

Charakterisierung und Anwendung Dihydrophenazin-basierter Leuchtstoffe und Koordinationspolymere

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Zusammenfassung

Phenazine und Flavine stellen vielseitige Stoffklassen natürlicher und synthetisch dargestellter, stickstoffhaltiger Heterocyclen dar. Aufgrund ihrer Struktur weisen sowohl Flavin als auch Dihydrophenazin(-Derivate) einzigartige physikalisch-chemische Eigenschaften auf. Dabei stehen besonders ihre ausgeprägten photophysikalischen Eigenschaften im Vordergrund. Aufgrund dieser Eigenschaften konnten sich beide Stoffklassen unter anderem in der organischen Chemie, Textilindustrie und Biochemie als bedeutende Farbstoffe etablieren.

Der erste Teil der Arbeit beschreibt die Einlagerung verschiedener Farbstoffe in metallorganische Gerüstverbindungen (*engl.* **metal organic frameworks**, MOFs). Die dargestellten Farbstoff@MOF-Komposite wurden charakterisiert und hinsichtlich ihrer photophysikalischen Eigenschaften detaillierter untersucht. Im Rahmen der Komposit-Synthese wurden die beiden Flavinfarbstoffe 10-Methyl-isoalloxazin (MIA) und 6-Fluoro-10-methyl-isoalloxazin (6F-MIA) in die MOFs MIL-53(Al) und MOF 5 eingelagert. Bei MIL-53(Al) (mikrokristallines Pulver) erfolgte die Farbstoffeinlagerung über eine postsynthetische, diffusionsbasierte Methode, bei MOF-5 erfolgte die Einlagerung über eine *in-situ*-Methode. Anschließende spektroskopische Analysen konnten nachweisen, dass sich die photophysikalischen Eigenschaften der Farbstoffe@MOF-Komposite ähnlich verhalten wie die Flavin-Farbstoffe in Lösungen. Die Emissionswellenlänge, Lebenszeit sowie Quantenausbeute bewegen sich dabei in vergleichbaren Größenordnungen, weshalb hier von festen homogenen Lösungen gesprochen werden kann.

Der Schwerpunkt der Promotion liegt auf der Synthese, Charakterisierung und Anwendung von Dihydrophenazin-basierten Leuchtstoffen und MOFs. Aufbauend auf dem literaturbekannten TADF-Emitter (*engl.* **thermally activated delayed fluorescence**) 4,4'-(Phenazin-5,10-diyl)dibenzonitril (pBN) wurden zwei weitere Dihydrophenazinderivate mittels Buchwald-Hartwig-Kupplung dargestellt und hinsichtlich ihrer photophysikalischen Eigenschaften analysiert. Der Dihydrophenazin-Kern (Donorgruppe) wurde hierbei mit verschiedenen Arylbromiden (Akzeptorgruppe) kombiniert. Die photophysikalischen Eigenschaften der neuen (TADF-)Emitter 3,3'-(Phenazin-5,10-diyl)dibenzonitril (mBN) und 4,4'''-(Phenazin-5,10-diyl)bis([1,1'-biphenyl]-4-carbonitril) (BPN) hängen dabei maßgeblich vom Substitutionsmuster der Benzonitrilgruppe ab und davon, ob es sich bei den Substituenten um Benzo- oder Biphenylnitrilgruppen handelt. mBN verfügt über schwach ausgeprägte TADF-Eigenschaften, während BPN einen konventionellen fluoreszenten Emitter darstellt.

4,4'-(Phenazin-5,10-diyl)dibenzonitril (später: Methylester) wurde in einem weiterführenden Syntheseschritt zu einer Carbonsäure hydrolysiert. Die Dicarbonsäuren eignen sich aufgrund ihrer linearen, symmetrischen Struktur ideal als bifunktionelle Linker für Koordinations-

polymere und MOFs. Die dargestellte Dicarbonsäure wurde anschließend mit Kobalt(II)-nitrat-Hexahydrat zu einem einzigartigen Koordinationspolymer und mit Zink(II)-nitrat-Hexahydrat zu neuartigen MOFs und Koordinationspolymeren umgesetzt.

Veröffentlichungen

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Abkürzungsverzeichnis

1D	eindimensional
2D	zweidimensional
3D	dreidimensional
A	Akzeptor(-Gruppe/Substituent)
AAS	Atomabsorptionsspektrometrie
bspw.	beispielsweise
bzw.	beziehungsweise
°C	Grad Celsius
CBP	4,4'-Bis(<i>N</i> -carbazolyl)-1,1'-biphenyl
CX31	Palladium-Katalysator - [1,3-Bis-(2,6-diisopropylphenyl)-imidazol-2-yliden]-chloro-[3-phenylallyl]-palladium(II)
CT	<i>engl.</i> charge-transfer
CTF	kovalente Triazin-Gerüste, (<i>engl.</i> covalent triazine frameworks)
D	Donor(-Gruppe/Substituent)
DCM	Dichlormethan
DEF	<i>N,N</i> -Diethylformamid
DHP	5,10-Dihydrophenazin
DMF	<i>N,N</i> -Dimethylformamid
EQE _{max}	externe Quantenausbeute, (<i>engl.</i> external quantum efficiency)
et al.	und andere, (<i>lat.</i> et alia)
etc.	übriger, der übrige, „und so weiter“ (<i>lat.</i> et cetera)
eV	Elektronenvolt
FAD	Flavinadenindinukleotid
FMN	Flavinmononukleotid
h	Stunde, (<i>engl.</i> hour)
HKUST	Universität für Wissenschaft und Technologie Hongkong (<i>engl.</i> Hong Kong University of Science and Technology)
HOMO	höchstbesetztes Molekülorbital (<i>engl.</i> highest occupied molecular orbital)
IC	innere Konversion (<i>engl.</i> internal conversion)
ISC	<i>engl.</i> intersystem crossing
LE	lokal angeregt, (<i>engl.</i> locally excited)
LUMO	niedrigstes unbesetztes Molekülorbital (<i>engl.</i> lowest unoccupied molecular orbital)
µs	Microsekunde

MMM	Metallorganische Gerüstverbindung aus mehreren (Übergangs)metallen (<i>engl.</i> mixed-metal metal-organic framework)
MOF	Metallorganische Gerüstverbindung (<i>engl.</i> metal-organic framework)
ms	Millisekunde
MS	Massenspektrometrie (<i>engl.</i> mass spectrometry)
NMR	Kernspinresonanz (<i>engl.</i> nuclear magnetic resonance)
ns	Nanosekunde
OLED	organische Leuchtdiode (<i>engl.</i> organic light emitting diode)
PCN	Phenazin-1-carboxamid
PDT	photodynamischen (Tumor-)Therapie (<i>engl.</i> photodynamic therapy)
PL	Photolumineszenz (<i>engl.</i> photoluminescence)
PLQY	Quantenausbeute (<i>engl.</i> photoluminescence quantum yield)
PNMOF	<i>engl.</i> polymer-nucleated metal-organic framework
ppm	Anteile pro Million (<i>engl.</i> parts per million)
RISC	<i>engl.</i> reverse intersystem crossing
S	Singulettzustand (<i>engl.</i> singlet state)
SBU	sekundäre Baueinheit (<i>engl.</i> secondary building unit)
sogn.	sogenannt
T	Triplettzustand (<i>engl.</i> triplet state)
TADF	thermisch aktivierte verzögerte Fluoreszenz, (<i>engl.</i> thermally activated delayed fluorescence)
XPS	Röntgenphotoelektronenspektroskopie (<i>engl.</i> X-ray photoelectron spectroscopy, XPS)
z.T.	zum Teil

Einleitung

1 Lumineszenz und TADF

Bei der Anregung eines Atoms, Moleküls oder (kristallinen) Festkörpers durch elektromagnetische Strahlung kommt es zu einer Wechselwirkung bzw. Absorption der Strahlung, sofern die Energie dieser Strahlung resonant zu einem Übergang in dem Atom, Molekül oder Festkörper ist. Die Atome, Moleküle oder Festkörper werden hierbei in höhere Energieniveaus, sogenannte angeregte Zustände überführt. Um diese ablaufenden photophysikalischen Prozesse zu visualisieren, hat Alexander Jablonski 1933 ein einfaches Termschema vorgestellt, das im Laufe der Jahrzehnte immer weiter differenziert wurde (Abbildung 1).¹⁻³

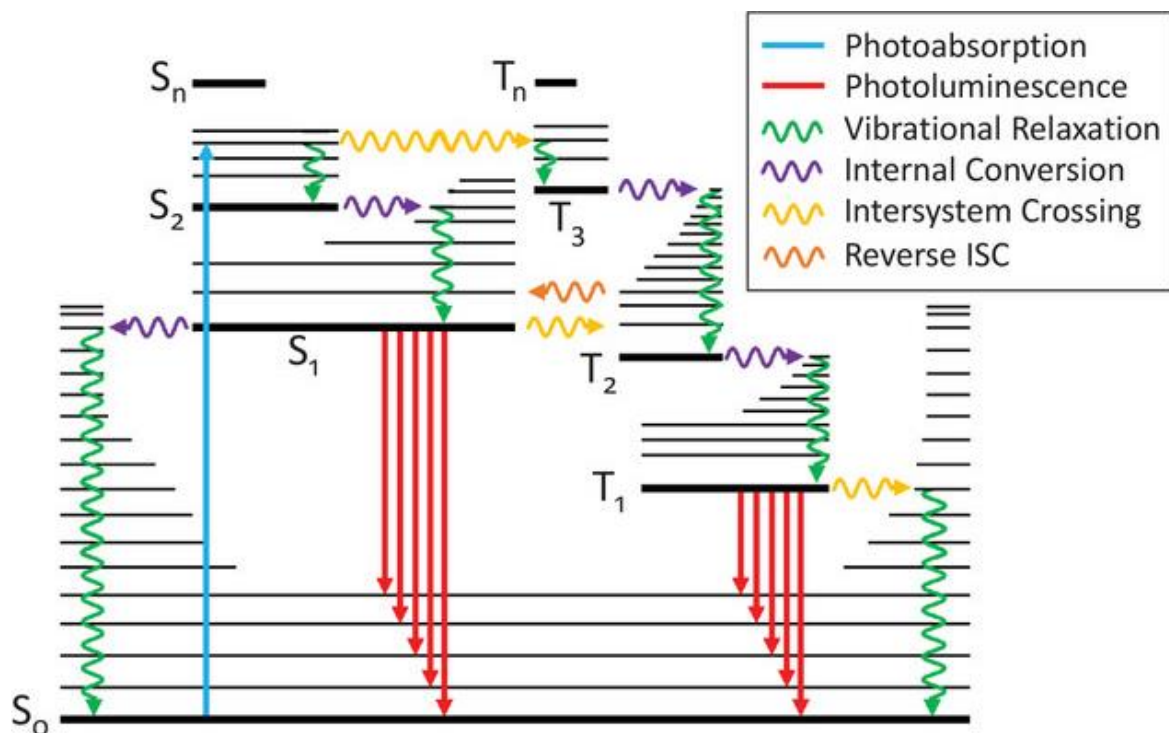


Abbildung 1: Jabłoński Diagramm. Nachdruck aus Ref. ⁴, mit Genehmigung, © 2023 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Bei der Absorption eines Photons durch ein organisches Molekül bzw. Luminophor findet eine Anregung aus den Schwingungsniveaus des Grundzustandes (S_0 , Singulett-Zustand) in einen elektronisch höheren Singulettzustand (S_n) statt ($n = 1, 2, 3$, etc.). Den Singulettzuständen S_n können dabei energetisch unterschiedliche Schwingungsniveaus zugeordnet werden. Die Schwingungsniveaus können ihrerseits wiederum in energetisch unterschiedliche Rotationsniveaus unterteilt werden. Da die Energiedifferenzen zwischen den Rotationsniveaus jedoch durch Wellenlängen im Mikrowellenbereich überbrückt werden, können diese im Rahmen dieser Diskussion vernachlässigt werden. Bei einer Anregung in einen Singulettzustand S_{n+1} , verlieren die Moleküle durch interne Konversion (*engl.* internal

conversion, IC) und vibronische Relaxation (VR) überschüssige Schwingungsenergie und kehren systematisch in den Schwingungsgrundzustand des energetisch niedrigeren elektronischen Singulettzustands (S_1) zurück. Dieser Vorgang wiederholt sich so lange, bis der energetisch niedrigste Singulettzustand (S_1) erreicht ist. Diese Relaxationsprozesse zeichnen sich durch Zeitkonstanten im Bereich von 10^{-12} bis 10^{-13} s aus, was signifikant unter den Zeitkonstanten von strahlenden Prozessen, typischerweise im Nanosekundenbereich, liegt. Diese Prozesse verhindern effektiv eine Emission aus elektronisch höheren Singulettzuständen. Michael Kasha beschrieb diese elektronischen Übergänge erstmals im Jahr 1950.⁵ Es existieren jedoch Ausnahmen, bei denen strahlende Prozesse aus energetisch höher angeregten Singulettzuständen S_{n+1} beobachtet werden können. Solche Emissionen treten auf, wenn beispielsweise der energetische Abstand zwischen S_2 und S_1 verhältnismäßig groß ist oder der $S_0 \rightarrow S_2$ -Übergang eine hohe Oszillatorstärke aufweist.

Aus dem Singulettzustand S_1 erfolgt schließlich eine Relaxation in den Grundzustand S_0 , wobei Energie in unterschiedlicher Form freigesetzt werden kann. Einerseits kann es zu Photolumineszenz kommen, andererseits aber auch zu einem strahlungslosen Übergang, bei dem die Energie in Form von Wärme an die Umgebung dissipiert wird. Darüber hinaus kann ein Energie- bzw. Ladungstransfer auf andere Moleküle stattfinden, wodurch beispielsweise photochemische Reaktionen katalysiert werden können. Allerdings kann es auch zu einer Fluoreszenzlöschung durch sogenanntes Quenching kommen. Hierbei können verschiedene Quenching-Effekte auftreten wie bspw. dynamisches und statisches Quenching, Resonanzenergietransfer aber auch andere Misch- und Nebeneffekte.^{1,2,6,7}

Bei der Anregung unter Absorption externer elektromagnetischer Strahlung und der Relaxation aus dem angeregten Zustand unter Emission von Licht wird der Prozess als Photolumineszenz bezeichnet. Die Photolumineszenz wird wiederum in Fluoreszenz und Phosphoreszenz unterteilt. Bei der Fluoreszenz handelt es sich um einen spinerlaubten Übergang aus dem niedrigsten Energieniveau des angeregten Singulettzustands S_1 in die Schwingungsniveaus des Grundzustands S_0 . Die typische Fluoreszenzlebensdauer τ_F bewegt sich dabei im Nanosekundenbereich. Bei der Phosphoreszenz handelt es sich um einen spinverbotenen Übergang aus dem angeregten Triplettzustand T_1 in die Schwingungsniveaus des Grundzustands S_0 . Zuvor findet unter Veränderung der Multiplizität ein strahlungsloser Übergang (*engl.* intersystem crossing, ISC) vom niedrigsten Energieniveau des angeregten Singulettzustands S_1 in den angeregten Triplettzustand T_1 statt. Die typische Phosphoreszenzlebensdauer τ_P bewegt sich dabei im Millisekundenbereich. Eine Sonderform der Fluoreszenz stellt die sogenannte thermisch aktivierte verzögerte Fluoreszenz (*engl.* thermally activated delayed fluorescence, TADF) dar. Dabei kommt es unter Einfluss von thermischer Energie zu einem umgekehrten ISC (*engl.* reverse intersystem crossing, RISC), wobei ein Molekül aus dem Triplettzustand T_1 zurück in den angeregten Singulettzustand S_1

überführt wird. Aus dem Singulettzustand S_1 kann wiederum unter spontaner Emission ein Übergang in die Schwingungsniveaus des Grundzustandes S_0 erfolgen. Der TADF-Mechanismus ist besonders relevant im Bereich der Elektrolumineszenz, da damit interne Quantenausbeuten von bis zu 100% unter gleichzeitig verhältnismäßig niedrigen Abklingzeiten im Mikrosekundenbereich möglich sind.^{1,2,8–10} Die Arrhenius-Gleichung beschreibt den Zusammenhang zwischen der RISC-Ratenkonstante (k_{RISC}^T), dem ΔE_{ST} -Wert und der Temperatur (T).

$$k_{RISC}^T \propto \exp(-\Delta E_{ST}/k_B T)$$

(k_B : Boltzmann-Konstante)

Mithilfe der Arrhenius-Gleichung kann beispielsweise der ΔE_{ST} -Wert aus experimentellen Daten errechnet werden. Für effizientes RISC sollte ΔE_{ST} idealerweise in der Größenordnung thermischer Energien um Raumtemperatur ($k_B T \sim 0.03$ eV) sein, typischerweise zwischen 0.1 – 0.2 eV.^{1,8–11}

2 Flavine und deren Derivate

Flavine stellen eine bedeutende Stoffgruppe in der Natur dar. Die Grundstruktur besteht aus einem heterozyklischen Isoalloxazin-Ringsystem (Abbildung 2). Dieses Ringsystem weist stark fluoreszierende Eigenschaften auf. Flavine bzw. Riboflavine (Vitamin B₂) treten oft in Verbindung mit Proteinen auf, den sogenannten Flavoproteinen (Oxidoreduktasen). Die Flavinnukleotide (Flavinadenindinukleotid (FAD), Flavinmononukleotid (FMN)) stellen dabei jeweils einen entscheidenden Kofaktor in Enzymen dar. Zudem spielen Flavinnukleotide eine wichtige Rolle in der Atmungskette von Zellen. Neben ihrer Funktion als Kofaktoren sind Flavine auch aufgrund ihrer photochemischen und photophysikalischen Eigenschaften von großem Interesse. In wässriger Lösung weisen Flavine eine starke Absorption im ultravioletten und sichtbaren Bereich auf. Die Absorptionsspektren weisen typischerweise vier Peaks mit hohen molaren Extinktionskoeffizienten ($\epsilon > 10^4$ M⁻¹cm⁻¹) auf, was auf $\pi \rightarrow \pi^*$ -Übergänge hinweist. Die genaue Position der Absorptionsmaxima und die Absorptivität hängen dabei stark von der chemischen Struktur des Flavinderivats und der chemischen Umgebung ab.^{12–17} Flavine haben vielfältige Anwendungen: in der (analytischen) Chemie als Farbindikatoren, in der Medizin als wichtige Kofaktoren bei enzymatischen Prozessen und in der Textilindustrie als Farbstoffe. Aufgrund ihrer photochemischen und photophysikalischen Eigenschaften sind sie zudem in der Photovoltaik von Interesse.^{13,15,16}

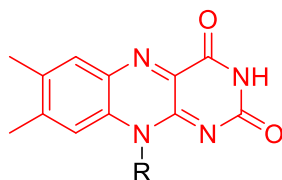


Abbildung 2: Allgemeine Struktur von Flavin.

(Der Flavinkern ist rot hervorgehoben; Vitamin B₂: R: Ribitylgruppe)

3 Phenazine und deren Derivate

Phenazine stellen eine vielseitige Stoffklasse natürlicher und synthetisch dargestellter, stickstoffhaltiger Heterocyclen dar. Die Grundstruktur des Phenazins stellt ein planares, aromatisches System dar, bestehend aus drei zusammenhängenden konjugierten Sechsringen. Phenazin leitet sich formal vom Pyrazin durch Anellierung zweier Benzogruppen ab (Dibenzo[*b,e*]pyrazin) (Abbildung 3). Aus der molekularen Struktur des Phenazins ergeben sich interessante physikochemische Eigenschaften. Phenazin ist anfällig für Oxidation, da die so gebildeten Radikale im ausgedehnten aromatischen System resonanzstabilisiert werden können.^{18–20}

Historisch betrachtet spielen Phenazinderivate in zwei Anwendungsbereichen eine zentrale Rolle: in der Pharmazie und als Farbstoff. So stellt der erste synthetisch hergestellte blaue Farbstoff das Phenazinderivat Mauvein dar, wobei es sich bei Mauvein genau genommen um eine Mischung aus mehreren verschiedenen Phenazinderivaten handelt (Abbildung 3). Mauvein wurde 1856 zufällig von William Henry Perkin entdeckt, als er versuchte, Chinin zu synthetisieren.^{21,22}

Perkin und der Phenazinfarbstoff Mauvein legten den Grundstein für die moderne Farbstoffforschung und -industrie. Vier Jahre nach Perkins Entdeckung gelang es Methurin-Joseph Fordos das Phenazinderivat Pyocyanin (5-Methylphenazin-1-on) zu isolieren (Abbildung 3). Bei Pyocyanin handelt es sich um einen antibakteriellen Naturstoff, der ähnlich dem Mauvein eine intensive blaue Farbe aufweist.^{23–25}

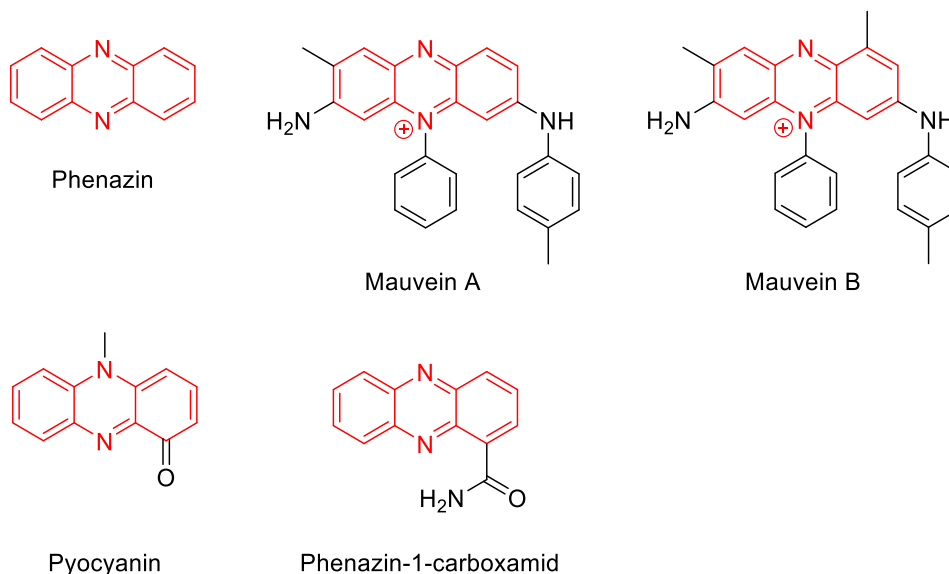


Abbildung 3: Phenazin, Mauvein A, Mauvein B und Pyocyanin.
(Der Phenazinkern ist rot hervorgehoben)

Als Farbstoffe und in der Pharmazie zeigen sich die beiden wichtigsten Eigenschaften von Phenazin und deren Derivaten. Zum einen verfügen sie über hervorragende optische Eigenschaften: Hohe Quantenausbeuten, schmale Emissionsbanden und eine kleine Stokes-Verschiebung. Grundsätzlich befinden sich Absorptions-, Anregungs-, und Emissionswellenlängen der meisten Phenazinderivate überwiegend im sichtbaren Bereich. Aufgrund der ausgezeichneten photophysikalischen Eigenschaften wurden in der Vergangenheit eine Vielzahl neuer Farbstoffe auf Basis der Phenazingrundstruktur entwickelt. Zwar spielen Phenazinderivate in der heutigen Farbstoffindustrie eine untergeordnete Rolle, dennoch stehen sie aufgrund ihres Potentials nach wie vor im Fokus der Forschung.^{26–31} Neben der Funktion als Farbstoff spielen Phenazine in der Pharmazie eine wichtige Rolle, da sie aufgrund ihrer Redoxempfindlichkeit ein breites Spektrum an biologischen Aktivitäten aufweisen. Phenazin-1-carboxamid (PCN) ist bspw. ein katalytisch wirksames Carbonsäureamidderivat, das vom Bakterium *Pseudomonas chlororaphis* (PCL1391) auf natürlichem Wege produziert wird. Phenazin-1-carboxamid ist aufgrund seiner Redoxaktivität in der Lage, in Bodenmineralien enthaltenes Eisen(III) zu reduzieren. Über die Reduktion kann bioverfügbares Eisen(II) im Boden angereichert werden.³² Eine andere Einsatzmöglichkeit von Phenazinderivaten ist bspw. die Verwendung als Photosensibilisatoren in der photodynamischen (Tumor-)Therapie (PDT). Inzwischen sind weit über 6000 natürliche und synthetische Phenazinderivate bekannt, mit zum Teil bemerkenswerten pharmakologischen Wirkungen.^{20,33,34}

Phenazin und deren Derivate können über unterschiedliche Syntheserouten dargestellt werden. Der klassische Syntheseweg erfolgt über die Wohl-Aue-Reaktion, die erstmals 1901

von Alfred Wohl und Wilhelm Aue publiziert wurde. Hierbei wird Nitrobenzol mit Anilin basenkatalysiert kondensiert.³⁵ Über diese Syntheseroute können sowohl reines Phenazin als auch, abhängig von der Wahl der Edukte, verschiedene Phenazinderivate dargestellt werden. Ein weiterer, modernerer Ansatz mit höheren Ausbeuten ist die Synthese mittels einer palladiumkatalysierte Buchwald-Hartwig-Kupplung. Auch über die Buchwald-Hartwig-Kupplung ist die Synthese verschiedener Phenazinderivate möglich (Abbildung 4). Beide Syntheserouten finden gegenwärtig noch Anwendung.^{35–38}

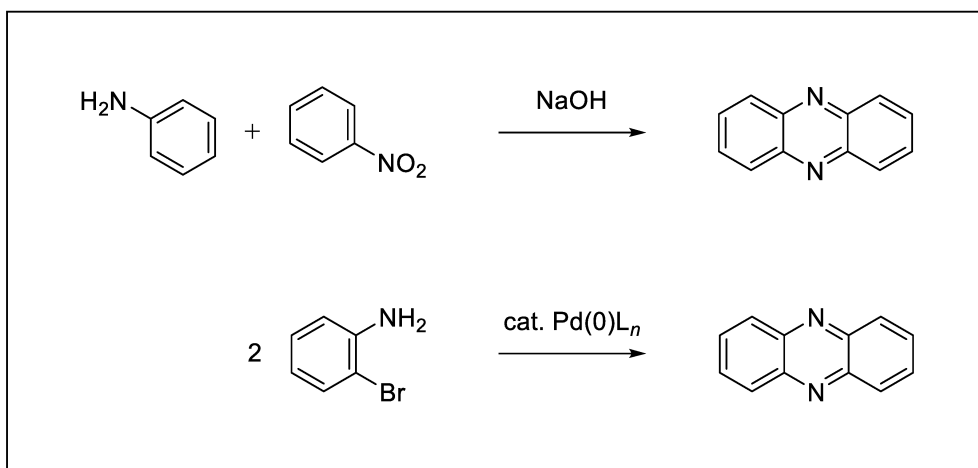


Abbildung 4: Wohl-Aue-Reaktion (oben) und Buchwald-Hartwig-Reaktion (unten).

4 Design von TADF-Emittern

Der in Kapitel 1 beschriebene Mechanismus der thermisch aktivierten verzögerten Fluoreszenz (*engl.* thermally activated delayed fluorescence, TADF) wurde erstmals 1961 von Parker und Hatchard detailliert anhand von Eosin-Lösungen beschrieben.³⁹ Die eigentliche Entdeckung geht allerdings auf das Ende der 1920er zurück, als Perrin an Uranylsalzen forschte.⁴⁰ Das Konzept wurde jedoch erst Jahrzehnte später von Adachi et al. wiederaufgegriffen und auf organische Luminophore übertragen, motiviert durch den potentiellen Einsatz in organischen Leuchtdioden (OLEDs).^{10,41} Eine der wichtigsten Eigenschaften von organischen TADF-Emittern sind die theoretisch zu erwartenden internen Quantenausbeuten von 100%, die gleichzeitig in OLEDs hohe externe Quantenausbeuten (*engl.* external quantum efficiency, EQE_{max}) von über 40% erlauben. Durch den Einsatz rein organischer TADF-Emitter können die bis dato verwendeten, kostspieligen phosphoreszierenden Metallkomplexe auf Basis von Ir(III) und Ru(II) in Displays substituiert werden. Weitere beachtliche Vorteile der organischen Emitter sind die ressourceneffiziente Synthese, die Aufreinigungsmöglichkeiten (bspw. Rekristallisation) und insbesondere die Optimierungsmöglichkeiten der photophysikalischen Eigenschaften durch die synthetische Flexibilität.^{8,9,42–44}

Abbildung 5 beschreibt den schematischen Aufbau von TADF-Emittern. Ein entscheidender Faktor für einen effizienten TADF-Emitter ist ein geringer ΔE_{ST} -Wert. Der ΔE_{ST} -Wert (die Singulett-Triplett-Energielücke) beschreibt – wie eingangs beschrieben – den energetischen Unterschied zwischen dem ersten angeregten Singulettzustand (S_1) und dem ersten angeregten Triplettzustand (T_1) eines Moleküls, im vorliegenden Beispiel eines TADF-Emitters. Ein geringer ΔE_{ST} -Wert korreliert dabei mit der Austauschwechselwirkung und diese ist wiederum von der Orbitalüberlappung des höchsten besetzten Molekülorbitals (*engl.* highest occupied molecular orbital, HOMO) mit dem niedrigsten unbesetzten Molekülorbitals (*engl.* lowest unoccupied molecular orbital, LUMO) abhängig. Eine geringe Orbitalüberlappung und damit ein kleiner ΔE_{ST} lässt sich auf zwei Arten realisieren: (a) durch eine effektive räumliche Trennung von HOMO und LUMO oder (b) durch eine torsional eingeschränkte Geometrie, die die Orbitalwechselwirkungen geometrisch begrenzt.

Neben dem sterischen Anspruch der einzelnen Gruppen unterscheiden sie sich auch in ihrer Donor- bzw. Akzeptorstärke. Über die selektive Wahl der Donor- und Akzeptor-Gruppen kann der ΔE_{ST} , die Emissionswellenlänge, Abklingzeit und Quantenausbeute gezielt gestaltet und optimiert werden. Als Donor-Gruppen werden typischerweise arylierte *N*-heterozyklische Verbindungen wie Dihydrophenazine, Dihydroacridine, 10*H*-Phenoxazin, 9*H*-Carbazole sowie Diphenylamine verwendet. Klassische Akzeptor-Gruppen stellen Benzophenone, Sulfone, Triazine, Tetrazole, Triazole, Oxadiazole und Nitril-substituierte Aromaten (bspw. Benzonitrile) dar (Abbildung 5). Zusätzlich zu den genannten Gruppen können zahlreiche weitere elektronenreiche oder -arme Gruppen für TADF-Emitter verwendet werden.^{8,42,44}

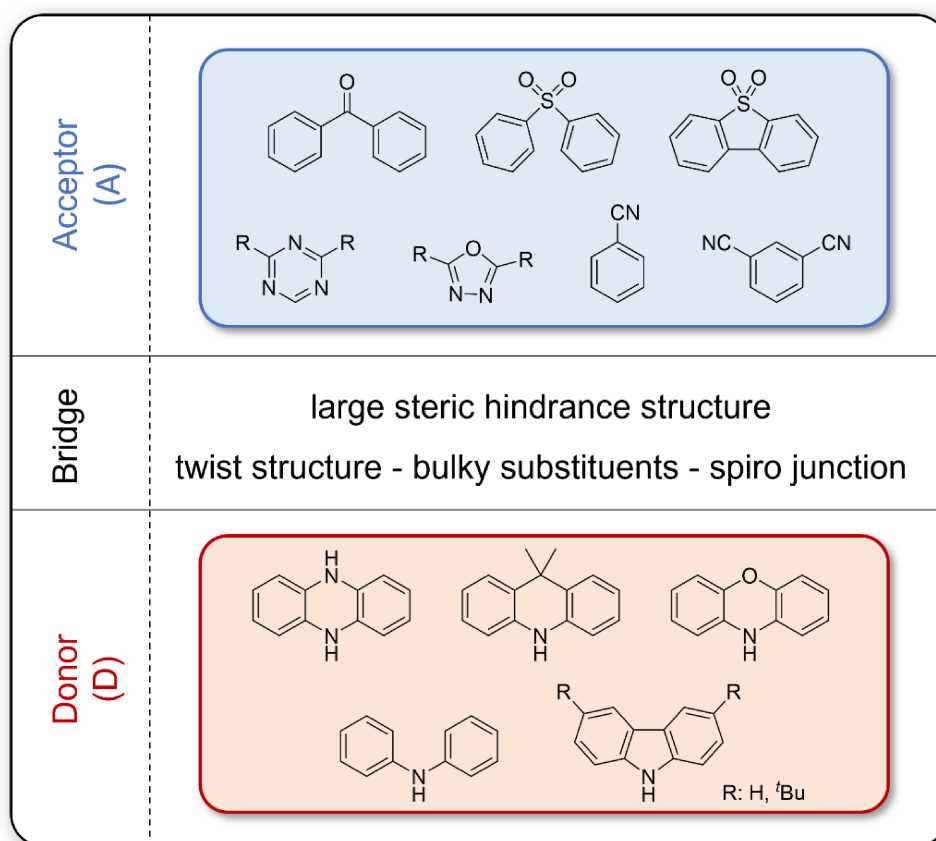


Abbildung 5: Auswahl an Donor- und Akzeptorgruppen für ein zielgerichtetes Design von TADF-Emitter.

Die Donor- und Akzeptor-Gruppen können mithilfe geeigneter Kupplungsreaktionen miteinander verknüpft werden. Klassischerweise kommen hierbei übergangsmetall-katalysierte Kreuzkupplungen wie die Heck-Reaktion, Suzuki-, Kumada-, Negishi-, Sonogashira-, Stille- oder Buchwald-Hartwig-Kupplung zum Einsatz. Diese Kreuzkupplungen haben in den letzten Jahrzehnten die Synthese von komplexen Naturstoffen, supramolekularen Synthesebausteinen, Polymeren und Leitstrukturen in der pharmazeutischen Chemie erheblich vereinfacht. Auf diese Weise können aus kleinen, modularen Moleküleinheiten vergleichsweise einfach komplexe Zielverbindungen dargestellt werden.

Bei den Metalkatalysatoren handelt es sich in der Regel um Kupfer-, Nickel- und Palladiumkatalysatoren, aber auch Eisen- und Rutheniumkatalysatoren finden Anwendung; wobei Palladiumkatalysatoren am weitesten verbreitet sind.^{45–48} Die Kreuzkupplungen unterscheiden sich dabei im Wesentlichen durch die verwendeten Übergangsmetalle und Liganden, lassen sich aber grundsätzlich in vier Reaktionsschritte unterteilen: Oxidative Addition (A_{Ox}), Transmetallierung, *trans-cis*-Isomerisierung und reduktive Eliminierung (E_{Red}). Abbildung 6 beschreibt den vereinfachten Katalysezyklus anhand der (Teil-)Synthese des TADF-Emitters 4,4'-(Phenazin-5,10-diyl)dibenzonitril. Im ersten Schritt reagiert die aktive

(lineare) Palladium-(0)-Spezies mit dem Elektrophil. Das Palladium wird dabei oxidiert und bildet einen stabileren Palladium-(II)-Komplex. Die Elektrophile stellen Halogenkohlenwasserstoffe (z.B.: Alkyl-, Alkenyl, Alkynyl- oder Arylhalogenide) oder Triflate dar. Die Transmetallierung ist der geschwindigkeitsbestimmende Schritt und unterscheidet sich mechanistisch abhängig vom verwendeten Nucleophil. Bei der Transmetallierung koordiniert das Nucleophil an den Palladium-(II)-Komplex und die Abgangsgruppe (Halogenid oder Triflat) wird in Form eines (Metall-)Salzes abgespalten. Die Nucleophile können neben Organometallverbindungen auch Alkene (Heck) oder Alkine (Sonogashira) darstellen oder wie in Abbildung 6 gezeigt, sekundäre Amine. Bei der anschließenden Isomerisierung wechselt der Komplex von der *trans*- in die *cis*-Konfiguration. Abhängig vom Nucleophil bzw. Intermediat ist der Isomerisierungsschritt nicht in allen Fällen erforderlich. Abschließend erfolgt eine reduktive Eliminierung, wobei das gewünschte Produkt abgespalten und die aktive Palladium-(0)-Spezies in den Katalysezyklus zurückgeführt wird.^{45–48}

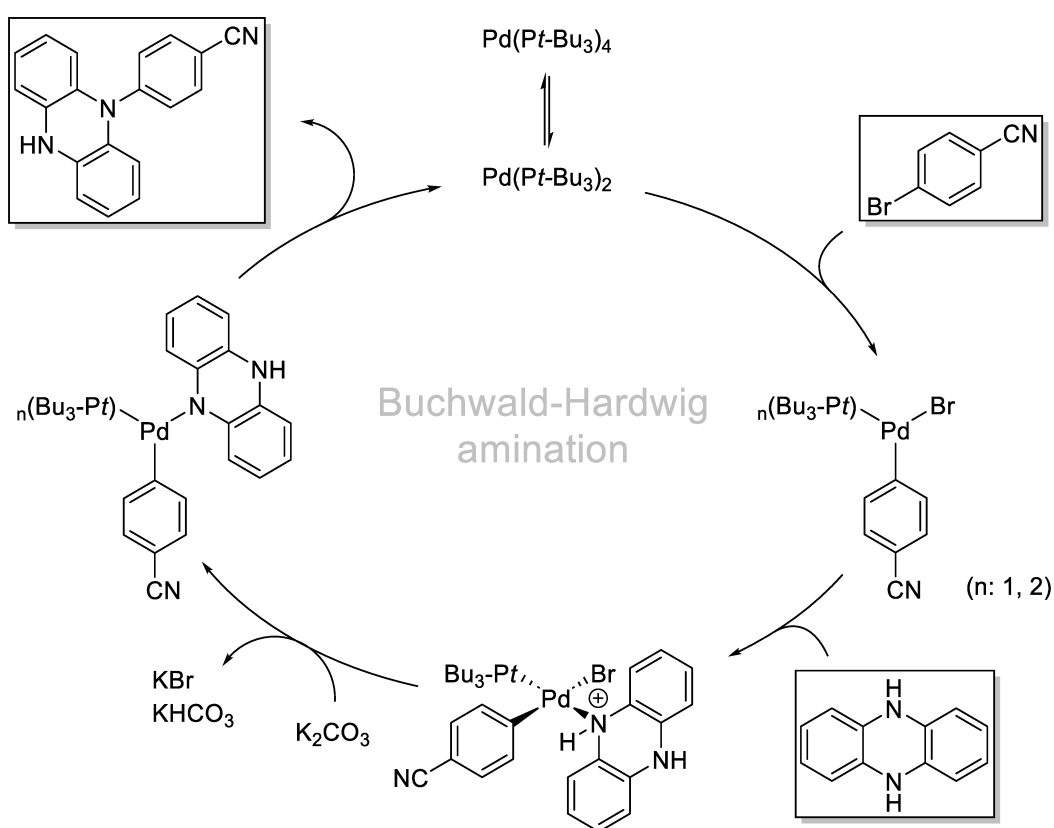


Abbildung 6: Vereinfachter Katalysezyklus einer Buchwald-Hartwig-Kreuzkupplung. Das Elektrophil stellt hier 4-Brombenzonitril und das Nucleophil Dihydrophenazin dar. Um den finalen TADF-Emitter 4,4'-(Phenazin-5,10-diyl)dibenzonitril zu erhalten, muss das (Zwischen)produkt 4-(phenazin-5(10H)-yl)benzonitril aufgrund der zweiten Aminogruppe einen weiteren Katalysezyklus durchlaufen.^{49,50}

4.1 Dihydrophenazin-basierte TADF-Emitter

Phenazine (und deren Derivate) können nicht nur als konventionelle Farbstoffe verwendet,^{51,52} sondern auch als TADF-Emitter konzipiert werden. TADF-Emitter auf Basis von Dibenzophenazin verfügen oftmals über bemerkenswerte photophysikalische Eigenschaften. Aufgrund der Hybridisierung der Stickstoffatome stellt der Dibenzophenazin-Kern die Akzeptorgruppe dar. Die Donorgruppen wiederum können beim finalen TADF-Emitter variieren. Effizienteste Donorgruppen stellen 9,9-Dimethyl-9,10-dihydroacridin, 10*H*-Phenoxazin und 3,6-Di-*tert*-butylcarbazol dar; so verfügt bspw. der TADF-Emitter **1PXZ-BP** in klassischen OLED-Devices über eine EQE_{max} von über 26 % (Abbildung 7).^{26–28}

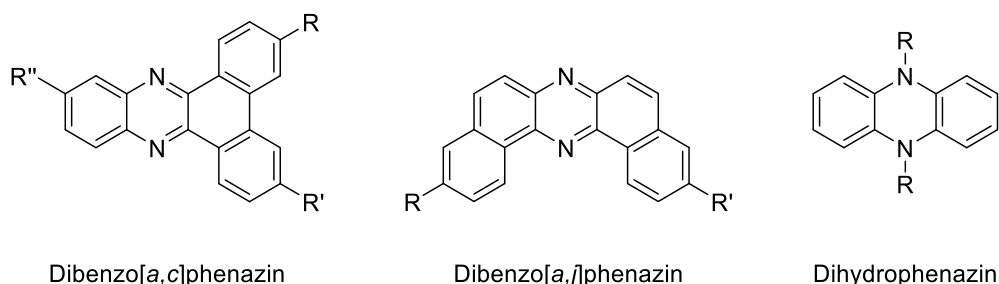


Abbildung 7: Beispielhafte TADF-Strukturmotive, abgeleitet von Phenazin.

(**1PXZ-BP**: Dibenzo[a,c]phenazin, R:10*H*-Phenoxazin, R':R'': H).

Neben TADF-Emittern auf Basis von Dibenzophenazin können auch solche auf Basis von Dihydrophenazin (DHP) designt werden.^{29,31} Mittels Arylierung der Positionen 5 und 10 können in Kombination mit geeigneten Akzeptorgruppen symmetrische TADF-Emitter mit einer Akzeptor-Donor-Akzeptor-Topologie (A-D-A) synthetisiert werden. Adachi et al. synthetisierte erstmals 2015 vier TADF-Emitter auf Basis von Dihydrophenazin. Dabei wurden systematisch verschiedene Akzeptorgruppen (1,2-Diphenylbenzimidazol, Benzonitril, 2-Phenylbenzo[d]thiazol und 2,4,6-Triphenyl-1,3,5-triazin) mit dem Dihydrophenazin-Kern mittels einer Buchwald-Hartwig-Reaktion miteinander gekuppelt. 4,4'-(Phenazin-5,10-diyl)dibenzonitril und 5,10-bis(4-(1-phenyl-1*H*-benzo[d]imidazol-2-yl)phenyl)-5,10-dihydrophenazin stellen hierbei die effizientesten TADF-Emitter dar. Die Emissionsmaxima der vier Emitter (6 wt% emitter:CBP (4,4'-Bis(N-carbazolyl)-1,1'-biphenyl)) reichen dabei von 537 bis 598 nm (grün – orange). Die theoretischen ΔE_{ST} -Werte reichen von 0 bis 0.19 eV und die TADF-Lebensdauer τ_d von 0.1 bis 50 ms. 5,10-bis(4-(1-phenyl-1*H*-benzo[d]imidazol-2-yl)phenyl)-5,10-dihydrophenazin weist die höchste EQE mit 12 % auf.²⁹ Auf den Ergebnissen von Adachi et al. aufbauend wurden die photophysikalischen Eigenschaften von Nitrilen als Akzeptorgruppe weitergehend analysiert. In der Arbeit von Janiak et al. wurde DHP mit den Akzeptorgruppen 3-Brombenzonitril und 4'-Bromo-[1,1'-biphenyl]-4-carbonitril umgesetzt. Die Ergebnisse zeigten, dass sowohl das Substitutionsmuster als auch eine Verlängerung der Verbrückung einen signifikanten Einfluss auf die photophysikalischen Eigenschaften der

Farbstoffe haben. Als Feststoff weist 3,3'-(phenazin-5,10-diyl)dibenzonitril lediglich schwach ausgeprägte TADF-Eigenschaften auf, während 4',4'''-(phenazin-5,10-diyl)bis([1,1'-biphenyl]-4-carbonitril) ein konventionelles Fluorophor darstellt. Die Veränderungen der photophysikalischen Eigenschaften können auf die Überlappung der HOMO/LUMO-Orbitale und die damit verbundenen ΔE_{ST} -Werte zurückgeführt werden.³⁰ Parallel zu der Arbeit von Janiak et al. analysierten Zedong et al. die TADF-Emitter 5,10-bis(4-(quinoxalin-6-yl)phenyl)-5,10-dihydrophenazin, 5,10-bis(4-(2,3-dimethylquinoxalin-6-yl)phenyl)-5,10-dihydrophenazin und 5,10-bis(4-(2,3-diphenylquinoxalin-6-yl)phenyl)-5,10-dihydrophenazin. Die drei Chinoxaline weisen ebenfalls sehr geringe ΔE_{ST} -Werte auf (15 - 19 meV). Die Emissionsmaxima der Emitter (3 wt% emitter:CBP) liegen dicht beieinander und reichen von 598 - 613 nm. Die absoluten internen Quantenausbeuten Φ_{PL} liegen zwischen 62 und 85 %, die TADF-Lebensdauern τ_{DF} zwischen 1,21 bis 2,25 μ s. Der TADF-Emitter 5,10-bis(4-(2,3-diphenylquinoxalin-6-yl)phenyl)-5,10-dihydrophenazin weist eine hohe EQE von fast 20 % auf.³¹ Abbildung 8 fasst schematisch alle literaturbekannten, auf DHP basierenden Luminophore zusammen.

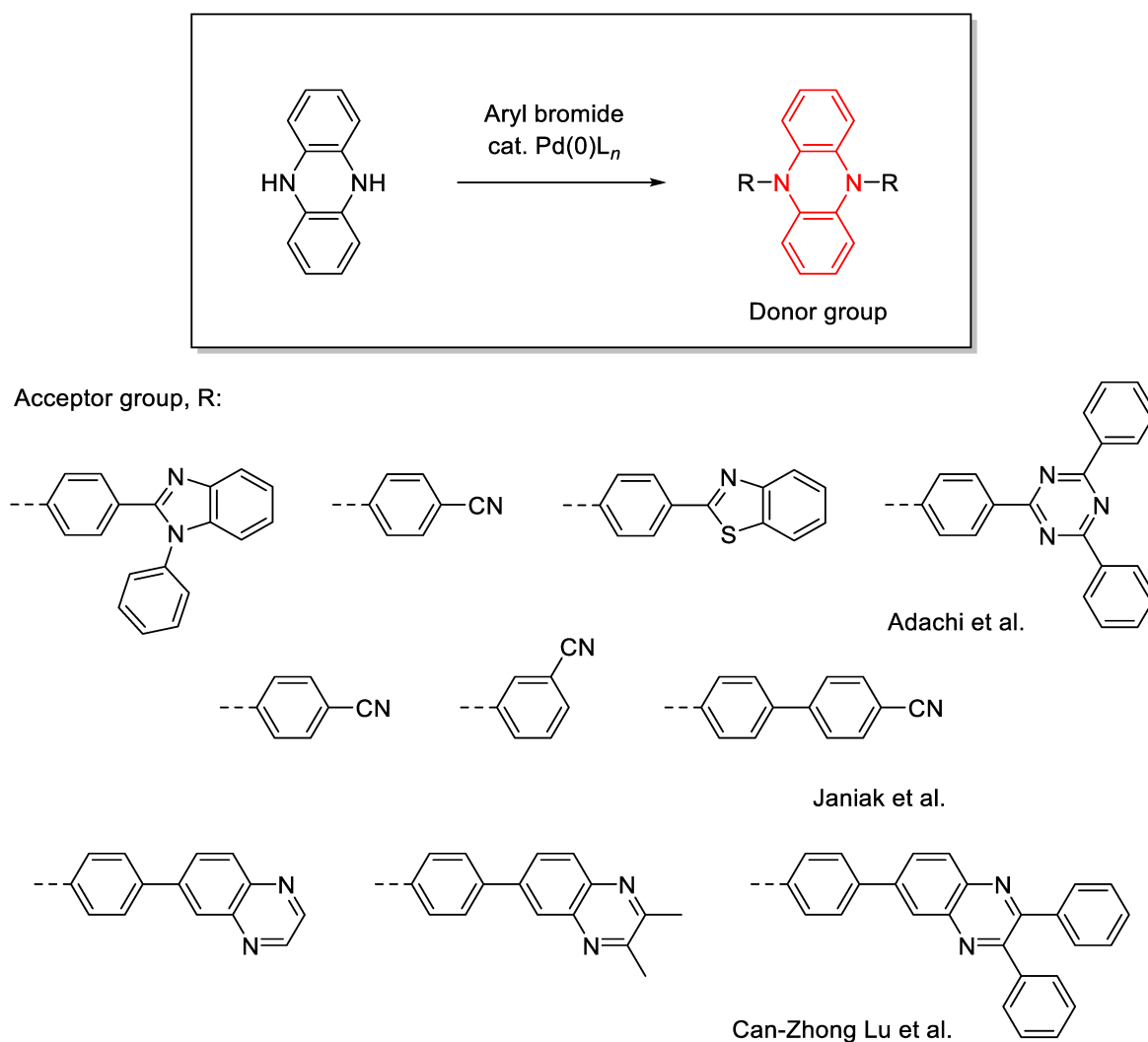


Abbildung 8: Literaturbekannte Dihydrophenazin-Luminophore mit unterschiedlichen Akzeptor-Gruppen.^{29–31}

5 Metallorganische Gerüstverbindungen

Metallorganische Gerüstverbindungen (*engl.* metal-organic frameworks, MOFs) sind nach IUPAC-Definition (*engl.* International union of pure and applied chemistry) potentiell poröse zwei/dreidimensionale Koordinationsnetzwerke, bestehend aus anorganischen (polynuklearen) Sekundärbausteinen (*engl.* secondary building units, SBUs) und organischen Liganden, die als Linker fungieren.⁵³ MOFs zeichnen sich durch ihren modularen Aufbau, ihre strukturelle Vielfalt, hohe Porosität und große spezifische Oberfläche aus. Durch die selektive Wahl verschiedener SBUs und Linker können Struktur und Funktion gezielt gestaltet werden. Abbildung 9 stellt den schematischen Aufbau von MOFs dar, wobei die SBUs vorwiegend aus Metallclustern bestehen und durch multifunktionale Linker miteinander verknüpft werden, sodass zwei/dreidimensionale Koordinationsnetzwerke entstehen.^{53–57}

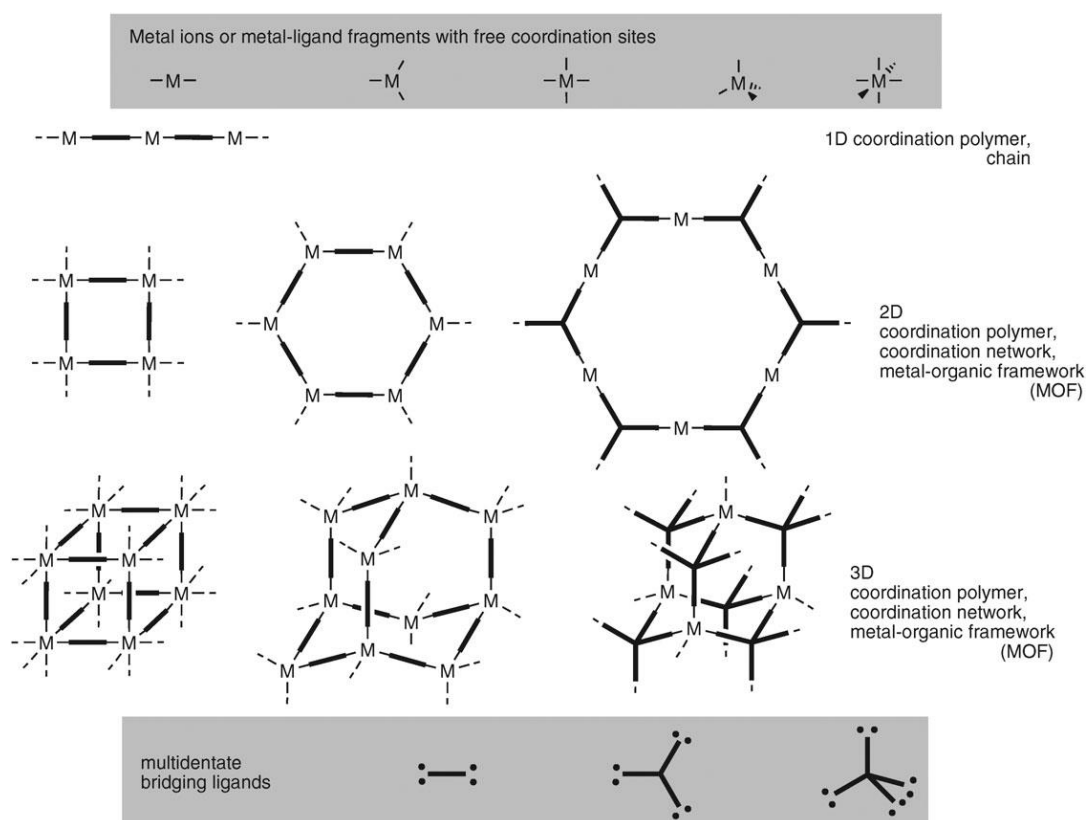


Abbildung 9: Schematischer Aufbau von Koordinationspolymeren (1D) und metallorganischen Gerüstverbindungen (2D & 3D). Nachgedruckt aus Ref. ⁵⁴, mit Genehmigung, © Copyright 2010 The Royal Society of Chemistry.

Die Geschichte der synthetischen metallorganischen Chemie geht auf den Anfang des 18ten Jahrhunderts zurück. Die erste literaturbekannte Koordinationsverbindung beschreibt das

anorganische Pigment Berliner Blau $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. Die damalige Synthese erfolgte jedoch ohne Kenntnis der chemischen Zusammensetzung und Struktur.^{58–60} Einer der wichtigsten Meilensteine der Koordinationschemie gelang Alfred Werner Ende des 19. Jahrhunderts. Werner legte mit seinen Arbeiten die konzeptionelle Grundlage der Koordinationschemie. „... auf Grund seiner Arbeiten über die Bindungsverhältnisse der Atome im Molekül, wodurch er ältere Forschungsgebiete geklärt und neue erschlossen hat, besonders im Bereich der anorganischen Chemie“ wurde Werner 1913 der Nobelpreis für Chemie verliehen.^{61–64} Seine Koordinationstheorie bildet bis heute die theoretische Basis der Komplexchemie. Ein weiterer wichtiger Schritt der Koordinationschemie gelang Hofmann bzw. Powell et al. Powell konnte Anfang der 1950er die Kristallstruktur von Hofmanns Clathratverbindungen $[\text{Ni}(\text{CN})_2(\text{NH}_3)](\text{C}_6\text{H}_6)$ aufklären und dadurch zum allgemeinen Verständnis von Koordinationsverbindungen beitragen. Bei Hofmanns Clathratverbindungen handelt es sich um 2D-Schichten, die abwechselnd aus oktaedrisch und quadratisch-planar koordinierten Ni(II)-Zentralatomen bestehen, die über Cyanidoliganden miteinander verknüpft werden. Zwischen den einzelnen Schichten befinden sich endständig an den oktaedrisch koordinierten Ni(II)-Zentralatomen Amminliganden.^{65–67} 1959 synthetisierten Saito et al. erstmals gezielt und systematisch kristalline Koordinationsnetzwerke. Dabei wurden Cu^{2+} -Ionen mit drei unterschiedlichen Dinitrilen (Succinonitril, Glutaronitril und Adiponitril) umgesetzt. Es resultierten 1D-, 2D- und 3D-Strukturen – abhängig von der Länge des gewählten Dinitrils.^{68–70} Die Arbeiten von Hoskins und Robson führten die ersten Gedanken der rationalen Synthese von dreidimensionalen Koordinationsnetzwerken weiter und demonstrierten anhand von $[\text{Cu}(\text{TCTPM})](\text{BF}_4)$ ($\text{TCTPM} = 4,4',4'',4'''$ tetracyanotetraphenylmethan) die einfachen und allgemeinen Grundsätze für das Design solcher Koordinationsnetzwerke.^{71–73} Der Begriff *metal-organic frameworks* (MOFs) wurde erstmals 1995 von Yaghi et al. im Zusammenhang mit den dreidimensionalen Koordinationsnetzwerken aus Kupfer und 4,4'-Bipyridin ($\text{Cu}(4,4'\text{-bpy})_{3/2} \cdot \text{NO}_3(\text{H}_2\text{O})_{3/2}$) sowie Cobalt und Trimesinsäure ($\text{CoC}_6\text{H}_3(\text{COOH})_{1/3})_3(\text{NC}_5\text{H}_5)_2 \cdot 2/3 \text{ NC}_5\text{H}_5$) etabliert.^{74,75} Ein weiterer Meilenstein gelang Yaghi et al. 1999 mit der Synthese von MOF-5 ($\text{Zn}_4\text{O}(\text{BDC})_3$). MOF-5 stellt ein Zink-Terephthalat dar, bestehend aus $[\text{Zn}_4\text{O}(\text{CO}_2)_6]$ -SBUs und dem Dicarboxylat der Terephthalsäure (BDC^{2-}). Allgemein kann die Struktur von MOF-5 als *Würfel* beschrieben werden. An jeder Ecke des Würfels befindet sich eine $[\text{Zn}_4\text{O}(\text{CO}_2)_6]$ -Einheit, die über einen Terephthalatlinker miteinander verknüpft sind. MOF-5 stellte zum Zeitpunkt der Veröffentlichung einen Porositätsrekord auf.⁷⁶ Darüber hinaus etablierte sich MOF-5 in der Literatur unter anderem als prototypisches MOF. Auf diesen MOFs aufbauend konzeptualisierte Yaghi erstmals übergreifende und allgemeingültige Designstrategien von Koordinationsnetzwerken. Basierend auf dem Prinzip des modularen Aufbaus von MOFs, sollen die beiden Grundbausteine Linker und SBU idealerweise beliebig miteinander kombinierbar sein, um gezielt MOFs mit gewünschten strukturellen und chemisch-

physikalischen Eigenschaften zu erhalten – vergleichbar mit dem Prinzip des Crystal Engineering.^{56,77}

Die Kombination von organischen Linkern mit (polynuklearen) SBUs ermöglicht die Synthese einer Vielzahl unterschiedlicher MOFs mit verschiedenen Strukturtypen. Um die Strukturbeschreibung zu erleichtern, werden MOFs in grundlegende Netzwerktopologien eingeteilt.⁷⁸ Bekannte Topologien sind bspw. die Diamantstruktur (**dia**, z.B.: MOF-808)^{68,79} oder der kubisch-primitive Strukturtyp (**pcu**, z.B.: MOF-5).^{76,80} Jede Topologie verfügt dabei über charakteristische Porengrößen und spezifische Oberflächen. Abbildung 10 zeigt exemplarisch verschiedene MOF-Topologien, die mittels gezielter Kombination aus Linker und SBU synthetisiert werden können. Inzwischen sind über 100000 verschiedene MOF-Strukturen bekannt.^{81,82}

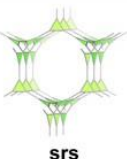
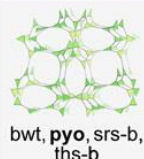
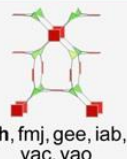
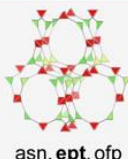
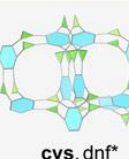
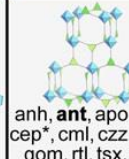
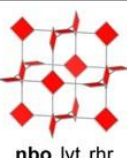
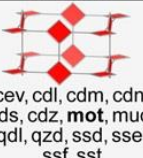
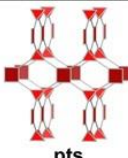
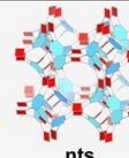
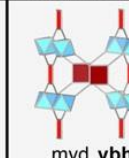
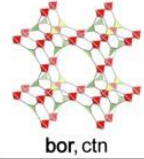
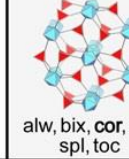
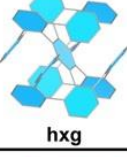
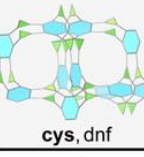
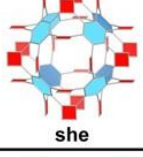
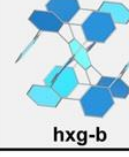
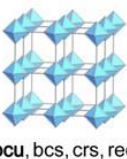
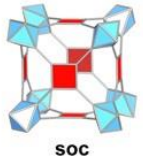
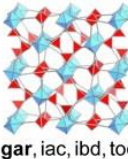
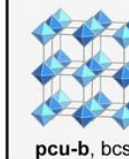
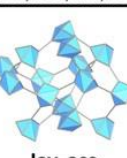
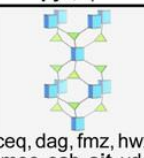
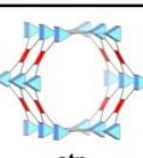
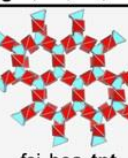
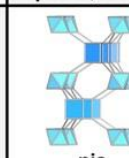
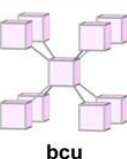
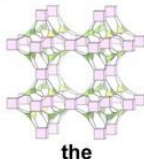
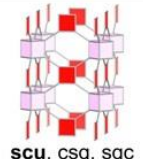
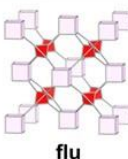
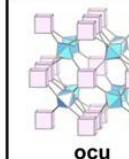
Building unit 1 \ Building unit 2	 2-c Linear	 3-c Triangle	 4-c Square	 4-c tet	 6-c Hexagon	 6-c oct
 3-c Triangle	 srs	 bwt, pyo, srs-b, ths-b	 fjh, fmj, gee, iab, yac, yao	 asn, ept, ofp	 cys, dnf*	 anh, ant, apo, brk, cep*, cml, czz, eea, qom, rtl, tsx, zzz
 4-c Square	 nbo, lvt, rhr	 pto, tbo	 cev, cdl, cdm, cdn, cds, cdz, mot, muo, qdl, qzd, ssd, sse, ssf, sst	 pts	 nts	 myd, ybh
 4-c tet	 dia, lcs, qtz, sod	 bor, ctn	 fgl, mog, pds, pth, pti, ptr, ptt	 bnl, byl, cag, cbt, coe, crb, fel, icm, kea, lon, pcl, qtz-b, sca, tpd, ucn	—	 alw, bix, cor, ing, spl, toc
 6-c Hexagon	 hxg	 cys, dnf	 she	—	 hxg-b	—
 6-c oct	 pcu, bcs, crs, reo	 pyr, spn	 soc	 gar, iac, ibd, toc	—	 pcu-b, bcs-b
 6-c trp	 lcy, acs	 ceq, dag, fmz, hwx, moo, sab, sit, ydq	 stp	 fsi, hea, tpt	 htp	 nia
 8-c cub	 bcu	 the	 scu, csq, sqc	 flu	—	 ocu

Abbildung 10: Schematische Darstellung unterschiedlicher Linker/SBU-Kombinationen und den resultierenden MOF-Netzwerktopologien. Die Abbildung stellt lediglich einen kleinen Ausschnitt möglicher Linker/SBU-Kombinationen dar. Nachdruck aus Ref. ⁸³, mit Genehmigung, © 2018 American Association for the Advancement of Science.

Seit den frühen 1990ern hat sich im allgemeinen Bereich der MOF-Forschung der Begriff der *retikulären Chemie* etabliert. Retikuläre Chemie (abgeleitet von *lat.* Reticulum = kleines Netz, Sieb) beschreibt die Verknüpfung von molekularen Bausteinen durch starke Bindungen zu porösen kristallinen mehrdimensionalen Gerüsten. Dies beschränkt sich allerdings nicht auf die zuvor beschriebenen metallorganischen Gerüstverbindungen, sondern umfasst auch sogn.

kovalente organische Gerüstverbindungen (*engl.* covalent organic frameworks, COFs). Kovalente organische Gerüstverbindungen beschreiben eine Klasse poröser, kristalliner Polymere, die zwei- oder dreidimensionale Strukturen durch Reaktionen zwischen molekularen organischen Bausteinen ausbilden. Aufgrund der kovalenten Bindungen weisen die Polymere eine hohe Stabilität auf.^{54,56,57,84}

5.1 Bausteine der Metallorganischen Gerüstverbindungen

5.1.1 Organische Linker

Wie bereits in Abschnitt 5 eingeführt, bestehen metallorganische Gerüstverbindungen aus zwei Grundbausteinen: anorganische (polynukleare) Sekundärbausteine (*engl.* secondary building units, SBUs) und organischen Liganden bzw. Linker. Die organischen Linker definieren die Metrik im MOF und zeichnen sich allgemein durch eine hohe Symmetrie aus. Der Aufbau der Linker kann durch ein vereinfachtes Konzept beschrieben werden, das aus drei modularen Bausteinen besteht: *Binding Group*, *Core Unit* und optionale *Extending Unit*. Die *Binding Unit* stellt endständige funktionelle Gruppen wie bspw. Carboxylat-, Azolat-, Phosphonat- und Sulfonat-Gruppen dar, die eine Koordination an SBUs ermöglichen. Carboxylatlinker stellen dabei die relevanteste Linkergruppe dar. Carboxylate haben entscheidende Vorteile im Vergleich zu neutralen *N-Donor*-Linkern wie bspw. Pyridine oder Nitrile: Carboxylate können aufgrund ihrer negativen Ladung andere positive Ladungen in SBUs ausgleichen, was zur Bildung ladungsneutraler MOFs führt. Darüber hinaus sorgen sie, aufgrund ihrer Chelateigenschaften für eine höhere strukturelle Rigidität und präzisere Ausrichtung. Carboxylate begünstigen zudem die Bildung stabiler polynuklearer SBUs. Aufgrund der starken Bindung zwischen den Carboxylatgruppen und den Metallzentren der SBUs verfügen entsprechende MOFs über eine vergleichsweise hohe thermische, mechanische und chemische Stabilität. Gleichzeitig weisen solche carboxylatbasierte MOFs dauerhaft poröse Strukturen mit hohen spezifischen Oberflächen auf.^{57,85–87}

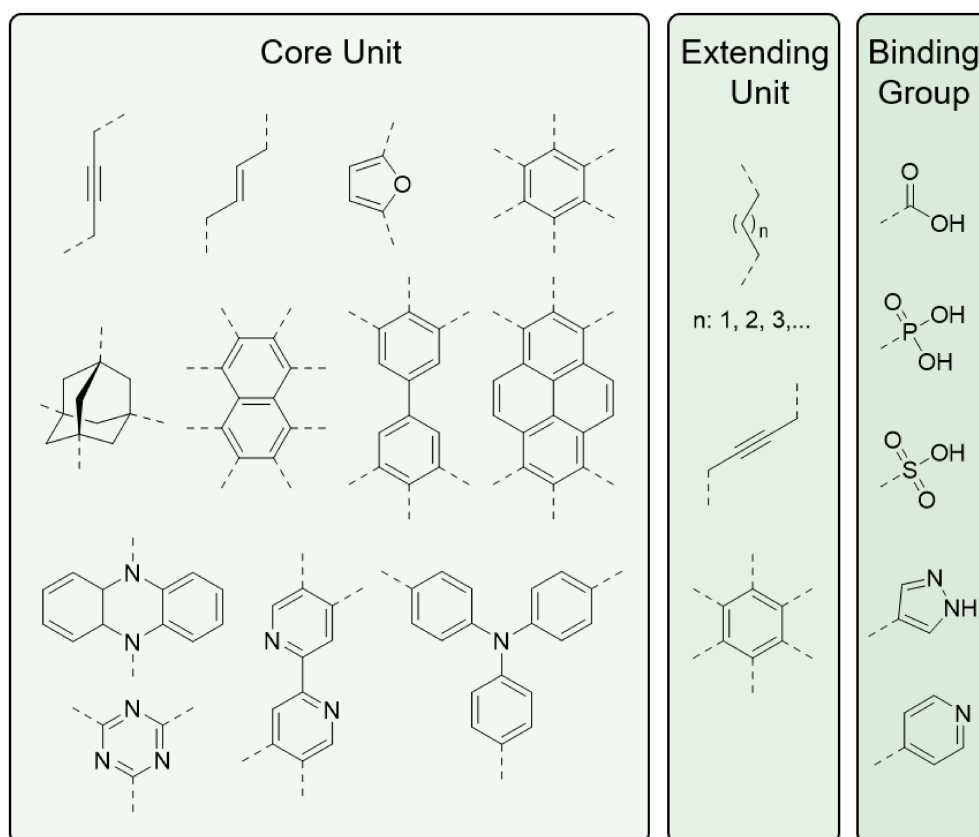


Abbildung 11: Schematische Darstellung der modularen Linker-Bausteine. Bei den hier dargestellten Bausteinen handelt es sich um eine allgemeine Zusammenstellung der gebräuchlichsten Strukturen.

Die *Core Unit* stellt das zentrale Strukturelement des Linkermoleküls dar und definiert nicht nur maßgeblich die Geometrie des finalen Linkers, sondern spielt auch bei der Linkersynthese eine entscheidende Rolle. Das zentrale Strukturelement des Linkers besteht in der Regel aus Kohlenwasserstoffen: (Cyclo)alkane, Alkene, Alkine und/oder Aromaten. Ferner existieren auch Linker, deren zentraler Strukturbausteine aus Heterocyclen oder Aminen besteht (Abbildung 12). Die *Core Units* können mittels einer *Extending Unit* erweitert werden. Dabei wird in drei verschiedene Gruppen unterschieden:

- *Lineare Gruppen*, die weder die Gesamtsymmetrie noch die Konnektivität verändern
- *Abgewinkelte Gruppen*, die die Gesamtsymmetrie ändern, aber nicht die Konnektivität
- *Verzweigte Gruppen*, die sowohl die Gesamtsymmetrie als auch die Konnektivität verändern

Mithilfe geeigneter Reaktionsmechanismen können die *Extending Unit* an den zentralen Strukturbaustein gekuppelt werden. Dabei kommen i.d.R. die gleichen Kupplungsreaktionen wie die bereits in Kapitel 4 beschriebenen zum Einsatz. Die Kreuzkupplungen sind in der präparativen organischen Chemie etablierte und zuverlässige Reaktionen, die die Synthese größerer Mengen mit hohen Ausbeuten ermöglichen. Die meisten *Extending Units* verfügen zusätzlich über geschützte *Binding Groups*. Klassische Schutzgruppen sind bspw. Methyl-

/Ethylester oder Trimethylsilyl). Entsprechend bedarf es für die Darstellung des finalen Linkers noch eines abschließenden Syntheseschritts in Form einer Entschützung.

Die Anzahl der *Extending Units* und der *Binding Groups* definiert die Anzahl der Verbindungen, die ein Linker zu benachbarten SBUs innerhalb eines MOFs ausbilden kann. Alle drei Linker-Bausteine können die Geometrie des finalen Linkers wesentlich beeinflussen und müssen entsprechend beim MOF-Design berücksichtigt werden.^{57,86}

Abbildung 12 beschreibt exemplarisch die zweistufige Synthese des MOF-Linkers 4,4',4'',4'''-(Pyren-1,3,6,8-tetrayl)tetrabenzoesäure. Ausgangsstoff bei der Synthese ist der polycyclische Aromat 1,3,6,8-Tetrabromopyren. In der ersten Stufe wird das 1,3,6,8-Tetrabromopyren (*Core Unit*) im Zuge einer Palladium-katalysierten Suzuki-Miyaura-Kupplung mit 4-Ethoxycarbonylphenylboronsäure (*Extending Unit* mit *Binding Group*) umgesetzt. Das Zwischenprodukt ist ein Carbonsäureester, der abschließend hydrolysiert bzw. entschützt wird. Das finale Produkt stellt eine symmetrische Carbonsäure dar.⁸⁸

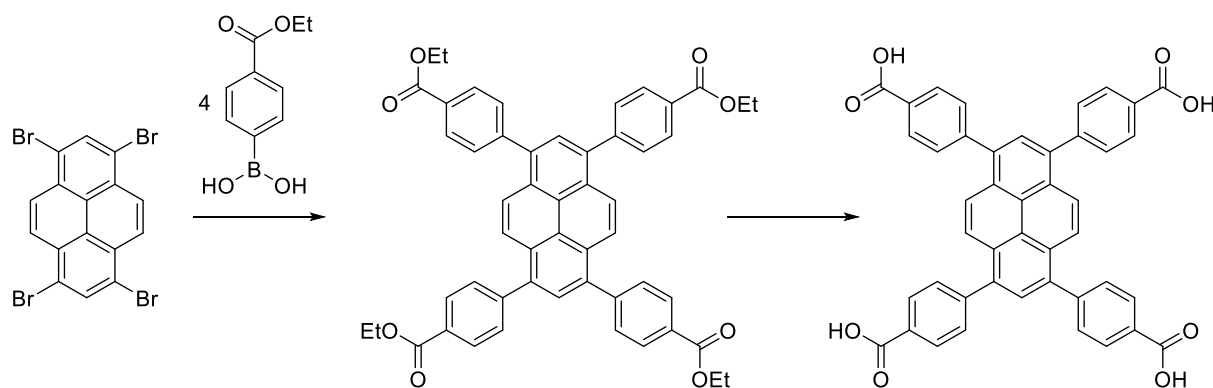


Abbildung 12. Beispielhafte Syntheseroute des Linkers 4,4',4'',4'''-(Pyren-1,3,6,8-tetrayl)tetrabenzoesäure.⁸⁸

5.1.2 Secondary building units (SBUs)

Der zweite elementare Bestandteil von MOFs sind die anorganischen polynuklearen Sekundärbausteine. Eingeführt wurde der Begriff 2005 um Zeolithe strukturell zu beschreiben. Das Konzept der SBUs dient allgemein der Vereinfachung und Klassifizierung von MOFs hinsichtlich ihrer Struktur bzw. Topologien. Die klar definierte Geometrie und die Gesamtkonnektivität der SBUs spielen eine entscheidende Rolle beim rationalen Design neuer MOFs nach geometrischen Konstruktionsprinzipien. Die geometrische und chemische Vielfalt der SBUs ermöglicht hierbei die Bildung einer Vielzahl unterschiedlicher MOF-Strukturen. Klassischerweise werden SBUs basierend auf ihrer Konnektivität n -c (n = Anzahl der Konnektivität) eingeteilt. Dabei müssen SBUs mindestens eine Konnektivität von 3-c aufweisen. Diese SBUs bilden zweikerniges Schaufelrad (*engl.* paddle wheel) $M_2(-CO_2)_3$ (z. B. $M = Cu^{2+}, Zn^{2+}$) dar.^{83,84} Ein Beispiel für eine entsprechende SBU findet sich im MOF PNMOF-3 ($Zn_4(NH_2BDC)_3(NO_3)(H_2O)_2$). Die Struktur besteht aus trigonalen Clustern, in denen zwei

Zinkatome durch die Carboxylatfunktionalitäten von drei NH_2BDC -Linkern verbrückt sind. Die verbleibenden Koordinationsstellen jedes Zinkatoms sind entweder mit einem Nitrat anion oder einem Wassermolekül besetzt, um die Ladungsneutralität der Gesamtstruktur zu gewährleisten. Daraus ergibt sich eine hexagonale, ekliptisch angeordnete Schichtstruktur mit der Topologie **hcb**.⁸⁹

In der MOF-Chemie sind SBUs mit einer Konnektivität von 4-c weit verbreitet. Diese SBU stellen ebenfalls ein zweikerniges Schaufelrad $\text{M}_2(-\text{CO}_2)_4$ (z.B. $\text{M} = \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Co}^{2+}$) dar. Hierbei ist jedes Metallion quadratisch-pyramidal von vier Sauerstoffatomen der verbrückenden Carboxylatfunktionalitäten und einem endständigen neutralen Liganden, meist Wasser, koordiniert. Aus entsprechenden SBU können in Kombination mit verschiedenen Linkern unterschiedliche MOF-Topologien hervorgehen. Eines der bekanntesten MOFs mit 4-c SBU ist HKUST-1 ($\text{Cu}_3(\text{TMA})_2$). Die Struktur setzt sich aus 4-c- $\text{Cu}_2(-\text{CO}_2)_4$ -SBU und Benzol-1,3,5-Tricarboxylat (TMA) zusammen. Das dreidimensionale MOF weist eine **tbo** Topologie auf, dass über quadratische Porenöffnungen ($9 \times 9 \text{ \AA}$) verfügt. Durch Aktivierung können die terminalen Wasserliganden entfernt werden, die axial an die SBU in HKUST-1 gebunden sind. Dadurch entstehen sog. *open metal sites*, deren Anwesenheit durch einen Farbwechsel des MOF von blau zu violett sichtbar ist.⁹⁰

6-c-SBU treten in der MOF-Chemie neben den zuvor beschriebenen 4-c-SBUs, am häufigsten auf. 6-c-SBU können aus verschiedenen Metallkationen hergestellt werden und unterschiedliche Geometrien aufweisen. Die Geometrien reichen von hochsymmetrischen oktaedrischen, trigonal prismatischen und hexagonal planaren Strukturen bis hin zu niedrigeren, stärker verzerrten Symmetrien. Einer der bekanntesten 6-c-SBU überhaupt ist der oktaedrische $\text{Zn}_4\text{O}(-\text{CO}_2)_6$ -SBU, der bspw. in der isoretikulären IRMOF-Reihe, MOF-150 oder MOF-177 vorkommt.^{76,91–93} Das MOF $\text{Zn}_4\text{O}(\text{TCA})_2$, auch bekannt als MOF-150 (TCA = 4,4',4''-Tricarboxytriphenylamin), verfügt über ein Netzwerk, bestehend aus dem trigonal-planarem Linker TCA und der oktaedrischen $\text{Zn}_4\text{O}(-\text{CO}_2)_6$ -SBU. Die dreidimensionale MOF-Struktur weist die Topologie **pyr-a** auf.⁹¹

Die genannten SBUs stellen lediglich eine kleine Auswahl möglicher SBU-Zusammensetzungen und Geometrien dar; auch können nahezu alle d- und f-Block-Elemente als SBU-Komponenten genutzt werden. Die Konnektivität von SBUs kann weit über 6-c hinausgehen. Darüber hinaus existieren in der MOF-Chemie neben den diskreten 0D-SBUs mit definierter Konnektivität auch eindimensionale unendliche Ketten-SBUs.^{94,95}

5.2 MOF-Synthese

Für die Darstellung von MOFs stehen verschiedene Synthesemethoden zur Auswahl. Die meisten Synthesen finden dabei in Lösung statt. Hierbei werden die Metallsalz- und Linkerlösungen entweder getrennt voneinander hergestellt und erst kurz vor der eigentlichen

Synthese miteinander vereint oder das Lösungsmittel wird direkt zu einer Mischung aus Metallsalz und Linker hinzugefügt. Eine entscheidende Rolle bei der Synthese spielen die Wahl des Lösungsmittels, die Reaktionstemperatur, -druck und -dauer sowie das Verhältnis der eingesetzten Stoffmengen. Eine erfolgreiche MOF-Synthese hängt allerdings von vielen zusätzlichen Reaktionsparametern wie bspw. Additiven, pH, Reaktivität, Redoxpotential, Löslichkeit etc. ab.^{96–98} Die solvothermale Methode ist aufgrund ihrer Einfachheit, synthetischen Flexibilität und Optimierungsmöglichkeiten die am häufigsten angewandte und etablierteste Methode in der MOF-Chemie. Die Reaktion findet zwischen dem Metallsalz und dem organischen Linker in einem geeigneten organischen Lösungsmittel statt. Je nach gewünschter Zielverbindung können auch mehrere Metallsalze, Linker oder Lösungsmittelmischungen verwendet werden. Klassische Lösungsmittel stellen Dimethylformamid, Diethylformamid, Acetonitril, Wasser, Aceton, Ethanol oder Methanol dar.⁹⁵ Solvothermale Reaktionen werden typischerweise oberhalb des kritischen Punkts eines Lösungsmittels in Autoklaven durchgeführt. Die solvothermale Methode ermöglicht hohe Ausbeuten und eine genaue Kontrolle der Kristallinität und der Größenverteilung der so erhaltenen Mikrokristallite des gewünschten Produkts.^{96–98}

Neben der solvothermalen Synthesemethode gibt es noch andere Methoden, wie bspw. die diffusionsbasierte, mechanochemische, elektrochemische oder Mikrowellenmethode. Jede dieser Methoden hat dabei ihre Vor- und Nachteile und sollte entsprechend der gewünschten Zielverbindung gewählt werden.⁹⁸

5.3 Mixed-metal metal-organic frameworks

Eine besondere Form der MOFs stellen sogenannte mixed-metal MOFs (MMMs) dar. Bei solchen MOFs bestehen die SBUs aus zwei oder mehreren verschiedenen Metallzentren, die unterschiedlich im MOF verteilt sein können. Ein Vorteil von mixed-metal MOFs gegenüber monometallischen MOFs ist, dass durch ein weiteres Metallkation die Eigenschaften noch spezifischer hinsichtlich der finalen Struktur und des Anwendungszwecks optimiert werden können. Durch die Kombination mehrerer Metallkationen können verschiedene Synergieeffekte entstehen und genutzt werden. Besonders interessant sind MMMs bei der (heterogenen) Katalyse, Gassorption und -speicherung.^{99–101}

MMMs sind primär über zwei verschiedene Synthesestrategien zugänglich. Eine vereinfachte Übersicht beider Strategien ist in Abbildung 13 dargestellt. Die erste Methode beschreibt die im letzten Abschnitt beschriebene solvothermale Synthese. Der Ablauf der Synthese verläuft prinzipiell analog, jedoch kommen hier mehrere Metallsalze zum Einsatz. Die Synthesestrategie zeichnet sich sowohl durch ihre Einfachheit als auch durch die geringe Anzahl an Syntheseschritten aus. Der Nachteil ist jedoch die fehlende Kontrolle über die endgültige Metallverteilung im MOF/MMM. Oftmals treten monometallische MOFs

phasensegregiert auf, während in einer weiteren Phase noch (Hydroxy)oxid-Cluster des zweiten Metallkations vorliegen. Vor diesem Hintergrund sind weiterführende Analysen wie bspw. Röntgenphotoelektronenspektroskopie (*engl.* X-ray photoelectron spectroscopy, XPS) oder Atomabsorptionsspektrometrie (AAS) notwendig. Eine homogene Metallverteilung in einem MMM wird am ehesten erreicht, wenn die eingesetzten Metallionen die gleichen Coulomb-Ladungen, Ionenradien und ein ähnliches chemisches Verhalten aufweisen. Es sind allerdings auch MMMs bekannt, die durch solvothermale Synthese hergestellt wurden und dabei zwei sehr unterschiedliche Metallionen enthalten.^{99,100,102,103}

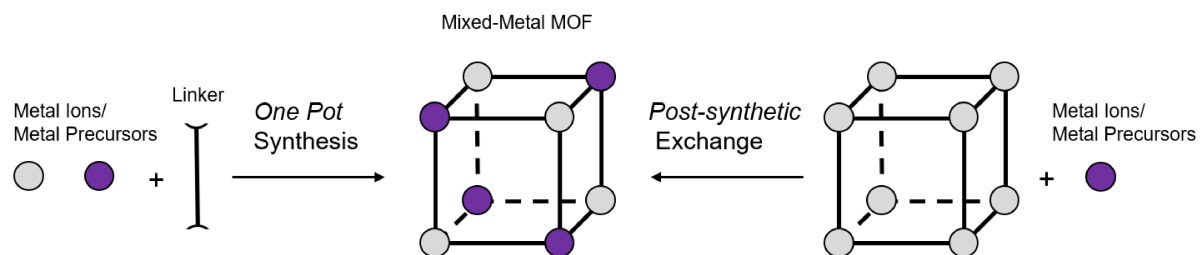


Abbildung 13: Schematische Syntheserouten von Mixed-metal MOFs. (Angelehnt an Ref.¹⁰⁰.)

Eine weitere Synthesestrategie ist die postsynthetische Modifikation bereits bestehender MOFs. Diese Syntheseroute ermöglicht die Darstellung von MMMs, die bei der solvothermalen Synthese aufgrund der unterschiedlichen Reaktivität der Metallionen nicht realisierbar sind. Die postsynthetischen Modifizierungen umfassen den Austausch von einzelnen Metallionen oder kompletter SBUs, die Einlagerung neuer Metalle oder die Modifizierung eines epitaktischen Wachstums. Mithilfe dieser Strategie ist es zudem möglich, gezielt definierte Prozentsätze neuer Metalle in MMMs einzubringen. Zusätzlich können mehr als zwei unterschiedliche Metalle in ein MMM eingebaut werden. Dies ermöglicht eine gezielte Anpassung des MMM an den späteren Anwendungszweck.^{99,104–107}

5.4 Anwendungsbereiche

MOF und andere retikuläre Gerüstverbindungen können aufgrund ihrer einzigartigen Eigenschaften in vielen verschiedenen Anwendungsbereichen wie den erneuerbaren Energien, Umweltanwendungen, Katalyse, Sensorik und Pharmazie/Medizin eingesetzt werden. Das breite Anwendungsspektrum wird durch ihre (kristallinen) Strukturen, großen spezifischen Oberflächen, maßgeschneiderten Porenöffnungen und Porengrößen sowie ihrer großen strukturellen Vielfalt bestimmt.^{108–110}

Die Hauptanwendung von MOFs, die in der Literatur beschrieben wird, ist die Speicherung und Abtrennung von Gasen. Eine hohe Oberfläche begünstigt die Adsorption von Gasen, während das große Porenvolumen die Gasmenge bestimmt, die in einem MOF gespeichert werden kann. Besonders hervorzuheben sind hier die Wasserstoff- und Methanspeicherung, sowie die CO₂-Abscheidung.^{111,112} Darüber hinaus können MOFs in der Pharmazie als Drug-

Delivery-Systeme eingesetzt werden. Mittels Einlagerung eines Therapeutikums in ein geeignetes MOF können Arzneimittel geschützt an den vorgesehenen Wirkort transportiert und dort gezielt freigesetzt werden. Durch die Funktionalisierung der Linker und die genaue Einstellung der Porengröße können MOFs auch gezielt an bestimmte Wirkstoffe angepasst werden.^{113,114} MOFs können zudem als Alternative für heterogene Katalysatoren betrachtet werden, die über die gleichen katalytischen Eigenschaften verfügen. Durch die gezielte Wahl der SBU und der organischen Linker können MOFs synthetisiert werden, die strukturell den konventionellen Katalysatoren ähneln und auch die gleiche katalytische Aktivität aufweisen. Das katalytisch-aktive Zentrum kann sich dabei sowohl am SBU selbst als auch am organischen Linker befinden.¹¹⁵ Weiterhin ist es möglich, die physikochemische Umgebung der gewünschten Katalyse anzupassen, vergleichbar mit dem *Induced-fit*-Modell bei Enzymen. Auf dieser Grundlage kann eine hoch selektive Katalyse ermöglicht werden.^{109,116}

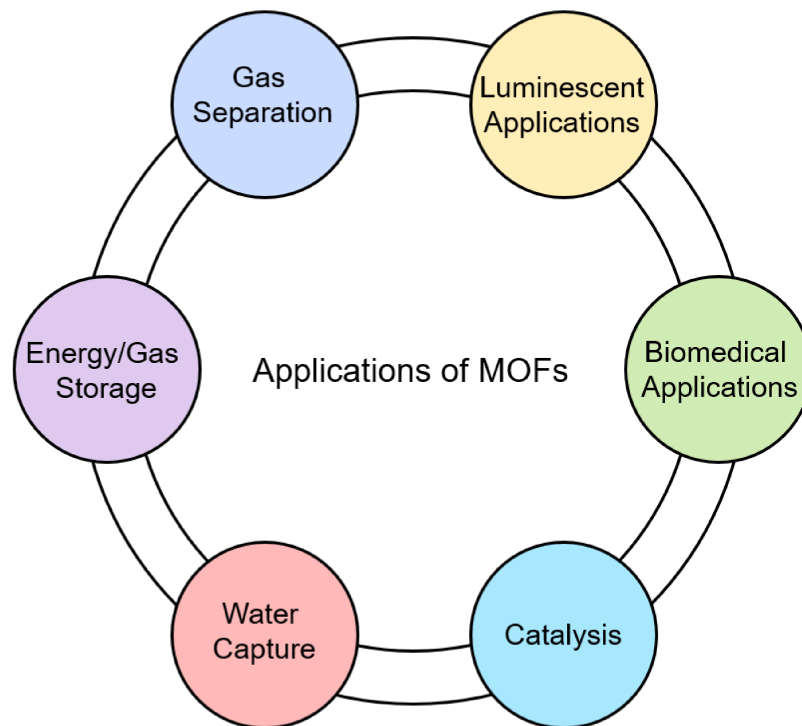


Abbildung 14: Allgemeine und vereinfachte Übersicht der Anwendungsbereiche von MOF. (Angelehnt an Ref. ¹¹⁷.)

6 Motivation

Ziel dieser Arbeit ist die Synthese und Charakterisierung neuartiger Dihydrophenazin-basierter Leuchtstoffe und metallorganischer Gerüstverbindungen (*engl.* metal-organic framework, MOFs). Die Ergebnisse sind hinsichtlich potentieller Anwendungen in der Optoelektronik und Sensorik von Interesse, insbesondere als TADF-Emitter (*engl.* thermally activated delayed fluorescence) in organischen Leuchtdioden (*engl.* organic light emitting diode, OLEDs). Ein weiterer Schwerpunkt liegt auf der Strukturaufklärung neuartiger Koordinationspolymere und MOFs sowie deren elektrochemischer Eigenschaften.

Zentrales Strukturelement stellt grundlegend der Heteroaromat Dihydrophenazin dar. Es handelt sich um ein kompaktes System mit einer hohen chemischen und physikalischen Stabilität sowie hervorragenden photophysikalischen Eigenschaften, gekennzeichnet durch einen modularen Aufbau und eine hohe synthetische Flexibilität. Ausgehend von diesem Strukturelement lassen sich mittels *kombinatorischer Chemie* eine Vielzahl linearer, symmetrischer Moleküle ableiten. Diese Moleküle eignen sich potenziell als organische TADF-Emitter, multifunktionelle MOF-Linker oder auch CTF-Monomere (*engl.* covalent triazine framework). Das Dihydrophenazin kann mittels einer palladiumkatalysierten Buchwald-Hartwig-Kupplung mit verschiedenen Arylhalogeniden zu den gewünschten Zielverbindungen umgesetzt werden. Die Arylhalogenide sollen entsprechend des finalen Verwendungszwecks verschiedene (endständige) funktionelle Gruppen aufweisen, wie beispielsweise Nitril- oder (evtl. daraus hydrolysierte) Carbonsäuregruppen.

Ziel ist die Synthese und Analyse der TADF-Eigenschaften mehrerer linearer, symmetrischer Dihydrophenazinderivate mit Akzeptor-Donor-Akzeptor-Topologie (A-D-A). Aufbauend auf dem literaturbekannten TADF-Farbstoff 4,4'-(Phenazine-5,10-diyl)dibenzonitril soll der Schwerpunkt dabei auf der Verwendung von Benzonitrilen als Akzeptorgruppen liegen. Ziel ist es, die Auswirkungen des Substitutionsmusters der Akzeptoreinheit auf die photophysikalischen Eigenschaften zu analysieren. Dabei sollen verschiedene Substitutionsmuster wie beispielsweise eine Meta-Substitution der Nitrilgruppe, zusätzliche Alkyl-/Phenylgruppen oder eine Verlängerung der Akzeptorgruppe betrachtet werden.

Ein weiteres Ziel ist die Synthese und Analyse linearer, bifunktionaler Linker für die Darstellung neuer Koordinationspolymere oder MOFs. Ein vielversprechender Kandidat ist das Dihydrophenazinderivat 4,4'-(Phenazin-5,10-diyl)dibenzoesäure, das in einer dreistufigen Synthese hergestellt werden soll. In Kombination mit dieser Dicarbonsäure sollen verschiedene Metallsalze zu kristallinen lumineszenten Koordinationspolymeren bzw. MOFs umgesetzt werden. Ausgangspunkt stellen die literaturbekannten Zr(IV)- und Cu(II)-MOF mit dem beschriebenen Linker dar. Darauf aufbauend sollen weitere Metallsalze, wie bspw. Zn(II)- und Co(II)-Nitrate, eingesetzt werden.

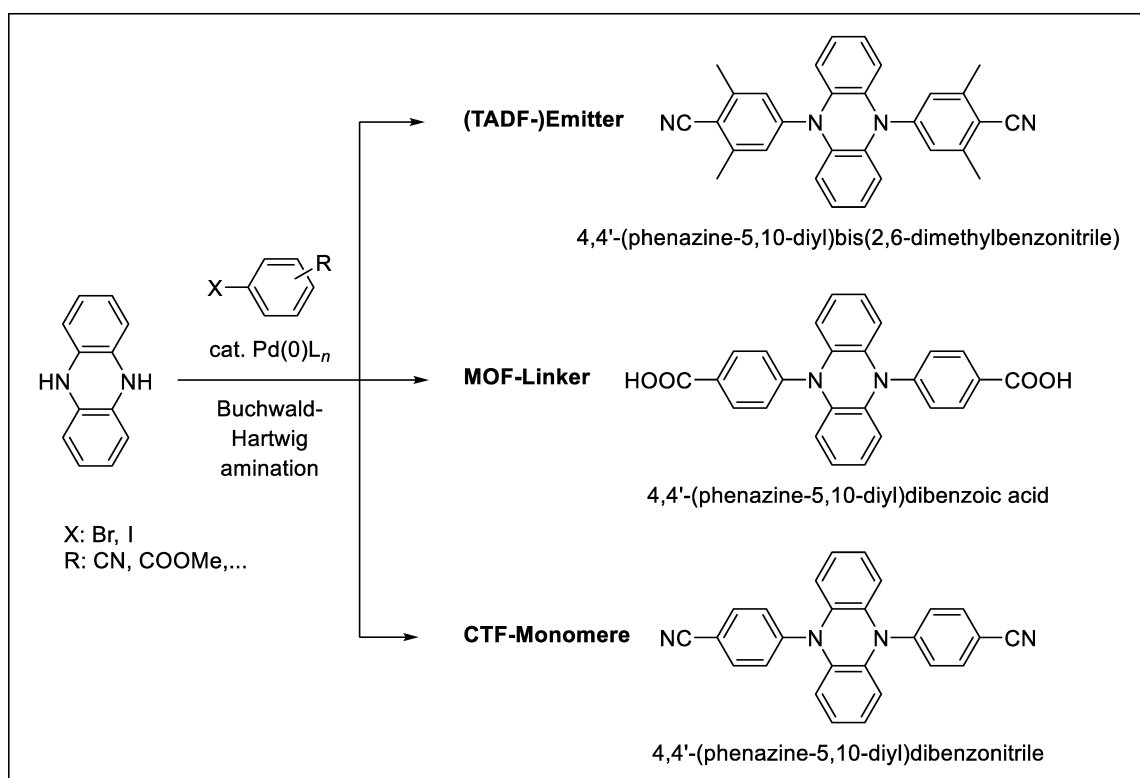


Abbildung 15: Schematischer Überblick zur Darstellung verschiedener beispielhafter Dihydrophenazin-Derivate. Das Beispiel 4,4'-(phenazin-5,10-diyl)dibenzonitril stellt sowohl ein CTF-Monomer als auch einen TADF-Emitter dar. Umgekehrt ist es auch möglich 4,4'-(phenazin-5,10-diyl)bis(2,6-dimethylbenzonitril) als CTF-Monomer zu verwenden.

7 Kumulativer Teil

In diesem Kapitel werden die Ergebnisse vorgestellt, die im Rahmen dieser Dissertation entstanden sind und in internationalen Fachjournalen eingereicht oder bereits veröffentlicht wurden. Im Rahmen dieser Dissertation konnten zwei Publikationen mit federführender Erstautorenschaft veröffentlicht werden. Ein weiteres Manuskript wurde zur Publikation eingereicht. Die Erstautorenschaften sind chronologisch nach dem Veröffentlichungsdatum geordnet.

Den Veröffentlichungen als Erstautor wird jeweils eine kurze Zusammenfassung mit Einordnung in den Kontext der Gesamtarbeit vorangestellt. Abschließend werden die Beiträge aller an den jeweiligen Veröffentlichungen beteiligten Autoren tabellarisch dargestellt. Es soll weiterhin darauf hingewiesen werden, dass die in den Veröffentlichungen verwendeten Literaturangaben in einem jeweils separaten Quellenverzeichnis aufgeführt sind. Zudem folgen die Nummerierungen von Abbildungen und Tabellen nicht der Nummerierung des Haupttextes, sondern der Nummerierung der jeweiligen Veröffentlichung. Die in der jeweiligen veröffentlichten Publikation vorhandenen Seitenzahlen werden ebenfalls angegeben.

7.1 Enhanced Solid-State Fluorescence of Flavin Derivatives by Incorporation in the Metal-Organic Frameworks MIL-53(Al) and MOF-5

Dietrich Püschel, Simon Hédé, Iván Maisuls, Simon-Patrick Höfert, Dennis Woschko, Ralf Kühnemuth, Suren Felekyan, Claus A. M. Seidel, Constantin Czekelius, Oliver Weingart, Cristian A. Strassert and Christoph Janiak

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Kurzzusammenfassung

Die Flavinderivate 10-Methyl-Isoalloxazin (MIA) und 6-Fluoro-10-Methyl-Isoalloxazin (6F-MIA) wurden in zwei unterschiedliche metallorganische Gerüstverbindungen (MOFs), MIL-53(Al) und MOF-5, eingelagert. Hierbei wurde eine postsynthetische, diffusionsbasierte Einlagerung in mikrokristallines MIL-53-Pulver und ein *in-situ*-Ansatz bei der Synthese von MOF-5 angewendet. Die maximale Farbstoffbeladung betrug bis zu 5.2 Gew.-% (6F-MIA@MOF-5). Ergebnisse der zeitaufgelöste Fluoreszenzspektroskopie zeigten, dass die Fluoreszenzlebensdauer von Flavin@MOF 4 ± 1 ns beträgt, was mit der Lebensdauer in Lösung vergleichbar ist. Im Vergleich zu den festen Flavinfarbstoffen mit weniger als 1 ns aber deutlich verlängert, wodurch das Konzept der "*festen Lösungen*" für Farbstoff@MOF-Komposite bestätigt wird. Die Fluoreszenzquantenausbeute (Φ_F) der Flavin@MOF-Komposite ist etwa halb so groß wie in Lösung, aber deutlich höher als die Flavinfarbstoffe im Feststoff. Sowohl die Fluoreszenzlebensdauer als auch die Quantenausbeute von Flavin@MOF nehmen mit der Flavinbeladung in MIL-53 aufgrund der Bildung verschiedener J-Aggregate ab. Theoretische Berechnungen mit Hilfe von *plane-wave*- und QM/MM-Methoden stimmen zudem gut mit den experimentellen Ergebnissen überein.

MIA@MOF-Strukturen zeigen keine π - π -Wechselwirkungen mit den Porenwänden, sondern nur schwache van-der-Waals-Wechselwirkungen, was die erhöhte Fluoreszenzlebensdauer und Quantenausbeute der Flavine in den Kompositen im Vergleich zu den reinen Feststoffen erklärt.

Um die Orientierung der Flavine in MOFs zu analysieren, wurden Fluoreszenzanisotropie-Bilder von einzelnen Flavin@MOF-5-Kristallen und einem *static ensemble* von Flavin@MIL53-Mikrokristallen gemessen. Auf Grundlage der Bildinformationen, Anisotropieverteilungen und der Gesamtkurve der zeitaufgelösten Anisotropiekurven in Kombination mit theoretischen Berechnungen kann nachgewiesen werden, dass alle fluoreszierenden Flavinmoleküle eine definierte und ziemlich homogene Orientierung im MOF-Gerüst haben. Zusammenfassend lässt sich sagen, dass die Einlagerung von Flavinen in MOFs zu Festkörpermateriale mit erhöhter Steifigkeit, stabilisierter Konformation, definierter Ausrichtung und verringerten Aggregationen der Flavine führt, was wiederum zu einer erhöhten Fluoreszenzlebensdauer und Quantenausbeute sowie kontrollierbaren photolumineszenten und photophysikalischen Eigenschaften führt.

Anteile an der Publikation

- Durchführung der Synthese und Charakterisierung der Flavinfarbstoffe durch Prof. Dr. C. Czekelius.
- Durchführung der Synthese und Charakterisierung der Flavin@MOF-Komposite durch S.-P. Höfert.
- Selbstständige Synthese und Charakterisierung von Mil-53(Al) und MOF-5 mittels PXRD.
- Reproduktion und Charakterisierung der Flavin@MOF-5-Komposite mittels NMR, UV/Vis, IR, in Kooperation mit Dr. D. Woschko.
- Durchführung der spektroskopischen Messungen der Flavin@MOF-Komposite sowie Auswertung, graphische Darstellung und Interpretation der Ergebnisse durch Dr. R. Kühnemuth, Dr. S. Felekyan, Prof. Dr. C. A. M. Seidel sowie Dr. I. Maisuls und Prof. Dr. C. A. Strassert.
- Durchführung der theoretischen Berechnungen der Flavin@MOF-Komposite sowie graphischen Darstellung und Interpretation der Ergebnisse durch Dr. S. Hede und Dr. O. Weingart.
- Anfertigung eines ersten Manuskripts und der *supporting information* für eine wissenschaftliche Publikation basierend auf den experimentellen und theoretischen Ergebnissen.
- Die Publikation wurde im internationalen Journal *Molecules* mit Prof. Dr. C. Janiak eingereicht.
- Überarbeitung des Manuskripts durch Prof. Dr. C. Janiak, insbesondere durch Prof. Dr. C. A. M. Seidel.

Article

Enhanced Solid-State Fluorescence of Flavin Derivatives by Incorporation in the Metal-Organic Frameworks MIL-53(Al) and MOF-5

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Abstract: The flavin derivatives 10-methyl-isoalloxazine (MIA) and 6-fluoro-10-methyl-isoalloxazine (6F-MIA) were incorporated in two alternative metal-organic frameworks, (MOFs) MIL-53(Al) and MOF-5. We used a post-synthetic, diffusion-based incorporation into microcrystalline MIL-53 powders with one-dimensional (1D) pores and an in-situ approach during the synthesis of MOF-5 with its 3D channel network. The maximum amount of flavin dye incorporation is 3.9 wt% for MIA@MIL-53(Al) and 1.5 wt% for 6F-MIA@MIL-53(Al), 0.85 wt% for MIA@MOF-5 and 5.2 wt% for 6F-MIA@MOF-5. For the high incorporation yields the probability to have more than one dye molecule in a pore volume is significant. As compared to the flavins in solution, the fluorescence spectrum of these flavin@MOF composites is broadened at the bathochromic side especially for MIA. Time-resolved spectroscopy showed that multi-exponential fluorescence lifetimes were needed to describe the decays. The fluorescence-weighted lifetime of flavin@MOF of 4 ± 1 ns also corresponds to those in solution but is significantly prolonged compared to the solid flavin dyes with less than 1 ns, thereby confirming the concept of “solid solutions” for dye@MOF composites. The fluorescence quantum yield (Φ_F) of the flavin@MOF composites is about half of the solution but is significantly higher compared to the solid flavin dyes. Both the fluorescence lifetime and quantum yield of flavin@MOF decrease with the flavin loading in MIL-53 due to the formation of various J-aggregates. Theoretical calculations using plane-wave and QM/MM methods are in good correspondence with the experimental results and explain the electronic structures as well as the photophysical properties of crystalline MIA and the flavin@MOF composites. In the solid flavins, π -stacking interactions of the molecules lead to a charge transfer state with low oscillator strength resulting in aggregation-caused quenching (ACQ) with low lifetimes and quantum yields. In the MOF pores, single flavin molecules represent a major population and the computed MIA@MOF structures do not find π -stacking interactions with the pore walls but only weak van-der-Waals contacts which reasons the enhanced fluorescence lifetime and quantum yield of the flavins in the composites compared to their neat solid state. To analyze the orientation of flavins in MOFs, we measured fluorescence anisotropy images of single flavin@MOF-5 crystals and a static ensemble flavin@MIL53 microcrystals, respectively. Based on image information, anisotropy distributions and overall curve of the time-resolved anisotropy curves combined with theoretical calculations, we can prove that all fluorescent flavins species have a defined and rather homogeneous orientation in the MOF framework. In MIL-53, the transition dipole moments of flavins are orientated along the 1D channel axis, whereas in MOF-5 we resolved an

average orientation that is tilted with respect to the cubic crystal lattice. Notably, the more hydrophobic 6F-MIA exhibits a higher degree order than MIA. The flexible MOF MIL-53(Al) was optimized essentially to the experimental large-pore form in the guest-free state with QuantumEspresso (QE) and with MIA molecules in the pores the structure contracted to close to the experimental narrow-pore form which was also confirmed by PXRD. In summary, the incorporation of flavins in MOFs yields solid-state materials with enhanced rigidity, stabilized conformation, defined orientation and reduced aggregations of the flavins, leading to increased fluorescence lifetime and quantum yield as controllable photo-luminescent and photo-physical properties.

Keywords: flavins; 10-methyl-isoalloxazine; metal-organic framework (MOF); MIL-53; MOF-5; fluorescence; flavin@MOF; solid solution; dye anisotropy; fluorescence lifetime; multiparametric fluorescence microscopy

1. Introduction

Flavins represent a ubiquitous group of compounds in nature [1–4]. The basic structure consists of an isoalloxazine ring system (Figure 1) that has strong fluorescent properties [4,5]. Besides the well-known vitamin B2, flavins or riboflavins occur predominantly in combination with proteins as the so-called flavoproteins [1,6,7]. Flavoproteins play an important role in the respiratory chain of cells [1]. In addition, light-dependent biological processes such as flowering and circadian rhythm often employ this class of chromophore [8,9]. Flavins that are not bound to proteins are of great interest due to their photochemical and photophysical properties [10]. As in nature, flavins are used as photo-redox catalysts due to their redox properties [11,12]. In aqueous solution, all flavins exhibit strong absorptions in the ultraviolet and visible range. The absorption spectra typically show four bands with high molar absorptivities ($>10^4 \text{ L}^{-1} \text{ mol cm}^{-1}$) which are attributed to $\pi \rightarrow \pi^*$ excitations [12–14]. The exact position of the absorption maxima, the absorptivity and the photoluminescence quantum yield depend significantly on the chemical structure of the flavin derivative and the chemical-physical environment, including solvatochromic effects [11,12,15,16].

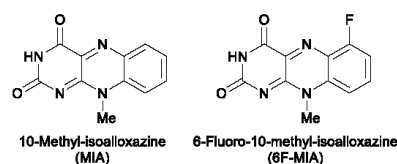


Figure 1. 10-Methyl-isoalloxazine (MIA) and the mono-fluorinated derivative 6-fluoro-10-methyl-isoalloxazine (6F-MIA) [17].

In their neat solid state, the photoluminescence of dye molecules is often quenched by nonradiative processes. The incorporation of luminescent dye molecules into metal-organic frameworks (MOFs) as a dye@MOF composite tries to exploit the photophysical properties of single molecules in a well-defined solid-state environment for applications such as white-light emission, upconversion, non-linear optics, biological fluorescent imaging, chemical sensing, optical thermometry and others [18–23]. The structure and pore environment of MOF compounds can be designed by the selection of organic linkers and the metal cluster secondary building units (SBUs) [24–31]. Through incorporation into MOFs, the dye molecules could be protected from dynamic quenching, e.g., by O_2 or solvent interactions. Aggregation-caused quenching (ACQ) of the dye in the solid-state is also effectively prevented by the confinement of separated single molecules in the pore system [18,32]. This protection could ensure consistent luminescence even under harsh environmental conditions. Conversely, targeted quenching of dyes by the selective addi-

tional adsorption of analyte species in dye@MOF composites could be interesting in sensor technologies [18,33–40].

A prerequisite for the MOF as a host for a dye guest with unchanged fluorescence is a minimal interference of MOF and dye. If the MOF should just act as a host matrix then ideally the MOF should show no fluorescence and color. Accordingly, aluminum-based MIL-53, $[\text{Al}(\text{OH})(\text{bdc})]$ (bdc = benzene-1,4-dicarboxylate) [41–50] and zinc-based MOF-5, $[\text{Zn}_4\text{O}(\text{bdc})_3]$ [51,52] are promising host networks (see Section S3, Supplementary materials for structure details).

The crystalline MOF host structures are often seen to give also a highly-ordered packing of the chromophore guests. Such an optimal alignment in host-guest MOF hybrid materials would be needed for polarized nonlinear optical responses [20,53] or to tune exciton coupling [54]. Yet, a correlation between photoresponse and anisotropy of dye guest molecules in ordered host matrices appears to be seldom done, e.g., in clays [55,56]. Here we chose the prototypical and well-characterized MOFs MIL-53(Al) with its periodic one-dimensional channels and MOF-5 with its three-dimensional orthogonal channel structure (Figure 2) for a proof-of-principle analysis of the anisotropy of encapsulated flavin dye molecules in these MOFs.

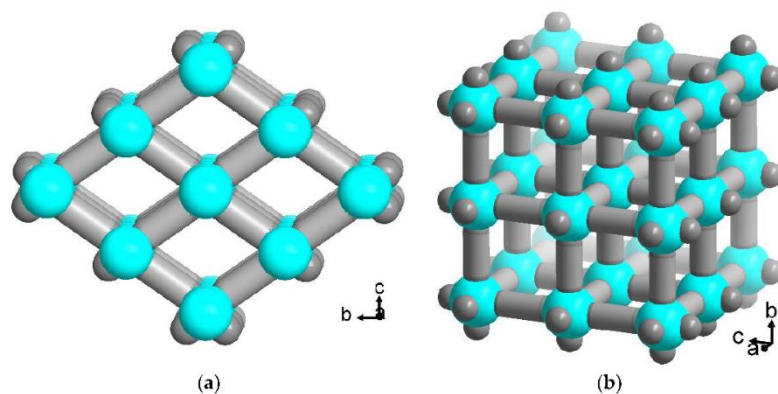


Figure 2. Schematic presentation of the periodic channel structures in (a) MIL-53, $[\text{Al}(\text{OH})(\text{bdc})]$ and (b) MOF-5, $[\text{Zn}_4\text{O}(\text{bdc})_3]$ (bdc = benzene-1,4-dicarboxylate) (The inorganic building units $[\text{AlO}_6]$ and $[\text{Zn}_4(\text{O})(\text{O}_2)_6]$, respectively, are represented in cyan and the bdc linker schematically as a grey rod; see Section S3, Supplementary materials for structure details). (Structure images were drawn with Diamond [57] from the deposited cif files under CCDC-no./Refcode 220476/SABVUN [41] and 256966/SAHYOQ [52,58]).

Furthermore, single crystals with an average diameter of 100 μm can be obtained for MOF-5 which allow the imaging of the embedded flavin with confocal laser scanning microscopy (CLSM) [59].

To the best of our knowledge we are not aware of flavin@MOF composites. Here, we report the incorporation of the flavin derivatives 10-methyl-isoalloxazine (MIA) and 6-fluoro-10-methyl-isoalloxazine (6F-MIA) (Figure 1) in the prototypical MOFs MIL-53 and MOF-5 and analyze the effects of the flavin@MOF composites on emission wavelength, the fluorescence lifetimes and photoluminescence quantum yields in comparison to the neat solid state and solution. The electronic structures of crystalline MIA, MIA@MIL-53 and MIA@MOF-5 and the resulting luminescent properties were calculated with plane-wave and QM/MM methods and compared with the experimental data.

2. Results and Discussion

The incorporation of the flavin derivatives 10-methyl-isoalloxazine (MIA) and 6-fluoro-10-methyl-isoalloxazine (6F-MIA) into MIL-53 and MOF-5 was carried out using a post-synthetic, diffusion-based incorporation into microcrystalline MIL-53 powders and an in situ embedding during MOF-5 synthesis.

2.1. Flavin@MIL-53 Synthesis

For the post-synthetic wet infiltration of MIL-53, different quantities of a saturated MIA or 6F-MIA solution in chloroform were added to the activated MOF MIL-53-lp and the suspension stored on an orbital shaker until all the solvent had been evaporated. The flavin@MIL-53 composites were washed with chloroform and then dried at 60 °C under dynamic vacuum. The MIA@MIL-53 composites contained 0.4 to 2.7 wt% of the flavin in the MOF and the 6F-MIA@MIL-53 composites between 0.1 to 1.5 wt% (see Supplementary Materials for details).

To further verify the incorporation of the flavins in the MOFs, nitrogen adsorption isotherms were recorded at 77 K (Figure S16). For very small amounts of incorporated flavin in MIL-53 (<1 wt% for MIA and 0.1 wt% for 6F-MIA), a slight increase in the internal surface area may occur (Table 1), which can be attributed to an additional washing effect exerted by shaking in the flavin solution. The proportional decrease in BET surface area and pore volume (Table 1) with an increase in flavin amount indicates successful incorporation into the network. The initial S_{BET} value of 1130–1150 m²/g for MIL-53 decreases to 80 m²/g (MIA@MIL-53) and 40 m²/g (6F-MIA@MIL-53), corresponding to a nearly nonporous structure which is due to pore blocking by occupation of the pore mouths with the flavin molecules. For the small wt% of the flavin the pore volume of the large-pore form of MIL-53 cannot be completely filled. Based on the crystallographic density ρ in the crystal structure of MIA of $\rho = 1.6 \text{ g/cm}^3$ [60] and $1/\rho = 0.63 \text{ cm}^3/\text{g}$, the maximum flavin loading of ~4 wt%, that is 0.04 g(flavin)/g(composite), would only occupy a volume of 0.025 cm³/g or about 6% of the determined total pore volume of ~0.5 cm³/g in neat MIL-53.

Table 1. Results of nitrogen sorption measurements for MIL-53 and flavin@MIL-53.

Compound	Flavin Loading [wt%] ^a	S_{BET} [m ² /g]	$V_{\text{pore(total)}}$ [cm ³ /g] ^b	$V_{\text{pore(micro;NLDFT)}}$ [cm ³ /g] ^c
MIL-53-lp literature	-	1150 [61]	0.53	0.53
	-	1140 [41]	n.a.	n.a.
MIL-53-lp synthesized	-	1130	0.45	0.43
MIA@MIL-53	0.4	1290	0.52	0.50
	0.8	1130	0.47	0.46
	1.6	1000	0.43	0.43
	2.0	890	0.41	0.42
	2.7	340	0.17	0.20
	3.9	80	0.05	0.09
6F-MIA@MIL-53	0.1	1150	0.49	0.49
	0.5	890	0.41	0.42
	1.0	600	0.28	0.30
	1.5	40	0.02	0.04

^a Calculated by UV-VIS from initial flavin concentration. ^b Total pore volume at $p/p_0 = 0.50$ for pores $\leq 2 \text{ nm}$.

^c Micropore volume calculated from NLDFT for pores $\leq 2 \text{ nm}$.

When we consider the MIL-53 formula unit of $[\text{Al}(\text{OH})\text{bdc}]$ ($M = 208.11 \text{ g/mol}$), then there is one channel segment of 13 Å (which is about the length of a MIA molecule) for 8 formula units. At a loading of 4 wt% MIA@MIL-53 we have 0.04 g MIA (0.175 mmol) in 0.96 g MIL-53 (4.6 mmol). Thus, the molar ratio of MIA molecules to the channel segments of 13 Å is $0.175/(4.6/8) = 0.3$ or ~3.3 channel segments per MIA molecule. In other words, on average at this loading the MIA molecules can be $\sim 2 \times 13 \text{ Å} = 26 \text{ Å}$ apart, that is separated

by 26 Å. At a loading of 1.5 wt% 6F-MIA@MIL-53, we have 0.015 g MIA (0.06 mmol) in 0.985 g MIL-53 (4.7 mmol). Thus, the molar ratio of 6F-MIA molecules to the channel segments of 13 Å is $0.06:(4.7/8) = 0.1$ or ~10 channel segments per 6F-MIA molecule. On average at this loading the 6F-MIA molecules can be $\sim 9 \times 13 \text{ Å} = 117 \text{ Å}$ separated along a channel. Other diffusion-based incorporations into MOFs have shown that in such a post-synthetic modification the molecules remain trapped close to the pore mouths [59]. For MIL-53 with its flexibility and breathing mode, formation of the narrow-pore form can also occur upon activation, which precedes the nitrogen sorption measurement.

The phase analysis of the flexible MIL-53 network structure after flavin insertion and before activation by powder X-ray diffraction (PXRD) shows a superposition of the three MIL-53 phases from the comparison of the MIA@MIL-53 composites with the simulated MIL-53-as, MIL-53-np and MIL-53-lp diffractograms (Figure S17a). The samples with the two highest loadings (2.7 wt% and 3.9 wt% for MIA, 1.0 wt% and 1.5 wt% for 6F-MIA) were measured before and after activation (Figure S17b). The incorporated flavin affects the phase which the flexible MIL-53 network assumes. A loading of up to 2.7 wt% MIA gives only the narrow-pore form after activation which is understandable if the flavin molecules would occupy little of the inner pore volume and do not penetrate deep into the channels. At a loading of 3.9 wt% MIA, a superposition of the large- and narrow-pore form remains (Figure S17b). The comparison of the 6F-MIA@MIL-53 composites with the simulated MIL-53 PXRDs patterns show good matches with the MIL-53-lp form, independently of incorporated flavin amounts (Figure S18a). For 1.0 wt% 6F-MIA@MIL-53 after activation the PXRD is also a superposition of the large- and narrow-pore phases (Figure S18b). At the maximum loading of 1.5 wt% of 6F-MIA, almost no change in the diffractogram is evident upon activation, indicating retention of the large-pore form with just a trace formation of the narrow-pore phase (Figure S18b).

2.2. Flavin@MOF-5 Synthesis

The flavins were incorporated in situ into MOF-5, that is during the MOF formation, in order to achieve a uniform distribution and pore filling of the flavins throughout the network [51,59]. From a comparison of the dimensions of MIA and 6F-MIA ($4 \times 8.5 \times 12 \text{ Å}$) (Figure S12) with the pore diameter of 15 Å in MOF-5, which is larger than its pore window size ($8 \times 8 \text{ Å}$) (Figure S15), the flavin molecules can be very well incorporated during the crystal formation. By using concentrated solutions of the flavins in dimethylformamide (DMF), cubic single crystals with an edge length up to 1 mm were synthesized according to a protocol by Han et al. [62].

The incorporated flavin amounts were determined to 0.85 wt% for MIA@MOF-5 by UV/Vis spectroscopy from the supernatant solution (Section S1.2) and to 5.2 wt% for 6F-MIA@MOF-5 by postsynthetic digestion ^1H NMR (Section S1.2). The higher amount of 6F-MIA is explained by the very good solubility of 6F-MIA in DMF for a saturated solution of $c_{6\text{F-MIA}} = 2640 \text{ mg}\cdot\text{L}^{-1}$ whereas MIA was much less soluble, giving only $c_{\text{MIA}} = 272 \text{ mg}\cdot\text{L}^{-1}$ as a saturated solution (Section S2). From the crystallographic density of MIA of $\rho = 1.6 \text{ g}/\text{cm}^3$ [60] and $1/\rho = 0.63 \text{ cm}^3/\text{g}$, the 6F-MIA loading of 0.052 g(6F-MIA)/g(composite) would still occupy only a volume of $0.03 \text{ cm}^3/\text{g}$ or about 3% of the total pore volume of $\sim 1.0 \text{ cm}^3/\text{g}$ in neat MOF-5 [52]. The MOF-5 formula unit is $[\text{Zn}_4\text{O}(\text{bdc})_3]$ ($M = 769.87 \text{ g/mol}$). There is 1 “pore” per formula unit. At a loading of 0.85 wt% MIA@MOF-5 we have 0.0085 g MIA (37 μmol) in 0.9915 g MOF-5 (1.3 mmol). Thus, the molar ratio of MIA molecules to pores is 0.037:1.3 or 0.029 (MIA per pore), or ~34 pores for each MIA molecule. At a loading of 5.2 wt% 6F-MIA@MOF-5 we have 0.052 g MIA (0.21 mmol) in 0.95 g MOF-5 (1.2 mmol). Thus, the molar ratio of 6F-MIA molecules to pores is 0.21:1.2 or 0.18 (6F-MIA per pore), that is on average 5.7 pores for each MIA molecule.

Powder X-ray diffraction shows a good match between the flavin@MOF-5 composites, synthesized MOF-5 crystals and the simulated MOF-5 diffractogram (Figure S19).

The large flavin@MOF-5 crystals were analyzed by confocal laser scanning microscopy (CLSM) for the distribution of MIA (Figure 3) and 6F-MIA (Figure 4) in the MOF. The fluorescence images of the sectional planes support an even incorporation of the flavin dyes throughout the whole MOF crystals during the in situ synthesis.

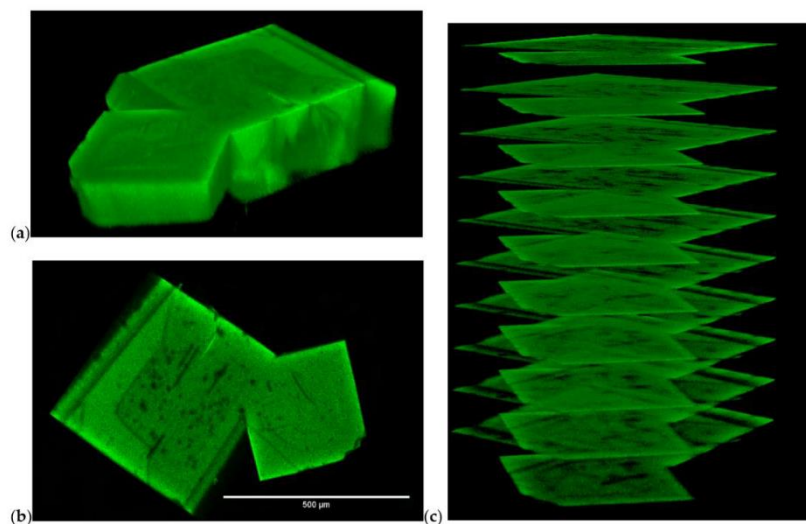


Figure 3. Confocal images of MIA@MOF-5. (a) Confocal laser scanning microscopy 3D profile, (b) sectional plane at 200 μm from top, and (c) stack of sectional planes of MIA@MOF-5 (cw excitation at $\lambda_{\text{ex}} = 458$ nm, $\lambda_{\text{em}} = 530$ –555 nm). Every sectional plane corresponds to a measurement thickness of 4 μm, which corresponds to the optical resolution of the used objective UPLSAPO10X/0.4NA.

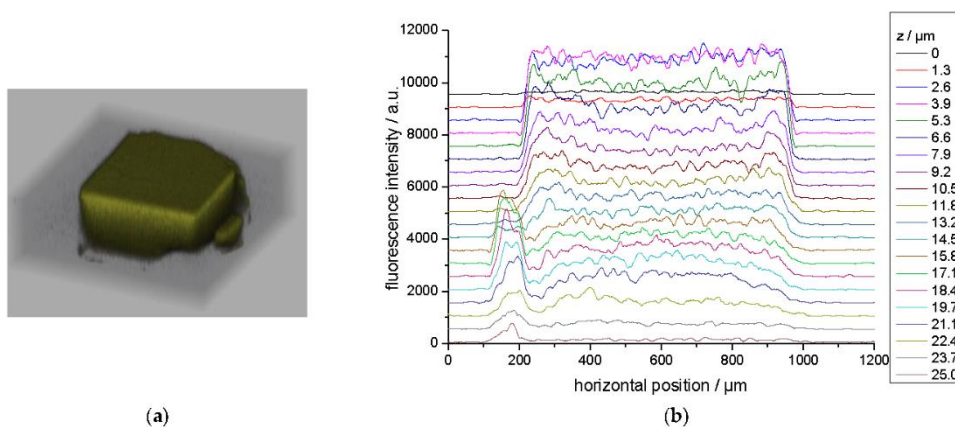


Figure 4. (a) Confocal laser scanning microscopy 3D profile for a height z of 25 μm, (b) line profile along z of 6F-MIA@MOF-5 (cw excitation at $\lambda_{\text{ex}} = 458$ nm, $\lambda_{\text{em}} = 530$ –555 nm, objective UPLSAPO10X/0.4NA). The fluorescence intensity decreases with the depth due to the inner filter effect.

2.3. Fluorescence Spectroscopy and Photophysics

Before discussing the fluorescence properties of the flavin@MOF composites in detail, it is important to consider which fluorescent species can be expected upon incorporation in MOFs. Since we varied the loading rate of incorporated flavins, we computed the probability p that a certain occupation number of flavins per site could be incorporated in MOFs assuming a random distribution of dyes. Using the average numbers of flavins per site $n_{av}(\text{flavins}/\text{site})$ approximated in Sections 2.1 and 2.2, our computation shows that the probability $p(> one)$ that more than one flavin is incorporated per site can be significant for our conditions (Table 2). The probability $p(> one)$ is higher in MIL-53 already at low loading as compared to MOF-5. In this context, it is important to take into account that organic chromophores with an extended π system can stack in solution with increasing concentration so that H- or J-aggregates of variable composition and structural arrangements can be formed. Due to the affinity of these chromophores to associate, the computed probabilities $p(> one)$ represent only lower limits that will be even higher in reality. Thus, flavin confinement in MOF composites could lead to J- or H-aggregates of variable stoichiometry. Notably, the emission properties of the chromophore aggregates critically depend on the strength of the excitonic coupling and on charge transfer interactions which can be influenced by their orientation stoichiometry and chemical structure. Therefore, we can expect variable fluorescent species for flavin@MOFs. Accordingly, we investigated in the following, whether the measured fluorescence spectra, lifetimes and anisotropies indicate the presence of multiple fluorescent species that could be related to aggregates.

Table 2. Probability p that a certain occupation number of flavins per site is confined in MOFs assuming a random distribution of flavins^a.

	MIA@MOF-5 0.85 wt%	6F MIA@MOF-5 5.2 wt%	MIA@MIL-53 3.9 wt%	6F MIA@MIL-53 1.5 wt%
$n_{av}(\text{flavins}/\text{site})$	0.029	0.18	0.3	0.1
$p(one)$	98.7%	92.0%	86.9%	95.5%
$p(two)$	1.3%	7.6%	12.1%	4.3%
$p(\geq three)$	0.0%	0.4%	1.0%	0.1%

^a: Site corresponds to a pore in MOF-5 and to a channel segment in MIL-53, respectively. Since the channel in MIL-53 is infinite, we cannot speak of “pores” as in MOF-5. Therefore, we define the length of a channel segment that is needed to host a MIA via the length of MIA molecule of ≈ 13 Å.

The fluorescence spectra at room temperature of both flavins, in a solution of 1:1 DCM/MeOH and in solid amorphous powder, are compared with their composites (bold lines) in Figure 5 for measurements at room temperature. Additional fluorescence spectra at 77 K were measured for all compounds and are compared with the corresponding spectra at room temperature in the supplementary materials Section S5, Figures S20–S23. The fluorescence spectrum of solid MIA is strongly red shifted with respect to the solution in 1:1 DCM/MeOH, while this shift is much weaker for 6F-MIA where a shoulder appears around 650 nm. The fluorescence spectra of flavin@MOF composites reveal a broadening at the bathochromic side that is stronger for higher loadings. We conclude that a mixture of emitters (flavin monomers and aggregates) exists. Due to the bathochromic shift of the spectra and the presence of shoulders for lower emission energies, we identify fluorescent J-aggregates as additional emitters. Consistently, the presence of bathochromically shifted emitters was enhanced for high flavin loadings at 77 K.

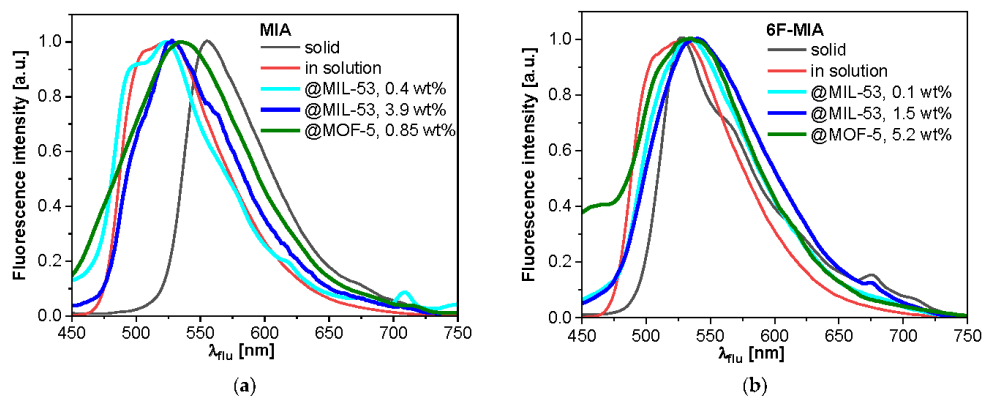


Figure 5. Normalized fluorescence spectra at room temperature of (a) MIA and (b) 6F-MIA in their neat solid state, in 1:1 DCM/MeOH solution and for the flavin@MOF composites; wt% refers to the flavin loading. Since the fluorescence signal of flavin@MOF composites with low loading is weak, the contributions of scattered excitation light at short emission wavelengths becomes relevant, which causes additional shoulders in the spectra at short wavelengths.

Next, we analyzed the fluorescence lifetimes and quantum yields. Table 3 summarizes fluorescence lifetimes (τ), quantum yields (Φ_F) and the wavelengths of the fluorescence maxima ($\lambda_{F,max}$) of the flavin dyes MIA, 6F-MIA and the flavin@MOF composites, which were measured with a time-resolved fluorescence spectrometer front-face sample holder (fluorescence spectra in Figures 5 and S20–S23) and multiparameter fluorescence image spectroscopy (MFIS) with polarization resolved detection, both using single photon timing electronics. All measured time-resolved fluorescence decays of both instruments are displayed in Figures S23–S33. The time-resolved fluorescence measurements in the fluorescence spectrometer and the confocal microscope with multiparameter fluorescence detection (see Section 3) gave consistent results. All fluorescence decays of flavin@MOF composites are multi-exponential. In addition to three fluorescence lifetimes in the ns range, polarisation-resolved MFIS detected a significant fraction of depolarized signal (i.e., fluorescence and not scattered excitation light) with a lifetime of 30 ps, which indicates the presence of strongly quenched fluorescent species. This agrees with the drop of the fluorescence quantum yields, Φ_F , observed for flavin@MOF composites. Notably, the fluorescence lifetimes of solid flavins are all in low picosecond time ranges, too. This finding agrees also with the quantum-chemical calculations presented in Section 2.4. below and in supplementary material section S6. Although the fluorescence quantum yields, Φ_F , in flavin@MOF composites indicate partially quenched fluorescence species, the Φ_F values are up to 8 times higher than for solid flavins. Moreover, in agreement with Table 2, we observe a qualitative correlation between lower fractions of quenched species for low loadings and $n_{av}(flavins/site)$. The flavin's tendency of forming J-aggregates is already visible in solution measurements of pure dyes. While at least three fluorescent species (most likely a small fraction of fluorescent aggregates) are detectable by up to three lifetimes in the solvent 1:1 DCM/MeOH dissolving flavins only moderately, a single fluorescent species is detectable in water, where flavins are dissolved well. In 1:1 DCM/MeOH, the longest lifetime with species fraction between 10 and 20% is in the range of 8 to 10 ns that is longer than the lifetime of the dye in water. The solid-state measurements and quantum-chemical calculation suggest that weakly and strongly fluorescent aggregates can coexist.

Table 3. Photophysical data for MIA, 6F-MIA and the flavin@MOF composites with $\lambda_{exc} = 405$ nm (TCSPC) or 440 nm (confocal MFIS) at room temperature (RT) unless indicated otherwise.

Compound	$\lambda_{E,max}$ [nm] ^a	τ_1 (x_1), τ_2 (x_2), τ_3 (x_3) [ns] ^b	τ_F [ns] ^b	τ_x [ns] ^b	x_{sq} ^g	Φ_F [%] ^c
MIA in solution:						
DCM/MeOH (RT)	527 ^d	10.2 (0.20), 6.1 (0.62), 2.9 (0.19)	7.1	6.3 ^d		28 ^d
DCM/MeOH (77 K) ^h	487/513	7.5 (1)	7.5	7.5		54
water	524 ^e	5.0 (1)	5.0	5.0 ^e		22
MIA solid	555, theo: 540 ⁱ	3.5 (0.01), 0.8 (0.12), 0.2 (0.87)	0.8	0.3		<2
0.4 wt% MIA@MIL-53	523	7.2 (0.22), 4.0 (0.51), 1.7 (0.27)	5.0	4.1		15
3.9 wt% MIA@MIL-53	527, theo: 509 ⁱ	7.6 (0.17), 4.0 (0.51), 1.3 (0.32)	4.9	3.7		11
		6.2 (0.13), 2.5 (0.33), 0.7 (0.53) ^g	3.6 ^g	2.1 ^g	0.87 ^g	
0.85 wt% MIA@MOF-5	533, theo: 528 ⁱ	9.5 (0.10), 4.2 (0.55), 1.3 (0.35)	5.1	3.7		6
		8.6 (0.10), 3.2 (0.65), 1.3 (0.24) ^g	4.7 ^g	3.3 ^g	0.79 ^g	
6F-MIA in solution:						
DCM/MeOH (RT)	530 ^d		3.6	3.6 ^d		13 ^d
DCM/MeOH (77 K) ^h	486/514	4.6 (0.17), 3.4 (0.83), 6.0 (0.41), 3.1 (0.59)	4.7	4.3		26
water	533 ^e	3.6 (1) ^e	3.6	3.6 ^e		12 ^e
6F-MIA solid	527	0.5 (0.01), 0.2 (0.05), 0.05 (0.94)	0.1	0.06		<2
0.1 wt% 6F-MIA@MIL-53	534	5.9 (0.13), 2.6 (0.46), 0.8 (0.41)	3.4	2.3		5
1.5 wt% 6F-MIA@MIL-53	538	6.7 (0.09), 2.5 (0.36), 0.6 (0.55)	3.5	1.9		3
		6.7 (0.07), 2.4 (0.39), 0.8 (0.53) ^g	3.2 ^g	1.9 ^g	0.87 ^g	
5.2 wt% 6F-MIA@MOF-5	510	7.0 (0.12), 3.2 (0.59), 0.8 (0.29)	4.1	3.0		8
		6.2 (0.21), 2.6 (0.70), 1.1 (0.09) ^g	4.0 ^g	3.2 ^g	0.79 ^g	

^a: Maximum of the fluorescence wavelength. ^b: Fluorescence lifetimes: $\tau(x_i)$ lifetime of species i (fraction), τ_F fluorescence-weighted average lifetime, τ_x species-weighted average lifetime. Raw time-resolved fluorescence decays with fits and obtained parameters are shown in the supplementary materials Section S5 Figures S24–S33 except for the MFIS data marked by ^g. ^c: Fluorescence quantum yield. Precision $\pm 2\%$. ^d: In DCM/MeOH 1:1 (DCM = dichloromethane). ^e: Mono-exponential fits from time-correlated single photon counting by Reiffers et al. [17]. ^f: Computations in this work. ^g: From confocal multi-parameter fluorescence image spectroscopy (MFIS) with pulsed excitation at 440 nm and $\lambda_{em} = 502$ –538 nm. Global fits to p- and s-polarized decays required 4 fluorescence lifetime components. The shortest lifetime component (<30 ps, close to the instrumental resolution but distinct from scatter due to its smaller anisotropy) was not considered in the calculation of the average lifetimes and amplitudes were rescaled to the bright species with $\tau >$ instrument response function (FWHM ≈ 0.5 ns). The non-rescaled amplitude fractions x_{sq} of the lifetime component with $\tau_{sq} < 30$ ps amount to 87% (dye@MIL-53) and 79% (dye@MOF-5) of all species, indicating a significant amount of strongly quenched dyes in both matrices. Raw time- and polarization-resolved fluorescence decays with fits and obtained parameters are shown in the supplementary materials Section S5 Figure S34. ^h: Measured in a 1:1 DCM/MeOH glassy matrix at 77 K.

We applied confocal multi-parameter fluorescence image spectroscopy (MFIS) to map also the spatial and orientation dependence of the fluorescence properties for the microcrystalline sample of flavin@MIL-53 and large single crystals of flavin@MOF-5.

The average fluorescence lifetime $\langle\tau\rangle_F$ of MIA@MIL-53 (3.9 wt%) (Figure 6a, panel 1) and a crystal of MIA@MOF-5 (Figure 6b panel 1) yielded 4.5 and 4.7 ns, respectively. For 6F-MIA@MIL-53 (1.5 wt%) and 6F-MIA@MOF-5 the values of $\langle\tau\rangle_F$ are 3.5 and 4.5 ns (Figure 6c,d panel 1), respectively. These results are consistent with the lifetimes measured in the fluorescence spectrometer. The average fluorescence lifetime values of the chromophores in flavin@MOF composites are similar to the values in aqueous solution (Table 3). Interestingly, the fluorescence lifetime of MIA is affected by the location in the crystal. The lifetime of MIA is slightly but significantly longer in the center of the MOF-5 crystal (Figure 6b—the false colors for lifetime values are darker in the middle (5.5 ns)). This positional effect explains the surprising result that the fluorescence lifetime distribution of MIA is broader in MOF-5 than in MIL-53 crystals (Figure 6b vs. a). Being aware that deactivation processes of MIA and 6F-MIA in solution include fluorescence, intersystem crossing and internal conversion with different relative efficiencies [17], we note that both methods for lifetime analysis indicate that MIA is the less sensitive derivative as compared to 6F-MIA.

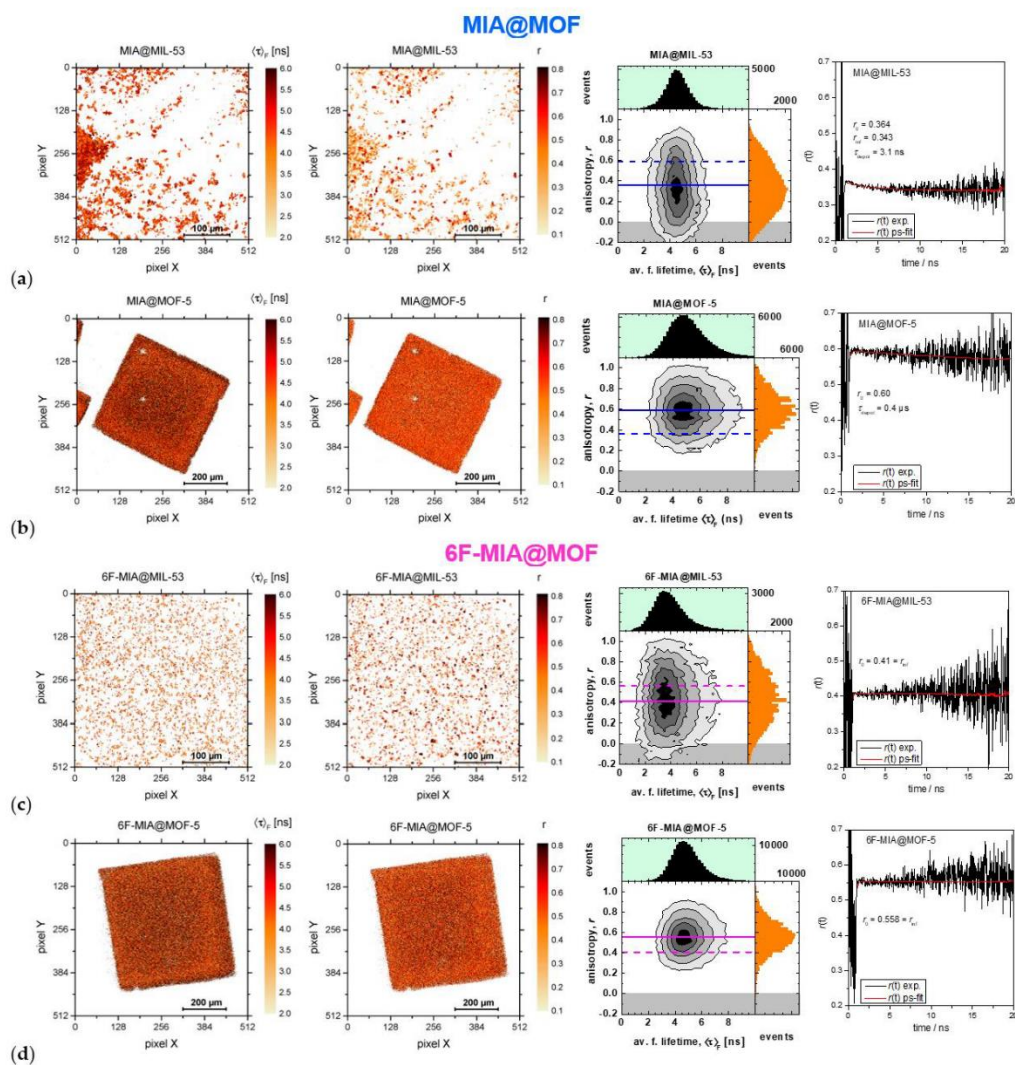


Figure 6. Images of MIA and 6F-MIA in two MOFs obtained by confocal multi-parameter fluorescence image spectroscopy (MFIS) (see Section 3). (Panel 1) Image of fluorescence-weighted average lifetime; (Panel 2) Image of experimental steady state fluorescence anisotropy r ; (Panel 3) Interrelation $\langle\tau\rangle_F - r$ in the 2D diagram of the parameter images in panels 1 and 2 with a full horizontal line for the average anisotropy $\bar{r}$ of the sample and second dashed line of other MOF composite as reference; and (Panel 4) Time-resolved fluorescence anisotropy curves $r(t)$ to resolve the fundamental anisotropy r_0 and the depolarization time τ_{depol} that are displayed in the individual panels 4. (a) MIA@MIL-53 (3.9 wt%), (b) MIA@MOF-5, (c) 6F-MIA@MIL-53 (1.5 wt%) and (d) 6F-MIA@MOF-5. For flavin@MOF-5 five slices in the center of the z-stack were selected to generate the decay histograms, for flavin@MIL53 all photons from the images were used. The acquisition conditions were $\lambda_{\text{ex}} = 440$ nm (pulsed@32MHz, objective UPLSAPO10X/0.4NA for MIL-53 and objective UPLSAPO20X/0.75NA for MOF-5), $\lambda_{\text{f}} = 502\text{--}538$ nm, under air.

With higher loading of the flavins into MIL-53, $\lambda_{F,max}$ shifts to slightly longer wavelengths (Table 3). A similar shift is seen for MIA when going from an aqueous to a DCM/MeOH solution and oppositely for 6F-MIA between a DCM/MeOH and water solution. In general, conditions where the flavin molecules come closer together enable charge transfer processes and self-quenching between them, resulting in spectral shifts and broadening of the emission bands with loss of fine structure and reduction of the fluorescence quantum yield. It is known that the photophysical properties of a chromophore in a MOF are influenced by the geometric restrictions imposed by the framework structure [18]. In all flavin@MOF composites, a strong increase in both lifetimes and quantum yields compared to the neat solid flavin is observed. In the case of MIA@MIL-53 and MIA@MOF-5 a ~10-fold increase in lifetime and a 3 to 5-fold increase in quantum yield can be observed compared to solid MIA. For the 6F-MIA@MOF composites, these increases are even more evident, with a ~50-fold increase in lifetime and ~3-fold increase in quantum yield. Compared to the neat solid flavins the incorporation of the molecules within the MOFs reduces the nonradiative decay rates, leading to increased fluorescence intensities, lifetimes, and quantum yields. This effect is especially prominent in MFIS. The photophysical parameters of the flavin@MOF composites correspond to the data of the flavins in solution (Table 3) fostering the concept of “solid solutions” for dye@MOF composites.

From the MFIS analysis, it is evident that microcrystals of flavin@MIL-53 vary significantly in both size and polarization properties (Figure 6a,c panel 2). The orientational distributions of both flavin chromophores is indicated by a broad distribution of the fluorescence anisotropies r due to varying size and orientation of the flavin@MIL-53 microcrystallites (Figure 6a,c). The anisotropies are calculated according to Schaffer et al. [63]. For this discussion of the r -distributions, it is important to consider the broadening of the distributions due to shot noise caused by the relatively small average number of photons per pixel ($\overline{N_p}(\text{MIA}) = 35$) and $\overline{N_p}(6\text{F-MIA}) = 200$). 6F-MIA@MIL-53 exhibits the broadest r -distribution reaching its upper limit ($r = 1$) and lower limit ($r = 0$). To reduce shot noise, we integrated the signal of the whole image to compute time-resolved anisotropy curves $r(t)$ (Figure 6a,c panel 4). This was accomplished by global fits with iterative deconvolution of the instrumental function (grey curves in Figure S34) to p- and s-polarized decays as described in ref. [63,64]. The fits required 4 fluorescence lifetime components (lifetimes and species fractions are compiled in Table 3) and one (two for MIA@MIL-53) depolarization correlation time.

It is especially remarkable, that $r(t)$ of 6F-MIA@MIL-53 starts at a fundamental anisotropy $r_0 = 0.4$ and exhibits no decay. This is direct proof the MFIS images resolve the distribution of particles whose orientation on the surface is static and random so that the isotropic average of r is obtained, which is usually mathematically derived in text books [65] considering the case of fluorophores in solution. Three arguments (the anisotropy of pixels of some MIA and 6F-MIA@MIL-53 microcrystals reaches one (see Figure 6a,c, panels 2 and 3 and Figure S35), geometric constraints of available space in MIL-53 and quantum-chemical calculations (see below)) allow us to conclude that transition dipole moments for absorption and fluorescence (TDM) (see supplementary materials Section S6.5 Figure S42) of the various fluorescent MIA and 6F-MIA species must be oriented along the one-dimensional channel of MIL-53 with no large deviation among each other. Considering MIA@MIL-53, the fundamental anisotropy $r_0 = 0.364$ is slightly smaller and an additional decay term with a depolarization time of 3.1 ns is observed. From this it is evident that the order of the MIA TDMs is slightly lower, but nevertheless quite similar for all fluorescent species. The TDMs are preferentially orientated along the channel axis.

In contrast to MIL-53, MOF-5 provides a very well defined and ordered porous framework with large flavin@MOF-5 crystals (Figures 3, 4 and 6b,d) as indicated by a narrow distribution of fluorescence anisotropies r , which are centered around mean anisotropy values: $\bar{r}(\text{MIA}) = 0.6$ (full blue line in Figure 6b, panel 3) and $\bar{r}(6\text{F-MIA}) = 0.56$ (full magenta line in Figure 6d, panel 3). Both flavin@MOF-5 samples show high anisotropies that indicate distinct oriented binding sites, excluding random orientation of the dye molecules in the

crystal. As for 6F-MIA@MIL53, no time-dependence of the anisotropy $r(t)$ was observed for 6F-MIA@MOF-5. MIA embedded in either of the two MOFs shows limited depolarization on the ns to μ s scale, which could have one or several of the following reasons: (i) constrained rotational motion, (ii) resonance energy transfer to chromophores in close vicinity and/or (iii) slightly differing orientations of fluorescent species with distinct lifetimes.

Due to the high symmetry of the cubic MOF-5 crystal for the x, y, z directions defined in the crystal parameters, it is feasible and appropriate to assume an identical rotation of the transition dipole moment of the MIA chromophore using the normalized rotation vector of the crystal $\mathbf{n}_{CA}$ in an angle axis representation that rotates the S_0 - S_1 absorption transition dipole moment A of the chromophore with respect to the crystal axis c by an angle ω_{CA} . For a cube, the directions of the four potential rotation vectors correspond to the respective body diagonals. Since the body diagonals are equivalent, we consider in the following only one rotation vector. Using the experimental observables for 6F-MIA@MOF-5 ($\bar{r}(6F\text{-MIA}) = 0.56$ (Figure 6d panel 3) and $\alpha = 8.2^\circ$ (Figure 6d panel 2)) and for MIA@MOF-5 ($\bar{r}(\text{MIA}) = 0.6$ (Figure 6b panel 3) and $\alpha = 65^\circ$ (Figure 6b panel 2)), a unique solution with an angle of the normalized rotation vector $\omega_{CA} = 13^\circ$ (for MIA) and $\omega_{CA} = 16^\circ$ (for 6F-MIA) is obtained that describes the average orientation of the TDM for absorption of all fluorescent species defined by the Euler angles relative to the crystal lattice $\theta_{CA} \sim 12 \pm 1$ and $\phi_{CA} \sim 40.5 \pm 1$, i. e., the TDM is not oriented along one of the crystal axes. This confirms that MOF-5 provides a suitable frame to incorporate flavins in a defined average orientation regardless of their aggregation.

2.4. QM/MM Excited State Computations

In the neat MIA crystal [60], we can identify two orientations of stacked neighboring molecules (Figure 7). In one orientation, π -stacking interactions occur between the terminal phenyl and the central and terminal ring of two adjacent MIA molecules (molecule no. 1 and 2 in Figure 7) with a centroid-centroid separation of 3.518 and 3.589 Å. The other π -stacking orientation involves only the terminal phenyl rings of two adjacent MIA molecules (no. 2 and 3) at a centroid-centroid distance of 3.561 Å.

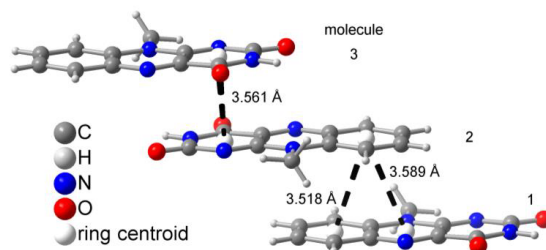


Figure 7. π - π stacking modes in crystalline MIA with centroid-centroid distances (graphics were drawn from the deposited cif file with CCDC Refcode MISALX [60]). The numbers 1, 2 and 3 differentiate the molecules for their different stacking interactions (see text).

Due to the different π -stacking modes in the crystal of neat MIA, QM/MM geometry optimizations of ground and excited state structures had to include at least three MIA molecules for a sensible description of interactions with all direct neighbors (see Section S6.1). Compared to the single MIA chromophore in vacuum ($\lambda_{\text{abs, max}} = 401$ nm), the calculated maximum absorption value in the crystal is 441 nm, thus significantly red-shifted. The calculated emission from S_1 state in the crystal occurs at ca. 540 nm, compared to ca. 555 nm in the solid-state experiment and 505 nm for MIA calculated in vacuum (Table 3) with a calculated small oscillator strength ($f = 0.025$) and an emission rate constant of $5.87 \cdot 10^6 \text{ s}^{-1}$. While for the single MIA molecule S_1 corresponds to a locally π -excited state, orbital analysis for the three-molecule MIA complex reveals a dominating charge-

transfer character. Here, electron density is relocated between the two molecules that overlap with two aromatic rings (number 1 and 2 in Figure 7). This is the main reason for the loss in fluorescence emission intensity in the crystalline state.

Optimization of MIL-53-lp with QuantumEspresso (QE) revealed essentially the same results as the experimental structures (Table S3). Compared to the reported orthorhombic large-pore form MIL-53-lp (CCDC 220476 [41]) the computed guest-free MIL-53-lp structure after optimization has nearly the same cell axes lengths within 0.7 Å (Figure S40, Table S3). With one MIA molecule per unit cell, the structure becomes more similar to the reported narrow-pore form (Figure S41, Table S3). A variation of lattice parameters upon adsorption in MIL-53 was also seen, e.g., upon loading with xylene isomers [66], short linear alkanes [67] or methane [68].

The position of the MIA molecule is optimized with its length along the channel direction and close to the center of the channel (Figure 8). There are no evident short and strong supramolecular interactions but the MIA molecule is held in place by weak C-H...O, C-H... π , C-H...C, N-H...O, O-H...O and O-H...C interactions. Even the N-H...O and O-H...O contacts have rather long H...X distances above 2.5 Å (Figure 8).

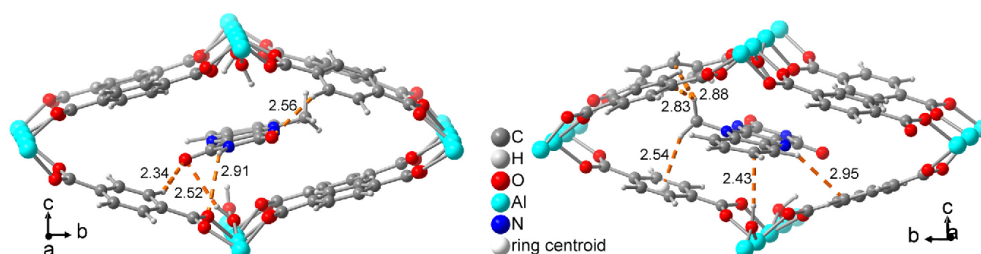


Figure 8. Computed structure of MIA@MIL-53 viewed from both ends of the MIA molecule with indication of the weak C-H...O, C-H... π , C-H...C, N-H...O, O-H...O and O-H...C interactions (H...X distances in Å, distances above 3 Å are not shown).

For neat MOF-5, we note a slight compression of the unit cell constants upon optimization by ca. 0.2 Å in each direction, compared to the experimental values [51,58]. The cell size does not significantly change when MIA is inserted. Due to the tilted arrangement of the phenyl rings, MOF-5 offers two different types of cages to host the MIA chromophore (Figure 9a). In one cage, the hydrogen atoms of the phenyl linkers point inwards toward the center of the pore (left pore with orange sphere in Figure 9a,b). We refer to this possibility as *inward-cage*. In the second alternative, the hydrogen atoms of the phenyls face *outwards*, thus offering a wider pore (right pore with green sphere in Figure 9a,c and pore in Figure S15d). The energy for MIA incorporated in the *inward-cage* is ca. 15.3 kJ/mol lower than in the *outward-cage* because of increased attractive van-der-Waals interactions. The computed binding energy of MIA is ca. 49 kJ/mol in the *inward-complex* and ca. 35 kJ/mol in the *outward-configuration*, suggesting that complexation in the *inward-cage* is preferred. There is, however, no evident supramolecular interaction in either case. The MIA molecule is computed in the center of the pores, along the horizontal channel direction (Figure 9b,c). All distances from MIA to the framework walls are larger than 3.0 Å, except for two C-H...H-C contacts in the *inward-cage* position (Figure 9b) with an H...H distance of 2.5–2.6 Å. The next-nearest distances are four C-H...O contacts of ~3.2 Å, also in the *inward-cage* position.

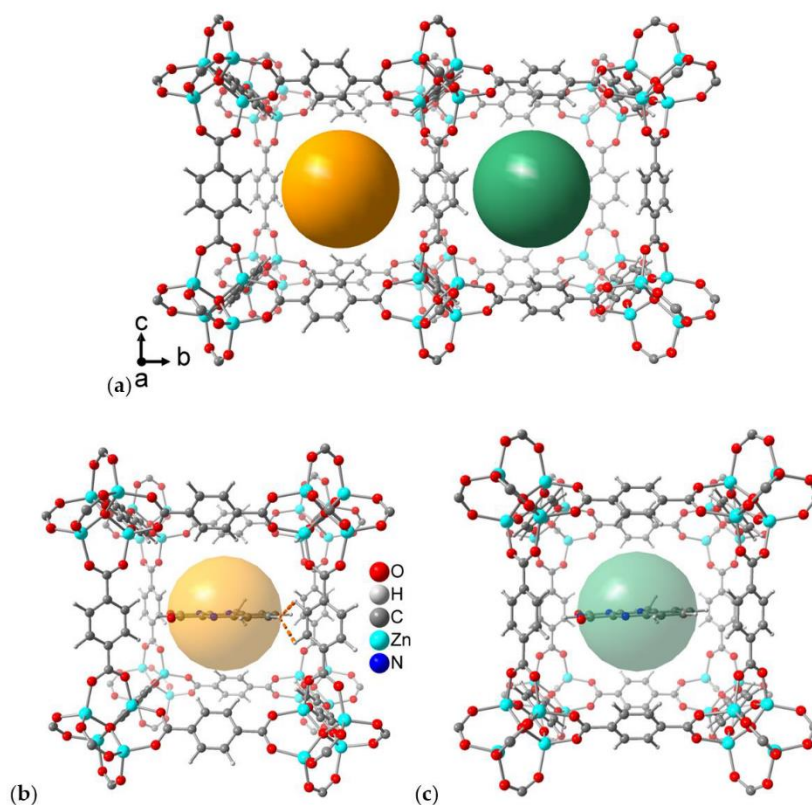


Figure 9. (a) Alternating neighboring pores in MOF-5 with different cages for binding MIA. Orange pore at left: Linker phenyl hydrogens face *inwards* toward the center of the pore. Green pore at right: outward position of linker phenyls. (b) Computed MIA molecule in the *inward*-cage in MOF-5 with the only two supramolecular contacts below 3.0 Å (two C-H...H-C contacts) indicated as dashed orange lines. (c) Computed MIA molecule in the *outward*-cage for which there are no supramolecular contacts below 3.0 Å.

In the MIA@MIL-53 complex, the ground state QM/MM optimization converges to essentially the same structure as with plane-wave methods. The lowest excitation wavelength is 414 nm with an oscillator strength f of 0.265 and local π -excitation character, corresponding to HOMO-LUMO excitation. The computed emission wavelength from the S_1 state is 509 nm ($f = 0.209$) (Figure 10) with an emission rate constant of $5.39 \cdot 10^7 \text{ s}^{-1}$, about ten times larger than in the neat MIA crystal. The absorption and emission wavelength values are slightly blue-shifted with respect to the experimental measurement (523 to 527 nm, depending on the MIA wt%). The oscillator strength compares well with the value for MIA in vacuum ($f = 0.243$), demonstrating that the MOF environment efficiently increases fluorescence emission by preventing quenching due to π -stacking.

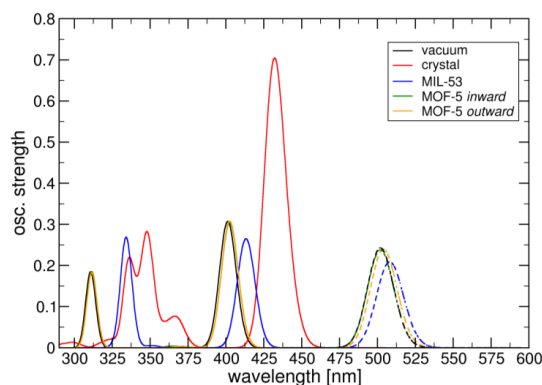


Figure 10. DFT/MRCI computed absorption (full lines) and emission (dashed lines) signatures of MIA in vacuum, neat crystal and MOF environments.

For MOF-5, we find no significant change in absorption and emission wavelength values depending on the mode of complexation. In the more stable *inward* form, maximum wavelength absorption occurs at 402 nm ($f = 0.305$), while emission from S_1 is at 502 nm ($f = 0.238$) with a rate constant of $6.30 \cdot 10^7 \text{ s}^{-1}$. Similar to MIL-53, the S_1 -excitation shows the same characteristics as in vacuum.

3. Materials and Methods

3.1. Chemicals and Equipment

Reagents were obtained from commercial sources (Table S1) and used without further purification. All flavin derivatives [17,69,70] and metal-organic frameworks [41,62,66,71] were synthesized and purified according to the literature.

Powder X-Ray diffractograms (PXRD) were measured on a Bruker D2 phaser benchtop diffractometer (Bruker, Ettlingen/Karlsruhe, Germany, 300 W, 30 kV, 10 mA) at ambient temperature using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate of $0.0125^\circ/\text{s}$. The measurements were performed with a flat silicon, low-background sample holder. This Bragg–Brentano geometry broadens the beam spot at low angles so that only a fraction of the diffraction radiation reaches the detector with reflections measured at $2\theta < 7^\circ$ have lower than expected intensity.

Nitrogen physisorption isotherms were obtained at 77 K on a Nova 4200e S/N volumetric gas sorption analyzer from Quantachrome (Boynton Beach, FL, USA), equipped with degassing and three analyses stations. Before the gas sorption experiment, the sample was weighed into a glass tube capped with a septum. The tube was connected to the degassing port of the Nova instrument and degassed under dynamic vacuum of $1 \cdot 10^{-2}$ mbar at a temperature of 120°C for 3 h, then weighed again and transferred to an analysis port of the Nova device.

The Brunauer–Emmett–Teller (BET) surface areas were calculated from the nitrogen adsorption isotherms in the p/p_0 range from 0.017 to 0.07. Total pore volumes were calculated from the nitrogen sorption isotherm at $p/p_0 = 0.95$.

Fluorescence microscopy. Characterization of the incorporated fluorophores by confocal laser scanning and multi-parameter fluorescence image spectroscopy (CLSM and MFIS [72]) (condition g in Table 3) was carried out with a modified Olympus Fluoview 1000 inverse confocal microscope system (Olympus, Hamburg, Germany) with an internal 405 nm laser and a 6-channel single photon detector on dye@MIL-53 ($20 \times$ objective) and dye@MOF-5 ($10 \times$ objective). For the excitation of CLSM a cw argon laser with a wavelength of 458 nm was used. For MFIS, the acquisition conditions were $\lambda_{\text{ex}} = 440 \text{ nm}$ (pulsed@32MHz, objective UPLSAPO10X/0.4NA for MIL-53 and objec-

tive UPLSAPO20X/0.75NA for MOF-5), $\lambda_{em} = 502\text{--}538$ nm, under air. Experimental anisotropy decays in Figure 6 were calculated from the measured p- and s-polarized fluorescence decays (Figure S34) after subtracting the observed background according to: $r = (GF_{\parallel} - F_{\perp}) / ((1 - 3I_1)GF_{\parallel} + (2 - 3I_2)F_{\perp})$. The correction factors, taking into account polarization mixing in high-NA objectives were $I_1 = 0.0308$ and $I_2 = 0.0368$ [73]. The model curves (red lines in Figure 6) are constructed in the same way from the fits to the decays. Global fits by iterative reconvolution of the instrumental function (grey curves) to p- and s-polarized decays required 4 fluorescence lifetime components (Table 3 main document) and one (two for MIA@MIL-53) rotational correlation time. The offsets in the decays are caused by afterpulsing of the detectors and taken into account by the fitting routine. The G-factor, compensating differences in the detection efficiencies in the two polarization channels, of $G = 0.97$ was determined by fitting polarized fluorescence decays of an aqueous solution of Rhodamine 110. The doped MOFs were studied under air.

Steady-state excitation and emission spectra were recorded on a FluorTime 300 spectrometer from PicoQuant (Berlin, Germany) equipped with a 300 W ozone-free Xe lamp (250–900 nm), a 10 W Xe flash-lamp (250–900 nm, pulse width <10 μ s) with repetition rates of 0.1–300 Hz, an excitation monochromator (Czerny–Turner 2.7 nm/mm dispersion, 1200 grooves/mm, blazed at 350 nm and 600 g/mm), diode lasers (pulse width <80 ps) operated by a computer-controlled laser driver PDL-820 (repetition rate up to 80 MHz, burst mode for slow and weak decays), two emission monochromators (Czerny–Turner, selectable gratings blazed at 500 nm with 2.7 nm/mm dispersion and 1200 grooves/mm, or blazed at 1250 nm with 5.4 nm/mm dispersion and 600 grooves/mm) with adjustable slit width between 0 mm and 10 mm, Glan–Thompson polarizers for excitation (Xe-lamps) and emission, a Peltier-thermostated sample holder (−40–105 °C), and two detectors, namely a PMA Hybrid 40 (transit time spread FWHM <120 ps, 200–900 nm) and a R5509-42 NIR-photomultiplier tube (transit time spread FWHM 1.5 ns, 300–1400 nm) from Hamamatsu. The signal-to-noise ratio (optical noise) is typically better than 29000:1, as measured with double monochromators in the excitation and emission light path. Steady-state photoluminescence spectra and fluorescence lifetimes were recorded in TCSPC mode by a PicoHarp 300 (minimum base resolution 4 ps), whereas phosphorescence was measured in the MCS mode by a TimeHarp 300, where up to several ms can be detected. Emission spectra were corrected for source intensity (lamp and grating) by standard correction curves. For samples with lifetime in the ns order, an instrument response function calibration (IRF) was performed using a diluted Ludox[®] solution. The lifetime analysis was performed using the commercial EasyTau 2.2 software. The quality of the fit was assessed by minimizing the reduced chi squared function (χ^2) and visual inspection of the weighted residuals and their autocorrelation. Absolute photoluminescence quantum yields were measured with a Hamamatsu Photonics measurement system (C9920-02) equipped with a L9799-01 CW Xenon light source (150 W), a monochromator, a C7473 photonic multi-channel analyzer, an integrating sphere and employing the U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan). All solvents used were of spectrometric grade (Uvasol[®]).

3.2. Flavin@MIL-53 Synthesis

Post synthetic wet infiltration was performed by adding different quantities (1 to 15 mL) of saturated solutions of the flavins in chloroform ($c_{MIA} = 69.5$ mg·L^{−1}, $c_{6F-MIA} = 20.25$ mg·L^{−1}) to activated microcrystalline MIL-53 powders (20 mg) in 25 mL glass vials. The different suspensions were stored on an orbital shaker until all the solvent had been evaporated. The flavin@MIL-53 composites were washed three times with chloroform for 5 min at each washing step and then dried at 60 °C under dynamic vacuum. Since the filtrate was already colorless after the first washing process, all of the dye from the initial solution was incorporated in the solid MIL-53 sample. The MIA@MIL-53 composites contained 0.4 to 2.7 wt% of the flavin in the MOF and the 6F-MIA@MIL-53 composites between 0.1 to 1.5 wt% (see also Section S1.2).

3.3. Flavin@MOF-5 Synthesis

In situ MOF-5 crystallization was performed by synthesizing the host network in saturated solutions of the flavins in dimethylformamide, DMF ($c_{\text{MIA}} = 272 \text{ mg}\cdot\text{L}^{-1}$, $c_{6\text{F-MIA}} = 2640 \text{ mg}\cdot\text{L}^{-1}$). The amount of incorporated flavin was then quantified using UV/Vis or postsynthetic digestions ^1H NMR. The MIA@MOF-5 composites contained 0.85 wt% (UV/Vis) and 6F-MIA@MOF-5 composites contained 5.2 wt% (^1H NMR) of the flavin (see also Section S1.2).

3.4. Computational Methods

Crystal structures of MIA (CCDC Refcode MISALX [60]), MIL-53(Al) (CCDC no./Refcode 220476/SABVUN for -MIL-53-lp [41]) and MOF-5 (CCDC-no./Refcode 256966/SAHYOQ [52,58]) were extracted from experimental data. The geometries were optimized with Quantum Espresso (QE) [74] using RRKJ-pseudopotentials [75], the generalized gradient approximation (GGA) with PBE-exchange correlation [76], Grimme-type D3-dispersion corrections [77] and a kinetic energy cutoff of 40 eV. SCF computations were performed including only the gamma point. For the optimization of the MIA crystal the cell parameters were frozen to the experimental values. MIL-53(Al) and MOF-5 were optimized without any constraints. To obtain the MOF-MIA complexes, one MIA molecule was placed into the center of the unit cell. To fit the MIA chromophore, the MIL53 the unit cell was replicated three times in a-direction, comprising a $3 \times 1 \times 1$ supercell. The resulting geometries were then fully relaxed using the aforementioned methodologies. These structures were used as input structures for QM/MM cluster model computations.

Atomic partial charges for the MIA chromophore were computed with Gaussian16 [78] using RHF, the 6-31G* basis set and the Merz-Kollmann scheme [79]. Periodic charges for the frameworks were generated with the REPEAT method [80] implemented in CP2K [81]. Atoms herein were described with DZVP-MOLOPT-GTH basis sets and corresponding GTH-PBE pseudopotentials [82]. Force field parameters for MIA were obtained from the Generalized Amber Force Field (GAFF). MOF-5 force field parameters were adapted from a previous work by Vanduyfhuys et al. [83]. MIL-53(Al) parameters were computed with the FFTK program suite [84] using cluster models optimized with Gaussian16 (see Section S6.2 for details).

Finite cluster models were generated for each structure using the previously optimized geometries. The MOF structures were saturated accordingly (see Sections S6.2 and S6.3 for details). The MIA crystal cluster was prepared by replicating the unit cell eight times in each direction, thus including 1024 individual MIA molecules with a cell size of ca. $40 \times 50 \times 60 \text{ \AA}^3$. The size of the MIL-53 cluster was ca. $60 \times 30 \times 30 \text{ \AA}^3$, the MOF-5 cluster had ca. $98 \times 98 \times 98 \text{ \AA}^3$.

For QM/MM geometry optimizations, the COBRAMM2.0 package [85] was employed, choosing Gaussian16 [78] for the computation of the QM part (MIA) and AMBER16 [86] for the MM part (i.e., the surrounding). The QM-part was described with the PBE0 functional. The MIA crystal model was computed with different sizes for the central QM part, including 1, 2 and 3 stacked MIA molecules (see Section S6.1) and the 6-31G* basis set. The QM part was allowed to fully relax while the remaining atoms were frozen to their initial positions. MOF structures were calculated with one MIA molecule as the QM part in the center of the clusters using the TZVP basis set. MIA and direct neighbors in the MM part were movable during optimization, while the rest of the cluster was kept fixed. In the case of MOF-5, the metal centers positions were additionally kept frozen.

Spectral properties were computed with the DFT/MRCI [87] program using the R2016 Hamiltonian [88]. Orbitals for MRCI were computed at the B3LYP/TZVP level using Turbomole [89]. The initial reference space was chosen by computing single and double excitations from eight electrons in eight orbitals. An energy selector of $0.8 E_h$ and the *tight* parameter set were chosen. A second run was performed with the same parameters to obtain an updated reference space and the final values for energies and oscillator strengths.

4. Conclusions

The flavin derivatives 10-methyl-isalloxazine (MIA) and 6-fluoro-10-methyl-isalloxazine (6F-MIA) were successfully encapsulated in the metal-organic frameworks (MOFs) MIL-53 and MOF-5. The incorporation of flavin@MOF composites was verified by BET surface measurements and powder X-ray diffraction. In the case of the flavin@MOF-5 composites, the incorporation was also demonstrated spectroscopically by homogeneous images obtained by confocal laser scanning microscopy (Figures 3 and 4). The photophysical properties of the flavin@MOF composites are significantly dependent on the specific molecular environment. Compared to the neat dyes in their solid states, the lifetime and quantum yield increase significantly in solution and in the dye@MOF composite. At least four fluorescent MIA species are present in the MOF composites. The lower lifetimes and quantum yield in the solid state of the dyes can be attributed to aggregation-caused quenching (ACQ). The fluorescence lifetimes and quantum yields of the flavins in liquid solution and in the “solid MOF solution” are of comparable orders. The electronic structures of MIA in its crystal environment, of MIA in MIL-53 and MIA in MOF-5 were investigated with plane-wave and QM/MM methods. In the crystalline state, π -stacking interactions of neighboring MIA chromophores change the nature of the first excited state from a local π - π (HOMO-LUMO) electronic excitation with high fluorescence intensity to a charge transfer state with low oscillator strength. The channels in the investigated metal-organic frameworks provide an environment for the incorporation of MIA as separated molecules, thus preventing π -stacking interactions between MIA molecules. The strong reduction of ACQ explains the enhanced fluorescence lifetime and quantum yield compared to the neat MIA crystal. The MIL-53 framework adapts towards the narrow-pore form when the MIA chromophore binds, thereby enhancing van-der-Waals contacts between the chromophore and the framework walls. Together with fluorescence anisotropy images and decays in Figure 6a,c, we can conclude that the transition dipole moments of the MIA derivatives are preferentially oriented along the one-dimensional channel axis. MOF-5 is a rather rigid framework but offers a narrower and wider pore environment for MIA with similar absorption and emission characteristics. In the preferred MIA position in the narrower pore, the hydrogen atoms of the phenyl linkers point towards the MIA-chromophore, thus enhancing host-guest van-der-Waals interactions. Together with fluorescence anisotropy images and decays in Figure 6b,d, we can conclude that the transition dipole moments of the MIA derivatives are not preferentially oriented along the three-dimensional cubic lattices but tilted in a similar manner (see Euler angles as described in Section 2.3).

The MOF environment influences the photophysical properties of the host chromophores. For 6F-MIA the non-radiative processes are significantly reduced. For MIA the location within the crystal becomes relevant. Further studies by fluorescence correlation spectroscopy (FCS) and transient state imaging microscopy (TRAST) will unravel the nature of these processes (internal conversion, IC or intersystem crossing, ISC). Moreover, we will also study the influence of the MOF environment on the photostability of the chromophores.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/molecules28062877/s1>. Section S1: Materials and methods; Section S2: MIA and 6F-MIA absorption spectra and calibration curves (Figures S4–S11); Section S3: Structure descriptions (Figures S12–S15); Section S4: Nitrogen adsorption isotherms and powder X-ray diffractograms (Figures S16–S19); Section S5: Photophysical characterization of the dyes and dye@MOF (Figures S20–S35); Section S6: Theoretical calculations (Figures S36–S42). References [90–93] are cited in the supplementary materials.

Author Contributions: Conceptualization: C.J. and S.-P.H.; methodology: D.P., O.W. and S.-P.H.; validation: S.-P.H., S.H. and D.P.; formal analysis: D.P., S.H., I.M., S.-P.H., R.K. and C.J.; investigation: D.P., S.H., I.M., S.-P.H., D.W. and R.K.; resources: C.A.M.S., C.C., O.W., C.A.S. and C.J.; data curation: D.P., S.H., I.M., S.-P.H. and R.K.; writing—original draft preparation: S.-P.H., S.H., C.A.M.S., O.W., D.P. and C.J.; writing—review and editing: C.J., R.K., O.W., C.A.M.S., C.C. and C.A.S.; visualization:

D.P., S.H., S.-P.H., R.K., S.F., C.A.M.S. and C.J.; supervision: C.A.M.S., C.C., O.W., C.A.S. and C.J.; project administration: O.W. and C.J.; funding acquisition: I.M., C.A.M.S., C.C., O.W., C.A.S. and C.J. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare that they have no known competing financial interest or personal relationship that could have appeared to influence the work reported in this paper.

Sample Availability: Samples of the compounds will not be available.

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Supplementary Material

Enhanced solid-state fluorescence of flavin derivatives by incorporation in the metal-organic frameworks MIL-53(Al) and MOF-5

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Section S1: Materials and methods

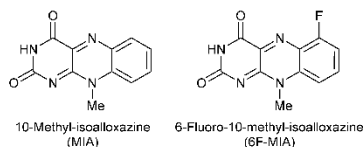
Commercially available reagents (Table S1) were used without further purification. All reagents were used in reagent grade without further purification. The solvents were purchased in reagent grade or purified by conventional methods. For reactions requiring an inert atmosphere the glassware was dried in a compartment dryer at 120 °C and standard Schlenk techniques were used to work under a dry nitrogen atmosphere. Degassing of solvents was done by purging with dry nitrogen for 30 minutes.

Table S1. Sources for starting materials and solvents.

Reagent	Manufacturer
Zinc nitrate hexahydrate	ACROS Organics
Terephthalic acid	Alfa Aesar
Ethanol	CHEMSOLUTE
<i>N,N</i> -dimethylformamide	Honeywell
<i>N,N</i> -diethylformamide	Honeywell
Aluminum nitrate nonahydrate	CARL ROTH

Section S1.1: Synthesis of flavins

Flavins were prepared from the corresponding 2-methylamino-anilines by condensation with alloxan hydrate. *N*-Methylation of 2-nitro-anilines was performed by alkylation of the corresponding trifluoroacetamides with dimethylsulfate following a procedure by Brown and Rizzo [1]. 10-Methyl-isoalloxazine (MIA) (Scheme S1) was prepared following a protocol reported by Imada, Murahashi and coworkers [2]. 6-Fluoro-10-methyl-isoalloxazine (6F-MIA) (Scheme S1) [3] was prepared following a modified protocol reported by Averill and co-workers [4].



Scheme S1. 10-Methyl-isoalloxazine (MIA) and 6-fluoro-10-methyl-isoalloxazine (6F-MIA).

Section S1.2: MOF syntheses and flavin incorporation

Preparation of saturated MIA and 6F-MIA dye solutions

The MIA or 6F-MIA dye was mixed in chloroform or DMF and dissolved for 30 min at 40 °C using ultrasound. When a clear homogeneous solution was obtained, this process was repeated until no more dye could be dissolved. The saturated chloroform solutions ($C_{\text{MIA}} = 69.5 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{6F-MIA}} = 20.25 \text{ mg}\cdot\text{L}^{-1}$; see Section S2) or DMF solutions ($C_{\text{MIA}} = 272 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{6F-MIA}} = 2640 \text{ mg}\cdot\text{L}^{-1}$; see Section S2) were then filtered at room temperature and used for the syntheses.

Synthesis of MIL-53(Al) according to Alaerts et al. and Loiseau et al. [5,6]

Aluminum nitrate nonahydrate (3.75 g, 10.0 mmol), terephthalic acid (0.83 g, 5.0 mmol) and dist. water (7.16 mL) were mixed in a 60 mL Teflon-lined stainless-steel autoclave, which was heated at 220 °C for 72 h including a 3 h heating ramp and 3 h cooling ramp. After cooling to room temperature, the white raw product was washed three times with water (10 mL). The white solid was dispersed in DMF and heated under reflux to 160 °C for 48 h to remove the incorporated terephthalic acid from the pores. The product was finally washed three times with hot ethanol (10 mL each). Yield 46 %.

10-Methyl-isoalloxazine (MIA) and 6-fluoro-10-methyl-isoalloxazine (6F-MIA) incorporation into MIL-53

Post-synthetic wet infiltration was performed by adding 1 to 15 mL from the concentrated solutions of the dyes in chloroform to 20 mg activated powders of the microcrystalline MIL-53. After brief mixing, slow evaporation at room temperature was used to promote diffusion of the dyes into the MOF pores.

MOF-5 single crystal synthesis according to Han et al. and Eddaoudi et al. [7,8]

Zinc nitrate hexahydrate (511 mg, 1.72 mmol) and terephthalic acid (96 mg, 0.58 mmol) were dissolved in dimethylformamide, DMF (5 mL). The solution was transferred to Pyrex tubes, which were placed in a programmable oven at 85 °C for 72 h including a 2.5 h heating ramp and 3.5 h cooling ramp. The colorless crystals obtained were washed with DMF (5 mL each) twice daily for three days and with ethanol (5 mL each) twice daily for another three days. After washing, the MOF-5 crystals were filtered and dried under vacuum (15 h at 120 °C). Yield 58 %. The MOF-5 were stored under nitrogen until further investigations.

MOF-5 single crystal synthesis with 10-methyl-isoalloxazine (MIA)

MIA (5.0 mg, 0.022 mmol) was added to DMF (5 mL) and sonicated at 60 °C for 30 min. The solution was then filtered to obtain a homogeneous MIA-saturated DMF solution with $c_{\text{MIA}} = 272 \text{ mg}\cdot\text{L}^{-1}$ (Section S2). Zinc nitrate hexahydrate (175.5 mg, 0.59 mmol) and terephthalic acid (31.0 mg, 0.19 mmol) were dissolved in the MIA-DMF solution (5 mL). The solution was then placed in a programmable oven at 85 °C for 72 h including a 2.5 h heating ramp and 3.5 h cooling ramp. Yellow discolored cubic crystals were obtained. The crystals were washed three times with DMF (5 mL), filtered and dried under vacuum (15 h at 120 °C). Yield 42.3 mg (MIA@MOF-5), 39.9 mg MOF-5 after deduction of MIA content (see below), ~90% MOF-5 based on terephthalic acid. The dry MIA@MOF-5 composites were stored under nitrogen until further investigations. For longer storage (> 4 weeks), the non-washed crystals were stored in the mother liquor at 4 °C. When needed, the crystals were then worked up as described above.

The 10-fold diluted supernatant DMF solution gave an absorption at 436 nm of 0.892 from which a residual MIA concentration of $0.892/0.04467 = 19.97 \text{ mg L}^{-1}$ (Figure S5), thus 199.7 mg L^{-1} for the original supernatant could be obtained. Hence, from 1.36 mg of MIA in 5 mL of the saturated MIA-DMF solution 1.00 mg of MIA was still present in the supernatant after MOF-5 formation or 0.36 mg MIA were incorporated in 39.94 mg MOF-5 ($42.3 \text{ mg} - 0.36 \text{ mg}$), representing $0.36 / (0.36 + 39.94) = 0.85 \text{ wt\%}$.

MOF-5 single crystal synthesis with 6-fluoro-10-methyl-isalloxazine (6F-MIA)

6F-MIA (20 mg, 0.081 mmol) was added to DMF (5 mL) and sonicated at 60 °C for 30 min. The solution was then filtered to obtain a homogeneous 6F-MIA-saturated DMF solution with $C_{6F-MIA} = 2640 \text{ mg L}^{-1}$ (Section S2). Zinc nitrate hexahydrate (175.5 mg, 0.59 mmol) and terephthalic acid (31.0 mg, 0.19 mmol) were dissolved in the 6F-MIA-DMF solution (5 mL). The solution was then placed in a programmable oven at 85 °C for 72 h including a 2.5 h heating ramp and 3.5 h cooling ramp. Yellow discolored cubic crystals were obtained. The crystals were washed three times with DMF (5 mL each), filtered and dried under vacuum (15 h at 120 °C). Yield 40.5 mg (6F-MIA@MOF-5), 29.3 mg MOF-5 after deduction of 6F-MIA, ~57% MOF-5 based on terephthalic acid.

The dry 6F-MIA@MOF-5 composites were stored under nitrogen until further investigations. For longer storage (> 4 weeks), the non-washed crystals were stored in the mother liquor at 4 °C. When needed, the crystals were then worked up as described above.

The 20-fold diluted supernatant DMF solution gave an absorption at 425 nm of 0.544 from which a residual 6F-MIA concentration of $0.544/0.0272 = 20.0 \text{ mg L}^{-1}$ (Figure S9), thus 400 mg L^{-1} for the original supernatant could be obtained. Hence, from 13.2 mg of 6F-MIA in 5 mL of the saturated MIA-DMF solution 2.0 mg of 6F-MIA was still present in the supernatant after MOF-5 formation or 11.2 mg MIA were adsorbed onto or incorporated in 29.3 mg MOF-5 ($40.5 \text{ mg} - 11.2 \text{ mg}$), representing $11.2 / (11.2 + 29.3) = 27.6 \text{ wt\%}$, albeit before the washing process three times with DMF (5 mL each).

However, digestive dissolution in DMSO- d_6 /DCI of 6F-MIA@MOF-5 gave a loading of 5.2 wt%.

The MIA@MOF-5 and 6F-MIA@MOF-5 composites were dissolved in 0.8-0.9 mL DMSO- d_6 upon addition of ~0.1 mL 35% DCI/D₂O. The solution ¹H NMR spectra were recorded on a Bruker Avance III-300 MHz spectrometer. Chemical shifts are referenced to the residual proton solvent signal (2.50 ppm for DMSO- d_6).

The digestion ¹H NMR spectrum of 6F-MIA@MOF-5 (Figure S1a) shows a small signal for the N-methyl group of 6F-MIA (cf. Scheme S1).

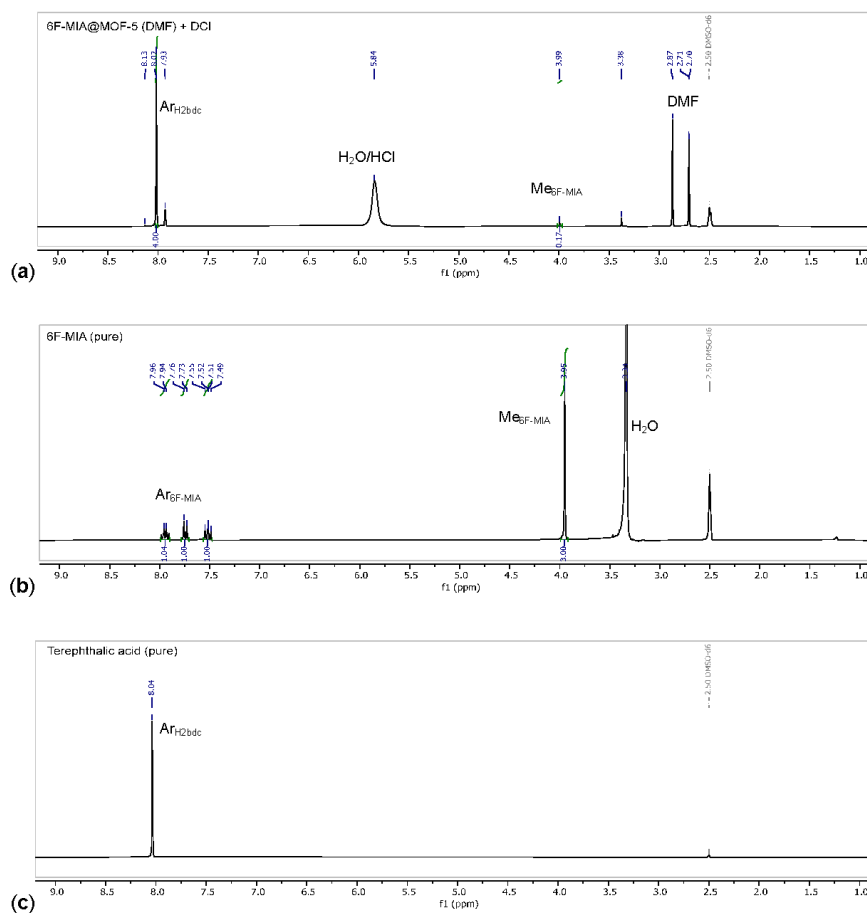


Figure S1. ^1H NMR spectra in DMSO-d_6 at 300 MHz of (a) 6F-MIA@MOF-5 upon digestive dissolution with DCI/D $_2$ O, (b) 6F-MIA and (c) terephthalic acid.

The integral of 4.00 for the terephthalic acid signal (4 aromatic protons) has to be divided by 12 as there are three terephthalate (bdc) linkers in the $[\text{Zn}_4\text{O}(\text{bdc})_3]$ formula unit of MOF-5. The integral of 0.17 for the N-methyl group (3 protons) of 6F-MIA has to be divided by 3. This normalization then gives the molar ratio of MOF-5 formula units to 6F-MIA molecules:

$$4/12 : 0.17/3 = 1:0.17 = 5.88 \text{ mol } [\text{Zn}_4\text{O}(\text{bdc})_3] \text{ for each mol of 6F-MIA.}$$

With $M = 769.87 \text{ g/mol}$ for $[\text{Zn}_4\text{O}(\text{bdc})_3]$ and $M = 246.20 \text{ g/mol}$ for 6F-MIA

there are $246.20 \text{ g 6F-MIA per } 5.88 \text{ mol} \times 769.87 \text{ g/mol} = 4528.6 \text{ g MOF-5.}$

This gives a 6F-MIA@MOF-5 loading of $246.20 / (246.20 + 4528.6) \times 100\% = 5.2 \text{ wt\%}.$

In view of the much smaller content of MIA@MOF-5 of at most 0.85 wt% from UV/Vis difference measurements no N-methyl signal is seen in the digestion ^1H NMR spectra of MIA@MOF-5.

As an explanation of the obtained large loading of 6F-MIA from the UV/Vis absorption difference measurement we suggest that a sizeable amount of 6F-MIA from the concentrated solution was adsorbed on the outer surface or in the pore mouths. This 6F-MIA content could easily be removed when the crystals were washed three times with DMF (5 mL). The much better solubility of 6F-MIA with $c_{6\text{F-MIA}} = 2640 \text{ mg}\cdot\text{L}^{-1}$ compared to MIA with only $c_{\text{MIA}} = 272 \text{ mg}\cdot\text{L}^{-1}$, both for saturated solutions, will also lead to a more facile postsynthetic removal of 6F-MIA through the washing cycles.

Infrared (IR) spectra of flavin@MOF

The Fourier transform infrared (FT-IR) spectra were collected with a Bruker Tensor 37 instrument with KBr or attenuated total reflection (ATR) technique. The spectra are collected in Figure S2 and Figure S3.

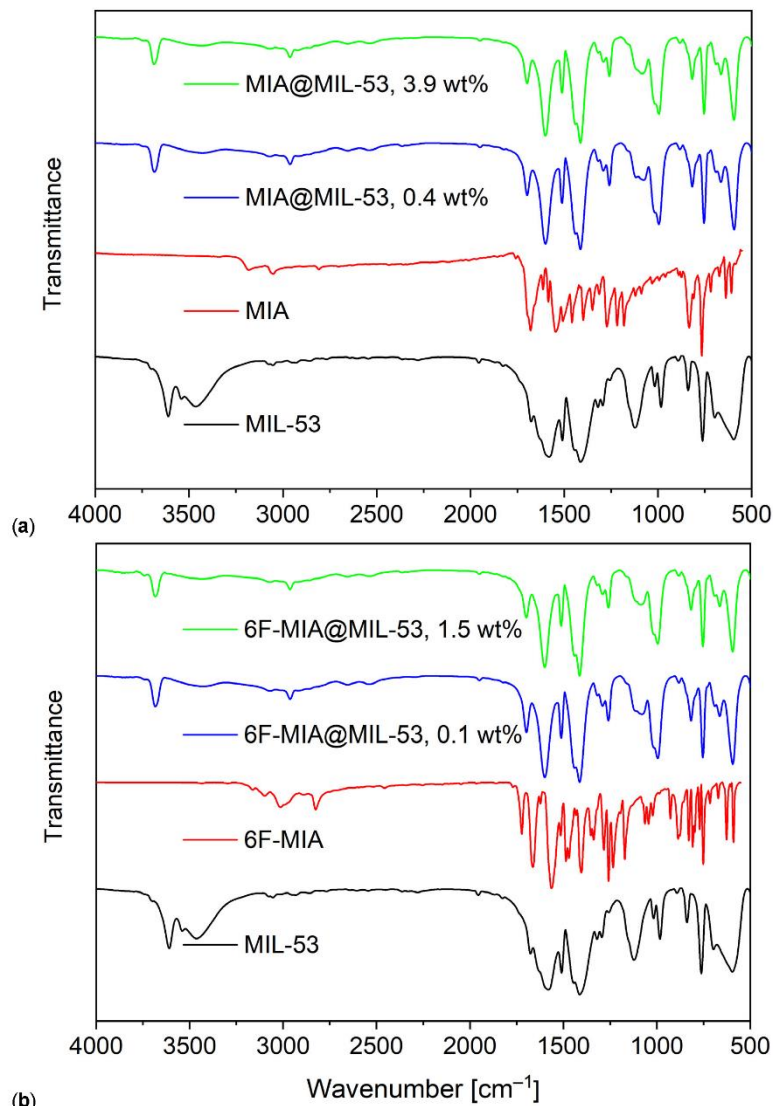


Figure S2. IR spectra of (a) MIL-53 (KBr), MIA (ATR) and MIA@MIL-53 (KBr) and (b) MIL-53 (KBr), 6F-MIA (ATR) and 6F-MIA@MIL-53 (KBr).

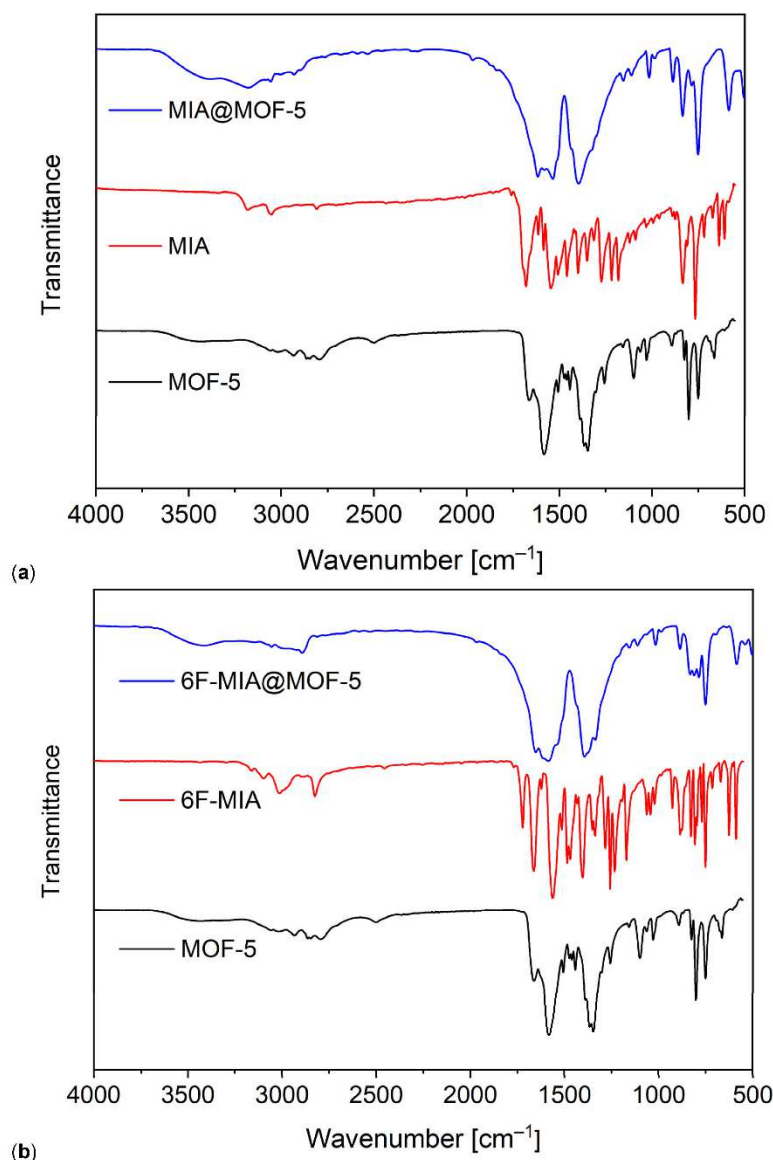


Figure S3. IR spectra of (a) MOF-5 (KBr), MIA (ATR) and MIA@MOF-5 (KBr) and (b) MOF-5 (KBr), 6F-MIA (ATR) and 6F-MIA@MOF-5 (KBr).

Neat MIL-53 features broad signals which we see as evidence for the superposition of the three MIL-53 phases MIL-53-as, MIL-53-np and MIL-53-lp (and intermediate phases) as is also evident from

the powder X-ray diffractograms (cf. Figure S14a). In the flavin@MIL-53 composites the bands sharpen and become more distinct with all composites giving nearly identical spectra (Figure S2). This is due to the formation of the same phase from the sample preparation as KBr pellets. The superposition of the flavin bands and the low amounts of flavins in MIL-53 do not allow a detection of flavin bands in the composites.

MOF-5 on the other hand has more distinct bands in its neat form whereas in the composites the band between 1000 and 1750 cm^{-1} have considerably broadened (Figure S3). Distinct bands remain only in the region between 750 to 1000 cm^{-1} where C=C- and C-H-bending vibrations occur. Also, MIA and 6F-MIA have bands in the same region. Upon close inspection the flavin-only bands at 606 and 833 cm^{-1} (MIA) and 588 and 828 cm^{-1} (6F-MIA) are also localized in the composites (Table S2).

Table S2. Listing of IR wavenumbers of MOF-5, MIA, 6F-MIA and flavin@MOF-5 composites.

Wavenumber [cm^{-1}]	MOF-5 (KBr)	MIA (ATR)	MIA@MOF-5 (KBr)	6F-MIA (ATR)	6F-MIA@MOF-5 (KBr)
C=C bending, C-H bending		606 ++	590 ++	588 ++	586 ++
	660 +	636 ++		625 ++	
	750 ++	765 +++	751 +++	750 +++	750 +++
	800 +++			808 ++	810 ++
				828 ++	835 ++
		833 ++	837 ++		
	892 +		889 +	885 ++	887 +
	1025 +		1012 +		1014 +
	1096 ++				
C-H stretching, O-H bending	1250-1450 +++, b (1343)	1216 ++	1230-1470 +++, b (1390)	1257 +++	1250-1470 +++, b (1390)
C-H/O-H stretching	1450-1670 +++, b (1578)	1454 +++	1470-1750 +++, b (1531,1616)	1564 +++	1480-1750 +++, b (1585)
		1680 ++		1722 ++	
	2495 +				
C-H/O-H stretching	2790-3100 +, b	2800-3180 +, b	2925-3530 +, b (3175)	2823 +	2900-3400 +, b
				3010 +	

Section S2: MIA and 6F-MIA absorption spectra and calibration curves (Figure S4-Figure S11)

For the concentration determination of the saturated solution of MIA in DMF, a stock solution with a concentration of $100 \text{ mg}\cdot\text{L}^{-1}$ MIA in DMF was prepared, diluted to lower concentrations and measured by UV/Vis spectroscopy (Figure S4).

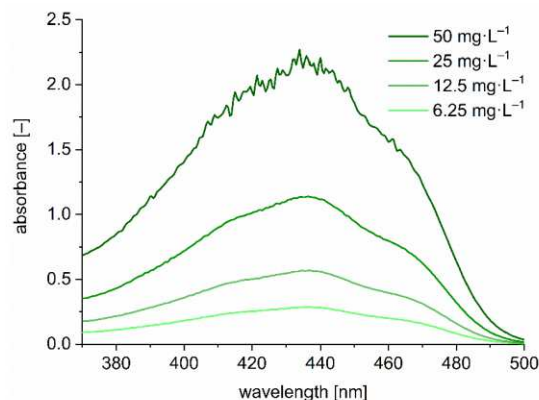


Figure S4. UV/Vis spectra of differently concentrated solutions of MIA in DMF in the range from 370 to 500 nm.

Using the maxima of the absorption spectra at 436 nm, a calibration curve was derived (Figure S5).

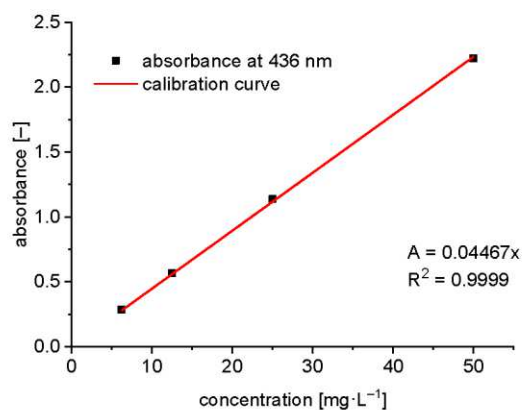


Figure S5. Calibration line for MIA in DMF from the absorbance at 436 nm.

The concentration of the **saturated MIA-DMF solution** was determined as follows: The saturated MIA-DMF solution was diluted by a factor of 1:10 to obtain an absorbance at 436 nm of 1.214 within the calibration range giving a concentration of $27.2 \text{ mg}\cdot\text{L}^{-1}$ for the tenfold-diluted solution. Taking this dilution into account, a concentration of $272 \text{ mg}\cdot\text{L}^{-1}$ was calculated for the saturated MIA-DMF solution.

For the concentration determination of the saturated solution of MIA in chloroform, a stock solution of $4 \text{ mg} \cdot \text{L}^{-1}$ of MIA in chloroform was prepared and diluted. This was followed by the recording of the UV/Vis spectra of the solution series (Figure S6).

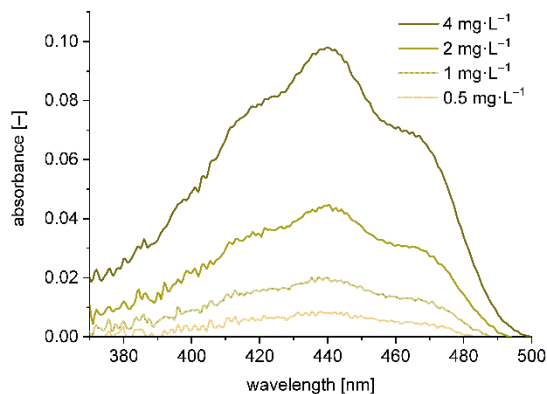


Figure S6. UV/Vis spectra of differently concentrated solutions of MIA in chloroform in the range from 370 to 500 nm.

From the absorbance maxima at 440 nm the calibration curve was obtained (Figure S7).

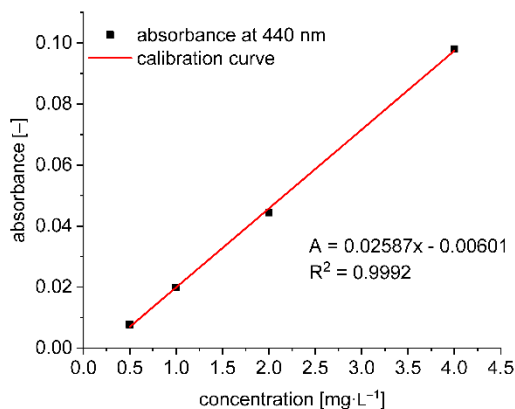


Figure S7. Calibration line for MIA in chloroform from the absorbance at 440 nm.

Subsequently, the concentration of the **saturated MIA-CHCl₃ solution** was determined as follows: The saturated MIA-CHCl₃ solution was diluted by a factor of 1:25 to obtain an absorbance at 440 nm of 0.078 within the calibration range giving a concentration of $2.78 \text{ mg} \cdot \text{L}^{-1}$ for the 25-fold-diluted solution. Taking this dilution into account, a concentration of $69.5 \text{ mg} \cdot \text{L}^{-1}$ was calculated for the saturated MIA-CHCl₃ solution.

To determine the concentration of the saturated solution of 6F-MIA in DMF, a stock solution with a concentration of $100 \text{ mg} \cdot \text{L}^{-1}$ of 6F MIA in DMF was prepared and the UV/Vis-spectra were recorded for the dilution series (Figure S8).

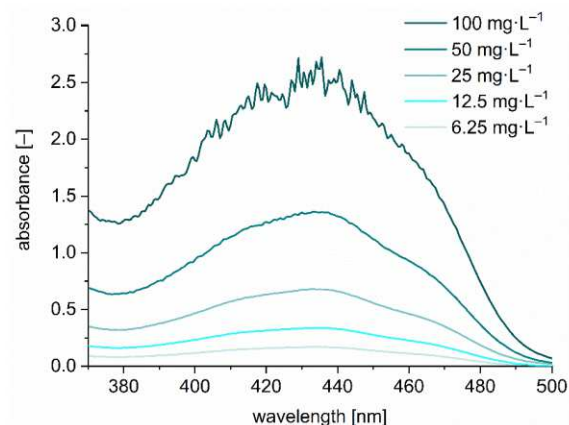


Figure S8. UV/Vis spectra of different concentrated solutions of 6F-MIA in DMF in the range from 370 to 500 nm.

From the absorbance maxima at 435.5 nm the calibration curve was obtained (Figure S9).

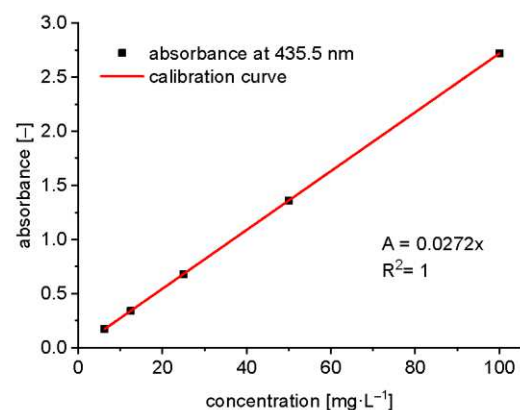


Figure S9. Calibration line for 6F-MIA in DMF from the absorbance at 435.5 nm.

The concentration of the **saturated 6F-MIA-DMF solution** was determined as follows: The saturated 6F-MIA-DMF solution was diluted by a factor of 1:50 to obtain an absorbance at 435.5 nm of 1.436 within the calibration range giving a concentration of $52.8 \text{ mg} \cdot \text{L}^{-1}$ for the 50-fold-diluted solution. Taking this dilution into account, a concentration of $2640 \text{ mg} \cdot \text{L}^{-1}$ was calculated for the saturated 6F-MIA-DMF solution.

The concentration of the saturated solution of 6F-MIA in chloroform was determined by starting from a solution with a concentration of $2.4 \text{ mg} \cdot \text{L}^{-1}$ 6F MIA in chloroform, from which a dilution series was prepared and the UV/Vis spectra were recorded (Figure S10).

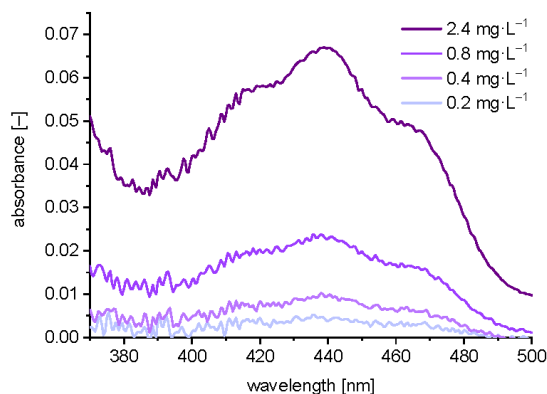


Figure S10. UV/Vis spectra of differently concentrated solutions of 6F-MIA in chloroform in the range from 370 to 500 nm.

The calibration line was derived from the maxima of the absorption at 440 nm (Figure S11).

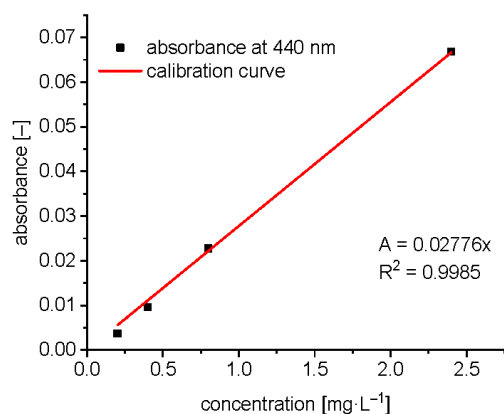


Figure S11 Calibration line for 6F-MIA in chloroform from the absorbance at 440 nm.

Subsequently, the **saturated 6F-MIA-CHCl₃ solution** was diluted by a factor of 1:12.5 to obtain an absorbance at 440 nm of 0.045 within the calibration range giving a concentration of $1.62 \text{ mg} \cdot \text{L}^{-1}$ for the 12.5-fold-diluted solution. Taking this dilution into account, a concentration of $20.25 \text{ mg} \cdot \text{L}^{-1}$ was determined for the saturated 6F-MIA-CHCl₃ solution.

Section S3: Structure descriptions (Figure S12 - Figure S15)

Section S3.1: Structure of 10-methyl-isoalloxazine (MIA) (Figure S12)

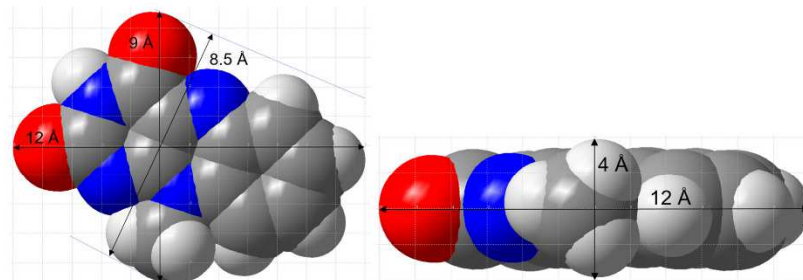


Figure S12. Top view and side view of a 10-methyl-isoalloxazine (MIA) molecule in space-filling presentation with the molecular dimensions indicated (the grid unit is 1 Å). (Structures were drawn with Diamond [9] from the deposited cif file under CCDC-no./Refcode MISALX [10]).

Section S3.2: Additional structure description of MIL-53(Al) (Figure S13 and Figure S14)

The MIL-53(Al) structure with the formula unit $[\text{Al}(\text{OH})(\text{bdc})]$ (bdc = benzene-1,4-dicarboxylate, terephthalate) is a very flexible, 'breathing'-type network, that is, it can assume different shapes and porosities depending on the presence or absence of host-guest interactions (Figure S13) [5, 11]. The secondary or here infinite building unit (SBU, IBU) in MIL-53 is a linear chain of $\{\text{MO}_6\}$ octahedra ($\text{M} = \text{Al}, \text{In}, \text{Ga}, \text{Cr}, \text{Fe}$). The Al^{3+} centers are octahedrally coordinated by terephthalate linkers and bridging $\mu\text{-OH}$ groups, giving chains of trans- $\mu\text{-OH}$ -connected vertex-bridged $\{\text{AlO}_6\}$ octahedra. The hydroxido-bridging and carboxylate-bridging occurs along the direction of the metal chains (Figure S13a). These chains are connected perpendicular to the chain direction through the ditopic terephthalate linkers to a three-dimensional network with channels running parallel to the $\{\text{MO}_6\}$ chains (Figure S13b). Each benzene-1,4-dicarboxylate ligand bridges between four Al atoms. This forms a three dimensional network consisting of rhombic-shaped channels with a significant breathing effect [5, 11, 12, 13, 14, 15, 16, 17, 18].

MIL-53 can be found in three different crystalline forms which are usually differentiated as MIL-53as, MIL-53ht = MIL-53lp and MIL-53lt = MIL-53np with as = *as synthesized*, ht = *high temperature* lp = *large pore*, lt = *low temperature* and np = *narrow pore* (Figure S13). After the hydrothermal synthesis as-synthesized MIL-53-as is obtained. By heating to a temperature between 275 °C and 420 °C (without vacuum), MIL-53 can be activated by the removal of guest molecules. This leads to the large-pore (lp) structure MIL-53-lp. Upon the uptake of water molecules from the air at ambient conditions, the narrow-pore (np) MIL-53-np is formed (Figure S13). The transformation between MIL-53-lp to MIL-53-np is reversible and is commonly referred to as the 'breathing effect'. For the large-pore (lp) form the diagonals for the rhombohedral channel cross section are 8.4 x 12 Å (Figure S14).

When incorporating the flavin derivatives, the MIL-53-lp form can be used as the van-der-Waals dimensions of MIA molecules are approximately $4 \times 8.5 \times 12 \text{ \AA}$ (Figure S12) with the width of $8.5 \text{ \AA}$ being the critical dimension for the diffusion through the rhombohedral MIL-53 channels.

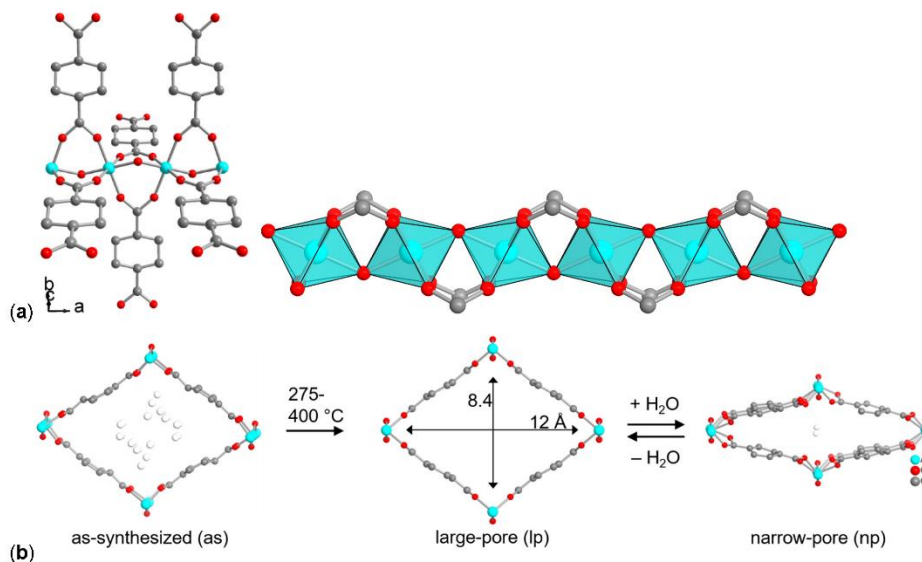


Figure S13. (a) Terephthalato- and hydroxido-bridged metal strand of $[\text{Al}(\text{OH})(\text{bdc})]$ as an infinite subunit. (b) Sections of the packing diagram with a flexible, 'breathing' network adapting to guest molecules. The pore structures of MIL-53(Al) are viewed along the channel direction. The channels can contain guest molecules in the as-synthesized or narrow-pore form or be empty in the similar large-pore structure. The as-synthesized, and the narrow-pore form also indicate the (disordered) guest molecules (hydrogen atoms are not shown). The high temperature for the transition from as-synthesized to large-pore form is due to the removal of residual terephthalic acid. The dimensions along the diagonals of the rhombic opening include the van-der-Waals radii of the atoms (see also Figure S14). Adsorption of water from air at room temperature transforms the structure into the narrow-pore / low-temperature form (right). Hydrogen atoms are not shown. (Structure images were drawn with Diamond [9] from the deposited cif files under CCDC-no./CSD-Refcodes 220475/SABVOH for MIL-53-as, 220476/SABVUN for -MIL-53-lp and 220477/SABWAU for MIL-53-np [6]).

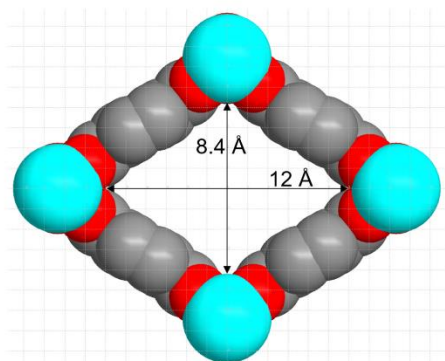
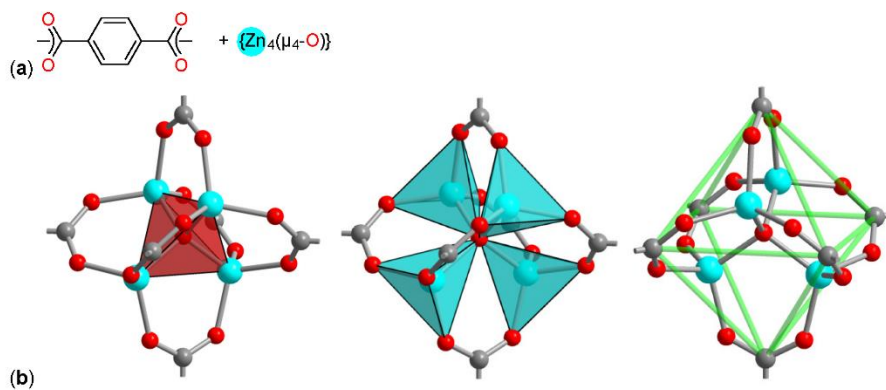
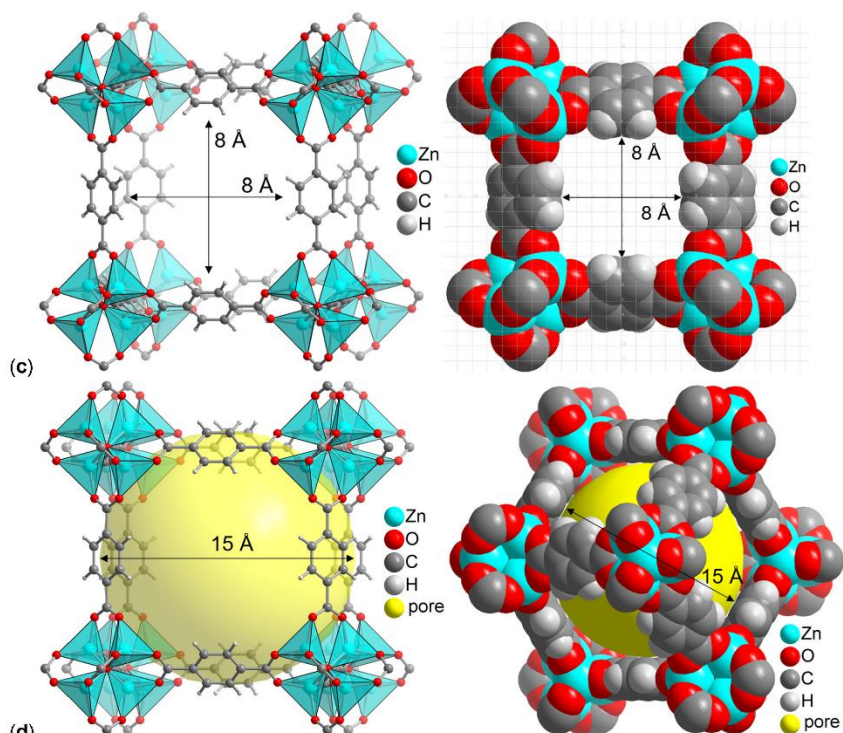


Figure S14. MIL-53(Al)-lp (large pore) in space-filling mode viewed along the channel direction. The dimensions along the diagonals of the rhombic opening include the van-der-Waals radii of the atoms (the grid unit is 1 Å).

Section S3.3: Additional structure description of MOF-5 (Figure S15)

MOF-5 (also named IRMOF-1), $[Zn_4O(bdc)_3]$ with bdc = benzene-1,4-dicarboxylate, terephthalate) is one of the best known and prototypical MOFs [19]. The structure of MOF-5 is constructed of tetrahedral $\{Zn_4O\}$ secondary building units where six carboxylate groups of the terephthalate linkers span the six edges of the $\{Zn_4O\}$ tetrahedron in an octahedral fashion to give a 3D primitive cubic (**pcu**) structure with orthogonal channels along each axis of a cartesian coordinate system with channel cross-sections (window size) of 8×8 Å and a pore diameter of 15 Å (Figure S15) [8]. Activated MOF-5 has a high surface area (3000 m²/g) and high thermal stability (up to 400 °C) [19].





(d)
Figure S15. (a) Benzene-1,4-dicarboxylate, terephthalate, bdc and μ_4 -oxido bridged tetranuclear zinc cluster as building blocks for MOF-5 (IRMOF-1), $3D-[Zn_4O(bdc)_3]$.
 (b) $\{Zn_4O\}$ SBU with six carboxylate groups in MOF-5, emphasizing the tetrahedral environment of the central μ -oxido atom, the tetrahedral Zn coordination and the carboxylate carbon atom positions at the vertices of an octahedron.
 (c) Section of the MOF-5 **pcu** framework in ball-and-stick and space-filling mode viewed along one of channel directions. The edge-to-edge dimensions of the square opening (cross-section) of 8×8 Å extend to the van-der-Waals radii of the atoms (the grid unit is 1 Å). (d) The pore diameter of 15 Å extends to the van-der-Waals surface of the framework atoms. At right, view along the cube diagonal. The objects in (b) to (d) are not drawn to scale. (Structure images were drawn with Diamond [9] from the deposited cif file under CCDC-no./Refcode 256966/SAHYOQ [19,20].)

Section S4: Nitrogen adsorption isotherms and powder X-ray diffractograms (Figure S16 - Figure S19)

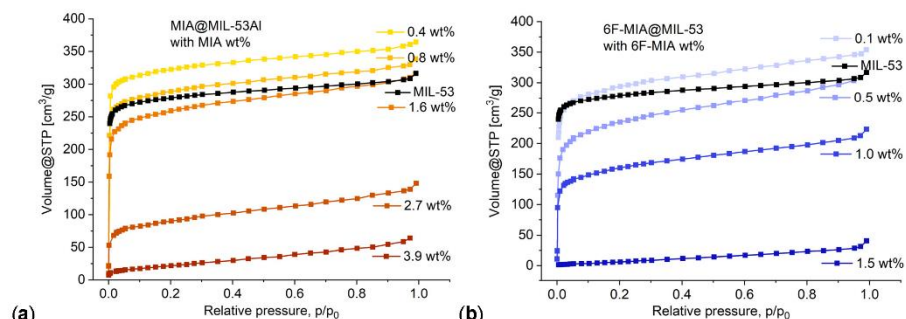


Figure S16. Nitrogen adsorption isotherms (77 K) of (a) MIA@MIL-53 and (b) 6F-MIA@MIL-53 with different flavin amounts.

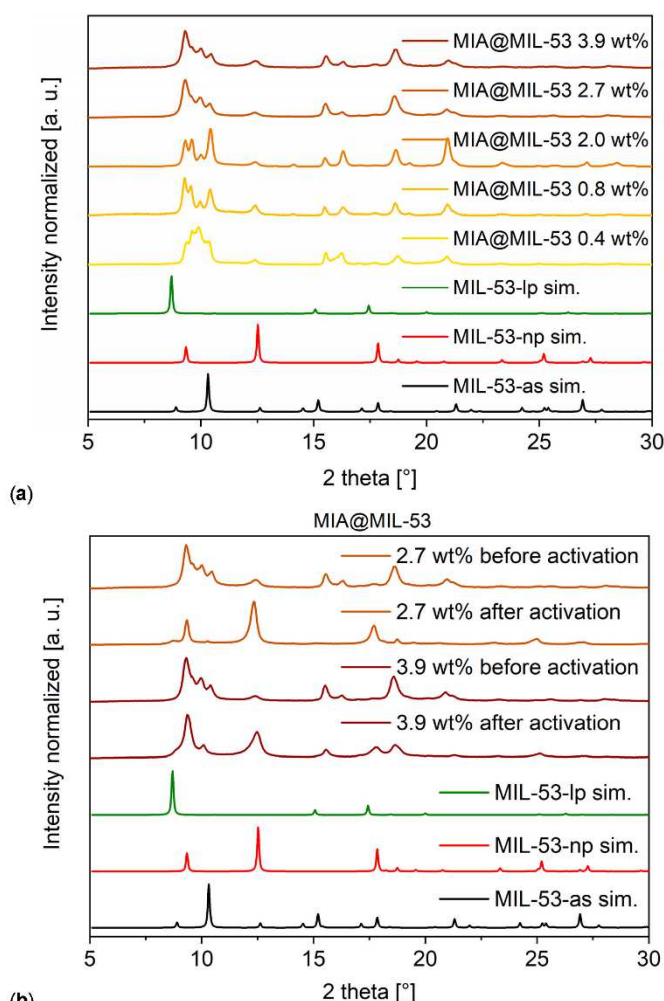


Figure S17. Comparison of the PXRD patterns of MIA@MIL-53 with varying flavin amounts (a) *before* activation and (b) *before and after* activation for 2.7 wt% and 3.9 wt% with the simulated PXRDs for MIL-53-as, -np and -lp based on the deposited cif files under CCDC-no./Refcode 220475/SABVOH for MIL-53-as, 220476/SABVUN for MIL-53-lp and 220477/ SABWAU for MIL-53-np [6].

The slight shift in the corresponding peak positions between the experimental and simulated diffractograms in Figure S17 is due to different cell constants from the formation of the experimental MIA@MIL-53 phases which only approximate the published MIL-53-as, -lp and -np phases. The simulated patterns from these published MIL-53-as, -lp and -np phases are based on Rietveld

refinements of PXRDs from a specific sample treatment protocol [6], which understandably differs from our treatment of the composite samples. An X-ray thermodiffractogram of MIL-53-as in ref. [6] illustrates the peak shift in the diffractograms with temperature. Hence, the experimental diffractograms of flavin@MIL-53 reflect 'breathing' phases which can only approximate the literature phases obtained at different conditions. Yet, the peak pattern allows for an unequivocal phase assignment.

The transition from as-synthesized to large-pore form required high temperature (cf. Figure S13), due to the removal of residual terephthalic acid. When the terephthalic acid is already removed through the washing steps concomitant with the flavin insertion, then there is only volatile solvent remaining in the as-synthesized form. Subsequently, the transition from as-synthesized to large-pore and further to narrow-pore form can occur upon sample storage and preparation under ambient air conditions. The reflections indicate a phase mixture that additionally varies with the different amounts of flavin incorporated.

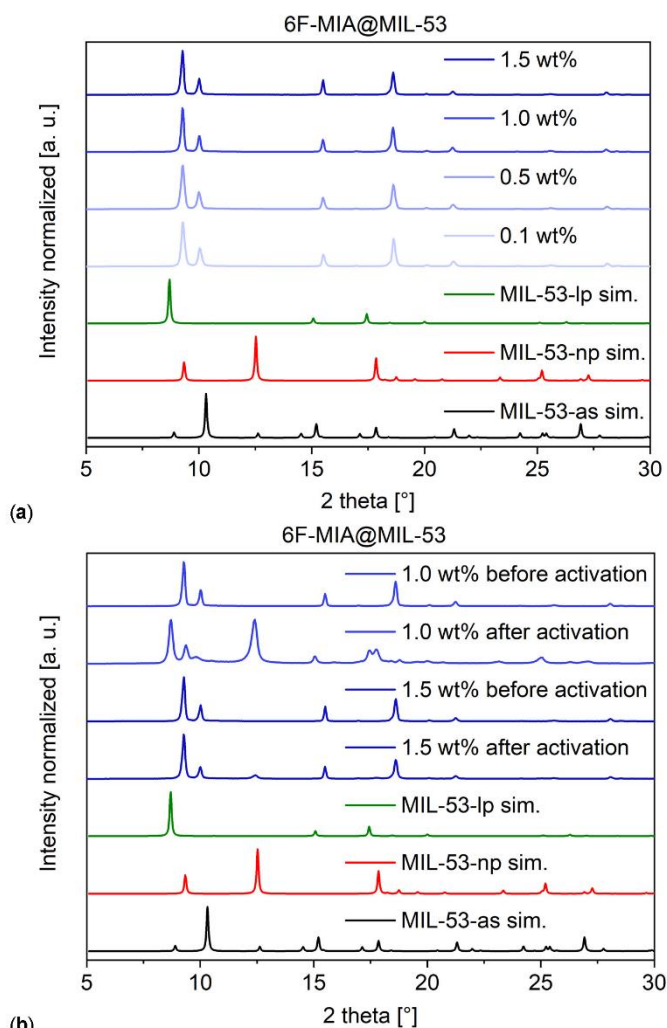


Figure S18. Comparison of the PXRD patterns of 6F-MIA@MIL-53 with varying flavin amounts (a) *before* activation and (b) *before and after* activation for 1.0 wt% and 1.5 wt%. The simulated PXRDs are based on the deposited cif files under CCDC-no./Refcode 220475/SABVOH for MIL-53-as, 220476/SABVUN for MIL-53-lp and 220477/ SABWAU for MIL-53-np [6].

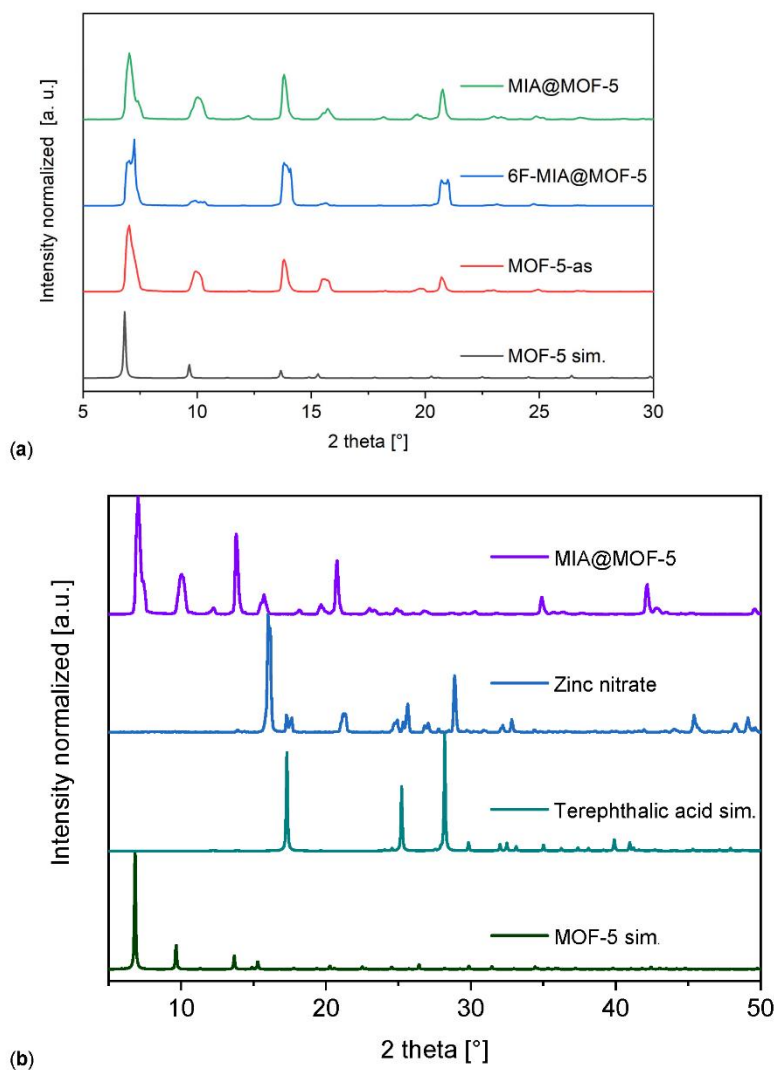


Figure S19. Comparison of the PXRD patterns of (a) MIA@MOF-5 and 6F-MIA@MOF-5 with simulated MOF-5; (b) MIA@MOF-5 with the measured patterns of zinc nitrate hexahydrate and simulated terephthalic acid and MOF-5. (Note the different 2theta range in (a) and (b). The simulated PXRDs are based on the deposited cif files under CCDC-no./Refcode 1269122/TEPHTH for terephthalic acid [21] and CCDC-no./Refcode 256966/SAHYOQ for MOF-5 [20,22].

Section S5: Photophysical characterization of the dyes and dye@MOF (Figure S20 - Figure S35)

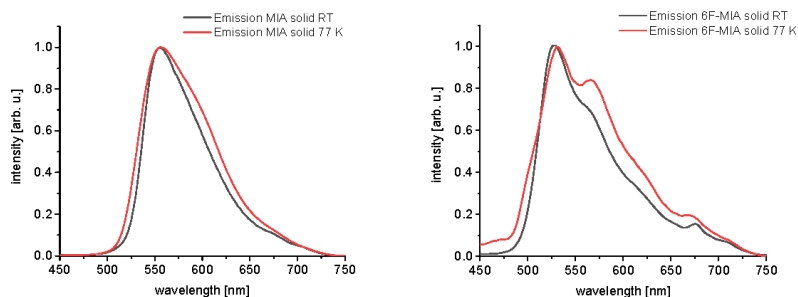


Figure S20. Photoluminescence spectra of MIA (left) and 6F-MIA (right) (λ_{exc} = 440 nm) at room temperature, RT, (black) and at 77 K (red).

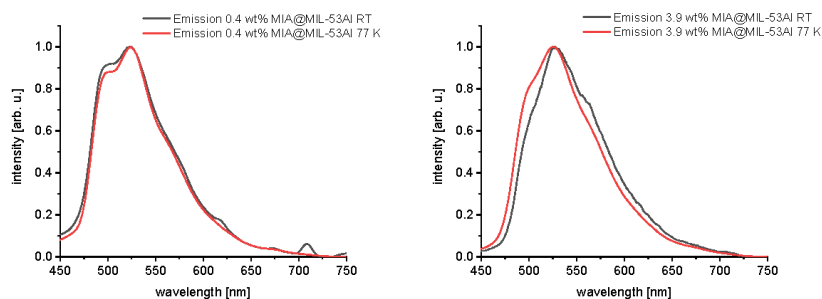


Figure S21. Photoluminescence spectra of MIA@MIL53Al with 0.4 wt % loading (left) and 3.9 wt % loading (right) (λ_{exc} = 440 nm) at room temperature, RT, (black) and at 77 K (red).

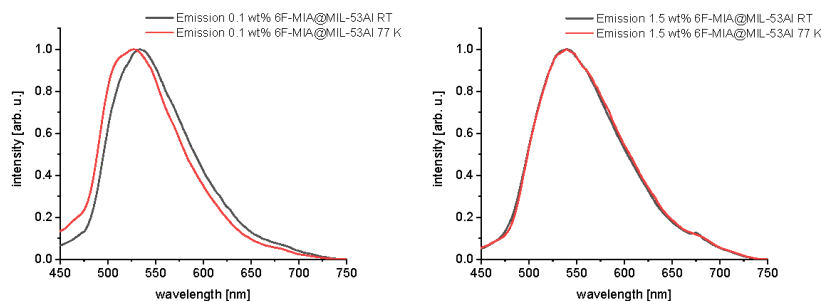


Figure S22. Photoluminescence spectra of 6F-MIA@MIL53Al with 0.1 wt % loading (left) and 1.5 wt % loading (right) (λ_{exc} = 440 nm) at room temperature, RT, (black) and at 77 K (red).

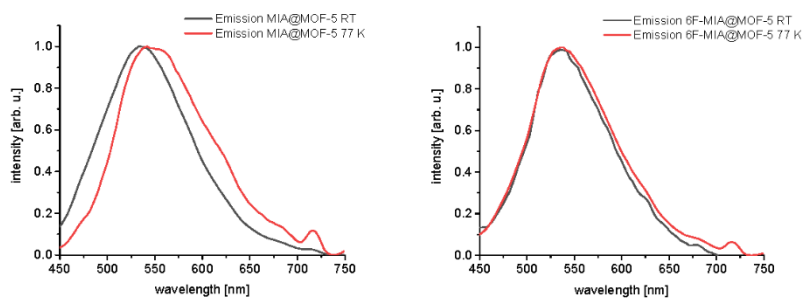


Figure S23. Photoluminescence spectra of MIA@MOF-5 (left) and 6F-MIA@MOF-5 (right) ($\lambda_{\text{exc}} = 440 \text{ nm}$) at room temperature, RT, (black) and at 77 K (red).

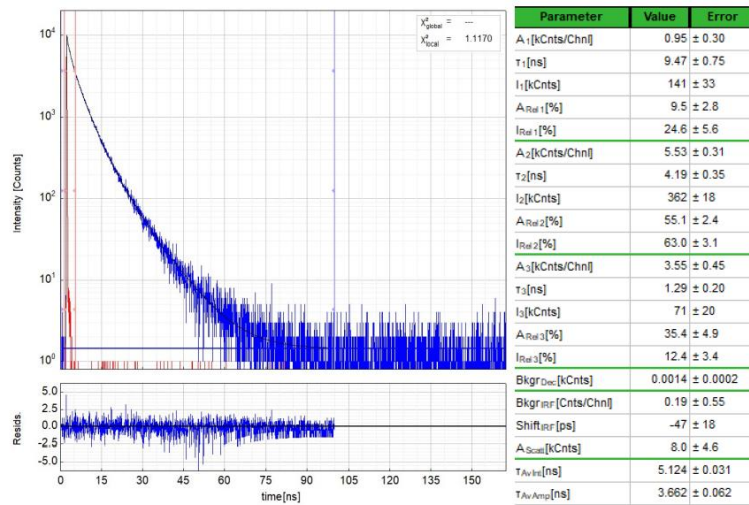


Figure S24. Left: Raw time-resolved photoluminescence decay (blue) of MIA@MOF-5 in the solid state at 298 K and the instrument response function (red), including the residuals ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 530$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits. Here, τ_{av_int} is the intensity-weighted average lifetime (τ_F) and τ_{av_amp} is amplitude-weighted average lifetime (τ_x).

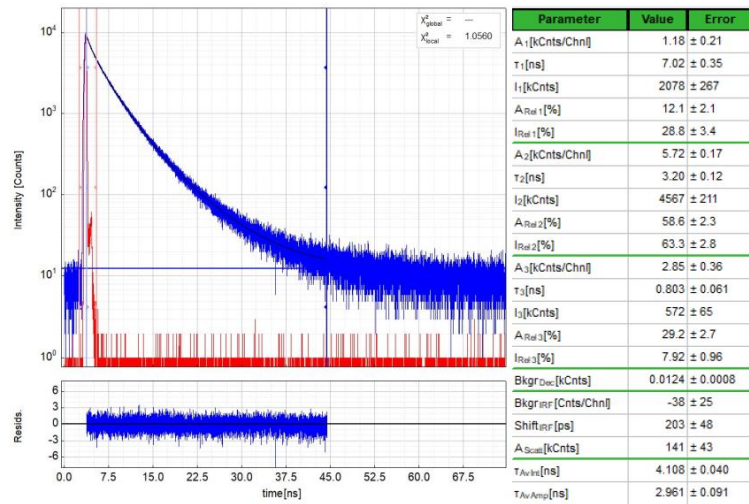


Figure S25. Left: Raw time-resolved photoluminescence decay (blue) of 6F-MIA@MOF-5 in the solid state at 298 K and the instrument response function (red), including the residuals ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 510$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits. Here, τ_{av_int} is the intensity-weighted average lifetime (τ_F) and τ_{av_amp} is amplitude-weighted average lifetime (τ_x).

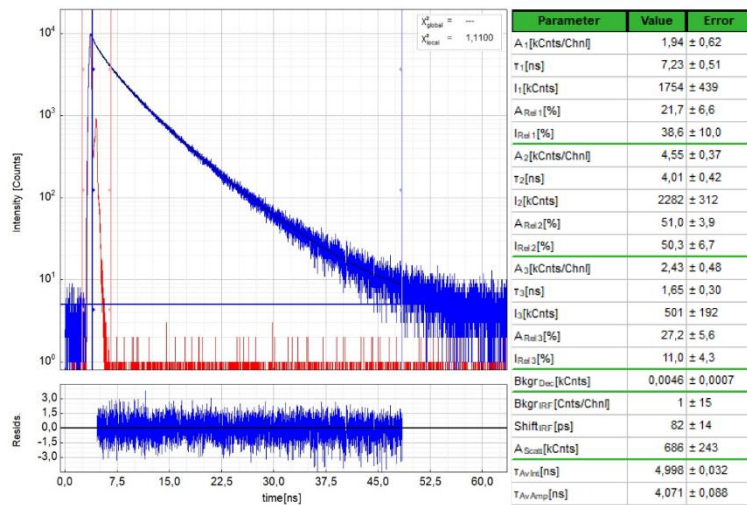


Figure S26. Left: Raw time-resolved photoluminescence decay (blue) of 0.4 wt% MIA@MIL-53 in the solid state at 298 K and the instrument response function (red), including the residuals ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 520$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits. Here, τ_{av_int} is the intensity-weighted average lifetime (τ_F) and τ_{av_amp} is amplitude-weighted average lifetime (τ_x).

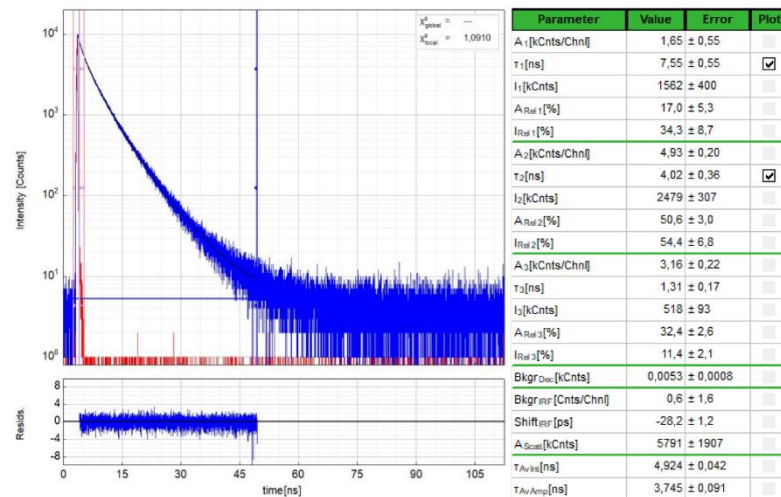


Figure S27. Left: Raw time-resolved photoluminescence decay (blue) of 3.9 wt% MIA@MIL-53 in the solid state at 298 K and the instrument response function (red), including the residuals ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 525$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits. Here, τ_{av_int} is the intensity-weighted average lifetime (τ_F) and τ_{av_amp} is amplitude-weighted average lifetime (τ_x).

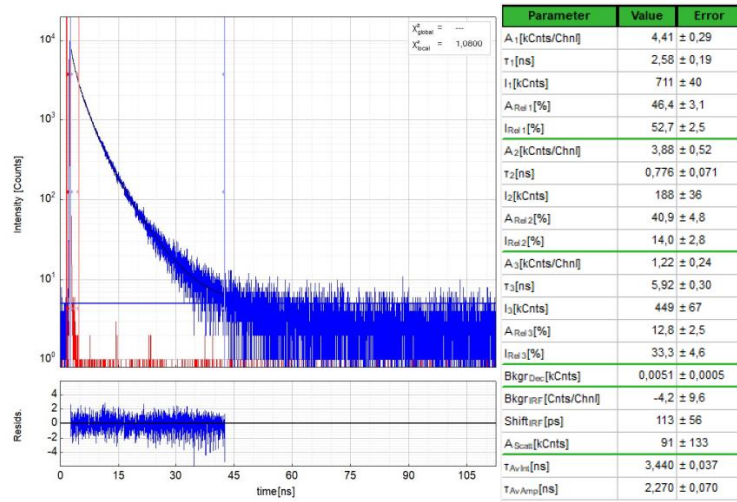


Figure S28. Left: Raw time-resolved photoluminescence decay (blue) of 0.1 wt% 6F-MIA@MIL-53 in the solid state at 298 K and the instrument response function (red), including the residuals ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 535$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits. Here, τ_{av_int} is the intensity-weighted average lifetime (τ_F) and τ_{av_amp} is amplitude-weighted average lifetime (τ_A).

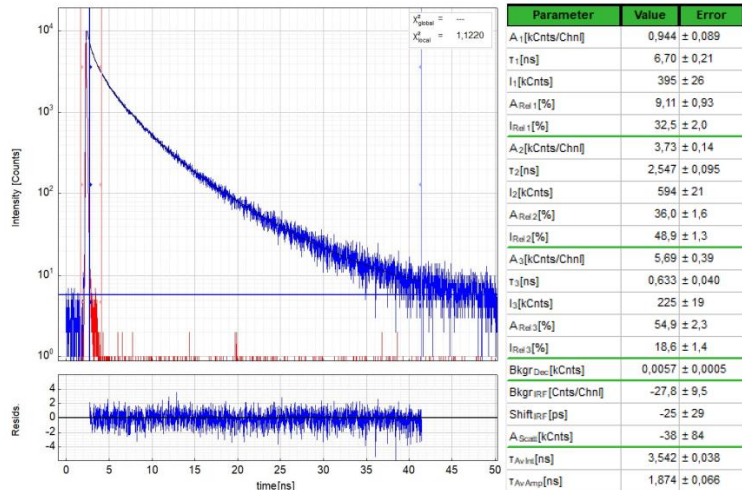


Figure S29. Left: Raw time-resolved photoluminescence decay (blue) of 1.5 wt% 6F-MIA@MIL-53 in the solid state at 298 K and the instrument response function (red), including the residuals ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 535$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits. Here, τ_{av_int} is the intensity-weighted average lifetime (τ_F) and τ_{av_amp} is amplitude-weighted average lifetime (τ_A).

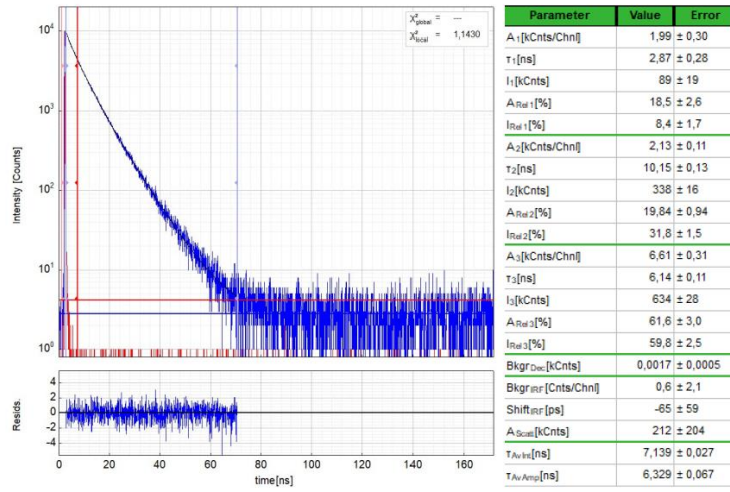


Figure S30. Left: Raw time-resolved photoluminescence decay (blue) of MIA in a DCM/MeOH 1:1 fluid solution at 298 K and the instrument response function (red), including the residuals ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 525$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits. Here, $\tau_{av, int}$ is the intensity-weighted average lifetime (τ_F) and $\tau_{av, amp}$ is amplitude-weighted average lifetime (τ_x).

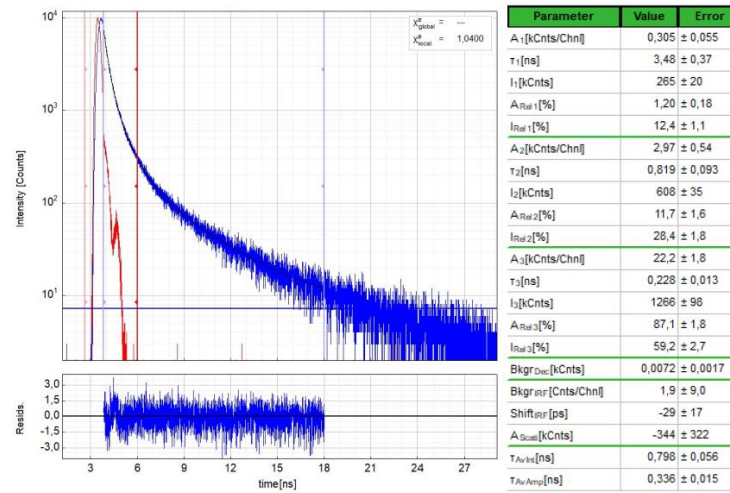


Figure S31. Left: Raw time-resolved photoluminescence decay (blue) of MIA in the solid state at 298 K and the instrument response function (red), including the residuals ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 550$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits. Here, $\tau_{av, int}$ is the intensity-weighted average lifetime (τ_F) and $\tau_{av, amp}$ is amplitude-weighted average lifetime (τ_x).

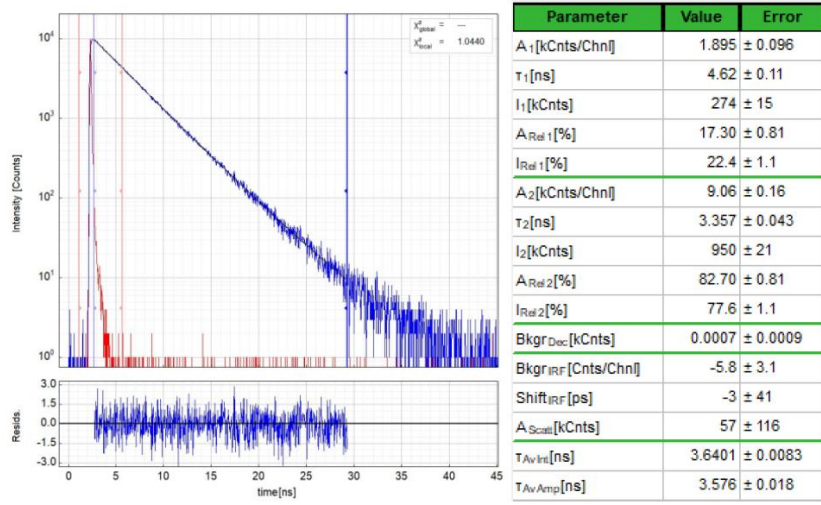


Figure S32. Left: Raw time-resolved photoluminescence decay (blue) of 6F-MIA in a DCM/MeOH 1:1 fluid solution at 298 K and the instrument response function (red), including the residuals ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 525$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits. Here, τ_{av_int} is the intensity-weighted average lifetime (τ_F) and τ_{av_amp} is amplitude-weighted average lifetime (τ_x).

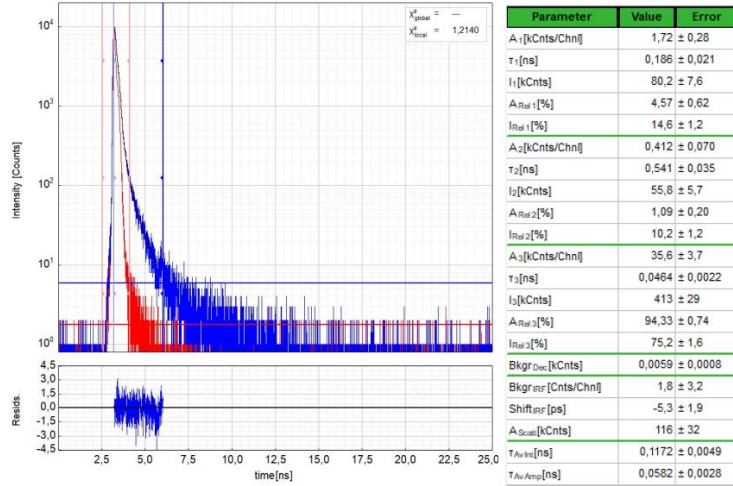


Figure S33. Left: Raw time-resolved photoluminescence decay (blue) of 6F-MIA in the solid state at 298 K and the instrument response function (red), including the residuals ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 550$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits. Here, τ_{av_int} is the intensity-weighted average lifetime (τ_F) and τ_{av_amp} is amplitude-weighted average lifetime (τ_x).

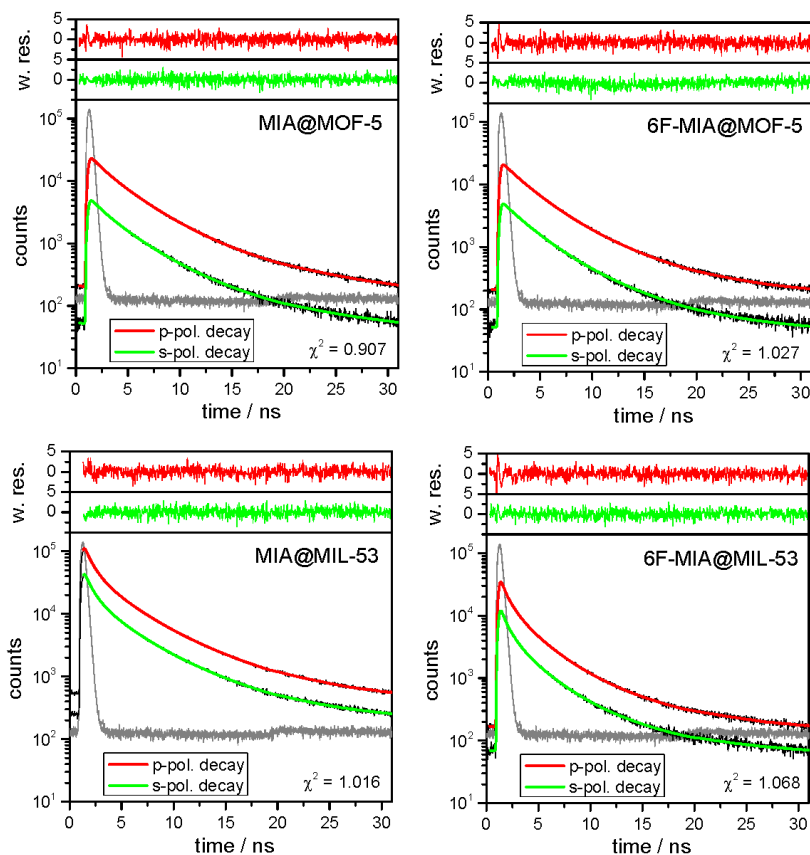


Figure S34. Time-correlated polarization-resolved single-photon data of the flavin@MOF composites imaged by confocal multi-parameter fluorescence image spectroscopy (MFIS) with pulsed excitation at 440 nm and $\lambda_{em} = 502\text{-}538$ nm (Figure 6, main document). Global fits by iterative reconvolution of the instrumental function (grey curves) to p- and s-polarized decays required 4 fluorescence lifetime components (lifetimes and species fractions are compiled in Table 3 of the main document) and one (two for MIA@MIL-53) rotational correlation time. The corresponding equations are described in ref. [23]. The offsets in the decays are caused by afterpulsing of the detectors and taken into account by the fitting routine. The G-factor, compensating differences in the detection efficiencies in the two polarization channels, of $G = 0.97$ was determined by fitting polarized fluorescence decays of an aqueous solution of Rhodamine 110. For flavin@MOF-5 five slices in the center of the z-stack were selected to generate the decay histograms, for flavin@MIL53 all photons from the images were used.

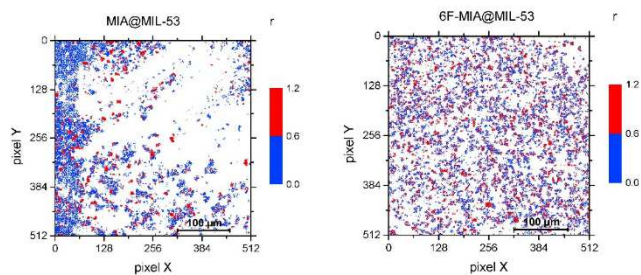


Figure S35. MFIS images of flavin@MIL-53 displaying experimental steady state fluorescence anisotropy r of Figure 6 with a distinct color scheme to highlight that one microcrystal has a unique anisotropy, i.e. r is a unique feature for each crystal that is related to its orientation. For further information, see discussion of Figure 6 in the main text section 2.3.

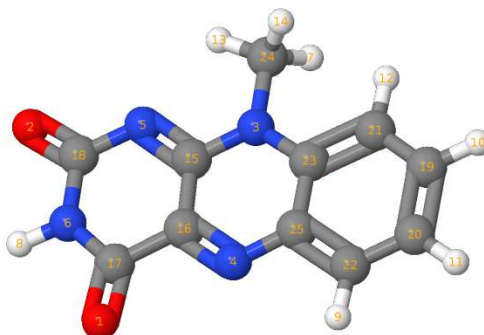
Section S6: Theoretical calculations (Figure S36 - Figure S42)

Force Field parameters are in the AMBER20 format and units.

Section S6.1: Force Field MIA

Atom number FF atom type

O	1	Oc
O	2	Oc
N	3	Na
N	4	Nc
N	5	Nc
N	6	N
H	7	H1
H	8	Hn
H	9	Hm
H	10	Hm
H	11	Hm
H	12	Hm
H	13	H1
H	14	H1
C	15	Cd
C	16	Cd
C	17	Co
C	18	Co
C	19	Cm
C	20	Cm
C	21	Cm
C	22	Cm
C	23	Cm
C	24	C3
C	25	Cm



MASS

om	16.0000.434
n	14.0100.530
nc	14.0100.530
na	14.0100.530
hn	1.0080.161
h1	1.0080.135
hm	1.0080.135
c2	12.0100.616
cd	12.0100.360
c3	12.0100.878
cm	12.0100.360

BOND STRETCHING

om-c2	637.70	1.218
n-hn	403.20	1.013

n -c2	427.60	1.379
nc-c2	416.90	1.387
nc-cd	525.40	1.317
nc-cm	467.70	1.352
na-cd	425.80	1.380
na-c3	327.70	1.463
na-cm	420.50	1.384
h1-c3	330.60	1.097
hm-cm	345.80	1.086
c2-cd	371.00	1.468
cd-cd	419.80	1.428
cm-cm	461.10	1.398

ANGLE BENDING

om-c2-n	74.220	123.050
om-c2-nc	73.910	123.180
om-c2-cd	69.140	123.930
n -c2-nc	71.580	117.110
n -c2-cd	69.070	112.700
nc-cd-na	74.900	112.220
nc-cd-cd	71.570	112.560
nc-cd-c2	67.620	121.880
nc-cm-cm	69.460	119.720
na-cd-cd	68.580	117.770
na-c3-h1	49.830	108.780
na-cm-cm	69.080	118.340
hn-n -c2	48.330	117.550
h1-c3-h1	39.240	108.460
hm-cm-cm	48.180	119.880
c2-n -c2	63.740	127.080
c2-nc-cd	66.680	120.490
c2-cd-cd	63.620	122.690
cd-nc-cm	72.480	104.880
cd-na-c3	61.880	126.460
cd-na-cm	67.400	113.150
c3-na-cm	62.320	124.360
cm-cm-cm	66.620	120.020

TORSION

om-c2-n -hn	1	2.500	180.000	-2.000
om-c2-n -hn	1	2.000	0.000	1.000
om-c2-n -c2	1	2.500	180.000	2.000
om-c2-nc-cd	1	4.000	180.000	2.000
om-c2-cd-nc	1	2.875	180.000	2.000
om-c2-cd-cd	1	2.875	180.000	2.000
n -c2-nc-cd	1	4.000	180.000	2.000
n -c2-cd-nc	1	2.875	180.000	2.000

n -c2-cd-cd	1	2.875	180.000	2.000
nc-c2-n -hn	1	2.500	180.000	2.000
nc-c2-n -c2	1	2.500	180.000	2.000
nc-cd-na-c3	1	1.700	180.000	2.000
nc-cd-na-cm	1	1.700	180.000	2.000
nc-cd-cd-nc	1	4.000	180.000	2.000
nc-cd-cd-c2	1	4.000	180.000	2.000
nc-cd-cd-na	1	4.000	180.000	2.000
nc-cm-cm-na	1	3.625	180.000	2.000
nc-cm-cm-cm	1	3.625	180.000	2.000
nc-cm-cm-hm	1	3.625	180.000	2.000
na-cd-nc-c2	1	4.750	180.000	2.000
na-cd-cd-c2	1	4.000	180.000	2.000
na-cm-cm-cm	1	3.625	180.000	2.000
na-cm-cm-hm	1	3.625	180.000	2.000
hn-n -c2-cd	1	2.500	180.000	2.000
h1-c3-na-cd	1	0.000	0.000	2.000
h1-c3-na-cm	1	0.000	0.000	2.000
hm-cm-cm-cm	1	3.625	180.000	2.000
hm-cm-cm-hm	1	3.625	180.000	2.000
c2-n -c2-cd	1	2.500	180.000	2.000
c2-nc-cd-cd	1	4.750	180.000	2.000
c2-cd-nc-cm	1	4.750	180.000	2.000
cd-nc-cm-cm	1	4.800	180.000	2.000
cd-cd-na-c3	1	1.700	180.000	2.000
cd-cd-na-cm	1	1.700	180.000	2.000
cd-na-cm-cm	1	0.300	180.000	2.000
cd-cd-nc-cm	1	4.750	180.000	2.000
c3-na-cm-cm	1	0.300	180.000	2.000
cm-cm-cm-cm	1	3.625	180.000	2.000

OUT-OF-PLANE

c2-c2-n -hn	1.1	180.0	2.0
c3-cm-na-cd	1.1	180.0	2.0
n -nc-c2-om	10.5	180.0	2.0
cd-n -c2-om	10.5	180.0	2.0
c2-cd-cd-nc	1.1	180.0	2.0
cd-na-cd-nc	1.1	180.0	2.0
cm-cm-cm-nc	1.1	180.0	2.0
cm-cm-cm-na	1.1	180.0	2.0
cm-cm-cm-hm	1.1	180.0	2.0

NON-BONDED

om	1.6612	0.2100
n	1.8240	0.1700
nc	1.8240	0.1700
na	1.8240	0.1700

hn	0.6000	0.0157
h1	1.3870	0.0157
hm	1.4590	0.0150
c2	1.9080	0.0860
cd	1.9080	0.0860
c3	1.9080	0.1094
cm	1.9080	0.0860

Section S6.2: Force Field MIL-53(Al)

-Metal residue (Al):

Atom number FF atom type

Al	1	Al
----	---	----

-Linker (C₈O₄H₄):

Atom number FF atom type

O	1	Oc
O	2	Oc
O	3	Oc
O	4	Oc
H	5	Ha
H	6	Ha
H	7	Ha
H	8	Ha
C	9	Co
C	10	Cp
C	11	Ca
C	12	Ca
C	13	Ca
C	14	Ca
C	15	Cp
C	16	Co

-Hydroxy bridge (OH):

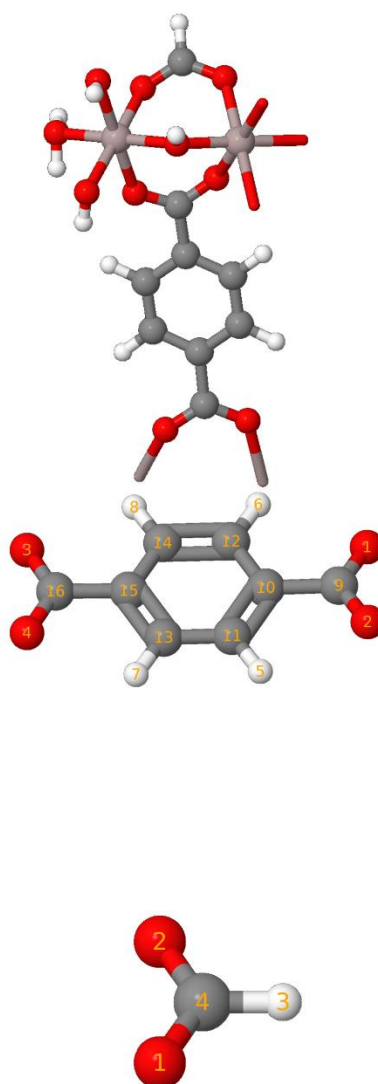
Atom number FF atom type

O	1	Oh
H	2	Ho

-Border residue (CO₂H):

Atom number FF atom type

O	1	Oc
O	2	Oc
H	3	H5
C	4	Co



- Border Hydroxy (OH):

Atom number FF atom type

O	1	Oy
H	2	Hy

- Border water (OH₂):

Atom number FF atom type

O	1	Ow
H	2	Hw
H	3	Hw

MASS

al	26.982	0.520
oh	16.000	0.465
oc	16.000	0.465
od	16.000	0.465
ow	16.000	0.465
oy	16.000	0.465
co	12.010	0.360
cp	12.010	0.360
ca	12.010	0.360
ho	1.008	0.135
ha	1.008	0.135
h5	1.008	0.135
hw	1.008	0.135
hy	1.008	0.135

BOND STRETCHING

al-oh	226.383	1.807
al-oc	191.193	1.905
al-od	185.625	1.910
al-oy	179.614	1.802
oh-ho	483.767	0.948
oy-hy	619.790	0.958
oc-co	532.656	1.264
od-co	515.050	1.268
co-cp	323.272	1.482
cp-ca	394.916	1.397
ca-ca	394.916	1.397
ca-ha	271.310	1.200
co-h5	319.400	1.115
al-ow	226.383	1.807

ANGLE BENDING

al-oh-al	267.297	125.491
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al-oh-ho	88.822	114.648
al-oy-hy	17.242	122.255
al-oc-co	94.016	133.962
al-od-co	94.016	133.962
oc-al-oc	56.898	179.890
od-al-od	55.952	179.789
oh-al-oh	61.380	179.487
oc-al-od	180.099	91.440
od-al-oh	9.883	90.324
oh-al-oc	221.271	90.942
oy-al-oy	46.500	90.000
oy-al-oh	63.653	90.000
oy-al-oc	63.653	90.000
oy-al-od	63.653	90.000
oy-al-ow	46.500	90.000
oc-co-oc	290.609	124.241
od-co-od	287.813	123.089
oc-co-cp	290.848	117.674
od-co-cp	290.848	117.674
co-cp-ca	284.293	120.197
cp-ca-ca	136.436	120.261
cp-ca-ha	82.144	121.174
ca-cp-ca	136.436	120.261
ca-ca-ha	82.144	121.174
oc-co-h5	55.501	123.760
od-co-h5	55.501	123.760
ow-al-oc	221.271	90.942
ow-al-od	221.271	90.942
ow-al-oh	221.271	90.942
ow-al-ow	55.952	179.789
al-ow-hw	88.822	114.648

TORSION

al-oc-co-cp	1	1.516	180.000	2.000
al-od-co-cp	1	1.516	180.000	2.000
al-oc-co-h5	1	1.516	180.000	2.000
oc-co-cp-ca	1	2.175	180.000	-2.000
oc-co-cp-ca	1	0.300	0.000	3.000
od-co-cp-ca	1	2.175	180.000	-2.000
od-co-cp-ca	1	0.300	0.000	3.000
co-cp-ca-ca	1	6.650	180.000	2.000
co-cp-ca-ha	1	6.650	180.000	2.000
cp-ca-ca-ha	1	6.650	180.000	2.000
ca-cp-ca-ha	1	6.650	180.000	2.000
ha-ca-ca-ha	1	6.650	180.000	2.000

OUT-OF-PLANE

cp-oc-oc-co	1.100	180.0000	2.000
co-ca-ca-cp	1.100	180.0000	2.000
ca-cp-ha-ca	1.100	180.0000	2.000
ca-ca-ca-ha	1.100	180.0000	2.000
co-ca-cp-ca	1.100	180.0000	2.000
ca-ca-cp-co	1.100	180.0000	2.000

NON-BONDED

al	2.36	0.115918
oh	1.82	0.059034
oc	1.82	0.059034
od	1.82	0.059034
oy	1.82	0.059034
ow	1.82	0.059034
co	1.94	0.055927
cp	1.94	0.055927
ca	1.94	0.055927
ho	1.60	0.016013
ha	1.60	0.016013
hw	1.60	0.016013
h5	1.60	0.016013
hy	1.60	0.016013

Section S6.3: Force Field MOF-5

-Metal residue (Zn_4O):

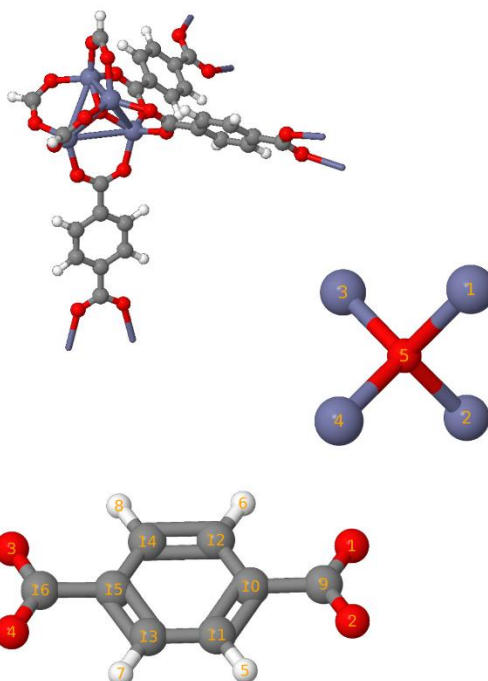
Atom number FF atom type

Zn	1	Zn
Zn	2	Zn
Zn	3	Zn
Zn	4	Zn
O	1	Os

-Linker ($\text{C}_8\text{O}_4\text{H}_4$):

Atom number FF atom type

O	1	O
O	2	O
O	3	O
O	4	O
H	5	Ha
H	6	Ha
H	7	Ha
H	8	Ha
C	9	C
C	10	Ca

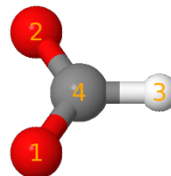


C	11	Ca
C	12	Ca
C	13	Ca
C	14	Ca
C	15	Ca
C	16	C

-Border residue (CO₂H):

Atom number FF atom type

O	1	O
O	2	O
H	3	H5
C	4	C



MASS

zn	65.38	0.999
o	16.00	0.434
os	16.00	0.465
c	12.01	0.616
ca	12.01	0.360
ha	1.008	0.135
h5	1.008	0.135

BOND STRETCHING

c-o	637.70000	1.2183
o-zn	61.13030	2.0150
zn-os	61.13030	2.0750
ca-o	542.26172	1.2850
ca-ca	471.78208	1.3800
c-ca	348.08312	1.4800
h5-c	319.40000	1.1150

ANGLE BENDING

zn-os-zn	28.76720	109.471
o-zn-os	21.57540	111.300
o-zn-o	15.82196	107.600
c-o-zn	30.92474	131.200
o-c-o	46.02752	125.500
ca-ca-c	52.50014	120.000
o-c-ca	56.09604	117.000
h5-c-o	55.50125	123.760

TORSION

ca-ca-c-o	1	1.0	180.0	2.0
os-zn-o-c	1	5.0	180.0	2.0

zn-os-zn- o	1	5.0	180.0	2.0
zn- o- c- c	1	5.0	180.0	2.0
zn -o- c-ca	1	5.0	180.0	2.0
zn-o -c -h5	1	1.6	180.0	2.0

OUT-OF-PLANE

o -o -c -ca	16.54	180.0	2.0
ca-ca-ca-ha	1.1	180.0	2.0
c -ca-ca-ca	1.1	180.0	2.0
ca-o -c -o	1.1	180.0	2.0

NON-BONDED

zn	2.29	0.276
os	1.82	0.059
o	1.82	0.059
c	1.94	0.056
ca	1.94	0.056
ha	1.62	0.020

Section S6.4: QM part, MM part

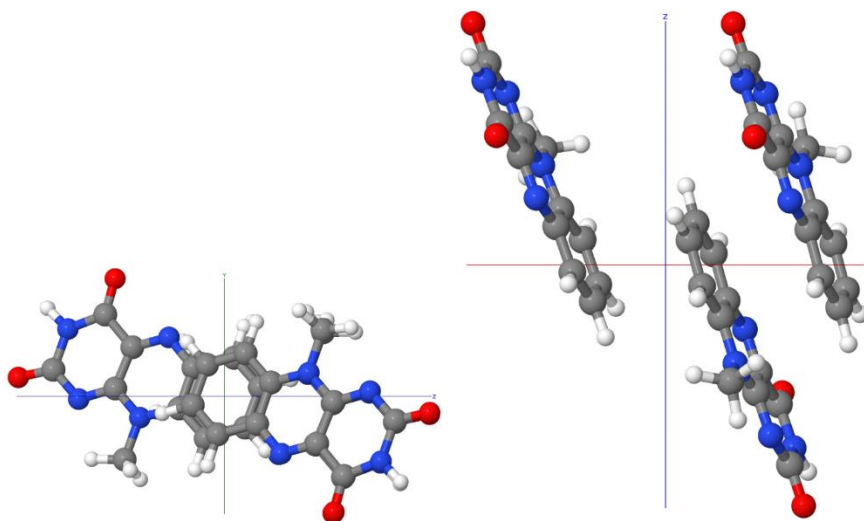


Figure S36. QM-Layer including three MIA molecules. During QM/MM-optimization only QM atoms were allowed to move (mobile layer), the remaining atom position were fixed at their optimized values from the corresponding plane-wave calculation with QuantumEspresso [24]. (left: view along X axis, right: view along Y axis).

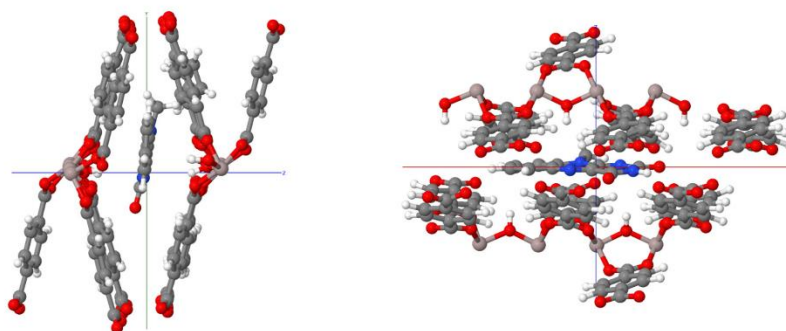


Figure S37. The mobile layer in MIL-53(Al) contains MIA and all residues that have at least 1 atom in a radius of 7.5 Å around the MIA chromophore (QM layer (MIA) and movable MM portion (MOF), left: view along X axis, right: view along Y axis). The remaining atoms (not shown) were fixed at their optimized positions from the plane-wave computation with QuantumEspresso [24].

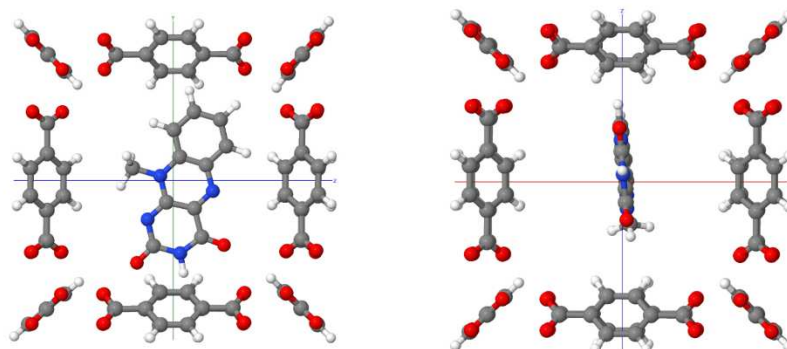


Figure S38. The mobile layer in both *inward* and *outward* pores of MOF-5, containing MIA and all residues that have at least one atom within a radius of 5.0 Å around the MIA chromophore. Zn₄O residues and the remaining portion of the MOF were kept fixed at their plane-wave optimized positions. (QM layer (MIA) and medium layer (MOF), left: view along X axis, right: view along Y axis).

Cluster for MIL-53(Al) Force Field generation:

The same cluster as presented in the work of Vanduyfhuys et al. [25] was used to generate the MIL-53(Al) force field (Figure S39). The total charge was -1 . It was first geometry-optimized with the B3LYP hybrid functional and the 6-311++G(d,p) basis set, followed by vibrational analysis using the Gaussian16 package [26].

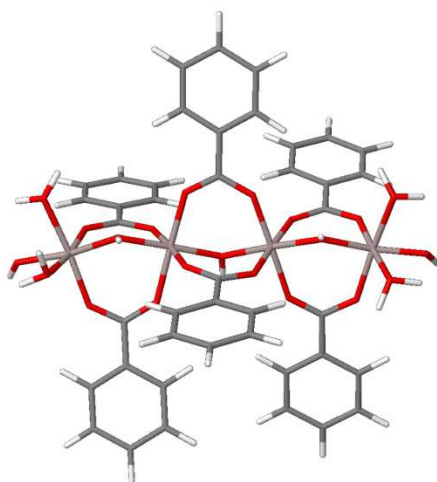


Figure S39. Cluster model of Vanduyfhuys et al. [25] used for generating the MIL-53(Al) force field used in this work.

Table S3. Crystallographic data for MIL-53 phases (powder data with Rietveld refinement from literature) and MIL-53 (computed).

Compound	experiment. MIL-53-lp ^a	computed MIL-53-lp ^b	experiment. MIL-53-np ^{a,c}	computed MIA@MIL-53 ^b
Crystal system	orthorhombic	unconstrained (triclinic)	monoclinic	unconstrained (triclinic)
Space group	<i>Imma</i>	unconstrained (<i>P1</i>)	<i>Cc</i>	unconstrained (<i>P1</i>)
a [Å]	6.6085(9)	6.8904	19.513(2)	20.1698 ^d
b [Å]	16.675(3)	16.4224	7.612(1)	18.8673
c [Å]	12.813(2)	13.5000	6.576(1)	8.9399
α [°]	90	90	90	89.92
β [°]	90	90	104.24(1)	90.31
γ [°]	90	90	90	87.29
V [Å ³]	1411.95(40)	1527.62	946.74(10)	3398.21

^a CCDC no. 220476 (lp), 220477 (np) [6]. ^b Cell parameters refined through Quantum Espresso.

^c The cell setting/orientation of the coordinate system in the experimental structure of MIL-53-np is different from those of the other three (exp. and comput.) structures. To facilitate a comparison of the axes lengths, matching directions are given in the same color. ^d Note that in computed MIA@MIL-53 the *a* axis (channel direction) was extended to about three times the corresponding axis length in experimental MIL-53-lp or -np (ca. 6.6 Å) to accommodate separated MIA molecules with their length of 12 Å (cf. Figure S12).

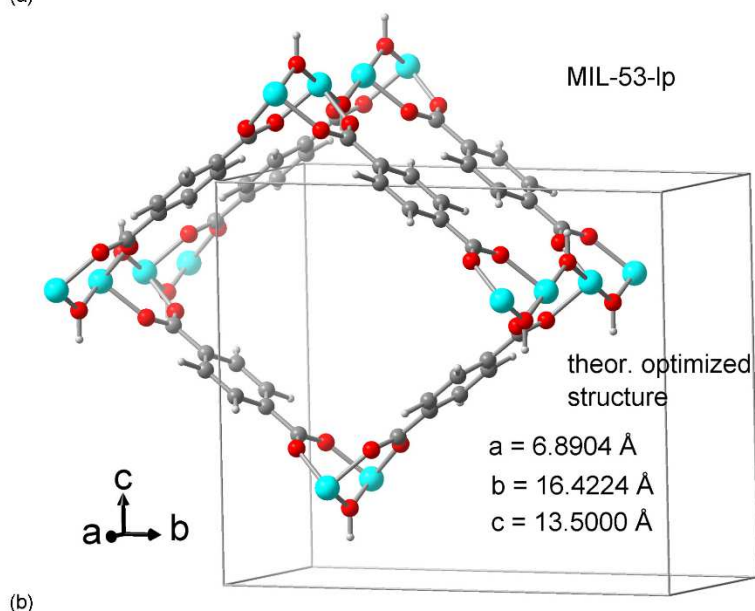
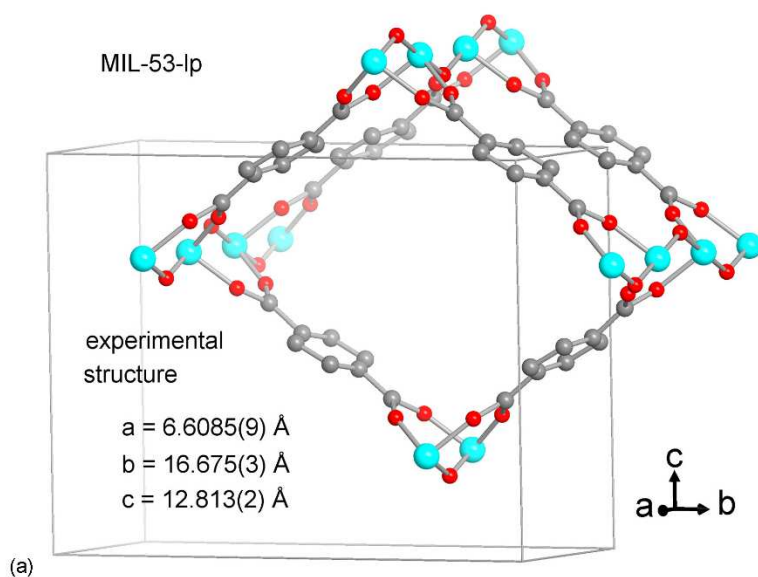


Figure S40. Sections of the structures with the cell edges and cell constants of MIL-53-lp from (a) experimental Rietveld refinement (CCDC no./Refcode 220476/SABVUN) [6] and (b) from theoretical optimization with QuantumEspresso (see also Table S3). Compared to the experimental orthorhombic large-pore form MIL-53-lp the computed guest-free MIL-53-lp structure after optimization widens by ca. 0.3 Å and 0.7 Å in a- and c-directions, respectively, while it shrinks by ca. 0.25 Å in the b-direction, with the cell angles remaining at 90°

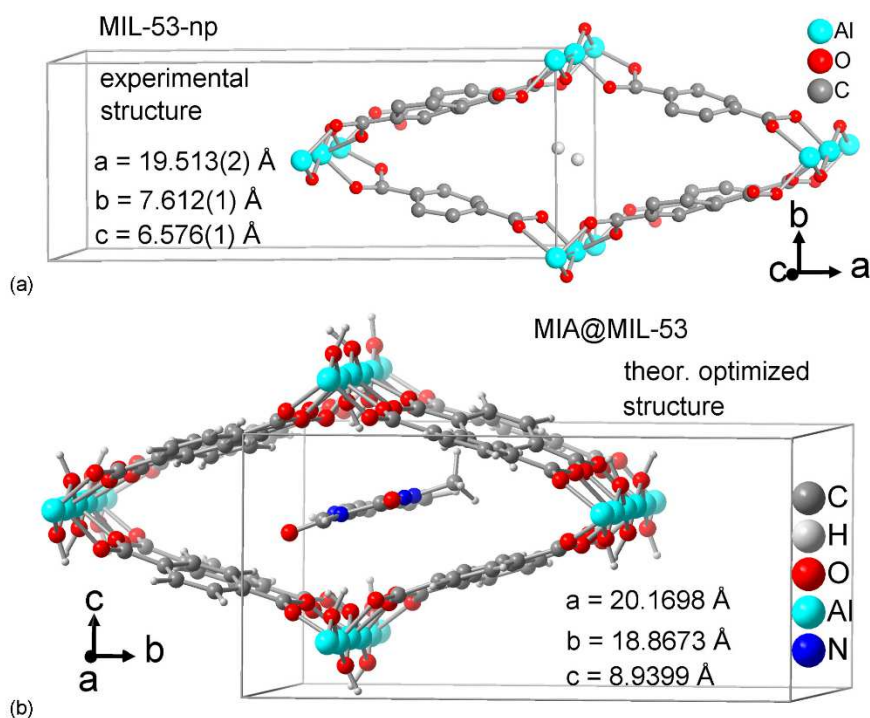


Figure S41. Sections of the structures with the cell edges and cell constants of (a) MIL-53-np from experimental Rietveld refinement (CCDC no./Refcode 220477/SABWAU) [6] and of (b) MIA@MIL-53 from theoretical optimization with QuantumEspresso. The theoretical cell setting/orientation of the coordinate system in (b) is the same as in the MIL-53-lp structures in Figure S40 but different to the MIL-53-np structure in (a). However, the axis parallel to the channel direction in MIA@MIL-53 (*a* axis, ca. 20 Å) was extended to about three times the corresponding axis length in experimental MIL-53-lp or -np (ca. 6.6 Å) to accommodate separated MIA molecules in the channels (cf. MIA length of 12 Å in Figure S12) (see also Table S3).

Section S6.5: Transition dipole moments of MIA

The orientations of the transition dipole moment vector (TDM) were obtained from the quantum-chemical calculations for $S_0 \rightarrow S_1$ (absorption) and for $S_1 \rightarrow S_0$ (fluorescence) (see example in Figure S42). The vector coordinates are as follows:

MIA in vacuum			
TDM	x	y	z
Absorption ($S_0 \rightarrow S_1$)	1.8176223	-0.4546537	0.7971484
Emission ($S_1 \rightarrow S_0$)	1.6719799	-0.3554352	0.7142668
Difference ($S_0 \rightarrow S_1$)	0.1456424	-0.0992185	0.0828816
Angle = 1.9°			

MIA@MIL-53			
TDM	x	y	z
Absorption ($S_0 \rightarrow S_1$)	1.7076416	0.9172188	-0.1371604
Emission ($S_1 \rightarrow S_0$)	1.5876942	-0.9185493	-0.1183539
Difference ($S_0 \rightarrow S_1$)	0.1199474	0.0013305	-0.0188065
Angle = 1.8°			

MIA@MOF-5			
TDM	x	y	z
Absorption ($S_0 \rightarrow S_1$)	0.0462862	-2.0319814	-0.0827332
Emission ($S_1 \rightarrow S_0$)	-0.0345843	-1.8358583	-0.1126006
Difference ($S_0 \rightarrow S_1$)	0.0808705	-0.1961231	
Angle = 2.7°			

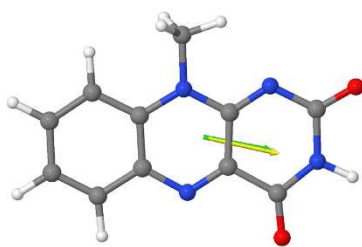


Figure S42. Transition dipole moments of MIA@MIL-53. Yellow arrow for $S_0 \rightarrow S_1$ (absorption) and green arrow for $S_1 \rightarrow S_0$ (fluorescence).

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7.2 Molecular design of phenazine-5,10-diyl dibenzonitriles and the impact on their thermally activated delayed fluorescence properties

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Kurzzusammenfassung

Die photophysikalischen Eigenschaften der Verbindungen 3,3'-(Phenazin-5,10-diyl)dibenzonitril (mBN) und 4',4'''-(Phenazin-5,10-diyl)bis([1,1'-Biphenyl]-4-carbonitril) (BPN) werden vorgestellt, analysiert und mit denen des bekannten TADF-Emitters 4,4'-(Phenazin-5,10-diyl)dibenzonitril (pBN) verglichen. Als Feststoff weist pBN deutliche TADF-Eigenschaften auf. Im Gegensatz dazu sind die TADF-Eigenschaften bei mBN nur schwach ausgeprägt. BPN stellt hingegen einen herkömmlichen fluoreszenten Emitter dar. Dies lässt sich auf die Überlappung der Phenazindiyl- und Benzonitril-Einheiten in diesen drei Molekülen zurückführen, die nur in pBN effizient funktioniert. Alle drei Moleküle lumineszieren nur schwach in Toluol, Tetrahydrofuran (THF) oder Dichlormethan (CH_2Cl_2). Die stärkste Lumineszenz tritt in Toluol bei gelber (pBN und mBN) bis orangener (BPN) Emission auf. Die Emissionsmaxima $\lambda_{\text{em,max}}$ in Toluol unterscheiden sich leicht zwischen pBN (562 nm) und mBN (572 nm) und überlappen in THF (634 nm) bzw. CH_2Cl_2 (~660 nm). Die breitbandige Emission ist stark lösungsmittelabhängig und deutet auf einen CT-Charakter des angeregten Zustands hin. BPN zeigt eine schwache lösungsmittelabhängige Photolumineszenz (604 nm in Toluol, 589 nm in THF und 587 nm in CH_2Cl_2). Zusammen mit der beobachtbaren vibronischen Feinstruktur in den Niedrigtemperaturspektren des Pulvers kann abgeleitet werden, dass die Emission in BPN von einem lokalisierten elektronischen Zustand (LE) ausgeht, der für die TADF-Eigenschaften ungünstig ist. Dies zeigt, dass selbst kleine Änderungen in der Molekülstruktur der Dihydrophenazine einen signifikanten Einfluss auf deren TADF-Eigenschaften haben können.

Anteile an der Publikation

- Konzeption des Forschungsvorhabens in Kooperation mit Jun.-Prof. Dr. M. Suta und Durchführung der Literaturrecherche.
- Synthese und Charakterisierung der Leuchtstoffe mittels NMR, HR-ESI-MS, EA und Schmelzpunktbestimmung, mit Unterstützung von L. Pfeifer.
- Spektroskopische Messungen der Leuchtstoffe am Feststoff.
- Selbständige Auswertung, graphische Darstellung und Interpretation der entsprechenden experimentellen Rohdaten.
- Durchführung der Kristallstrukturanalyse und Verfeinern der Einkristall-Röntgenstrukturdaten der Leuchtstoffe durch T. Heinen; graphische Darstellung und Interpretation der Ergebnisse durch Prof. Dr. C. Janiak, bei pBN mit Unterstützung und Polymorph-Analyse durch Dr. I. Boldog.
- Durchführung der spektroskopischen Messungen der Leuchtstoffe in Lösung sowie Auswertung, graphische Darstellung und Interpretation der Ergebnisse durch Dr. J. Wiefermann und Prof. Dr. T. J. J. Müller
- Durchführung der theoretischen Berechnungen der Leuchtstoffe sowie graphischen Darstellung und Interpretation der Ergebnisse durch Dr. S. Hede und Dr. O. Weingart.
- Anfertigung eines Manuskripts und der *supporting information* für eine wissenschaftliche Publikation basierend auf den experimentellen und theoretischen Ergebnissen.
- Überarbeitung des Manuskripts nach den Kommentaren der Co-Autoren.
- Erstellung des *cover letters* in Kooperation mit Jun.-Prof. Dr. Markus Suta
- Gestaltung des *graphical abstract* des Manuskripts.
- Die Publikation wurde im internationalen Journal *Journal of Materials Chemistry C* mit Jun.-Prof. Dr. M. Suta eingereicht.
- Überarbeitung des Manuskripts in Kooperation mit Jun.-Prof. Dr. M. Suta und Prof. Dr. C. Janiak.



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Molecular design of phenazine-5,10-diyl-
dibenzonitriles and the impact on their thermally
activated delayed fluorescence properties†Dietrich Püschel,^a Julia Wiermann,^b Simon Hédé,^c Tobias Heinen,^a Leo Pfeifer,^a
Oliver Weingart,^b Markus Suta,^b Thomas J. J. Müller^b and
Christoph Janiak^b

The photoluminescence properties of the compounds 3,3'-(phenazine-5,10-diyl)dibenzonitrile (**mBN**) and 4',4'''-(phenazine-5,10-diyl)bis([1,1'-biphenyl]-4-carbonitrile) (**BPN**) are presented and compared to those of the known fluorophore 4,4'-(phenazine-5,10-diyl)dibenzonitrile (**pBN**), which has been reported to show thermally activated delayed fluorescence (TADF). In the solid state, **pBN** shows clear TADF properties. In contrast, TADF is only weakly pronounced in **mBN**, and **BPN** is a conventional fluorescent emitter. This is discussed in terms of the provided through-space overlap between donating phenazinediyl and accepting benzonitrile units in these three molecules, which is only effective in **pBN**. These compounds are only weakly luminescent in toluene, tetrahydrofuran (THF) or dichloromethane (CH₂Cl₂) solution, most intensively in toluene, with yellow (**pBN** and **mBN**) to orange (**BPN**) colors of the emission. The emission maxima $\lambda_{em,max}$ in toluene differ slightly between **pBN** (562 nm) and **mBN** (572 nm) and overlap in THF (634 nm) and CH₂Cl₂ (~660 nm), respectively. Their emission is broad-banded and strongly solvent-dependent and thus indicates a CT-type nature of the excited state. **BPN** shows weak solvent-dependent photoluminescence (604 nm in toluene, 589 nm in THF, and 587 nm in CH₂Cl₂) and together with an observable vibronic structure in the low temperature spectra of the powder, it can be concluded that emission in **BPN** occurs from a localized electronic (LE) state non-beneficial for TADF properties. This demonstrates that even tiny modifications in the molecular templating structure of the phenazines can significantly affect their TADF properties.

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Introduction

The phenomenon of thermally activated delayed fluorescence (TADF) was first described in detail by Parker and Hatchard in 1961¹ and discovered even earlier by Perrin in 1929 on uranyl salts.^{2,3} After a long period of time without application, the concept has been re-introduced by Adachi *et al.* in the 2010s to

motivate the usage of new organic chromophores in organic light-emitting diodes (OLEDs) with the goal to replace common phosphorescent expensive noble-metal complex emitters.^{4,5} Since then, the field of organic TADF chromophores has received a lot of attention worldwide with vivid development over the last decade.^{6–13} A key advantage of TADF emitters in OLEDs is the high quantum efficiency based on harvesting of both spin singlet and triplet excitons, which formally allows achieving internal quantum efficiencies of ~100% and high external quantum efficiencies (EQEs) of up to ~40%.^{5,6,14–17} This high efficiency can be achieved because the lowest excited singlet state (S₁) and lowest excited triplet state (T₁) are energetically sufficiently close that reverse intersystem crossing (rISC) can be thermally triggered.^{18–23} The energy difference ΔE_{ST} of both energy levels is typically less than 0.1 eV for the current highly efficient organic TADF emitters.^{14,24–27} The smaller the energy gap ΔE_{ST} between S₁ and T₁ the higher the equilibrium population of the higher excited S₁ state, which governs up to 25% of the internal quantum efficiency in cases of electric injection of charge carriers.

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† Electronic supplementary information (ESI) available: Sources of chemicals, synthesis, crystal structure details, supramolecular interaction analysis, photo-physical properties, and quantum chemical calculations. CCDC 2238744, 2222499 and 2222500. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3tc01228j>



Small organic molecules such as TADF emitters have the advantage that they can be synthesized in high purity or can be optimally purified by recrystallisation and/or sublimation. In addition, the molecules can be modified and optimized in a large variety to lead to high luminous efficacies of light-emitting devices containing these compounds. Ideally, the emitters should have high color purity and narrow emission bands.^{24,28}

It has been shown that the photoluminescence (PL) efficiency of donor-acceptor TADF compounds can be controlled and optimized by the selective choice of specific donor and acceptor moieties.^{29–31} Furthermore, systems with donor-acceptor-donor (D-A-D)³² and acceptor-donor-acceptor type (A-D-A) topologies have proven to be a beneficial combination.^{33,34}

The phenazine-5,10-diyl molecule with two nitrogen atoms in the central 1,4-dihydrodiazine core is an excellent donor moiety.³⁵ By arylation of the 5 and 10 positions, 5,10-di-aryl derivatives are obtained. The variation of acceptor groups attached to the nitrogen atoms of phenazine-5,10-diyl has been well investigated in this symmetrical A-D-A system. Benzonitrile has been found to be the most effective acceptor in these designed TADF emitters.^{33,35} Compound 4,4'-(phenazine-5,10-diyl)dibenzonitrile (Fig. 1), which is derived from 5,10-dihydrophenazine (DHPZ) as the strong electron donor and two *para*-benzonitrile moieties as strong electron acceptor units, has an energy gap of $\Delta E_{ST} = 0.10$ eV and a photoluminescence quantum yield of 35.2% with the corresponding EQE of 5–8%. It is an established TADF emitter.³³

Here, we analyze the effect of a change in the nitrile substitution pattern from a *para* to *meta* configuration and an elongation of the phenyl to a biphenyl group on the photophysical properties with special emphasis on potential TADF properties. This offers the possibility of deriving structure-property relationships and to formulate molecular design rules to control desirable TADF parameters such as ΔE_{ST} by simple chemical inspection. Thus, we synthesized and investigated the luminescence properties of 3,3'-(phenazine-5,10-diyl)dibenzonitrile (**mBN**) and 4',4'''-(phenazine-5,10-diyl)bis([1,1'-biphenyl]-4-carbonitrile) (**BPN**) and compared them to those of the

literature-known TADF emitter 4,4'-(phenazine-5,10-diyl)dibenzonitrile (**pBN**) (Fig. 1). We analyzed the optical properties both in the solid state and in solution to identify the overall nature of the radiative transition and to verify if aggregation-induced effects in the powder lead to significant changes in the TADF properties. This is usually relevant for applications such as emitting materials in OLEDs, in which thin films are used rather than dissolved dyes. In particular, the presented dyes have high melting points (**mBN** = 284 °C, **pBN** and **BPN** > 300 °C) and can be even processed by sublimation, which is beneficial for applications.

Results and discussion

For the synthesis of the phenazine-5,10-diyl dibenzonitriles, phenazine was first reduced to dihydrophenazine following established literature procedures (see the ESI† for details).^{33,36} Then, Buchwald-Hartwig coupling with 4-bromobenzonitrile, 3-bromobenzonitrile, or 4'-bromo-[1,1'-biphenyl]-4-carbonitrile forms the products 4,4'-(phenazine-5,10-diyl)dibenzonitrile (**pBN**), 3,3'-(phenazine-5,10-diyl)dibenzonitrile (**mBN**) or 4',4'''-(phenazine-5,10-diyl)bis([1,1'-biphenyl]-4-carbonitrile) (**BPN**), respectively (Fig. 1). The dihydrophenazine derivatives are obtained in good to high yields of 65–78%. Their purity and identity were confirmed by ¹H NMR, mass spectrometry, combustion analysis and single-crystal structures.

The crystal structure of **pBN** was only published recently (α -polymorph, space group $P2_1$, no. 4)³⁷ and another β -polymorph (space group $P\bar{1}$, no. 2) has been determined in parallel in this work (see the ESI† for details). Both **pBN** polymorphs consist of two types of molecules, namely a 'linear' one and a *trans*-bent 'distorted one' (ratios 1:1 in β - and 1:2 in α -polymorph), with a characteristic non-linearity of the latter associated with the weak, but clearly distinguishable pyramidalicity at the N atoms of the phenazinediyl core (Fig. 2a). In both molecules of β -**pBN** and also in crystalline **mBN** (Fig. 2b), the center of the pyrazine ring coincides with an inversion center; hence, the pyrazine rings are planar by symmetry (see the ESI† for crystallographic details). The dihedral angles between the benzonitrile aryl group and the pyrazine core or phenazine plane are 75.08(5)° or 76.41(4)° in β -**pBN** molecule 1, 79.37(5)° or 79.93(4)° in β -**pBN** molecule 2, 86.67(5)° or 85.80(3)° in **mBN**, respectively. The fused benzo and pyrazine rings are almost coplanar with a small interplanar angle of 2.79(4)°, 1.07(5)° in β -**pBN** molecule 1,2 and 1.71(4)° in **mBN**.

Photophysical properties

Solution. UV-Vis absorption and emission spectra were recorded in solvents of different polarity. For each compound, the absorption maxima in the different solvents are located at around the same wavelengths (Table 1 and Fig. 3).

Compound **pBN** has the strongest absorption maximum at ~320 nm with a pronounced tailing shoulder at 371 nm and a weak one at 427 nm. In toluene, the absorption at 371 nm is a distinct band (Table 1 and Fig. 3a). In comparison to **pBN**, for **mBN** the strongest absorption bands are redshifted to

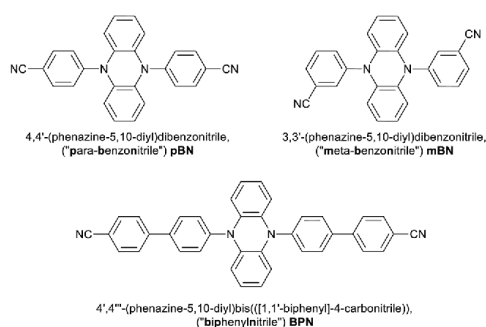


Fig. 1 Chemical formulae of the investigated phenazine-5,10-diyl dibenzonitriles in this work.



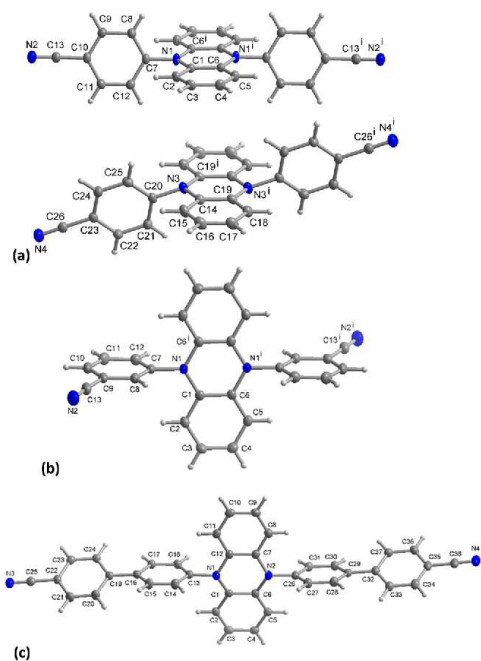


Fig. 2 Molecular structures of (a) **pBN** with linear molecule 1 and trans-bent molecule 2, (b) **mBN** and (c) **BPN** (CHCl_3 solvent molecule omitted) in the crystalline state (50% thermal ellipsoids, H atoms with arbitrary radii). Symmetry transformation in (a) $i = -x + 1, -y + 1, -z$; (b) $i = -x + 1, -y, -z + 2$.

~ 331 nm with a weak shoulder at ~ 380 nm. For **BPN**, an additional redshift of the strongest band to ~ 373 nm and the tailing shoulder to 427 nm is observed. This band and shoulder coincide with the two shoulders in **pBN**. The molar absorption coefficients of the strongest absorptions above 300 nm are relatively low and in the range of $6000\text{--}8000\text{ L mol}^{-1}\text{ cm}^{-1}$ (and even lower for **pBN** in toluene and **BPN** in THF) (Table 1).

In toluene, the absorption spectra for **pBN** and **BPN** are very similar and the longest wavelength absorption maxima appear as incompletely resolved shoulders at 427 nm (Fig. 3a). The comparable lowest energetic absorption of **mBN** is located at 381 nm (Table 1). This can also be rationalized by DFT/MRCI calculations (see the Theoretical Calculations section).

The compounds are only weakly luminescent in solution, yet, most intensively in toluene. Unlike the absorption spectra, the emission bands of the three compounds recorded upon excitation at each absorption maximum ($\lambda_{\text{exc}} = \lambda_{\text{max,abs}}$) show a pronounced solvatochromicity. For **pBN** and **mBN**, the emission maxima differ by 10 nm in toluene with $\lambda_{\text{em}} = 562$ nm and 572 nm, respectively, but lie closely together in THF ($\lambda_{\text{em}} = 634$ nm) and CH_2Cl_2 ($\lambda_{\text{em}} = 660$ nm) (Table 1 and Fig. 3). The bathochromic shift from toluene to THF and CH_2Cl_2 of

the emission bands indicates a positive emission solvatochromism (see also Fig. S17 and S19, ESI†).

Compared to the **pBN** and **mBN** compounds, the emission maximum for **BPN** with its biphenyl π -system is bathochromically shifted to 604 nm in toluene but hypsochromically to 589 nm in THF and to 587 nm in CH_2Cl_2 . In CH_2Cl_2 , there is also a second emission band observable at 760 nm. For **BPN**, the hypsochromic emission shift from toluene to THF and CH_2Cl_2 represents a negative emission solvatochromism (see also Fig. S21, ESI†).

Compared to the solid-state (at 25°C), the λ_{max} values for **pBN** (558 nm) and **mBN** (551 nm) differ depending on the solvent. In the solid state, the emission maxima of **pBN** and **mBN** are located at similar wavelengths. The emission maximum of **BPN** (596 nm) is at a comparable wavelength to the values in solution and indicates limited solvatochromism.

The emission bands of the chromophores in toluene are narrow, with full width at half maximum (FWHM) values ranging from 0.44 to 0.47 eV (Table 1). The FWHM values only increase slightly for **pBN** and **mBN** from toluene to THF and CH_2Cl_2 (to 0.50–0.56 eV). Emission intensities are low for these molecules in toluene, and the CIE coordinates in toluene comply with the observable yellow (**pBN**, **mBN**) to orange (**BPN**) colors of the emission. In THF the CIE coordinates account for orange emission colors (Table 1 and Fig. S18, S20 and S22, ESI†). In CH_2Cl_2 , the CIE coordinates match the observable orange emission colors of all compounds (Table 1).

Luminescence decay times are in a typical range for fluorescent organic chromophores.³⁹ For **pBN** and **mBN**, the decay times decrease from toluene (5.7 ns and 8.9 ns) to THF (2.5 and 1.7 ns, respectively) and further to CH_2Cl_2 (1.0 and 1.6 ns, respectively) (Table 1). If the decay was purely radiative, the decay time should expectedly increase with redshifted emission wavelength based on the λ_{em}^3 dependence of the radiative decay time. On the other hand, the increasing refractive index of the solvents from toluene over THF to CH_2Cl_2 leads to a local field enhancement and thus compensates the pure wavelength dependence of the radiative decay time.⁴⁰ Finally, redshifted broad-band luminescence is more strongly prone to non-radiative relaxation and consequently lower quantum yields. The general decrease in emission brightness of **pBN/mBN** from toluene to CH_2Cl_2 indicates that it is the non-radiative pathway that is most relevant to the observed decrease of the photoluminescence decay time.

For **BPN**, the decay time first increases from toluene (6.7 ns) to THF (12.0 ns) along with the hypsochromic shift and then decreases again in CH_2Cl_2 (5.5/0.5 ns) in line with the lower intensity in emission which, however, is not visible anymore. The increase in decay time from toluene to THF is not readily expected given the slightly blue-shifted emission wavelength and similar photophysical properties such as FWHM and Stokes shift of **BPN** in THF compared to toluene (Table 1). However, the molar absorption coefficients in THF are lowered by a factor of almost 3 compared to those in toluene. If the difference in refractive indices between toluene and THF is considered, this could explain the difference in factor of almost



Table 1 Photophysical data for compounds **pBN**, **mBN**, and **BPN** in different solvents at room temperature

Compound	$\lambda_{\text{max,abs}}/\text{nm}$ ($\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{em}}/\text{nm}$	τ/ns	Stokes shift ^a / cm^{-1}	FWHM ^b / cm^{-1} (eV)	CIE ^c
pBN						
Toluene	427sh (900) 371 (1800) 318 (2700)	562	5.7	5600	3624 (0.45)	0.450, 0.530
THF	427sh (1700) 370sh (3800) 318 (7200)	634	2.5	7600	4018 (0.50)	0.572, 0.422
Dichloromethane	427sh (2100) 372sh (4200) 321 (7700) ^d 255 (42600) ^d	659	1.0	8200	4436 (0.55)	0.567, 0.418
mBN						
Toluene	381sh (2400) 331 (6800)	572	8.9	8800	3746 (0.47)	0.468, 0.513
THF	383sh (1900) 329 (5900)	634	1.7	10 300	4101 (0.51)	0.556, 0.422
Dichloromethane	384sh (2600) 332 (7400) 250 (54200) ^d	662	1.6	10 900	4517 (0.56)	0.561, 0.432
BPN						
Toluene	427sh (2800) 375 (6600)	604	6.7	6900	3564 (0.44)	0.544, 0.451
THF	428sh (1000) 373 (1900)	589	12.0	6400	3739 (0.46)	0.525, 0.446
Dichloromethane	427sh (2500) 373 (6500) 271sh (71900) 255 (98000) ^d	587 760	5.5 0.5	6400	6442 (0.8)	0.463, 0.449

^a $\Delta\tilde{\nu} = \frac{1}{\lambda_{\text{max,abs}}} - \frac{1}{\lambda_{\text{max,em}}}$. ^b FWHM = full width at half maximum. ^c Refers to a transparent solution of the respective compound, not an OLED device. ^d In toluene and THF, the absorption measurement starts above 285 nm because of solvent absorption below 285 nm.

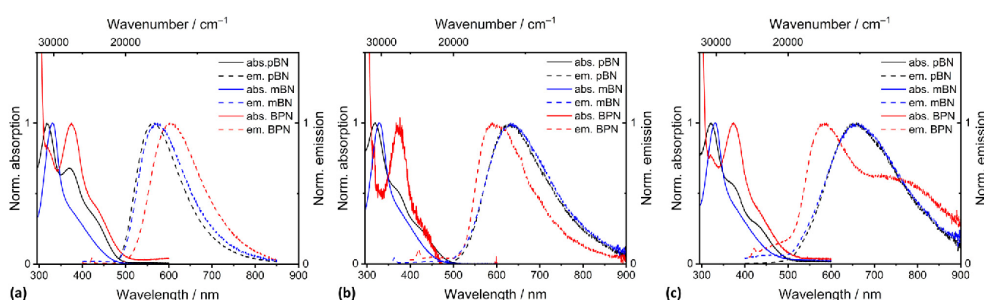


Fig. 3 Absorption and emission spectra ($\lambda_{\text{exc}} = \lambda_{\text{max,abs}}$) of **pBN**, **mBN** and **BPN** recorded in (a) toluene, (b) THF, and (c) dichloromethane. $c = 10^{-5} \text{ mol L}^{-1}$, $T = 293 \text{ K}$.

2 in the luminescence decay times of the luminescence of **BPN** in these two solvents.

In addition, all chromophores show a higher energy absorption maximum of around 250 nm (Fig. S17, S19, S21, ESI† and Table 1), which might be assigned to π - π^* transitions. This absorption is only seen in dichloromethane because toluene and THF are not transparent at this wavelength. While the molar absorption coefficients of the longest wavelength absorption bands were low, the higher energy absorption bands are characterized by molar absorption coefficients of up to $98000 \text{ L mol}^{-1} \text{cm}^{-1}$. The spectral features of the ground state,

as reflected by the absorption characteristics, indicate that **pBN** and its phenylene expanded congener **BPN** are not only similar, but the ground state is largely insensitive to the change of polarity. Due to steric effects, a significant twist of the *N*-aryl substituents can be plausibly assumed in the ground state as is also indicated by single crystal structural data (Fig. 2). Yet, the electron-withdrawing nitrile substituent is positioned in conjugation with the phenazine-5,10-diyl nitrogen atoms. For **mBN**, this conjugative pathway is excluded due to the *meta*-positioning of the nitrile group, as indicated by the hypsochromic shift with respect to the maxima of the former two chromophores.



The spectral features of the excited states of the constitutional isomers **pBN** and **mBN** represented by the spectral ranges of their emission are mutually more similar than for the phenylene expanded system **BPN**. The positive emission solvatochromicity of the former indicates a polar excited state arising from a charge transfer from the phenazinediyl donor to the benzonitrile acceptor. The expansion of the π -system in **BPN** leads to negative emission solvatochromicity and hence to a less polar excited state. However, peculiar for the latter system is the occurrence of a second longer wavelength emission band at 760 nm in dichloromethane, which could either indicate a twisted intramolecular charge transfer (TICT) state^{41–44} or phosphorescence. Especially the latter type of transition should, however, be strongly prone to non-radiative relaxation in solution. **BPN** can be divided into a donor (phenazinediyl) and an acceptor (biaryl) moiety linked by a single bond. Upon excitation from the ground state, the locally excited (LE) state with a planar conformation can rapidly equilibrate with an intramolecular twisted charge transfer state of lower energy.⁴⁵ This often results in dual emission with a high energy band through relaxation of the LE state (587 nm) and a low energy band by relaxation of the TICT state (760 nm). In a less polar solvent, like THF, the LE state is slightly energetically increased, but due to lower solvent polarity, the TICT state cannot be stabilized. Only in dichloromethane can the twisted CT state be stabilized and therefore be observed. This might explain the recorded negative emission solvatochromicity. The phenomenon of TICT has previously been observed for biphenyls and terphenyls.^{46,47}

Solid state. The solid-state luminescence/emission spectra were measured as a function of temperature from 79 K to 473 K to investigate potential TADF properties. The luminescence intensity of all phenazinediyl derivatives decreases with increasing temperatures (see Fig. S11, ESI†). At 79 K, **pBN** shows a broad emission with a maximum at $\lambda_{\text{em}} \approx 565$ nm and a shoulder peak at around 590 nm (Fig. 4a). With higher temperatures, the emission band evolves into a more symmetric Gaussian band shape. An interesting peculiarity is that the emission maximum shows an initial thermally induced blue shift between 79 K and 273 K before it shows a red shift above 273 K. This observation indicates thermal occupation of

a higher excited emissive state already in the low-temperature domain before.

mBN features an emission maximum at $\lambda_{\text{em}} \approx 537$ nm with a shoulder at 522 nm upon excitation at $\lambda_{\text{exc}} = 420$ nm at 79 K. With increasing temperature, the shoulder is not resolved anymore due to vibronic broadening. The barycenter of the emission band becomes thermally redshifted (Fig. 4b) in the whole regarded temperature range. The location of the emission maximum at shorter wavelengths compared to **pBN** at 79 K is assigned to the *meta* position of the nitrile functionalities that limits effective linear charge transfer from the phenazinediyl unit mediated through the phenyl moieties and thus, should lead to expectedly less pronounced TADF properties.

The emission spectra of solid **BPN** at 79 K show a vibronic fine structure (Fig. 4c). The maximum is located at $\lambda_{\text{em}} \approx 583$ nm and is also redshifted with increasing temperature accompanied by a loss in the resolution of the vibronic fine structure. Together with the findings of nearly no solvatochromism of the respective emission of **BPN** in toluene, THF, and CH_2Cl_2 , the observation of vibronic structure in the powder luminescence spectra at low temperatures indicate emission from a LE state. Both this observation and the redshifted luminescence in **BPN** compared to **mBN/pBN** can be rationalized by the donor-acceptor distances in the molecule due to the presence of the additional phenylene moiety (see Fig. 1). Charge transfer interaction strength roughly scales inversely exponentially with the donor-acceptor distance, which should be expectedly weakened in the large **BPN** molecule.⁴⁸ In addition, the twisted configuration between the intermediate phenyl ring and the benzonitrile moiety additionally minimizes orbital overlap thereby localizing electron density.

Fig. 5 depicts the temperature-dependent time-resolved luminescence of the three phenazinediyl derivatives. **pBN** shows clear signatures of TADF such as a prompt component in the ns range ($\tau_{\text{p}}(79 \text{ K}) = 11 \text{ ns}$; $\tau_{\text{p}}(273 \text{ K}) = 6.2 \text{ ns}$) and delayed time component in the μs range ($\tau_{\text{d}}(79 \text{ K}) = 2.0 \mu\text{s}$; $\tau_{\text{d}}(273 \text{ K}) = 0.3 \mu\text{s}$) as well as a temperature-dependent amplitude ratio between the prompt and delayed component. This is in line with the observable thermally-assisted blueshift of the emission below 272 K (Fig. 4a). From the delayed components at low temperatures ($T < 220 \text{ K}$), an effective singlet-triplet gap of

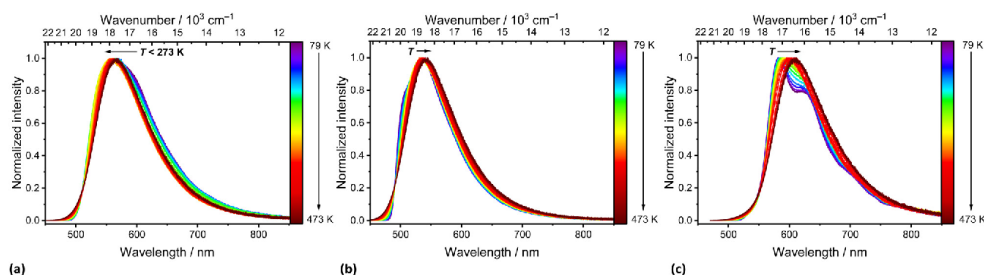


Fig. 4 Temperature-dependent emission spectra of solid (a) **pBN**, (b) **mBN**, and (c) **BPN** upon excitation at $\lambda_{\text{exc}} = 420$ nm (a, b) and 450 nm (c). Temperature intervals were $\Delta T = 25 \text{ K}$.



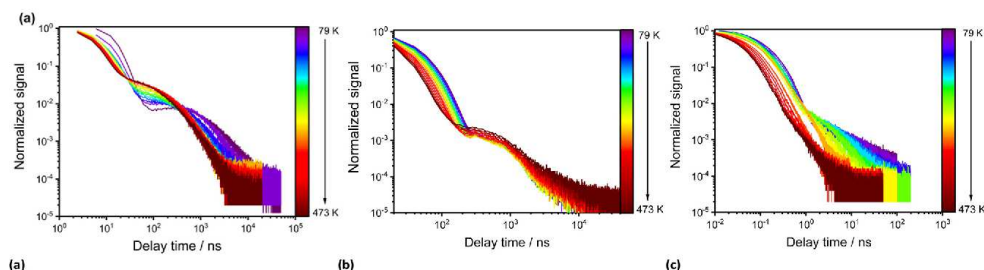


Fig. 5 Temperature-dependent time-resolved photoluminescence of solid (a) **pBN**, (b) **mBN** and (c) **BPN** upon excitation at $\lambda_{exc} = 450$ nm. Temperature intervals were $\Delta T = 25$ K.

$\Delta E_{ST} = (174 \pm 3) \text{ cm}^{-1} = (21.5 \pm 0.4) \text{ meV}$ was derived (Fig. S14, ESI†), which is in agreement with the spectroscopically deduced value of $\Delta E_{ST} \approx 200 \text{ cm}^{-1}$ (25 meV) based on the energy difference of the emission maxima at 79 K and 273 K of **pBN** (Fig. S16, ESI†). Our derived energy gap is lower than the literature-reported value of $\Delta E_{ST} = 806 \text{ cm}^{-1}$ (100 meV), which refers, however, to a 6 wt% **pBN**:*m*-CBP doped thin film and was solely estimated based on the energy difference between noisy spectra.³³ In a neat powder, additional intermolecular interactions and aggregate formation expectedly decrease the energy gap consistent with our finding. Another aspect that can affect the energy gap by means of the effective orbital overlap is the relative twisting angle of the benzonitrile moieties to the central dihydrophenazine residue. This angle is fixed in a crystalline solid and may differ from the respective angle upon doping into a thin film. In contrast, **mBN** (Fig. 4b) shows weak TADF properties with a more dominant prompt ($\tau_p(79 \text{ K}) = 33 \text{ ns}$; $\tau_p(273 \text{ K}) = 24 \text{ ns}$) and weakly defined delayed component ($\tau_d(79 \text{ K}) = 0.9 \mu\text{s}$; $\tau_d(273 \text{ K}) = 0.6 \mu\text{s}$) with an average singlet-triplet gap of $\Delta E_{ST} = (38 \pm 6) \text{ cm}^{-1} = (4.7 \pm 0.8) \text{ meV}$ (Fig. S15, ESI†). No TADF properties are observed for **BPN** (Fig. 4c) and it shows conventional fluorescence with decay times in the ns range ($\tau_p(79 \text{ K}) = 14 \text{ ns}$; $\tau_p(273 \text{ K}) = 8.6 \text{ ns}$). Unfortunately, no non-radiative intersystem crossing rates are readily accessible with our spectroscopic equipment that would allow a more detailed analysis of the TADF kinetics. It is, however, evident that only **pBN** is a potent TADF emitter with reasonable photoluminescence quantum yield ($\phi_{PL} = 35.8\%$) if doped into a thin film (as the literature-reported 6 wt% **pBN**:*m*-CBP doped film).³³ Its absolute quantum yield in powdered form is much lower ($\phi_{PL} = 1.00\%$), which is understandable given the close contacts between the molecules within the crystalline solid (see section S4 in the ESI†) and agrees with the significant quenching of the luminescence at room temperature (see Fig. S11, ESI†). A similar low quantum yield of only 3.3% was found for **pBN** in aerated toluene solution with no observation of any delayed fluorescence at all.³³ From the time-resolved photoluminescence of **pBN** at room temperature (see Fig. 5), we derive that the prompt and delayed components have almost equal contributions ($\phi_p(\text{pBN}) = 0.46\%$, $\phi_d(\text{pBN}) = 0.54\%$), also in agreement with the findings in a thin film.³³ Similarly, the absolute quantum yields of powdered **mBN** ($\phi_{PL} = 3.10\%$; $\phi_p(\text{mBN}) = 2.97\%$, $\phi_d(\text{mBN}) = 0.13\%$) are low and

dominantly stem from prompt fluorescence according to the time-resolved luminescence at room temperature (see Fig. 5). This again indicates that **mBN** is just at the boundary of being a TADF emitter. Finally, also the fluorescence of powdered **BPN** ($\phi_{PL} = 2.80\%$) is significantly quenched at room temperature, which makes these compounds not readily applicable organic emitters if used as neat powders and requires dilution or doping into thin films.

Theoretical calculations

The DFT/MRCI-computed vertical excitation energies to the HOMO-LUMO S_1 -state in **pBN**, **BPN** and **mBN** in a vacuum are 402, 415 and 401 nm, respectively. **BPN** and **pBN** have zero oscillator strength of the $S_0 \rightarrow S_1$ transition, and the computed value for f in **mBN** is weak (0.01) (Table S4, ESI†). This results from a lack of overlap between the participating orbitals (Fig. S31, ESI†). The first states with noticeable intensity are S_4 in **BPN** ($f = 0.10$) and in **pBN** ($f = 0.09$) and S_6 in **mBN** ($f = 0.14$) (Fig. 6). Similar findings hold true for the S_1 structures and the corresponding vertical emission from this state. In the S_1 geometry, the phenazine moiety flattens and becomes essentially planar (Fig. S26, ESI†).

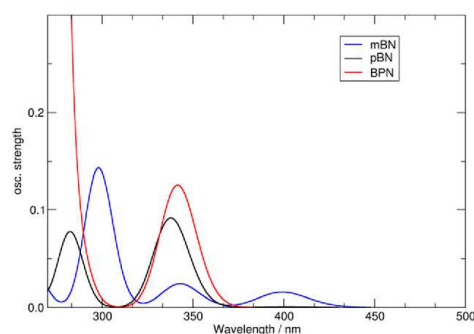


Fig. 6 DFT/MRCI computed static absorption spectra of **pBN**, **mBN** and **BPN** in vacuum.



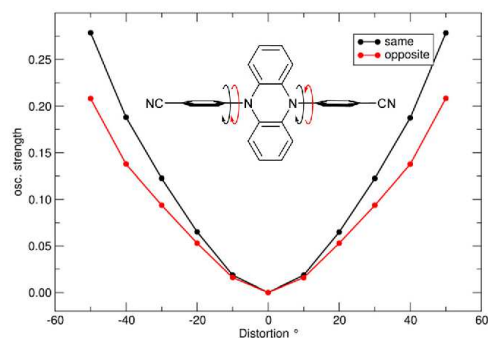


Fig. 7 Unrelaxed dihedral scan for phenyl-rotation in **pBN** showing oscillator strength (same and opposite directions of phenyl ring rotation, the starting point corresponds to the perpendicular arrangement (90°) of phenazine and phenyl rings); see also Fig. S26 (ESI†) for the energy profile.

Notably, the lowest triplet state at the S_0 geometry is not of HOMO-LUMO character but rather mixed in all models (Table S4, ESI†).

The oscillator strength of both S_1 absorption and emission are, however, tuned by motion of the phenyl rings with respect to the phenazine core as depicted in Fig. 7.

Hence, low-frequency normal mode vibrations ($\sim 21 \text{ cm}^{-1}$, Fig. S28, ESI†) increase the absorption intensity and slightly shift the corresponding bands, which appear in our zero-point energy (ZPE) simulated absorption spectrum as shoulders at ca. 405 nm (**mBN**) and 415 nm (**pBN**) (Fig. 8).

Through ZPE sampling, we note only a slight enhancement in the emission intensity ($f < 0.002$, Fig. S29, ESI†). Here, the normal mode including torsion of the phenyl rings is shifted towards slightly higher frequencies (34 vs. 21 cm^{-1}). The emission bands gain additional intensity ($f \sim 0.008$) after including temperature effects. In our simulation at 300 K the emission bands appear at 547 nm (**mBN**) and 573 nm (**pBN**). Thermal sampling at the S_0 geometry leads to unphysical

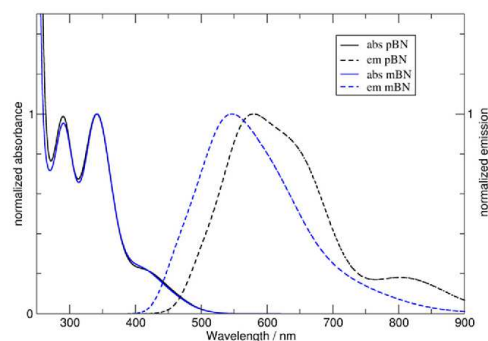


Fig. 8 Combined calculated absorption and emission spectra from vibrational sampling in toluene.

distortions indicating the limits of the harmonic approximation in this model.

Variations in phenyl torsions furthermore affect the singlet-triplet gap, this finding is visualized in Fig. S29 (ESI†). The effect is significantly stronger in **pBN**, where ΔE_{ST} decreases from 105 meV to 34 meV by rotation of one phenyl moiety by only -15° (left graph in Fig. S30, ESI†). Fixation in this position through an external force (such as exerted in a rigid crystal structure) may enable efficient tuning of its emission properties and offers an explanation for the difference between the originally reported value of $\Delta E_{ST} = 100 \text{ meV}$ in the 6 wt% **mBN**:*m*-CBP doped thin film and our slightly smaller value (22 meV).³³

Conclusions

The investigated compounds 3,3'-(phenazine-5,10-diyl)dibenzonitrile (**mBN**) and 4,4'''-(phenazine-5,10-diyl)bis([1,1'-biphenyl]-4-carbonitrile) (**BPN**) do not show any evident TADF behavior compared to 4,4'-(phenazine-5,10-diyl)dibenzonitrile (**pBN**) known from the literature. This indicates that even slight changes in the molecular structure have a significant effect on the photophysical properties of the molecules. Thus, **pBN** exhibits unique TADF properties both in the solid state and in liquid solution. In the solid state, **pBN** exhibits a decay time that is in the microsecond range over the entire temperature range measured, along with a blue shift of the emission maximum at temperatures below 220 K. The effective singlet-triplet gap here is $\Delta E_{ST} = (174 \pm 3) \text{ cm}^{-1} = (21.5 \pm 0.4) \text{ meV}$ as derived from temperature-dependent time-resolved luminescence data. **mBN** only exhibits very weak TADF properties with an effective estimated exchange energy gap below 10 meV. We assign this marked difference between **pBN** and **mBN** in their TADF behavior to the minimized orbital overlap in the latter case given by the *meta*-substitution pattern of the nitrile functionalities. Apart from that, the two emitters are strongly related, which is reflected in their similar emission wavelengths and solvatochromism. The emission spectra are broad and featureless, which indicates a CT-like character of the electronic transition in both compounds. In contrast, **BPN** is a conventional fluorescent emitter and shows a vibronic fine structure indicating an emissive localized state. Their emission maxima are strongly dependent on the solvent, indicating a CT-like character of the excited state. Overall, it can be seen that TADF donor-acceptor-type emitters follow clear electronic guidelines that can be structurally controlled on a molecular scale and within the solid.

Materials and methods

The purity of the compounds was determined by NMR spectroscopy, elemental analysis, high-resolution mass spectrometry and single crystal structure analysis (for details, see the ESI†).

Solid state optical measurements were performed using an FLS1000 photoluminescence spectrometer from Edinburgh Instruments equipped with a 450 W Xe arc lamp as an excitation source, double excitation and emission monochromators



in Czerny–Turner configuration and a thermoelectrically cooled ($-20\text{ }^{\circ}\text{C}$) photomultiplier tube PMT-980 from Hamamatsu. The emission spectra were corrected with respect to the grating efficiency and PMT sensitivity, while excitation spectra were additionally corrected with respect to the lamp intensity. Time-resolved photoluminescence was excited with pulsed laser diodes EPL-450 (Edinburgh Instruments, temporal pulse width: 90 ps, 0.15 mW average incident peak power) or VPL-450 (Edinburgh Instruments, 90 mW average incident peak power in CW mode) with adjustable temporal pulse width (0.1 ms...1 ms) and variable trigger frequency (0.1 Hz...5 MHz) as pulsed excitation sources. The detection mode for the time-resolved measurements was time-correlated single photon counting. Absolute quantum yields at room temperature were measured with a BenFlect[®] covered integrating sphere and excitation wavelength of 420 nm in all three regarded compounds.

Solution state absorption spectra were recorded in toluene, tetrahydrofuran and CH_2Cl_2 of high-performance liquid chromatography (HPLC) grade at 293 K on a PerkinElmer UV/Vis/NIR Lambda 19 spectrometer. For the determination of the molar extinction coefficients ϵ absorption measurements at five different concentrations were carried out. Emission spectra and fluorescence lifetimes were recorded in toluene, tetrahydrofuran and CH_2Cl_2 of HPLC grade at 293 K using an Edinburgh FS5 spectrometer. As light sources a 150 W xenon lamp as well as pulsed EPLED-320 (Edinburgh Instruments, 313.5 nm, temporal pulse width: 950 ps, 3 μW average incident peak power) and EPL-375 (Edinburgh Instruments, 372.2 nm, temporal pulse width: 76 ps, 0.15 mW average incident power) laser sources were used.

Computations

Single-molecule structures of **pBN**, **mBN** and **BPn** were geometry-optimized with Gaussian16,⁴⁹ taking the crystal structure data as input. Calculations were performed with the PBE0 functional,⁵⁰ the TZVP basis set⁵¹ and Grimme D3 dispersion corrections⁵² in vacuum and in toluene solvent applying the PCM model. TD-DFT was used for the excited S_1 and T_1 states. Vibrational analysis ensured that the obtained structures were true minima with no imaginary frequencies. For the computation of spectral properties, the optimized structures were recomputed at the BH-LYP/TZVP level of theory using Turbomole 7.5.⁵³ Solvation was considered with the COSMO model.⁵⁴ A DFT/MRCI computation was then performed with the R2022 Hamiltonian,⁵⁵ the tight parameter set and an energy selector of $0.8E_{\text{h}}$. The starting wavefunction was computed including eight orbitals and eight electrons with single and double excitations. An updated reference space was obtained by performing a second run with the same parameters to yield the final values for energies and oscillator strengths. Combined unrelaxed scans along the dihedral angles involving the phenyl rings were applied to document changes in ΔE_{ST} and oscillator strengths f .

Vibrational effects in emission and absorption data were considered by sampling the vibrational modes (zero-point-energy (ZPE) sampling) generating 200 structures for each molecule and state in **pBN** and **mBN**. Thermal sampling at a temperature of

300 K was performed in addition to the S_1 structures. After orbital computation with BH-LYP and the SV(P) basis, the resulting geometries were processed with DFT/MRCI and the R2016 Hamiltonian⁵⁶ using the same selector choices stated above. The final spectra with vibrational contributions were obtained by Gaussian broadening using a FWHM of 0.3 eV.

Author contributions

Conceptualization: D. P. and M. S.; methodology: D. P., J. W., T. H. and M. S.; validation: D. P.; formal analysis: D. P., J. W., T. H., L. P. and M. S.; investigation: D. P., J. W., T. H., L. P. and M. S.; resources: M. S., T. J. J. M. and C. J.; data curation: D. P., J. W., T. H. and M. S.; writing – original draft preparation: D. P. and J. W.; writing – review and editing: D. P., M. S., T. J. J. M. and C. J.; visualization: D. P., J. W. and C. J.; supervision: C. J.; project administration: C. J.; funding acquisition: M. S., T. J. J. M. and C. J.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationship that could have appeared to influence the work reported in this paper.

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Electronic Supplementary Information (ESI)

Molecular design of thermally activated delayed fluorescence properties of phenazine-5,10-diyl-dibenzonitriles†

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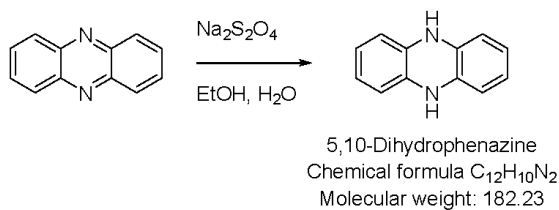
S1 Sources of chemicals

Commercially available reagents were used without further purification.

Items	Manufacturer
Phenazine, 97 %	BLDpharm
3-Bromobenzonitrile	BLDpharm
4-Bromobenzonitrile	fluorochem
4'-Bromo-[1,1'-biphenyl]-4-carbonitrile, 95 %	BLDpharm
Palladium(II) acetate, 98 %	Sigma-Aldrich
Tri- <i>tert</i> -butyl-phosphine	Sigma-Aldrich
Sodium dithionite	VWR Chemicals
Sodium chloride, ≥ 99.5 %	Sigma-Aldrich
Magnesium sulfate	VWR Chemicals
Potassium carbonate	Riedel-de Haen
Toluene, ≥ 99.7 %	Sigma-Aldrich
Ethanol, ≥ 99.8 %	Honeywell
Dichloromethane, ≥ 99.9 %	Sigma-Aldrich
Chloroform, ≥ 99.8 %	Fisher Chemical
n-Hexane, ≥ 99.0 %	VWR Chemicals
Cyclohexane, ≥ 99.8 %	Fisher Chemical

S2 Synthesis

S2.1 5,10-Dihydrophenazine

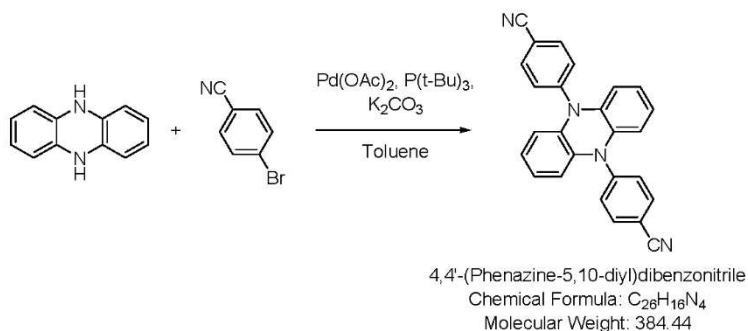


Starting materials	$M / \text{g} \cdot \text{mol}^{-1}$	$\rho / \text{g} \cdot \text{cm}^{-3}$	eq	n / mmol	m / g	V / mL
Phenazine	180.21	-	1.0	27.7	5.00	-
Sodium dithionite	174.11	2.38	10.0	277.0	48.2	-

Following literature procedures,^{1,2} phenazine was dissolved in ethanol (125 mL), sodium dithionite in de-ionized water (500 mL) and both solutions were combined and heated under stirring and reflux for three hours or overnight. The precipitate was filtered off and washed three times with deionized water. Finally, the solid was dried at 20 °C in vacuum (1×10^{-3} mbar) for 16 h. The product (yield 4.75 g, 94 %) was obtained as a light green solid and was used without further purification. Important: The dihydrophenazine solid must be stored under a protective gas atmosphere (nitrogen or argon), otherwise it re-oxidizes which is evidenced by slowly turning dark blue and then black.

[^1H NMR] (600 MHz, CDCl_3) δ = 8.27 (dd, J = 6.8, 3.5 Hz, 1H), 7.86 (dd, J = 6.8, 3.4 Hz, 1H), 6.12 (s, 2H), 1.57 (s, 3H).

S2.2 4,4'-(Phenazine-5,10-diyl)dibenzonitrile (pBN)



Starting materials	<i>M</i> / g·mol ⁻¹	<i>ρ</i> / g·cm ⁻³	eq	<i>n</i> / mmol	<i>m</i> / g	<i>V</i> / mL
5,10-Dihydrophenazine	182.22	-	1.00	5.49	1.00	-
4-Bromobenzonitrile	182.02	-	2.20	12.1	2.20	-
Potassium carbonate	138.20	2.43	6.00	32.9	4.55	-
Palladium(II) acetate	224.51	-	5 mol%		0.061	-
Tri- <i>tert</i> -butyl-phosphine	202.32	0.83	10 mol%		0.111	134

Following literature procedures,^{1,2} 5,10-dihydrophenazine, 4-bromobenzonitrile and potassium carbonate were dissolved in degassed toluene (20 mL). Palladium(II) acetate and tri-*tert*-butylphosphine were dissolved in degassed toluene (20 mL). Both solutions were combined under stirring. Under nitrogen inert gas the reaction mixture was heated with stirring to reflux for 24 hours. After cooling to room temperature, water (60 mL) was added to the reaction mixture and the water/toluene mixture extracted three times with chloroform (3 x 200 mL). The organic phases were combined, washed with a brine, dried over magnesium sulfate (5 min) and concentrated using a rotary evaporator. After addition of n-hexane (20 mL), a golden yellow insoluble precipitate was formed. The precipitated raw product was filtered off and washed three times with 60 mL each of a mixture of n-hexane/chloroform (2:1) and dried at 20 °C under vacuum (1x10⁻³ mbar) for 16 h. The product was obtained as a golden yellow crystalline solid (yield 1.6 g, 76 %). Ideally, the product occurs as small yellow-gold crystals. To increase the yield, the crystallisation solution can be concentrated and purified by column chromatography (dichloromethane/cyclohexane 10:1).



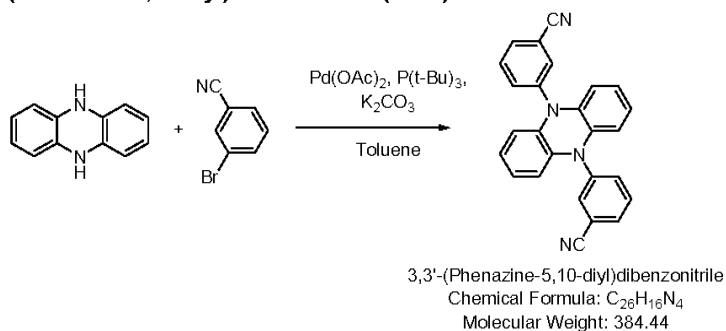
[¹H NMR] (600 MHz, C₆D₆) δ = 6.96 (d, *J* = 8.2 Hz, 4H), 6.71 (d, *J* = 8.2 Hz, 4H), 6.41 – 6.37 (m, 4H), 5.69 (dt, *J* = 7.9, 3.9 Hz, 4H).

[HR-ESI-MS] (*m/z*): Calc. for [M⁺]: 384.1375 – found: 384.1370

[EA] Calc. for C₂₆H₁₆N₄: C 81.20, H 4.20, N 14.57 – found: C 80.7, H 4.21, N 14.39 %

[M.p] > 300 °C

S2.3 3,3'-(Phenazine-5,10-diyl)dibenzonitrile (mBN)



Starting materials	<i>M</i> / g·mol ⁻¹	<i>ρ</i> / g·cm ⁻³	eq	<i>n</i> / mmol	<i>m</i> / g	<i>V</i> / mL
5,10-Dihydrophenazine	182.22	-	1.00	5.49	1.00	-
3-Bromobenzonitrile	182.02	-	2.20	12.1	2.20	-
Potassium carbonate	138.20	2.43	6.00	32.9	4.55	-
Palladium(II) acetate	224.51	-	5 mol%		0.061	-
Tri- <i>tert</i> -butylphosphine	202.32	0.83	10 mol%		0.111	134

Following the procedure in S2.2 the starting materials 5,10-dihydrophenazine, 3-bromobenzonitrile and potassium carbonate were dissolved in toluene (20 mL). Palladium(II) acetate and tri-*tert*-butylphosphine were dissolved in toluene (20 mL). Both solutions were combined under stirring. Under nitrogen inert gas the reaction mixture was heated with stirring to reflux for 24 hours.³ After cooling to room temperature, water (60 mL) was added to the reaction mixture and the water/toluene mixture extracted three times with chloroform (3 × 200 mL). The organic phases were combined, washed with a saturated aqueous NaCl solution (~ 25 %), dried over magnesium sulfate (5 min) and concentrated using a rotary evaporator. After 3 d and slow evaporation of the solvent, yellow crystals precipitated. The precipitated raw product was filtered off and washed three times with 60 mL each of a mixture of *n*-hexane/chloroform (2:1) and dried at 20 °C under vacuum (1×10⁻³ mbar) for 16 h. The product was obtained as small yellow crystals (yield 1.67 g, 79 %). To increase the yield, the crystallization solution can be concentrated and purified by column chromatography (dichloromethane/cyclohexane 10:1).



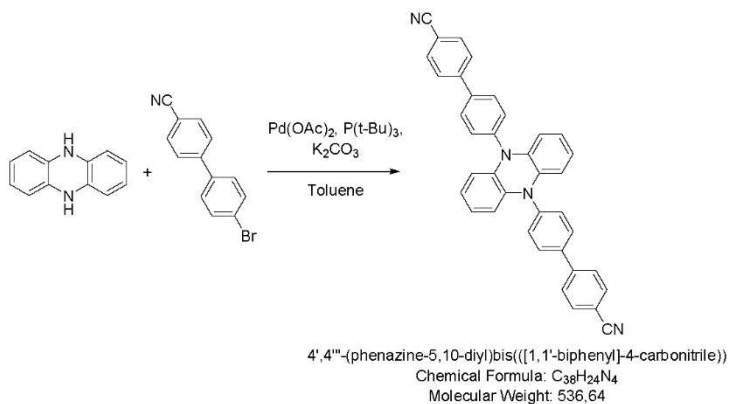
[¹H NMR] (300 MHz, C₆D₆) δ = 7.47 (s, 2H), 7.45 – 7.30 (m, 6H), 6.53 - 6.47 (m, 4H), 5.80 - 5.73 (m, 4H)

[HR-ESI-MS] (*m/z*): Calc. for [M⁺]: 384.1375 – found: 384.1367

[EA] Calc. for C₂₆H₁₆N₄: C 81.20, H 4.20, N 14.57 – found: C 81.41, H 4.27, N 14.51 %

[M.p] 284 °C

S2.4 4',4'''-(Phenazine-5,10-diyl)bis([1,1'-biphenyl]-4-carbonitrile) (BPN)



Starting materials	<i>M</i> / g·mol ⁻¹	<i>ρ</i> / g·cm ⁻³	eq	<i>n</i> / mmol	<i>m</i> / g	<i>V</i> / mL
5,10-Dihydrophenazine	182.22	-	1.00	5.49	1.00	-
4'-Bromo-[1,1'-biphenyl]-4-carbonitrile	258.12	-	2.20	12.0	3.10	-
Potassium carbonate	138.20	2.43	6.00	32.9	4.55	-
Palladium(II) acetate	224.51	-	8 mol%		0.098	-
Tri- <i>tert</i> -butylphosphin	202.32	-	16 mol%		0.178	-

Following the procedure in S2.2 the starting materials 5,10-dihydrophenazine, 4'-bromo-[1,1'-biphenyl]-4-carbonitrile, and potassium carbonate were dissolved in degassed toluene (20 mL). Palladium(II) acetate and tri-*tert*-butylphosphine were dissolved in degassed toluene (20 mL). Both solutions were combined under stirring. Under nitrogen inert gas the reaction mixture was heated with stirring to reflux for 48 hours. The solvent toluene was removed by rotary evaporator. The crude product (dark orange/brown to black) was dissolved and resuspended in hot chloroform and filtered using a short (10 cm) filter column (silica). The filter cake was washed with hot chloroform until the filtrate became colorless (approximately 250 mg of product dissolves in 1 L of hot chloroform). The chloroform filtrates were combined and the solvent concentrated to about 200 mL using a rotary evaporator. The crystallized product was filtered and washed three times with chloroform (20 mL). The product was obtained as fine orange crystals (yield 2.06 g, 70 %).



[¹H NMR] (600 MHz, C₆D₆) δ = 7.54 – 7.49 (m, 1H), 7.32 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 7.14 – 7.10 (m, 25H), 7.10 – 7.05 (m, 1H), 7.03 – 6.97 (m, 1H).

[HR-ESI-MS] (*m/z*): Calc. for [M⁺]: 536.2001 – found: 536.1998

[EA] Calc. for C₃₈H₂₄N₄: C 85.05, H 4.51, N 10.44 – found: C 85.67, H 4.43, N 10.52 %

[M.p] > 300 °C

S3 Crystal structure details

The sample of β -pBN crystallized via slow evaporation of a CHCl_3 solution as yellow elongated blocks/needles with a nearly rectangular (rather trapeze) cross section. A suitable crystal was mounted on a microloop in a drop of immersion oil. For 4,4'-(phenazine-5,10-diyl)dibenzonitrile (pBN, β -polymorph) the data was collected using ϕ and ω -scans on a Bruker Kappa APEX 2 CCD X-ray diffractometer with a microfocus sealed tube, Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), and a multilayer mirror monochromator. For the compounds 3,3'-(phenazine-5,10-diyl)dibenzonitrile (mBN) and 4,4'''-(phenazine-5,10-diyl)bis([1,1'-biphenyl]-4-carbonitrile) (BPN) the single-crystal diffraction data was collected using ω -scans on a Rigaku XtaLAB Synergy S four-circle diffractometer with a Hybrid Pixel Array Detector and a PhotonJet X-ray source for Cu- $K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) with a multilayer mirror monochromator. The data were collected under a cold nitrogen gas-stream (Oxford Cryostream liquid nitrogen cooling system) at 140 K (β -pBN) or 100 K (mBN, BPN). Data reduction and absorption correction were performed with APEX2,⁴ SAINT⁵ and SADABS on the Bruker device and by CrysAlisPro on the Rigaku diffractometer [6]. Structures were solved by direct methods with SHELX-2018 and refined with full-matrix least squares refinements on F^2 using SHELXL [7] in OLEX2 [8]. Crystal data and details on the structure refinement are given in Table S1 and Table S2. All hydrogen atoms were positioned geometrically and refined using riding models with $U_{\text{iso}}(\text{H}) = 1.2 \cdot U_{\text{eq}}$. For structure BPN the chloroform solvent molecule was disordered over two positions and refined in a 66:34 ratio. Graphics were drawn with the program Diamond.⁹

Table S1. Crystal data and structure refinement for α - and β -polymorph of pBN.

	α -pBN reported previously ¹⁰	β -pBN reported here
Identification code	wq_2_2	mo_th_dp_paralink_0m_a
CCDC number	2156760	2238744
Empirical formula	$\text{C}_{26}\text{H}_{16}\text{N}_4$	$\text{C}_{26}\text{H}_{16}\text{N}_4$
Formula weight / g mol^{-1}	384.43	384.43
Temperature / K	149.99(10)	140.0(10)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$ (no. 4)	$\bar{P}1$ (no. 2)
$a / \text{\AA}$	9.16980(10)	9.2154(7)
$b / \text{\AA}$	25.87320(10)	9.8882(8)
$c / \text{\AA}$	13.00690(10)	11.5256(9)
$\alpha / ^\circ$	110.2310(10) $^\circ$	105.439(4)
$\beta / ^\circ$	90	100.122(4)
$\gamma / ^\circ$	90	104.034(4)
Volume / $\text{\AA}^3$	2895.53(4)	949.16(13)
Z	6	2
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.323	1.345
μ / mm^{-1}	0.630	0.082
$F(000)$	1200	400
Crystal size / mm^3	$0.08 \times 0.07 \times 0.05$	$0.24 \times 0.15 \times 0.1$
Radiation	Cu $K\alpha$ ($\lambda = 1.54184 \text{ \AA}$)	Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$)
2θ range for data collection / $^\circ$	3.416 to 67.080	1.90 to 30.51
Index ranges	$-10 \leq h \leq 10, -30 \leq k \leq 30, -15 \leq l \leq 15$	$-13 \leq h \leq 13, -14 \leq k \leq 14, -16 \leq l \leq 16$
Reflections collected	77636	19393
Independent reflections	10131 ($R_{\text{int}} = 0.0284$)	5723 ($R_{\text{int}} = 0.0304$)

Data/restraints/parameters	10131 / 1 / 812	5723 / 0 / 271
Final R indexes [$I \geq 2\sigma(I)$] ^a	$R_1 = 0.0281$, $wR_2 = 0.0751$	$R_1 = 0.0508$, $wR_2 = 0.1257$
Final R indexes [all data] ^a	$R_1 = 0.0288$, $wR_2 = 0.0757$	$R_1 = 0.0760$, $wR_2 = 0.1398$
Goodness-of-fit on F^2 ^b	1.043	1.060
Largest diff. peak/hole / e Å ⁻³	0.114 and -0.229	0.326 and -0.263
Absolute structure parameter	0.2(3)	

^a Full-matrix least-square refinement on F^2 as implemented in SHELX. $R_1 = [\sum(|F_o| - |F_c|)/\sum|F_o|]$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$, a and b are refined parameters. ^b Goodness-of-fit $S = [\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$.

Table S2. Crystallographic details for structures **mBN** and **BPN · CHCl₃**.

	mBN	BPN · CHCl₃
Identification code	DP-metaLinker	DP-LinkerA2
CCDC number	2222499	2222500
Empirical formula	C ₂₆ H ₁₆ N ₄	C ₃₉ H ₂₅ Cl ₃ N ₄
Formula weight / g mol ⁻¹	384.43	655.98
Temperature / K	100.0(1)	100.0(1)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$\bar{P}1$ (no. 2)
a / Å	12.7220(4)	9.4403(2)
b / Å	7.6706(2)	12.0125(2)
c / Å	11.0125(3)	14.3830(3)
α / °	90	80.303(2)
β / °	113.828(4)	82.611(2)
γ / °	90	78.921(2)
Volume / Å ³	983.06(6)	1569.97(6)
Z	2	2
ρ_{calc} / g cm ⁻³	1.299	1.388
μ / mm ⁻¹	0.618	2.922
$F(000)$	400.0	676.0
Crystal size / mm ³	0.64 × 0.39 × 0.2	0.18 × 0.06 × 0.04
Radiation	Cu $K\alpha$ ($\lambda = 1.54184$ Å)	Cu $K\alpha$ ($\lambda = 1.54184$ Å)
2θ range for data collection/°	3.798 to 78.680	3.133 to 79.754
Index ranges	$-13 \leq h \leq 16$, $-9 \leq k \leq 7$, $-13 \leq l \leq 13$	$-12 \leq h \leq 11$, $-14 \leq k \leq 15$, $-17 \leq l \leq 17$
Reflections collected	11223	45762
Independent reflections	2024 [$R_{\text{int}} = 0.0229$, $R_{\text{sigma}} = 0.0143$]	6294 [$R_{\text{int}} = 0.0476$, $R_{\text{sigma}} = 0.0257$]
Data/restraints/parameters	2024/0/136	6294/0/460
Final R indexes [$I \geq 2\sigma(I)$] ^a	$R_1 = 0.0360$, $wR_2 = 0.0950$	$R_1 = 0.0418$, $wR_2 = 0.1000$
Final R indexes [all data] ^a	$R_1 = 0.0377$, $wR_2 = 0.0963$	$R_1 = 0.0526$, $wR_2 = 0.1037$
Goodness-of-fit on F^2 ^b	1.047	1.057
Largest diff. peak/hole / e Å ⁻³	0.14/-0.21	0.20/-0.28

^a Full-matrix least-square refinement on F^2 as implemented in SHELX. $R_1 = [\sum(|F_o| - |F_c|)/\sum|F_o|]$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$, a and b are refined parameters. ^b Goodness-of-fit $S = [\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$.

Comparison of α - and β -polymorph of pBN

Both polymorphs consist of two type of molecules, namely the 'linear' one and the 'distorted one' (ratios 1:1 in β -pBN and 1:2 in α -pBN), with a characteristic non-planarity of the latter associated with the weak, but clearly distinguishable, pyramidalicity of the N atoms (Table S3), constituting the dihydrophenazine core (Figure S1 and Figure 2 in the main text).

Table S3. Listing of angular distortions of the independent pBN molecules constituting the structures of the two known α - and β -polymorphs expressed as the sum of the C-N-C angles at the N atoms of the phenazinediyl core.

α -pBN (reported earlier)		β -pBN (reported here)	
Molecule 1, ('linear')	$\Sigma(\angle\text{CNC}) / ^\circ$ ^a	Molecule 1, (linear)	$\Sigma(\angle\text{CNC}) / ^\circ$ ^a
N(1)	360.0	N(1)	359.8
N(2)	359.3	N(2)	359.8
Molecule 2, ('distorted')	$\Sigma(\angle\text{CNC}) / ^\circ$ ^{a,b}	Molecule 2, ('distorted')	$\Sigma(\angle\text{CNC}) / ^\circ$ ^{a,b}
N(1)	356.5	N(1)	355.8
N(2)	358.7	N(2)	355.8
Molecule 3, ('distorted')	$\Sigma(\angle\text{CNC}), ^\circ$ ^{a,b}		
N(1)	359.9 ^a		
N(2)	357.3		

^a $\Sigma(\angle\text{CNC}) = \angle\text{C1NC2} + \angle\text{C2NC3} + \angle\text{C3NC2}$, i.e. the sum of all angles between bonded atoms, with N atoms serving a vertex of the angles; a measure of non-planarity, with 360° corresponding to a planar case.

^b Due to the significant distortion of the phenazine moiety the geometry of the N-atom environment is nearly planar, but the direction of the N-C_{Ph} bond is still significantly off the least squares plane for atoms constituting the phenazinediyl plane, i.e. the molecule is notwithstanding characteristically non-linear.

The α - and β -polymorphs could be rationalized as being both constituted from layers of molecules of the same type, following the ABBABB... and ABAB... patterns (Figure S1a,b), where A and B are the layers consisting of 'linear' and 'disordered' molecules, respectively only. The packing efficiency is only slightly better in the β -polymorph compared to the α -polymorph, with the respective densities being 1.345 vs. 1.323 g cm⁻³ (Table S1).

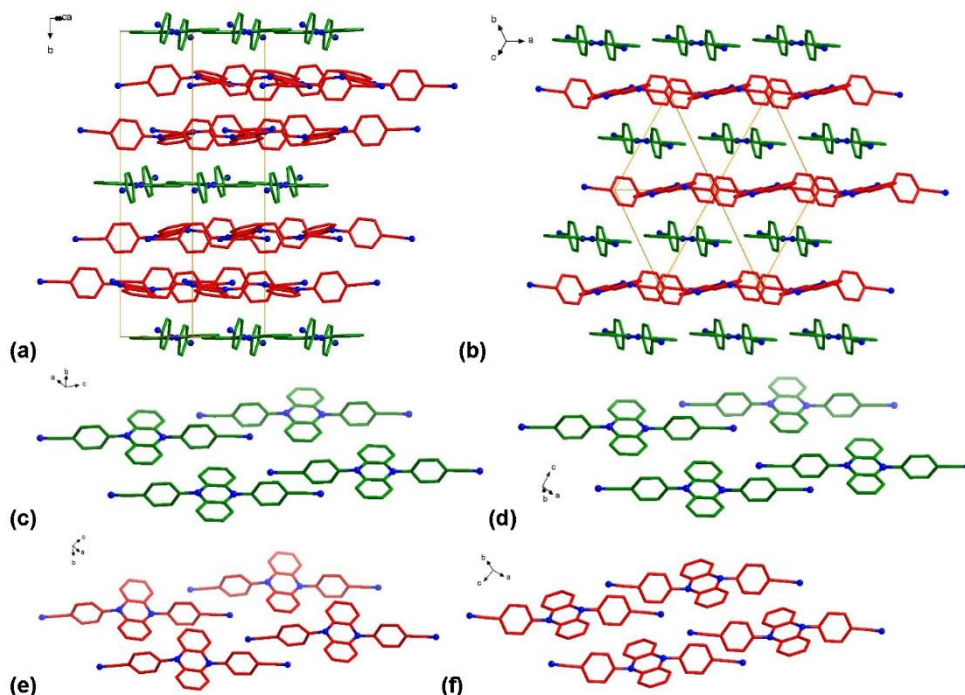
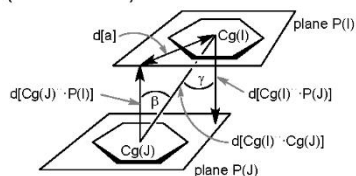


Figure S1. Comparison of the packing diagrams in the structures of **pBN**. The previously reported polymorph **α-pBN**¹⁰ (monoclinic, $P2_1$ (no. 4), $Z' = 3$; crystallization by slow evaporation of a hexane/dichloromethane solution) left panes: **(a)**, **(c)**, **(e)**. The **β-pBN** reported here (triclinic, $P\bar{1}$ (no. 2), $Z' = 1$; crystallization by slow evaporation of a solution in CHCl_3) right panes: **(b)**, **(d)**, **(f)**. The linear molecules are depicted in green, the distorted ones in red.

S4 Supramolecular interaction analysis

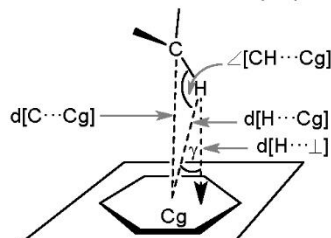
The supramolecular packing interactions have been analyzed for compounds **β-pBN**, **mBN** and **BPN** with PLATON.^{11,12,13}

The PLATON-listing "Analysis of Short Ring-Interactions" for possible π -stacking interactions yielded no π - π -stacking interactions in **β-pBN** or **mBN** and only one in **BPN**. π -Stacking, especially significant π -stacking would mean rather short centroid-centroid contacts ($< 3.8 \text{ \AA}$), near parallel ring planes ($\alpha < 10^\circ$ to $\sim 0^\circ$ or even exactly 0° by symmetry), small slip angles ($\beta, \gamma < 25^\circ$) and vertical displacements (slippage $< 1.5 \text{ \AA}$) which translate into a sizable overlap of the aryl-plane areas (Scheme S1).^{14,15}



Scheme S1. Graphical presentation of the parameters used for the description of π - π stacking.

However, from the "Analysis of X-H...Cg(Pi-Ring) Interactions ($H...Cg < 3.0 \text{ \AA} - \gamma < 30.0^\circ$) significant intermolecular C-H... π contacts were found in **mBN**, which start around 2.57 Å for the (C-)H...ring centroid distances with H-perp starting below 2.5 Å and C-H...Cg $> 135^\circ$ (Scheme S2) [16].



Scheme S2. Graphical presentation of the parameters used for the description of CH- π interactions.

Furthermore, there are C-H...N contacts in the solid-state packing arrangements of all three compounds.

Compound β -pBN:

Figure S2 gives an approximate view along the N...N axis in **β -pBN** to illustrate the planar nature of the pyrazine ring in both the linear and distorted molecule of **β -pBN** and shows the packing diagram.

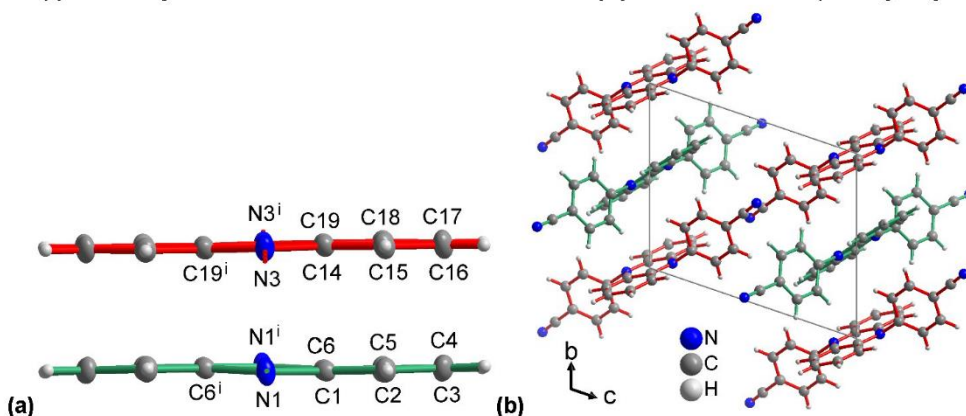


Figure S2. (a) Approximate view along the N...N axis in the linear (green) and distorted (red) molecules of **β -pBN** and (b) packing diagram. The linear molecules are depicted with green bonds, the distorted ones with red bonds.

Intermolecular C-H... π contacts in the packing of **β -pBN** (shown in Figure S3):

Analysis of X-H...Cg(Pi-Ring) Interactions ($H...Cg < 3.0 \text{ \AA}$, $\gamma < 30.0 \text{ Deg}$)

===== Cg(J)

= Center of gravity of ring J (Plane number above)

- H-Perp = Perpendicular distance of H to ring plane J

- Gamma = Angle between Cg-H vector and ring J normal

- X-H...Cg = X-H-Cg angle (degrees)

- X...Cg = Distance of X to Cg (Angstrom)

- X-H, Pi = Angle of the X-H bond with the Pi-plane (i.e. Perpendicular = 90 degrees, Parallel = 0 degrees)

X-H(I)	Res(I)	Cg(J) [ARU(J)]	H...Cg	H-Perp	Gamma	X-H...Cg	X...Cg	X-H, Pi
C4 -H4	[1]-> Cg3	[1455.01]	2.85	2.83	7.02	154	3.7317(18)	59
C12 -H12	[1]-> Cg8	[2676.02]	2.89	2.84	10.84	145	3.7073(17)	63
C21 -H21	[2]-> Cg1	[2666.01]	2.64	2.55	14.71	138	3.4020(17)	56

C21	-H21	[2]-> Cg4	[2666.01]	2.80	2.55	24.51	120	3.3799(17)	55
C21	-H21	[2]-> Cg6	[2666.01]	2.64	2.55	14.36	138	3.4020(16)	54
C22	-H22	[2]-> Cg2	[2666.01]	2.50	2.50	3.24	144	3.3203(17)	58
C22	-H22	[2]-> Cg4	[2666.01]	2.81	2.49	27.47	119	3.3798(16)	57

[1455] = -1+X,Y,Z
[2676] = 1-X,2-Y,1-Z
[2666] = 1-X,1-Y,1-Z

Cg(1) = centroid of N1-C1-C6-N1i-C1i-C6i
Cg(2) = centroid of C1-C2-C3-C4-C5-C6
Cg(3) = centroid of C7-C8-C9-C10-C11-C12
Cg(4) = centroid of N1-C1-C2-C3-C4-C5-C6-N1i-C1i-C6i
Cg(6) = centroid of N1-C1-C2-C3-C4-C5-C6-N1i-C1i-C2i-C3i-C4i-C5i-C6i corresponds to Cg(1)
Cg(8) = centroid of C14-C15-C16-C17-C18-C19

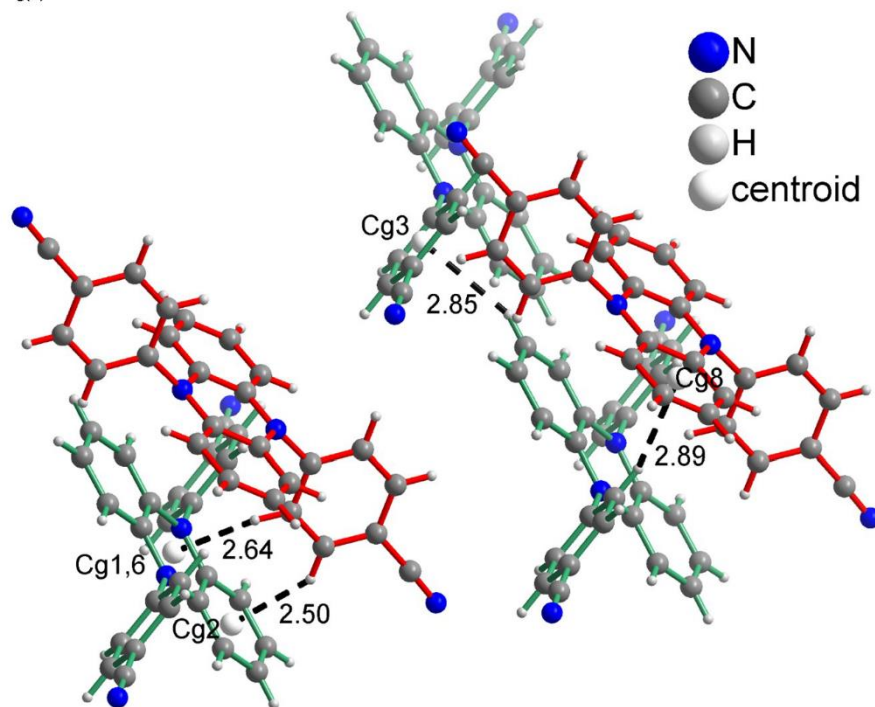


Figure S3. Intermolecular C-H... π contacts in **β -pBN**. Cg = ring centroids and distances (in Å) according to the Table above. The linear molecules are depicted with green bonds, the distorted ones with red bonds.

Intermolecular C-H...N contacts in the packing of **β -pBN** (shown in Figure S4)

Analysis of Potential Hydrogen Bonds and Schemes with $d(D...A) < R(D)+R(A)+0.50$, $d(H...A) < R(H)+R(A)-0.12$ Ang., $D-H...A > 100.0$ Deg

Nr	Typ	Res	Donor	H...	Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
1	1	C2	-H2	..N2	[2776.01]		0.95	2.55	3.363(2)	143
2	2	C15	-H15	..N4	[2666.02]		0.95	2.59	3.441(2)	150

[2776.] = [2_776] = 2-x,2-y,1-z
[2666.] = [2_666] = 1-x,1-y,1-z

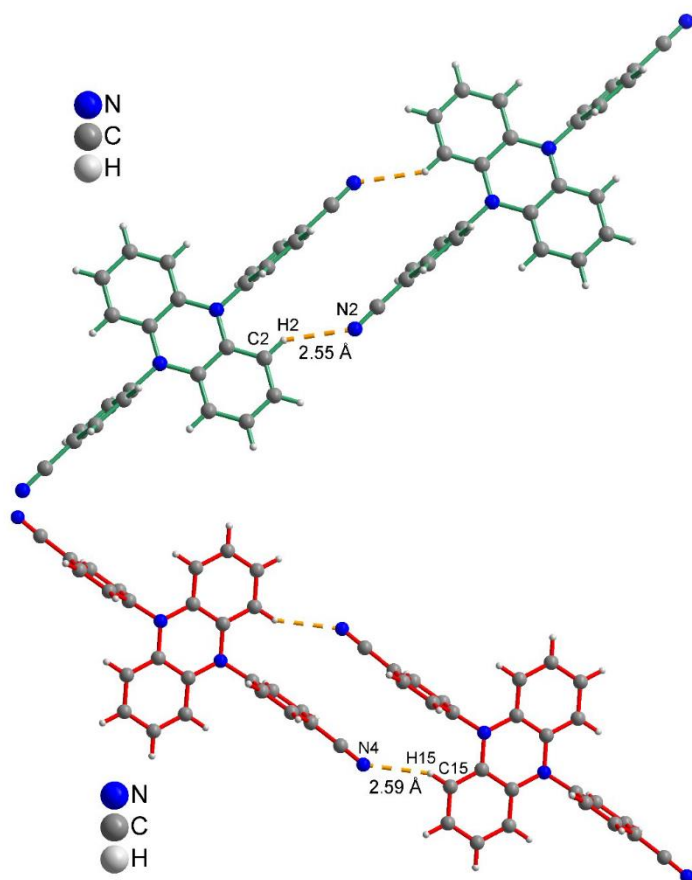


Figure S4. Inter-molecular C-H...N contacts in β -pBN according to the Table above. The linear molecules are depicted with green bonds, the distorted ones with red bonds.

Compound mBN:

Figure S5 gives an approximate view along the N...N axis in **mBN** to illustrate the planar nature of the pyrazine ring in **mBN** and shows the packing diagram.

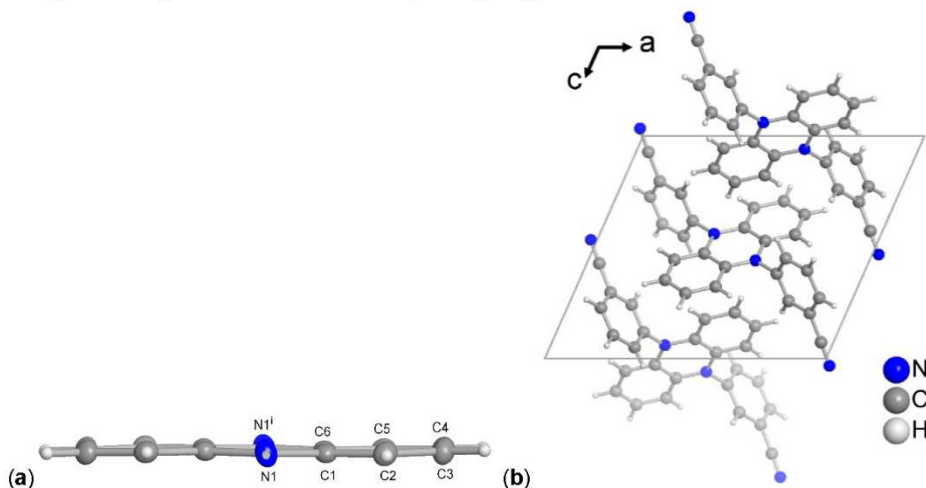


Figure S5. (a) Approximate view along the N...N axis in **mBN** and (b) packing diagram.

Intermolecular C-H... π contacts in the packing of **mBN** (shown in Figure S6):

Analysis of X-H...Cg(Pi-Ring) Interactions (H...Cg < 3.0 Ang. - Gamma < 30.0 Deg)

===== Cg(J)

= Center of gravity of ring J (Plane number above)

- H-Perp = Perpendicular distance of H to ring plane J

- Gamma = Angle between Cg-H vector and ring J normal

- X-H...Cg = X-H-Cg angle (degrees)

- X...Cg = Distance of X to Cg (Angstrom)

- X-H, Pi = Angle of the X-H bond with the Pi-plane (i.e. Perpendicular = 90 degrees, Parallel = 0 degrees)

X-H(I)	Res(I)	Cg(J) [ARU(J)]	H...Cg	H-Perp	Gamma	X-H...Cg	X...Cg	X-H, Pi
C(2) -H(2)	[1]-> Cg(2)	[2656,01]	2.95	2.82	16.89	135	3.6779(11)	52
C(3) -H(3)	[1]-> Cg(1)	[2656,01]	2.57	2.49	15.07	148	3.4194(12)	67
C(3) -H(3)	[1]-> Cg(4)	[2656,01]	2.66	2.48	21.65	136	3.4142(11)	67
C(3) -H(3)	[1]-> Cg(6)	[2656,01]	2.57	2.48	15.80	148	3.4194(11)	67

[2656] = 1-X, 1/2+Y, 3/2-Z

[4554] = X, 1/2-Y, -1/2+Z

Cg(1) = centroid of N1-C1-C6-N1i-C1i-C6i

Cg(2) = centroid of C1-C2-C3-C4-C5-C6

Cg(4) = centroid of N1-C1-C2-C3-C4-C5-C6-N1i-C1i-C6i

Cg(6) = centroid of N1-C1-C2-C3-C4-C5-C6- N1i-C1i-C2i-C3i-C4i-C5i-C6i = corresponds to Cg(1)

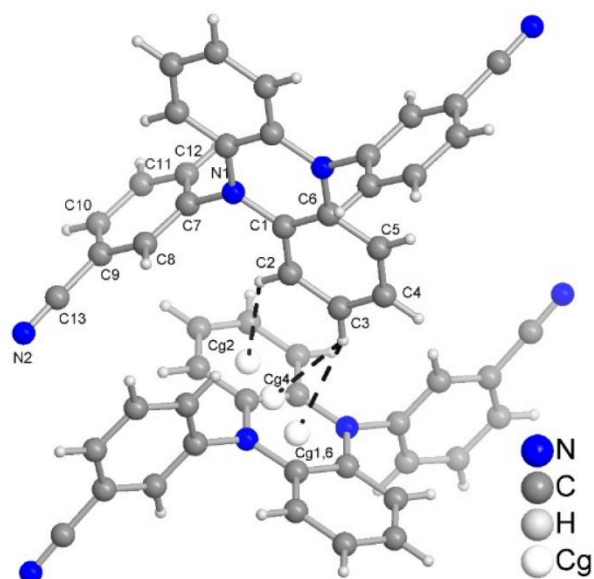


Figure S6. Intermolecular C-H $\cdots$ π contacts in **mBN**. Symmetry transformation $i = -x+1, -y, -z+2$. Cg = ring centroids according to the Table above.

Intermolecular C-H $\cdots$ N contacts in the packing of **mBN** (shown in Figure S7)

Analysis of Potential Hydrogen Bonds and Schemes with $d(D\cdots A) < R(D)+R(A)+0.50$, $d(H\cdots A) < R(H)+R(A)-0.12$ Ang., $D-H\cdots A > 100.0$ Deg

Nr	Typ	Res	Donor	H...	Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
1	1	C(4)	-H(4)	..	N(2)	[4655.01]	0.95	2.61	3.3597(17)	136

[4655.] = [4_666] = $1+x, 1/2-y, 1/2+z$

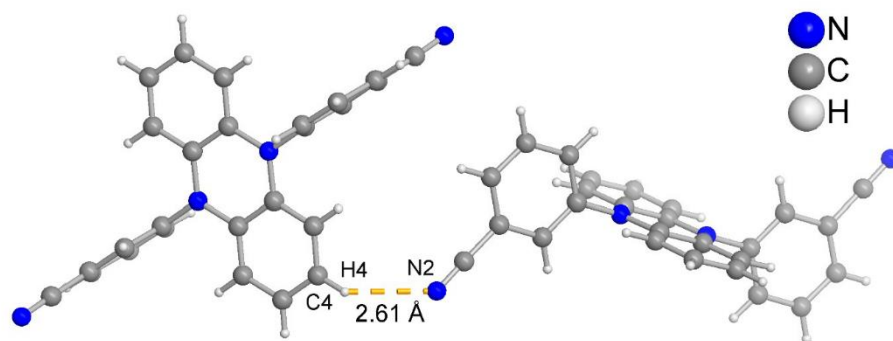


Figure S7. Intermolecular C-H $\cdots$ N contact in **mBN** according to the Table above.

Compound BPN:

Figure S8 depicts the molecular structure of **BPN** with the chloroform solvent of crystallization, gives an approximate view along the N···N axis in **BPN** to illustrate the bending and shows the packing diagram.

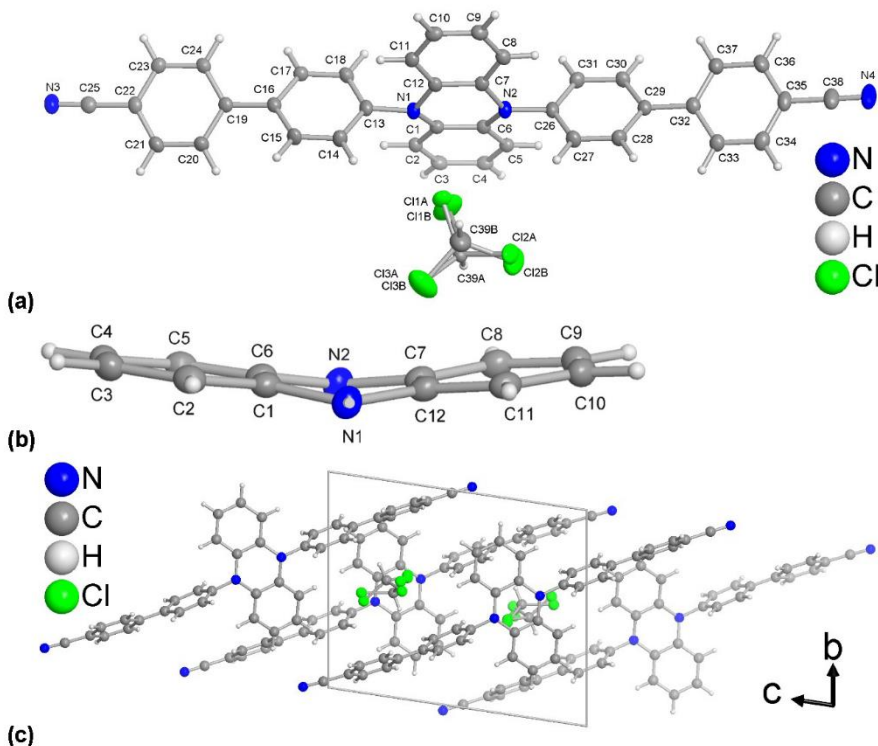


Figure S8. (a) Molecular structure of **BPN** showing also the disordered CHCl₃ solvent molecule in the crystalline state (50% thermal ellipsoids, H atoms with arbitrary radii). (b) Approximate view along the N···N axis in **BPN** to illustrate the bending by 16.00° of the two pyrazine halves in **BPN**. The angles in **BPN** between the benzene ring planes and the anellated half of the pyrazine ring are 2.71° (C1-C6) and 1.19° (C7-C12). (c) Section of the packing diagram.

Intermolecular π - π -Stacking interactions in the packing of **BPN** (shown in Figure S9a):

Analysis of Short Ring-Interactions with Cg-Cg Distances < 6.0 Å, Alpha < 20.000 Deg. and Beta < 60.0 Deg.

- Cg(I) = Plane number I (= ring number in () above)
- Alpha = Dihedral Angle between Planes I and J (Deg)
- Beta = Angle Cg(I)→Cg(J) or Cg(I)→Me vector and normal to plane I (Deg)
- Gamma = Angle Cg(I)→Cg(J) vector and normal to plane J (Deg)
- Cg-Cg = Distance between ring Centroids (Å.)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Å.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Å.)
- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Å.).
- P,Q,R,S = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

Cg(I)	Res(I)	Cg(J)	[ARU(J)]	Cg-Cg	Alpha	Beta	Gamma	CgI_Perp	CgJ_Perp	Slippage
Cg(5)	[1]	→ Cg(7)	[1564.01]	3.7043(10)	5.87(8)	28.3	22.4	3.4247(7)	3.2626(7)	1.754
Cg(7)	[1]	→ Cg(5)	[1546.01]	3.7041(10)	5.87(8)	22.4	28.3	3.2625(7)	3.4246(7)	1.412

(Cg-Cg contacts above 4.9 Å have been omitted.)

[1564] = X, 1+Y, -1+Z
 [1546] = X, -1+Y, 1+Z
 Cg(5) = centroid of C19-C20-C21-C22-C23-C24
 Cg(7) = centroid of C32-C33-C34-C35-C36-C37

Intermolecular C-H... π contacts in the packing of BPN (shown in Figure S9b):

Analysis of X-H...Cg(Pi-Ring) Interactions (H...Cg < 3.0 Ang. - Gamma < 30.0 Deg)

===== Cg(J)

= Center of gravity of ring J (Plane number above)

- H-Perp = Perpendicular distance of H to ring plane J

- Gamma = Angle between Cg-H vector and ring J normal

- X-H...Cg = X-H-Cg angle (degrees)

- X...Cg = Distance of X to Cg (Angstrom)

- X-H, Pi = Angle of the X-H bond with the Pi-plane (i.e. Perpendicular = 90 degrees, Parallel = 0 degrees)

X-H(I)	Res(I)	Cg(J) [ARU(J)]	H...Cg	H-Perp	Gamma	X-H...Cg	X...Cg	X-H, Pi
C(17) -H(17)	[1] -> Cg(2)	[2666.01]	2.71	2.69	6.49	154	3.5831(18)	62
C(28) -H(28)	[1] -> Cg(3)	[2567.01]	2.80	2.68	17.19	169	3.7406(19)	64

[2666] = 1-X, 1-Y, 1-Z

[2567] = -X, 1-Y, 2-Z

Cg(2) = centroid of C1-C2-C3-C4-C5-C6

Cg(3) = centroid of C7-C8-C9-C10-C11-C12

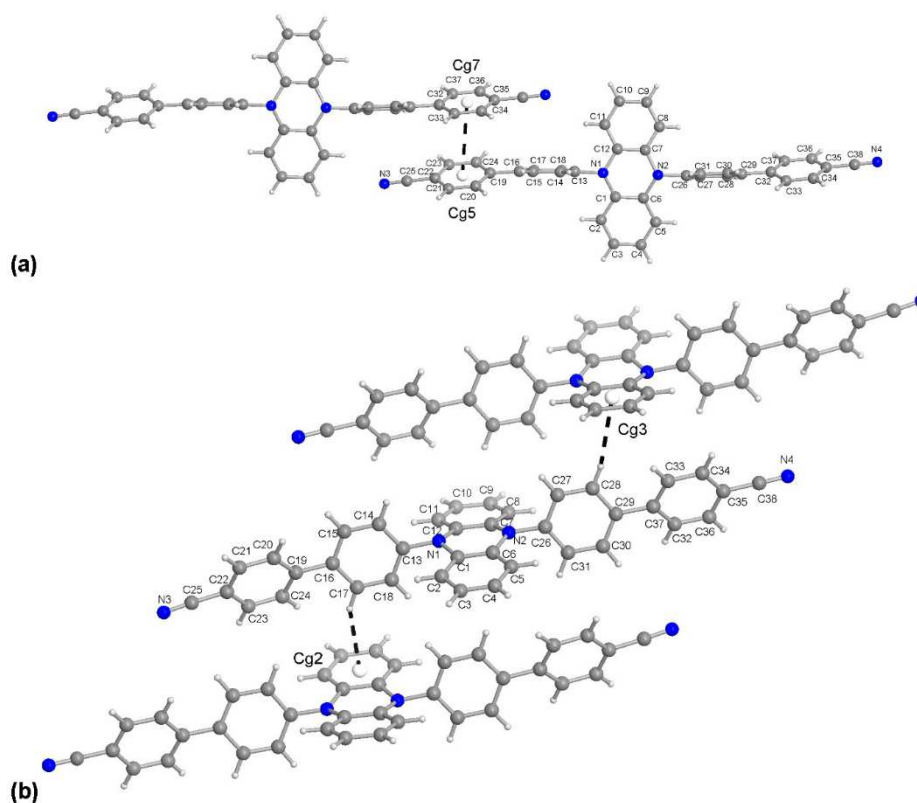


Figure S9. (a) π - π -Stacking interactions and **(b)** intermolecular C-H $\cdots$ π contacts in **BPN**. Cg = ring centroids according to the Table above.

Intermolecular C-H $\cdots$ N contacts in the packing of **BPN** (shown in Figure S10)

Analysis of Potential Hydrogen Bonds and Schemes with $d(D\cdots A) < R(D)+R(A)+0.50$, $d(H\cdots A) < R(H)+R(A)-0.12$ Ang., $D-H\cdots A > 100.0$ Deg

=====							
Nr	Typ	Res Donor	H...Acceptor [ARU]	D - H	H...A	D...A	D - H...A
1	1	C(5)	-H(5) ...N(3) [1546.01]	0.95	2.55	3.395(2)	149
3	1	C(11)	-H(11) ...N(4) [1564.01]	0.95	2.53	3.365(2)	147
[1564.] = [1_564] = x,1+y,-1+z							
[1546.] = [1_546] = x,-1+y,1+z							

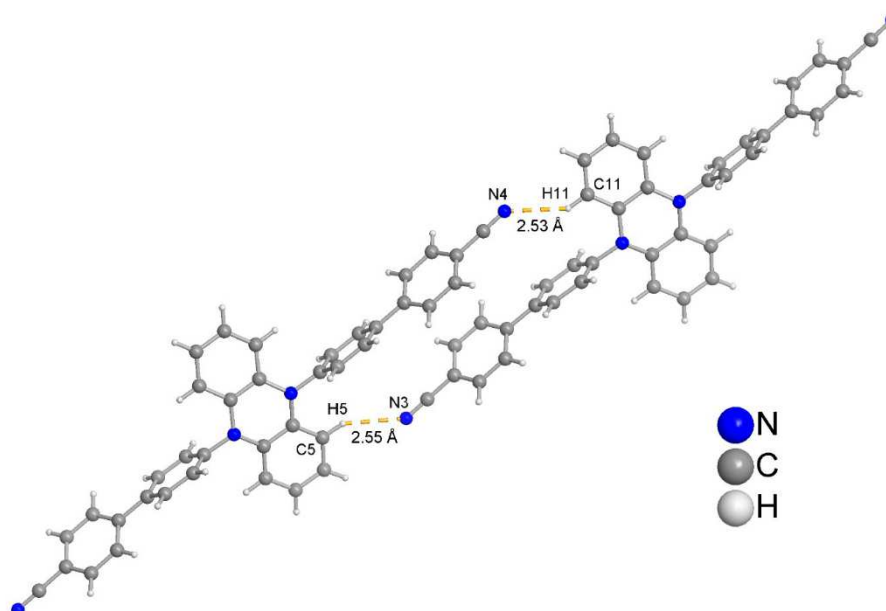


Figure S10. Intermolecular C-H $\cdots$ N contacts in **BPN** according to the Table above.

S5 Photophysical properties

Emission spectra (Solid state)

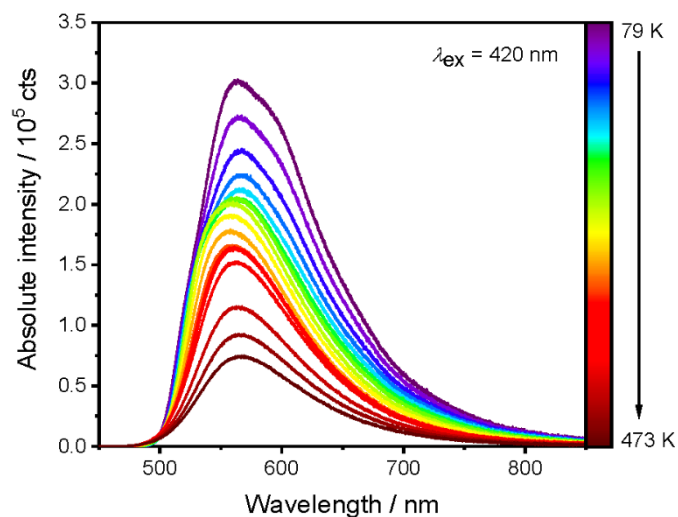


Figure S11. Temperature-dependent emission spectrum of powdered pBN. Excitation wavelength is indicated. Temperature intervals were $\Delta T = 25$ K.

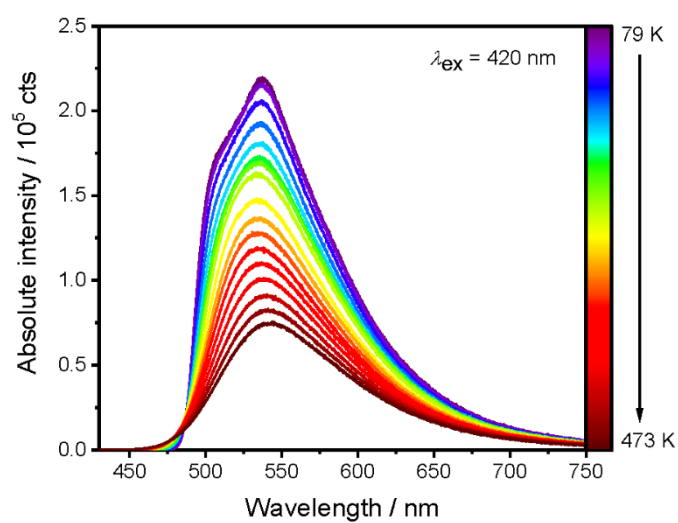


Figure S12. Temperature-dependent emission spectrum of powdered mBN. Excitation wavelength is indicated. Temperature intervals were $\Delta T = 25$ K.

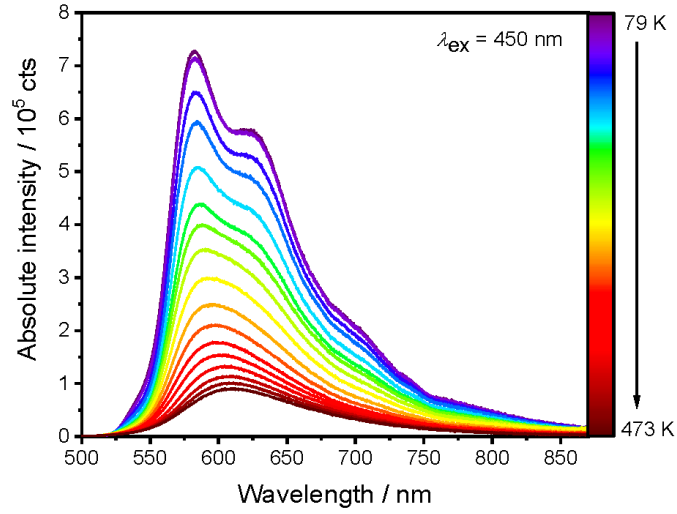


Figure S13. Temperature-dependent emission spectrum of powdered **BPN**. Excitation wavelength is indicated. Temperature intervals were $\Delta T = 25$ K.

Arrhenius plots (Solid state)

The temperature-dependent delayed components were fitted to an Arrhenius law in the low temperature range:

$$k_{\text{delayed}}(T) = k_{d0} \exp \left(-\frac{\Delta E_{ST}}{k_B T} \right) \quad (1)$$

with k_{d0} as a pre-factor, ΔE_{ST} as the effective singlet-triplet energy gap, k_B as the Boltzmann constant and T as the absolute temperature. In the cases of **pBN** and **mBN**, the prompt and delayed components were obtained from the time-resolved luminescence by biexponential fits over the whole dynamic range,

$$I(t, T) = A_{\text{prompt}} \exp(-k_{\text{prompt}}(T) \cdot t) + A_{\text{delayed}} \exp(-k_{\text{delayed}}(T) \cdot t) \quad (2)$$

with $I(t, T)$ as the time-dependent intensity at a given temperature T , A_{prompt} and A_{delayed} as the amplitudes of the prompt and delayed component, respectively, and $k_{\text{prompt}}(T)$ and $k_{\text{delayed}}(T)$ as the (eventually temperature-dependent) decay rate constants of the prompt and delayed fluorescence, respectively.

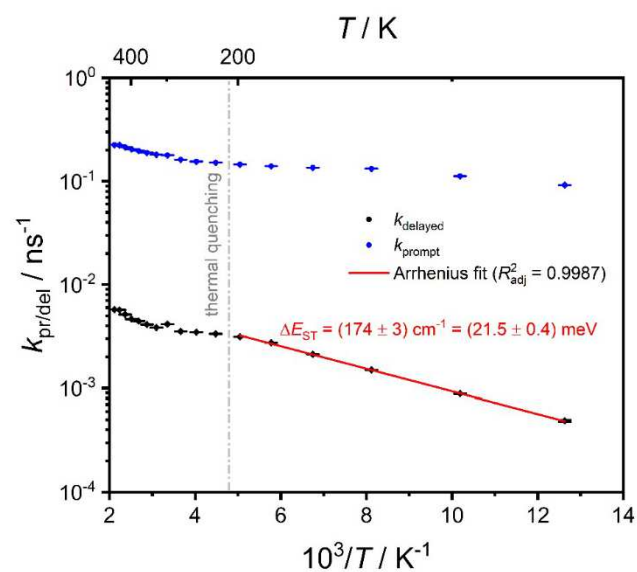


Figure S14. Arrhenius plot of the temperature-dependent time-resolved luminescence data of pBN.

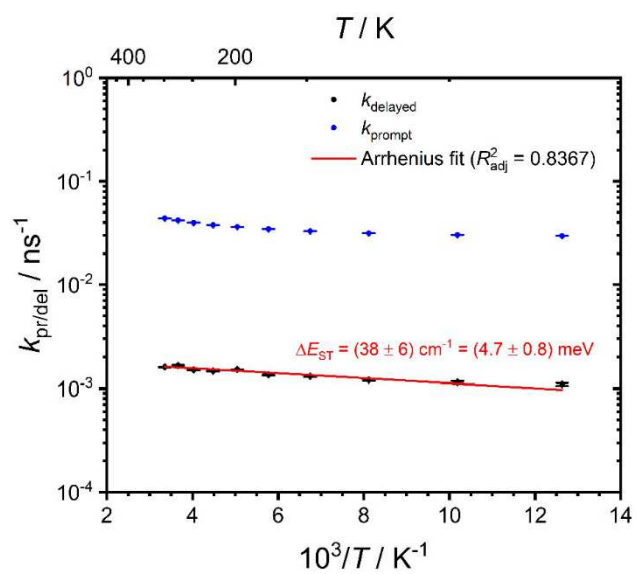


Figure S15. Arrhenius plot of the temperature-dependent time-resolved luminescence data of mBN.

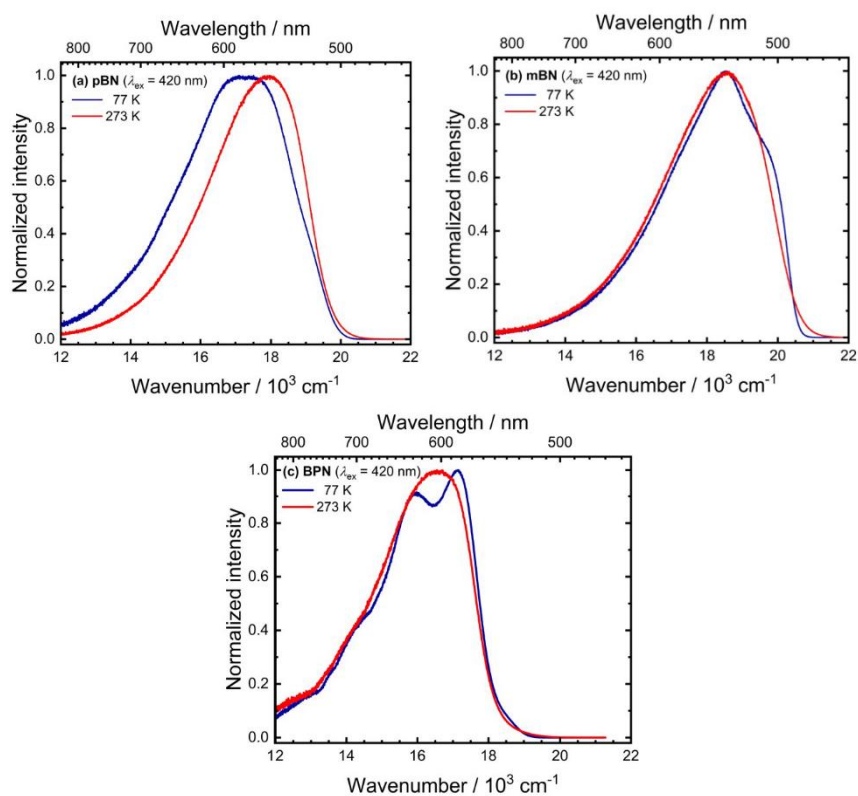


Figure S16. Photoluminescence spectra in wavenumber scale (including Jacobian λ^2 intensity correction) for (a) pBN, (b) mBN, and (c) BPN at 77 K (blue) and 273 K (red).

Absorption and emission spectra (solution state)

Compound **pBN**:

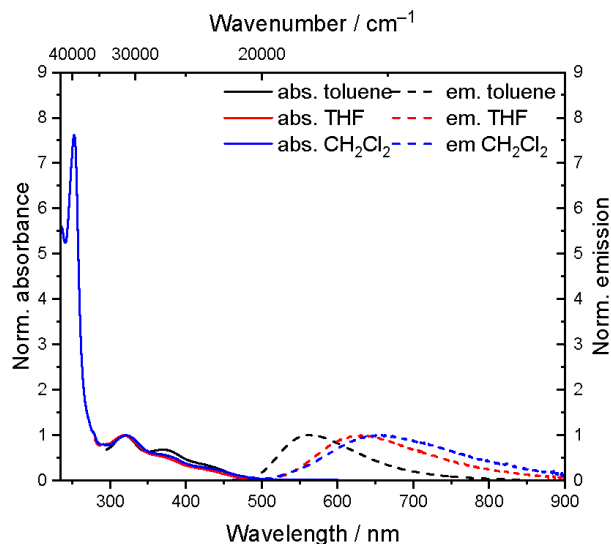


Figure S17. Absorbance and emission spectra of **pBN** recorded in solvents with different polarity ($c = 10^{-5}$ mol/L, $T = 293$ K).

Compound **pBN** possesses in toluene (318 nm, $\epsilon = 2700$ L mol⁻¹ cm⁻¹), THF (318 nm, $\epsilon = 7200$ L mol⁻¹ cm⁻¹) and dichloromethane (321 nm, $\epsilon = 7700$ L mol⁻¹ cm⁻¹) one distinct absorption maximum, which is accompanied by two shoulders around 370 nm and 427 nm with weaker intensity (Figure S17, Table 1). In dichloromethane a maximum at higher energy at 255 nm with a molar absorption coefficient of 42600 L mol⁻¹ cm⁻¹ is detected (Table 1).

While the absorbance spectra are almost indifferent to the change of solvent polarity regarding their absorption maxima, the emission is strongly affected by solvent polarity and a distinct positive emission solvatochromicity can be observed in solvents of higher polarity (Table 1).¹⁷ The broad emission bands (full width at half maximum (FWHM) from 3624 cm⁻¹ (0.45 eV) to 4426 cm⁻¹ (0.55 eV) are redshifted from toluene (562 nm) over THF (634 nm) to dichloromethane (659 nm) and a pronounced increase of the Stokes shifts from 9200 to 16000 cm⁻¹ can be determined. The bathochromic emission shift with increasing solvent polarity indicates a significant charge transfer character of the excited state. CIE coordinates reveal yellow to orange emission colors (Figure S18). Emission is not intense and hardly visible to the eye in THF and dichloromethane. Luminescence lifetimes are in a typical range for organic chromophores¹⁸, and decrease with increasing solvent polarity from toluene ($\tau = 5.7$ ns) over THF ($\tau = 2.5$ ns) to dichloromethane ($\tau = 1.0$ ns). This observation indicates high non-radiative rate constants in each solvent.

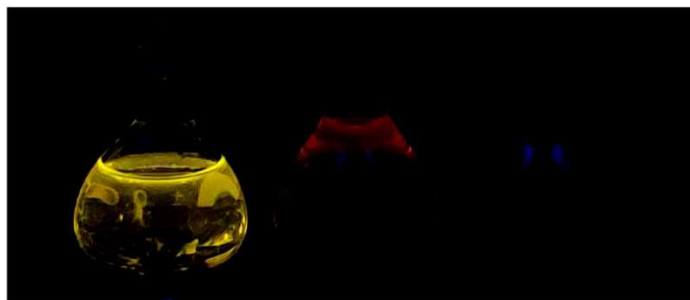


Figure S18. Emission of **pBN** in toluene, THF and dichloromethane (from left to right) ($c = 10^{-4}$ mol/L, $\lambda_{\text{exc}} = 365$ nm).

Compound mBN:

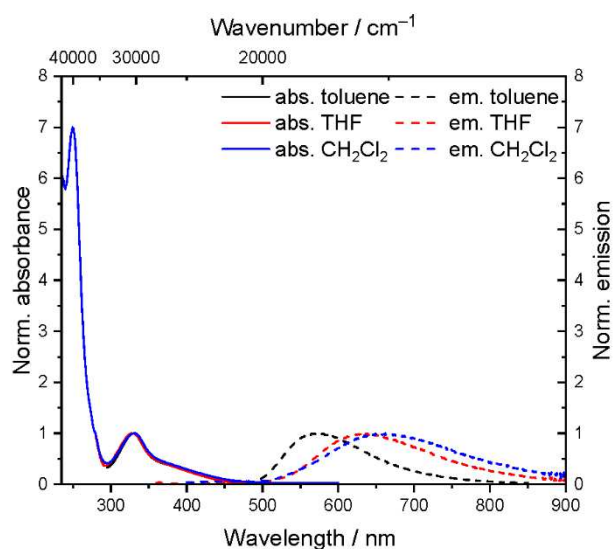


Figure S19. Absorbance and emission spectra of **mBN** recorded in solvents with different polarity ($c = 10^{-5}$ mol/L, $T = 293$ K).

Compound **mBN** possesses in toluene (331 nm, $\epsilon = 6800$ L mol $^{-1}$ cm $^{-1}$) and THF (329 nm, $\epsilon = 5900$ L mol $^{-1}$ cm $^{-1}$) a distinct longest wavelength absorption maximum that is accompanied by broad tailing shoulder around 380 nm with weaker intensity (Figure S19, Table 1). In dichloromethane, the higher energy absorption band at 250 nm with a molar absorption coefficient of 54200 L mol $^{-1}$ cm $^{-1}$ is found (Table 1). Also, in dichloromethane a shoulder around 380 nm can be identified.

While the absorption spectra are almost indifferent to the change of solvent polarity, the emission is strongly affected by solvent polarity and a distinct positive emission solvatochromism can be

observed in solvents of higher polarity (Table 1).¹⁷ The broad emission bands (full width at half maximum (FWHM) from 3746 cm^{-1} (0.47 eV) to 4517 cm^{-1} (0.56 eV) are redshifted from toluene (572 nm) over THF (634 nm) to dichloromethane (662 nm) and a pronounced increase of the Stokes shifts from 12700 to 15000 cm^{-1} can be determined. The bathochromic emission shift with increasing solvent polarity indicates a significant charge transfer character of the excited state. CIE coordinates indicate an orangish-yellow color in emission (Figure S20, Table 1). Emission intensity strongly decreases with increasing solvent polarity. Already in toluene the emission is very weak, being not visible to the eye in THF and dichloromethane (Figure S20). Furthermore, the luminescence lifetimes fall into the typical range for organic chromophores,¹⁸ and the lifetimes decrease from toluene ($\tau = 8.9\text{ ns}$) over THF ($\tau = 1.7\text{ ns}$) to dichloromethane ($\tau = 1.6\text{ ns}$). These observations indicate high non-radiative rate constants in each solvent.



Figure S20. Emission of **mBN** in toluene, THF and dichloromethane (from left to right) ($c = 10^{-4}\text{ mol/L}$, $\lambda_{\text{exc}} = 365\text{ nm}$).

Compound BPN:

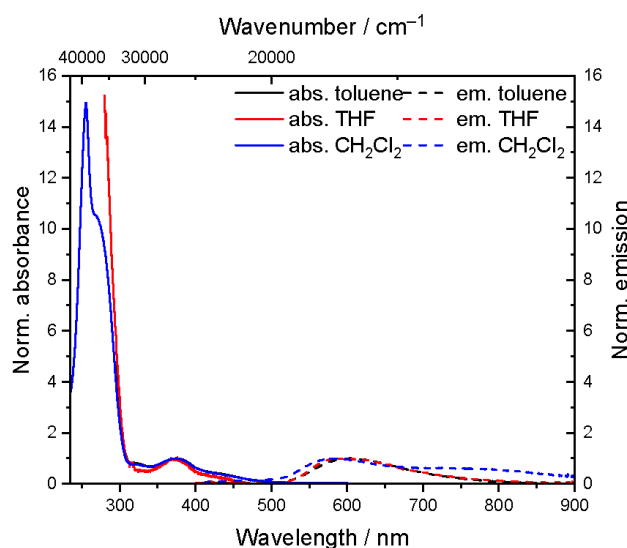


Figure S21. Absorbance and emission spectra of **BPN** recorded in solvents with different polarity ($c = 10^{-5}$ mol/L, $T = 293$ K).

Compound **BPN** possesses in toluene (375 nm, $\epsilon = 6600$ L mol⁻¹ cm⁻¹) and THF (373 nm, $\epsilon = 1900$ L mol⁻¹ cm⁻¹) a distinct longest wavelength absorption maximum that is accompanied by tailing shoulder around 427 nm with weaker intensity (Figure S21, Table 1). In dichloromethane, the higher energy absorption band at 255 nm with a molar absorption coefficient of 98000 L mol⁻¹ cm⁻¹ is found (Table 1). Also, in dichloromethane a shoulder around 427 nm and 271 nm can be identified. While the absorbance spectra are almost indifferent to the change of solvent polarity, the emission is strongly affected by solvent polarity and a distinct negative emission solvatochromism can be observed in solvents of higher polarity (Table 1).¹⁷ The broad emission bands (full width at half maximum (FWHM) from 3564 cm⁻¹ (0.44 eV) to 6442 cm⁻¹ (0.88 eV) are blueshifted from toluene (604 nm) over THF (589 nm) to dichloromethane (587 nm) and a decrease of the Stokes shifts from 10100 to 9800 cm⁻¹ can be determined. The hypsochromic emission shift with increasing solvent polarity indicates a stabilization of the excited state in apolar solvents. Dual emission in dichloromethane might be caused by a twisted intramolecular charge transfer (TICT) state.¹⁹ Upon photonic excitation the LE state equilibrates rapidly with the TICT state at lower energy.²⁰ This results in two emission maxima, one at higher energy (587 nm, emission from the LE state) and one at lower energy (760 nm, emission from the TICT state). The CIE coordinates clearly indicate orange emission colors (Figure S22). The intensity of the emission is low in THF and dichloromethane, in toluene it is stronger, but not that intense (Figure S22). Furthermore, the luminescence lifetimes fall

into the typical range for organic chromophores,¹⁸ and range from 5.5 ns (toluene) to 12.0 ns (THF).



Figure S22. Emission of **BPN** in toluene, THF and dichloromethane (from left to right) ($c = 10^{-4}$ mol/L, $\lambda_{\text{exc}} = 365$ nm).

Luminescence decay times (Solution state)

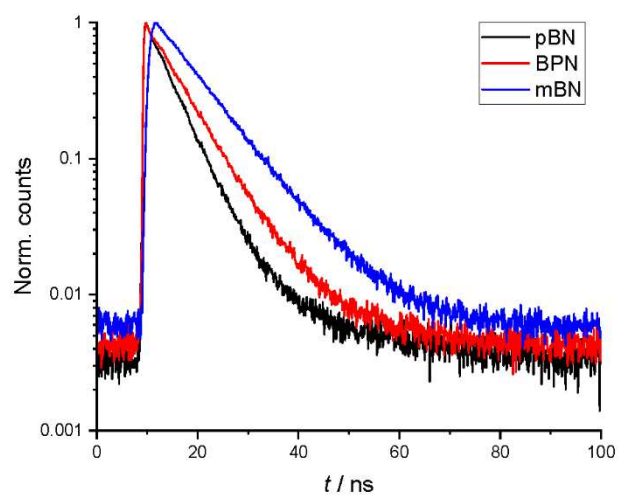


Figure S23. Photoluminescence decays for **pBN**, **mBN** and **BPN** recorded in toluene ($c = 10^{-4}$ mol/L, $T = 293$ K).

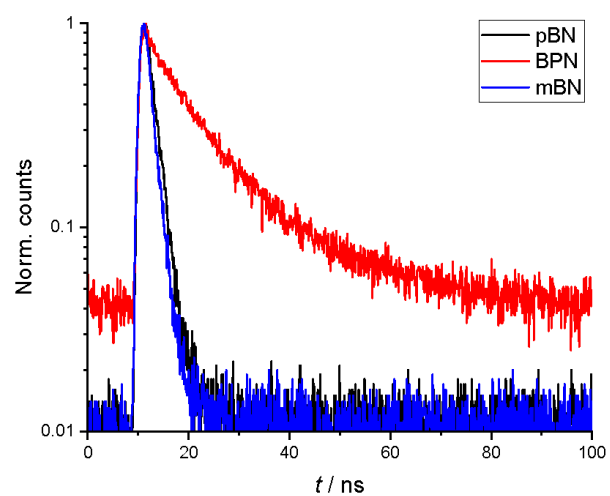


Figure S24. Photoluminescence decays for pBN, mBN and BPN recorded in THF ($c = 10^{-4}$ mol/L, $T = 293$ K).

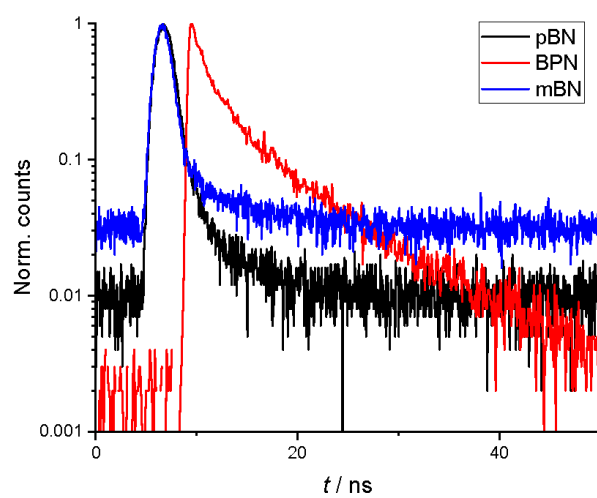


Figure S25. Photoluminescence decays for pBN, mBN and BPN recorded in dichloromethane ($c = 10^{-4}$ mol/L, $T = 293$ K).

S6 Data of quantum chemical calculations

Table S4. Computed absorption and emission data for **BPN**, **mBN** and **pBN** in vacuum. Oscillator strengths f are only given when > 0 , adiabatic energies are given in bold italics.

Molec.	Geom.	State	Spectral line / nm	Energy / eV	Composition
BPN	S₀	S ₀	-	0.00	92% GS
		S ₁	415	2.98	81% H-L
		S ₂	412	2.00	81% H-(L+1)
		S ₃	362	2.42	42% H-(L+2), 30% H-(L+4), 17% H-
		S ₄	343 $f = 0.10$	3.61	42% H-(L+3), 35% H-(L+5)
		T ₁	-	2.92	64% H-(L+2), 26% H-(L+7), 20% H-
		T ₂	-	2.95	53% H-L, 12% H-(L+8)
	S₁	S ₀	-	0.00	91% GS
		S ₁	544	2.28 <i>2.49</i>	84% H-L
		T ₁	-	2.34	84% H-L
	T₁	S ₀	-	0.00	91% GS
		S ₁	-	2.28	84% H-L
		T ₁	-	2.24 <i>2.44</i>	84% H-L
pBN	S₀	S ₀	-	0.00	94% GS
		S ₁	401	3.09	88% H-L
		S ₂	398	3.11	87% H-(L+1)
		S ₃	351	3.53	71% H-(L+2), 18% H-(L+4)
		S ₄	338 $f = 0.09$	3.67	77% H-(L+3)
		T ₁	-	3.01	41% H-(L+2), 38% H-(L+4)
		T ₂	-	3.06	80% H-L
	S₁	S ₀	-	0.00	93% GS
		S ₁	-	2.57 <i>2.70</i>	89% H-L
		T ₁	-	2.54	89% H-L
	T₁	S ₀	-	0.00	93% GS
		S ₁	-	2.58	89% H-L
		T ₁	-	2.54 <i>2.67</i>	89% H-L
mBN	S₀	S ₀	-	0.00	94% GS
		S ₁	402 $f = 0.01$	3.08	78% H-L
		S ₂	398 $f = 0.01$	3.11	78% H-(L+1)
		S ₃	351 $f = 0.01$	3.54	73% H-(L+2)
		S ₄	344 $f = 0.01$	3.60	73% H-(L+3), 11% H-(L+2)
		S ₅	310	4.00	80% H-(L+4)
		S ₆	296 $f = 0.14$	4.20	82% H-(L+5)
		T ₁	-	2.89	37% H-(L+1), 26% H-(L+4), 20%
		T ₂	-	3.01	59% H-L, 24% H-(L+1)
	S₁	S ₀	-	0.00	93% GS
		S ₁	497	2.49 <i>2.68</i>	89% H-L
		T ₁	-	2.41	81% H-L
	T₁	S ₀	-	0.00	93% GS
		S ₁	-	2.51	89% H-L
		T ₁	-	2.41 <i>2.59</i>	79% H-L

	S_0	S_1
BPN	8.78°	0.01°
mBN	10.95°	1.49°
pBN	11.43°	0.01°

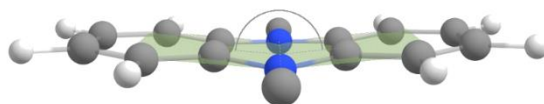
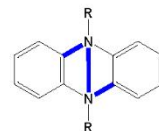


Figure S26. Phenazine-core planarization. Table entries denote the C-N-N-C dihedral angle in S_0 and S_1 geometries computed at the (TD)-DFT PBE0 level of theory.

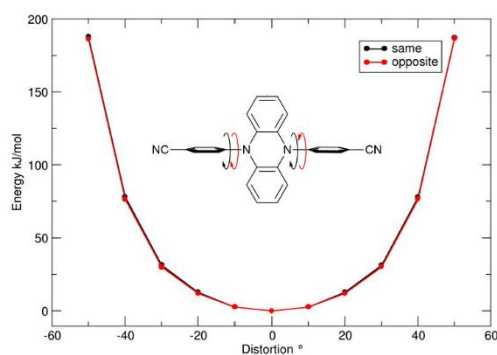


Figure S27. Unrelaxed dihedral scan for phenyl-rotation in **pBN** showing the energy profile (same and opposite directions phenyl rotation, the starting point corresponds to the perpendicular arrangement (90°) of phenazine and phenyl rings).

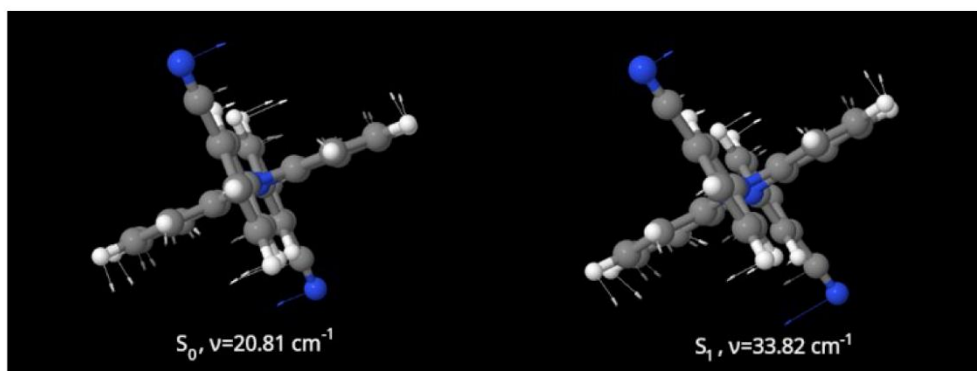


Figure S28. Normal mode vibrations including phenyl torsions in **mBN** (same direction) in S_0 (left) and S_1 (right) geometries.

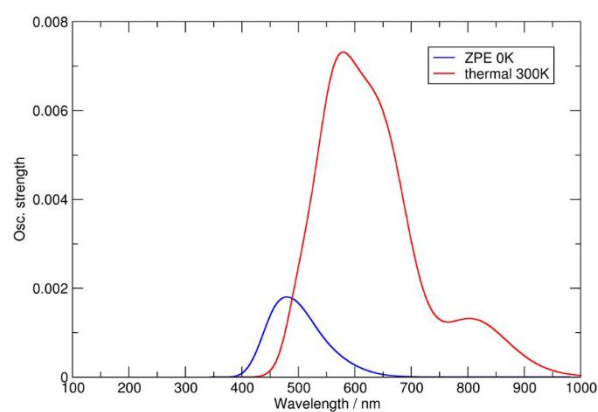


Figure S29. Computed emission in **pBN** at 0 K and 300 K (vacuum).

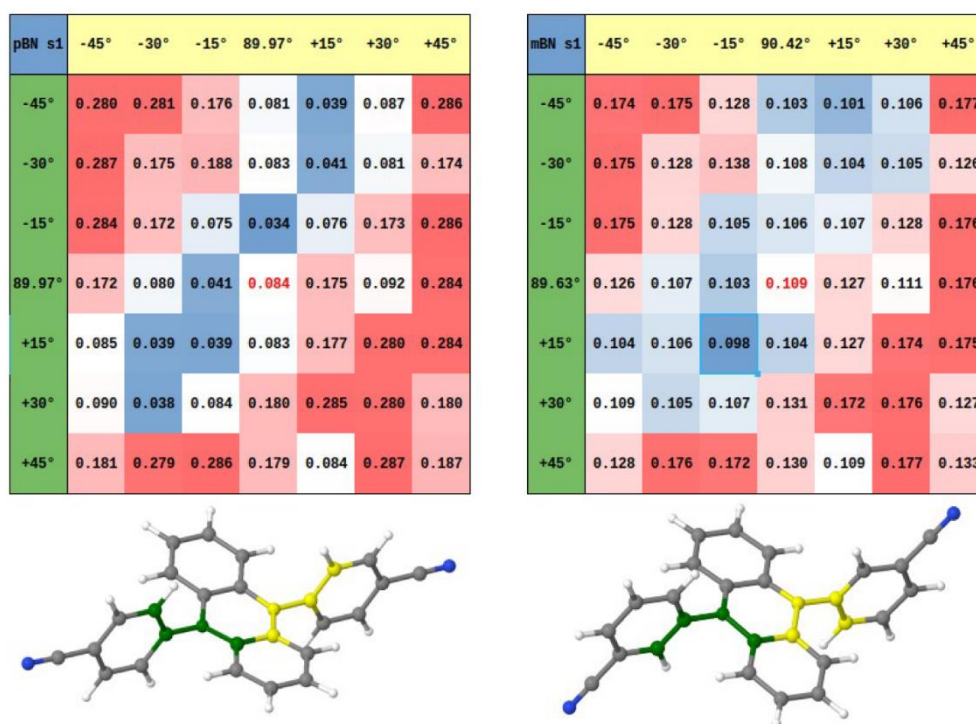


Figure S30. Modulation of ΔE_{ST} in **mBN** and **pBN**.

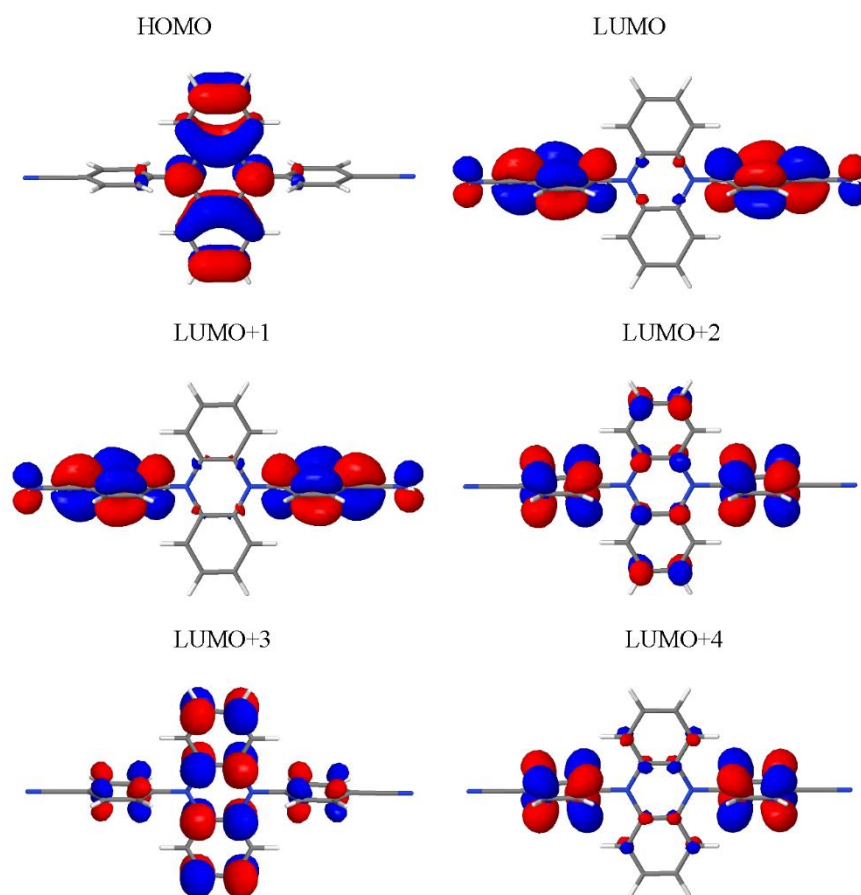


Figure S31. BH-LYP-computed orbitals involved in **pBN** excitations.

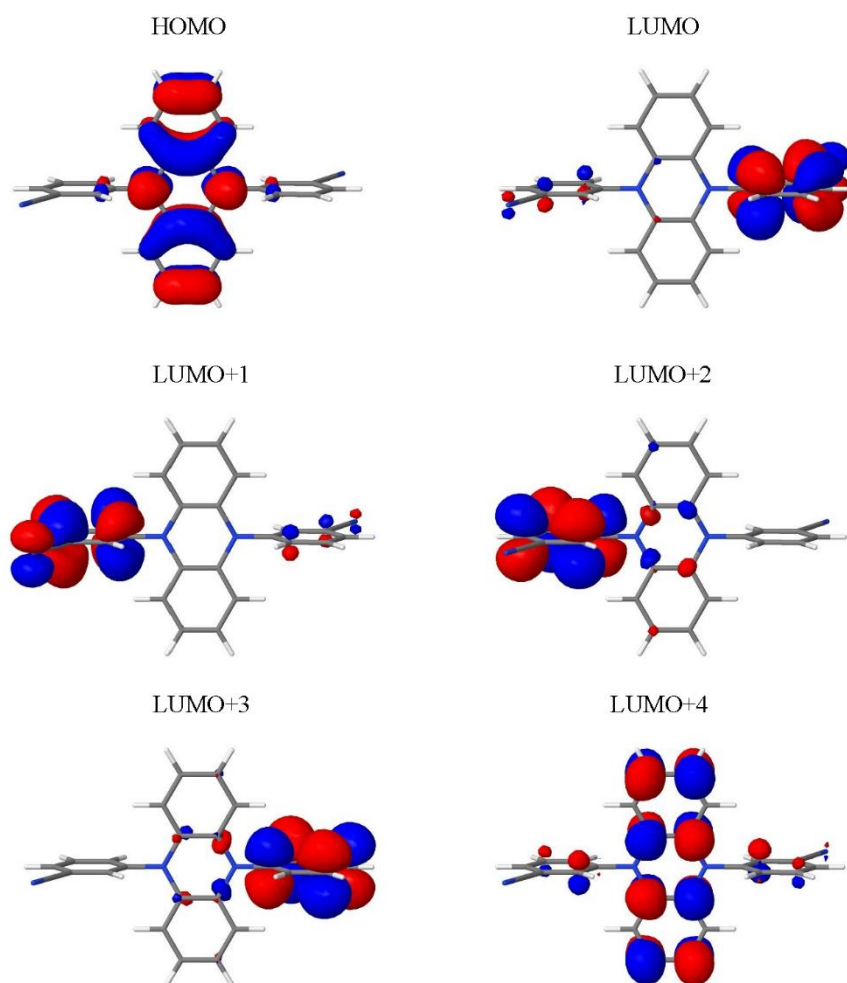


Figure S32. BH-LYP-computed orbitals involved in **mBN** excitations.

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7.3 Zinc and Cobalt Coordination Polymers Based on the Redox-Active Linker 4,4'-(Phenazine-5,10-diyl)dibenzoate: Structures and Electrochemical Properties

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Kurzzusammenfassung

Die neuen Koordinationspolymere $[\text{Zn}(\text{PZDB})(\text{DEF})_2]_n$ (Zn-PZDB) und $[\text{Co}(\text{HPZDB})_2(\text{DEF})_2]_n$ (Co-HPZDB) (H_2PZDB = 4,4'-(Phenazin-5,10-diyl)dibenzoesäure, DEF = *N,N*-Diethylformamid) wurden mittels Solvothermalsynthese aus den Metallsalzen und dem linearen H_2PZDB -Linker synthetisiert. Zn-PZDB besteht aus *zickzack*-Ketten, wobei das Zn-Ion tetraedrisch von zwei DEF-Molekülen und zwei Carboxyl-O-Atomen des verbrückenden PZDB^{2-} -Linkers koordiniert wird. Die Kristallstruktur von Co-PZDB stellt ein zweidimensionales (2D) Koordinationsgitter dar. Das Co^{2+} -Ion wird oktaedrisch von zwei DEF-Molekülen und vier Carboxyl-Sauerstoffatomen der einfach deprotonierten HPZDB-Linkermoleküle koordiniert. Farbloses Zn-PZDB und rotes Co-PZDB färben sich an der Luft grün, was auf die Oxidation des Linkers zurückzuführen ist, wobei ein $(\text{H})\text{PZDB}^+$ -Radikalkation entsteht. Die UV/Vis/NIR-Spektroelektrochemie zeigte, dass Me_2PZDB zwei reversible Ein-Elektronen-Oxidationen durchläuft, die charakteristische Absorptionsbanden erzeugen. Ähnliche spektroskopische Veränderungen wurden bei der Oxidation von Zn-PZDB und Co-HPZDB beobachtet. Die chemische Oxidation mit SbCl_5 führte zu den gleichen Farbveränderungen zusammen mit EPR-Signalen, die typisch für Radikalkationen auf Ligandenbasis sind. Diese Ergebnisse deuten darauf hin, dass der PZDB-Linker die primäre Redoxstelle ist. Auf die Ligandenoxidation folgt der Zerfall der Koordinationspolymere.

Anteile an der Publikation

- Konzeption des Forschungsvorhabens und Durchführung der Literaturrecherche.
- Synthese und Charakterisierung der organischen Dicarbonsäure mittels NMR, HR-ESI-MS, IR, EA und Schmelzpunktbestimmung.
- Synthese und Charakterisierung der Koordinationspolymere mittels EA, PXRD, IR und TGA, mit Unterstützung von N. Hufnagel und N. Assahub.
- Spektroskopische Messungen der Koordinationspolymere am Feststoff.
- Selbständige Auswertung, graphische Darstellung und Interpretation der entsprechenden experimentellen Rohdaten.
- Durchführung der TGA-Messungen durch T. Strothmann und N. Assahub.
- Durchführung der Kristallstrukturanalyse und Verfeinern der Einkristall-Röntgenstrukturdaten der Koordinationspolymere durch T. Heinen, Dr. D. Jordan und Dr. I. Boldog; graphische Darstellung und Interpretation der kristallographischen Ergebnisse durch Prof. Dr. C. Janiak.
- Durchführung der XPS-Messungen der Koordinationspolymere sowie Auswertung, graphische Darstellung und Interpretation der Ergebnisse durch Dr. T. H. Y. Beglau.
- Durchführung der elektrochemischen Messungen sowie Auswertung, graphische Darstellung und Interpretation der Ergebnisse durch M. Nau und Prof. Dr. R. F. Winter.
- Anfertigung eines Manuskripts und der *supporting information* für eine wissenschaftliche Publikation basierend auf den experimentellen Ergebnissen.
- Überarbeitung des Manuskripts nach den Kommentaren der Co-Autoren.
- Gestaltung des *graphical abstract* des Manuskripts.
- Die Publikation wurde im internationalen Journal *European Journal of Inorganic Chemistry* mit Prof. Dr. C. Janiak eingereicht.
- Überarbeitung des Manuskripts in Kooperation mit Prof. Dr. R. F. Winter und Prof. Dr. C. Janiak.

Zinc and Cobalt Coordination Polymers Based on the Redox-Active Linker 4,4'-(Phenazine-5,10-diyl)dibenzoate: Structures and Electrochemical Properties

Dietrich Püschel, Moritz Nau, Nabil Assahub, Thi Hai Yen Beglau, Nils Hufnagel, Dustin Jordan, Tobias Heinen, Till Strothmann, Markus Suta, Rainer F. Winter,* and Christoph Janiak*

The novel coordination polymers $[\text{Zn}(\text{PZDB})(\text{DEF})_2]_n$ (Zn-PZDB) and $[\text{Co}(\text{HPZDB})_2(\text{DEF})_2]_n$ (Co-HPZDB) ($\text{H}_2\text{PZDB} = 4,4'$ -(phenazine-5,10-diyl)dibenzoic acid, $\text{DEF} = N,N$ -diethylformamide) are synthesized solvothermally from the metal nitrate salts and the linear H_2PZDB linker with the redox-active phenazine-5,10-diyl core. Zn-PZDB is composed of zigzag chains with the Zn ion tetrahedrally coordinated by two diethylformamide (DEF) molecules and two carboxyl O-atoms from the bridging PZDB^{2-} linker. The crystal structure of Co-PZDB represents a two-dimensional (2D) coordination grid. The Co^{2+} ion is octahedrally coordinated by two DEF molecules and four carboxyl oxygen atoms of the semi-deprotonated HPZDB^- linker molecules. Yellow Zn-PZDB

and red Co-PZDB turn green upon air exposure, which is due to linker oxidation, forming the $(\text{H})\text{PZDB}^+$ radical cation. UV/Vis/NIR spectroelectrochemistry reveals that Me_2PZDB undergoes two reversible one-electron oxidations, producing characteristic absorption bands. Similar spectroscopic changes are observed upon oxidation of Zn-PZDB and Co-HPZDB . Chemical oxidation with SbCl_5 yields the same color changes together with electron paramagnetic resonance signals typical of ligand-based radical cations. These findings indicate that the PZDB linker is the primary redox site. Ligand oxidation is followed by disintegration of the coordination polymers.

1. Introduction

The synthesis and design of coordination polymers (CPs) and metal-organic frameworks (MOFs) have gained significant attention in recent years due to their unique architectures and diverse functional properties. CPs are crystalline solids with infinite chains or networks in one, two, or three dimensions, maintained by coordination bonds between metal ions or metal clusters and organic

bridging ligands denoted as linkers.^[1,2] MOFs are a subclass of CPs with potential porosities, often due to the utilization of spatially elongated linkers.^[3,4] These materials have significant potential for various applications in luminescence, biomedicine, gas adsorption, as well as gas storage and separation.^[5–10] Organic polycarboxylate anions have been established as widely used linkers for CPs and MOFs. They favor the formation of multinuclear clusters that act as secondary building units (SBUs) with a fixed coordination geometry and connectivity, often rendering them electroneutral by compensating the charge at the metal or cluster cations. The targeted construction of CPs nevertheless warrants a rational design and sensible use of polytopic linkers.^[8,11,12]

Redox-active CPs and MOFs enable the investigation of charge transfer mechanisms and applications in chemosensing, electrocatalysis, and optoelectronics. The integration of redox-active ligands or multivalent metal centers facilitates the tuning of electronic, magnetic, and spectroscopic properties. However, challenges such as structural instability during redox cycling necessitate careful design of metal-ligand systems. Advances such as post-synthetic modifications and the incorporation of redox-active guests often serve the purpose of improving stability and functionality. These materials show great potential for technologies such as batteries and catalysis, with ongoing research focused on optimizing CPs and MOFs for enhanced performance and durability.^[13–15] Examples for redox-active ligands in coordination polymers and networks are substituted 4,4'-bipyridinium ligands, so-called viologens,^[16,17] guanidines,^[18,19] and linkers with tetrathiafulvalene (TTF) cores.^[20–23]

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The use of carboxylate linkers that are also redox-active, such as phenazine-based linkers, for the synthesis of novel CPs and MOFs provides a further opportunity to exploit redox properties. Phenazines feature a dibenzo-annelated pyrazine core and are known for their inherent redox activity. Phenazines are easily reduced to 5,10-dihydrophenazines, which, when combined with further conversions, provide access to a rich variety of dihydrophenazine derivatives (Scheme 1).^[24] Dihydrophenazines (DHPs), and in particular *N,N*-substituted diaryl-phenazin-5,10-diyls are electron-rich and form stable radical cations under irradiation, heating, electrolysis, or treatment with a suitable chemical oxidant. Due to their remarkable redox activity and their stable radical cations,^[25,26] DHPs exhibit unique optical, electronic, magnetic, and catalytic properties.^[27–29] Several diaryl DHPs have been reported as promising photoredox catalysts for visible light-activated atom transfer radical polymerization.^[30]

Dihydrophenazine-based organic polymers,^[27,31] coordination cages,^[32] and MOFs have been investigated as heterogeneous catalysts.^[28,33] DHP-based 2D and 3D covalent organic frameworks (COFs) were found as efficient heterogeneous photocatalysts for the radical ring-opening polymerization of vinylcyclopropanes.^[31] The UiO-type MOF [Zr₆(μ₃-O)₄(μ₃-OH)₄(PZDB)₆] was successfully employed as a heterogeneous donor component for enhanced catalytic electron donor acceptor photoactivation.^[28] [Zn₂(PZDB)₂(DABCO)]·4DMF was applied as a heterogeneous catalyst for aza-Diels-Alder reactions (DABCO = 1,4-diazabicyclo[2.2.2]octane).^[34] Further, DHP-based coordination cages^[35] and porous organic polymers GT-POP-1 (precursor: 4,4'-(phenazine-5,10-diyl)dibenzonitrile), POP1/2 and POP2-Ni (precursor: 5,10-bis(4-vinylphenyl)-5,10-dihydrophenazine) have been studied with respect to their electrochemical properties.^[36,37]

In addition to their use as heterogeneous catalysts, dihydrophenazines represent a promising, inexpensive, and environmentally friendly alternative as a cathode material in batteries.^[38–40] For instance, molecular DHP derivatives can be embedded in polymers to enhance the electrochemical properties.^[41] The lithium salt of PZDB^{2–} (Li₂-PZDB) can be used as a bipolar active material for organic symmetric battery cells, serving both as a cathode and an anode. The dihydrophenazine moiety is cathode-active, while

the benzoate moiety is anode-active.^[42] Hence, it is of interest to develop new (coordination) polymers based on DHP and investigate their electrochemical properties.

In this work, we present the synthesis and characterization of two new coordination polymers based on the DHP-derived redox-active linker PZDB^{2–}.

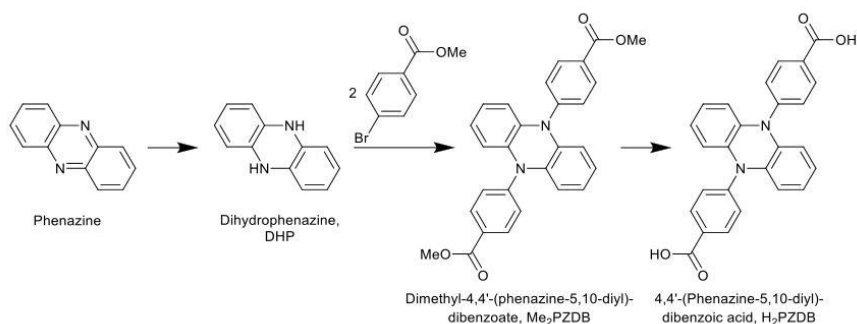
2. Results and Discussion

The synthesis of the linker acid 4,4'-(phenazine-5,10-diyl)dibenzoic acid (H₂PZDB) is illustrated in Scheme 1. The first step in the synthesis is the reduction of phenazine to DHP. In the second step, the DHP is subjected to a palladium-catalyzed Buchwald-Hartwig coupling with methyl 4-bromobenzoate. The intermediate ester (Me₂PZDB) is subsequently hydrolyzed to give the free dicarboxylic acid H₂PZDB with an overall yield of up to 75%.^[42] Its purity and identity were confirmed by ¹H NMR, ¹³C NMR, infrared and high-resolution mass spectrometry, elemental analysis and single-crystal structure analysis (see ESI for details).

The free acid H₂PZDB could be crystallized from DMSO as a DMSO solvate, H₂PZDB·2DMSO as yellow platelets in the triclinic space group *P* $\bar{1}$ (no. 2). In the crystal structure, the pyrazine centroid coincides with the inversion center, rendering half of the molecule as the crystallographic unique asymmetric unit (Figure 1). The annelated benzo and pyrazine rings are nearly coplanar (dihedral angle 0.76(6)°). The dihedral angle between the benzoic acid aryl group and the pyrazine ring is 79.36(7)°, similar to phenazine-5,10-diyl-dibenzonitriles.^[43] The intermolecular packing is controlled by C–H... π contacts (see ESI for details).

The reactions of zinc(II) or cobalt(II) nitrate with H₂PZDB under solvothermal conditions in diethylformamide (DEF) resulted in the formation of yellow thin platelet crystals of [Zn(PZDB)(DEF)]₂_n (Zn-PZDB) (Figure S8, Supporting Information), or hexagonal dark red-purple crystals of [Co(HPZDB)(DEF)]₂_n·DEF (Co-HPZDB) (Figure S19, Supporting Information).

Zn-PZDB crystallizes in the monoclinic space group *C*2/c (no. 15) in a structure determination at 298 K and in the triclinic space group *P* $\bar{1}$ (no. 2) at 150 K. The room-temperature structure



Scheme 1. Synthesis route to the linker 4,4'-(phenazine-5,10-diyl)dibenzoic acid (H₂PZDB).

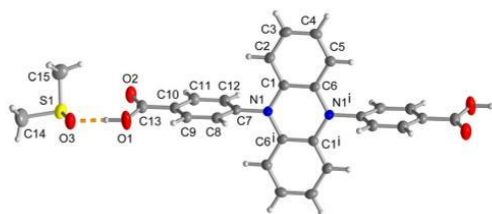


Figure 1. Molecular structure of $\text{H}_2\text{PZDB-2DMSO}$ in the crystal (50% thermal ellipsoids, H atoms with arbitrary radii). Hydrogen bonding interaction (dashed orange line) with $\text{O1-H1} = 0.93(3) \text{ \AA}$, $\text{H1}\cdots\text{O3} = 1.65(3) \text{ \AA}$, $\text{O1}\cdots\text{O3} = 2.578(2) \text{ \AA}$, $\text{O1-H1}\cdots\text{O3} = 176^\circ$. Symmetry code $i = -x + 2, -y + 1, -z + 2$.

has a crystallographically unique Zn atom (on a two-fold rotation axis and glide plane), one unique DEF molecule and half a linker (inversion center at the pyrazine centroid) (Figure S12 and S17a,

Supporting Information). The lower-symmetry low-temperature structure has two crystallographically different Zn atoms, four DEF ligands and two linkers, none of them on a special position (Figure 2, Figure S13 and S17b, Supporting Information). Other than that, the two polymorphic structures from the single-crystal-to-crystal transition are almost identical, with only minor differences in the bond lengths and atomic parameters. The structure of catena-[bis(*N,N*-diethylformamide)- μ -4,4'-(phenazine-5,10-diyl)dibenzoato- $\kappa^2\text{O},\text{O}'$ -zinc(II)], Zn-PZDB, is a one-dimensional zigzag chain. A topological analysis (carried out with the program *TopCryst*^[44]) assigns the topology **2C1**, which is a very common topology for such zigzag structures.^[45] The distance between the Zn(II) ions in a chain is $19.3 \text{ \AA}$, with a $\text{Zn}\cdots\text{Zn}\cdots\text{Zn}$ angle of 114° . The tetrahedral coordination environment of Zn is composed of two carboxylate oxygen atoms from two monodentate PZDB^{2-} linkers and two oxygen atoms from two DEF molecules. One-dimensional zigzag chains of Zn(II) or Co(II) ions

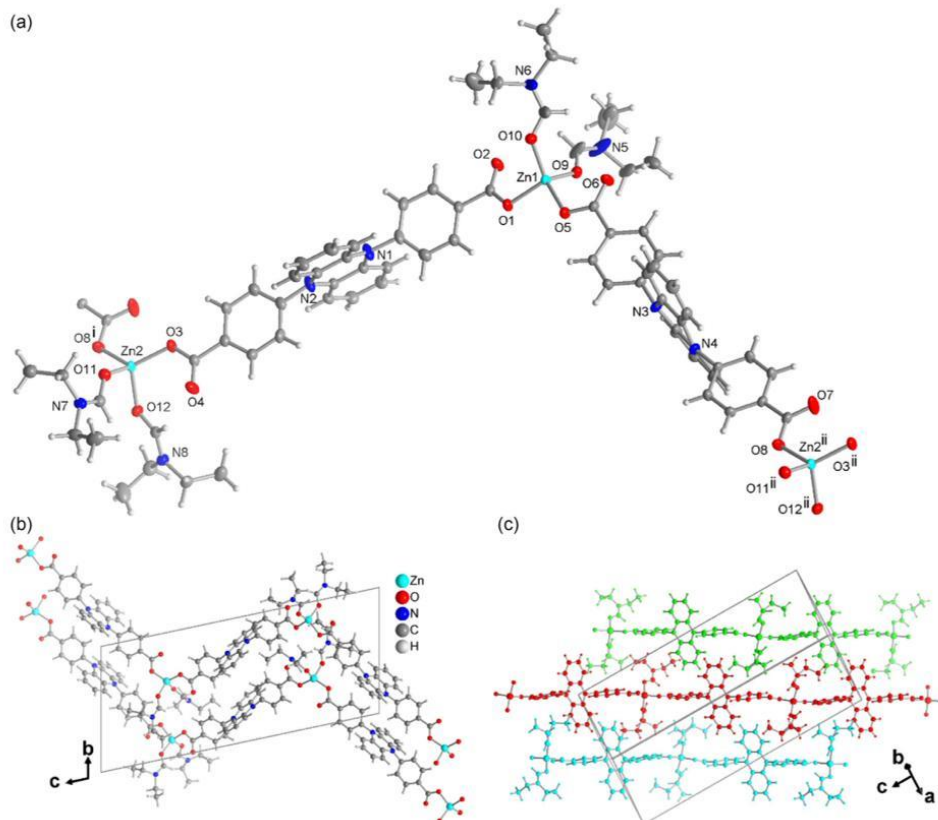


Figure 2. a) Expanded asymmetric unit of Zn-PZDB (150 K structure) with the two symmetry-independent Zn atoms and PZDB^{2-} linkers (50% thermal ellipsoids, H atoms with arbitrary radii). Symmetry transformations: 1) $x - 1, y + 1, z + 1$; 2) $x + 1, y - 1, z - 1$. b,c) Chain arrangement in Zn-PZDB. In (c) three different chains are depicted in different colors to help to visualize the "tongue-and-groove" interdigitation motif for the inter-chain packing. See (Figure S13, Supporting Information) for full atom labeling in the asymmetric unit.

with carboxylate ligands are frequently observed in dicarboxylate coordination polymers, as exemplified by $[\text{Zn}(\text{BDC})(\text{DMP})_2(\text{H}_2\text{O})]_n$ and $[\text{Co}(\text{BDC})(\text{DMP})_2]_n$ (BDC^{2-} = benzene-1,4-dicarboxylate, terephthalate, DMP = 3,5-dimethylpyrazole) or $[\text{Zn}(\text{DHBD})_2(\text{PYAOX})_2]_n$ (DHBD^{2-} = 2,5-dihydroxyterephthalate, PYAOX = pyridine-2-amidoxime).^[45,46]

In the low-temperature structure the $\text{Zn}-\text{O}_{\text{carb}}$ bonds range from 1.928(2) to 1.947(2) Å, while the $\text{Zn}-\text{O}_{\text{DEF}}$ bonds are slightly longer, between 1.968(2) and 2.007(2) Å. The $\text{O}-\text{Zn}-\text{O}$ angles lie in between $96.82(7)^\circ$ and $125.07(7)^\circ$ (Table S4; see S3, Supporting Information for room-temperature structure). Each PZDB^{2-} linker bridges two zinc ions. The benzoate aryl groups (bzate) and the annelated benzo (bz) groups on the pyrazine (py) ring are slightly *cis*-bent to each other. The angles between the ring centroids (Ct) are $\text{Ct}_{\text{bzate}}-\text{Ct}_{\text{py}}-\text{Ct}_{\text{bzate}} = 177^\circ$ and 172° and $\text{Ct}_{\text{bz}}-\text{Ct}_{\text{py}}-\text{Ct}_{\text{bz}} = 175^\circ$ and 171° for the PZDB^{2-} linkers with N1/N2 and N3/N4, respectively. The dihedral angles between the benzoate aryl groups and the pyrazine ring vary from $82.4(1)^\circ$ to $88.9(1)^\circ$. Adjacent Zn-PZDB chains are arranged parallel to each other. In the room-temperature structure, the chains lie in the $\{4\ 0\ -4\}$ lattice planes, in the low-temperature structure in the $\{1\ -1\ 2\}$ planes (Figure S18, Supporting Information).

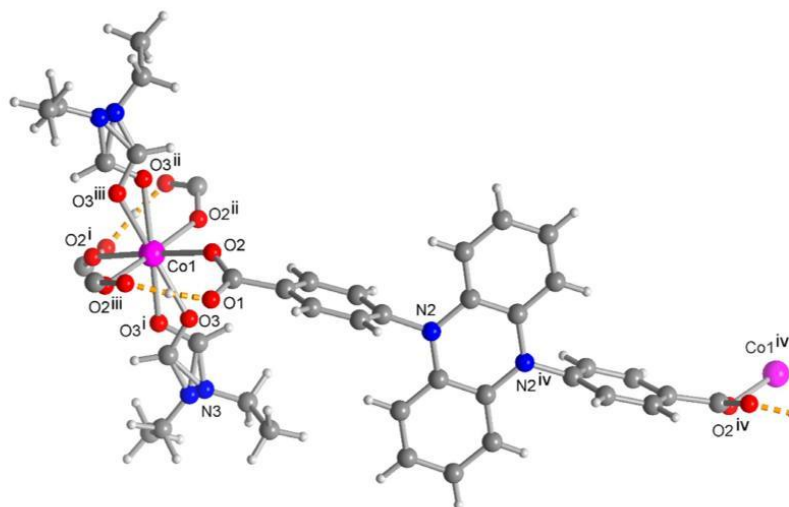
There are no $\pi-\pi$ interactions between the aromatic rings to organize the inter-chain packing. Instead, the packing of adjacent chains is controlled by a few weak $\text{C}-\text{H}\cdots\text{O}_{\text{carb}}$ interactions and by van-der-Waals interactions through the mutual interdigitation, or a "tongue-and-groove" motif of the "tongues" of the diethyl groups from DEF and the annellated benzo groups of the

phenazine rings into the "grooves" formed by these alternating "tongues" of the adjacent chains. Evidently, the DEF ligands keep the chains at a certain distance so that no $\pi-\pi$ or $\text{C}-\text{H}\cdots\pi$ interactions develop between the aromatic rings. The dense packing of the parallel chains prevents the occlusion of solvent of crystallization.

In view of the important role of the DEF ligands, we crystallized Zn-PZDB also from *N,N*-dimethylformamide (DMF). The structure, which is essentially identical to the one from DEF, is only presented and discussed in the Supporting Information (Section S5, Figure S16 and S17, Supporting Information).

Co-HPZDB crystallizes in the orthorhombic space group *Cmce* (no. 68). The structure is composed of two-dimensional layers with square-lattice (**sql**) topology based on the repeating formula unit $\text{Co}(\text{HPZDB})_2(\text{DEF})_2$. Noteworthy, the linker is a mono-deprotonated mono-anion HPZDP^- . Two mono-ionic HPZDP^- linkers per formula unit give a charge-balanced formula unit with $\text{Co}(\text{II})$. The asymmetric unit of Co-HPZDB contains half a HPZDB^- linker, a $\text{Co}(\text{II})$ ion and one molecule of DEF, with two-fold rotations axes passing through the centroid of the pyrazine ring and the Co atom. Figure 3 shows the extended asymmetric unit with the coordination environment of the $\text{Co}(\text{II})$ ion in Co-HPZDB.

The $\text{Co}(\text{II})$ ion is sixfold coordinated by four carboxylate and two DEF oxygen atoms in a distorted octahedral geometry. The $\text{Co}-\text{O}(\text{DEF})$ bond (2.109(6) Å) is slightly longer than the charge-supported $\text{Co}-\text{O}(\text{carboxylate})$ bond (2.086(3) Å). The $\text{O}-\text{Co}-\text{O}$ angles range from $76.6(2)^\circ$ to $178.0(2)^\circ$. The oxygen atoms of the unique carboxyl group in Co-HPZDB have large



thermal ellipsoids, which are evidence of a tilt disorder that was also separately refined with two independent A and B oxygen positions (see Figure S26, Supporting Information for further details).

The mono-deprotonated HPZDP[−] linkers connect two Co atoms and the non-deprotonated carboxyl group, −COOH forms an H-bond to the *cis*-positioned, deprotonated carboxylate group COO[−] around the Co atom. The distance between the two O atoms in the O(−H)⋯O hydrogen bond is 2.44 Å. Due to the high symmetry in the X-ray structure with only a single unique carboxyl group, the H atom will be seen at both carboxyl groups of the HPZDP[−] linker and will, thus, be half-occupied. Because of the additional tilt-disorder of the carboxyl groups (see Figure S26, Supporting Information), this half-occupied H atom could not be located and was arbitrarily placed at a maximum of electron density found at midpoint between the symmetry-related O1 atoms (cf. Figure 3), but the actual O—H⋯O bond will be unsymmetric. Such an H-bond between a non-deprotonated and deprotonated carboxyl group around a metal center has rarely been observed. A search in the Cambridge structure data base yields only two examples with Co: [Co₂(dps)₂(5-Br-Hip)₄]_n (dps = 4,4'-dipyridylsulfide, 5-Br-H₂ip = 5-bromoisophthalate),^[47] and bis[3-(4-carboxyphenoxy)propionato-κO]bis[3-(4-carboxyphenoxy)propionic acid-κO]bis(pyridine-κN)cobalt(II),^[48] Further, there is a coordination polymeric Mn network {[Mn₃(HBTC)₂(H₂BTC)₂(DMF)₄(H₂O)₂]-4DMF}_n (H₃BTC = benzene-1,3,5 tricarboxylic acid).^[49]

In the C₂-symmetric HPZDB[−] linker, the angles between the ring centroids (Ct) are Ct_{bzate}−Ct_{py}−Ct_{bzate} = 173° and Ct_{bz}−Ct_{py}−Ct_{bz} = 179°. The dihedral angle between the benzoic acid aryl group and the pyrazine ring is almost perpendicular (89.41°). The bridging action of four HPZDB[−] linkers around cobalt gives rise to a two-dimensional (2D) network with square-lattice (sql) topology (Figure 4a). The layers in the network lie parallel to

the crystallographic *ab* plane. The linkers and their phenazine rings form two planes in each layer (Figure 4b). Parallel networks are arranged in a staggered fashion so that no voids or channels are formed. The distance between the cobalt(II) ions within a layer is 17.7 Å. The Co⋯Co⋯Co angles are 61° and 119°, respectively. The distance between the individual layers is 4.9 Å.

Powder X-ray diffraction (PXRD) analyses indicated that as-synthesized Zn-PZDB and Co-HPZDB have a high crystalline phase purity according to the good matches between the experimental and simulated patterns from single-crystal structure data, respectively (Figure 5). However, both coordination polymers exhibit a significantly different PXRD pattern after a 24 h exposure to air (Figure S22, Supporting Information). This is accompanied by a change in color from the original yellow in Zn-PZDB and dark red-purple in Co-HPZDB to dark green (Figure S8 and S20, Supporting Information). The observed color change is attributed to the oxidation of the diarylphenazine core. This phenomenon has been previously observed in other dihydrophenazine derivatives.^[50,51] The formation of a stable radical cation results in a shift in the charge balance or charge neutrality within the CPs, which contributes to the decomposition of both CPs. Under the employed experimental conditions, the structural disintegration of the coordination polymers upon linker oxidation is irreversible. Neither PXRD nor visual inspection revealed any signs of reassembly or partial structural recovery. The green color of the oxidized material remains unchanged for several weeks and even months under ambient conditions, which suggests that the oxidized phase is stable in the long term. It is also noteworthy that reassembly processes in coordination polymers typically require carefully controlled conditions, such as solvent-mediated recrystallisation or the re-introduction of linkers or metal centres. These conditions were not present in the experimental setup, which further supports the observed irreversibility.

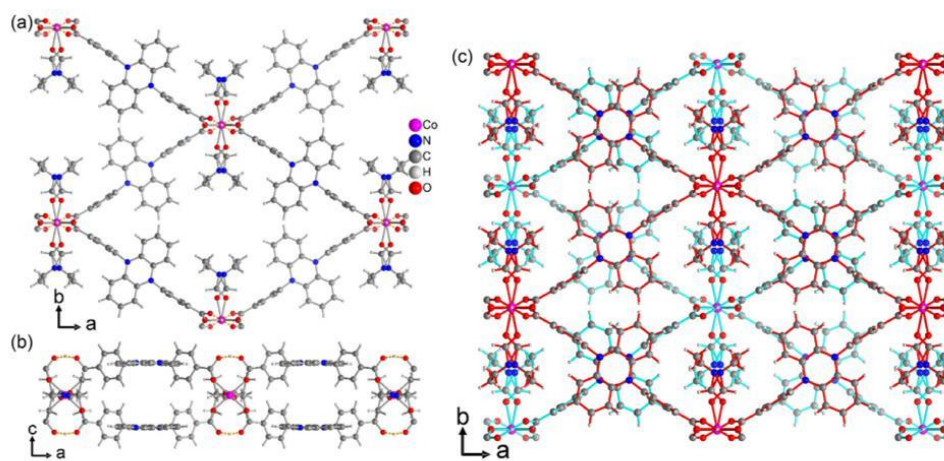


Figure 4. a,b) Section of a single-layer arrangement in Co-HPZDB with (a) top-down view (along the *c* axis), and (b) side view (along *b* axis). In c) the two different layers are depicted in different colors to help to visualize the staggered motif for the inter-layer packing.

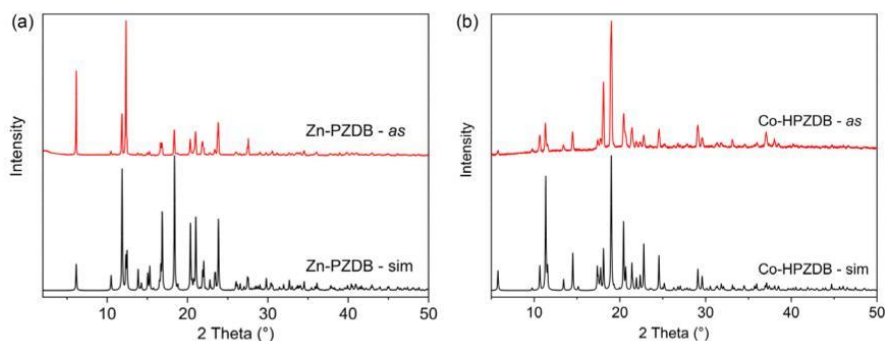


Figure 5. Comparison of the experimental (as = as synthesized) and simulated powder X-ray diffractogram of a) Zn-PZDB (simulation from room-temperature structure), and b) Co-HPZDB. The diffractograms were measured directly after washing and before drying.

Solid-state luminescence/emission spectra were measured at room temperature in order to investigate the photophysical properties. Zn-PZDB exhibits a broad emission with a maximum at 595 nm upon excitation at 400 nm (Figure 6a). Additionally, a small shoulder at 804 nm can be resolved. Unlike Zn-PZDB, Co-HPZDB exhibits a markedly red-shifted emission profile, characterized by a weak and broad emission peak with a maximum at 858 nm upon excitation at 450 nm (Figure 6b), which could be related to a localized $d-d'$ transition of the Co^{2+} ions in an octahedral ligand field. Time-resolved photoluminescence spectra of Zn-PZDB and Co-HPZDB reveal a decay in the nanosecond range as well as a delayed component in the μs range with lower amplitudes (see Figure S28, S29, and S31, Supporting Information). In agreement to various dihydrophenazine derivatives,^[24,43] both coordination polymers also show both prompt and delayed fluorescence at room temperature indicating that also ligand-centered luminescence can be detected.

For Zn-PZDB, we attribute the observed photoluminescence to ligand-centered singlet and triplet excited states, consistent within the nature of the dihydrophenazine linker. This

assignment is supported by the absence of low-lying metal-centered states in Zn(II), which has a $3d^{10}$ configuration and is thus, photophysically inactive. In Co-HPZDB, the situation is more complex due to the open-shell $3d^7$ high-spin configuration of Co(II). The emission maximum at 850 nm suggests a different origin. Based on the energy and the redox-active nature of the mono-deprotonated HPZDP⁻ ligand, we consider a metal-to-ligand charge transfer (MLCT) process as a most plausible mechanism—especially because Co(III) in an octahedral coordination with a d^6 low-spin configuration would be very much stabilized. This is supported by prior studies on Co-based coordination compounds showing MLCT-type emissions in the red to near-infrared region.^[52,53] While $d-d$ transitions cannot be fully excluded, their typically spin-forbidden nature in intermediate ligand fields and the concomitant low emission energies lead to longer radiative decay times and thus, make nonradiative relaxation at room temperature a very favorable mechanism. The detection of an emission signal at room temperature despite those challenging conditions may imply a different origin. Furthermore, the emission at long wavelengths

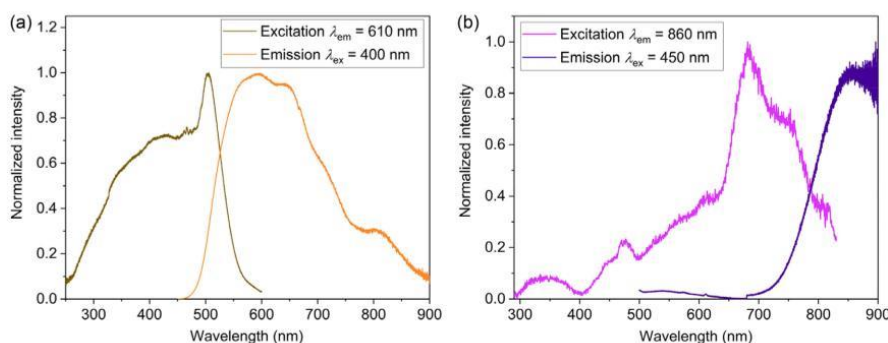


Figure 6. Excitation and emission spectra of powdered a) Zn-PZDB from DEF, and b) Co-HPZDB at room temperature.

compared to the Zn congener is unusual for ligand-centered luminescence alone, additionally supporting a CT-based excited state. Future CASSCF calculations could give more profound insight here.

The thermal stability of Zn-PZDB and Co-HPZDB was investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere (Figure S11 and S24, Supporting Information). TGA of Zn-PZDB indicates a 30% weight loss at $\approx 180^\circ\text{C}$, which corresponds to the release of two DEF molecules (theoretical 29.4%) with a boiling point of $176\text{--}177^\circ\text{C}$.^[54] The remaining 60% corresponds to PZDB, which does not undergo complete combustion, and metallic Zn (theoretical 61.1%). The residual mass of 10% agrees with the theoretical mass of Zn of 9.5%. For Co-HPZDB, the initial loss of 9.5% corresponds to the loss of one DEF molecule (theoretical 9.1%). The loss of the second DEF overlaps partially with the loss of PZDB, resulting in a combined loss of 83% (theoretical 84.9%). The residual mass of 6% agrees with the theoretical mass of Co of 5.3%.

X-ray photoelectron spectroscopy (XPS) has been performed to investigate the chemical composition and chemical state of Co, N, C, and O in Co-HPZDB. The XPS survey spectrum in the range of binding energies from 0 to 1100 eV in Figure 7 confirmed the presence of the elements Co, N, C, and O. Figure 8 shows the high-resolution XPS spectra of C 1s, O 1s, N 1s, Co 2p. The high-resolution C 1s XPS spectrum exhibits three individual peaks at binding energy values of 284.8, 285.7, and 288.8 eV, which could be assigned to C=C/C—C/C—H, C—N, and O—C=O bonds, respectively corresponding to the arene ring and the carboxylic group in the linker HPZDB.^[55] The high-resolution O 1s XPS spectrum is divided into three components, which are composed of oxygen bonded to cobalt (Co—O) and the carboxylic group (O=C—O) of HPZDB[−], and absorbed water molecules (—OH) at the binding energy values of 530.8, 531.8, and 532.9 eV, respectively.^[56] The N 1s high-resolution XPS spectrum shows that in Co-HPZDB, N exists in two chemical states of the phenazine imine (C=N—C) and DEF amide (N—(C=O)—) at the binding energy of 399.0 and

399.7 eV, respectively.^[57,58] The Co 2p spectrum displayed two main peaks of Co 2p_{3/2} (780.6 eV) and Co 2p_{1/2} (796.3 eV) with their shake-up satellite peaks (785.6 and 801.2 eV), which can be assigned to Co²⁺ species (Figure 8d).^[59]

2.1. Spectroelectrochemistry of Me₂PZDB and the Coordination Polymers

The typical green coloration observed upon prolonged exposure of the two new CPs to air is highly suggestive of linker oxidation with the concomitant formation of the associated PZDB⁺ radical cation with an overall charge of -1 , considering the deprotonated benzoate groups.^[26,50,60] This will likely decrease the binding capabilities of the bridging PZDB^{2−} ligands, thereby opening an avenue for CP degradation. In order to probe experimentally for linker oxidation, we first subjected its dimethyl ester Me₂PZDB to chemical or electrolytic oxidation and measured its UV/Vis/NIR spectrum as a point of comparison with the oxidized samples of Zn-PZDB and Co-HPZDB. Like other 5,10-diaryl-5,10-dihydrophenazines,^[25,26,50,51,61–63] Me₂PZDB undergoes two consecutive, chemically and electrochemically reversible one-electron oxidations at half-wave potentials of -130 and 620 mV on the ferrocene/ferrocenium potential scale (Figure S32, Supporting Information). Oxidation past the first anodic peak to the corresponding radical cation inside a spectroelectrochemical cell in the presence of the 1,2-dichloroethane/0.1 mol L^{−1} NBu₄⁺ PF₆[−] electrolyte caused the growth of new bands at 448 and 475 nm and a vibrationally structured band at lower energy with individual peaks at 572, 629, 685, and 761 nm (Figure S34, Supporting Information). All of these features are typical of 5,10-diphenyl-5,10-dihydrophenazine radical cations;^[50,63] they are almost identical to those reported for the closely related *N,N'*-diphenyldihydrophenazine (DPPZ).^[63]

In order to monitor the spectroscopic changes accompanying the oxidation of the insoluble Zn-PZDB and Co-HPZDB CPs, we also employed UV/Vis/NIR spectroelectrochemistry. To these ends, an optically transparent ITO electrode was covered with a thin layer of a slurry of the corresponding CP in the ionic liquid 3-butyl-1-methyl-1H-imidazol-3-ium hexafluorophosphate (BMIM⁺ PF₆[−]). The cell was then assembled and filled with an aqueous NaNO₃ solution as the electrolyte (for details, see the Experimental Section). On applying a gradually increasing positive potential to the ITO electrode, we observed very similar spectroscopic changes as with dissolved Me₂PZDB (see Figure S34, Supporting Information), that is, the growth of new bands at 443, 470, 623, 681, and 755 nm for Zn-PZDB (Figure 9a), or at 443, 472, 630, 687, and 758 nm for Co-HPZDB (Figure S36, Supporting Information). The continuous baseline drift to positive absorbance values during this process hints at the release of the oxidized linker into the ionic liquid. In agreement with this proposition, reduction of the oxidized CPs did not restore the initial state. When subjected to electrolysis under identical conditions, the free H₂PZDB linker provided practically superimposable spectroscopic changes (see the insert of Figure 9a). As a further test for linker oxidation, we subjected dispersions of Zn-PZDB

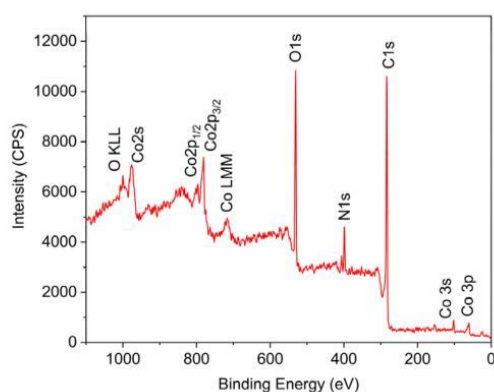


Figure 7. XPS survey spectrum of Co-HPZDB.

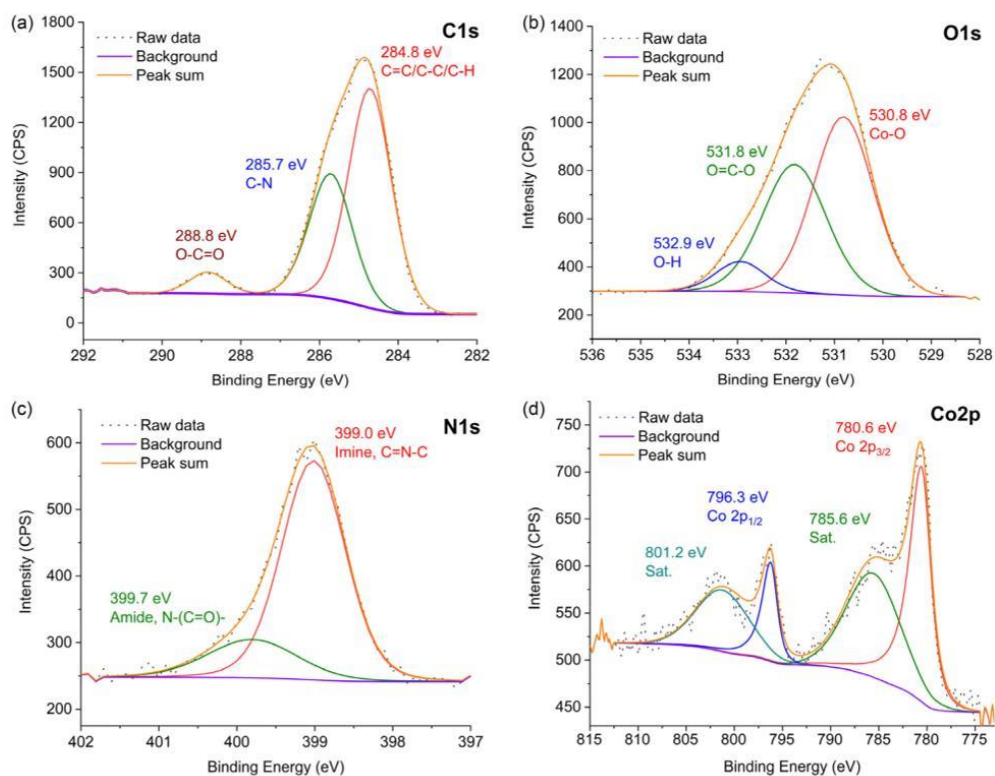


Figure 8. XPS high-resolution spectra of a) C 1s, b) O 1s, c) N 1s, and d) Co 2p.

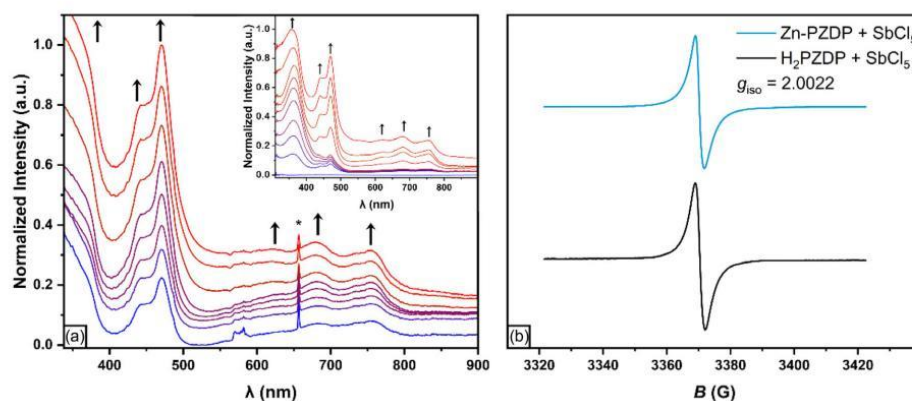


Figure 9. a) UV-Vis spectroelectrochemistry of Zn-PZDB and of H₂PZDB (insert) with oxidation progressing from blue to red lines, measured as pastes in the ionic liquid 3-butyl-1-methyl-1H-imidazol-3-ium hexafluorophosphate (BMIM⁺ PF₆⁻) applied to an ITO-coated glass plate with an aqueous 1 mmol L⁻¹ NaNO₃ solution as supporting electrolyte at r. t. The asterisk marks an artifact due to the used setup. b) EPR spectra of dispersions of H₂PZDP (black) and Zn-PZDP (blue) in CH₂Cl₂ after addition of sub-stoichiometric amounts of SbCl₅ measured with a microwave frequency of 9.404 GHz.

(see Figure 9b) (for Co-HPZDB see Figure S36, Supporting Information) and of H₂PZDB in CH₂Cl₂ to oxidation with sub-stoichiometric amounts of SbCl₅. In both cases, we observed a rapid color change to a deep blue-green and the concomitant growth of an intense, isotropic EPR resonance signal at a *g*-value of 1.9935, which is typical of the DPPZ⁺ radical cation (see Figure 9b, right panels).^[63]

All these results indicate that the PZDB linker constitutes the primary redox site of these CPs, and that linker oxidation triggers their degradation. This does, however, *per se* not disqualify our new CPs as, for example, photo-redox catalysts, as long as the resulting electron hole is rapidly transferred to a substrate.

3. Conclusion

In summary, this study details the synthesis, structural characterization and redox behavior of two unique coordination polymers (CPs), Zn-PZDB and Co-HPZDB, utilizing the linker acid 4,4'-(phenazine-5,10-diyl)dibenzoic acid (H₂PZDB). The crystallization of H₂PZDB in dimethyl sulfoxide (DMSO) yielded yellow platelets of H₂PZDB·2DMSO in the triclinic space group *P* $\bar{1}$ (no. 2). Solvothermal reactions of H₂PZDB with Zn(II) or Co(II) nitrate yielded Zn-PZDB and Co-HPZDB. Zn-PZDB crystallizes in monoclinic and triclinic space groups with a 2C1 topology, forming one-dimensional zigzag chains composed of Zn(II) ions coordinated by two monodentate carboxylate ligands and two DEF molecules. The structural details revealed tetrahedral Zn coordination with minor differences in distances and angles between the monoclinic and triclinic forms. Co-HPZDB crystallizes in the orthorhombic space group *Ccce* (no. 68) with a *sql* topology, forming two-dimensional layers with disordered octahedral cobalt coordination. Each Co(II) ion is coordinated by two DEF molecules and two HPZDB[−] linkers, with hydrogen bonding and stacking interactions extending to a three-dimensional supramolecular structure. Upon exposure to air, the CPs exhibit a green coloration, indicative of the oxidation of the (H)PZDB^{−/2−} linkers, which lead to the degradation of the CPs. UV/Vis/NIR spectroelectrochemical studies of Me₂PZDB showed two reversible one-electron oxidations, producing characteristic absorbance bands. Similar spectroscopic changes were observed for Zn-PZDB and Co-HPZDB upon oxidation, indicating the presence of oxidized linker. Chemical oxidation with SbCl₅ was employed to confirm the formation of (H)PZDB^{0/+} radicals, evidenced by a rapid color change and isotropic EPR resonance signals. The findings indicate that the (H)PZDB linker is the primary redox site, and its oxidation triggers CP degradation. However, this redox activity does not necessarily disqualify the CPs from applications such as photo-redox catalysis, provided that the resulting electron hole can be efficiently transferred to a substrate. Thus, the study does not only provide a comprehensive synthesis and characterization of the CPs, but also highlights their potential utility in catalytic applications despite the challenges posed by linker oxidation.

4. Experimental Section

All chemicals were commercially obtained and used without further purification (see ESI, Section S1 for details of commercial suppliers). The water used was deionized.

Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker FT-IR Tensor 37 spectrometer in the attenuated total reflection (ATR) mode in the range of 4000–550 cm^{−1}.

Thermogravimetric analyses (TGA) were performed on a Netzsch Tarsus TG 209 instrument under nitrogen from room temperature to 1000 °C with a heating rate of 5 °C min^{−1} in Al₂O₃ crucibles.

NMR spectra were obtained on a Bruker Avance III-300 (Bruker, Billerica, MA, USA) (¹H: 300 MHz; ¹³C{¹H}: 75 MHz) in CDCl₃, C₆D₆ and DMSO-*d*₆. The spectra were referenced on the residual solvent peak (¹H NMR δ = 7.26 ppm for CDCl₃, 7.16 ppm for C₆D₆ and 2.50 ppm for DMSO-*d*₆).

Elemental analyses were performed using an Elementar Vario MICRO Cube analyzer. Due to technical limitations, it was not possible to shield the samples from ambient air and moisture during weighing and handling, leading to deviations.

X-ray photoelectron spectroscopy (XPS) was carried out using a ULVAC-PHI VersaProbe II microfocus spectrometer equipped with an Al K α X-ray source (1486.8 eV). The spectra were analyzed with the Casa XPS software, version 2.3.19PR1.0 from Casa Software Ltd, Teignmouth, UK.

Powder X-ray diffraction (PXRD) measurements were performed at room temperature using a Rigaku Miniflex 600 powder diffractometer (Rigaku, Tokyo, Japan) with Cu K α 1 radiation (λ = 1.5406 Å, 40 kV, 15 mA, 600 W) covering a 2θ range of 2°–50°. The analysis utilized a flat silicon low-background holder with a small indent for placing the sample.

Solid-state luminescence measurements were carried out using an FLS1000 photoluminescence spectrometer from Edinburgh Instruments. The system featured a 450 W Xe arc lamp as the excitation source, double grating monochromators in Czerny-Turner configuration in both the excitation and emission compartment, and a thermoelectrically cooled photomultiplier tube (PMT-980) from Hamamatsu, maintained at −20 °C. Emission spectra were corrected for both grating efficiency and PMT sensitivity, while excitation spectra were additionally corrected to account for fluctuations of the lamp intensity. Time-resolved photoluminescence was recorded using pulsed laser diodes EPL-450 (Edinburgh Instruments, temporal pulse width: 90 ps, 0.15 mW average incident peak power) or VPL-450 (Edinburgh Instruments, operating at 90 mW average incident peak power in continuous-wave mode) with adjustable pulse widths (0.1–1 ms) and variable trigger frequencies (0.1 Hz to 5 MHz). Time-correlated single photon counting (TCSPC) was employed as the detection mode for time-resolved measurements.

For single-crystal X-ray diffraction suitable crystals were selected with care under a polarized-light microscope, coated with protective oil, and mounted on a cryo-loop. The data were acquired using a Rigaku XtaLAB Synergy diffractometer equipped with a Hybrid Pixel Array Detector and a microfocus sealed X-ray tube PhotonJet (Cu) X-ray source (λ = 1.54184 Å). Cell refinement, data reduction, and absorption correction were performed using CRYSLISPRO. The structure was determined with SHELXT and further refined with SHELXL, utilizing OLEX2 as the interface. Figures were generated using the DIAMOND 4.0 software. Additional crystal data can be found in the Supporting Information.

Deposition Numbers 2 453 691 (for H₂PZDB·2DMSO), 2 453 692 (for Zn-PZDB, 150 K), 2 453 693 (for Zn-PZDB, 298 K), 2 453 694 (for Zn-PZDB with DMF), 2 453 695 (for Co-HPZDB, non-disordered), 2 453 696 (for Co-HPZDB, disordered) contain the supplementary crystallographic data for this article. These data are provided free of charge by the joint Cambridge Crystallographic Data Center and Fachinformationszentrum Karlsruhe Access Structures service.^[64]

Cyclic voltammetry of Me₂PZDP was conducted under an argon atmosphere. The voltammograms were recorded using a BASi Epsilon potentiostat and a custom-built cell as previously described.^[65] A platinum working electrode ($\varnothing = 1.1$ mm, BASi) was used. The platinum electrode was polished before each measurement series with diamond pastes from Buehler & Wirtz (grain sizes 1 and 0.25 μm). Spiral-shaped AgCl and Pt wires were used as the reference and counter electrode. The supporting electrolyte was a 0.1 mol L⁻¹ solution of nBu₄N⁺ PF₆⁻ in CH₂Cl₂. The redox potentials were referenced against the FcH/FcH⁺ redox couple ($E_{1/2} = 0.000$ V).

UV-Vis/NIR spectroscopy and spectroelectrochemical measurements were acquired with a TIDAS fiber optic diode array spectrometer, which consists of a combination of MCS UV/NIR and PGS NIR instruments from j&m Analytik AG. For the determination of the extinction coefficients, a quartz cell with an optical path length of 0.2 cm was used. A Wenking Pos 2 potentiostat from intelligent controls GmbH was used for spectroelectrochemical measurements on dissolved samples in combination with a custom-made optically transparent electrochemical thin-layer cell (OTTLE) according to Hartl's design.^[66] The OTTLE cell consists of a working and counter electrode made of Pt grids and a thin silver wire as a pseudo reference electrode, sandwiched in between two optically transparent CaF₂ windows. 1,2-C₂H₄Cl₂ was used as the solvent with 0.1 mol L⁻¹ nBu₄N⁺ PF₆⁻ as the supporting electrolyte. Spectroelectrochemical measurements of insoluble Zn-PZDP, Co-HPZDP, and H₂PZDP were recorded as pastes of the analyte with the ionic liquid BMIM⁺ PF₆⁻ applied on an ITO-coated, electrically conductive transparent plate as the working electrode. The latter was assembled in a Teflon cell together with a platinum and Ag/AgCl wire as counter and pseudo reference electrode, respectively. An aqueous NaNO₃ solution (1 mmol L⁻¹) was used as supporting electrolyte. The potential was applied using a BASi Epsilon potentiostat, and the UV/Vis spectra were continuously recorded upon applying a potential sweep at a scan rate of 2 mV s⁻¹. Both CPs were generally oxidized under inert atmosphere (except for the control experiment in Figure S36, Supporting Information). The paste with the ionic liquid had to be prepared under ambient atmosphere. After assembling the cell, we flushed the setup with argon, as to be able to conduct the spectroelectrochemical measurement under inert gas atmosphere, and in the absence of oxygen. Based on the initial UV-Vis absorption spectrum we can confirm the fully reduced sample was present at the start of the experiment.

EPR spectra were recorded under inert atmosphere using a X-band tabletop spectrometer MiniScope MS 400 by Magnettech GmbH.

Synthesis

5,10-Dihydrophenazine: Phenazine (5.0 g, 27.7 mmol) was dissolved in ethanol (125 mL), sodium dithionite (48.2 g, 277 mmol) in de-ionized water (500 mL), and both solutions were combined and heated under stirring and reflux for 3 h or overnight. The precipitate was filtered off and washed three times with deionized water. Finally, the solid was dried at 20 °C in vacuum (1×10^{-3} mbar) for 16 h. The product (yield 4.75 g, 94%) was obtained as a light green solid and was used without further purification. Important: The dihydrophenazine solid must be stored under a protective gas atmosphere (nitrogen or argon), otherwise it re-oxidizes which is evidenced by a gradual color change to dark blue and then black. [¹H NMR] (600 MHz, CDCl₃) δ (ppm) = 8.27 (dd, $J = 6.8, 3.5$ Hz, 1 H), 7.86 (dd, $J = 6.8, 3.4$ Hz, 1 H), 6.12 (s, 2 H).

Dimethyl-4,4'-(phenazine-5,10-diyl)dibenzoate (Me₂PZDB): 5,10-Dihydrophenazine (1.0 g, 5.49 mmol), methyl-4-bromobenzoate (2.6 g, 12.1 mmol) and anhydrous potassium carbonate (1.52 g, 11.0 mmol) were dissolved in degassed xylene (25 mL). Palladium

(II) acetate (62 mg, 5 mol%) and tri-*tert*-butylphosphine (111 mg, 10 mol%) were dissolved in degassed xylene (25 mL). Both solutions were combined under stirring. Under nitrogen inert gas the reaction mixture was heated under stirring to reflux for 48 h. After cooling to room temperature, water (100 mL) was added to the reaction mixture and the water/xylene mixture was extracted three times with dichloromethane (3×150 mL). The organic phases were combined and dried over magnesium sulfate (30 min). All solvents were removed using a rotary evaporator. The crude product was washed three times with ethanol (100 mL). The product was finally filtered and dried in vacuo at 60 °C for 16 h (yield 2.25 g, 91%). [¹H NMR] (300 MHz, C₆D₆) δ (ppm) = 8.11 (d, $J = 8.4$ Hz, 4 H), 7.06 (d, $J = 8.5$ Hz, 4 H), 6.35 (dd, $J = 5.9, 3.4$ Hz, 4 H), 5.81 (dd, $J = 5.9, 3.4$ Hz, 4 H), 3.52 (s, 6 H). [¹³C NMR] (75 MHz, C₆D₆) δ (ppm) = 166.0, 145.2, 136.6, 132.9, 131.0, 130.1, 122.0, 113.9, 52.5. [HR-ESI-MS] $m/z = 450.1582$ (calculated for ¹²C₂₈ ¹H₂₂ ¹⁴N₂ ¹⁶O₄ 450.1580). [IR] (ATR) ν (cm⁻¹) = 2955 (m), 1723 (s), 1590 (m), 1483 (s), 1344 (s), 1285 (s), 1265 (s), 1110 (w), 1095 (w), 724 (w), 701 (w). [EA] Calc. for C₂₈H₂₂N₂O₄: C 74.65, H 4.92, N 6.22 – found: C 74.78, H 4.93, N 6.11%. [M.p] 296 °C.

4,4'-(Phenazine-5,10-diyl)dibenzoic acid (H₂PZDB): Dimethyl-4,4'-(phenazine-5,10-diyl)dibenzoate (450.5 mg, 1.0 mmol) was dissolved in 1,4-dioxane (30 mL). Lithium hydroxide (419.6 mg, 10.0 mmol) was dissolved separately in 15 mL of water and added to the reaction mixture, which was then heated overnight under reflux (100 °C). With the assistance of a pipette, hydrochloric acid was carefully added the following day until a pH value of $\approx 1-2$ was reached. Afterwards, 100 mL of water were added to the mixture and stirred for another 3 h. The formed yellow precipitate was filtered off and washed with water. Finally, the orange solid obtained was dried in vacuo at 60 °C for 16 h (yield 0.372 g, 88%). Single crystals suitable for X-ray crystallography were grown from a saturated DMSO solution. [¹H NMR] (300 MHz, DMSO-*d*₆) δ (ppm) = 8.20 (d, $J = 8.4$ Hz, 4 H), 7.54 (d, $J = 8.4$ Hz, 4 H), 6.37 (dd, $J = 5.9, 3.4$ Hz, 4 H), 5.67 (dd, $J = 5.9, 3.4$ Hz, 4 H). [¹³C NMR] (75 MHz, DMSO-*d*₆) δ (ppm) = 166.7, 144.1, 135.6, 132.5, 130.6, 130.5, 121.5, 113.2. [HR-ESI-MS] $m/z = 422.1269$ (calculated for ¹²C₂₆ ¹H₁₈ ¹⁴N₂ ¹⁶O₄ 422.1267). [IR] (ATR) ν (cm⁻¹) = 3454 (m), 1692 (s), 1656 (m), 1593 (m), 1484 (s), 1418 (w), 1346 (s), 1280 (s), 1119 (w), 1091 (w), 735 (w). [EA] Calc. for C₂₆H₁₈N₂O₄: C 73.92, H 4.30, N 6.63 – found: C 73.10, H 4.36, N 6.42%. [M.p] > 350 °C.

Zn-PZDB: Zinc nitrate hexahydrate (800 mg, 2.69 mmol) and 4,4'-(phenazine-5,10-diyl)dibenzoic acid (100 mg, 0.24 mmol) were added to 10 mL of DEF in a Pyrex tube (20 mL). The reaction mixture was then placed in an ultrasonic bath at 40 °C for ≈ 30 min until a homogeneous solution was obtained. The reaction was carried out for 72 h at 85 °C (plus 3 h heating/3 h cooling) in a programmable synthesis oven. Subsequently, the crude product was washed three times with DEF (5 mL each). The crystalline MOF was finally dried by high vacuum (1×10^{-3} mbar) for 16 h and stored under inert gas atmosphere. The final product was obtained as clear yellow crystals. Yield: 26.0%, 42.8 mg, [EA] Calc. for C₃₆H₃₈N₄O₆Zn: C 62.84, H 5.57, N 8.14 – found: C 62.23, H 5.38, N 8.16%. [IR] (ATR) ν (cm⁻¹) = 2978 (w), 2919 (w), 2881 (w), 1573 (s), 1482 (m), 1401 (m), 1331 (s), 1281 (m), 1264 (m), 1088 (w), 1061 (w), 781 (m), 731 (m), 707 (w), 667 (w).

Co-HPZDB: Cobalt nitrate hexahydrate (800 mg, 2.75 mmol), lithium chloride (10 mg, 0.24 mmol) and 4,4'-(phenazine-5,10-diyl)dibenzoic acid (100 mg, 0.24 mmol) were added to 10 mL of DEF in a Pyrex tube (20 mL). The reaction mixture was then placed in an ultrasonic bath at 40 °C for ≈ 30 min until a homogeneous solution was obtained. The reaction was carried out for 72 h at 85 °C (3 h heating/3 h cooling) in a programmable synthesis oven. Subsequently, the crude product was washed three times with DEF (5 mL). The crystalline MOF was finally dried in high vacuum (1×10^{-3} mbar) for 16 h and stored under inert gas atmosphere. The product was obtained as a dark brown/purple crystalline solid. Yield: 11.8%, 31.5 mg. [EA] Calc. for C₆₂H₅₆CoN₄O₁₀: C 67.14, H 4.91, N 7.58 – found: C 67.32, H 5.12, N 7.55%. [IR] (ATR) ν

(cm⁻¹) = 3048 (w), 2985 (w), 2946 (w), 2910 (w), 2880 (w), 1639 (s), 1591 (s), 1483 (s), 1456 (m), 1386 (m), 1346 (m), 1284 (m), 1265 (m), 1215 (w), 1160 (w), 1092 (w), 1059 (w), 824 (m), 780 (m), 733 (s), 707 (m), 659 (m), 616 (w).

Supporting Information

The authors have cited additional references within the Supporting Information.^[67–74]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: coordination polymers · dihydrophenazine · radical cation · redox-active linker · spectroelectrochemistry

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Supporting Information (SI)

Zinc and Cobalt Coordination Polymers Based on the Redox-Active Linker 4,4'-(Phenazine-5,10-diyl)dibenzoate: Structures and Electrochemical Properties

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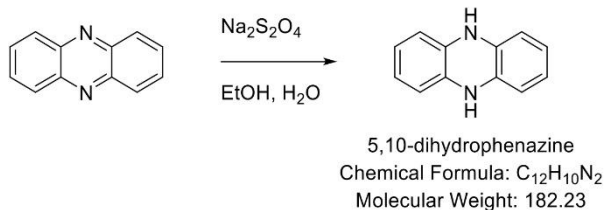
S1 Sources of chemicals

Commercially available reagents were used as received without further purification.

Items	Manufacturer
Phenazine, 97 %	BLDpharm
Methyl-4-bromobenzoate 98 %	BLDpharm
Palladium(II) acetate, 98 %	Sigma-Aldrich
Tri- <i>tert</i> -butyl-phosphine	Sigma-Aldrich
Potassium carbonate ≥ 99.5 %	Riedel-de Haen
Sodium dithionite ~85 %	VWR Chemicals
Sodium chloride, ≥ 99.5 %	Sigma-Aldrich
Magnesium sulfate	VWR Chemicals
Lithium hydroxide monohydrate	AppliChem
Xylene	Fisher Chemical
Ethanol, ≥ 99.8 %	Honeywell
Dichloromethane, ≥ 99.9 %	Sigma-Aldrich
Cyclohexane, ≥ 99.8 %	Fisher Chemical
Hydrochloric acid ≥ 37 %	Sigma-Aldrich
Cobalt nitrate hexahydrate ≥ 98 %	Carl Roth
Zinc nitrate hexahydrate 98 %	Acros Organics
Lithium chloride (anhydrous)	Fisher Chemical
<i>N,N</i> -Diethylformamide	Sigma-Aldrich
<i>N,N</i> -Dimethylformamide	Sigma-Aldrich

S2 Synthesis of 4,4'-(phenazine-5,10-diyl)dibenzoic acid (H₂PZDB)

S2.1 5,10-Dihydrophenazine



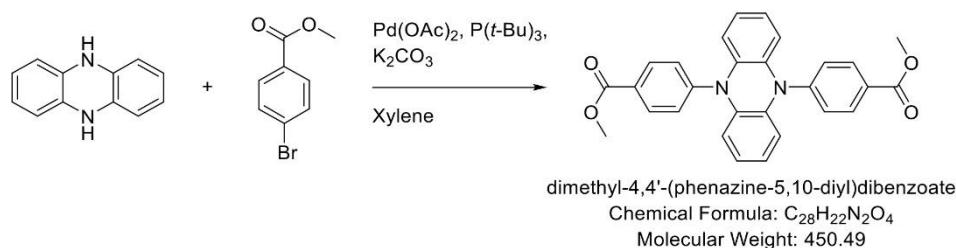
Starting materials	M [g·mol ⁻¹]	ρ [g·cm ⁻³]	eq	n [mmol]	m [g]
Phenazine	180.21	-	1.0	27.7	5.00
Sodium dithionite	174.11	2.38	10.0	277.0	48.2

Solvents: Ethanol, water (deionized)

Following our previous work,¹ phenazine was dissolved in ethanol (125 mL), sodium dithionite in de-ionized water (500 mL) and both solutions were combined and heated under stirring and reflux for three hours or overnight. The precipitate was filtered off and washed three times with deionized water. Finally, the solid was dried at 20 °C in vacuum (1x10⁻³ mbar) for 16 h. The product (yield 4.75 g, 94 %) was obtained as a light green solid and was used without further purification. Important: The dihydrophenazine solid must be stored under a protective gas atmosphere (nitrogen or argon), otherwise it re-oxidizes which is evidenced by slowly turning dark blue and then black.

[¹H NMR] (600 MHz, CDCl₃) δ = 8.27 (dd, *J* = 6.8, 3.5 Hz, 1H), 7.86 (dd, *J* = 6.8, 3.4 Hz, 1H), 6.12 (s, 2H).

S2.2 Dimethyl-4,4'-(phenazine-5,10-diyl)dibenzoate (Me₂PZDB)



Starting materials	M [g·mol ⁻¹]	ρ [g·cm ⁻³]	eq	n [mmol]	m [g]
5,10-Dihydrophenazine	182.22	-	1.00	5.49	1.00
Methyl-4-bromobenzoate	215.04	-	2.20	12.1	2.60
Potassium carbonate	138.20	2.43	6.00	11.0	1.52
Palladium(II) acetate	224.51	-	5 mol%	-	0.062
Tri- <i>tert</i> -butyl-phosphine	202.32	-	10 mol%	-	0.111

Solvents: Xylene, dichloromethane (DCM)

According to the literature,^{2,3} 5,10-dihydrophenazine, methyl-4-bromobenzoate and anhydrous potassium carbonate were dissolved in degassed xylene (25 mL). Palladium(II) acetate and tri-*tert*-butylphosphine were also dissolved in degassed xylene (25 mL). Both solutions were combined under stirring. Under nitrogen inert gas the reaction mixture was heated under stirring to reflux for 48 hours. After cooling to room temperature, water (100 mL) was added to the reaction mixture and the water/xylene mixture extracted three times with dichloromethane (3 x 150 mL). The organic phases were combined and dried over magnesium sulfate (30 min). All solvent was removed using a rotary evaporator. The crude product was washed three times with ethanol (in total 100 mL). The product was finally filtered and dried in vacuo at 60 °C for 16 h (yield 2.25 g, 91 %).

[¹H NMR] (300 MHz, C₆D₆) δ/ppm = 8.11 (d, *J* = 8.4 Hz, 4H), 7.06 (d, *J* = 8.5 Hz, 4H), 6.35 (dd, *J* = 5.9, 3.4 Hz, 4H), 5.81 (dd, *J* = 5.9, 3.4 Hz, 4H), 3.52 (s, 6H) (Figure S1).

[¹³C NMR] (75 MHz, C₆D₆) δ/ppm = 166.0, 145.2, 136.6, 132.9, 131.0, 130.1, 122.0, 113.9, 52.5 (Figure S2).

[HR-ESI-MS] *m/z* = 450.1582 (calculated for ¹²C₂₈ ¹H₂₂ ¹⁴N₂ ¹⁶O₄ 450.1580)

[IR] (ATR) *ν*/cm⁻¹ = 2955 (m), 1723 (s), 1590 (m), 1483 (s), 1344 (s), 1285 (s), 1265 (s), 1110 (w), 1095 (w), 724 (w), 701 (w) (Figure S3)

[EA] Calc. for C₂₈H₂₂N₂O₄: C 74.65, H 4.92, N 6.22 – found: C 74.78, H 4.93, N 6.11 %

[M.p] 296 °C

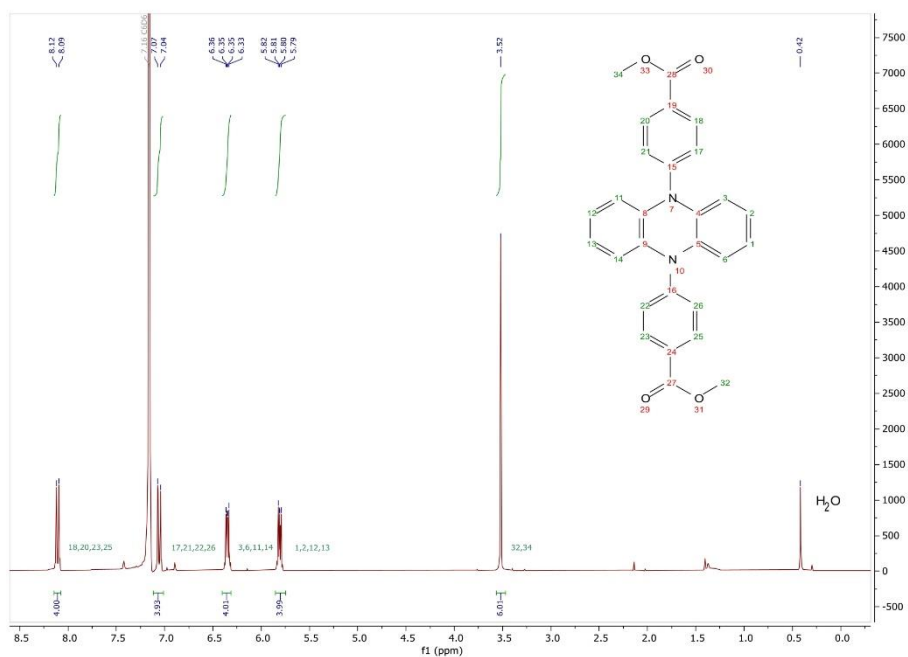


Figure S1. ¹H-NMR spectrum of dimethyl-4,4'-(phenazine-5,10-diyl)dibenzoate (300 MHz, C₆D₆).

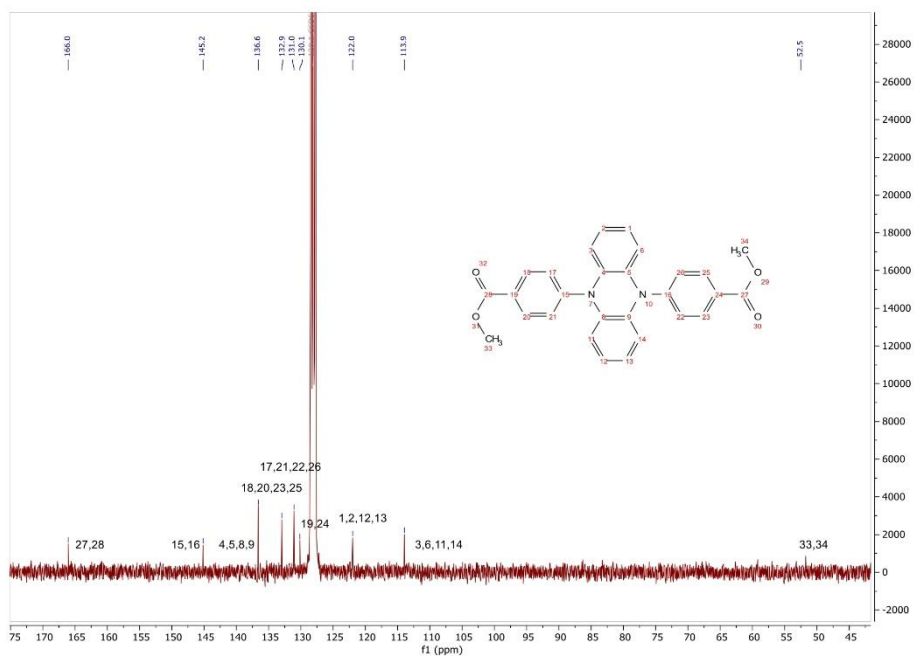


Figure S2. ¹³C-NMR spectrum of dimethyl-4,4'-(phenazine-5,10-diyl)dibenzoate (75 MHz, C₆D₆).

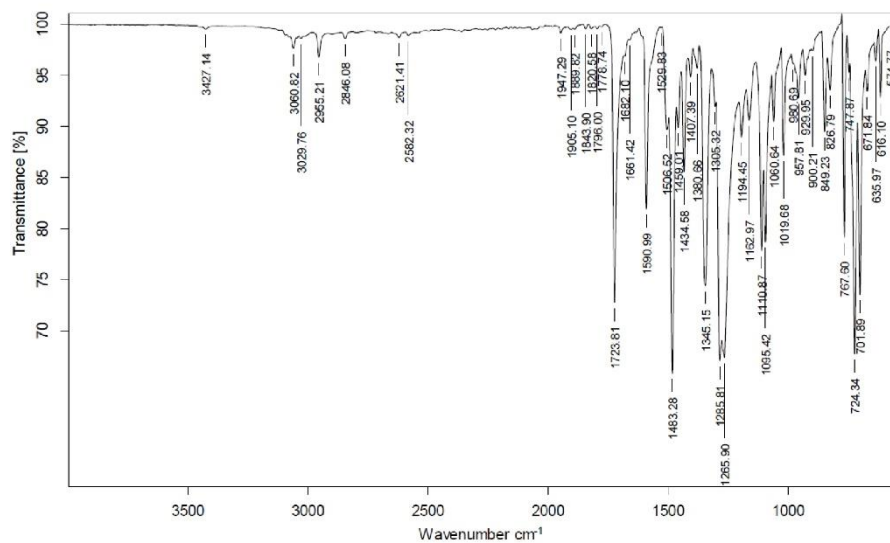
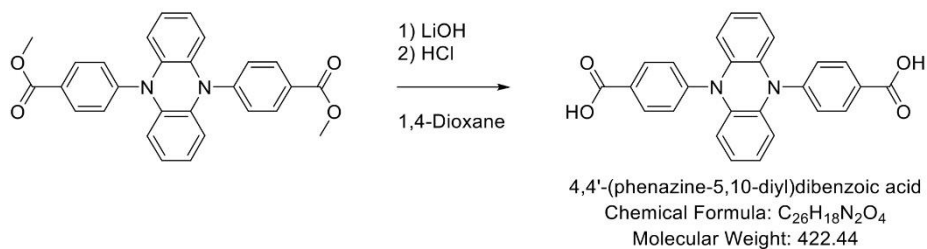


Figure S3. IR spectrum (ATR) of dimethyl-4,4'-(phenazine-5,10-diyl)dibenzoate.

S2.3 4,4'-(Phenazine-5,10-diyl)dibenzoic acid (H₂PZDB)



Starting materials	M [g·mol ⁻¹]	ρ [g·cm ⁻³]	n [mmol]	m [mg]	V [mL]
Dimethyl-4,4'-(phenazine-5,10-diyl)dibenzoate	450.49	-	1.00	450.5-	-
Lithium hydroxide monohydrate	41.96	1.46	10.0	419.6	-
Hydrochloric acid	36.46	1.19	0.065	-	~ 2.0

Solvents: 1,4-Dioxane, water (deionized)

Following the literature⁴, dimethyl-4,4'-(phenazine-5,10-diyl)dibenzoate was dissolved in 1,4-dioxane (30 mL). Lithium hydroxide was dissolved separately in 15 mL of water and added to the reaction mixture which was then heated overnight under reflux (100 °C). With the assistance of a pipette, hydrochloric acid was carefully added the following day until a pH value of ~1-2 was reached. Afterwards, 100 mL of water were added to the mixture and stirred for another 3 h. The formed yellow precipitate was filtered and washed with 100 mL of water. Finally, the orange solid obtained was dried in vacuo at 60 °C for 16 h (yield 0.372 g, 88 %).

The following analytical investigations were **not** done on the crystallized DMSO solvate.

[¹H NMR] (300 MHz, DMSO-d₆) δ/ppm = 8.20 (d, *J* = 8.4 Hz, 4H), 7.54 (d, *J* = 8.4 Hz, 4H), 6.37 (dd, *J* = 5.9, 3.4 Hz, 4H), 5.67 (dd, *J* = 5.9, 3.4 Hz, 4H) (Figure S4).

[¹³C NMR] (75 MHz, DMSO-d₆) δ/ppm = 166.7, 144.1, 135.6, 132.5, 130.6, 130.5, 121.5, 113.2 (Figure S5).

[HR-ESI-MS] *m/z* = 422.1269 (calculated for ¹²C₂₆ ¹H₁₈ ¹⁴N₂ ¹⁶O₄ 422.1267)

[IR] (ATR) *v*/cm⁻¹ = 3454 (m), 1692 (s), 1656 (m), 1593 (m), 1484 (s), 1418 (w), 1346 (s), 1280 (s), 1119 (w), 1091 (w), 735 (w) cm⁻¹ (Figure S6)

[EA] Calc. for C₂₆H₁₈N₂O₄: C 73.92, H 4.30, N 6.63 – found: C 73.10, H 4.36, N 6.42 %

[M.p] > 350 °C

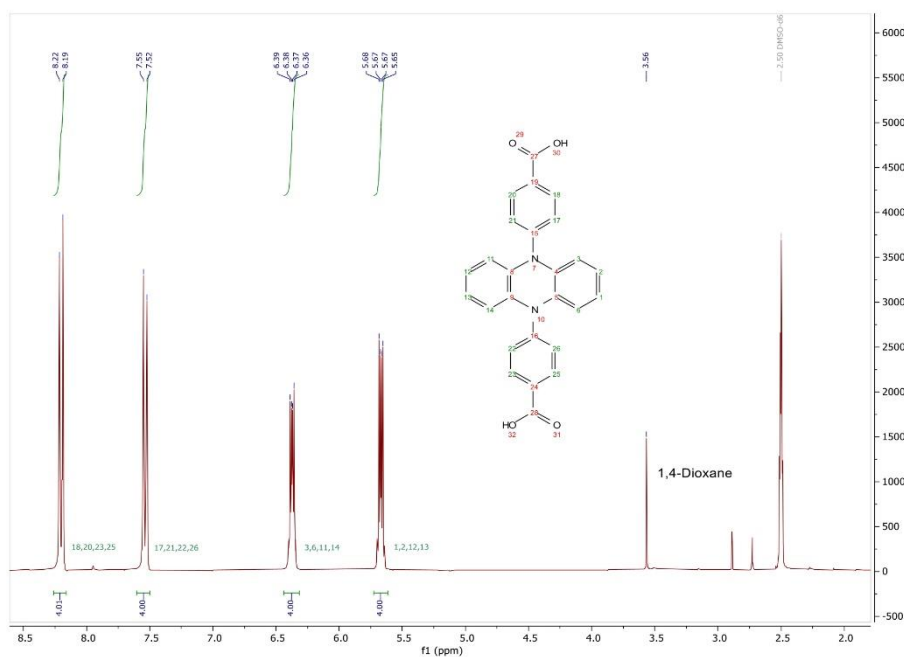


Figure S4. ¹H-NMR spectrum of 4,4'-(phenazine-5,10-diyl)dibenzoic acid (300 MHz, DMSO-d₆).

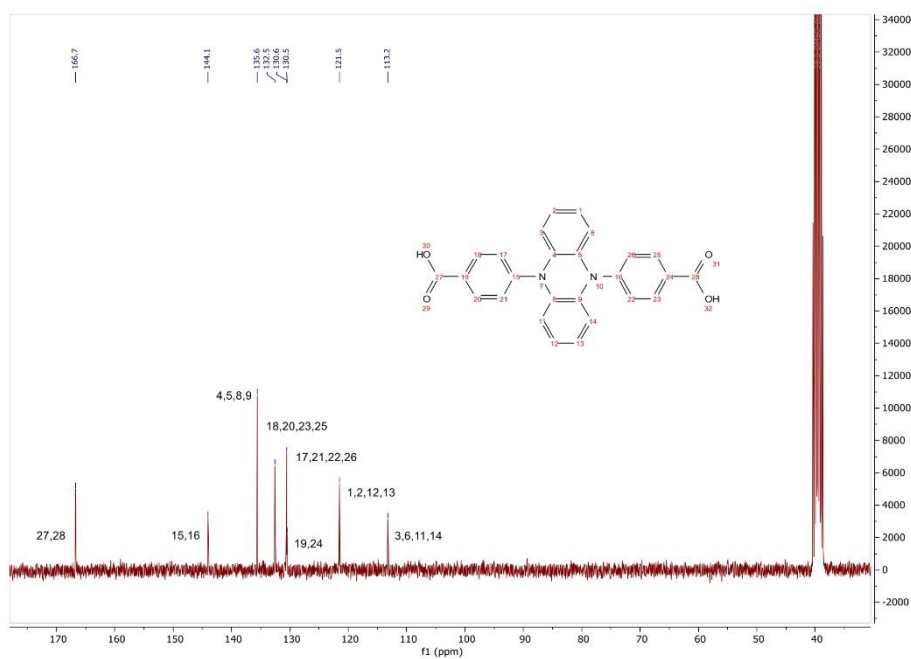


Figure S5. ¹³C-NMR spectrum of 4,4'-(phenazine-5,10-diyl)dibenzoic acid (75 MHz, DMSO-d₆).

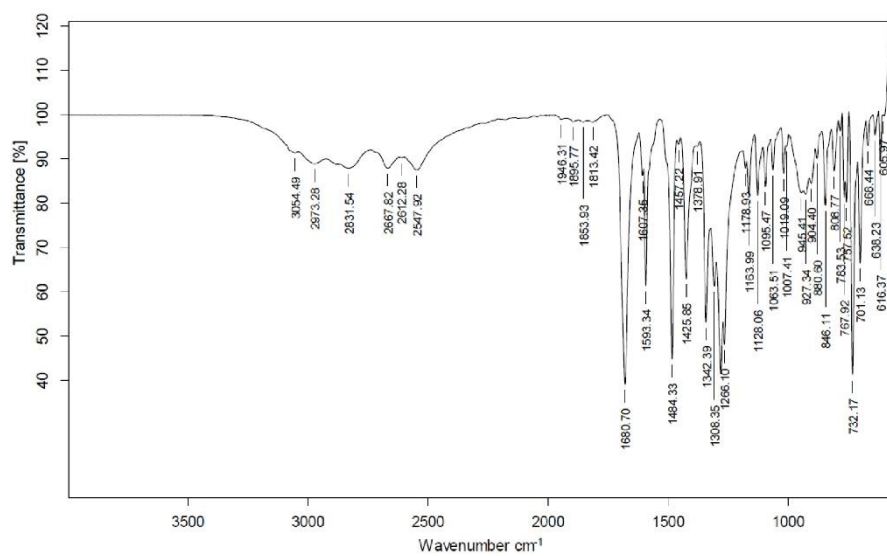


Figure S6. IR spectrum (ATR) of 4,4'-(phenazine-5,10-diyl)dibenzoic acid.

S3 4,4'-(Phenazine-5,10-diyl)dibenzoic acid dimethylsulfoxide solvate (H₂PZDB·2DMSO)

The dicarboxylic acid (100 mg) was dissolved in DMSO (50 mL). The solution was filtered and the filtrate was transferred to a 100 mL round bottom flask. The solution was heated at 80 °C, allowing the DMSO to evaporate slowly. After ~40 min, the product started to crystallize as long yellow platelets. The crystals obtained represent a DMSO solvate.

Details of the X-ray structure determinations of H₂PZDB·2DMSO (CCDC no. 2453691)*Crystal data*

C ₂₆ H ₁₈ N ₂ O ₄ ·2(C ₂ H ₆ OS)	Z = 1
<i>M_r</i> = 578.68	<i>F</i> (000) = 304
Triclinic, <i>P</i> [−] 1	<i>D_x</i> = 1.358 Mg m ^{−3}
<i>a</i> = 7.7816 (3) Å	Cu Kα radiation, λ = 1.54184 Å
<i>b</i> = 8.8985 (4) Å	Cell parameters from 3815 reflections
<i>c</i> = 11.0236 (4) Å	θ = 5.4–76.0°
α = 100.635 (3)°	μ = 2.10 mm ^{−1}
β = 97.096 (3)°	<i>T</i> = 150 K
γ = 106.318 (4)°	Plate, clear yellow
<i>V</i> = 707.44 (5) Å ³	0.14 × 0.08 × 0.06 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	2524 independent reflections
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	2150 reflections with <i>I</i> > 2σ(<i>I</i>)
Mirror monochromator	<i>R</i> _{int} = 0.038
Detector resolution: 10.0000 pixels mm ^{−1}	θ _{max} = 67.1°, θ _{min} = 4.2°
ω scans	<i>h</i> = −9→9
Absorption correction: gaussian, <i>CrysAlis PRO</i> 1.171.41.90a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	<i>k</i> = −10→10
<i>T</i> _{min} = 0.670, <i>T</i> _{max} = 1.000	<i>l</i> = −12→13
7782 measured reflections	

Refinement

Refinement on <i>F</i> ²	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: mixed
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.0382 <i>R</i> (<i>F</i> ²) = 0.0466	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.0964 <i>wR</i> (<i>F</i> ²) = 0.1002	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0441 <i>P</i>) ² + 0.2779 <i>P</i>] where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 1.042	(Δ/σ) _{max} < 0.001
2524 reflections	Δρ _{max} = 0.20 e Å ^{−3}
186 parameters	Δρ _{min} = −0.31 e Å ^{−3}
0 restraints	

S10

Geometric parameters (Å, °) for H₂PZDB·2DMSO

S1—O3	1.5082 (15)	O1—H1	0.93 (3)
S1—C15	1.762 (2)	O1—C13	1.323 (2)
S1—C14	1.780 (3)	O2—C13	1.205 (2)
		N1—C1	1.406 (2)
		N1—C6 ⁱ	1.406 (2)
		N1—C7	1.439 (2)
O3—S1—C15	106.16 (10)	N1 ⁱ —C6—C1	119.43 (16)
O3—S1—C14	103.90 (12)	C5—C6—N1 ⁱ	121.48 (16)
C15—S1—C14	98.06 (13)	C8—C7—N1	119.16 (17)
C13—O1—H1	108.5 (16)	C12—C7—N1	119.95 (17)
C1—N1—C6 ⁱ	121.40 (15)	O1—C13—C10	112.84 (16)
C1—N1—C7	119.38 (15)	O2—C13—O1	123.73 (17)
C6 ⁱ —N1—C7	119.21 (15)	O2—C13—C10	123.42 (17)
N1—C1—C6	119.16 (16)		
C2—C1—N1	121.63 (16)		
C6 ⁱ —N1—C1—C2	-179.76 (17)	N1—C7—C12—C11	179.86 (16)
C6 ⁱ —N1—C1—C6	-0.9 (3)	C1—N1—C7—C8	-99.8 (2)
C6 ⁱ —N1—C7—C8	79.4 (2)	C1—N1—C7—C12	80.1 (2)
N1—C1—C2—C3	179.51 (17)	C2—C1—C6—N1 ⁱ	179.77 (16)
N1—C1—C6—N1 ⁱ	0.9 (3)	C6 ⁱ —N1—C7—C12	-100.7 (2)
N1—C1—C6—C5	-178.07 (16)	C7—N1—C1—C2	-0.6 (3)
N1—C7—C8—C9	-178.26 (16)	C7—N1—C1—C6	178.28 (16)

Symmetry code: (i) -x+2, -y+1, -z+2.

Hydrogen-bond geometry (Å, °) for H₂PZDB·2DMSO

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15A···O3 ⁱⁱ	0.98	2.37	3.351 (3)	178
C15—H15C···O2	0.98	2.64	3.340 (3)	128
O1—H1···S1	0.93 (3)	2.70 (3)	3.5604 (16)	154 (2)
O1—H1···O3	0.93 (3)	1.65 (3)	2.5780 (19)	176 (3)

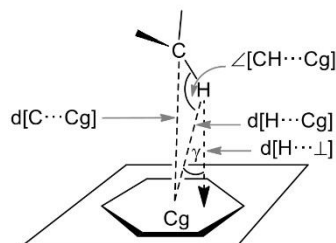
Symmetry code: (ii) -x, -y+2, -z+1.

Analysis of "Short Ring-Interactions" for possible π -stacking and C-H··· π contacts in H₂PZDB·2DMSO

The PLATON^{5,6} -listing "Analysis of Short Ring-Interactions" for possible π -stacking interactions yielded **no significant π -stacking** for H₂PZDB·2DMSO, that is no short centroid-centroid contacts (< 3.8 Å), near parallel ring planes (α < 10° to ~0° or even exactly 0° by symmetry), small slip angles (β , γ < 25°) and vertical displacements (slippage < 1.5 Å) which translate into a sizable overlap of the aryl-plane areas.

S11

Some C-H $\cdots\pi$ contacts were found for H₂PZDB·2DMSO. Significant intermolecular C-H $\cdots\pi$ contacts start below around 2.7 Å for the C-H $\cdots$ ring centroid distances with H-perp also starting at below 2.6-2.7 Å and C-H $\cdots$ Cg > 145° (Scheme S1, Table S1, Figure S7).^{7,8,9,10,11,12}



Scheme S1: Graphical presentation of the parameters used for the description of CH- π interactions.⁸

Table S1. Analysis of intermolecular C-H $\cdots$ Cg(Pi-Ring) Interactions (H $\cdots$ Cg < 3.0 Å - Gamma < 30.0 Deg) in H₂PZDB·2DMSO (see Scheme S1 for explanation).

- Cg(J) = Center of gravity of ring J (Plane number above)
- H-Perp = Perpendicular distance of H to ring plane J
- Gamma = Angle between Cg-H vector and ring J normal
- C-H..Cg = C-H-Cg angle (°)
- C..Cg = Distance of X to Cg (Å)
- C-H, Pi = Angle of the X-H bond with the π -plane (i.e. perpendicular = 90 degrees, parallel = 0 degrees)

X-H(I)	Res(I)	Cg(J)	[ARU(J)]	H..Cg	H-Perp	Gamma	X-H..Cg	X..Cg	X-H,Pi
C(9) -H(9)	[1] -> Cg(2)	[1455.01]		2.82	2.82	0.66	149	3.6672(19)	60
C(15) -H(15B)	[2] -> Cg(2)	[1454.01]		2.89	2.65	23.46	136	3.659(2)	51

[1454] = -1+X,Y,-1+Z

[2565] = X,1-Y,1/2+Z

Cg2 = centroid of ring C1-C2-C3-C4-C5-C6

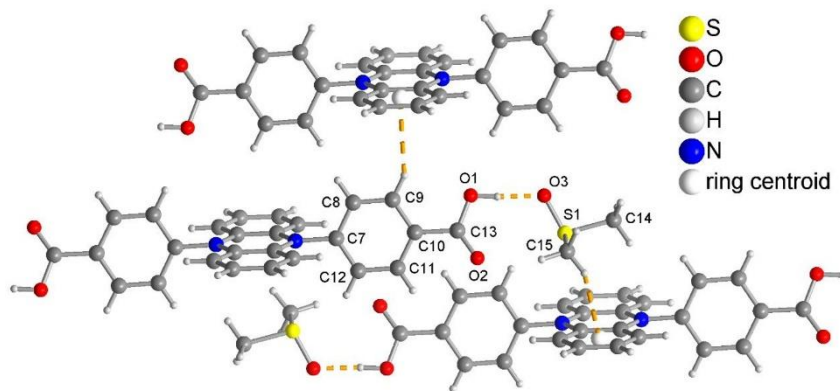


Figure S7. C-H $\cdots\pi$ interactions (and O-H $\cdots$ O interactions) in the packing of H₂PZDB·2DMSO in the crystal, indicated as dashed orange lines. Further details of these C-H $\cdots\pi$ interactions, including the symmetry transformations are listed in the above Table S1.

S4 [Zn(PZDB)(DEF)₂]_n (Zn-PZDB)

Zinc nitrate hexahydrate (Table S2) and 4,4'-(phenazine-5,10-diyl)dibenzoic acid (Table S2) were added to diethylformamide (DEF) (Table S2) in a Pyrex tube. The reaction mixture was then placed in an ultrasonic bath at 40 °C for ~30 min until a homogeneous solution was obtained. The reaction was carried out for 72 h at 85 °C (plus 3 h heating/3 h cooling) in a programmable synthesis oven. Subsequently, the crude product was washed three times with DEF (5 mL each). The crystalline CP was finally dried in high vacuum (1×10^{-3} mbar) for 16 h and stored under inert gas atmosphere. The final product was obtained as clear yellow crystals (yield 26 %, 43 mg, based on the large batch Table S2; the high concentration of zinc nitrate yielded the greatest quantity of product. At lower concentrations, the yield decreased significantly).

Elemental analysis C₃₆H₃₈N₄O₆Zn: calc C 62.84, H 5.57, N 8.14; found: C 62.23, H 5.38, N 8.16 %

Table S2. Overview of the different batch sizes.

Metal salt [mg]	Linker [mg]	Solvent [mL]	Pyrex tube size [mL]	Molar ratio	Yield
35 (0.12 mmol)	50 (0.12 mmol)	5	10	1:1	crystalline mixed phase
100 (0.34 mmol)	50 (0.12 mmol)	5	10	2.8:1	~ 4% crystalline mixed phase
200 (0.67 mmol)	50 (0.12 mmol)	5	10	5.6:1	~ 13%
400 (1.34 mmol)	50 (0.12 mmol)	5	10	11.2:1	19 - 25 %
800 (2.69 mmol)	100 (0.24 mmol)	10	20	11.2:1	20 - 26%

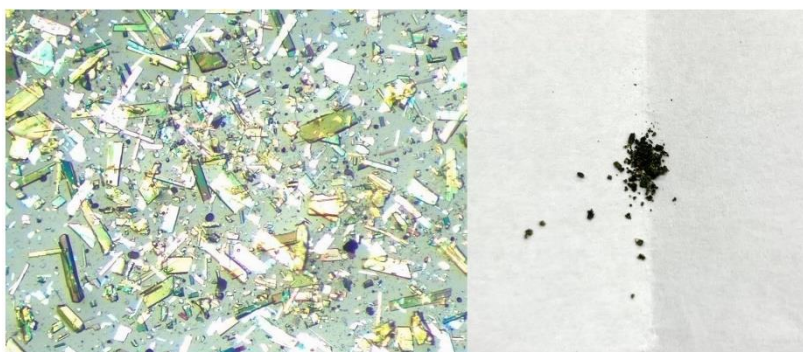


Figure S8. Polarizing light microscope images of the crystals of Zn-PZDB from DEF (the compound forms as thin platelets, left) and color after contact with air (right).

Powder X-ray diffraction (PXRD)

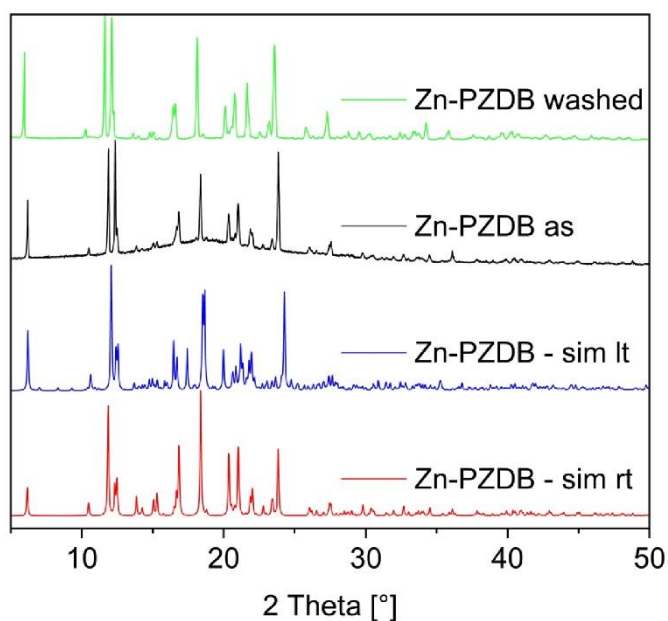


Figure S9. Comparison of the diffractograms (at room temperature) for the as synthesized (as) sample of Zn-PZDB from DEF and after washing, but before drying with the simulations for the room and low-temperature structures.

Infrared spectroscopy

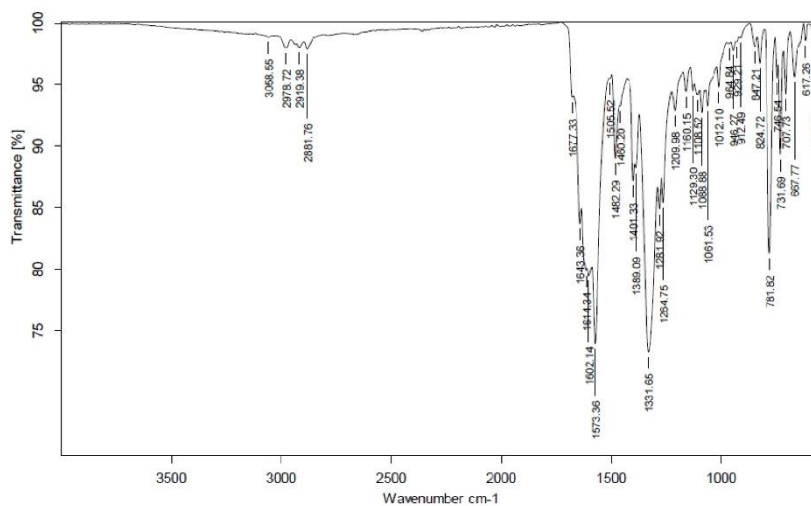
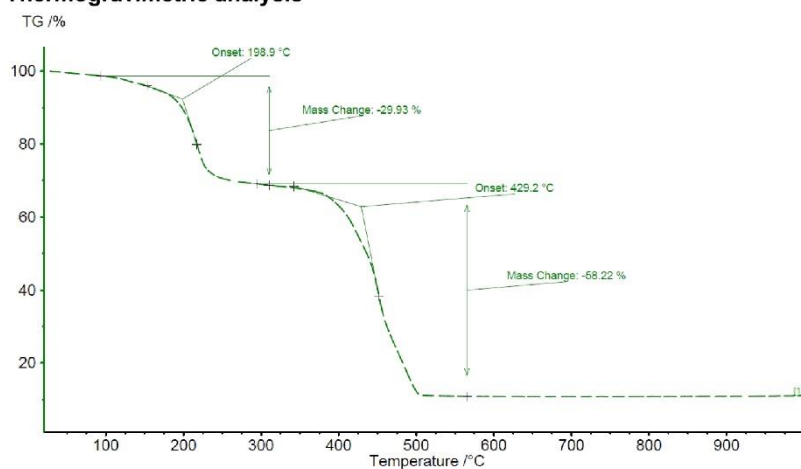


Figure S10. IR spectrum (ATR) of Zn-PZDB from DEF.

Thermogravimetric analysis



$[\text{Zn}(\text{PZDB})(\text{DEF})_2]_n$
$\text{C}_{36}\text{H}_{38}\text{N}_4\text{O}_6\text{Zn}$ - 688.06 g/mol
PZDB - $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_4$, 420.42 g/mol, 61.10 %
DEF - $\text{C}_5\text{H}_{11}\text{NO}$, 101.15 g/mol, 14.70 % ($\times 2 = 29.40$ %)
Zn - 65.38 g/mol, 9.50 %

Figure S11. TGA of Zn-PZDB from DEF under nitrogen atmosphere with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in Al_2O_3 -crucibles and mass percent of building groups.

Details of the X-ray structure determinations of

catena-[bis(N,N-diethylformamide)- μ -4,4'-(phenazine-5,10-diyl)dibenzoato- κ^2 O,O''-zinc(II)]

[Zn(PZDB)(DEF)₂]_n (Zn-PZDB) – room-temperature structure

Crystal data

C ₃₆ H ₃₈ N ₄ O ₆ Zn	$F(000) = 1440$
$M_r = 688.07$	$D_x = 1.367 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$a = 16.8843 (3) \text{ \AA}$	Cell parameters from 11503 reflections
$b = 6.8991 (1) \text{ \AA}$	$\theta = 3.1\text{--}76.2^\circ$
$c = 28.7416 (4) \text{ \AA}$	$\mu = 1.44 \text{ mm}^{-1}$
$\beta = 93.307 (1)^\circ$	$T = 298 \text{ K}$
$V = 3342.43 (9) \text{ \AA}^3$	Block, clear yellow
$Z = 4$	$0.25 \times 0.18 \times 0.08 \text{ mm}$

Data collection

Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer	2978 independent reflections
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	2615 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{\text{int}} = 0.033$
Detector resolution: $10.0000 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 67.0^\circ$, $\theta_{\text{min}} = 3.1^\circ$
ω scans	$h = -19\text{--}20$
Absorption correction: gaussian, <i>CrysAlis PRO</i> 1.171.41.90a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$k = -7\text{--}8$
$T_{\text{min}} = 0.490$, $T_{\text{max}} = 1.000$	$l = -34\text{--}34$
19301 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.0639$ $R(F^2) = 0.0690$	H-atom parameters constrained
$wR[F^2 > 2\sigma(F^2)] = 0.1935$ $wR(F^2) = 0.2004$	$w = 1/[\sigma^2(F_o^2) + (0.1217P)^2 + 4.9375P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.048$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2978 reflections	$\Delta\rho_{\text{max}} = 0.81 \text{ e \AA}^{-3}$
215 parameters	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
7 restraints	

S16

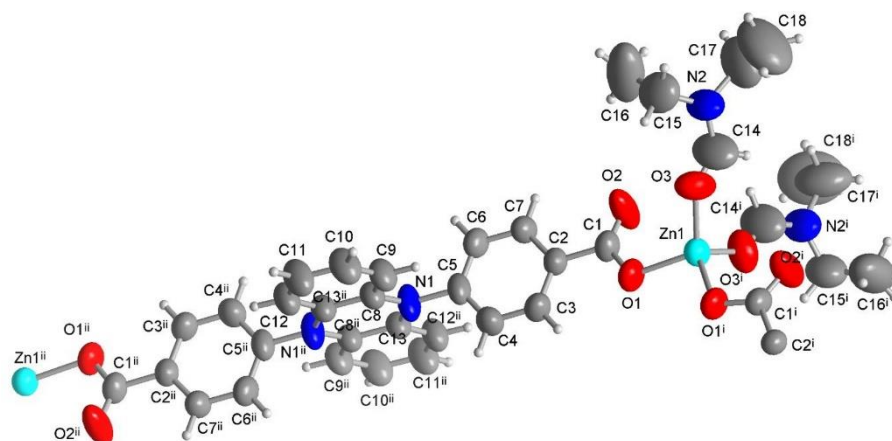


Figure S12. Expanded asymmetric unit of Zn-PZDB room-temperature structure (50% thermal ellipsoids, H atoms with arbitrary radii). Symmetry transformations: (i) $-x+1, y, -z+1/2$; (ii) $-x+3/2, -y+5/2, -z+1$.

Table S3. Geometric parameters ($\text{\AA}$, $^\circ$) for Zn-PZDB – room-temperature structure

Zn1—O1 ⁱ	1.941 (3)	O1—C1	1.273 (4)
Zn1—O1	1.941 (3)	O2—C1	1.201 (5)
Zn1—O3 ⁱ	1.972 (3)		
Zn1—O3	1.972 (3)		
O1 ⁱ —Zn1—O1	98.04 (16)	O1 ⁱ —Zn1—O3 ⁱ	111.34 (14)
O1—Zn1—O3 ⁱ	113.82 (13)	O1—Zn1—O3	111.34 (14)
O1 ⁱ —Zn1—O3	113.83 (13)	O3 ⁱ —Zn1—O3	108.6 (3)

Symmetry codes: (i) $-x+1, y, -z+1/2$; (ii) $-x+3/2, -y+5/2, -z+1$

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$) for Zn-PZDB – room-temperature structure

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C4—H4 $\cdots$ O2 ⁱⁱⁱ	0.93	2.41	3.155 (6)	137
C17—H17A $\cdots$ O1 ^{iv}	0.97	2.50	3.444 (9)	163

Symmetry code: (iii) $x, y+1, z$; (iv) $-x+1, y-1, -z+1/2$.

[Zn(PZDB)(DEF)₂]_n (Zn-PZDB)—low-temperature structure

Crystal data

C ₇₂ H ₇₆ N ₈ O ₁₂ Zn ₂	Z = 2
<i>M_r</i> = 1376.14	<i>F</i> (000) = 1440
Triclinic, <i>P</i> [−] 1	<i>D_x</i> = 1.406 Mg m ^{−3}
<i>a</i> = 8.8316 (2) Å	Cu Kα radiation, λ = 1.54184 Å
<i>b</i> = 13.6072 (3) Å	Cell parameters from 16404 reflections
<i>c</i> = 29.1437 (5) Å	θ = 3.1–77.6°
α = 100.867 (2)°	μ = 1.48 mm ^{−1}
β = 91.613 (2)°	<i>T</i> = 150 K
γ = 108.277 (2)°	Block, clear yellow
<i>V</i> = 3251.64 (12) Å ³	0.29 × 0.19 × 0.09 mm

Data collection

Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer	11580 independent reflections
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	9335 reflections with <i>I</i> > 2σ(<i>I</i>)
Mirror monochromator	<i>R</i> _{int} = 0.068
Detector resolution: 10.0000 pixels mm ^{−1}	θ _{max} = 67.1°, θ _{min} = 3.1°
ω scans	<i>h</i> = −10→10
Absorption correction: for a sphere <i>CrysAlis PRO</i> 1.171.41.90a (Rigaku Oxford Diffraction, 2020) Spherical absorption correction using equivalent radius and absorption coefficient. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	<i>k</i> = −16→16
<i>T</i> _{min} = 0.822, <i>T</i> _{max} = 0.827	<i>l</i> = −32→34
41525 measured reflections	

Refinement

Refinement on <i>F</i> ²	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.0426 <i>R</i> (<i>F</i> ²) = 0.0565	H-atom parameters constrained
<i>wR</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.1053 <i>wR</i> (<i>F</i> ²) = 0.1132	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0534 <i>P</i>) ² + 0.7955 <i>P</i>] where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 1.037	(Δ/σ) _{max} = 0.002
11580 reflections	Δρ _{max} = 0.59 e Å ^{−3}
895 parameters	Δρ _{min} = −0.44 e Å ^{−3}
7 restraints	

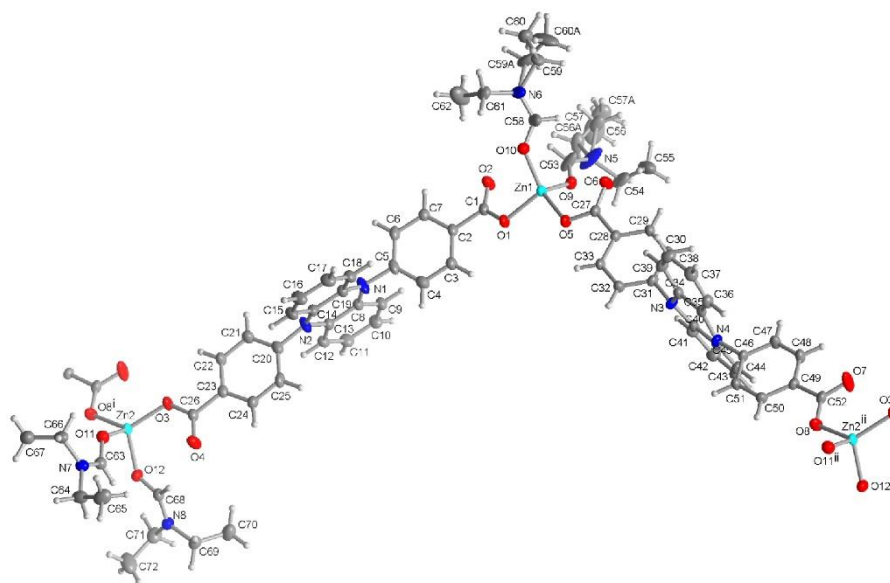


Table S4. Geometric parameters (Å, °) for Zn-PZDB – low-temperature structure

Symmetry codes: (i) $x-1, y+1, z+1$; (ii) $x+1, y-1, z-1$.

Hydrogen-bond geometry (Å, °) for Zn-PZDB – low-temperature structure.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C21—H21 $\cdots$ O2 ⁱⁱⁱ	0.95	2.37	3.233 (3)	151
C32—H32 $\cdots$ O8 ^{iv}	0.95	2.57	3.410 (3)	148
C47—H47 $\cdots$ O6 ^v	0.95	2.53	3.141 (3)	122
C51—H51 $\cdots$ N4 ^{iv}	0.95	2.66	3.577 (3)	162
C58—H58 $\cdots$ O7 ^v	0.95	2.38	3.180 (4)	142
C64—H64A $\cdots$ O5 ^{vi}	0.99	2.52	3.433 (3)	154
C65—H65C $\cdots$ O6 ^{vii}	0.98	2.59	3.571 (4)	175
C68—H68 $\cdots$ O4	0.95	2.27	3.046 (3)	139

Symmetry codes: (iii) $-x+2, -y+2, -z+1$; (iv) $-x+2, -y, -z$; (v) $-x+3, -y+1, -z$; (vi) $-x+1, -y+1, -z+1$; (vii) $-x+2, -y+1, -z+1$.

S5 [Zn(PZDB)(DMF)₂]_n (Zn-PZDB from DMF)

Zinc nitrate hexahydrate (0.0211 mg, 0.071 mmol) and 4,4'-(phenazine-5,10-diyl)dibenzoic acid (10 mg, 0.024 mmol) were added to 5 mL of dimethylformamide (DMF) in a Pyrex tube (10 mL). The reaction mixture was then placed in an ultrasonic bath at 40 °C for ~30 min until a homogeneous solution was obtained. The reaction was carried out for 144 h at 85 °C (plus 0.5 h heating/24 h cooling) in a programmable synthesis oven. Subsequently, the crude product was washed three times with DMF (5 mL each). The crystalline CP was finally dried in high vacuum (1×10^{-3} mbar) for 16 h and stored under inert gas atmosphere. The final product was obtained as clear yellow crystals (yield 29 %, 2.85 mg).

Elemental analysis C₃₂H₃₀N₄O₆Zn: calc. C 60.81, H 4.78, N 8.87; found C 55.53, H 4.33, N 7.96 %

The crude product exhibits a phase-pure crystalline structure (Figure S14). Individual transparent yellow crystals (in the form of small platelets) were picked from this phase mixture and subjected to measurement. The reaction conditions and batch size were based on the experience gained from the aforementioned experimental approaches of Zn-PZDB in DEF. The crystals represent a coordination polymer analogous to structure to [Zn(PZDB)(DEF)₂]_n, with the exception of the replacement of DEF molecules with DMF molecules. Despite various washing cycles and cleaning methods with different solvents (DMF, DEF, ethanol, acetone), the CHN analysis remained at variance. Also, no large amounts could be obtained as attempted upscaling led to mixtures.

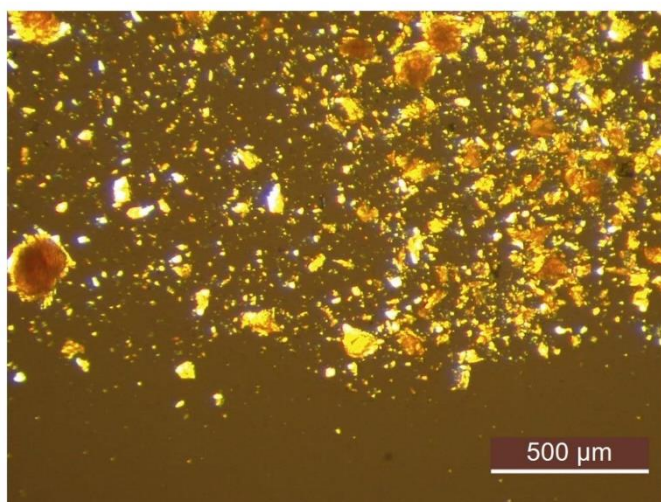
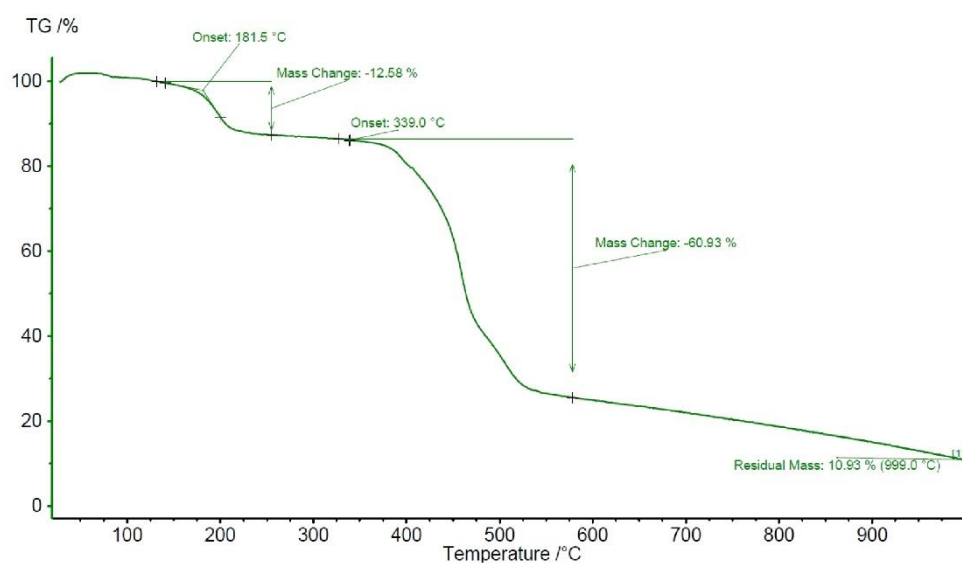


Figure S14. Light microscope images of the crystals of Zn-PZDB from DMF.

Thermogravimetric analysis of $[\text{Zn}(\text{PZDB})(\text{DMF})_2]_n$



$[\text{Zn}(\text{PZDB})(\text{DMF})_2]_n$
$\text{C}_{32}\text{H}_{30}\text{N}_4\text{O}_6\text{Zn} - 632.00 \text{ g/mol}$
PZDB - $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_4$, 420.42 g/mol, 66.52 %
DMF - $\text{C}_3\text{H}_7\text{NO}$, 73.09 g/mol, 11.56 % ($\times 2 = 23.12 \%$)
Zn - 65.38 g/mol, 10.35 %

Figure 15. TGA of Zn-PZDB from DMF under nitrogen atmosphere with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ in Al_2O_3 -crucibles and mass percent of building groups.

Details of the X-ray structure determinations of catena-[bis(N,N-dimethylformamide)-4,4'-(phenazine-5,10-diyl)dibenzoatozinc(II)], [Zn(PZDB)(DMF)₂]_n

Crystal data

C ₁₂₈ H ₁₂₀ N ₁₆ O ₂₄ Zn ₄	<i>F</i> (000) = 1312
<i>M_r</i> = 2527.87	<i>D_x</i> = 1.440 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Cu <i>K</i> α radiation, λ = 1.54184 Å
<i>a</i> = 16.8810 (4) Å	Cell parameters from 11054 reflections
<i>b</i> = 6.83856 (14) Å	θ = 3.4–77.0°
<i>c</i> = 25.5519 (7) Å	μ = 1.61 mm ⁻¹
β = 98.923 (2)°	<i>T</i> = 100 K
<i>V</i> = 2914.06 (12) Å ³	Plate, clear yellow
<i>Z</i> = 1	0.15 × 0.1 × 0.04 mm

Data collection

Rigakua XtaLAB Synergy, Dualflex, HyPix diffractometer	9865 measured reflections
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	9865 independent reflections
Mirror monochromator	8402 reflections with <i>I</i> > 2σ(<i>I</i>)
Detector resolution: 10.0000 pixels mm ⁻¹	θ _{max} = 79.1°, θ _{min} = 2.9°
ω scans	<i>h</i> = -20→21
Absorption correction: gaussian <i>CrysAlis PRO</i> 1.171.42.58a (Rigaku Oxford Diffraction, 2022) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	<i>k</i> = -8→8
<i>T</i> _{min} = 0.761, <i>T</i> _{max} = 1.000	<i>l</i> = -32→32

Refinement

Refinement on <i>F</i> ²	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.0484 <i>R</i> (<i>F</i> ²) = 0.0573	H-atom parameters constrained
<i>wR</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.1307 <i>wR</i> (<i>F</i> ²) = 0.1381	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0887 <i>P</i>) ² + 1.2423 <i>P</i>] where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 1.037	(Δ/σ) _{max} = 0.001
9865 reflections	Δρ _{max} = 0.55 e Å ⁻³
393 parameters	Δρ _{min} = -0.85 e Å ⁻³
0 restraints	

Special details

<i>Refinement.</i> Refined as a 2-component twin.

S23

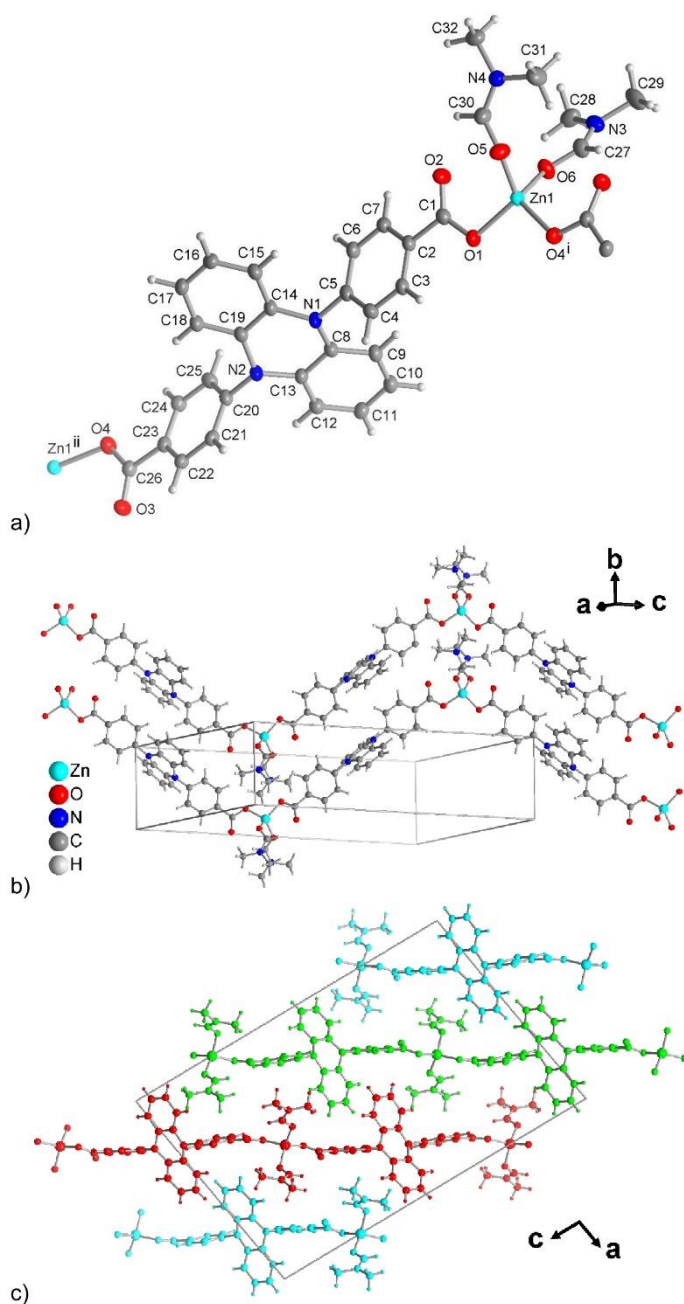


Figure S16. Expanded asymmetric unit of Zn-PZDB from DMF (50% thermal ellipsoids, H atoms with arbitrary radii). Symmetry transformations: (i) $x+1/2, -y+3/2, z-1/2$; (ii) $x-1/2, -y+3/2, z+1/2$. b) and c) Chain arrangement in Zn-PZDB from DMF. In c) the three different chains are depicted in different colors to help to visualize the 'tongue-and-groove' motif for the inter-chain packing. Compare to Figure 2 in the main text.

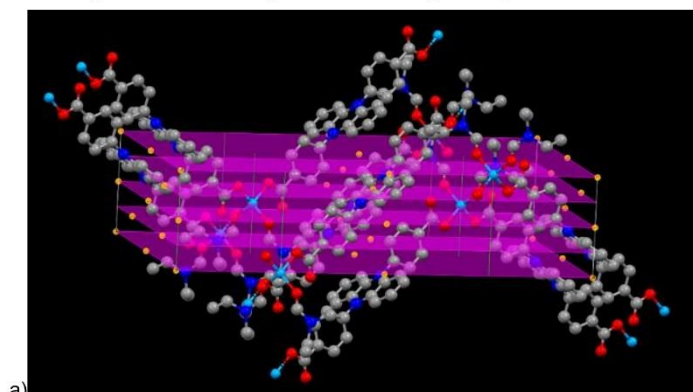
The atom positions within the unit cell and the packing in Zn-PZDB from DMF can be seen as intermediate between the low- and room-temperature structure from DEF. In Zn-PZDB from DMF none of the atoms or pyrazine centroid sits on a special position (as in the DEF-low-temperature structure) (cf. Figure S13). Yet, in its layer arrangement of having every second plane parallel to (4 0 4) occupied, it resembles the room-temperature structure (Section S6, Figure S18c)

Geometric parameters (Å, °) for [Zn(PZDB)(DMF)₂]_n

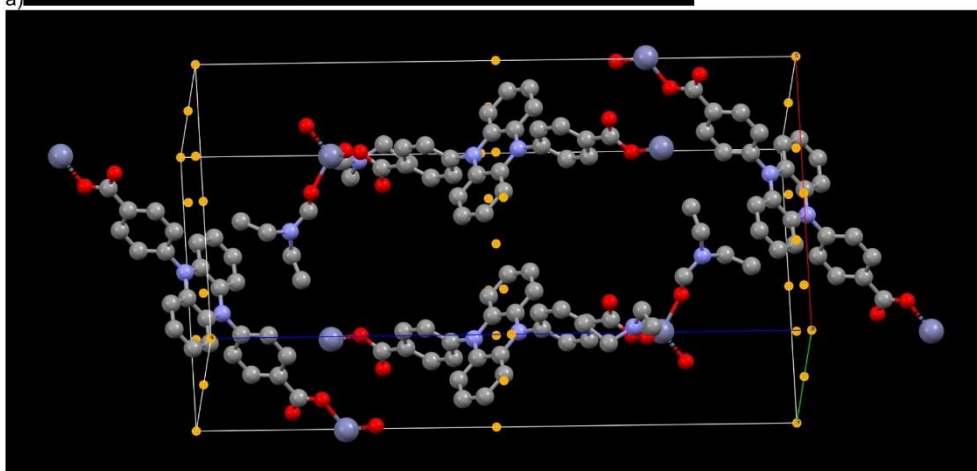
Zn1—O5	1.972 (2)	O5—C30	1.252 (4)
Zn1—O1	1.941 (2)	O1—C1	1.288 (3)
Zn1—O6	1.977 (2)	O6—C27	1.256 (4)
Zn1—O4 ⁱ	1.933 (2)	O3—C26	1.233 (4)
		O4—C26	1.292 (3)
		O2—C1	1.234 (4)
O5—Zn1—O6	105.96 (10)	O4 ⁱ —Zn1—O6	115.98 (9)
O1—Zn1—O5	118.94 (9)	C30—O5—Zn1	127.5 (2)
O1—Zn1—O6	109.51 (9)	C1—O1—Zn1	109.34 (18)
O4 ⁱ —Zn1—O5	104.02 (9)	C27—O6—Zn1	125.9 (2)
O4 ⁱ —Zn1—O1	102.80 (8)	C26—O4—Zn1 ⁱⁱ	119.41 (18)

Symmetry codes: (i) $x+1/2, -y+3/2, z-1/2$; (ii) $x-1/2, -y+3/2, z+1/2$.

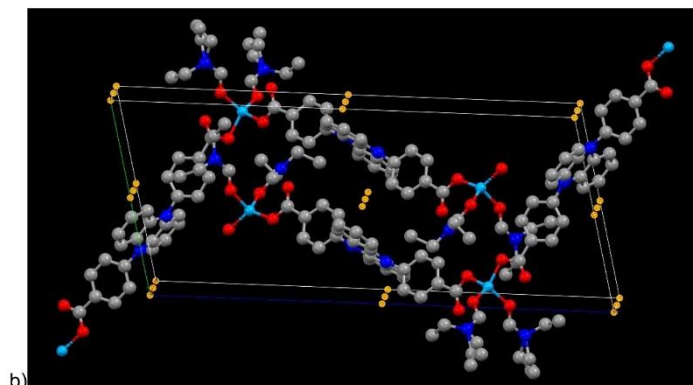
S6 Comparison of the crystal structure packing in Zn-PZDB from DEF and from DMF



a)



DEF – room temp., $C2/c$



b)

DEF – low temp., $P\bar{1}$

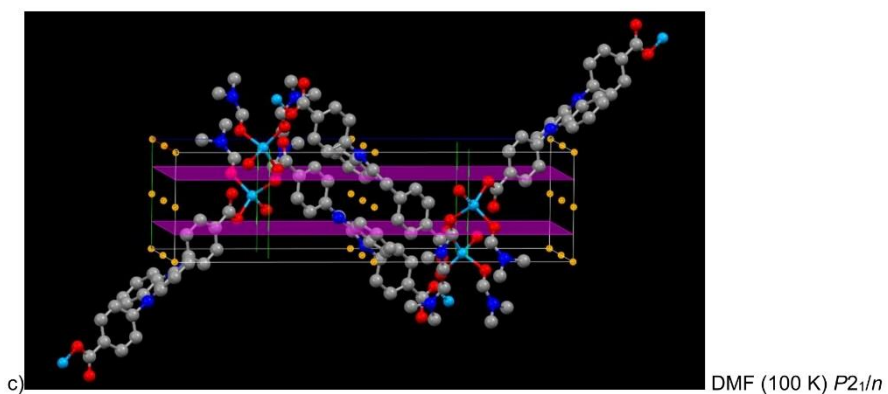


Figure S17. a, b) Unit cell packing diagrams of Zn-PZDB from DEF: a) room-temperature structure, showing the relevant inversion centers (yellow dots), two-fold rotation axes (green lines) and glide planes (pink layers) (the latter two pass through the Zn atoms marked in light-blue). b) Low-temperature structure showing the inversion centers (yellow dots). Hydrogen atoms are not shown for clarity. c) Unit cell packing diagram of Zn-PZDB from DMF showing the relevant inversion centers (yellow dots), 2-fold screw axes (green lines) and glide planes (pink layers)

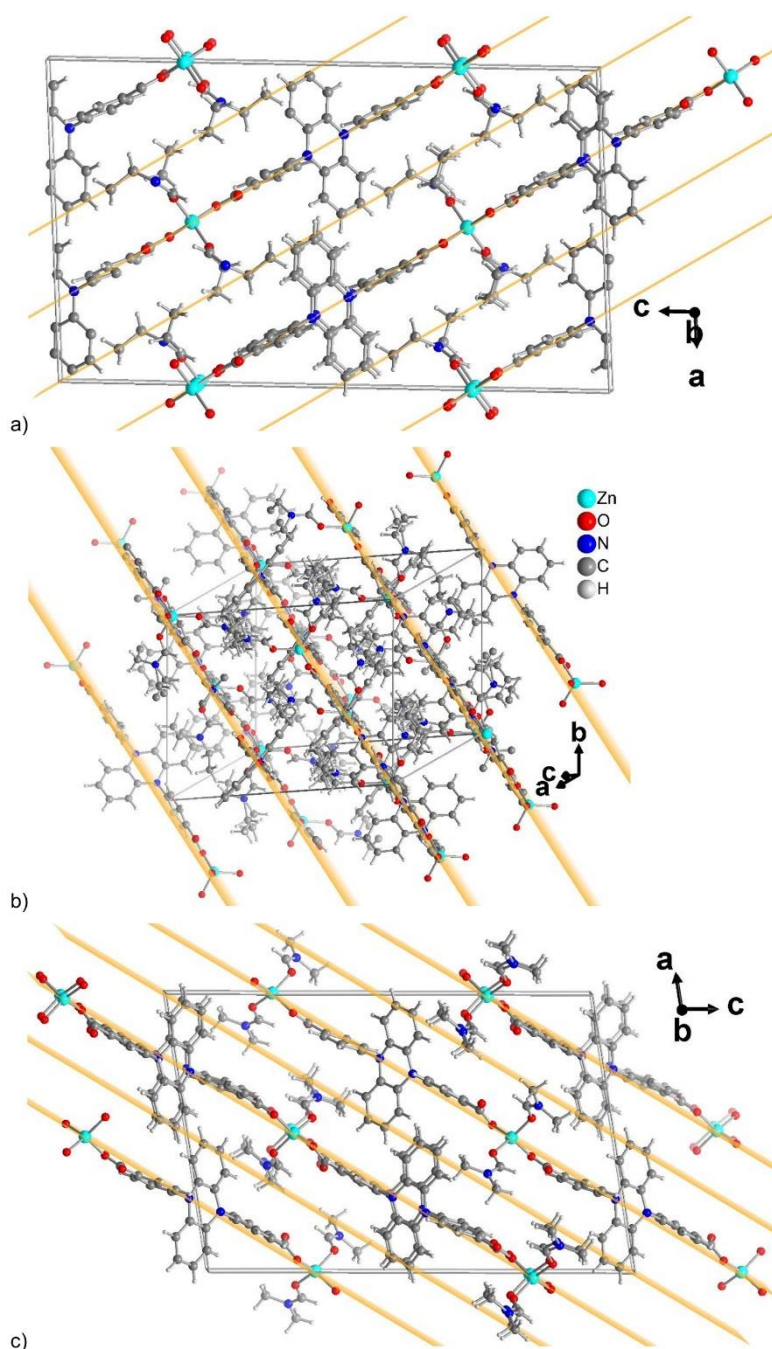


Figure S18. Packing diagrams of Zn-PZDB from DEF: a) Set of planes parallel to $(4\ 0\ -4)$ where the chains lie in every second plane in the room-temperature structure of Zn-PZDB from DEF. b) Set of planes parallel to $(1\ -1\ 2)$ where the chains lie in the low-temperature structure of Zn-PZDB from DEF. c) Zn-PZDB from DMF: Set of planes parallel to $(4\ 0\ 4)$ where the chains lie in every second plane.

S7 [Co(HPZDB)₂(DEF)₂]_n·DEF (Co-HPZDB)

Cobalt nitrate hexahydrate (800 mg, 2.75 mmol) and 4,4'-(phenazine-5,10-diyl)dibenzoic acid (100 mg, 0.24 mmol) were added to 10 mL of diethylformamide (DEF) in a Pyrex tube (20 mL). The reaction mixture was then placed in an ultrasonic bath at 40 °C for ~30 min until a homogeneous solution was obtained. The reaction was carried out for 72 h at 85 °C (3 h heating/3 h cooling) in a programmable synthesis oven. Subsequently, the crude product was washed three times with DEF (5mL). The crystalline CP was finally dried in high vacuum (1×10^{-3} mbar) for 16 h and stored under inert gas atmosphere. The product was obtained as a dark red-purple crystalline solid (yield 12 %, 31.5 mg, Figure S19).

Elemental analysis C₆₂H₅₄CoN₆O₁₀: calc. C 67.14, H 4.91, N 7.58; found C 67.32, H 5.12, N 7.55 %

The high excess of metal salt used originated from several approaches in which the metal-to-linker ratio was varied systematically. Reactions performed with a large excess of the linker yielded products with the highest phase-purity.

The compound is stable for a short time (approx. 30 min) in air, depending on crystal size. As time passes, the crystals become opaque and increasingly dark green. The compound decomposes immediately during grinding in air or upon drying for 3 h at 130 °C.

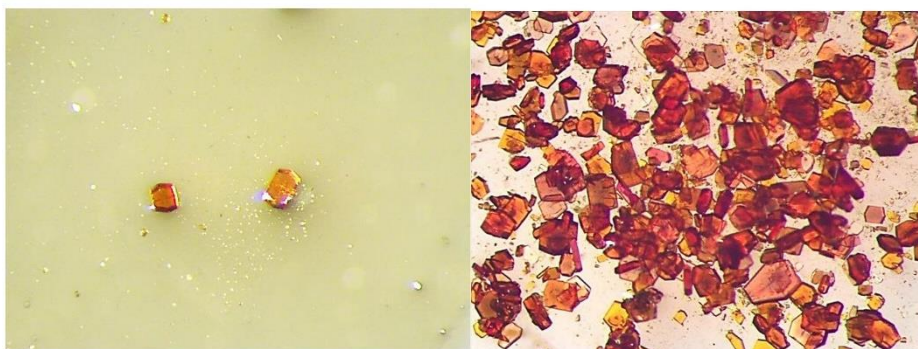


Figure S19. Microscope images of Co-HPZDB crystals: Two individual crystals (left) and a section of an entire batch (right).



Figure S20. Dark red-purple crystalline solid of Co-HPZDB (left), and color after grinding and air contact (right).

Co metal analysis by atom absorption spectroscopy (AAS)

Sample	Co-PZDB (1)		Co-PZDB (2)
Sample mass	10.1 mg		12.7 mg
Theoretical Co mass (percent)	0.54 mg (5.34%)		0.68 mg (5.34%)
Found Co mass	0.54 mg		0.67 mg

S29

Powder X-ray diffraction (PXRD)

Figure S21 compares the diffractogram simulated from the crystal structure with the measured diffractogram. The sample was prepared as described above and measured immediately.

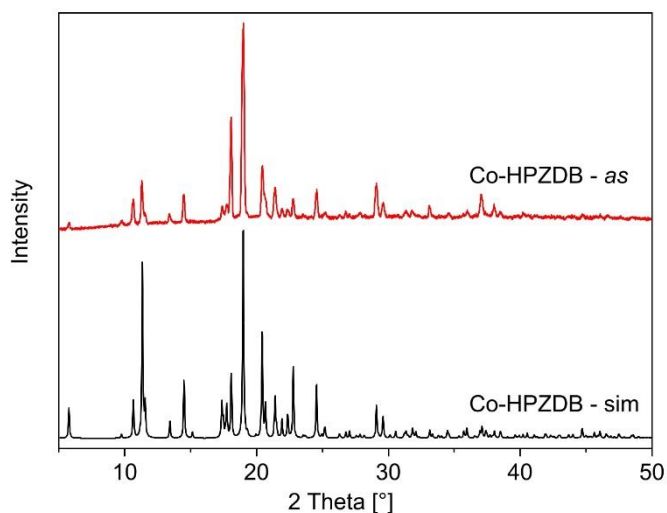


Figure S21. Comparison of the experimental diffractogram of the as-synthesised sample (as, ground and measured immediately) and the simulated PXRD for Co-HPZDB.

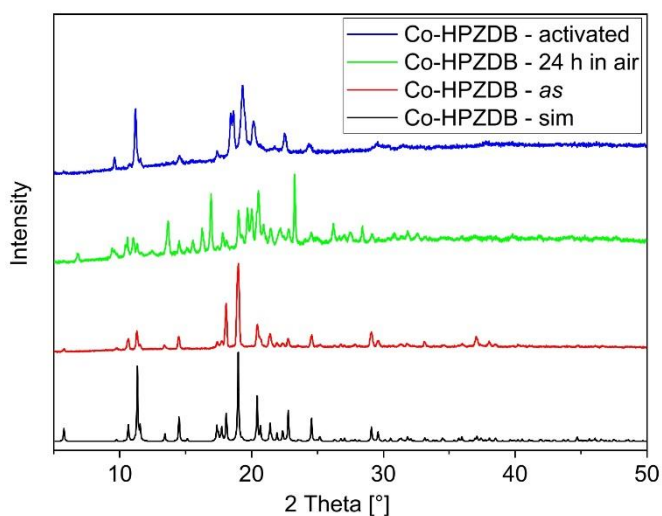


Figure S22. Comparison of PXRDs of Co-HPZDB sim (simulated, based on the crystal structure), as-synthesised (as; washed with DEF and measured immediately) 24 h in air (measured after 24-hour air contact) and activated (activation was achieved by 3 h, 130 °C, 1×10^{-3} mbar)

S30

Infrared spectroscopy

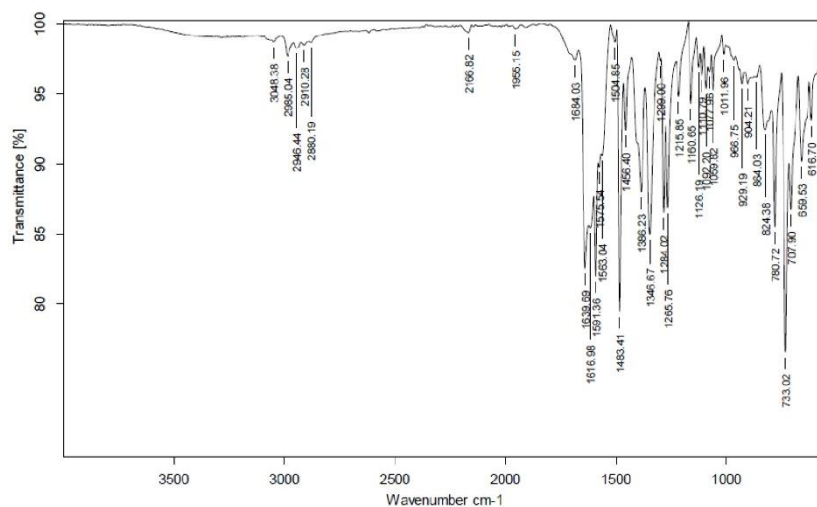
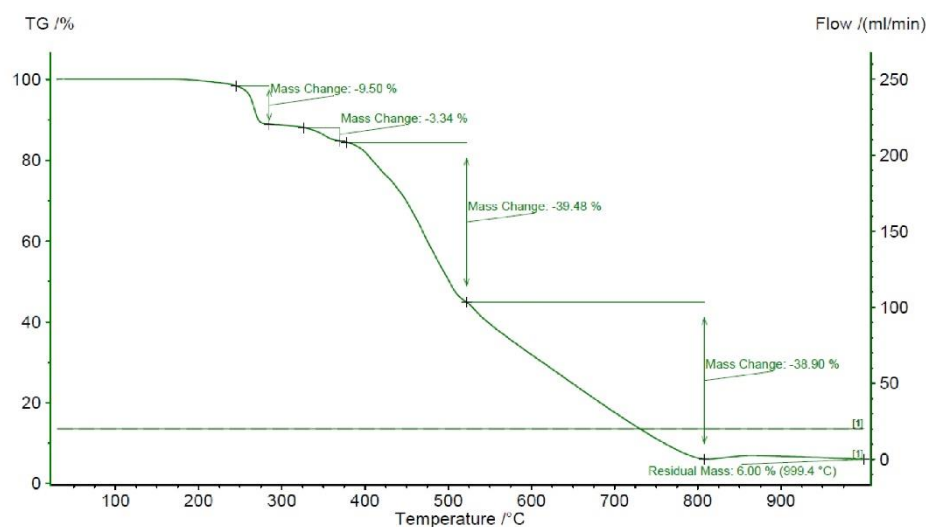


Figure S23. IR spectrum (ATR) of Co-HPZDB.

Thermogravimetric analysis



$[\text{Co}(\text{HPZDB})_2(\text{DEF})_2]_n$
$\text{C}_{62}\text{H}_{56}\text{CoN}_6\text{O}_{10}$ - 1104.05 g/mol
HPZDB - $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_4$, 421.43 g/mol, 38.17 % ($x_2 = 76.34\%$)
DEF - $\text{C}_5\text{H}_{11}\text{NO}$, 101.15 g/mol, 9.16 % ($2x = 18.32\%$)
Co - 58.93 g/mol, 5.34 %

Figure S24. TGA of Co-HPZDB under nitrogen with a heating rate of 5°C min^{-1} in Al_2O_3 -crucibles.

Details of the X-ray structure determination of

catena-[bis(N,N-diethylformamide- κ O)-bis- μ -(phenazine-5,10-diyl(4-phenylcarboxylate- κ O))(4-phenylcarboxylic acid- κ O))cobalt(II)], [Co(HPZDB)₂(DEF)₂]_n (Co-HPZDB)

Crystal data

C ₆₂ H ₅₆ CoN ₆ O ₁₀	$D_x = 1.353 \text{ Mg m}^{-3}$
$M_r = 1104.05$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
Orthorhombic, Cc	Cell parameters from 2516 reflections
$a = 30.5108 (13) \text{ \AA}$	$\theta = 2.9\text{--}67.4^\circ$
$b = 18.1091 (10) \text{ \AA}$	$\mu = 3.03 \text{ mm}^{-1}$
$c = 9.8074 (11) \text{ \AA}$	$T = 300 \text{ K}$
$V = 5418.8 (7) \text{ \AA}^3$	Block, clear reddish violet
$Z = 4$	$0.14 \times 0.10 \times 0.07 \text{ mm}$
$F(000) = 2308$	

Data collection

Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer	1851 reflections with $I > 2\sigma(I)$
Radiation source: sealed	$R_{\text{int}} = 0.052$
ω scans	$\theta_{\text{max}} = 67.1^\circ$, $\theta_{\text{min}} = 4.9^\circ$
Absorption correction: multi-scan <i>CrysAlis PRO</i> 1.171.43.98a (Rigaku Oxford Diffraction, 2023) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$h = -36 \rightarrow 22$
$T_{\text{min}} = 0.459$, $T_{\text{max}} = 1.000$	$k = -21 \rightarrow 20$
9319 measured reflections	$l = -11 \rightarrow 11$
2385 independent reflections	

Refinement – non-disordered

Refinement on F^2	Primary atom site location: iterative
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.0741$ $R(F^2) = 0.0968$	H atoms treated by a mixture of independent and constrained refinement
$wR[F^2 > 2\sigma(F^2)] = 0.1545$ $wR(F^2) = 0.1648$	$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 17.0922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.079$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2385 reflections	$\Delta\rho_{\text{max}} = 0.611 \text{ e \AA}^{-3}$
196 parameters	$\Delta\rho_{\text{min}} = -0.358 \text{ e \AA}^{-3}$
16 restraints	

Geometric parameters (Å, °) for Co-HPZDB – non-disordered refinement

Co1—O2 ⁱ	2.086 (3)	Co1—O3	2.109 (6)
Co1—O2	2.085 (3)		
Co1—O2 ⁱⁱ	2.086 (3)		
Co1—O2 ⁱⁱⁱ	2.086 (3)		
O2—Co1—O3	76.56 (19)	O2 ⁱ —Co1—O2 ⁱⁱ	95.2 (2)
O2 ⁱⁱⁱ —Co1—O3	95.0 (2)	O2 ⁱⁱ —Co1—O2 ⁱⁱⁱ	178.0 (2)
O2 ⁱ —Co1—O3	101.45 (19)	O2—Co1—O2 ⁱ	178.0 (2)
O2 ⁱⁱ —Co1—O3	87.0 (2)	O2—Co1—O2 ⁱⁱ	84.9 (2)
O2 ⁱ —Co1—O2 ⁱⁱⁱ	84.9 (2)	C1—O2—Co1	139.1 (3)
O2—Co1—O2 ⁱⁱⁱ	95.2 (2)	C21—O3—Co1	122.8 (5)
Co1—O3—C21—N3	166 (2)	O1—C1—O2—Co1	-50.8 (9)
C2—C1—O2—Co1	127.1 (4)		

Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $x, -y+3/2, -z+3/2$; (iii) $-x+1, -y+3/2, z$.

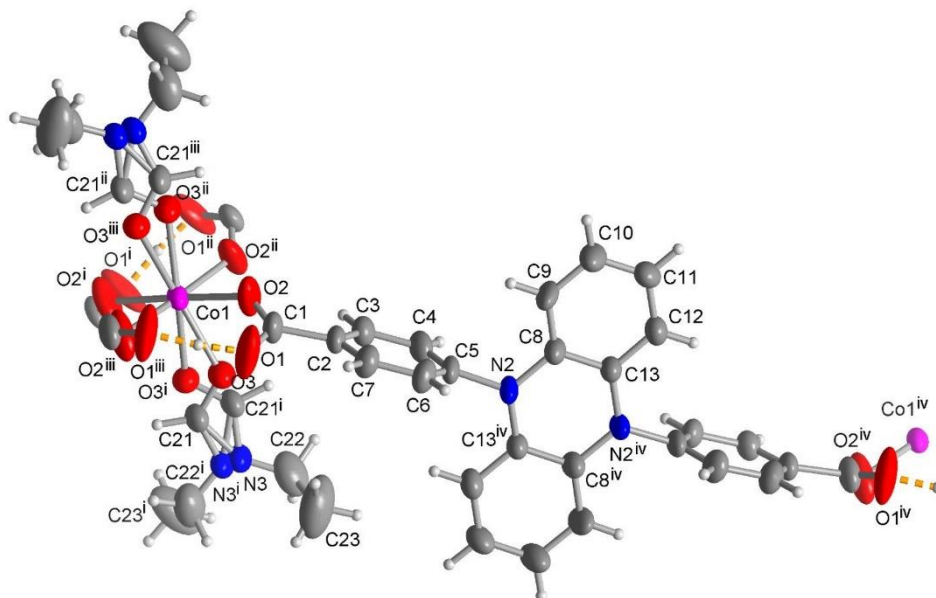


Figure S25. Expanded asymmetric unit of Co-HPZDB, non-disordered refinement (50% thermal ellipsoids, H atoms with arbitrary radii). Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $x, -y+3/2, -z+3/2$; (iii) $-x+1, -y+3/2, z$; (iv) $-x+1/2, -y+1, z$. The large thermal ellipsoids of O1 and O2 are evidence of a tilt disorder which was separately refined with two independent A and B oxygen positions (Figure S26).

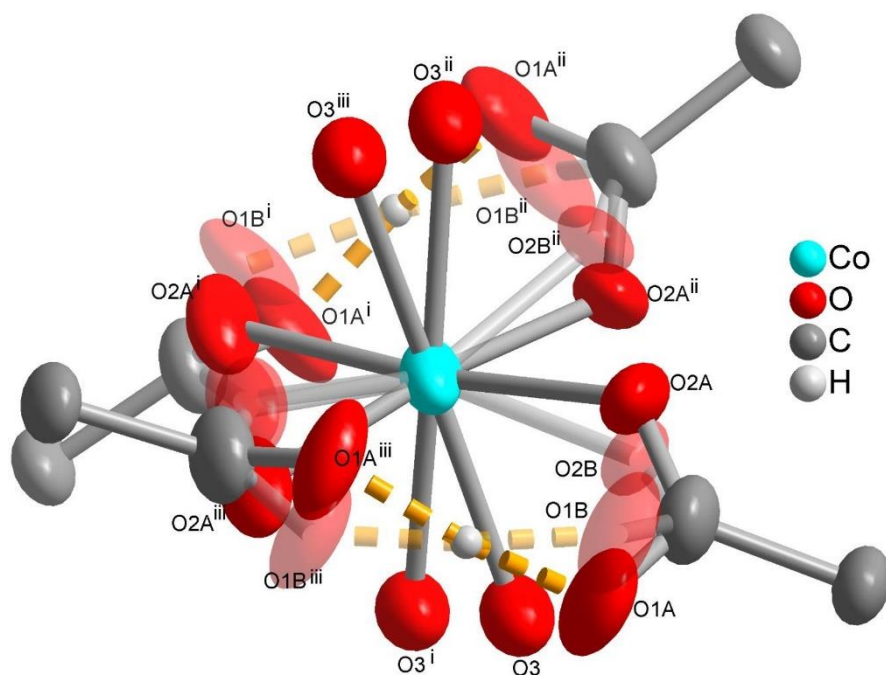


Figure S26. Oxygen atom coordination sphere around Co in Co-HPZDB with a refinement of O1 and O2 in two independent A and B positions each to account for the large thermal ellipsoids, that is, the tilt disorder in the carboxylate groups (cf. Figure S25). In the so-called "disordered refinement", the A position refined to a site-occupation fraction of 0.666(16) and the B position to 0.333(16), hence, the B positions and their bonds are depicted half transparent. The ellipsoids from the anisotropic refinement are shown with 50% probability, H atoms with arbitrary radii). Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $x, -y+3/2, -z+3/2$; (iii) $-x+1, -y+3/2, z$.

Refinement - disordered

Refinement on F^2	Primary atom site location: iterative
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.0699$ $R(F^2) = 0.0928$	H atoms treated by a mixture of independent and constrained refinement
$wR[F^2 > 2\sigma(F^2)] = 0.1437$ $wR(F^2) = 0.1533$	$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 13.0196P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.104$	$(\Delta/\sigma)_{\max} < 0.001$
2385 reflections	$\Delta\rho_{\max} = 0.533 \text{ e } \text{\AA}^{-3}$
215 parameters	$\Delta\rho_{\min} = -0.331 \text{ e } \text{\AA}^{-3}$
53 restraints	

Geometric parameters ($\text{\AA}$, $^\circ$) for Co-HPZDB – disordered refinement

Co1—O2A ⁱ	2.144 (7)	Co1—O2B	1.995 (12)
Co1—O2A ⁱⁱⁱ	2.144 (7)	Co1—O2B ⁱ	1.995 (12)
Co1—O2A ⁱⁱ	2.144 (7)	Co1—O2B ⁱⁱ	1.995 (12)

Co1—O2A	2.144 (7)	Co1—O2B ⁱⁱⁱ	1.995 (12)
Co1—O3	2.110 (5)		
O2B—Co1—O2A ⁱⁱⁱ	82.6 (3)	O2A—Co1—O2A ⁱⁱ	173.0 (5)
O2B ⁱⁱⁱ —Co1—O2A ⁱⁱⁱ	17.2 (4)	O2A ⁱ —Co1—O2A ⁱⁱⁱ	173.0 (5)
O2B ⁱⁱ —Co1—O2A ⁱⁱⁱ	95.8 (3)	O2A ⁱⁱ —Co1—O2A ⁱ	87.1 (4)
O2B ⁱ —Co1—O2A ⁱⁱⁱ	169.5 (6)	O2A—Co1—O2A ⁱ	93.3 (4)
O3—Co1—O2A	81.3 (3)	O2A—Co1—O2A ⁱⁱⁱ	87.1 (4)
O3—Co1—O2A ⁱ	90.4 (3)	O2A ⁱⁱ —Co1—O2A ⁱⁱⁱ	93.3 (4)
O3—Co1—O2A ⁱⁱ	105.8 (3)	C1—O2B—Co1	144.0 (11)
O3—Co1—O2A ⁱⁱⁱ	82.7 (3)	C1—O2A—Co1	131.3 (6)
Co1—O2B—C1—C2	166.3 (16)	C2—C1—O2A—Co1	119.8 (6)
Co1—O2B—C1—O1B	-13 (2)	O1A—C1—O2A—Co1	-58.5 (9)
Co1—O3—C21—N3	166.1 (18)		

Symmetry codes: (i) $-x+1, -y+3/2, z$; (ii) $-x+1, y, -z+3/2$; (iii) $x, -y+3/2, -z+3/2, z$.

Table S5. Overview of the crystallographic data of the metal-PZDB coordination polymers.^a

Compound	Zn-PZDB 150 K	Zn-PZDB 298 K	Zn-PZDB with DMF	Co-HPZDB - non- disordered	Co-HPZDB - disordered
Moiety formula	[Zn ₂ (PZDB) ₂ (DEF) ₄] _n	[Zn(PZDB)(DEF) ₂] _n	[Zn(PZDB)(DMF) ₂] _n	[Co(HPZDB) ₂ (DEF) ₂] _n	[Co(HPZDB) ₂ (DEF) ₂] _n
Empirical formula	C ₇₂ H ₇₆ N ₈ O ₁₂ Zn ₂	C ₃₆ H ₃₈ N ₄ O ₆ Zn	C ₁₂₈ H ₁₂₀ N ₁₆ O ₂₄ Zn ₄	C ₆₂ H ₅₆ CoN ₆ O ₁₀	C ₆₂ H ₅₆ CoN ₆ O ₁₀
Formula weight	1376.14	688.06	2527.87	1104.05	1104.05
Temperature/K	150	298	100	300	300
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> cce	<i>C</i> cce
<i>a</i> /Å	8.8316 (2)	16.8843 (3)	16.8810 (4)	30.5108 (13)	30.5108 (13)
<i>b</i> /Å	13.6072 (3)	6.8991 (1)	6.83856 (14)	18.1091 (10)	18.1091 (10)
<i>c</i> /Å	29.1437	28.7416 (4)	25.5519 (7)	9.8074 (11)	9.8074 (11)
α /°	100.867 (2)	90	90	90	90
β /°	91.613 (2)	93.307 (1)	98.923 (2)	90	90
γ /°	108.277 (2)	90	90	90	90
Volume/Å ³	3251.64 (12)	3342.43 (9)	2914.06 (12)	5418.8 (7)	5418.8 (7)
<i>Z</i>	2	4	1	4	4
ρ_{calc} /mm ³	1.406	1.432	1.440	1.353	1.353
μ /mm ⁻¹	1.48	1.44	1.61	3.03	3.03
<i>F</i> (000)	1440	1432	1312	2308	2308
2 θ range for data collection	6.2 - 134.2	6.2 - 134.0	5.9 - 158.0	9.8 - 134.2	9.8 - 134.2
Reflections collected	41525	19301	9865	9319	9319
Independent reflections	11580	2978	9865	2385	2385
Data/restraints/parameters	11580/7/895	2978/7/215	9865/0/393	2385/ 16/196	2385/ 53/215
Goodness-of-fit on <i>F</i> ²	1.04	1.04	1.04	1.08	1.10
<i>wR</i> (<i>F</i> ²) ^b	0.113	0.195	0.138	0.165	0.153
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.043	0.064	0.048	0.074	0.070
CCDC no.	2453692	2453693	2453694	2453695	2453696

^a Differences between related structure determinations or refinements, such as solvent type, temperature, disorder refinement with restraints, parameters and subsequent *R* values are highlighted in bold.

^b $w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 13.0196P]$ where $P = (F_o^2 + 2F_c^2)/3$

S8 Luminescence spectroscopy

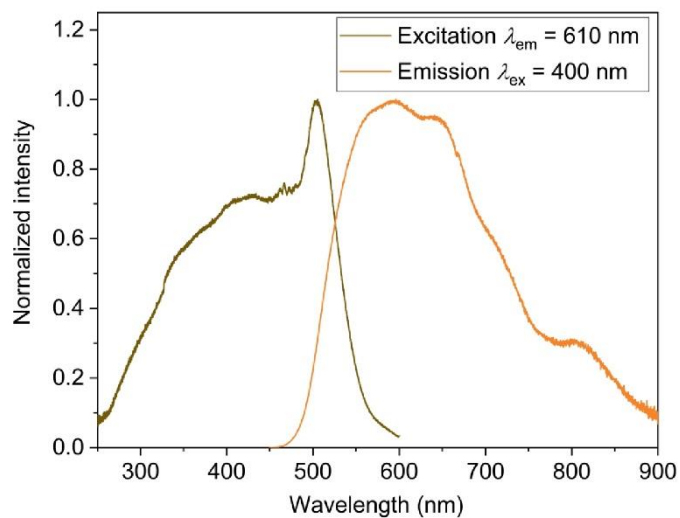


Figure S27. Excitation ($\lambda_{em} = 610$ nm, dark yellow) and emission ($\lambda_{ex} = 400$ nm, orange) spectrum of powdered Zn-PZDB from DEF at room temperature.

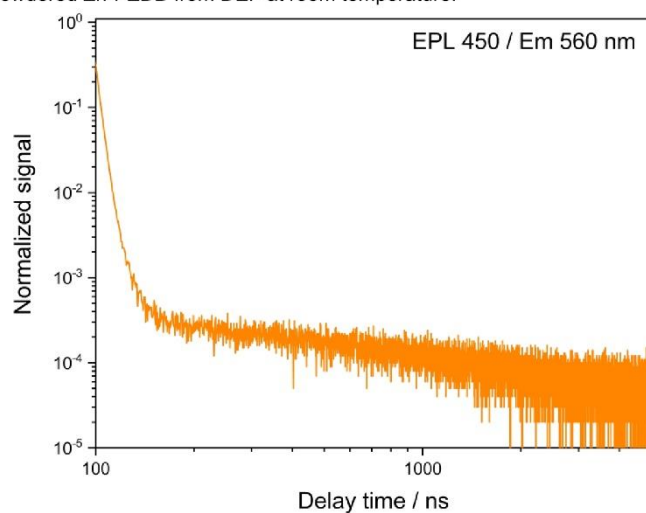


Figure S28. Time-resolved photoluminescence signal ($\lambda_{ex} = 450$ nm, $\lambda_{em} = 560$ nm) of powdered Zn-PZDB from DEF at room temperature.

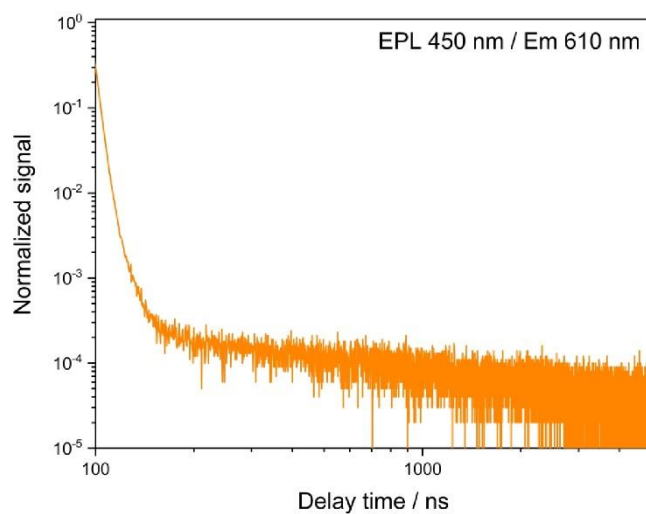


Figure S29. Time-resolved photoluminescence signal ($\lambda_{\text{ex}} = 450 \text{ nm}$, $\lambda_{\text{em}} = 610 \text{ nm}$) of powdered Zn-PZDB from DEF at room temperature.

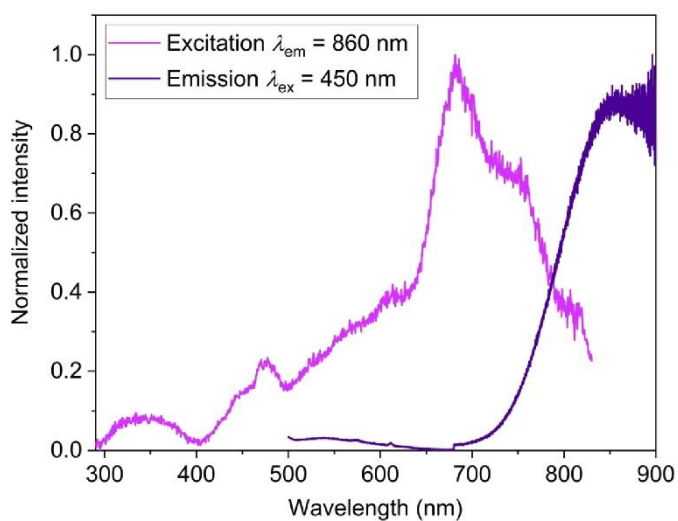


Figure S30. Excitation ($\lambda_{\text{em}} = 860 \text{ nm}$, purple) and emission ($\lambda_{\text{ex}} = 450 \text{ nm}$, violet) spectrum of powdered Co-HPZDB at room temperature.

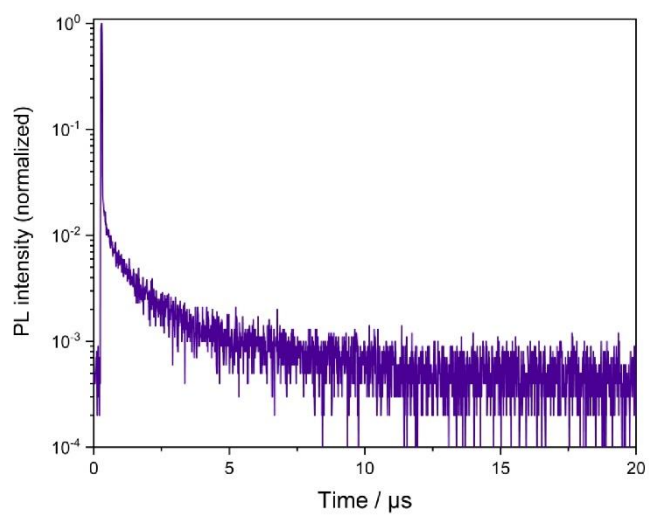


Figure 31. Time-resolved photoluminescence signal ($\lambda_{\text{ex}} = 450 \text{ nm}$, $\lambda_{\text{em}} = 555 \text{ nm}$) of powdered Co-HPZDB at room temperature.

S9 Electrochemical measurements

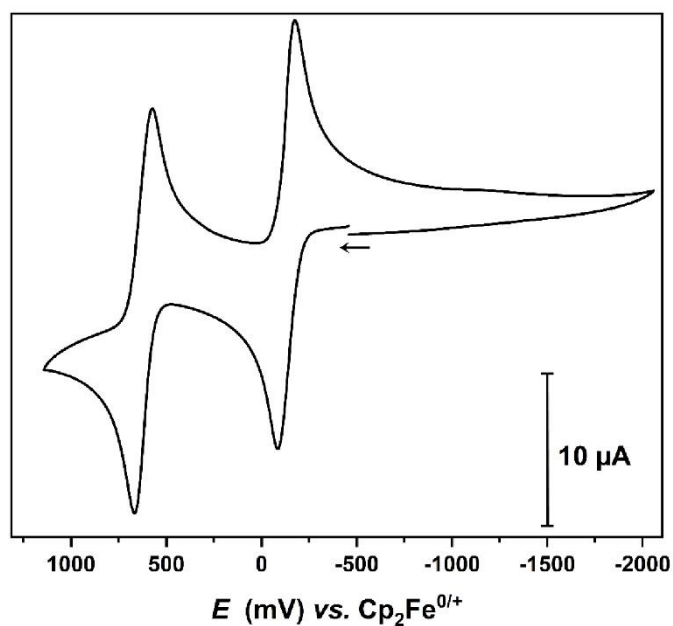


Figure S32. Cyclic voltammogram of Me_2PZDP in $0.1 \text{ mM } n\text{Bu}_4\text{N}^+ \text{PF}_6^-$ in CH_2Cl_2 and at r. t. at a scan rate of 100 mVs^{-1} .

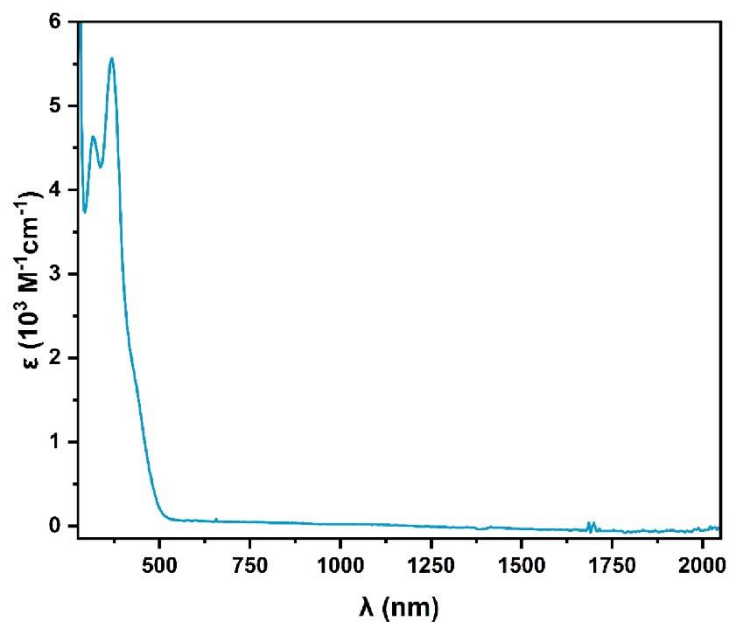


Figure S33. UV-Vis absorption spectrum of Me_2PZDP in CH_2Cl_2 .

S40

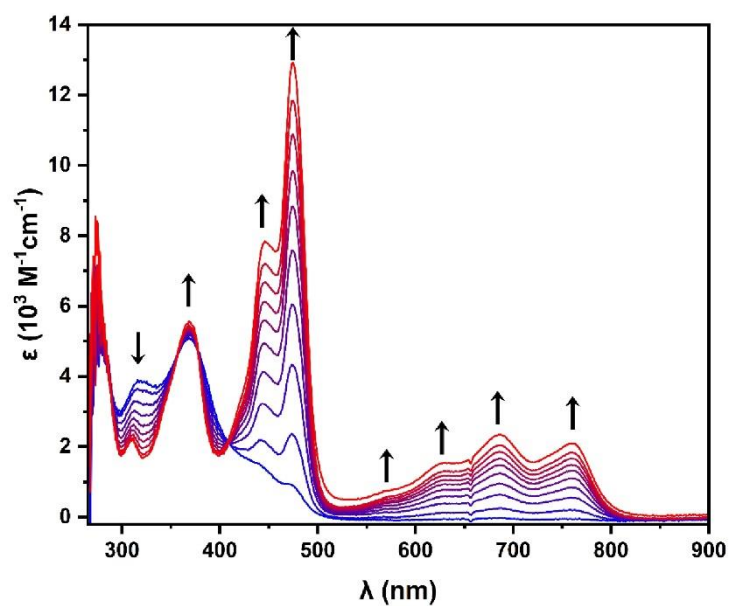


Figure S34. UV-Vis spectroelectrochemistry of Me₂PZDB with oxidation proceeding from blue to red color, measured in CH₂Cl₂ with 0.1 mM ⁿBu₄N⁺PF₆⁻ as supporting electrolyte at r. t.

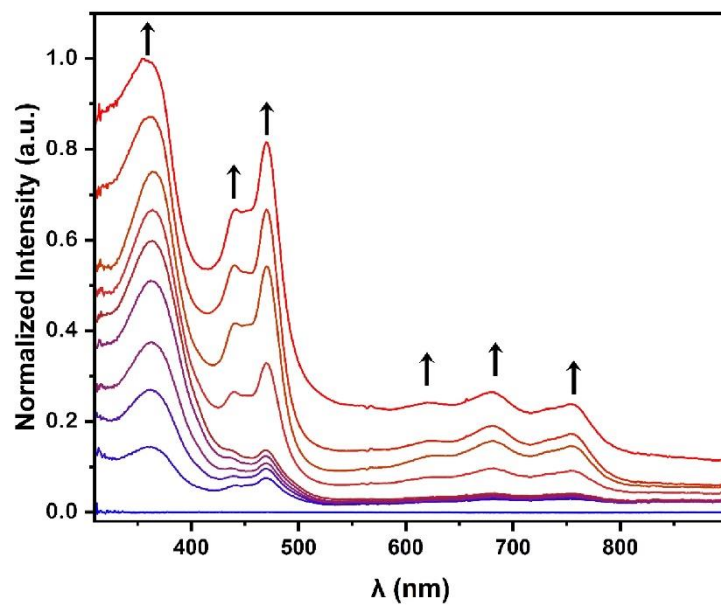


Figure S35. UV-Vis spectroelectrochemistry of H₂PZDB with oxidation proceeding from blue to red color, measured as a paste in ionic liquid applied to an ITO-coated glass plate with an aqueous 1 mM NaNO₃ solution as supporting electrolyte at r. t.

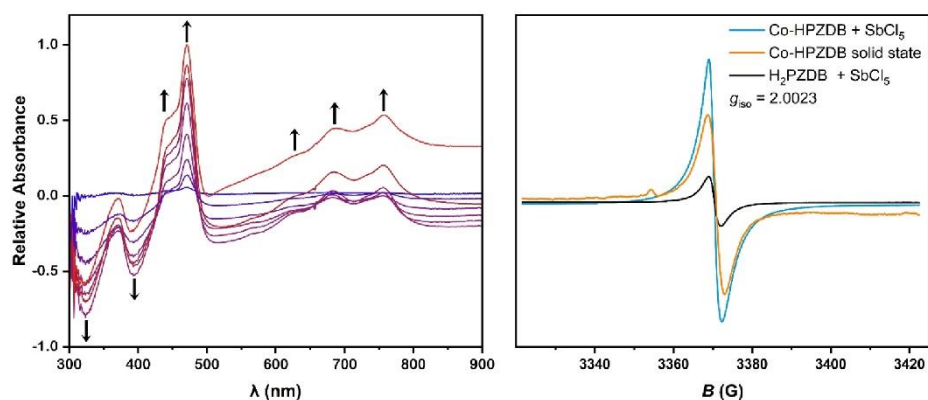


Figure S36. Left: Spectroscopic changes in the UV-Vis absorption spectra during electrolysis of Co-HPZDB with oxidation, measured as a paste in the BMIM⁺ PF₆⁻ ionic liquid applied to an ITO-coated glass plate with an aqueous 1 mmol/L NaNO₃ solution as supporting electrolyte at r. t. Conversion progresses from blue to red line color. Spectroscopic changes with respect to the initial state are indicated by positive/negative absorbance. Right: EPR spectra of H₂PZDB after addition of sub-stoichiometric amounts of SbCl₅ oxidant (black curve), of solid Co-HPZDB after exposure to air (orange curve), and of crystalline Co-HPZDB after treatment with SbCl₅ (blue curve).

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8 Zusammenfassung und Ausblick

Die dargestellten Farbstoff@MOF-Komposite wurden strukturell und hinsichtlich ihrer photophysikalischen Eigenschaften umfassend analysiert. Im Rahmen der Kompositsynthese wurden die beiden Flavinfarbstoffe 10-Methyl-isoalloxazin (MIA) und 6-Fluoro-10-methyl-isoalloxazin (6F-MIA) in die MOFs MIL-53(Al) und MOF-5 eingelagert. Bei MIL-53(Al) (mikrokristallines Pulver) erfolgte die Farbstoffeinlagerung über einen postsynthetischen, diffusionsbasierten Ansatz, bei MOF-5 hingegen erfolgte die Einlagerung über einen *in-situ*-Ansatz. Anschließende spektroskopische Analysen konnten nachweisen, dass sich die photophysikalischen Eigenschaften der Farbstoffe@MOF-Komposite ähnlich verhalten wie die Flavinfarbstoffe in Lösungen. Die Emissionswellenlänge, Abklingzeit sowie die Quantenausbeute bewegen sich dabei in vergleichbaren Größenordnungen, weshalb hier von *festen homogenen Lösungen* gesprochen werden kann.

Der Schwerpunkt der dieser Arbeit lag auf der Darstellung, Charakterisierung und Anwendung von Dihydrophenazin-basierten Leuchtstoffen und Koordinationspolymeren. Ausgangsprodukt war durchgehend der polycyclische Heteroaromat Phenazin, der in einem ersten Syntheseschritt zu Dihydrophenazin reduziert wurde. Das Dihydrophenazin konnte anschließend mit unterschiedlichen Arylhalogeniden im Zuge einer Buchwald-Hartwig-Kupplung zu symmetrischen (TADF-)Emittlern und linearen bifunktionellen (MOF-)Linkern in hohen Ausbeuten umgesetzt werden. Abbildung 16 beschreibt die schematische, konzeptionelle Syntheseroute der neuen Dihydrophenazinderivate.

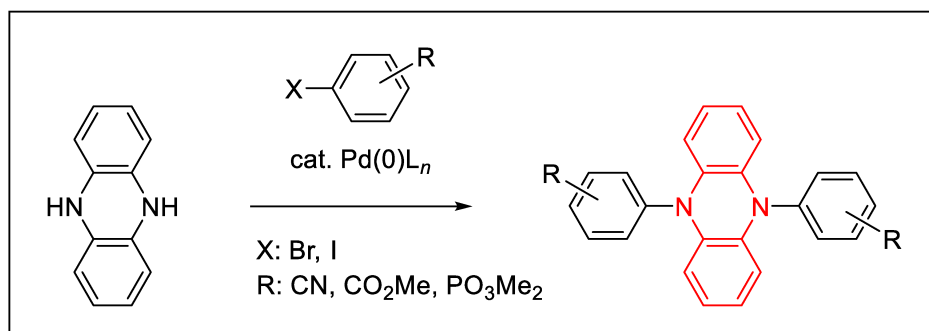


Abbildung 16: Schematische Syntheseroute neuer Dihydrophenazinderivate.

Im Zuge der Promotion konnten folgende Arylbromide erfolgreich zu (TADF-)Emittlern umgesetzt werden (Abbildung 17). Der Dihydrophenazinkern stellt hierbei die Donorgruppe dar, während die beiden Nitrilgruppen die Akzeptorgruppen darstellen. Entsprechend weisen alle (TADF-)Emitter eine Akzeptor-Donor-Akzeptor-Topologie (A-D-A) auf.

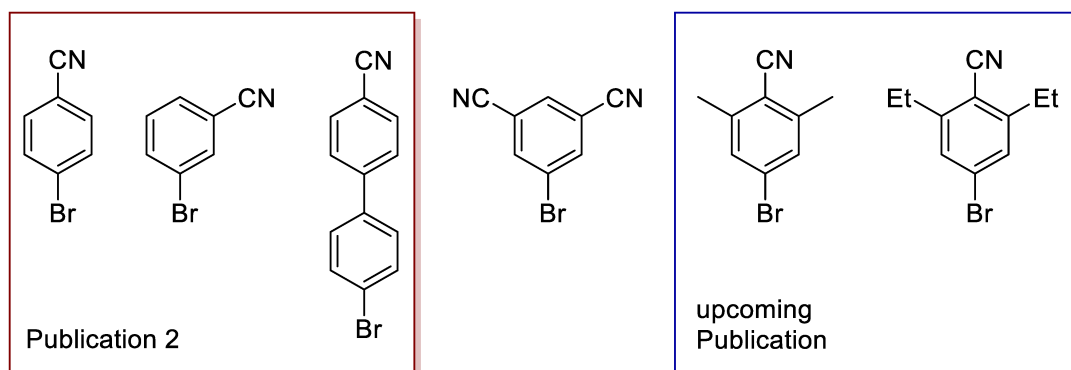


Abbildung 17: Übersicht erfolgreich umgesetzter Arylbromide zu potentiellen TADF-Emittern.

Die zweite Veröffentlichung beschreibt die Darstellung und Charakterisierung neuer (TADF)-Emitter auf Basis des Dihydrophenazinkerns. Aufbauend auf dem literaturbekannten TADF-Farbstoff 4,4'-(Phenazine-5,10-diyl)dibenzonitril (pBN) wurden zwei weitere Emitter (3,3'-(Phenazin-5,10-diyl)dibenzonitril (mBN) und 4',4'''-(Phenazin-5,10-diyl)bis([1,1'-biphenyl]-4-carbonitril) (BPN) dargestellt und hinsichtlich ihrer photophysikalischen Eigenschaften analysiert und miteinander verglichen. Als Feststoff weist lediglich der literaturbekannte Emitter pBN eindeutige TADF-Eigenschaften auf, mBN verfügt über schwach ausgeprägte TADF-Eigenschaften, während BPN einen herkömmlichen fluoreszenten Emitter darstellt. Dies kann auf die orbitale Überlappung der Phenazindiyl- und Benzonitril-Einheiten in pBN und mBN zurückgeführt werden, die lediglich in pBN effizient funktioniert. Dies verdeutlicht, dass selbst geringfügige Änderungen in der Molekülstruktur der Dihydrophenazine einen signifikanten Einfluss auf ihre TADF-Eigenschaften haben können.

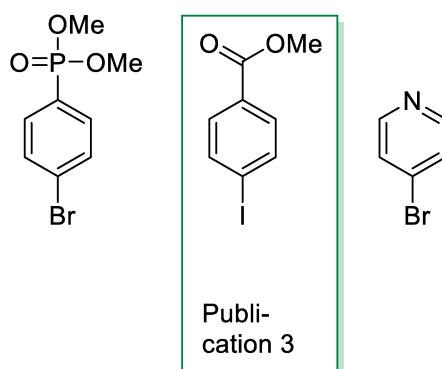


Abbildung 18: Übersicht erfolgreich umgesetzter Arylhalogenide zu bifunktionellen Linkern.

Die dritte Veröffentlichung baut auf dem vorgestellten Konzept (Abbildung 16) auf und beschreibt die Darstellung und Charakterisierung von linearen, bifunktionellen Linkern für neuartige Koordinationspolymere und MOFs. Die Nitrilgruppen des 4'-(Phenazine-5,10-diyl)dibenzonitrils (später der entsprechende Methylester) wurden in einem weiteren Syntheseschritt zu Carbonsäuren hydrolysiert. Die dargestellte Dicarbonsäure konnte

anschließend mit Kobalt(II)-nitrat-Hexahydrat zu einem einzigartigen Koordinationspolymer und mit Zink(II)-nitrat-Hexahydrat zu neuartigen MOFs und Koordinationspolymeren umgesetzt werden.

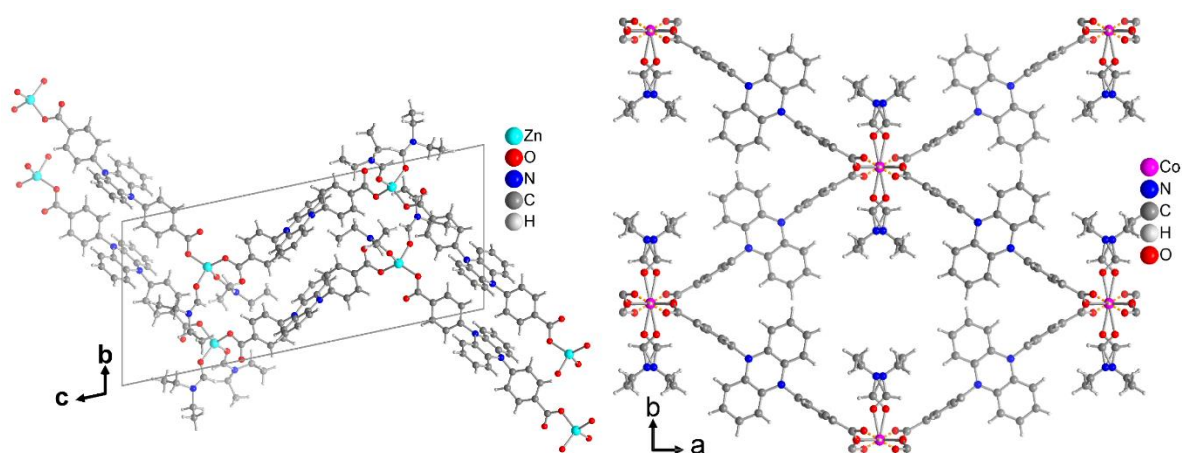


Abbildung 19: Die dargestellten Koordinationspolymere $[Zn(PZDB)(DEF)_2]_n$ (Zn-PZDB, links) und $[Co(HPZDB)_2(DEF)_2]_n$ (Co-HPZDB, rechts) (H_2PZDB = 4,4'-(Phenazin-5,10-diyl)dibenzoesäure, DEF = *N,N*-Diethylformamid).

Darüber hinaus konnten auch lineare, symmetrische Linker mit Phosphorsäureester und Pyridingruppen als *binding groups* dargestellt werden.

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