

Azol-basierte Koordinationspolymere und Metall-organische
Gerüstverbindungen – Strukturanalyse und Eigenschaften

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Ich versichere an Eides statt, dass die vorliegende Dissertation von mir selbstständig und ohne unzulässige fremde Hilfe unter Beachtung der „Grundsätze zur Sicherung guter wissenschaftlicher Praxis“ an der Heinrich-Heine-Universität Düsseldorf erstellt worden ist.

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„The universe is only as large as our perception of it. When we cultivate our awareness, we are expanding the universe. This expands the scope, not just of the material at our disposal to create from, but of the life we get to live.“

– Rick Rubin, The Creative Act: A Way of Being

I. Kurzzusammenfassung

In der vorliegenden Arbeit wurde sowohl der Einfluss von Templat-Effekten hinsichtlich der Struktur motive (erster Teil) als auch der Einfluss der $\text{-C}\equiv\text{C-}$ Dreifachbindung auf die Sorptionseigenschaften von Pyrazolat-basierten Metall-organischen Gerüstverbindungen (zweiter Teil) untersucht.

Im ersten Teil wurden sieben neue Koordinationsnetzwerke $[\text{Fe}(\text{tbbt})_3](\text{BF}_4)_2$ (**1**), $[\text{Co}(\text{tbbt})_3](\text{BF}_4)_2$ (**2**), $[\text{Fe}(\text{tbbt})_3](\text{ClO}_4)_2$ (**3**), $[\text{Co}(\text{tbbt})_3](\text{ClO}_4)_2$ (**4**), $[\text{Fe}(\text{NCS})_2(\text{tbbt})_2]$ (**5**), $[\text{Co}(\text{NCS})_2(\text{tbbt})_2]$ (**6**) und $[\text{Fe}(\text{H}_2\text{O})_2(\text{tbbt})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (**7**) mit dem Linker 1,1'-(*trans*-2-buten-1,4-diyl)bis-1,2,4-triazol (tbbt) synthetisiert. Die Verbindungen **1–4** bestehen aus drei sich gegenseitig durchdringenden, symmetriebezogenen 3D-Netzwerken, bei dem jedes einzelne Netzwerk ein primitives, nahezu kubisches Gitter (**pcu**) darstellt. In **5** und **6** liegen zweidimensionalen **sql**-Schichten vor, welche von eindimensionalen Ketten durchdrungen werden. In **7** werden nicht-interpenetrierte, zweidimensionale **sql**-Schichten ausgebildet. Die Interpenetration der Verbindungen **1–6** wird über Wasserstoffbrückenbindungen zwischen den Anionen und dem tbbt-Linker gesteuert. Dies lässt auf einen Templat-Effekt der entsprechenden (nicht-)koordinierten Anionen als Grund für die Interpenetration schließen. In **7** stabilisieren die Wasserstoffbrückenbindungen der Bromid-Ionen, der Aqua-Liganden und der Kristallwassermoleküle die Struktur. Es ist offensichtlich, dass die (nicht-)koordinierten Anionen eine wesentliche Rolle bei der Bildung der Netzwerke spielen und die Interpenetration steuern.

Im zweiten Teil konnte in Kombination mit dem Linker 1,2-bis(1*H*-pyrazol-4-yl)ethin (H_2bpe) die Struktur von $[\text{Zn}(\text{bpe})] \cdot 1.8\text{DMF}$ (HHUD-5), dem orthorhombischen Polymorph des zuvor veröffentlichten tetraedrischen $[\text{Zn}(\text{bpe})] \cdot 1.2\text{DMF}$, und die Struktur von $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ (HHUD-6), einem neuen Mitglied der isoretikulären Serie $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2\text{L}_6]$ (L = Bis-pyrazolat oder Carboxylat-Pyrazolat), aufgeklärt werden. Die BET-Oberfläche des Zn-MOFs liegt bei $2135 \text{ m}^2/\text{g}$ und die des Ni-MOFs bei $1415 \text{ m}^2/\text{g}$. Der Vergleich mit den CO_2 -, CH_4 - und H_2 -Aufnahmen beider MOFs mit den isoretikulären MOFs mit dem leicht längeren 4,4'-(1,4-phenylen)bis(pyrazolat) Linker, welcher eine Phenyleneinheit anstelle der Acetyleneinheit aufweist, zeigt einen vermeintlichen Vorteil der $\text{-C}\equiv\text{C-}$ Dreifachbindung, welcher sich durch höhere Gasaufnahmen auszeichnet. Neben Dampfsorptionsexperimenten mit volatilen organischen Verbindungen wurde die Stabilität beider MOFs gegenüber Wasser im Rahmen von Wasserdampfsorption und weiteren Stabilitätstests untersucht und hierbei die Hydrophobie des bpe^{2-} -Linkers bestätigt.

II. Abstract

In the present work, both the influence of template effects on the structure motifs (first part) and the influence of the $\text{-C}\equiv\text{C-}$ triple bond on the sorption properties of pyrazolate-based metal-organic frameworks (second part) were investigated.

In the first part, seven new coordination networks $[\text{Fe}(\text{tbbt})_3](\text{BF}_4)_2$ (**1**), $[\text{Co}(\text{tbbt})_3](\text{BF}_4)_2$ (**2**), $[\text{Fe}(\text{tbbt})_3](\text{ClO}_4)_2$ (**3**), $[\text{Co}(\text{tbbt})_3](\text{ClO}_4)_2$ (**4**), $[\text{Fe}(\text{NCS})_2(\text{tbbt})_2]$ (**5**), $[\text{Co}(\text{NCS})_2(\text{tbbt})_2]$ (**6**) and $[\text{Fe}(\text{H}_2\text{O})_2(\text{tbbt})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (**7**) were synthesized with the linker 1,1'-(*trans*-2-butene-1,4-diyl)bis-1,2,4-triazole (tbbt). Compounds **1–4** consist of three interpenetrating, symmetry-related 3D networks in which each individual network represents a primitive nearly cubic lattice (**pcu**). In **5** and **6** there are two-dimensional **sql**-layers, which are interpenetrated by one-dimensional chains. In **7**, non-interpenetrated, two-dimensional **sql**-layers are formed. The interpenetration of compounds **1–6** is controlled by hydrogen bonds between the anions and the tbbt linker. This suggests a template effect of the corresponding (non-)coordinated anions as the reason for the interpenetration. In **7**, the hydrogen bonds of the bromide ions, the aqua ligands and the crystal water molecules stabilize the structure. It is obvious that the (non-)coordinated anions play an essential role in the formation of the networks and control the interpenetration.

In the second part, in combination with the linker 1,2-bis(1*H*-pyrazol-4-yl)ethyne (H_2bpe), the structure of $[\text{Zn}(\text{bpe})] \cdot 1.8\text{DMF}$ (HHUD-5), the orthorhombic polymorph of the previously published tetrahedral $[\text{Zn}(\text{bpe})] \cdot 1.2\text{DMF}$, and the structure of $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ (HHUD-6), a new member of the isorecticular series $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2\text{L}_6]$ (L = bis-pyrazolate or carboxylate-pyrazolate), was elucidated. The BET surface area is $2135 \text{ m}^2/\text{g}$ for the Zn-MOF and $1415 \text{ m}^2/\text{g}$ for the Ni-MOF. The comparison of the CO_2 , CH_4 , H_2 uptakes of both MOFs with the isorecticular MOFs with the slightly longer 4,4'-(1,4-phenylene)bis(pyrazolate) linker, which has a phenylene unit instead of the acetylene unit, suggests an advantage of the $\text{-C}\equiv\text{C-}$ triple bond, which is characterized by higher gas uptakes. In addition to vapor sorption experiments with volatile organic compounds, the stability of both MOFs towards water was investigated by means of water vapor sorption and further stability tests, which also show a hydrophobicity of the bpe^{2-} linker.

III. Publikationsliste

Dustin N. Jordan, Tim Müller, Robert Oestreich, Till Strothmann, Istvan Boldog, Christoph Janiak:

“Metal–organic Azolate Frameworks with an Acetylene-bis-pyrazolate Linker: Assessing the Role of the Triple-bond Spacer in Gas and Vapor Sorption”

Cryst. Growth Des. **2024**, *24*, 3837–3854. DOI: 10.1021/acs.cgd.4c00165

Dustin N. Jordan, Patrick G. Straßburg, Dennis Woschko, Luca M. Carrella, Laure P. Cuignet, Katharina Eickmeier, Richard Dronskowski, Yann Garcia, Eva Rentschler, Christoph Janiak:

“Interpenetration Phenomena via Anion Template Effects in Fe(II) and Co(II) Coordination Networks with a Bis-(1,2,4-triazole) Ligand”

Polymers **2023**, *15*, 3286. DOI: 10.3390/polym15153286

Alicia Marco, Pezhman Ashoo, Samanta Hernández-García, Pedro Martínez-Rodríguez, Natalia Cutillas, Annette Vollrath, Dustin Jordan, Christoph Janiak, Fernando Gandía-Herrero, José Ruiz:

“Novel Re(I) complexes as potential selective theranostic agents in cancer cells and in vivo in *Caenorhabditis elegans* tumoral strains”

J. Med. Chem. **2024**, DOI: 10.1021/acs.jmedchem.3c01869

Aysenur Limon, Dustin N. Jordan, Till Strothmann, Laure P. Cuignet, Yann Garcia, Christoph Janiak:

“Single-Crystal Structure Analysis of Three Novel Iron(II) Coordination Polymers with Bridging 1,3,5-Tris((1*H*-1,2,4-triazol-1-yl)methyl)benzene”

Crystals **2023**, *13*, 1574. DOI: 10.3390/cryst13111574

Christian Jansen, Niels Tannert, Dirk Lenzen, Marco Bengsch, Simon Millan, Anna Goldman, Dustin N. Jordan, Linda Sondermann, Norbert Stock, Christoph Janiak:

“Unravelling gas sorption in the aluminum metal-organic framework CAU-23: CO₂, H₂, CH₄, SO₂ sorption isotherms, enthalpy of adsorption and mixed-adsorptive calculations”

Z. Anorg. Allg. Chem. **2022**, *648*, e202200170. DOI: 10.1002/zaac.202200170

IV. Inhaltsverzeichnis

I. Kurzzusammenfassung.....	I
II. Abstract.....	II
III. Publikationsliste	III
IV. Inhaltsverzeichnis	IV
V. Abkürzungsverzeichnis	V
1. Einleitung.....	1
1.1 Koordinationspolymere	1
1.1.1 Triazol-basierte Koordinationspolymere.....	6
1.1.2 Spin-Crossover	7
1.2 Metall-organische Gerüstverbindungen	12
1.2.1 Metall-azolat Gerüstverbindungen	15
1.2.2 Adsorptionsprozesse und Isothermenprofile	17
2. Zielsetzung und Motivation	22
3. Kumulativer Teil.....	23
3.1 Interpenetration Phenomena via Anion Template Effects in Fe(II) and Co(II) Coordination Networks with a Bis-(1,2,4-triazole) Ligand.....	23
3.2 Metal-organic Azolate Frameworks with an Acetylene-bis-pyrazolate Linker: Assessing the Role of the Triple-bond Spacer in Gas and Vapor Sorption.....	68
3.3 Beiträge an weiteren Veröffentlichungen.....	127
4. Zusammenfassung.....	130
5. Literaturverzeichnis	142

V. Abkürzungsverzeichnis

ADI	Adiponitril
Alfum	Aluminiumfumarat
bdc	1,4-Benzoldicarboxylat
BET	Brunauer, Emmett, Teller
BIPY	4,4'-Bipyridin
Boc ₂ bpe	1,2-Bis(1-boc-pyrazol-4-yl)ethin
bspw.	Beispielsweise
bzw.	Beziehungsweise
CALF	Calgary Framework (dt. Calgary Gerüstverbindung)
CAU	Christian-Albrechts-Universität zu Kiel
CCDC	Cambridge Crystallographic Data Center (dt. Cambridge Datenzentrum für Kristallographie)
CFSE	Crystal field stabilization energy (dt. Kristallfeldstabilisierungsenergie)
COF	Covalent-organic framework (dt. Kovalent-organische Gerüstverbindung)
Di-Boc	Di- <i>tert</i> -butyl dicarbonat
DMF	<i>N,N</i> -Dimethylformamid
dt.	Deutsch
et al.	Et alia (dt. und andere)
ggf.	Gegebenenfalls
H ₂ bpb	1,4-Bis(1 <i>H</i> -pyrazol-4-yl)benzol
H ₂ bpe	1,2-Bis(1 <i>H</i> -pyrazol-4-yl)ethin
HHUD	Heinrich-Heine-Universität Düsseldorf
HoA	Heat of adsorption (dt. Adsorptionswärme)
HS	High-spin
HSAB	Hard and soft acids and bases (dt. Harte und weiche Säuren und Basen)
HTFA	Trifluoressigsäure
IAST	Ideal adsorbed solution theory (dt. Theorie der idealen adsorbierten Lösung)
inkl.	Inklusive

IUPAC	International Union of Pure and Applied Chemistry (dt. Internationale Union für reine und angewandte Chemie)
LS	Low-spin
MAF	Metal-azolate framework (dt. Metall-azolat Gerüstverbindung)
MIL	Matériaux de l'Institut Lavoisier (dt. Materialien des Lavoisier-Instituts)
MOF	Metal-organic framework (dt. Metall-organische Gerüstverbindung)
OAc	Acetat
pz	Pyrazolat
Ref.	Referenz
SBB	Supramolecular building blocks (dt. Supramolekulare Baueinheiten)
SBL	Supramolecular building layers (dt. Supramolekulare Schichten)
SBU	Secondary building unit (dt. Sekundäre Baueinheit)
SCO	Spin-Crossover
SCXRD	Single crystal X-ray diffraction (dt. Einkristall-Röntgendiffraktometrie)
tbbt	1,1'-(<i>Trans</i> -2-buten-1,4-diyl)bis-1,2,4-triazol
TCTPM	4,4',4'',4'''-Tetracyanotetraphenylmethan
UiO	Universitetet i Oslo (dt. Universität von Oslo)
VOC	Volatile organic compounds (dt. volatile organische Verbindungen)
z.B.	Zum Beispiel
ZIF	Zeolitic-imidazolate framework (dt. Zeolitisch-imidazolate Gerüstverbindung)

1. Einleitung

1.1 Koordinationspolymere

Während bereits zu Beginn des 18. Jahrhunderts in Berlin zufällig das erste, heute unter dem Namen „Berliner Blau“ bekannte Koordinationspolymer $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ synthetisiert wurde, liegt die Basis für die Entwicklung der Koordinationspolymere hin zu einer umfangreich analysierten Stoffgruppe in den gegen Ende des 19. Jahrhunderts gemachten Entdeckungen Alfred Werners, dem Begründer der Komplexchemie.¹⁻⁴ Gemäß der Definition der *International Union of Pure and Applied Chemistry* (IUPAC, dt. Internationale Union für reine und angewandte Chemie) stellen Koordinationspolymere alle Koordinationsverbindungen dar, welche sich aus wiederholenden Koordinationseinheiten bestehend in eine, zwei oder drei Dimensionen erstrecken.⁵ Koordinationspolymere enthalten einerseits Metallkationen, welche als Knotenpunkte fungieren, und andererseits mehrzählige Linkermoleküle, welche über mindestens zwei freie Koordinationsstellen verfügen. Die Metallkationen bzw. Metall-Cluster, welche auch als *secondary building units* (SBUs, dt. sekundäre Baueinheiten) bezeichnet werden, werden mit Hilfe der multidentaten Linker über deren freie Koordinationsstellen verbrückt (Abbildung 1).⁶⁻⁹

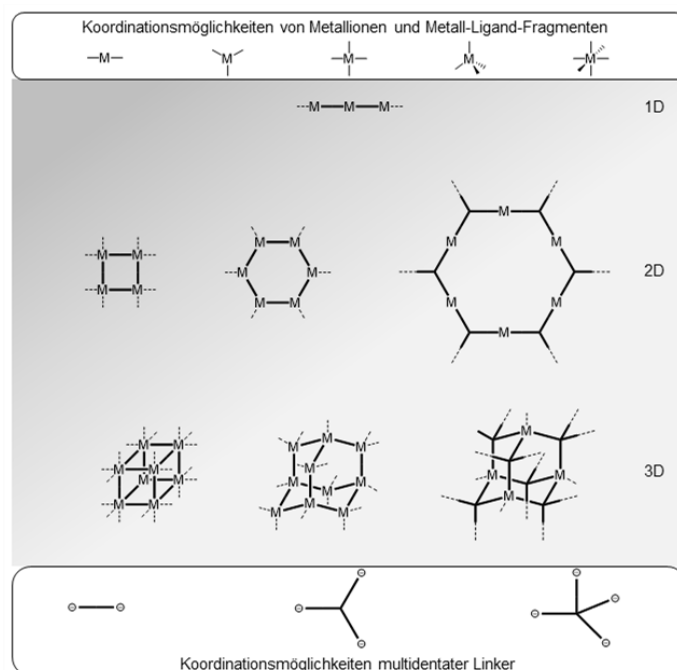


Abbildung 1. Schematische Abbildung von ein-, zwei und dreidimensionalen Koordinationspolymeren bestehend aus Metallionen und multidentaten, verbrückenden Linkermolekülen. Abbildung mit Genehmigung von Ref. 7 reproduziert und ins Deutsche übersetzt. ©Copyright 2010, The Royal Society of Chemistry.

Der Begriff *Koordinationspolymer* konnte bis ins Jahr 1916 zurückverfolgt werden, auch wenn bereits die Hofmann Clathrate (1897) als Vorläufer bekannt waren. Obwohl die ersten Koordinationspolymere bereits von Saito *et al.* (1959) veröffentlicht wurden,^{3,10,11} dauerte es bis in die 1990er Jahre für das Wachstum des Forschungsfeldes (Abbildung 2). Ursache hierfür waren die grundlegenden Veröffentlichungen von Robson und Hoskins, welche erstmalig unter Verwendung von rationalen Designprinzipien dreidimensionale, kationische Netzwerke, wie $[\text{Cu}^{\text{I}}(\text{TCTPM})](\text{BF}_4) \cdot x\text{C}_6\text{H}_5\text{NO}_2$ (TCTPM: 4,4',4'',4'''-Tetracyanotetraphenylmethan), durch die Verknüpfung tetra- oder oktaedrischer Zentren synthetisiert haben.^{12,13} Darauf aufbauend konnten sowohl Kitagawa *et al.* als auch Yaghi *et al.* zeigen, dass diese topologischen Designprinzipien systematisch für die Synthese ganzer Materialklassen mit spezifischen Strukturen und Eigenschaften verwendet werden können.^{14,15} Diese Erkenntnis führte letztendlich dazu, dass Yaghi *et al.* den Aufbau von (porösen) Netzwerkstrukturen über die gezielte Verknüpfung molekularer Bausteine, wie Metall-Cluster und organischen Liganden, durch gerichtete Bindungen in dem Konzept der „retikulären Chemie“ zusammengefasst hat.^{8,16} Im Zuge dessen wurde der Begriff *metal-organic frameworks* (MOFs, dt. Metall-organische Gerüstverbindungen) erstmalig im Jahre 1995 von Yaghi *et al.* für die Verbindungen $\text{Cu}(\text{BIPY})_{1.5} \cdot \text{NO}_3(\text{H}_2\text{O})_{1.5}$ (BIPY: 4,4'-Bipyridin) und $\text{CoC}_6\text{H}_3(\text{COOH}_{1/3})_3(\text{NC}_5\text{H}_5)_2 \cdot 2/3\text{NC}_5\text{H}_5$ verwendet und sollte zunächst lediglich die grundlegende Zusammensetzung aus Metallionen und organischen Liganden beschreiben. Seither hat sich dieser Begriff aber insbesondere für rigide, poröse Strukturen etabliert.^{17–19} Unabhängig von der Porosität lassen sich Koordinationspolymere in einer Vielzahl von potentiellen Anwendungsmöglichkeiten wiederfinden (Abbildung 3).²⁰

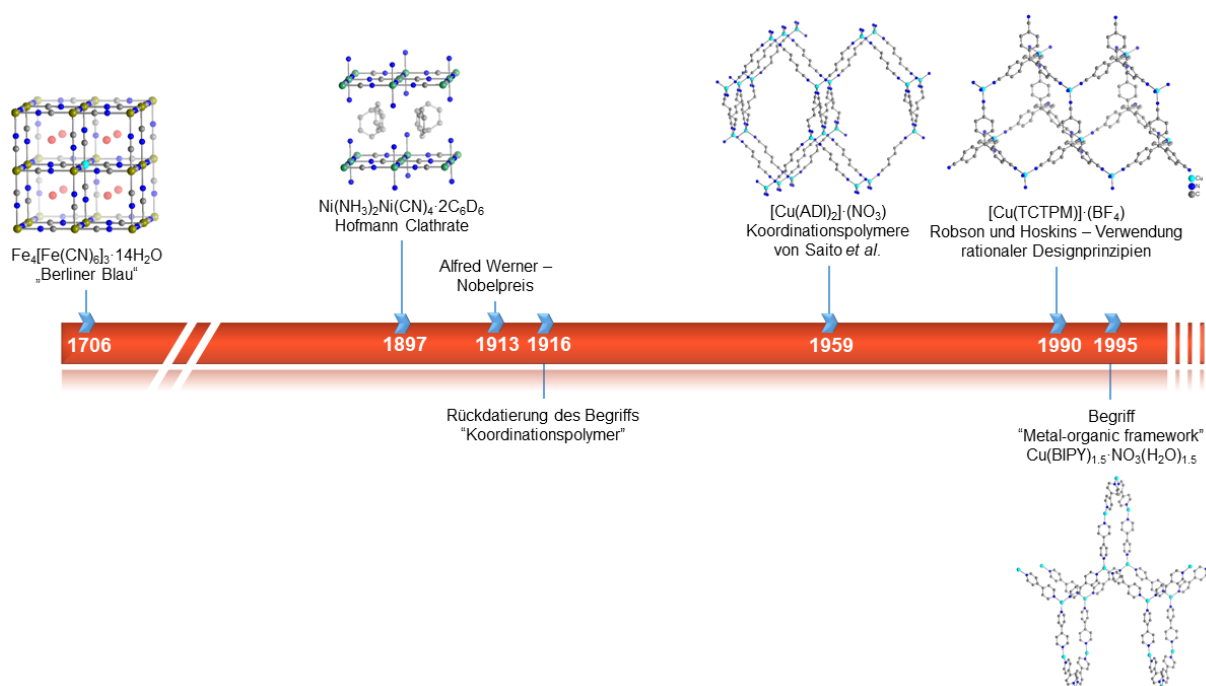


Abbildung 2. Historische Einordnung der Koordinationspolymere. Die Kristallstrukturdaten wurden aus der CCDC (*Cambridge Crystallographic Data Center*) Datenbank mit den folgenden Codes entnommen: $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$: ICSD 1277²¹; $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{D}_6$: HEMJIS²²; $[\text{Cu}(\text{ADI})_2] \cdot (\text{NO}_3)$ (ADI: Adiponitril): ADINCUI¹¹; $[\text{Cu}(\text{TCTPM})] \cdot (\text{BF}_4)$ (TCTPM: 4,4',4'',4'''-Tetracyanotetraphenylmethan): JARMEU10¹²; $\text{Cu}(\text{BIPY})_{1.5} \cdot \text{NO}_3(\text{H}_2\text{O})_{1.5}$ (BIPY: 4,4'-bipyridin): ZIBRAD¹⁷. Wasserstoffatome und Gastmoleküle bei den komplexeren Strukturen wurden aus Übersichtlichkeitsgründen nicht dargestellt (C: grau, N: blau, O: rot, Fe: oliv, Ni: grün, Cu: hellblau).

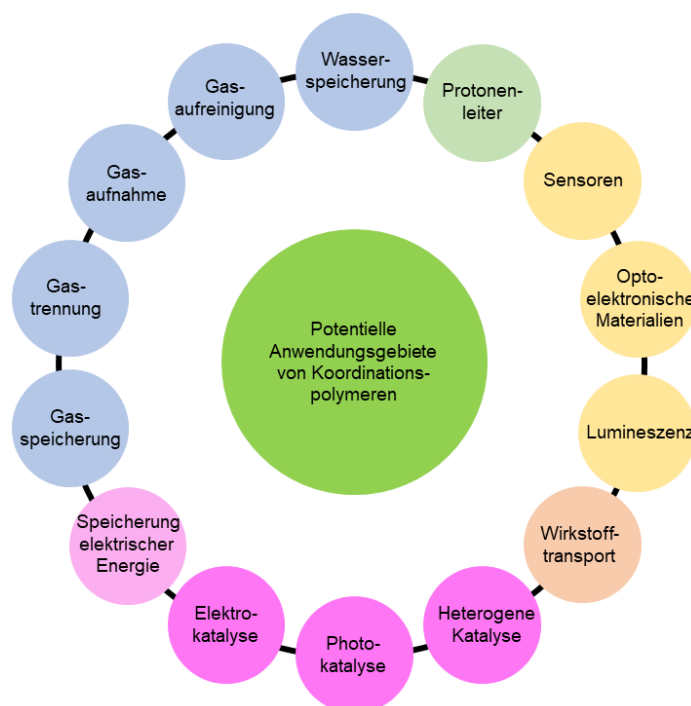


Abbildung 3. Übersicht von ausgewählten potentiellen Anwendungsgebieten von Koordinationspolymeren. Abbildung mit Genehmigung von Ref. 20 reproduziert und ins Deutsche übersetzt. ©Copyright 2017, The Royal Society of Chemistry.

Sowohl die supramolekulare Chemie, in welcher über spontane Selbstorganisationsprozesse gezielt größere Strukturen aufgebaut werden sollen,²³ als auch das *crystal engineering*, in welchem Verständnis über die Anordnung von Molekülen in Kristallen erlangt werden soll,²⁴ greifen auf eine Bandbreite nicht-kovalenter, intermolekularer Wechselwirkungen zurück, um das gemeinsame Ziel, neue Materialien mit spezifischen Eigenschaften herzustellen zu erreichen.^{1,25,26} Eine Möglichkeit diese gezielten Strukturen auszubilden liegt in der Verwendung von neutralen oder ionischen Verbindungen (Template), welche den Aufbau über intermolekulare Wechselwirkungen, wie z.B. koordinative Bindungen, Wasserstoffbrückenbindungen, π - π -stacking oder $X-H\cdots\pi$ -Wechselwirkungen, organisieren und ggf. sogar aus dem Produkt entfernt werden können. Diese Organisation des Strukturaufbaus über Template wird auch als Templat-Effekt bezeichnet.²⁷⁻³⁰

Während der Templat-Effekt von neutralen Lösungsmittelmolekülen, Kationen sowie Anionen gut dokumentiert ist, ist aufgrund weniger systematischer Arbeiten das Verständnis der Beeinflussung des Selbstorganisationsprozesses durch Template und deren gezielte Nutzung relativ gering.^{25,28,31-33}

Dass Template einen Einfluss auf die Strukturen haben, haben Dunbar *et al.* anschaulich verdeutlicht, indem diese durch die Auswahl der Anionen unterschiedliche Geometrien für Cyclophan-Komplexe aus $[Ni(CH_3CN)_6]X_2$ ($X = NO_3^-$, ClO_4^- , BF_4^- , SbF_6^-) und 3,6-Di(2-pyridyl)-1,2,4,5-Tetrazin erhalten haben (Abbildung 4).³⁴

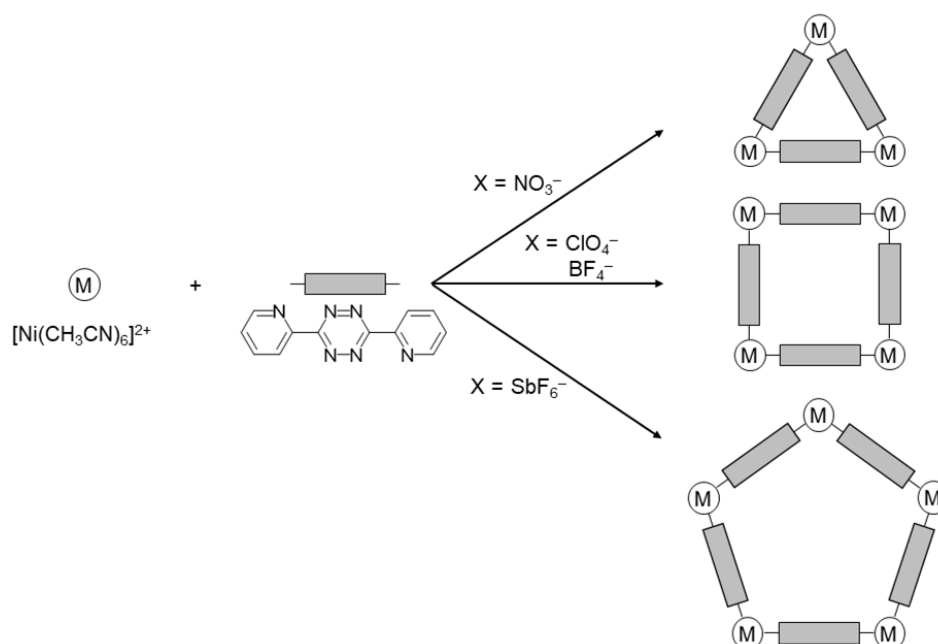


Abbildung 4. Schematische Darstellung des Einflusses unterschiedlicher Anionen auf die Struktur für die Reaktion von $[Ni(CH_3CN)_6]X_2$ mit 3,6-Di(2-pyridyl)-1,2,4,5-tetrazin aus der Arbeit von Dunbar *et al.*³⁴ Abbildung wurde mit Genehmigung von Ref. 30 reproduziert. ©Copyright 2006, Elsevier B.V.

Wenn Strukturen erhalten werden, ist es unausweichlich diese auch möglichst einfach beschreiben zu können. Während für diskrete Moleküle das Konzept zur Beschreibung der Kristallstrukturen als (Kugel-)Packungen der einen Art von Atomen, bei welchen andersartige Atome die Hohlräume der Struktur besetzen, verwendet wird, kann dieses Konzept auf theoretisch unendliche Strukturen nicht ausgeweitet werden.^{19,35} Um dennoch die Strukturen beschreiben zu können, wird in diesen Fällen auf das Konzept der Topologie zurückgegriffen. Während dieses Konzept die Strukturen erheblich vereinfacht, indem lediglich die Verknüpfungen zwischen den Bestandteilen und nicht ihre chemische Natur berücksichtigt wird, ermöglicht dieses Konzept auch das sogenannte *reverse engineering*, also das Konstruieren neuer Materialien auf Basis vorheriger Erkenntnisse.^{16,36–38}

Um die Topologie bestimmen zu können, müssen zunächst die Baueinheiten, welche die Knoten und Kanten darstellen, identifiziert werden. In Koordinationspolymeren sind dies typischerweise die anorganischen SBUs und die Linker, wobei auch größere Strukturfragmente als Baueinheiten verwendet werden können. Kanten bilden jeweils nur zwei Verknüpfungen aus, während Knotenpunkte Baueinheiten mit drei oder mehr Verbindungen darstellen. Die Konnektivität der Knoten mit x Verknüpfungen wird auch mit der Kurzschreibweise x -c (x -connected, dt. x -verknüpft) dargestellt.¹⁹ Die Identifikation der Topologie kann zusätzlich erschwert werden, wenn es zu Interpenetrationsphänomenen kommt. Interpenetration tritt auf, wenn zwei oder mehr unabhängige polymere Netzwerke ohne direkte Verbindungen, topologisch nur durch das Aufspalten von Bindungen separiert werden können.³⁹ In diesen Fällen werden die Strukturfragmente der einzelnen unabhängigen Netzwerke topologisch untersucht. Eine Vielzahl an Topologien, deren Bezeichnung mithilfe eines Drei-Buchstabencodes abgekürzt werden, wurden anhand von natürlichen Materialien, wie z.B. dem Diamanten (**dia**) oder Platin(II)sulfid (**pts**),⁴⁰ abgeleitet. Neueren Topologien wird ein eigener Code basierend auf dem Materialnamen oder einer spezifischen Konnektivität zugeteilt.⁴¹

Der supramolekulare Schichten-Ansatz (*supramolecular building layers*, SBL-Ansatz) beschreibt die Topologien anhand zweidimensionaler Schichten. Diesem SBL-Ansatz liegen fünf kantentransitive, periodische, zweidimensionale Schichten zu Grunde. Hervorzuheben sind hierbei die häufigsten Vertreter, die *square-lattice* (**sql**) und die *honeycomb* (**hcb**) Topologie, welche in etwa zwei Dritteln aller Fälle auftreten (Abbildung 5).⁴³ Auch dreidimensionale Strukturen können über den SBL-Ansatz beschrieben werden, indem diese als verbrückte zweidimensionale Schichten interpretiert werden. Seki *et al.* gehörten zu den Vorreitern, welche gezielt Kupfer(II)-terephthalat-basierte **sql**-Schichten an den axialen

Positionen mit Triethylendiamin zu dreidimensionalen Netzwerken verknüpft haben.⁴⁴ Im Rahmen des supramolekularen Baueinheiten-Ansatzes (*supramolecular building blocks*, SBB-Ansatz), welcher die Topologien anhand dreidimensionaler Strukturen beschreibt, können diese verknüpften **sql**-Schichten auch als *primitive cubic net* (**pcu**) Topologie, dem häufigsten Topologievertreter des SBB-Ansatzes, bezeichnet werden.^{42,43} Eine der zahlreichen weiteren Topologien im SBB-Ansatz stellt die *face-centered cubic lattice* (**fcu**) Topologie dar. Ein Wechsel von 6-c **pcu** zu 12-c **fcu** konnte beispielsweise in der Arbeit von Du *et al.* durch den Einsatz von Tetrafluorterephthalsäure anstelle der sterisch anspruchsvolleren Tetrafluorisophthalsäure erreicht und dadurch nochmals die Bedeutung der Konnektivität der Knotenpunkte unterstrichen werden (Abbildung 5).⁴⁵

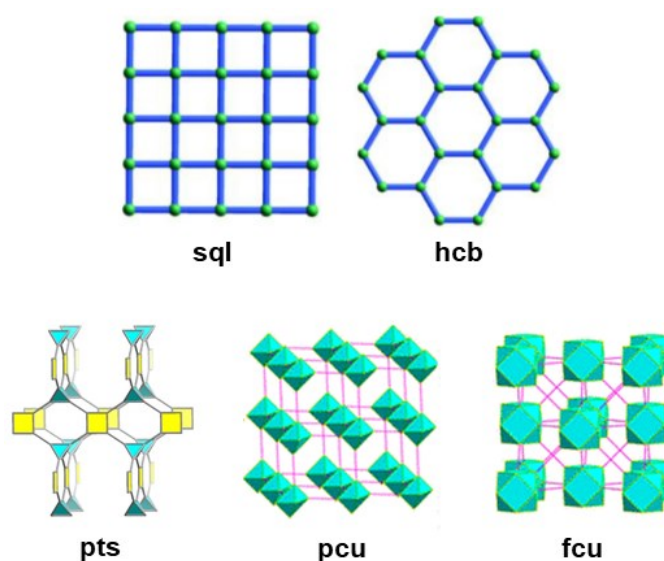


Abbildung 5. Schematischer Überblick der zweidimensionalen Topologien **sql** und **hcb** sowie der dreidimensionalen Topologien **pts**, **pcu** und **fcu**. Abbildung für **sql** und **hcb** mit Genehmigung von Ref. 42 nachgedruckt. ©Copyright 2014, The Royal Society of Chemistry. Abbildung für **pts** mit Genehmigung von Ref. 40 nachgedruckt. ©Copyright 2008, Springer Nature. Abbildung für **pcu** und **fcu** mit Genehmigung von Ref. 45 nachgedruckt. ©Copyright 2018, American Chemical Society.

1.1.1 Triazol-basierte Koordinationspolymere

Eine häufig für Koordinationspolymere eingesetzte Ligandenklasse stellen die N-heterozyklischen Triazole sowohl in der 1,2,3-Stellung als auch in der 1,2,4-Stellung dar. Im Vergleich zu den 1,2,3-Triazolen sind die 1,2,4-Triazole jedoch eine vielfältiger untersuchte Ligandenklasse. Eine Übersicht hierzu liefern Gamez *et al.*⁴⁶

1,2,4-Triazole können Metallionen in protonierter oder deprotonierter Form über fünf unterschiedliche Koordinationsmodi, bei denen mehr als ein Metallion beteiligt ist, koordinieren und somit zu einer Vielzahl an unterschiedlichen Strukturen führen

(Abbildung 6).⁴⁶ Je nach Verknüpfung von organischen Resten an den 1,2,4-Triazolen können diese somit die Koordinationsgeometrien der Pyrazolate und Imidazolate kombinieren.⁴⁷

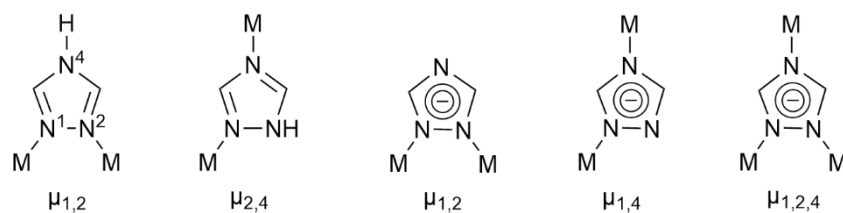


Abbildung 6. Unterschiedliche Koordinationsmodi von 1,2,4-Triazol und 1,2,4-Triazolat (M = Metallion).

Die ersten Koordinationspolymere mit 1,2,4-Triazolen lassen sich bis ins Jahr 1979 rückdatieren. Engelfriet *et al.* ist es gelungen mit 1,2,4-Triazol unterschiedliche Koordinationspolymere mit der Summenformel $M(C_2H_3N_3)_2(NCS)_2$ ($M = Co, Zn, Cu$) zu synthetisieren und strukturell aufzuklären.⁴⁸

Aus kristallographischer Sicht sind insbesondere flexible Bis-Triazol-Liganden interessant, da diese nicht nur diverse Koordinationsmöglichkeiten besitzen, sondern sich aufgrund der Flexibilität bei entsprechendem organischem Rückgrat in unterschiedlichen Konformationen befinden können und somit die Anzahl an möglichen Strukturen nochmals vergrößern.²⁶

Ogleich der zahlreichen Koordinationsmodi von 1,2,4-Triazol-Derivaten ist die Bandbreite an Materialien, welche für die häufigste untersuchte Anwendungsmöglichkeit im Rahmen des *Spin-Crossover*-Phänomens in Frage kommen, relativ gering und nahezu ausschließlich für den $\mu_{1,2}$ -Koordinationsmodus zu finden. Ein Grund hierfür könnte sein, dass mono-koordinierte 1,2,4-Triazol-Liganden ein schwaches Ligandenfeld ausbilden und somit nahezu ausschließlich im *high-spin*-Zustand vorliegen. In den Fällen in denen *Spin-Crossover* auftritt, ist der Triazol-Ring in supramolekularen Wechselwirkungen, welche diesen Effekt durch die Veränderung der Donorstärke kompensieren, involviert.⁴⁶ Als ein Beispiel für Bis-Triazol-basierte Koordinationspolymere, in denen ein Wechsel des Spinzustandes möglich ist, ist die von Tuchages *et al.* synthetisierte Verbindung $[Fe(4,4'\text{-Bis-1,2,4-Triazol})_3](ClO_4)_2$.⁴⁹

1.1.2 Spin-Crossover

Spin-Crossover (SCO) beschreibt den Wechsel der Spin-Konfiguration eines sechsfach-koordinierten, oktaedrischen $3d^4$ – $3d^7$ Übergangsmetallions von *low-spin* (LS) zu *high-spin* (HS) und *vice versa*. Diese Entropie-getriebene Elektronenumverteilung kann durch äußere Einflüsse, wie z.B. Temperaturänderung, Druck, Licht oder durch Gastmoleküle

induziert werden und geht mit strukturellen, elektronischen und magnetischen Änderungen einher.^{50–58}

Um dieses Phänomen genauer betrachten zu können, muss zunächst die Natur der d-Orbitale im Rahmen der Kristallfeldtheorie genauer beleuchtet werden (Abbildung 7). Während die d-Orbitale eines freien Ions in der Gasphase energetisch gleich, also entartet, vorliegen, wird die Orbitalenergie eines Ions im sphärischen Kristallfeld angehoben. Im oktaedrischen Kristallfeld resultiert eine energetische Orbitalaufspaltung aus der räumlichen Lage entsprechender Liganden durch repulsive Wechselwirkungen zwischen den d-Elektronen und den negativen Punktladungen der Liganden. Bei räumlicher Richtung der Elektronen auf die Liganden werden die entsprechenden Orbitale ($d_{x^2-y^2}$, d_{z^2}) energetisch weiter angehoben. Die Orbitale, bei denen die Elektronen nicht auf die Liganden gerichtet sind (d_{xy} , d_{xz} , d_{yz}), werden energetisch abgesenkt. Trotz Aufspaltung entspricht die Summe der Orbitalenergien im oktaedrischen Kristallfeld (*Oktaederaufspaltungsenergie* $\Delta_O = 10 Dq_O$) der Summe der Energie der entarteten Orbitale im sphärischen Kristallfeld.³⁵

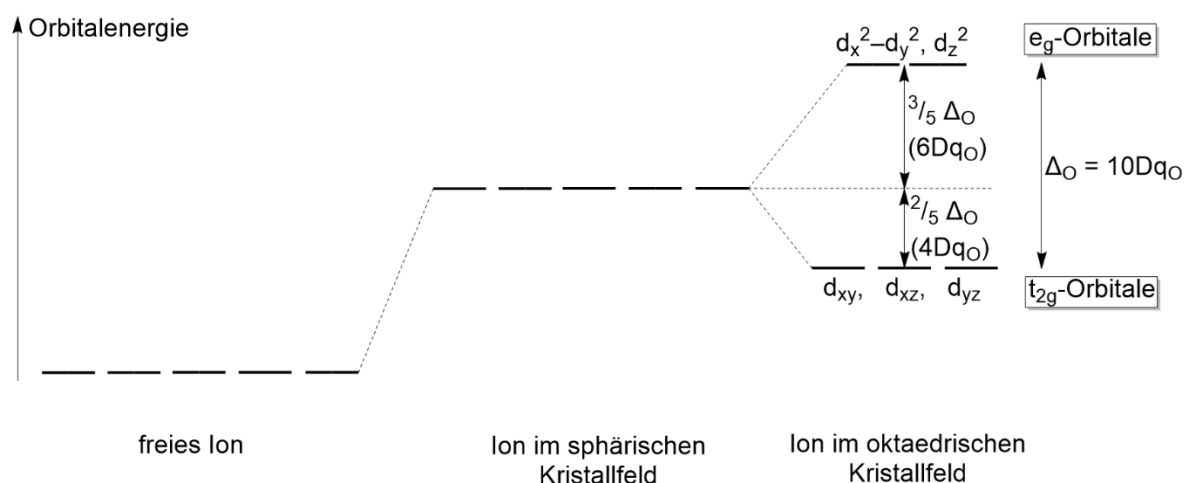


Abbildung 7. Schematische Darstellung der Orbitalenergie für ein freies Ion, der Anhebung im sphärischen Kristallfeld und der Aufspaltung im oktaedrischen Kristallfeld.

In oktaedrischen Komplexen mit bis zu drei d-Elektronen ($3d^1$ – $3d^3$) erfolgt die Verteilung auf jedes der drei t_{2g} -Orbitale gemäß der zweiten Hund'schen Regel, welche die maximale Spin-Multiplizität bei der Besetzung der Orbitale vorschreibt. Da die Energie bei der Besetzung der t_{2g} -Orbitale im Vergleich zum freien Ion im sphärischen Kristallfeld niedriger ist, kommt es zu einem Energiegewinn, welcher als *crystal field stabilization energy* (CFSE, dt. Kristallfeldstabilisierungsenergie) definiert wird. Für jedes Elektron in einem t_{2g} -Orbital eines oktaedrischen Komplexes kommt es zu einem Energiegewinn von $4 Dq_O$. Bei der Besetzung der e_g -Orbitale kommt es pro Elektron zu einem Energieverlust von $6 Dq_O$.³⁵

Bei Betrachtung der oktaedrischen Komplexe mit vier bis sieben Elektronen ($3d^4$ – $3d^7$) können die nun zusätzlichen Elektronen die Orbitale auf zwei Weisen besetzen. Im Falle einer $3d^4$ -Konfiguration kann das vierte Elektron das leere e_g -Orbital besetzen, sodass der *high-spin*-Komplex vorliegt. Mit *high-spin* wird immer der Zustand bezeichnet, welcher die maximale Anzahl an ungepaarten Elektronen aufweist. Alternativ kann dieses Elektron gemäß des Pauli-Prinzips eines der t_{2g} -Orbitale doppelt besetzen. In diesem Fall würde der Komplex im *low-spin*-Zustand vorliegen. Für diese Orbitalbesetzung muss zusätzlich die *Spinpaarungsenergie* P aufgebracht werden (Abbildung 8).³⁵

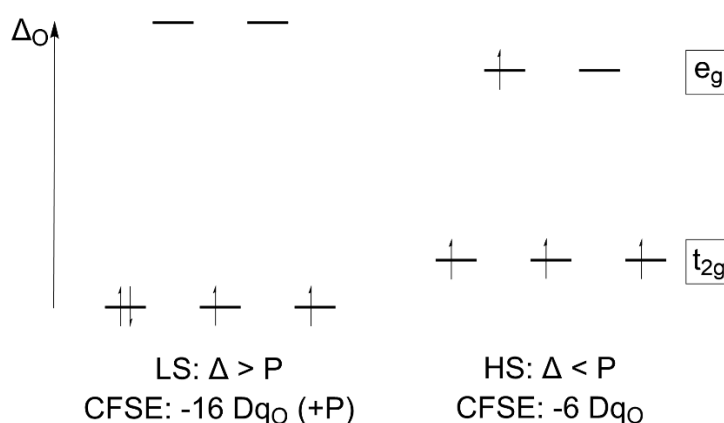


Abbildung 8. Besetzung der Orbitale und Kristallfeldstabilisierungsenergie (CFSE) für den *high-spin*- und *low-spin*-Zustand für eine $3d^4$ -Konfiguration im oktaedrischen Kristallfeld.

Für die Vorhersage, welcher der beiden Zustände vorliegt und ob sogar ein Wechsel (*Spin-Crossover*) möglich ist, muss die Beziehung zwischen der *Ligandenfeldstärke* Δ und der *Spinpaarungsenergie* P betrachtet werden.^{52,59} Für den Fall $\Delta < P$ liegt eine Verbindung im *high-spin*-Zustand vor, während für den *low-spin*-Zustand $\Delta > P$ gilt.^{52,35,60,61} Damit nun ein Wechsel zwischen beiden Zuständen möglich ist, müssen die Ligandenfeldstärke und die Spinpaarungsenergie in einem ähnlichen Bereich liegen, damit ein äußerer Einfluss diese Beziehung signifikant beeinflussen kann. Für $3d^4$ – $3d^7$ -Konfigurationen ist dies der Fall. Oktaedrische 4d- bzw. 5d-Metallkomplexe hingegen liegen nur im *low-spin*-Zustand vor. Während die Ligandenfeldstärke von Metallkomplexen derselben Gruppe mit identischer Ligandensphäre und Oxidationsstufe jeweils um etwa 50% zunimmt, ändert sich die Spinpaarungsenergie nicht signifikant. Die Konfiguration kann nun durch einen äußeren Einfluss nicht mehr gewechselt werden.⁶² Da im tetraedrischen Kristallfeld die Ligandenfeldstärke nur $4/9$ ($\sim 44.5\%$) der Stärke eines oktaedrischen Kristallfeldes entspricht, ist auch in tetraedrischen 3d-Komplexen kein *Spin-Crossover* bekannt.⁶²

Eisen(II) ist das meist untersuchteste Metallkation in Hinblick auf *Spin-Crossover* und den damit einhergehenden Eigenschaftsänderungen, wie Bindungslängen oder Farbe. Der *high-spin*-Zustand zeichnet sich eher durch Farblosigkeit und hellere Farbtöne (weiß-gelb bis orange) aus, während der *low-spin*-Zustand sich eher durch intensivere Farbtöne, wie lila oder rot, auszeichnet.^{53,56,63} Am häufigsten werden die d^6 - Fe^{2+} -Metallzentren oktaedrisch von sechs Stickstoff-Donor-Atomen umgeben.^{56,64,65} In diesen FeN_6 -Komplexen lassen sich drei häufig auftretende Verbindungsmuster feststellen. Einerseits gibt es neutrale Komplexe mit den Summenformeln $[\text{FeL}_y\text{X}_2]$ oder $[\text{FeX}_y]$ und andererseits kationische Komplexe in Form von $[\text{FeL}_y]^{2+}$.⁶⁵ Die neutralen, mehrzähligen Liganden L können basierend auf ihrer Länge die SCO-Eigenschaften signifikant beeinflussen, wobei auch mit vergleichsweise langen Liganden SCO beobachtet werden konnte.^{66–72} Die mono-anionischen Stickstoff-Donor-Liganden X , wie bspw. Isothiocyanat (NCS^-), liegen in den neutralen Komplexen am Eisen koordiniert vor. In den kationischen Komplexen liegen nicht-koordinierte Anionen, wie Tetrafluoroborat (BF_4^-), vor. Sowohl koordinierte als auch nicht-koordinierte Anionen können einen immensen Einfluss auf die SCO-Eigenschaften besitzen.^{60,73–75}

Eine der deutlichsten Änderungen beim Auftreten von *Spin-Crossover* sind die Metall-Ligand-Bindungslängen, deren Änderung über Röntgenstrukturanalysen gut beobachtet werden kann. Im Falle von $3d^6$ - Fe^{2+} nehmen die Fe–N-Bindungslängen im *high-spin*-Zustand um $0.2 \text{ \AA}$ (10%) zu. Hierdurch vergrößert sich das Volumen eines molekularen Eisen(II)-Komplexes um 3–4% (Abbildung 9).^{56,61,76} In Eisen(III)-Komplexen mit $3d^5$ -Konfiguration beträgt die Änderung der Bindungslängen nur noch knapp 5%.⁷⁶

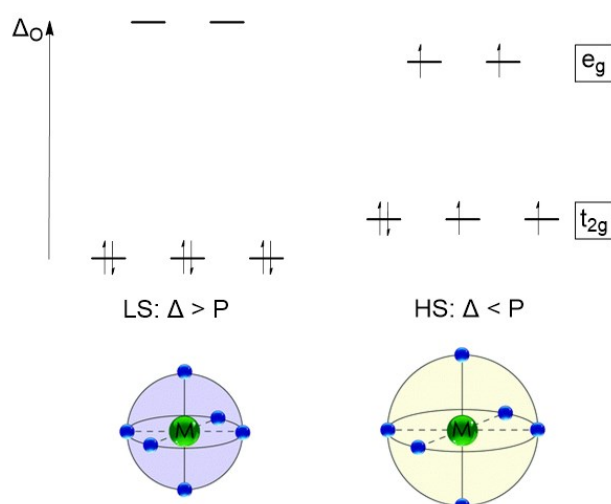


Abbildung 9. Schematische Darstellung der Orbitalbesetzung und strukturellen und visuellen Unterschiede des *high-spin*- und *low-spin*-Zustandes für Fe^{2+} . Unterer Teil der Abbildung (strukturelle und visuelle Unterschiede) mit Genehmigung von Ref. 56 entnommen. ©Copyright 2015, The Royal Society of Chemistry.

In Cobalt(II)-Komplexen sind SCO-Eigenschaften weniger untersucht, was vermutlich auch auf die eher graduell-verlaufenden Spin-Übergänge zurückzuführen ist. Neben einer Änderung der Co–N-Bindungslängen um ca. 5%, kommt es in der *low-spin*-Konfiguration aufgrund des einzelnen Elektrons im e_g -Orbital zur Jahn-Teller-Verzerrung des oktaedrisch koordinierten d^7 -Co²⁺-Kations (Abbildung 10).^{56,77–80}

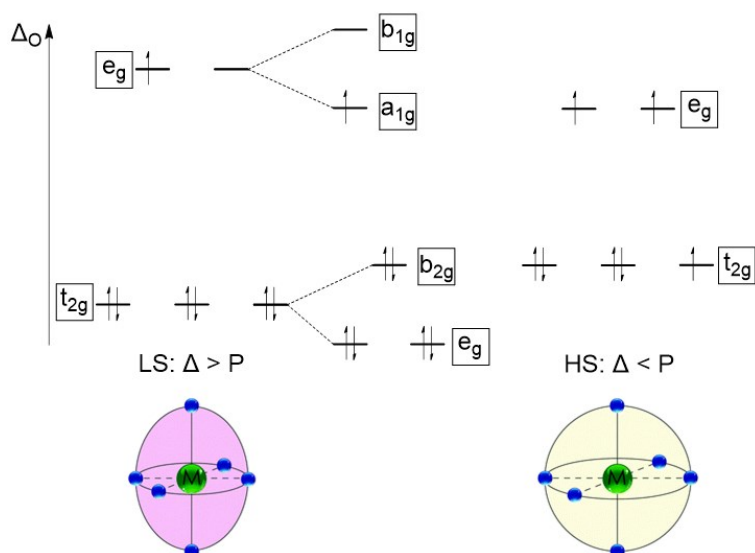


Abbildung 10. Schematische Darstellung der Orbitalbesetzung und strukturellen und visuellen Unterschiede des *high-spin*- und *low-spin*-Zustandes für Co²⁺ inkl. Jahn-Teller-Verzerrung. Unterer Teil der Abbildung (strukturelle und visuelle Unterschiede) in Anlehnung an Ref. 56 mit Genehmigung reproduziert. ©Copyright 2015, The Royal Society of Chemistry.

Der gängigste Parameter, auf welchen zur Induktion von *Spin-Crossover* zurückgegriffen wird, ist die Temperatur. Hierfür muss die *Differenz der Gibbs-Energien beider Spinzustände* ΔE_{HL} ungefähr der *Wärmeenergie* $k_B T$, zusammengesetzt aus der *Boltzmann-Konstante* k_B und der *Temperatur* T , entsprechen.^{55,81} Der enthalpisch begünstigte *low-spin*-Zustand ist bei niedrigeren Temperaturen stabil und der entropisch begünstigte *high-spin*-Zustand ist dementsprechend bei höheren Temperaturen stabil.^{56,76} Daraus folgt, dass der Spin-Übergang von *low-spin* zu *high-spin* endotherm und der Übergang von *high-spin* zu *low-spin* exotherm ist.⁸²

Die unterschiedlichen Arten von SCO werden im Folgenden anhand des temperaturabhängigen SCO beschrieben (Abbildung 11). Der graduelle SCO erfolgt vollständig, aber in einem breiten Bereich und ist somit potentiell in der Sensorik interessant (Abbildung 11a). Für binäre Schalter würde sich der abrupte SCO, welcher in einem sehr schmalen Temperaturbereich stattfindet, eignen (Abbildung 11b). Ein abrupter SCO mit thermaler Hysterese zeichnet sich dadurch aus, dass die zur Spin-Änderung notwendige Temperatur nicht gehalten werden muss, um den entsprechenden Zustand beizubehalten. Diese Bistabilität lässt diese Art des SCO für

Speicheranwendungen interessant werden (Abbildung 11c). Stufenweise Spin-Übergänge könnten für ternäre oder größere Schalter Anwendung finden (Abbildung 11d). Der unvollständige SCO hingegen ist der uninteressanteste SCO-Typ (Abbildung 11e).^{55,56,83–85}

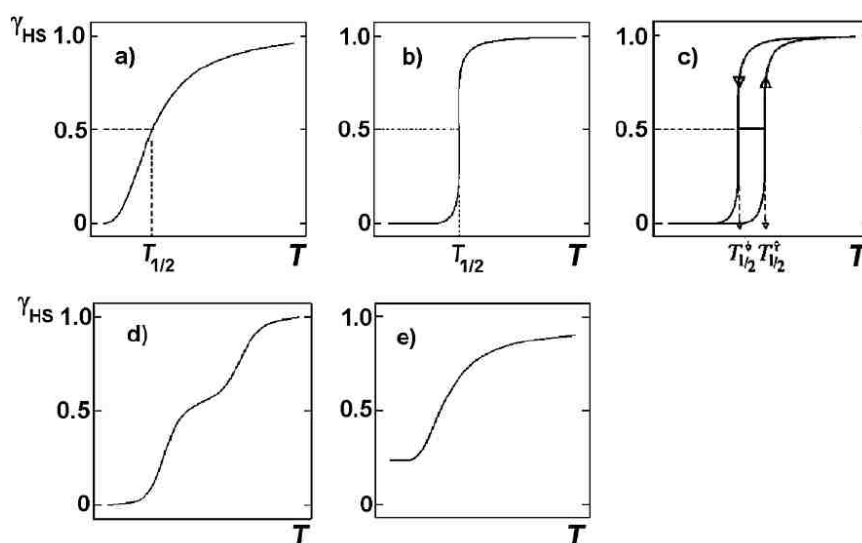


Abbildung 11. Überblick über die unterschiedlichen Arten des *Spin-Crossovers*: a) graduell, b) abrupt, c) abrupt mit Hysterese, d) stufenweise, e) unvollständig. Der Anteil an Molekülen im *high-spin*-Zustand γ_{HS} wird in Abhängigkeit der Temperatur T beschrieben. Abbildung wurde mit Genehmigung aus Ref. 86 entnommen. ©Copyright 2001, Wiley.

1.2 Metall-organische Gerüstverbindungen

Koordinationsnetzwerke bilden nach IUPAC-Definition eine Subkategorie der Koordinationspolymere und umfassen alle eindimensionalen Koordinationsverbindungen, bei denen mindestens zwei unabhängige Ketten miteinander quervernetzt sind, und zusätzlich alle zwei- bzw. dreidimensionalen Koordinationsverbindungen. Eine Unterkategorie dieser Koordinationsnetzwerke stellen die sogenannten *metal-organic frameworks* (MOFs, dt. Metall-organische Gerüstverbindungen) dar. Sie beinhalten dabei alle zwei- und dreidimensionalen Koordinationsnetzwerke, welche potentielle Porosität aufweisen (Abbildung 12).^{3,5} Gemäß IUPAC wurde eine einheitliche Begriffsdefinition für die Miko- (>2 nm), Meso- (2–50 nm) und Makroporosität (>50 nm) geschaffen.⁸⁷

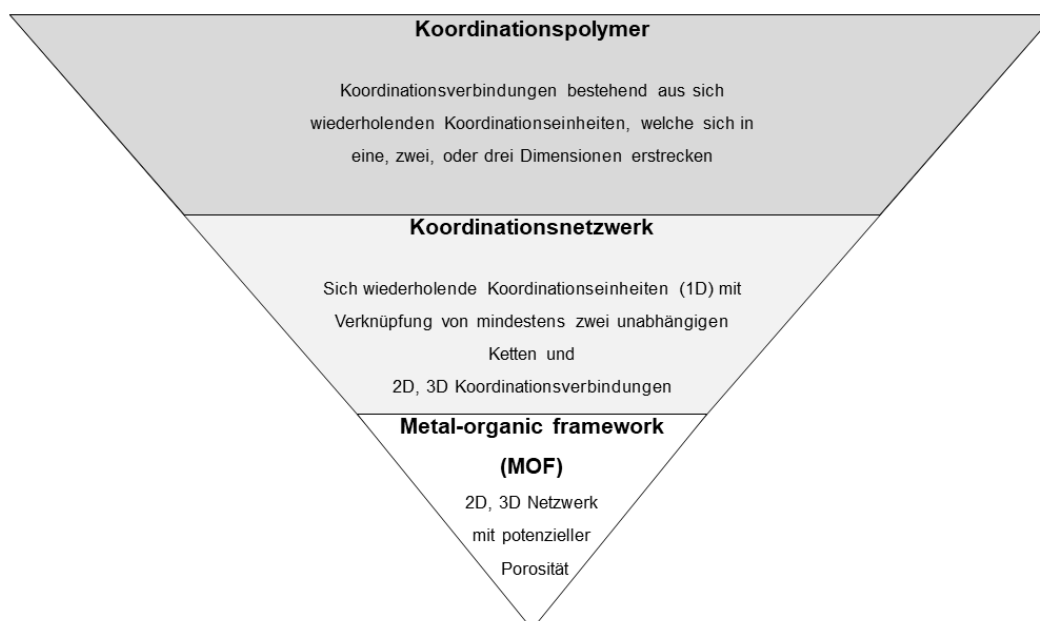


Abbildung 12. Schematischer Überblick über die hierarchische Begriffsabgrenzung von Koordinationspolymeren, Koordinationsnetzwerken und Metall-organischen Gerüstverbindungen (MOFs).

Neben anderen porösen Materialklassen, wie den rein organischen *covalent-organic frameworks* (COFs, dt. kovalent-organische Gerüstverbindungen) oder *zeolitic-imidazolate frameworks* (ZIFs, dt. zeolitisch-imidazolat Gerüstverbindungen) entstammen auch MOFs dem Konzept der retikulären Chemie.^{16,88,89}

Die große Anzahl an Kombinationsmöglichkeiten von Metallen und Linkern erlaubt es die Eigenschaften und Strukturen der MOFs über die Porengröße und Funktionalisierung der Porenoberfläche zu kontrollieren.^{90–93} Als Beispiele sind die beiden auf 1,4-Benzoldicarboxylat (bdc^{2-}) basierenden MOFs MOF-5 und UiO-66 (UiO = *Universitetet i Oslo*, dt. Universität von Oslo) zu nennen. Die eher uneinheitliche Nomenklatur von MOFs setzt sich hierbei weitgehend aus dem Kürzel des Instituts bzw. der Universität und einer fortlaufenden Zahl zusammen.

MOF-5 mit der Summenformel $[\text{Zn}_4\text{O}(\text{bdc})_3](\text{DMF})_x$ wurde 1999 von Yaghi *et al.* synthetisiert. Die SBU von MOF-5 besteht aus vier tetraedrischen ZnO_4 -Einheiten, welche über ein zentrales $\mu_4\text{-O}$ und je einem Carboxylat des bdc^{2-} -Linker verknüpft sind. In der hieraus resultierenden dreidimensionalen **pcu**-Struktur liegen zwei kubische Poren (9.2 Å und 13.8 Å) vor (Abbildung 13).⁹⁴ Im Jahr 2008 konnten Lillerud *et al.* mit demselben Liganden das auf Zirkonium-basierte UiO-66 mit der Summenformel $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_6]$ synthetisieren. Hierbei besteht der SBU-Kern aus $\text{Zr}_6\text{O}_4(\text{OH})_4$ -Einheiten, in welchen die dreieckigen Flächen des Zr_6 -Oktaeders abwechselnd von $\mu_3\text{-O}$ und $\mu_3\text{-OH}$ -Gruppen bedeckt sind. Alle Polyeder-Kanten werden durch insgesamt zwölf Carboxylat-Einheiten verbrückt, woraus die

$\{\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}\}$ -Cluster resultieren. Aus der **fcu**-Topologie ergeben sich zwei unterschiedliche Poren: Eine größere oktaedrische Pore (12 Å) sowie eine kleinere tetraedrische Pore (8 Å) (Abbildung 13).^{95,96}

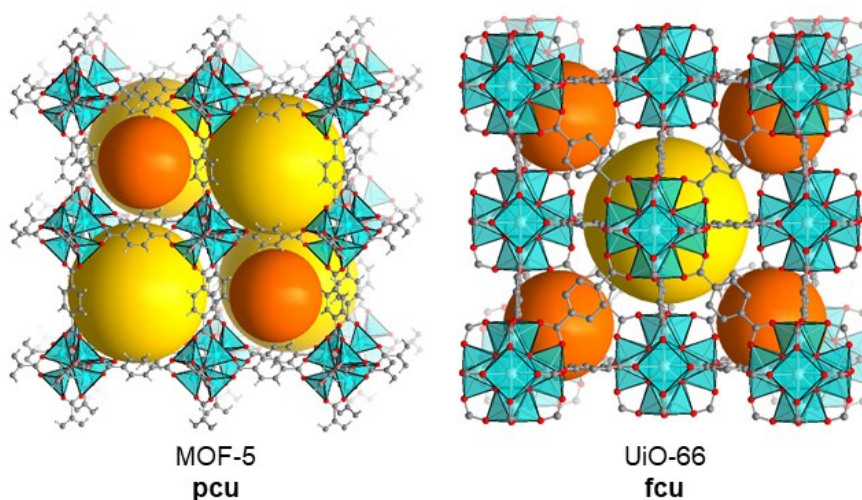


Abbildung 13. Strukturelle Darstellung von MOF-5 und UiO-66 inkl. Veranschaulichung der Poren in gelb, orange. Die Kristallstrukturdaten wurden aus der CCDC Datenbank mit den folgenden Codes entnommen: MOF-5: MIBQAR⁹⁷; UiO-66: RUBTAK⁹⁵.

Auf beiden Arbeiten aufbauend wurden jeweils isoretikuläre Serien entwickelt, in welchen grundsätzlich dieselbe Struktur durch die Beibehaltung der SBU erhalten wurden, aber durch die Verwendung von längeren oder auch funktionalisierten Linkern die Eigenschaften wie Porengröße oder Funktionalität beeinflusst wurden (Abbildung 14).^{95,98,99}

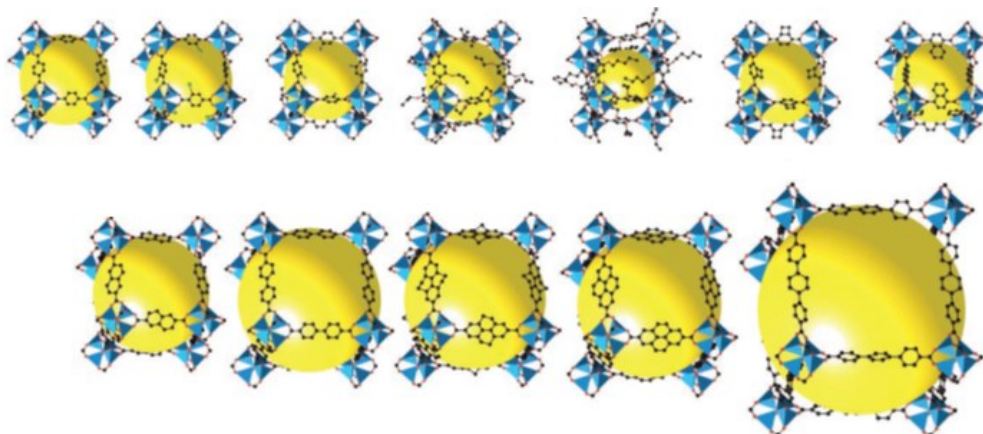


Abbildung 14. Isoretikuläre Serie von MOF-5. In gelb sind die Porengrößen dargestellt. Die Abbildung wurde mit Genehmigung von Ref. 98 nachgedruckt. ©Copyright 2002, American Association for the Advancement of Science.

Durch die fortlaufende Erweiterung der Substanzklasse der MOFs werden zwangsläufig kontinuierlich neue isoretikuläre Serien entstehen als auch bestehende Serien erweitert. Hierin spielen häufig neue Erkenntnisse, welche dazu führen, dass MOFs noch genauer auf ihre spätere potentielle Anwendung abgestimmt sind, eine bedeutende Rolle. So sollte insbesondere die

Porengröße beim MOF-Design für die Gas- und Dampfsorption berücksichtigt werden, da die Aufnahme durch kleine Mikroporen mit schmaler Porenverteilung signifikant gesteigert werden kann.^{90–93,100} Neben den Porengrößen zeigen mehrere Arbeiten, angestoßen von Farha *et al.* und weitergeführt von Janiak *et al.* (vgl. HHUD-MOFs, HHUD = Heinrich-Heine-Universität Düsseldorf), dass der Austausch von Phenylen-Einheiten durch Dreifachbindungen die Sorptionsaffinitäten erhöhen kann.^{101–105}

1.2.1 Metall-azolat Gerüstverbindungen

Aufgrund der häufig vorkommenden Hydrolyseanfälligkeit zersetzen sich MOFs häufig, wenn sie mit Wasser oder gar Luftfeuchtigkeit in Kontakt kommen. Carboxylat-basierte MOFs besitzen eine gewisse Stabilität gegenüber Hydrolyse, sofern basierend auf dem HSAB-Konzept (*hard and soft acids and bases*, dt. harte und weiche Säuren und Basen) hoch-valente Metall-Atome, also harte Säuren (z.B. Zr^{4+} , Cr^{3+} , Fe^{3+} , Al^{3+}), eingesetzt werden, welche in Zusammenhang mit O-Donor-Liganden, also harten Basen, starke koordinative Bindungen ausbilden.^{106–108} In Kombination mit niedriger-valenten Metall-Atomen, also weicheren Säuren (z.B. Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Fe^{2+}), können stabilere MOFs mit N-Donor-Liganden, also weicheren Basen, synthetisiert werden. Ein Beispiel stellen hierfür die Azolat-basierten MOFs, auch *metal-azolate frameworks* (MAFs, dt. Metall-azolat Gerüstverbindungen) genannt, dar. Neben einer thermischen Stabilität von häufig über 400 °C, zeichnen sich MAFs auch durch eine hohe chemische Resistenz gegenüber siedendem alkalischem Wasser und anderen Lösungsmitteln aus. Diese höhere Stabilität kann auf die höhere Basizität der Azolate in Kombination mit den entsprechenden Metallionen gemäß dem HSAB-Konzept, den kovalenteren Metall-Stickstoff-Bindungen sowie eine hydrophobere innere Oberfläche, welche bei vollständiger Deprotonierung und nicht-funktionalisierten Linker-Rückgrat weniger anfällig gegenüber polaren Spezies ist, zurückgeführt werden.^{89,109,110} Eines der vielversprechendsten MAFs und dadurch auch hervorzuheben ist $[\text{Zn}_2(1,2,4\text{-triazolat})_2(\text{oxalat})]$, auch CALF-20 (CALF = *Calgary Framework*) genannt.¹¹¹ CALF-20 ist ein langzeitstabiles MOF und zeichnet sich auch unter industriellen Bedingungen (100 °C, in Kombination mit Wasserdampf und sauren Gasen) durch eine ausgezeichnete CO_2 -Adsorption aus. Dadurch, dass CALF-20 auch im Kilogramm-Maßstab kostengünstig synthetisiert werden kann, gilt CALF-20 hinsichtlich der CO_2 -Filtration in industriellen Prozessen als potentiell Material der Zukunft.¹¹¹

Neben Triazol-basierten MOFs sind auch diverse andere N-Heterozyklen-basierte MOFs interessant. Einer der am häufigsten studierten N-Heterozyklen in der Koordinationschemie stellt Pyrazol dar, dessen gängigen Koordinationsmodi der deprotonierten Form mit denen des Carboxylats vergleichbar sind.^{89,110}

In Abbildung 15 sind einige SBUs für Pyrazolate beispielhaft dargestellt. In Kombination mit einwertigen Metall-Kationen, wie Cu^I , Ag^I oder Au^I , werden häufig trigonal-planare $\{\text{M}_3(\text{pz})_3\}$ -Cluster (pz = Pyrazolat) ausgebildet. Für eine Reihe zweiwertiger Kationen tritt die SBU häufig in Form von unterschiedlichen Typen von (Doppelstrang-)Ketten auf, in welchen die Metallionen tetraedrisch koordiniert vorliegen.⁸⁹ In diesem Kontext konnten mit Zink-Ionen und linearen Bis-Pyrazolaten zahlreiche isoretikuläre, dreidimensionale Netzwerke mit der **pts**-Topologie synthetisiert werden.^{112–114} Hervorzuheben sind hierbei die Arbeiten von Navarro *et al.* und Galli *et al.*, welche unter anderem mit 1,4-Bis(1*H*-pyrazol-4-yl)benzol (H_2bpb) und dem Acetylen-basierten analogen 1,2-Bis(1*H*-pyrazol-4-yl)ethin (H_2bpe) neue Zink-basierte MOFs synthetisiert haben. Aufgrund der tetraedrischen Raumgruppen liegen in diesen beiden Verbindungen quadratische Kanäle vor.^{113,114} Neben tetragonalen Raumgruppen können Zink-Bis-Pyrazolate auch in orthorhombischen Raumgruppen auskristallisieren. Das Strukturmotiv bleibt hierbei erhalten und der einzige Unterschied liegt in der Form der Poren bzw. Kanäle, welche in diesem Fall rhombisch statt quadratisch vorliegen.^{110,113,114}

Zusätzlich zu den SBUs, in welchen die Metall-Atome lediglich von Pyrazolaten verbrückt vorliegen, spielen auch polynukleare Cluster, bei denen die Metall-Atome sowohl von Pyrazolaten als auch von Oxido-, Hydroxido- oder Aqua-Liganden verknüpft werden, eine bedeutende Rolle. In diesem Zusammenhang können dreieckige, kubische, oktaedrische oder aber auch Kronenether-ähnliche SBUs entstehen (Abbildung 15). Die kubische SBU $\{\text{M}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{pz})_{12}\}$ ist bis dato nur in Kombination mit Nickel beobachtet worden.⁸⁹ In dieser SBU sitzen die Ni^{2+} -Kationen auf den Ecken des Würfels, die Würfelflächen sind hierbei von Ni-verbrückenden μ_4 -Hydroxido- bzw. μ_4 -Aqua-Liganden besetzt und zwölf Pyrazolat-Gruppen verbinden die Nickel-Atome entlang der Würfelseiten. Hierbei sei zu erwähnen, dass häufig für das Verhältnis von Hydroxid zu Wasser eine statistische Belegung von 2:1 und somit also die neutrale Form $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{pz})_{12}]$ angenommen wird. Für H_2bpb konnten Volkmer *et al.* zeigen, dass in dieser Verbindung die anionische Form $[\text{Ni}_8(\text{OH})_6(\text{bpb})_{12}]^{2-}$ vorliegt. Allerdings kann diese Form auch bei entsprechenden Bedingungen in die neutrale Form überführt werden, sodass ein Rückschluss auf die Ladung aller Verbindungen dieser Klasse nicht gezogen werden sollte.¹¹⁵ Unabhängig des

Hydroxid-Wasser-Verhältnisses ist diese kubische SBU aufgrund der starken Ni–N-Bindung insbesondere für die Synthese von hochporösen Netzwerken für diverse Anwendungsgebiete, wie Gas-Speicherung/Trennung, Magnetismus oder (Elektro-)Katalyse, interessant.^{116–124}

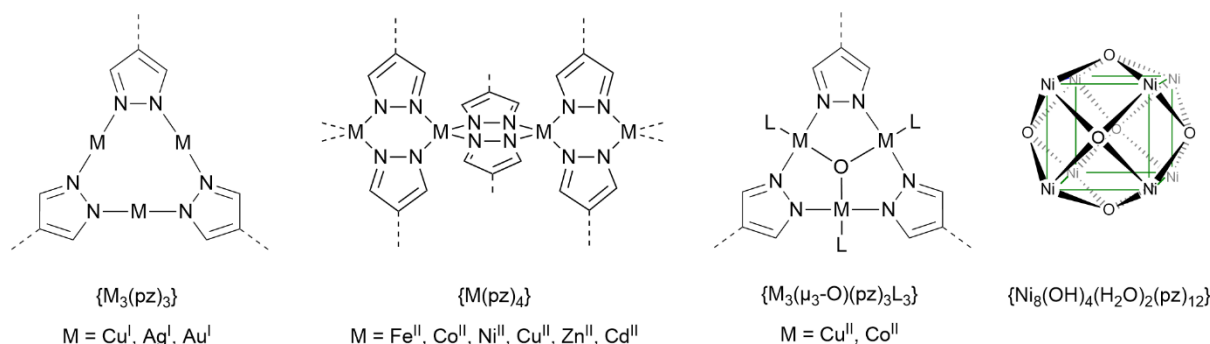


Abbildung 15. Auswahl von unterschiedlichen Pyrazolat-SBUs ohne und mit verbrückenden Sauerstoffatomen. Bei $\{Ni_8(OH)_4(H_2O)_2(pz)_{12}\}$ wurden die Pyrazolat-Einheiten, welche je zwei Ni-Atome des Ni_8 -Würfels (grüne Linien) verbrücken, aus Gründen der Übersichtlichkeit weggelassen. Die Abbildung wurde mit Genehmigung in Anlehnung an Ref. 125 reproduziert. ©Copyright 2024, American Chemical Society.

Die isoretikuläre Serie mit der Formel $[Ni_8(\mu_4-X)_6(\mu_4-L)_6]$ ($X = OH^-$, H_2O ; $L =$ Bis-Pyrazolat, Pyrazolat-Carboxylat) wurde von Galli *et al.* und Navarro *et al.* begründet und maßgeblich erweitert. Sie beinhaltet neben linearen Bis-Pyrazolaten auch lineare Pyrazolat-Carboxylate, welche sich aufgrund der ähnlichen Koordinationsmodi ebenfalls verwenden lassen. In dieser Serie mit der kubischen Ni_8 -SBU werden dreidimensionale Netzwerke ausgebildet.^{116,118} Aus der vorliegenden 12-c **fcu**-Topologie folgend, liegen sowohl oktaedrische als auch tetraedrische Poren vor, sodass eine Vergleichbarkeit mit der isoretikulären Bis-Carboxylat-basierten UiO-Serie gegeben ist.^{95,96}

1.2.2 Adsorptionsprozesse und Isothermenprofile

Die der Definition innewohnende potentielle Porosität von MOFs beschreibt zugleich eine der wichtigsten Eigenschaften. Aufgrund deren Porosität wurden im Laufe der Zeit unzählige Sorptionsisothermen zur Charakterisierung von MOFs für potentielle Anwendungsbereiche hinsichtlich der Speicherung und Trennung von Gasen, wie z.B. CO_2 , und Dämpfen, wie von volatilen organischen Verbindungen, unter anderem Benzol und Cyclohexan, aufgenommen.^{91,111–127}

Für gewöhnlich handelt es sich bei den Adsorptionsprozessen in MOFs um Physisorption, welche die schwachen Wechselwirkungen zwischen dem Adsorptiv, also dem zu adsorbierenden Stoff *vor* der Adsorption, und dem Adsorbens, dem Material, an dessen

Oberfläche die Adsorption stattfindet, beschreibt. Als Adsorbat wird das Adsorptiv *nach* erfolgter Adsorption bezeichnet.^{87,128,129} Im Kontrast dazu kommt es bei der Chemisorption zur Ausbildung chemischer Bindungen zwischen Adsorptiv und Adsorbens. Durch die Veränderung des Adsorbates, sind Chemisorptionsprozesse häufig irreversibel.¹³⁰

Für eine einheitliche Charakterisierung und eine bessere Vergleichbarkeit bzw. Einordnung von porösen Materialien wurden diverse Modelle entwickelt. In diesem Zusammenhang hat sich die Kennzahl der spezifischen Oberfläche etabliert. Gemäß der beiden meist-verwendeten Theorien von Langmuir oder Brunauer, Emmett und Teller (BET) kann diese Oberfläche basierend auf einer Gasmessung einer entgasten Probe in Anbetracht diverser Annahmen berechnet werden.^{131,132} Beide Theorien beschreiben die Physisorption. Während die Langmuir-Theorie auf der Adsorption einer Monolage des Adsorptivs beruht, basiert die BET-Theorie auf der Adsorption von Multilagen.¹³²

Standardmäßig werden die chemisch inerten Gase Stickstoff oder Argon zur Bestimmung der BET-Oberfläche bei der entsprechenden Siedetemperatur (77 K für N₂; 87 K für Ar), bei welcher die Wechselwirkungen zwischen Adsorptiv und Adsorbens zur Ausbildung von Multilagen am größten sind, verwendet. Obwohl Argon atomar vorliegt und hieraus resultierend kein Quadrupolmoment besitzt, wird Stickstoff aus ökonomischen Gründen bevorzugt verwendet.⁸⁷ Wenn die Poren weder für N₂ noch Ar zugänglich sind, kann die Oberfläche auch mit Hilfe von CO₂ bestimmt werden. Trotz vergleichbarer Größe eignet sich CO₂ in diesen Fällen besser, da die Messung bei höheren Temperaturen durchgeführt wird und somit mehr kinetische Energie zum Eindringen in die Poren vorhanden ist. Die Bestimmung der Oberfläche sollte hierbei allerdings eher mit der Langmuir-Theorie bestimmt werden, da durch CO₂···CO₂-Wechselwirkungen und dem hohen Quadrupolmoment die Multilagen-Adsorption maßgeblich beeinflusst wird.¹³³

Durch die Auftragung der Gas- bzw. Dampfaufnahme gegen den *relativen Druck* p/p_0 (p_0 = Sättigungsdampfdruck) können Isothermen erhalten werden, welche sich abhängig von der Porengröße unterscheiden lassen und daher von der IUPAC entsprechend kategorisiert werden (Abbildung 16).⁸⁷

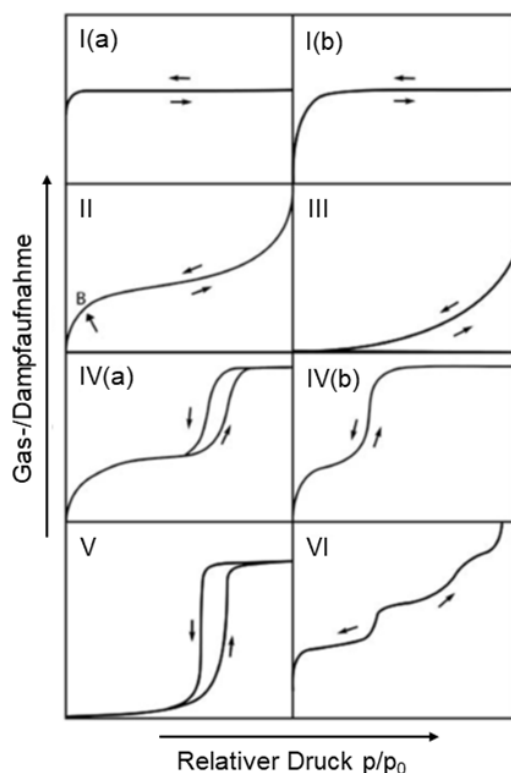


Abbildung 16. Klassifizierung der idealisierten Isothermen für mikroporöse (Typ I), nicht-poröse oder makroporöse (Typ II, III und VI) und mesoporöse Materialien (Typ IV, V) nach IUPAC. Abbildung wurde mit Genehmigung von Ref. 87 übernommen und ins Deutsche übersetzt. ©Copyright 2015, De Gruyter, IUPAC.

Typ I-Isothermen werden für mikroporöse Materialien erhalten. Für N_2 - oder Ar-Messungen werden Typ I(a)-Isothermen für Materialien mit Mikroporen unter 1 nm erhalten. Bei größerer Porengrößenverteilung und größeren Poren bis 2.5 nm werden Typ I(b)-Isothermen erhalten. Hierbei ist zu erwähnen, dass die BET-Theorie in Zusammenhang mit Typ I-Isothermen an ihre Grenzen kommt, sodass die erhaltenen Oberflächen eher mit Vorsicht zu betrachten sind.^{87,134} Die Isothermen des Typs II, III und VI werden für nicht-poröse und makroporöse Materialien erhalten und spielen für MOFs für gewöhnlich eine eher untergeordnete Rolle. Typ IV-Isothermen werden für mesoporöse Materialien erhalten. Je nach Porengröße (>4 nm) kann es durch Kapillarkondensation zum Auftreten einer Hysterese kommen (Typ IV(a)). Diese Hysteresen sind im Typ IV(b) nicht erkennbar. Aufgrund von vergleichsweise schwachen Wechselwirkungen ähnelt Typ V bei niedrigem relativem Druck einer Typ III-Isothermen. Bei höherem relativem Druck kommt es letztendlich zur Füllung der Poren. Diese Art von Isothermen kann unter anderem bei Wassersorptionsisothermen von hydrophobischen mikro- und mesoporösen Materialien beobachtet werden.⁸⁷ Da es sich hierbei um idealisierte Typen handelt, ist es in der Realität nicht unüblich auch Misch-Isothermen zu erhalten. In flexibleren Materialien können auch Effekte, wie *gate-opening* oder *breathing*, beobachtet werden, sodass

Vorschläge für eine Erweiterung der Kategorisierung mit zunehmender Charakterisierung poröser Materialien aufkommen. Während das *gate-opening* den Wechsel von nicht-porösen in poröse Phasen beschreibt, stellt der *breathing*-Effekt die Expansion bestehender Poren, vergleichbar mit der Atmung von Lebewesen, dar.¹³⁵

Durch zusätzliche Adsorbens-Adsorbat-Wechselwirkungen kommt es im Gegensatz zum idealisierten Fall, bei dem Adsorption und Desorption identisch verlaufen, häufig zu einer Verschiebung der Desorption hin zu niedrigerem relativem Druck. Diese Hysteresen wurden von der IUPAC klassifiziert (Abbildung 17).⁸⁷

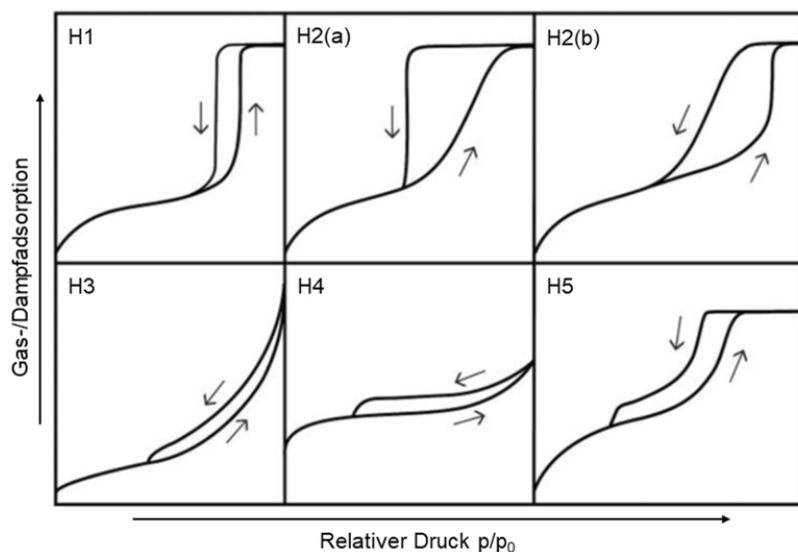


Abbildung 17. Klassifizierung der idealisierten Hysteresen nach IUPAC. Abbildung wurde mit Genehmigung von Ref. 87 übernommen und ins Deutsche übersetzt. ©Copyright 2015, De Gruyter, IUPAC.

Bedingt der Materialbeschaffenheit und Porengröße führt das (Nicht-)Vorhandensein diverser Netzwerkeffekte, wie Kondensation, Porenverstopfung bzw. Perlokation oder kavitationsbedingte Verdampfung, zu den unterschiedlichen charakteristischen Hysteresenformen.⁸⁷

Während die Aufnahmekapazität bereits aus der Isotherme ersichtlich ist, gibt es neben der spezifischen Oberfläche weitere Parameter, welche in Hinblick auf potentielle Anwendungen und der besseren Vergleichbarkeit eine relevante Rolle einnehmen. Zum einen zu nennen ist hierbei die *isosteric heat of adsorption* Q_{st} (HoA, dt. isosterische Adsorptionswärme), welche über zwei oder mehr Sorptionsisothermen bei unterschiedlichen Temperaturen mit einer Differenz von 10 K oder 20 K desselben Adsorptiv-Adsorbens-Paar berechnet wird.^{136,137} Zum anderen stellt die aus der *ideal adsorbed solution theory* (IAST, dt. Theorie der idealen adsorbierten Lösung) hervorgehende IAST-Selektivität, welche aus Sorptionsisothermen

derselben Temperatur mit unterschiedlichen Adsorptiven berechnet wird, einen weiteren wichtigen Parameter dar.¹³⁸ Für beide Parameter gilt, dass die entsprechenden Messungen an demselben Messgerät durchgeführt werden müssen. Zusätzlich dazu sollte für die IAST-Selektivität beachtet werden, dass die Adsorptive ähnliche Polaritäten besitzen, da sich diese ansonsten nicht wie eine ideale Lösung verhalten und somit die Aussagekraft verloren geht.¹³⁹

Für die Berechnung der HoA, welche näherungsweise die Adsorptiv-Adsorbens-Wechselwirkungen beschreibt, müssen die Isothermen nach der erfolgten Messung an ein theoretisches Isothermen-Modell gefittet werden. Hierfür lassen sich wahlweise leichtere Modelle, wie das Freundlich-Modell, erweiterte Modelle, wie das Freundlich-Langmuir-Modell oder aber auch rein-mathematische Modelle, wie der Fit mithilfe einer Virialfunktion, verwenden.^{136,137} Basierend auf Clausius-Clapeyron kann die *enthalpy of adsorption* ΔH_{ads} (dt. Adsorptionsenthalpie) über die folgende Gleichung (1) berechnet werden. Die *heat of adsorption* Q_{st} entspricht der negativen Adsorptionsenthalpie (Gleichung (2)).^{136,137}

$$\Delta H_{ads} = -R \left(\frac{T_2 \cdot T_1}{T_2 - T_1} \right) \ln \frac{p_2}{p_1} \quad (1)$$

$$Q_{st} = -\Delta H_{ads} \quad (2)$$

Für die IAST-Selektivität werden ebenfalls die Isothermen gefittet. Anhand des Modells wird dann die *adsorbierte Menge* x_i bei entsprechenden *molaren Gasanteil* y_i berechnet. Die *IAST-Selektivität* S wird dann wie folgt über Gleichung (3) bestimmt:¹³⁸

$$S = \frac{x_1/x_2}{y_1/y_2} \quad (3)$$

2. Zielsetzung und Motivation

Ziel dieser Arbeit ist die Untersuchung des Einflusses sowohl von Templaten hinsichtlich der ausgebildeten Strukturen von 1,2,4-Triazol-basierten Koordinationspolymeren als auch die Untersuchung des Einflusses der $\text{-C}\equiv\text{C-}$ Dreifachbindung auf die Sorptionseigenschaften von Pyrazolat-basierten Metall-organischen Gerüstverbindungen.

Das Ziel größere Strukturen gezielt über spontane Selbstorganisationsprozesse aufzubauen, kann über die Verwendung neutraler oder ionischer Verbindungen (Template), welche den Aufbau über intermolekulare Wechselwirkungen organisieren, erzielt werden. Zahlreiche Arbeiten haben sich bereits mit dem Templat-Effekt befasst, wobei aufgrund weniger systematischer Arbeiten das Verständnis, wie Template den Selbstorganisationsprozess beeinflussen und wie dies gezielt genutzt werden kann, relativ gering ist. Aus diesem Grund sollen die Anionen für die Synthese von Eisen- bzw. Cobalt-haltigen Koordinationspolymeren mit dem bereits literaturbekannten Linker 1,1'-(*trans*-2-buten-1,4-diyl)bis-1,2,4-triazol (tbbt) systematisch ausgetauscht und die erhaltenen Strukturen analysiert werden.

Mehrere Arbeiten, angestoßen von Farha *et al.* im Jahre 2012 und weitergeführt von Janiak *et al.* zeigten bereits, dass der Austausch von Phenyl-Einheiten durch $\text{-C}\equiv\text{C-}$ Dreifachbindungen die Adsorptionsaffinitäten von MOFs erhöhen können. Während in diesen Arbeiten Carboxylat-basierte MOFs untersucht wurden, soll im Rahmen dieser Arbeit mit den thermisch stabileren und weniger Hydrolyse-anfälligen Metall-azolaten Gerüstverbindungen analysiert werden. Für diese Untersuchung eignet sich der erstmalig 2023 von Galli *et al.* verwendete Ligand 1,2-Bis(1*H*-pyrazol-4-yl)ethin (H_2bpe). Neben den Sorptionseigenschaften wurden auch die Stabilitäten der isoretikulären Zink- bzw. Nickel-Serien bezogen auf die Hydrolyse-Anfälligkeit in der veröffentlichten Literatur diskutiert, sodass sich für eine Einordnung und Vergleichbarkeit der Eigenschaften im Rahmen dieser Arbeit auf die Erweiterung dieser Serien fokussiert wurde.

Für alle synthetisierten Verbindungen sollen die Strukturen aufgeklärt, die Topologien beschrieben und weitere Eigenschaften, wie z.B. Spin-Crossover für die 1,2,4-Triazol-basierten Koordinationspolymere oder den Gas- bzw. Dampf-Sorptionseigenschaften der Metall-azolaten Gerüstverbindungen, hinsichtlich potentieller Anwendungsmöglichkeiten untersucht werden.

3. Kumulativer Teil

Die Ergebnisse der Dissertation werden in den nachfolgenden Kapiteln dargelegt. Hierbei handelt es sich um Zeitschriftenaufsätze, welche in internationalen Journalen in Form von Erst-Autorschaften veröffentlicht wurden. Jede Publikation steht mit eigener Auflistung für sich. Hieraus folgt, dass sich die Nummerierung der Abbildungen, Tabellen und Schemata nicht dem Haupttext, sondern an der Publikation orientieren. Zum Ende jeder Publikation ist ein eigenständiges Literaturverzeichnis, welches nicht zum Literaturverzeichnis dieser Arbeit gehört, aufgeführt. In den weiteren Kapiteln werden die veröffentlichten Ergebnisse mit Eigenanteilen als Co-Autor dargelegt.

Jede Publikation wird durch den Titel, Autorenliste, Journalnamen und einer Kurzzusammenfassung eingeleitet. Des Weiteren werden die Anteile der Autoren an den Publikationen vorgestellt.

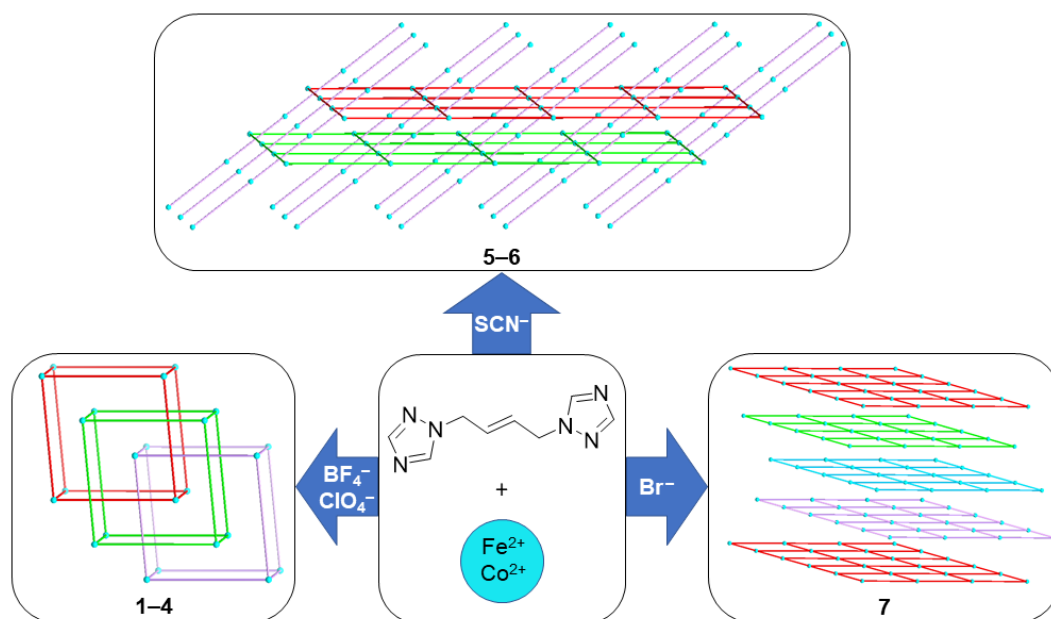
3.1 Interpenetration Phenomena via Anion Template Effects in Fe(II) and Co(II) Coordination Networks with a Bis-(1,2,4-triazole) Ligand

Diese Arbeit wurde veröffentlicht in:

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Kurzzusammenfassung:



Sieben neue Koordinationsnetzwerke [Fe(tbbt)₃](BF₄)₂ (**1**), [Co(tbbt)₃](BF₄)₂ (**2**), [Fe(tbbt)₃](ClO₄)₂ (**3**), [Co(tbbt)₃](ClO₄)₂ (**4**), [Fe(NCS)₂(tbbt)₂] (**5**), [Co(NCS)₂(tbbt)₂] (**6**) und [Fe(H₂O)₂(tbbt)₂]Br₂·2H₂O (**7**) wurden mit dem Linker 1,1'-(*trans*-2-buten-1,4-diyl)bis-1,2,4-triazol (tbbt) synthetisiert und strukturell untersucht. Die Struktur der Komplexe **1–4** besteht aus drei sich gegenseitig durchdringenden, symmetriebezogenen 3D-Netzwerken. Jedes einzelne 3D-Netzwerk bildet ein primitives, nahezu kubisches Gitter (**pcu**) mit BF₄⁻ oder ClO₄⁻ Anionen in den Zwischenräumen. Die Struktur der Verbindungen **5** und **6** setzt sich aus zweidimensionalen **sql**-Schichten, die parallel zueinander im AB-Schichttyp stehen, zusammen. Diese Schichten sind von eindimensionalen Ketten durchdrungen und haben beide die gleiche Summenformel [M(NCS)₂(tbbt)₂] (M = Fe, Co). Die Struktur von Verbindung **7** besteht aus parallelen, zweidimensionalen Schichten im ABCD-Schichttyp. Die Interpenetration der Verbindungen **1–6** wird nicht über π - π -Wechselwirkungen zwischen den Triazolringen oder C=C-Bindungen, wie hätte erwartet werden können, sondern über (Triazol)C–H $\cdots$ F₄B⁻, C–H $\cdots$ O₄Cl⁻ und C–H $\cdots$ SCN⁻ Wasserstoffbrückenbindungen gesteuert. Dies lässt auf einen Templat-Effekt der entsprechenden nicht-koordinierten oder koordinierten Anionen als Grund für die Interpenetration schließen. In **7** werden die (Triazol)C–H $\cdots$ Br⁻ Wechselwirkungen durch O–H $\cdots$ O und O–H $\cdots$ Br Wasserstoffbrückenbindungen unter Beteiligung der Aqua-Liganden und der Kristallwassermoleküle unterstützt. Es ist offensichtlich, dass die koordinierten und nicht-koordinierten Anionen eine wesentliche Rolle bei der Bildung der Netzwerke spielen und die Interpenetration steuern. Alle Eisen(II)

Koordinationsnetzwerke sind farblos, cremefarben bis gelb-orange und haben Metallionen bis zu 77 K im *high-spin*-Zustand. Verbindung **5** verweilt sogar bei Temperaturen bis zu 10 K im *high-spin*-Zustand.

Anteil an der Publikation:

- Dustin N. Jordan: Idee und Konzeptualisierung, Synthese und Optimierung der Verbindungen **1–7**, Lösung und Verfeinerung der Strukturen, Strukturelle Analyse, Charakterisierung der Materialien, Auswertung und Interpretation der Ergebnisse, Verschriftlichung und Revision des Manuskripts.
- Patrick G. Straßburg: Synthese und Charakterisierung der Verbindungen **1–3** und **5** im Rahmen seiner Bachelorarbeit unter Aufsicht von Dustin N. Jordan.
- Dennis Woschko: Lösung und Verfeinerung der Strukturen und Hilfe bei den anderen Verfeinerungen.
- Luca M. Carrella: Messung und Interpretation der temperaturabhängigen Messungen der magnetischen Suszeptibilität und Verschriftlichung des Manuskripts.
- Laure P. Cuignet: Idee und Konzeptualisierung und synthetische Vorarbeiten.
- Katharina Eickmeier: Hilfe bei den Druckexperimenten in der Diamantstempelzelle.
- Richard Dronskowski: Revision des Manuskriptes.
- Yann Garcia: Idee und Konzeptualisierung und Revision des Manuskriptes.
- Eva Rentschler: Revision des Manuskriptes.
- Christoph Janiak: Idee und Konzeptualisierung, Verschriftlichung und Revision des Manuskriptes.

Article

Interpenetration Phenomena via Anion Template Effects in Fe(II) and Co(II) Coordination Networks with a Bis-(1,2,4-triazole) Ligand

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Abstract: Seven new coordination networks, [Fe(tbbt)₃](BF₄)₂ (**1**), [Co(tbbt)₃](BF₄)₂ (**2**), [Fe(tbbt)₃](ClO₄)₂ (**3**), [Co(tbbt)₃](ClO₄)₂ (**4**), [Fe(NCS)₂(tbbt)₂] (**5**), [Co(NCS)₂(tbbt)₂] (**6**), and [Fe(H₂O)₂(tbbt)₂]Br₂·2H₂O (**7**), were synthesized with the linker 1,1'-(*trans*-2-butene-1,4-diyl)bis-1,2,4-triazole (tbbt) and structurally investigated. The structure of complexes **1–4** is composed of three interpenetrating, symmetry-related 3D networks. Each individual 3D network forms a primitive, nearly cubic lattice (**pcu**) with BF₄[−] or ClO₄[−] anions present in the interstitial spaces. The structure of compounds **5** and **6** is composed of two-dimensional **sql** layers, which are parallel to each other in the AB stacking type. These layers are interpenetrated by one-dimensional chains, both having the same formula unit, [M(NCS)₂(tbbt)₂] (M = Fe, Co). The structure of compound **7** consists of parallel, two-dimensional **sql** layers in the ABCD stacking type. The interpenetration in **1–6** is not controlled by π - π interactions between the triazole rings or C=C bonds, as could have been expected, but by (triazole)C-H $\cdots$ F₄B, C-H $\cdots$ O₄Cl, and C-H $\cdots$ SCN anion hydrogen bonds, which suggests a template effect of the respective non-coordinated or coordinated anion for the interpenetration. In **7**, the (triazole)C-H $\cdots$ Br anion interactions are supplemented by O-H $\cdots$ O and O-H $\cdots$ Br hydrogen bonds involving the aqua ligand and crystal water molecules. It is evident that the coordinated and non-coordinated anions play an essential role in the formation of the networks and guide the interpenetration. All iron(II) coordination networks are colorless, off-white to yellow-orange, and have the metal ions in the high-spin state down to 77 K. Compound **5** stays in the high spin state even at temperatures down to 10 K.

Keywords: coordination polymers; coordination networks; metal-organic frameworks; triazole ligand; iron(II); cobalt(II); interpenetration; template effect; C-H $\cdots$ X hydrogen bonds; spin-crossover effect

1. Introduction

According to the IUPAC definition, coordination polymers consist of repeating coordination entities extending in one, two, or three dimensions [1–3]. Controlling their structure, thus leading to the desired properties for potential applications, can be described as one of the greatest goals of supramolecular chemistry in general [4,5]. Among the promising ways to achieve specific topologies and structures are self-assembly processes involving metal

ions with different coordination geometries or radii and using counter anions or solvent molecules as templating agents [4,6–8]. While cations and anions as structure-guiding templates are well documented, a better understanding of their templating properties and their influence will eventually help to reach the ultimate aim of being able to control the structures and, therefore, the properties of the targeted products [8–17]. Examples for anion templating effects show that non-covalent interactions, like hydrogen-bonding, are involved [8,11,18,19].

The spin-crossover (SCO) phenomenon describes the transition from a low-spin (LS) to a high-spin (HS) state and vice versa of six-coordinated octahedral $3d^4$ – $3d^7$ metal ions induced by external stimuli like temperature, pressure, light irradiation, etc. [20–28]. Due to this entropy-driven electron redistribution through SCO, changes in chemical and physical properties like magnetism, color, structure, and dielectric behavior draws attention to potential applications such as switches, memory devices, sensors, or contrast agents [23,24,26,29–35]. Anions can play an important role in influencing these SCO properties [36–39].

Regarding SCO, iron(II) is by far the most studied metal ion concerning its property changes [23,26,40]. Most of these compounds have the d^6 - Fe^{2+} metal center surrounded by six nitrogen donor atoms, in which the metal–ligand bond lengths change by around 0.2 Å (10%) during spin transition [23,41]. SCO in cobalt(II) is less investigated, which could be ascribed to more gradual spin transitions [42–44]. Besides a bond length change by around 0.1 Å (5%), a significant Jahn–Teller distortion is expected for the LS state of an octahedrally coordinated d^7 - Co^{2+} metal ion [26,42,44–46].

1,2,4-triazole-based ligands are often used in coordination polymers and lead to interesting topologies, structures, and magnetic properties like SCO [5,47–49]. Previous studies show that the linker length can influence SCO properties and that, even with long ligands, SCO can be observed [43,50–55]. Here, we have synthesized Fe(II) and Co(II) coordination polymers with the bis-(1,2,4)-triazole ligand, 1,1'-(*trans*-2-butene-1,4-diyl)bis-1,2,4-triazole (tbbt), and different anions. The ligand tbbt was published first by Attaryan et al., and till now, there is only one mixed ligand structure known ($\text{Cd}(\text{tbbt})_2(\text{btc})_2 \cdot 2\text{H}_2\text{O}$, $\text{btc} = 1,3,5$ -benzenetricarboxylate) [56,57]. Therefore, this work is a continuation of previously published results with different 1,1'-linked bis(1,2,4)-triazoles [47,48,58–65].

2. Materials and Methods

All chemicals were commercially obtained and used without further purification (see Supplementary Materials, Section S1). The water used was deionized.

FT-IR spectra were collected using a Bruker TENSOR 37 IR spectrometer (Bruker, Billerica, MA, USA) in ATR mode (platinum ATR-QL, diamond) in the range 4000–500 cm^{-1} . NMR spectra were measured with a Bruker Avance III—300 (Bruker, Billerica, MA, USA) (^1H : 300 MHz; $^{13}\text{C}\{^1\text{H}\}$: 75 MHz). Elemental analyses were performed using a PerkinElmer 2400 series II elemental analyzer (PerkinElmer, Waltham, MA, USA) (accuracy of 0.5%). As coordination polymers cannot be recrystallized, any co-precipitate that cannot be removed by washing will affect the elemental analysis. It will be seen that out of the $8 \times 3 = 24$ CHN analysis values for the tbbt linker and the 7 complexes, 19 values lie within 0.5% deviation, 4 within 1%, and only one value deviates by 1.1% (C for compound 4). Thermogravimetric analyses were performed using a Netzsch TG209 F3 Tarsus (Netzsch, Selb, Germany) under a nitrogen atmosphere with a ramp of 5 K min^{-1} up to 600 °C. PXRD measurements were obtained with a Rigaku MiniFlex (Rigaku, Tokyo, Japan) (600 W, 40 kV, 15 mA) and Cu-K_α radiation ($\lambda = 1.54184$ Å) at room temperature. The increasing baseline below 5° 2Theta stems from the PXRD device measurement method with the low-background silicon holder. The highest reflex was normalized to 1. Simulated powder patterns were derived from the single-crystal data using MERCURY 2020.3.0 software [66].

Suitable single crystals were selected under a polarized-light Leica M80 microscope (Leica, Wetzlar, Germany) and mounted with oil on a cryo-loop. The data were obtained using a Rigaku XtaLAB Synergy S (Rigaku, Tokyo, Japan) diffractometer with a hybrid

pixel array detector and a micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray source ($\lambda = 1.54184 \text{ \AA}$). CRYSLISPRO was used for cell refinement, data reduction, and absorption correction [67]. The crystal structure was solved using OLEX2 with SHELXT, and the refinement was done with SHELXL [68–70]. Figures were drawn with DIAMOND 4.0 software [71]. The values for the distortion indices of the coordination polyhedra of 1–7 were calculated using OctaDist software [72]. For further information, see Supplementary Materials, Section S7.

SCO experiments were carried out as follows: single crystals of compounds 1–7 were selected and mounted with oil on a cryo-loop. The single crystals were cooled down to 80 K using the cryocooler of a Rigaku XtaLAB Synergy S diffractometer (Rigaku, Tokyo, Japan) at a rate of 0.5 K/min.

The temperature-dependent magnetic susceptibility of compound 5 was recorded using a Quantum Design SQUID magnetometer MPMS-XL7 (Quantum Design, San Diego, CA, USA). Measurements were made in a temperature range of 10 K to 300 K and under an applied external field of 0.1 Tesla. The temperature-dependent magnetic moments were corrected for the diamagnetic contribution of the holder, as well as for the diamagnetic contribution of the sample, which was determined using the Pascal constant.

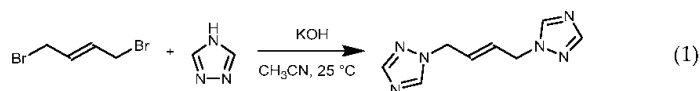
For powder pressure experiments, powders of compounds 1–7 were pressed with a 30-ton press, a P30 hydraulic press by Research Industrial Instrument Co. (London, England), under vacuum in a 13 mm press tool for KBr pellets by the LOT-Oriel Group (LOT-Oriel Group, Darmstadt, Germany) at a pressure of 9 t for 10 min.

Diamond anvil cell (DAC) experiments were performed in a Boehler-Almax-DAC Diacell® Bragg-LT(S) Plus (Almax easyLab Inc., Cambridge, MA, USA). Diamonds with 400 μm central tips and a tungsten carbide holder were used. The pressure inside the DAC was determined with the ruby fluorescence method. The corresponding ruby fluorescence spectrometer was based on the design by Y. Feng [73]. The light source was an LED with broadband emission around 565 nm. An Ocean Optics® HR2000+ Raman spectrometer (Ocean Optics, Dunedin, FL, USA) was used for detection.

2.1. Synthesis

2.1.1. Synthesis of 1,1'-(*trans*-2-butene-1,4-diyl)bis-1,2,4-triazole (tbbt)

The synthesis was carried out with a modified procedure from Shang et al. [74], as shown in Equation (1). Amounts of 4.0 g (57.9 mmol) of 1,2,4-triazole and 6.0 g (106.7 mmol) of KOH in 100 mL of acetonitrile were stirred for 30 min at 25 °C. A solution of 4.28 g (20.0 mmol) of *trans*-1,4-dibromo-2-butene in 60 mL of CH_3CN was added, and the resulting mixture was stirred for a further 30 min at 25 °C. After filtration, the solvent was removed in vacuo. The resulting oil was dissolved in 30 mL of deionized H_2O and washed with chloroform ($4 \times 50 \text{ mL}$). After the organic phase was dried with MgSO_4 and filtrated, the excess of solvent was removed by rotary evaporation. The obtained yellowish product was purified by vacuum sublimation for 24 h at 140 °C. (Note: tbbt can also be used without purification by vacuum sublimation.) Yield: 1.93 g (51%). Before the analyses, the sample was dried in vacuo at 60 °C, as otherwise water signals will be detected. $\text{C}_8\text{H}_{10}\text{N}_6$: calc. C = 50.5, H = 5.3, N = 44.2; exp.: C = 50.3, H = 5.4, N = 44.2. IR: $\tilde{\nu}$ [cm^{-1}]: 2450, 3120, 3098, 3007, 1846, 1802, 1766, 1743, 1558, 1512, 1442, 1387, 1258, 1344, 1312, 1269, 1245, 1219, 1170, 1148, 1075, 1008, 977, 960, 929, 872, 758, 678, 642. $^1\text{H-NMR}$ (300 MHz, DMSO-d_6): δ [ppm]: 8.50 (s, 2H), 7.98 (s, 2H), 5.83–5.80 (m, 2H), 4.86–4.83 (q, 4H). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75 MHz, DMSO-d_6): δ [ppm]: 151.56, 143.95, 128.52, 49.60.



2.1.2. Synthesis of $[\text{Fe}(\text{tbbt})_3](\text{BF}_4)_2$ (**1**)

(Catena-bis(μ -1,1'-(trans-2-butene-1,4-diyl)bis-1,2,4-triazole- $\kappa^2\text{N}_4,\text{N}_4'$)iron bis(tetrafluoroborate))

The amounts of 61 mg (0.18 mmol) of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and 103 mg (0.54 mmol) of tbbt were dissolved in 6 mL of H_2O and stored at rt. After 24 h, colorless single crystals were obtained, washed three times with H_2O (6 mL each), and stored in H_2O . Yield: 82 mg (57%). $\text{C}_{24}\text{H}_{30}\text{B}_2\text{F}_8\text{FeN}_{18}$: calc.: C = 36.0, H = 3.8, N = 31.5; exp.: C = 35.5, H = 3.8; N = 31.2. IR: $\tilde{\nu}$ [cm^{-1}]: 3145, 2165, 1752, 1520, 1473, 1443, 1375, 1358, 1313, 1276, 1209, 1175, 1122, 1050, 1013, 990, 969, 941, 880, 759, 677, 652.

2.1.3. Synthesis of $[\text{Co}(\text{tbbt})_3](\text{BF}_4)_2$ (**2**)

(Catena-bis(μ -1,1'-(trans-2-butene-1,4-diyl)bis-1,2,4-triazole- $\kappa^2\text{N}_4,\text{N}_4'$)cobalt bis(tetrafluoroborate))

Compound **2** was synthesized similar to **1** from 61 mg (0.18 mmol) of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and 103 mg (0.54 mmol) of tbbt. Yield: 93.6 mg (65%). $\text{C}_{24}\text{H}_{30}\text{B}_2\text{F}_8\text{CoN}_{18}$: calc.: C = 35.9, H = 4.1, N = 30.3; exp.: C = 35.4, H = 3.9, N = 31.2. IR: $\tilde{\nu}$ [cm^{-1}]: 3148, 3029, 2965, 1751, 1520, 1474, 1443, 1375, 1359, 1313, 1278, 1209, 1174, 1121, 1050, 1013, 991, 969, 941, 880, 759, 677, 652.

2.1.4. Synthesis of $[\text{Fe}(\text{tbbt})_3](\text{ClO}_4)_2$ (**3**)

(Catena-bis(μ -1,1'-(trans-2-butene-1,4-diyl)bis-1,2,4-triazole- $\kappa^2\text{N}_4,\text{N}_4'$)iron bis(perchlorate))

Please note that perchlorates are potentially explosive and must be handled with care. TGA shows an explosive decomposition at around 250 °C. In total, 46 mg (0.18 mmol) of $\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ and 103 mg (0.54 mmol) of tbbt were dissolved in 6 mL of H_2O and stored at rt. After 24 h, yellow single crystals were obtained, washed three times with H_2O (6 mL each), and stored in H_2O . Yield: 66 mg (44%). $\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{O}_8\text{FeN}_{18}$: calc.: C = 34.9, H = 3.7, N = 30.6; exp.: C = 34.1, H = 3.8, N = 29.9. IR: $\tilde{\nu}$ [cm^{-1}]: 3144, 2960, 2164, 2018, 1751, 1518, 1472, 1439, 1373, 1358, 1311, 1276, 1208, 1172, 1121, 1090, 1013, 989, 968, 939, 879, 759, 676, 651, 622.

2.1.5. Synthesis of $[\text{Co}(\text{tbbt})_3](\text{ClO}_4)_2$ (**4**)

(Catena-bis(μ -1,1'-(trans-2-butene-1,4-diyl)bis-1,2,4-triazole- $\kappa^2\text{N}_4,\text{N}_4'$)cobalt bis(perchlorate))

Please note that perchlorates are potentially explosive and should be handled with care. TGA shows an explosive decomposition at around 340 °C. In total, 33 mg (0.09 mmol) of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 2 mL of H_2O , while 35 mg (0.18 mmol) of tbbt was dissolved in 5 mL of H_2O . Both solutions were heated to their boiling points, combined, and cooled to rt at ambient conditions. Orange crystals were obtained overnight, washed three times with H_2O (7 mL each), and stored in H_2O . Yield: 34 mg (46%). $\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{O}_8\text{CoN}_{18}$: calc.: C = 34.8, H = 3.7, N = 30.4; exp.: C = 33.7, H = 3.7, N = 29.8. The jointly lower C and N analysis values may indicate the formation of a very small amount of cobalt(hydroxide)oxide co-precipitate. IR: $\tilde{\nu}$ [cm^{-1}]: 3146, 2960, 1749, 1519, 1472, 1440, 1373, 1312, 1277, 1208, 1172, 1091, 1077, 1013, 990, 968, 938, 878, 758, 677, 651, 622, 475.

2.1.6. Synthesis of $[\text{Fe}(\text{NCS})_2(\text{tbbt})_2]$ (**5**) (Catena-bis(thiocyanato- κN)-bis(μ -1,1'-(trans-2-butene-1,4-diyl)bis-1,2,4-triazole- $\kappa^2\text{N}_4,\text{N}_4'$)iron)

Compound **5** was synthesized according to Garcia et al. [75]. A solution of 90 mg (0.23 mmol) of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 51 mg (0.29 mmol) of ascorbic acid in 1.25 mL of H_2O was heated to near its boiling point and added to a hot solution of 35 mg (0.46 mmol) of NH_4SCN in 1 mL of H_2O . To this, a nearly boiling solution of 88 mg (0.46 mmol) of tbbt in 5 mL of H_2O was added dropwise. This final hot solution was cooled to rt within two days. The colorless crystals were washed with H_2O three times (6 mL each) and were stored in H_2O . Yield: 74 mg (58%). $\text{C}_{18}\text{H}_{20}\text{S}_2\text{FeN}_{14}$: calc.: C = 39.1, H = 3.7, N = 35.5, S = 11.6; exp.:

C = 38.9, H = 3.7, N = 35.5, S = 11.9. IR: $\tilde{\nu}$ [cm⁻¹]: 3144, 3104, 3026, 2949, 2867, 2847, 2071, 2050, 1822, 1792, 1770, 1734, 1690, 1518, 1470, 1439, 1426, 1391, 1377, 1339, 1318, 1278, 1206, 1182, 1127, 1075, 1033, 1013, 986, 969, 949, 899, 888, 868, 848, 788, 760, 698, 675, 643, 582.

2.1.7. Synthesis of [Co(NCS)₂(tbbt)₂] (6) (Catena-bis(thiocyanato-κN)-bis(μ-1,1'-(trans-2-butene-1,4-diyl)bis-1,2,4-triazole-κ²N4,N4')cobalt)

The amount of 16 mg (0.09 mmol) of Co(SCN)₂ was dissolved in 2 mL of H₂O, while 35 mg (0.18 mmol) of tbbt was dissolved in 5 mL of H₂O. Both solutions were heated to nearly their boiling points, combined, and cooled to rt over 48 h. The obtained orange crystals were washed three times with H₂O (7 mL each) and stored in H₂O. Yield: 36 mg (36%). C₁₈H₂₀S₂CoN₁₄: calc.: C = 38.9, H = 3.6, N = 35.3, S = 11.5; exp.: C = 38.5, H = 3.8, N = 35.2, S = 11.9. IR: $\tilde{\nu}$ [cm⁻¹]: 3145, 3105, 2949, 2852, 2081, 2058, 2015, 1825, 1792, 1770, 1734, 1689, 1519, 1471, 1440, 1425, 1392, 1378, 1339, 1319, 1279, 1205, 1177, 1127, 1069, 1034, 1014, 1007, 988, 970, 948, 916, 901, 889, 868, 847, 788, 760, 698, 675, 643, 582, 480, 467, 423.

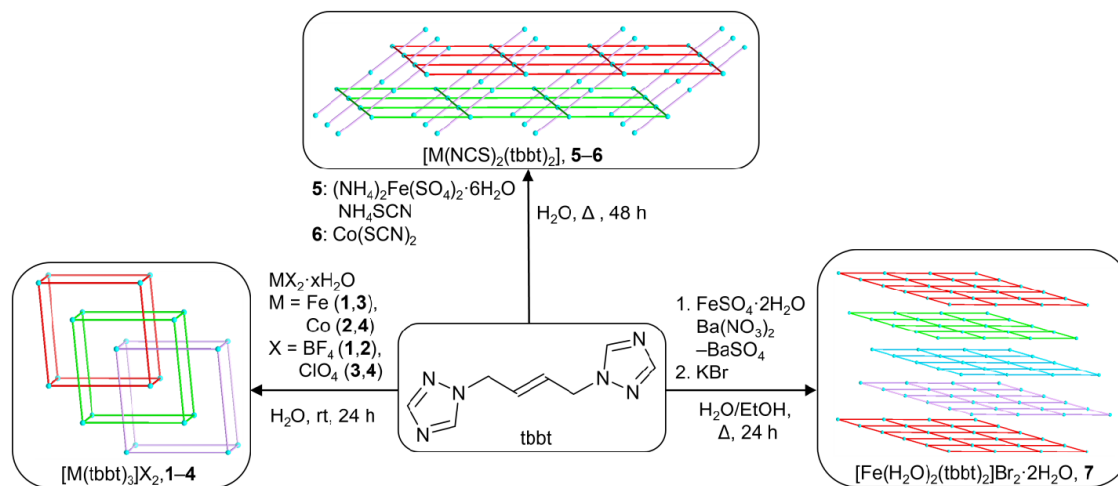
2.1.8. Synthesis of [Fe(H₂O)₂(tbbt)₂]Br₂·2H₂O (7) (Catena-diaqua-bis(μ-1,1'-(trans-2-butene-1,4-diyl)bis-1,2,4-triazole-κ²N4,N4')iron Dibromide Dihydrate)

Compound 7 was synthesized similar to Lavrenova et al. [76]. In total, 47 mg (0.25 mmol) of FeSO₄·2H₂O and 10 mg (0.06 mmol) of ascorbic acid were dissolved in 3 mL of H₂O, to which a solution of 66 mg (0.25 mmol) of Ba(NO₃)₂ in 3 mL of H₂O was added. The mixture was left for 2 h at rt; then, the BaSO₄ precipitate was filtered off, and 120 mg (1 mmol) of KBr was added to this solution, which was heated to nearly boiling and added to a nearly boiling solution of 95 mg (0.50 mmol) of tbbt in 3 mL of EtOH. The combined hot solution was cooled to rt at ambient conditions, and colorless crystals were obtained overnight. The crystals were washed with H₂O three times (6 mL each) and stored in H₂O. Yield: 131 mg (79%). C₁₆H₂₀FeN₁₂Br₂(H₂O)₂·2H₂O: calc.: C = 28.8, H = 4.2, N = 25.2; exp.: C = 28.4, H = 4.3, N = 25.2. IR: $\tilde{\nu}$ [cm⁻¹]: 3472, 3386, 3257, 3144, 3096, 2968, 2941, 2075, 1812, 1731, 1620, 1583, 1526, 1476, 1441, 1383, 1369, 1345, 1311, 1276, 1209, 1181, 1132, 1098, 1027, 1005, 980, 908, 880, 866, 776, 756, 707, 676, 655, 642, 574, 528, 486, 423.

3. Results and Discussion

The linker 1,1'-(trans-2-butene-1,4-diyl)bis-1,2,4-triazole (tbbt) was obtained from the reaction between 1,2,4-triazole and trans-1,4-dibromo-2-butene in acetonitrile, as depicted in Equation (1), and its identity was established by ¹H, ¹³C NMR and IR spectroscopy. Thermogravimetric analysis indicates a stability of tbbt of up to 200 °C (see Supplementary Materials, Section S2).

The synthesis of the metal–tbbt networks 1–7 is schematically presented in Scheme 1. Compounds 1–4 were initially synthesized with both 1:2 and 1:3 molar metal:ligand ratios. Even at the experimental M:L ratio of 1:2, the structures of 1–4 with an M:L formula ratio of 1:3 were obtained, as verified by identical powder X-ray diffractograms. However, at the ratio of 1:3, the quality of the single crystals for the X-ray analysis was usually better. The synthesis of 1–4 and 6 proceeds by the straightforward reaction of the metal salts and the tbbt linker in water. The synthesis of compound 5 includes the combination of three separately heated solutions of the metal salt, NH₄SCN, and linker. The synthesis of 7 includes the in situ formation of an intermediary product (ferrous nitrate) [76] at elevated temperature before the addition of tbbt. The combination of hot solutions in the case of 5–7 was necessary to avoid the rapid precipitation of 5–7 as powders, instead of the formation of single crystals upon slow cooling (Scheme 1). Images of the single crystals can be found in Supplementary Materials, Section S5. The colorless, off-white to yellow-orange color of the iron products and the yellow to orange color of the cobalt compounds signals their HS state [25].



Scheme 1. Schematic presentation of the synthesis of the coordination networks 1–7 with their formed structure topologies. The blue spheres represent the metal atoms and the different colors of the connecting lines differentiate the adjacent networks. The *anti*-conformeric tbtt linkers lie along the colored connecting lines except for the for the pink chains in 5 and 6, where there are two curved *syn*-conformeric linkers for each connecting line.

The IR spectra of compounds 1–7 (see Supplementary Materials, Section S3) show the characteristic bands of the linker for $\nu(C=C)$ at around 969 cm^{-1} and $\nu(C=N)$ at about 1515 cm^{-1} . Also, the indicative anion bands can be observed ($\nu(B-F)$: 1045 cm^{-1} for 1 and 2; $\nu(Cl-O)$: 1091 cm^{-1} , 936 cm^{-1} , 621 cm^{-1} for 3 and 4; $\nu(NCS)$: 2048 cm^{-1} for 5 and 6) [77]. Due to structural similarities, the IR spectra of 1–4 or 5 and 6, respectively, look almost identical.

Thermogravimetric analysis indicates a thermal stability of at least $250\text{ }^\circ\text{C}$ for 1–6 and around $80\text{ }^\circ\text{C}$ for 7 (see Supplementary Materials, Section S4). The main thermal decomposition step for 1–7 is attributed to the decomposition of the tbtt linker. The neat tbtt compound decomposes between ~ 180 and $280\text{ }^\circ\text{C}$ at a heating rate of 5 K min^{-1} (Figure S4). As a linker in the metal complexes 1–7, the decomposition starts at $\sim 250\text{ }^\circ\text{C}$ or even later, indicating a thermal stabilization upon metal coordination caused by rigidification of the molecule. The BF_4^- compounds 1 and 2 (dec. from $\sim 300\text{ }^\circ\text{C}$, Figures S12 and S13) or the NCS compounds 5 and 6 (dec. starting $\sim 250\text{ }^\circ\text{C}$, Figures S16 and S17) show almost similar stabilities and TGA traces. Decomposition of the BF_4^- anion leads to FeF_3 in 1, CoF_2 in 2, FeS_2 in 5, and CoS_2 in 6, whose mass fractions are close to the residual mass-% values at $600\text{ }^\circ\text{C}$. Perchlorate compounds 3 and 4 both undergo sudden sharp mass loss because of an explosive decomposition at about $250\text{ }^\circ\text{C}$ and $340\text{ }^\circ\text{C}$, respectively (Figures S14 and S15). Please note our warning that perchlorate salts are potentially explosive and must be handled with care! The first decomposition step in 7 is due to the loss of the four water molecules, while the second step at above $300\text{ }^\circ\text{C}$ is attributed to the ligand (Figure S18).

The pH stability of each compound was visually checked in an aqueous medium for one hour. Iron compounds 1, 3, 5, and 7 are stable within a range of pH 4 to 6, while the cobalt analogues 2, 4, and 6 are stable between pH 1 and 8. Below pH 3 and above pH 7, the crystals of the iron compounds very quickly turned from almost colorless to green. The cobalt compounds turn blue above pH 8 but retain their faint yellow-orange color down to pH 1.

The topology of the metal-linker networks was elucidated by single-crystal X-ray analysis as presented below. Additional crystal data and values of the distortion of the metal coordination polyhedra of 1–7 can be found in the Supplementary Materials, Sections

S6 and S7. Additional structure images are provided in the Supplementary Materials, Section S8. For each compound powder, X-ray diffraction patterns positively matched the corresponding simulated pattern from the single-crystal X-ray analysis and, thereby, supported the phase purity of each compound (see Supplementary Materials, Section S9).

3.1. Crystal Structures of $[M(tbbt)_3](BF_4)_2$ and $[M(tbbt)_3](ClO_4)_2$ ($M = Fe$ **1**, **3**; $M = Co$ **2**, **4**)

Crystallographic X-ray analysis shows compounds **1–4** to be isostructural, all crystallizing in the trigonal space group $P\bar{3}$. The asymmetric unit contains one M(II) atom ($M = Fe$, Co) (residing on an inversion center and a threefold rotation axis), one half-linker molecule (inversion center at the middle of the C=C bond) and half a BF_4^- or ClO_4^- anion on the threefold rotation axis with one of the B–F or Cl–O bonds coinciding with the rotation axis (Figure 1). The F and O atoms of the anion in **2–4** are slightly disordered, as indicated by the transparent F or O atoms in Figure 1. The octahedral coordination sphere of each Fe(II) and Co(II) metal ion is composed of six symmetry-related nitrogen donor atoms from six triazole rings of six tbbt molecules (Figure 1) and is only negligibly distorted (see Supplementary Materials, Section S7).

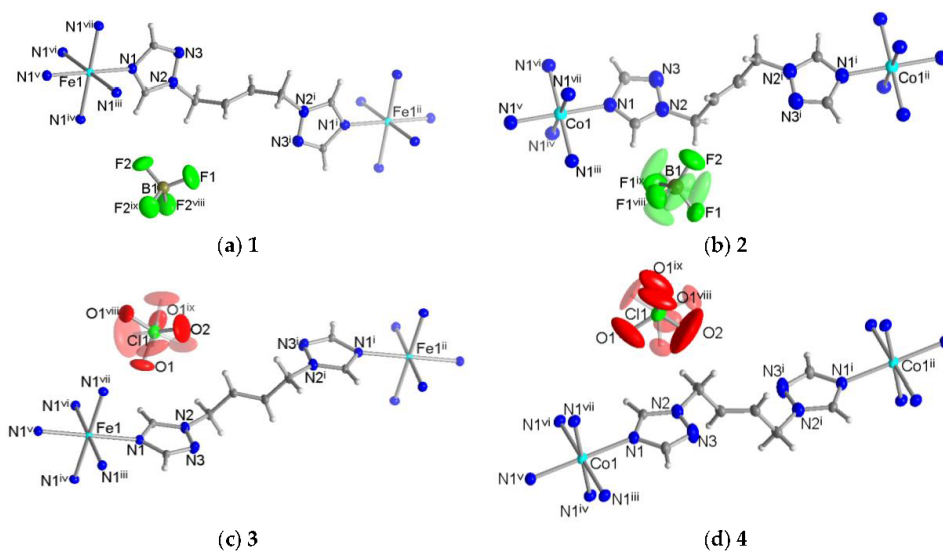


Figure 1. Extended asymmetric unit of (a) **1**, (b) **2**, (c) **3**, and (d) **4** (50% thermal ellipsoids and H atoms with arbitrary radii). The anion disorder is indicated by transparent atoms. The symmetry transformations are as follows: (a) i = 1 − x, 2 − y, 2 − z; ii = 1 + x, y, 1 + z; iii = −1 − x + y, 1 − x, z; iv = −1 + y, −x + y, 1 − z; v = −x, 2 − y, 1 − z; vi = 1 + x − y, 1 + x, 1 − z; vii = 1 − y, 2 + x − y, z; viii = −x + y, 1 − x, z; ix = 1 − y, 1 + x − y, z. (b) i = 2 − x, 1 − y, 2 − z; ii = x, −1 + y, 1 + z; iii = 1 − x + y, 1 − x, z; iv = 1 − y, x − y, z; v = 2 − x, 2 − y, 1 − z; vi = 2 − y, 1 + x − y, z; vii = 1 − x + y, 2 − x, z; viii = 1 − x + y, 1 − x, z; ix = 1 − y, x − y, z. (c) i = 1 − x, 1 − y, −z; ii = −1 + x, −1 + y, −1 + z; iii = 2 − y, 1 + x − y, z; iv = 1 + x − y, x, 1 − z; v = 2 − x, 2 − y, 1 − z; vi = y, 1 − x + y, 1 − z; vii = 1 − x + y, 2 − x, z; viii = 1 − y, 1 + x, z; ix = −x + y, 1 − x, z. (d) i = 1 − x, −y, 2 − z; ii = 1 + x, y, 1 + z; iii = −y, x − y, z; iv = −x + y, −x, z; v = −x, −y, 1 − z; vi = x − y, x, 1 − z; vii = y, −x + y, 1 − z; viii = 1 − x + y, 1 − x, z; ix = 1 − y, x − y, z.

The Fe–N bond lengths are 2.186(2) Å in **1** and 2.191(2) Å in **3**, which is the typical range of an iron(II) high-spin complex [26,75,78]. The Co–N bond lengths with 2.149(2) Å in **2** and 2.150(2) Å in **4** are also in the range of a cobalt(II) high-spin complex [78,79].

Two crystallographically equivalent metal(II) atoms are connected by one ligand molecule to establish a three-dimensional (3D) network, which forms a primitive, almost

cubic lattice (pcu) with two non-coordinated anions on each face (Figure 2a). The $M \cdots M$ distance along the connecting tbbt linker is between 13.9 Å and 14.0 Å. In view of the long linker and, consequently, large void space in a single 3D network, three such symmetry-related 3D networks interpenetrate (Figure 2b) [80–85], as was described in the literature for bis(1,2,4-triazole)- and bis(imidazole)metal compounds [58,86]. The BF_4^- or ClO_4^- anions in **1–4** control or guide the interpenetration of the 3D frameworks because each anion forms three (triazole)C–H $\cdots$ F (2.27 Å–2.48 Å), respectively, (triazole)C–H $\cdots$ O hydrogen bonds (2.37 Å–2.65 Å) with three tbbt ligands, each belonging to one of the three interpenetrating networks (Figure 2c). The BF_4^- or ClO_4^- anions give rise to the same structural motif in **1–4** because of their similar size, shape, and hydrogen-bonding capability. Consequently, different structures would be expected with other charge-compensating counter anions [87,88]. There are no voids in the structure. A calculation of voids with the Mercury program [66] yielded only about 11–13 Å³ or 1.2–1.4% of empty space per unit cell volume with a probe radius of 1.2 Å in **1–4**.

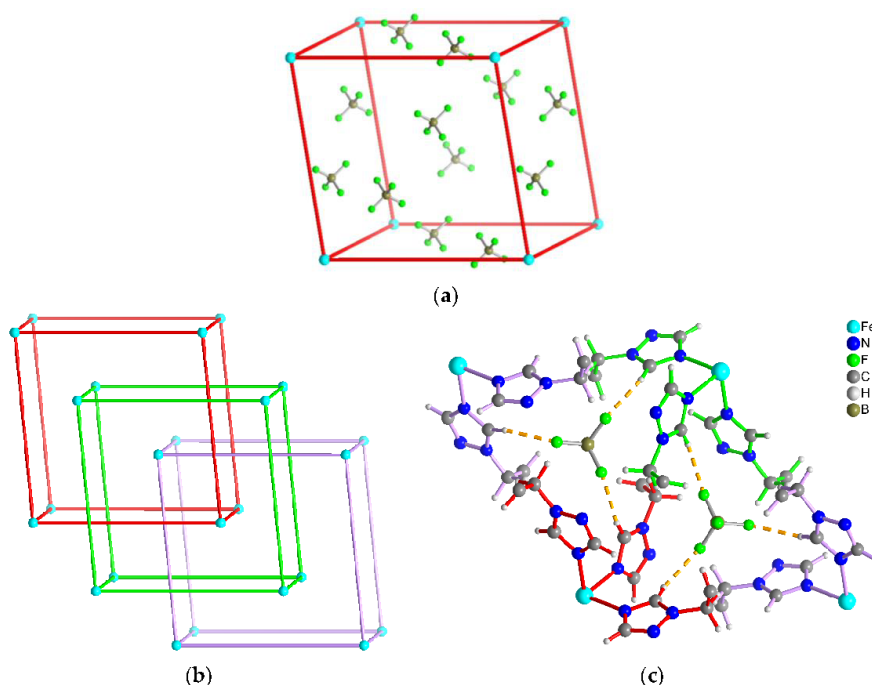


Figure 2. (a) Schematic presentation of the primitive lattice metal-linker topology (pcu) in **1** (identical to **2–4**) with the positions of the anions on the faces of the primitive lattice. (b) Threefold interpenetration of three symmetry-related primitive lattices, differentiated by color (the anions are not shown for clarity). (c) Interpenetration-guiding template effect of the BF_4^- (and similarly of the ClO_4^-) anions through (triazole)C–H $\cdots$ F hydrogen bonds (orange dashed lines) to triazole moieties from three different networks of **1** (for a presentation of the (triazole)C–H $\cdots$ O hydrogen bonds in the structure of **3**, see Figure S26, Supplementary Materials).

3.2. Crystal Structures of $[M(NCS)_2(tbbt)_2]$ ($M = Fe$ **5**; $M = Co$ **6**)

The isostructural compounds **5** and **6** crystallize in the triclinic space group $P\bar{1}$. The asymmetric unit contains two crystallographically different M(II) atoms ($M = Fe, Co$), each on an inversion center, one full and two half tbbt molecules (the latter have again an inversion center at the middle of the C=C bond), and a metal-coordinated isothiocyanate anion (Figure 3). Both metal atoms are coordinated in an octahedral fashion by four different

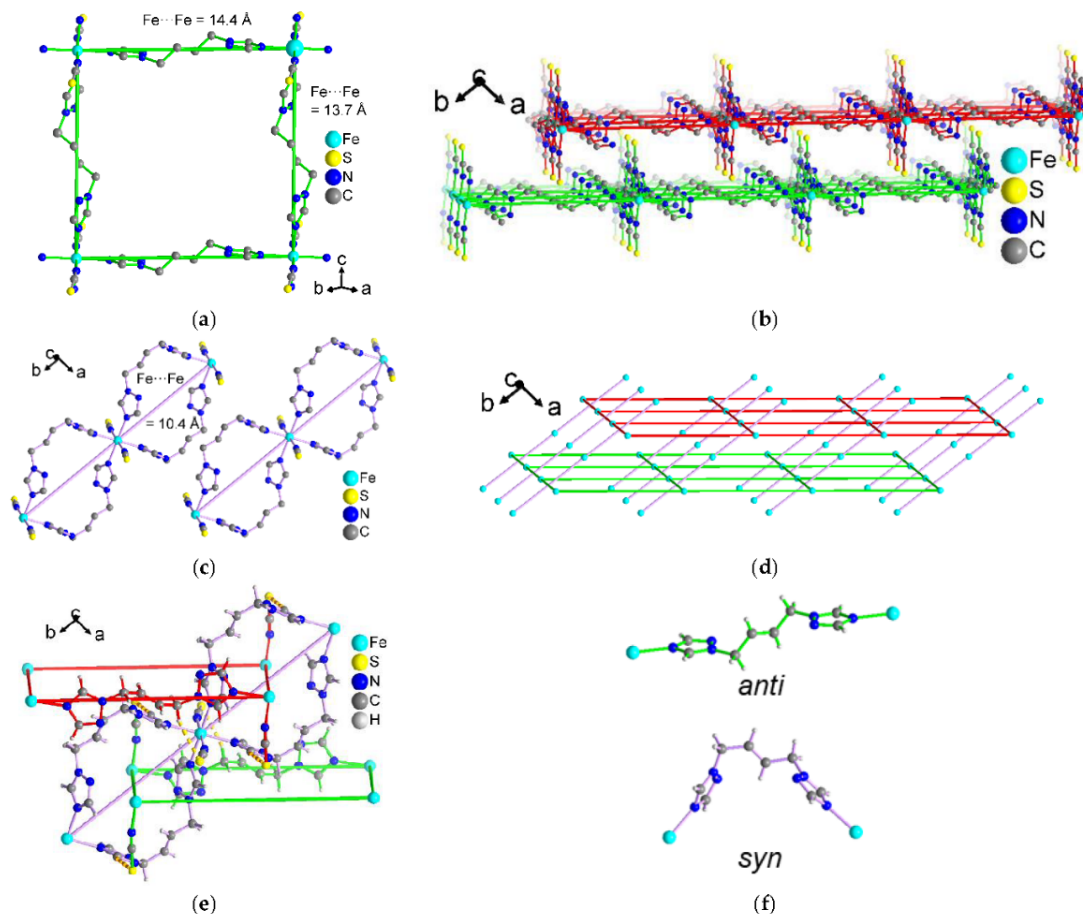


Figure 4. Packing arrangement in **5** ($M = \text{Fe}$) (identical in **6**, $M = \text{Co}$; hydrogen atoms omitted for clarity). Section of the **sql** layer substructure as (a) on-top view and (b) side view with two layers differentiated by red and green colors. (c) Two parallel chains. (d) Schematic arrangement of layers and chain (NCS ligands omitted). (e) Polycatenation organized by (triazole)C-H...S and (butene)C-H...S hydrogen bonds as orange and golden dashed lines, respectively. (f) *Anti* and *syn* conformation of the tbbt linker in the layers and in the chains, respectively.

3.3. Crystal Structure of $[\text{Fe}(\text{H}_2\text{O})_2(\text{tbbt})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (**7**)

Using bromide as the counter anion, a different structure motif was obtained. Compound **7** crystallizes in the orthorhombic space group $Fdd2$. The asymmetric unit contains one-half of an octahedrally coordinated iron(II) atom (on a twofold rotation axis), one full linker molecule, two halves of Fe-coordinated water molecules (aqua ligands), one non-coordinated crystal water molecule, and a bromine anion (Figure 5). In contrast to compounds **1–4** and similar to compounds **5** and **6**, the metal ion in compound **7** is only coordinated by four nitrogen donor atoms. Hence, a 3D framework cannot form, only a 2D metal-linker network. The potentially coordinating Br^- anion does not bind to iron and engages only in hydrogen bonding. Possibly, the coordination of the harder aqua ligand and the non-coordination of the softer bromine can be rationalized by the hard and soft acid and base concept if the Fe(II) ion is categorized on the harder acid site [91–93]. The

distortion of the octahedral coordination environment is stronger compared to compounds 1–6 (see Supplementary Materials, Section S7).

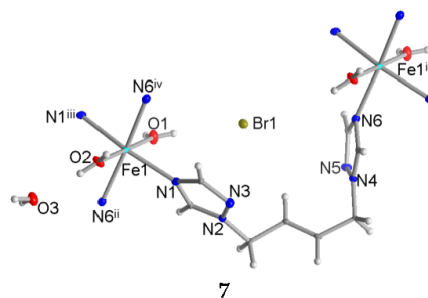


Figure 5. Extended asymmetric unit of **7** (50% thermal ellipsoids and H atoms with arbitrary radii). Symmetry transformations: i = $x, 1/2 + y, 1/2 + z$; ii = $x, -1/2 + y, -1/2 + z$; iii = $1 - x, 1 - y, z$; iv = $1 - x, 3/2 - y, -1/2 + z$.

The Fe–N1 bond length is 2.18(3) Å; the Fe–N6 bond length is slightly larger with 2.20(3) Å. Both bond lengths signal the high-spin state of Fe(II) in this compound [26,75,78]. The bond length between Fe and O2 with 2.098(2) Å is slightly shorter than the Fe–O1 bond length with 2.140(5) Å.

In **7**, corrugated **sql** layers are formed with a *syn* conformation of the linker (Figure 6a), whereas in 1–6, the **tbbt** linker was bridging the metal atoms in the networks with its *anti*-conformation (only the chains in **5** and **6** had the linker bridge in *syn*-conformation). In **7**, the *syn* conformation is responsible for the layer corrugation. Hence, in **7**, the Fe···Fe distance of 9.6 Å within the layer is considerably smaller than the approximately 14 Å in the 3D networks in 1–4 and in the layers in 5–6 but is as seen in the chains in 5–6. Consequently, no interpenetration or polycatenation occurs with the layers in **7**; instead, each pore in the layer is filled with four water molecules and two bromine anions (Figure 6b). These corrugated layers are arranged in an ABCD stacking type with a distance of 7.7 Å between the layer planes as defined by the Fe atoms (Figure 6c). This distance is almost 1.4 Å larger than in **5** and **6**. The different layers interdigitate because of their corrugated nature (Figure 6d). The hydrogen bond length between the coordinated and non-coordinated water molecules is 1.94(5) Å. The O–H···Br hydrogen bonds are between 2.48(4) Å and 2.61(4) Å. The (triazole)C–H···Br hydrogen bonds are 2.83(5) Å and 2.86(5) Å.

3.4. Spin-Crossover Properties

The LS state is enthalpically favored, hence more stable at lower temperatures, while the HS state is entropically favored and, therefore, more stable at higher temperatures [26]. Given that Fe(II) triazole complexes are known to be thermochromic, with a reddish-purple color in the LS state, compounds 1–7 were cooled from room temperature down to 77 K by immersing the vials containing off-white to yellow-orange samples into liquid nitrogen, but no color change was observed.

Considering the possibility of the occurrence of a so-called thermally induced excited spin-state trapping effect (TIESST effect), which describes a metastable HS state at low or even cryogenic temperatures on fast cooling [28,30,40,94,95], we even used a relatively low cooling rate (0.5 K/min) down to 80 K using the cryo-cooler device on the single-crystal X-ray diffractometer, but no SCO was observed.

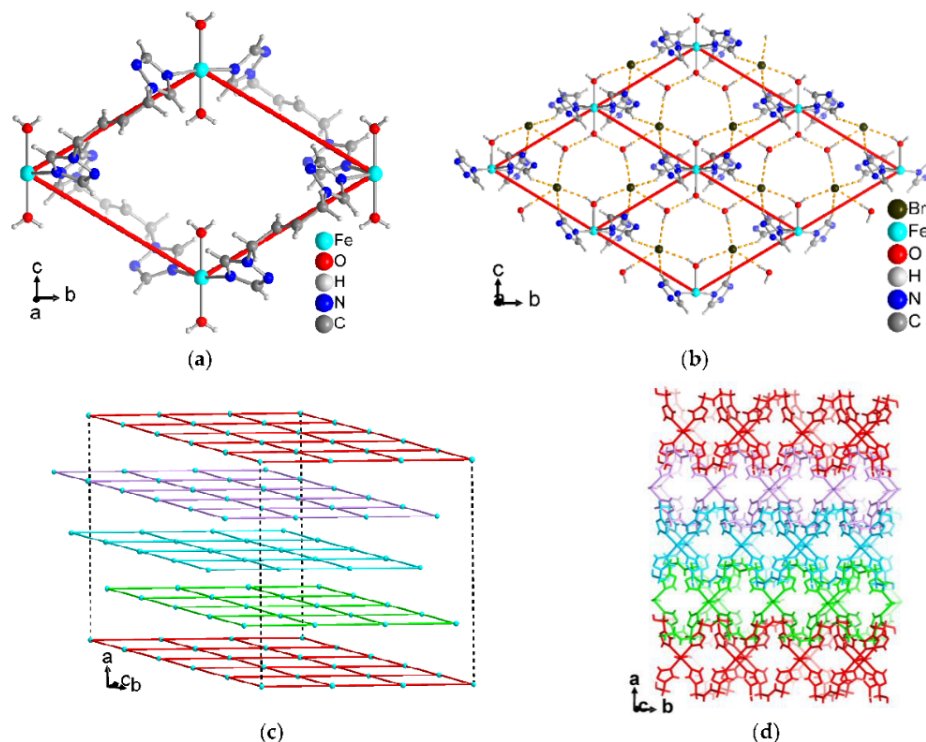


Figure 6. Illustration of a section of the **sql** layer in the structure of **7** with (a) a single opening depicting the *syn*-conformation of the tbbt linker and (b) showing the filling with crystal water molecules and bromide ions (hydrogen bonds as dashed orange lines; from the linker only the triazole part is shown for clarity). (c) ABCD stacking of the **sql** layers as represented by Fe atoms and their topological connections (the black dotted lines are guides to the eye). (d) ABCD stacking of the **sql** layers showing their interdigitation.

One explanation for a non-existing SCO in **1–7** could be that the SCO occurs at lower temperatures or is blocked by the strong rigidity of the networks, which prevent the significant shrinking of the iron(II) nitrogen bond lengths in the LS state. Another reason for the missing SCO could be the present distortion of the metal coordination sphere (see Supplementary Materials, Section S7), which can play a significant role in the stabilization of the LS state [96–99].

To test these assumptions, compound **5**, potentially the most structurally flexible of the iron compounds, was cooled even further to 10 K while performing SQUID measurements of the magnetic susceptibility (Figure 7).

However, even cooling to 10 K did not result in spin switching, and the compound remained in the high-spin state over the entire temperature range, suggesting that the network is still too rigid to allow SCO. A slight increase in the $\chi_M T$ value is observed upon cooling to about 50 K, indicating a weak ferromagnetic interaction. The decrease with further temperature decrease can be explained by weak intermolecular antiferromagnetic interactions and/or zero-field-splitting and/or saturation of the magnetization.

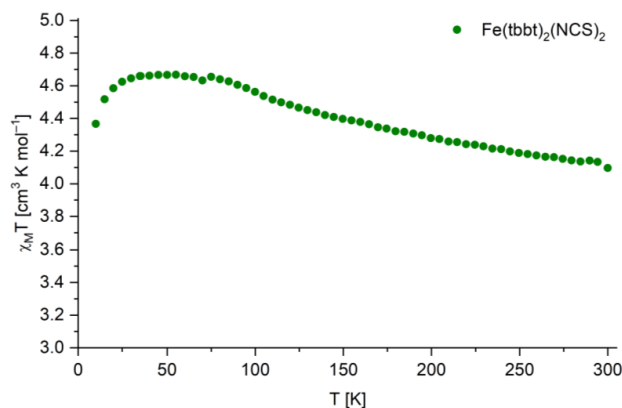


Figure 7. Temperature-variable magnetic susceptibility of compound 5.

Since pressure can increase the ligand field strength at the metal center by shortening the metal–ligand bond lengths, provided there is no change in the coordination polyhedron, it is well known that pressure can induce spin-crossover from the HS to the LS state [25,40,100,101]. Such a pressure-induced SCO remains less investigated because of the more challenging experimental requirements. We have thus examined the spin state of 1–7 under pressure [100,101]. Indeed, we were able to observe a color change from colorless to purple for compound 5. While single crystals of 5 switched back to colorless after removing the pressure, a powder of 5 kept the purple color (Figures S34 and S35). SQUID measurements of this purple powder do not indicate any spin transition (Figure S36). A possible explanation for this color change could be a partial oxidation of iron(II) to iron(III) and/or valence tautomerism.

4. Conclusions

In summary, seven new iron or cobalt coordination polymers based on a bis-1,2,4-triazole ligand 1,1'-(*trans*-2-butene-1,4-diyl)bis-1,2,4-triazole (tbbt) have been successfully synthesized and structurally characterized.

The use of BF_4^- or ClO_4^- metal salts with weakly coordinating anions leads to the formation of triply interpenetrated 3D **pcu** lattices (1–4). As the BF_4^- or ClO_4^- anions do not coordinate to the metal atoms, their close-to-octahedral coordination sphere consists of nitrogen donor atoms from six different bridging tbbt linkers, thereby providing 3D frameworks. Structure and interpenetration are not controlled by interactions between the triazole rings or double bonds, as expected, but by (triazole)C–H $\cdots$ F₄B and CH $\cdots$ O₄Cl hydrogen bonds through a template effect of the non-coordinated BF_4^- or ClO_4^- anions. In compounds 5 and 6, the used SCN^- is coordinated directly to the metal center, with only four N atoms from four tbbt linkers coordinating to the metal atoms. Consequently, these two structures are built of 2D **sql** layers and 1D double-bridged chains. The 2D layers are interpenetrated by the 1D chains, with the interpenetration again controlled and stabilized by hydrogen bonds from the linkers of the chains to the isothiocyanate groups in the layers. Thus, both in 1–4 and in 5 and 6, the anions exert an interpenetration-guiding template effect. When Br^- is used as a counter ion, like in 7, non-interpenetrated **sql** layers in an ABCD stacking type are obtained. In contrast to 1–6, the metal center is coordinated by four nitrogen atoms of linker molecules and two water molecules, instead of six nitrogen atoms. The bromine anion does not coordinate to the iron atoms. Instead, the presence of hydrogen-bonded Br^- and water molecules in the openings of the **sql** layers prevent any interpenetration in 7.

From the existing interpenetration-guiding template effects and various structural motifs, it was evident in this work that the coordinated and non-coordinated anions play an essential role in the formation of the corresponding networks.

SCO is not observable in any compound. The color change of **5** to purple under pressure seems not to correlate with any spin transition. To understand this behavior, further experiments will follow in subsequent research.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/polym15153286/s1>: Section S1: Used Chemicals; Section S2: Ligand analyses; Section S3: Infrared spectra of **1–7**; Section S4: Thermogravimetric analyses of **1–7**; Section S5: Crystal images of **1–7**; Section S6: Crystal data of **1–7**; Section S7: Distortion of the coordination polyhedra of **1–7**; Section S8: Additional structure images; Section S9: Powder X-ray diffraction patterns of **1–7**; Section S10: Pressure experiments of **5**; References [72,96–99,102–105] are cited in the Supplementary Materials.

Author Contributions: Conceptualization, D.N.J., L.P.C., Y.G. and C.J.; methodology, D.N.J., L.M.C. and L.P.C.; validation, D.N.J., L.M.C. and L.P.C.; formal analysis, D.N.J., P.G.S., D.W., L.M.C. and L.P.C.; investigation, D.N.J., P.G.S., D.W., L.M.C., L.P.C. and K.E.; resources, R.D., E.R. and C.J.; data curation, D.N.J., D.W. and L.M.C.; writing—original draft preparation, D.N.J.; writing—review and editing, Y.G., E.R. and C.J.; visualization, D.N.J. and C.J.; supervision, C.J.; project administration, C.J.; funding acquisition, C.J. All authors have read and agreed to the published version of the manuscript.

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Institutional Review Board Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The CCDC numbers 2280632–2280638 for **1–7** contain the supplementary crystallographic data reported in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (accessed on 30 July 2023).

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Conflicts of Interest: The authors declare no conflict of interest.

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Supplementary Materials

S1. Used chemicals

Table S1. Overview of used chemicals.

Chemical	Supplier	Purity
1,2,4-triazole	BLDpharm	97%
Acetonitrile	Riedel-de Haën	99,9%
Ascorbic acid	Roth	99%
Ba(NO ₃) ₂	lab inventory	–
Buffer solutions (pH 4 to 8)	AppliChem	–
Chloroform	Fisher	99,8%
Co(BF ₄) ₂ ·6H ₂ O	Alfa Aesar	96%
Co(ClO ₄) ₂ ·6H ₂ O	Strem Chemicals Inc.	–
Co(SCN)	Johnson Matthey Alfa Products	98%
DSMO-d ₆	Sigma-Aldrich	99,9%
Ethanol	Chemsolute	99,9%
Fe(BF ₄) ₂ ·6H ₂ O	abcr	97%
Fe(ClO ₄) ₂ ·xH ₂ O	Sigma-Aldrich	98%
FeSO ₄ ·2H ₂ O	Merck	p.a.
KBr	Riedel-de Haën	99,5%
KOH	Merck	p.a.
MgSO ₄	VWR Chemicals	98,0%
(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	Sigma-Aldrich	99%
NH ₄ SCN	Riedel-de Haën	99%
<i>trans</i> -1,4-dibromo-2-butene	BLDpharm	98%

S2 . Ligand analyses

Before the analyses the sample was dried in vacuo at 60 °C as otherwise water signals will be detected.

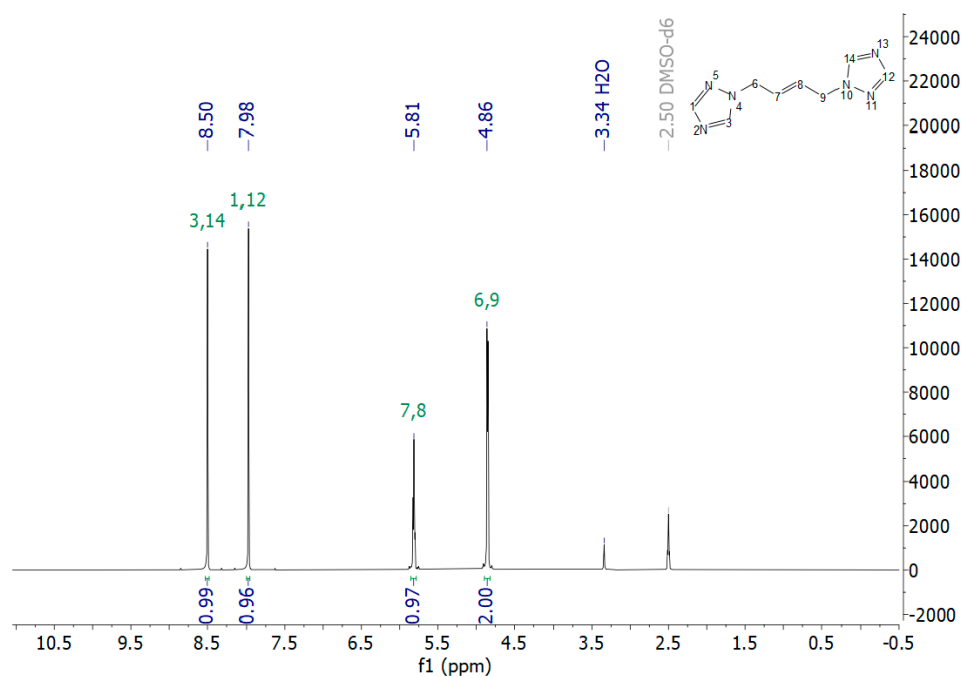


Figure S1. ¹H-NMR spectrum (300 MHz, DMSO-d₆) of tbbt. The water peak is due to the difficult-to-avoid water content of the used DMSO-d₆.

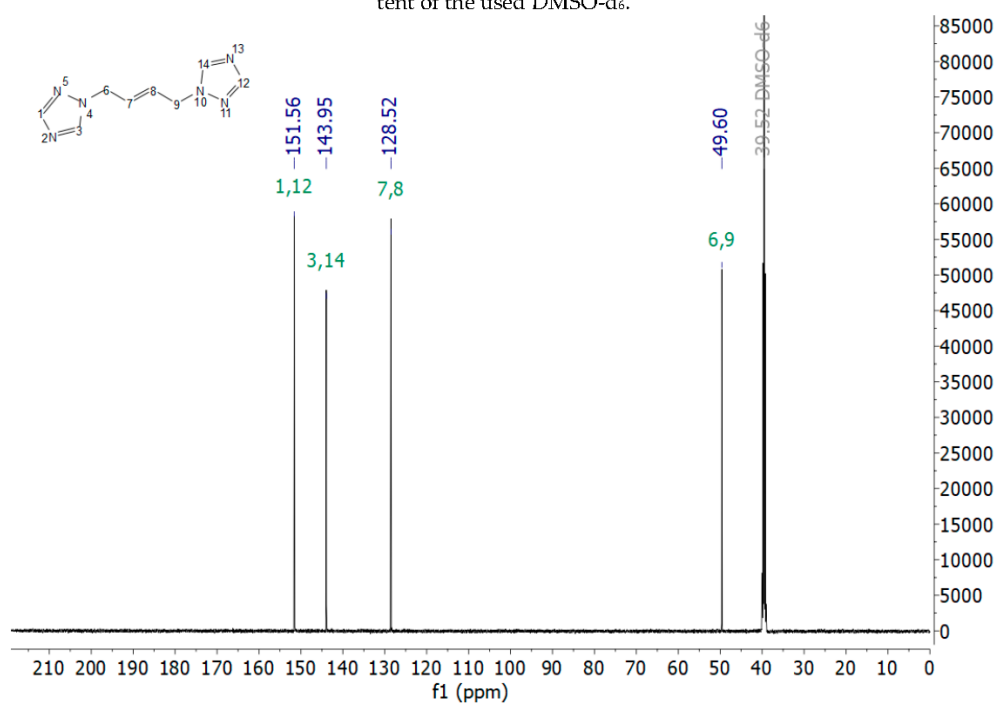


Figure S2. ¹³C{¹H}-NMR spectrum (75 MHz, DMSO-d₆) of tbbt.

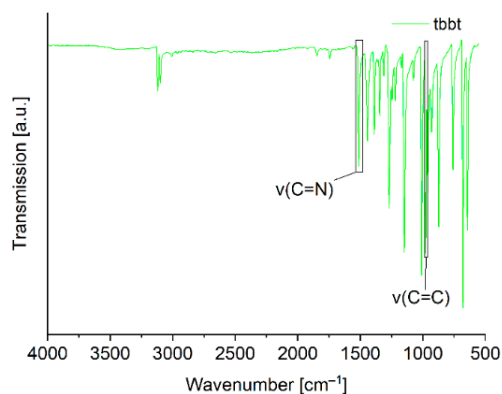


Figure S3. IR spectrum of tbbt (ATR).

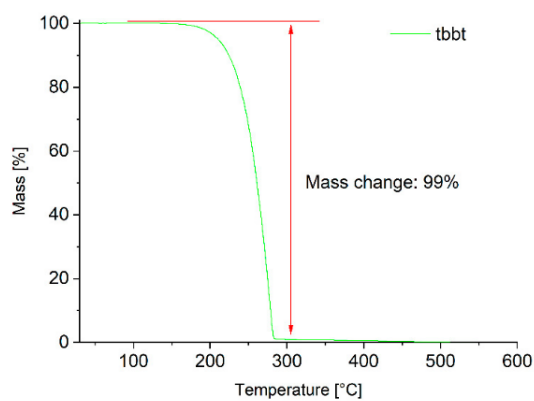


Figure S4. TGA of tbbt (heating rate 5 K min⁻¹). Before the analysis the sample was dried in vacuo at 60 °C as otherwise a mass loss of up to 8% below 100 °C will be detected due to absorbed water.

S3. Infrared spectra of 1-7

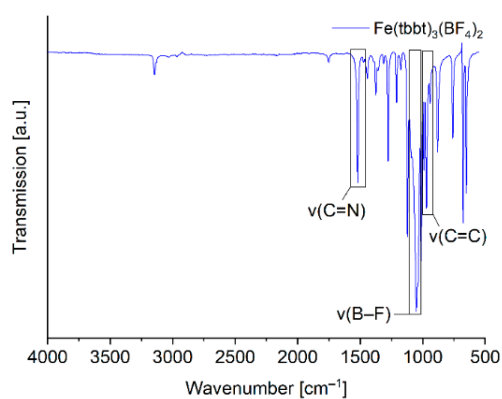


Figure S5. IR spectrum of 1 (ATR).

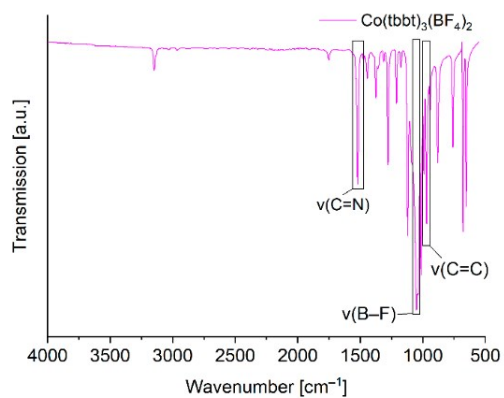


Figure S6. IR spectrum of **2** (ATR).

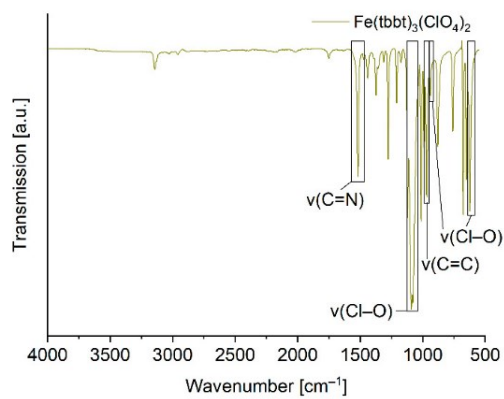


Figure S7. IR spectrum of **3** (ATR).

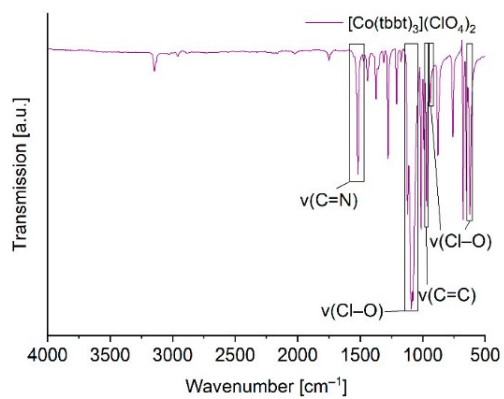


Figure S8. IR spectrum of **4** (ATR).

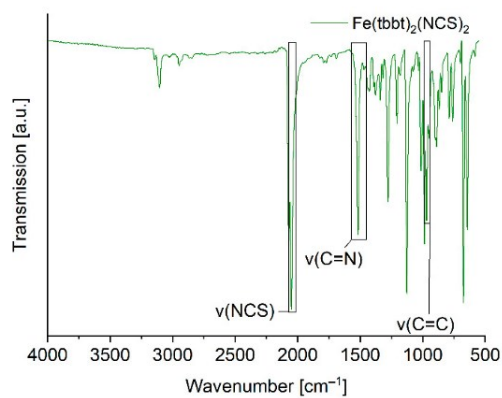


Figure S9. IR spectrum of **5** (ATR).

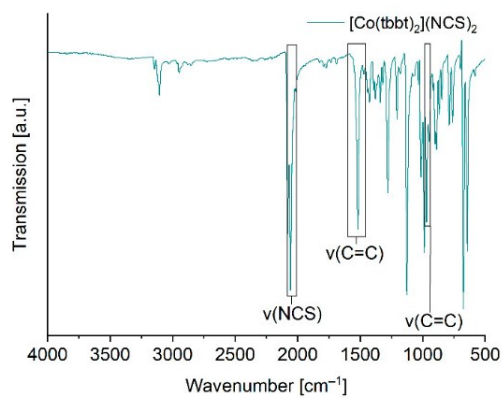


Figure S10. IR spectrum of **6** (ATR).

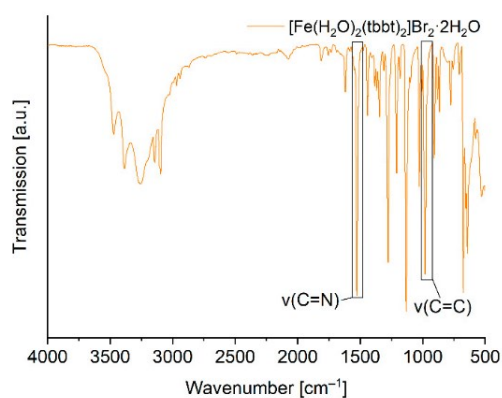


Figure S11. IR spectrum of **7** (ATR).

S4. Thermogravimetric analyses of 1-7

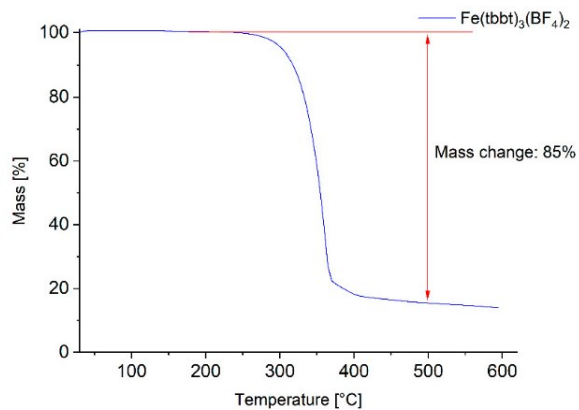


Figure S12. TGA of 1 (heating rate 5 K min⁻¹). The theoretical mass loss of three tbbt ligands would be 71%, leaving a residual mass for $\text{Fe}(\text{BF}_4)_2$ of 29%. Decomposition of BF_4 would leave a residual mass for FeF_2 of 12% and for FeF_3 of 14%.

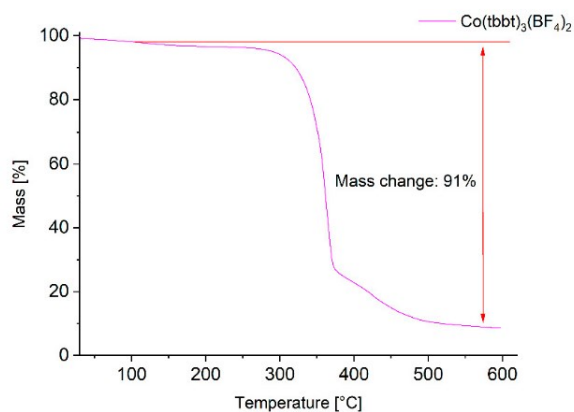


Figure S13. TGA of 2 (heating rate 5 K min⁻¹). The theoretical mass loss of three tbbt ligands would be 71%, leaving a residual mass for $\text{Co}(\text{BF}_4)_2$ of 29%. Decomposition of BF_4 would leave a residual mass for CoF_2 of 12%.

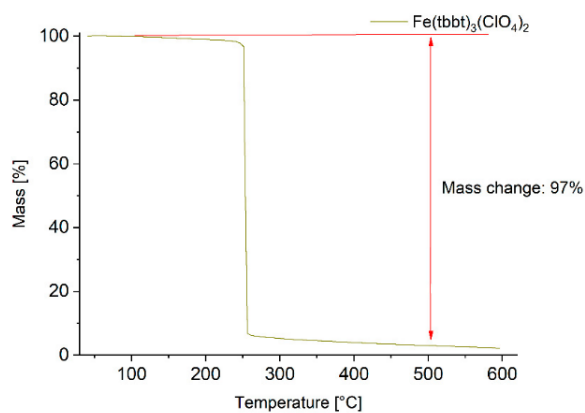


Figure S14. TGA of **3** (heating rate 5 K min⁻¹). The sudden sharp mass loss at about 250 °C with essentially no residual mass is due to an explosive decomposition which blew the sample out of the sample holder.

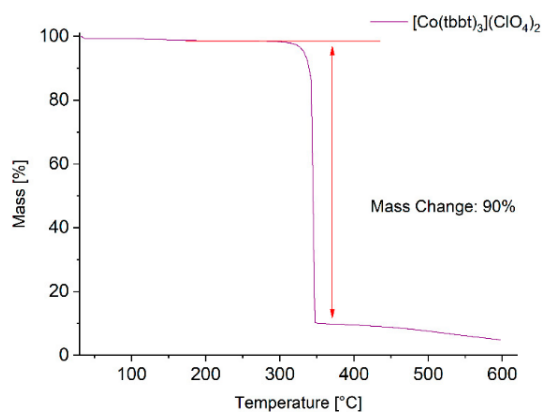


Figure S15. TGA of **4** (heating rate 5 K min⁻¹). The sudden sharp mass loss at about 340 °C with essentially no residual mass at 600 °C is due to an explosive decomposition which blew the sample out of the sample holder.

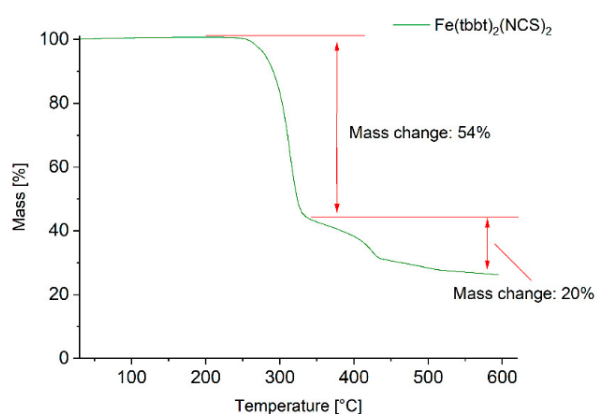


Figure S16. TGA of **5** (heating rate 5 K min⁻¹). The theoretical mass loss of two tbbt ligands would be 69%, leaving a residual mass for Fe(NCS)₂ of 31%. Decomposition of NCS would leave a residual mass for FeS or 16% or for FeS₂ of 22%.

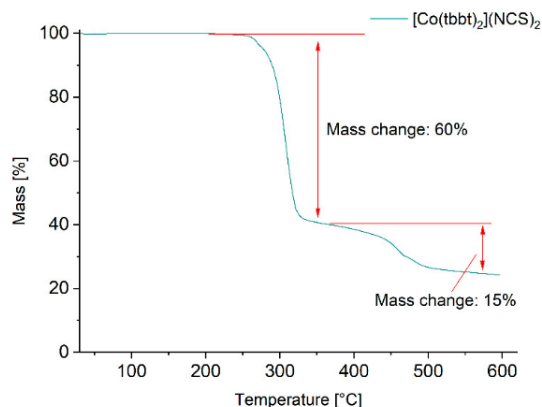


Figure S17. TGA of **6** (heating rate 5 K min⁻¹). The theoretical mass loss of two tbbt ligands would be 68%, leaving a residual mass for Co(NCS)₂ of 32%. Decomposition of NCS would leave a residual mass for CoS or 16% or for CoS₂ of 22%.

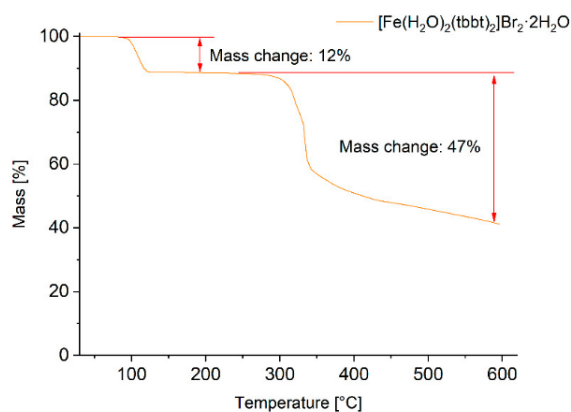


Figure S18. TGA of **7** (heating rate 5 K min⁻¹). The calculated mass loss of 4H₂O molecules per formula unit is 11% (obs. 12%). The calculated residual mass for FeBr₂ would be 32%. We note that the mass loss is not complete and still continuing with a strong negative slope at 600 °C.

S5. Crystal images

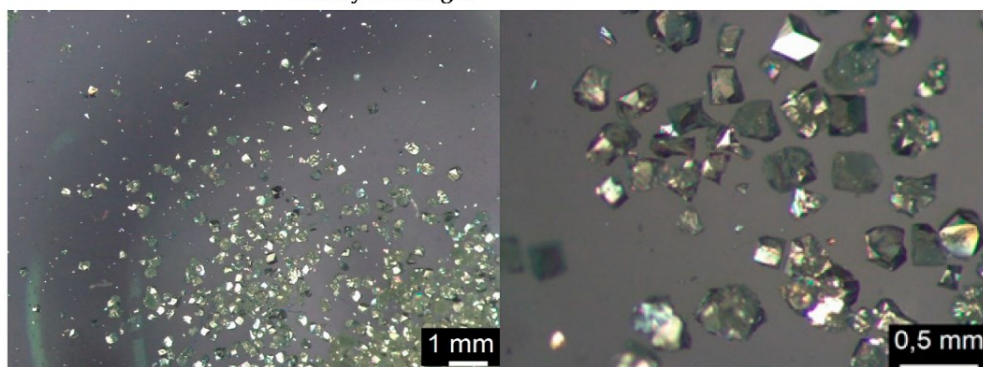


Figure S19. Crystal images of 1.

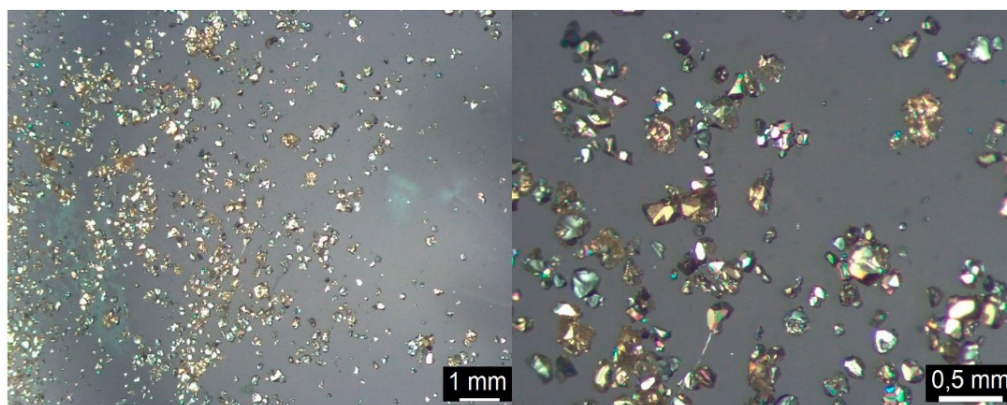


Figure S20. Crystal images of 2.

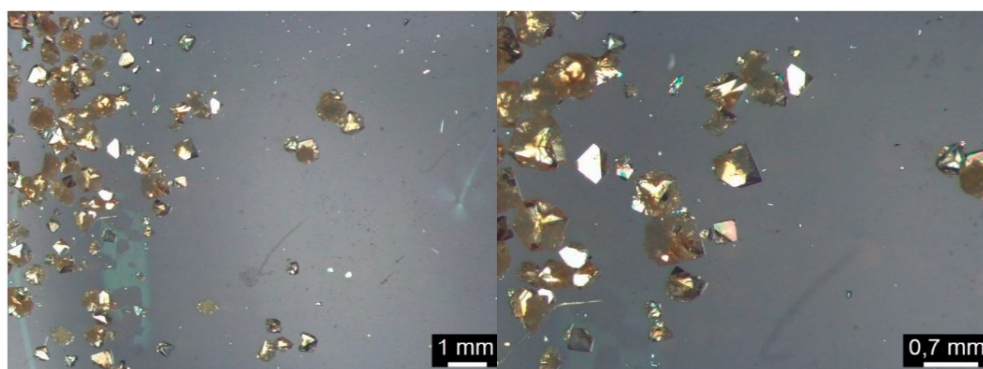


Figure S21. Crystal images of 3.

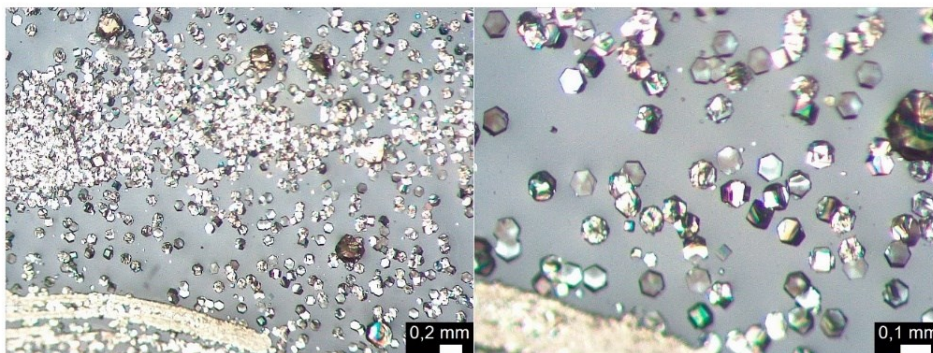


Figure S22. Crystal images of 4.

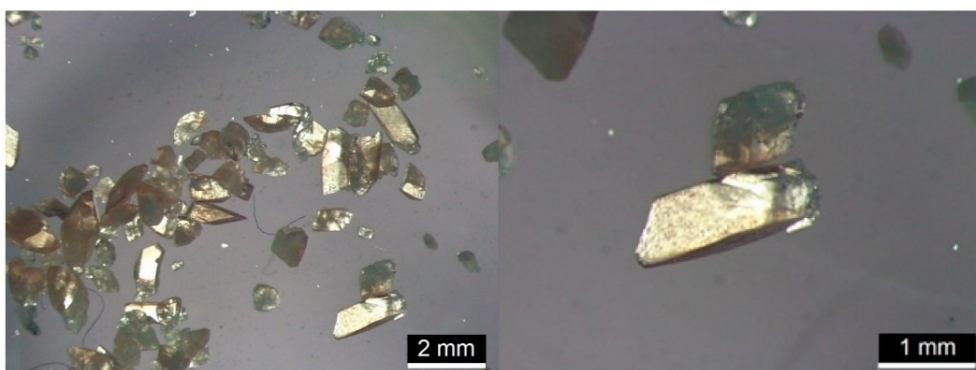


Figure S23. Crystal images of 5.

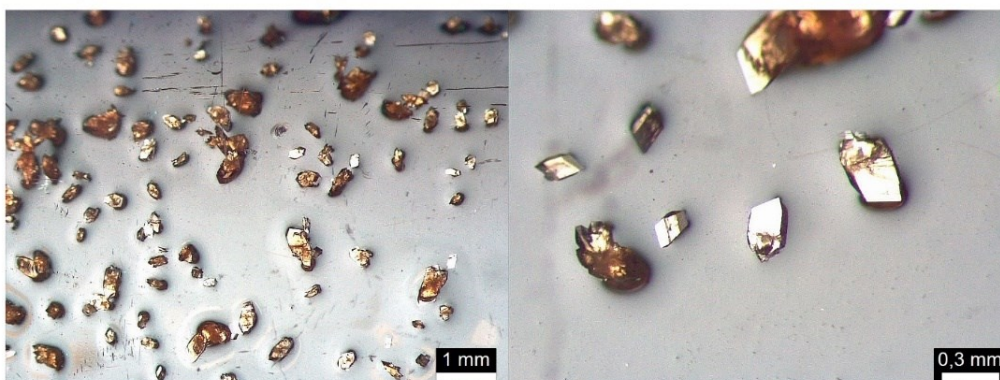


Figure S24. Crystal images of 6.

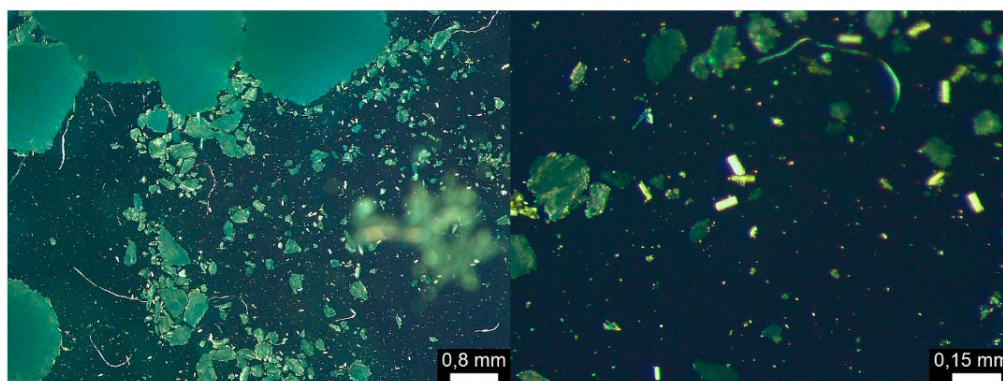


Figure S25. Crystal images of 7.

S6. Crystal data of 1-7

The CCDC numbers 2280632-2280638 for 1-7 contain the supplementary crystallographic data reported in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table S2. Crystal data for compounds 1–4.

	1	2	3	4
CCDC no.	2280632	2280633	2280634	2280635
Empirical formula	C ₂₄ H ₃₀ B ₂ F ₈ FeN ₁₈	C ₂₄ H ₃₀ B ₂ F ₈ CoN ₁₈	C ₂₄ H ₃₀ Cl ₂ O ₈ FeN ₁₈	C ₂₄ H ₃₀ Cl ₂ O ₈ CoN ₁₈
<i>M</i> [g/mol]	800.13	803.21	825.41	828.49
<i>T</i> [K]	100	100	100	100
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal
Space group	<i>P</i> $\bar{3}$	<i>P</i> $\bar{3}$	<i>P</i> $\bar{3}$	<i>P</i> $\bar{3}$
<i>a</i> [Å]	10.8198(3)	10.8024(0)	10.7561(0)	10.7538(4)
<i>b</i> [Å]	10.8198(3)	10.8024(0)	10.7561(0)	10.7538(4)
<i>c</i> [Å]	8.8597(3)	8.7938(0)	8.9294(0)	8.816(4)
α [°]	90	90	90	90
β [°]	90	90	90	90
γ [°]	120	120	120	120
<i>V</i> [Å ³]	898.23(6)	888.68(4)	894.66(9)	883.00(8)
<i>Z</i>	1	1	1	1
ρ_{calc} [g/cm ³]	1.479	1.501	1.532	1.558
μ [mm ⁻¹]	4.159	4.586	5.388	5.84
<i>F</i> (000)	408	409	424	425
Crystal size [mm ³]	0.07 × 0.09 × 0.10	0.24 × 0.3 × 0.44	0.23 × 0.31 × 0.31	0.11 × 0.06 × 0.03
λ (Cu <i>K</i> α) [Å]	1.54184	1.54184	1.54184	1.54184
No. of unique reflections	1077	1063	1067	1059
No. of reflections	5702	10906	5526	2960
<i>R</i> _{int}	0.032	0.031	0.031	0.030
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0538	0.0384	0.0337	0.043
<i>wR</i> (<i>F</i> ²)	0.1579	0.1101	0.0949	0.115

Table S3. Crystal data for compounds 5–7.

	5	6	7
CCDC no.	2280636	2280637	2280638
Empirical formula	C ₁₈ H ₂₀ S ₂ FeN ₁₄	C ₁₈ H ₂₀ S ₂ CoN ₁₄	C ₁₆ H ₂₀ FeN ₁₂ Br ₂ (H ₂ O) ₂ ·2H ₂ O
<i>M</i> [g/mol]	552.45	555.53	668.17
<i>T</i> [K]	100	100	101
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Fdd2</i>
<i>a</i> [Å]	8.8371(2)	8.8108(2)	30.9796(9)
<i>b</i> [Å]	10.3804(0)	10.3262(2)	16.4690(5)
<i>c</i> [Å]	13.6972(2)	13.6246(3)	9.9148(3)
α [°]	100.713(0)	100.394(2)	90
β [°]	100.685(0)	100.774(2)	90
γ [°]	97.114(0)	96.985(2)	90

$V [\text{\AA}^3]$	1196.36(3)	1182.18(5)	5058.6(3)
Z	2	2	8
$\rho_{\text{calc}} [\text{g}/\text{cm}^3]$	1.534	1.563	1.755
$\mu [\text{mm}^{-1}]$	7.020	7.68	8.91
$F(000)$	568	572	2699
Crystal size $[\text{mm}^3]$	$0.09 \times 0.14 \times 0.47$	$0.09 \times 0.06 \times 0.05$	$0.09 \times 0.06 \times 0.05$
$\lambda (\text{Cu } K\alpha) [\text{\AA}]$	1.54184	1.54184	1.54184
No. of unique reflections	4277	4218	1853
No. of reflections	21877	13910	4447
R_{int}	0.044	0.037	0.032
$R[F^2 > 2s(F^2)]$	0.0256	0.028	0.022
$wR(F^2)$	0.0662	0.063	0.049

Table S4. Selected bond lengths and bond angles for 1–7.

Compound 1			
Bond lengths $[\text{\AA}]$			
Fe1–N1	2.1858(2)	Fe1–N1 ^v	2.1858(2)
Fe1–N1 ⁱⁱⁱ	2.1858(2)	Fe1–N1 ^{vi}	2.1858(2)
Fe1–N1 ^{iv}	2.1858(2)	Fe1–N1 ^{vii}	2.1858(2)
Bond angles $[\circ]$			
N1 ^v –Fe1–N1 ^{iv}	89.18(8)	N1 ^{vi} –Fe1–N1 ⁱⁱⁱ	180.0
N1 ^{vii} –Fe1–N1 ⁱⁱⁱ	89.18(8)	N1 ^{iv} –Fe1–N1 ^{vi}	89.18(8)
N1 ^{vi} –Fe1–N1	90.82(8)	N1 ^{vii} –Fe1–N1	89.18(8)
N1 ^v –Fe1–N1 ^{vii}	90.82(8)	N1 ^{vii} –Fe1–N1 ^{vi}	90.82(8)
N1 ^{iv} –Fe1–N1	90.82(8)	N1 ⁱⁱⁱ –Fe1–N1	89.18(8)
N1 ^{iv} –Fe1–N1 ^{vii}	180.0	N1 ^v –Fe1–N1 ⁱⁱⁱ	90.82(8)
N1 ^{iv} –Fe1–N1 ⁱⁱⁱ	90.82(8)	N1 ^v –Fe1–N1	180.00(9)
N1 ^v –Fe1–N1 ^{vi}	89.18(8)		
Symmetry transformations: i = 1-x, 2-y, 2-z; ii = 1+x, y, 1+z; iii = -1-x+y, 1-x, z; iv = -1+y, -x+y, 1-z; v = -x, 2-y, 1-z; vi = 1+x-y, 1+x, 1-z; vii = 1-y, 2+x-y, z; viii = -x+y, 1-x, z; ix = 1-y, 1+x-y, z.			
Compound 2			
Bond lengths $[\text{\AA}]$			
Co1–N1	2.1490(2)	Co1–N1 ^v	2.1490(2)
Co1–N1 ⁱⁱⁱ	2.1490(2)	Co1–N1 ^{vi}	2.1490(2)
Co1–N1 ^{iv}	2.1490(2)	Co1–N1 ^{vii}	2.1490(2)
Bond angles $[\circ]$			
N1 ^{vi} –Co1–N1 ^v	90.76(6)	N1 ^{vii} –Co1–N1 ⁱⁱⁱ	90.76(6)
N1 ^{iv} –Co1–N1 ⁱⁱⁱ	89.24(6)	N1 ^v –Co1–N1 ^{vii}	90.76(6)
N1 ^{iv} –Co1–N1	90.76(6)	N1 ^v –Co1–N1	180.0
N1 ^{vi} –Co1–N1 ^{iv}	90.76(6)	N1 ^{iv} –Co1–N1 ^{vii}	180.0
N1 ^{vi} –Co1–N1	89.24(6)	N1 ⁱⁱⁱ –Co1–N1	90.76(6)
N1 ^v –Co1–N1 ^{iv}	89.24(6)	N1 ^{vi} –Co1–N1 ⁱⁱⁱ	180.0
N1 ^v –Co1–N1 ⁱⁱⁱ	89.24(6)	N1 ^{vii} –Co1–N1	89.24(6)
N1 ^{vi} –Co1–N1 ^{vii}	89.24(6)		
Symmetry transformations: i = 2-x, 1-y, 2-z; ii = x, -1+y, 1+z; iii = 1-x+y, 1-x, z; iv = 1-y, x-y, z; v = 2-x, 2-y, 1-z; vi = 2-y, 1+x-y, z; vii = 1-x+y, 2-x, z; viii = 1-x+y, 1-x, z; ix = 1-y, x-y, z.			

Compound 3			
Bond lengths [Å]			
Fe1—N1	2.1909(2)	Fe1—N1 ^v	2.1909(2)
Fe1—N1 ⁱⁱⁱ	2.1909(2)	Fe1—N1 ^{vi}	2.1909(2)
Fe1—N1 ^{iv}	2.1909(2)	Fe1—N1 ^{vii}	2.1909(2)
Bond angles [°]			
N1 ^{vi} —Fe1—N1	91.04(6)	N1 ^v —Fe1—N1 ^{iv}	88.96(6)
N1 ⁱⁱⁱ —Fe1—N1 ^{iv}	91.04(6)	N1—Fe1—N1 ^v	180.00(6)
N1 ⁱⁱⁱ —Fe1—N1 ^{vii}	88.96(6)	N1—Fe1—N1 ^{vii}	88.96(6)
N1 ^{vi} —Fe1—N1 ⁱⁱⁱ	180.0	N1 ⁱⁱⁱ —Fe1—N1 ^v	91.04(6)
N1 ^{vi} —Fe1—N1 ^{vii}	91.04(6)	N1 ^{iv} —Fe1—N1 ^{vii}	180.0
N1—Fe1—N1 ⁱⁱⁱ	88.96(6)	N1 ^{vi} —Fe1—N1 ^{iv}	88.96(6)
N1—Fe1—N1 ^{iv}	91.04(6)	N1 ^v —Fe1—N1 ^{vii}	91.04(6)
N1 ^{vi} —Fe1—N1 ^v	88.96(6)		

Symmetry transformations: : i = 1-x, 1-y, -z; ii = -1+x, -1+y, -1+z; iii = 2-y, 1+x-y, z; iv = 1+x-y, x, 1-z; v = 2-x, 2-y, 1-z; vi = y, 1-x+y, 1-z; vii = 1-x+y, 2-x, z; viii = 1-y, 1+x, z; ix = -x+y, 1-x, z.

Compound 4			
Bond lengths [Å]			
Co1—N1	2.1495(2)	Co1—N1 ^v	2.1495(2)
Co1—N1 ⁱⁱⁱ	2.1495(2)	Co1—N1 ^{vi}	2.1495(2)
Co1—N1 ^{iv}	2.150(2)	Co1—N1 ^{vii}	2.150(2)
Bond angles [°]			
N1—Co1—N1 ^{vi}	90.88(8)	N1 ^{vi} —Co1—N1 ⁱⁱⁱ	180.00(8)
N1 ⁱⁱⁱ —Co1—N1 ^{vii}	90.88(8)	N1—Co1—N1 ^{iv}	89.12(8)
N1 ⁱⁱⁱ —Co1—N1 ^{iv}	89.12(8)	N1 ^v —Co1—N1 ⁱⁱⁱ	90.88(8)
N1 ^v —Co1—N1 ^{vii}	89.12(8)	N1 ^{vi} —Co1—N1 ^v	89.12(8)
N1 ^{vi} —Co1—N1 ^{iv}	90.88(8)	N1 ^{vii} —Co1—N1 ^{iv}	180.00(1)
N1 ^v —Co1—N1 ^{iv}	90.88(8)	N1 ^{vi} —Co1—N1 ^{vii}	89.12(8)
N1—Co1—N1 ⁱⁱⁱ	89.12(8)	N1—Co1—N1 ^{vii}	90.88 (8)
N1—Co1—N1 ^v	180.0		

Symmetry transformations: : i = 1-x, -y, 2-z; ii = 1+x, y, 1+z; iii = -y, x-y, z; iv = -x+y, -x, z; v = -x, -y, 1-z; vii = x-y, x, 1-z; vi = y, -x+y, 1-z; vii = 1-x+y, 1-x, z; ix = 1-y, x-y, z.

Compound 5			
Bond lengths [Å]			
Fe1—N1	2.1751(1)	Fe2—N8 ^{iv}	2.1732(1)
Fe1—N1 ⁱ	2.1751(1)	Fe2—N8	2.1732(1)
Fe1—N4	2.2014(1)	Fe2—N13 ⁱⁱ	2.1944(1)
Fe1—N4 ⁱ	2.2014(1)	Fe2—N13 ^v	2.1944(1)
Fe1—N7	2.1394(1)	Fe2—N14 ^{iv}	2.1622(1)
Fe1—N7 ⁱ	2.1394(1)	Fe2—N14	2.1622(1)
Bond angles [°]			
N1—Fe1—N1 ⁱ	180.00(1)	N8 ^{iv} —Fe2—N8	180.0
N1 ⁱ —Fe1—N4	89.08(5)	N8 ^{iv} —Fe2—N13 ⁱⁱ	87.13(5)
N1—Fe1—N4	90.92(5)	N8—Fe2—N13 ⁱⁱ	92.87(5)

N1—Fe1—N4 ⁱ	89.08(5)	N8—Fe2—N13 ^v	87.13(5)
N1 ⁱ —Fe1—N4 ⁱ	90.92(5)	N8 ^{iv} —Fe2—N13 ^v	92.87(5)
N4 ⁱ —Fe1—N4	180.0	N13 ^v —Fe2—N13 ⁱⁱⁱ	180.00(8)
N7 ⁱ —Fe1—N1	89.77(5)	N14 ^{iv} —Fe2—N8	91.26(5)
N7 ⁱ —Fe1—N1 ⁱ	90.23(5)	N14—Fe2—N8	88.74(5)
N7—Fe1—N1 ⁱ	89.77(5)	N14 ^{iv} —Fe2—N8 ^{iv}	88.74(5)
N7—Fe1—N1	90.23(5)	N14—Fe2—N8 ^{iv}	91.26(5)
N7 ⁱ —Fe1—N4	90.31(5)	N14—Fe2—N13 ^v	88.97(5)
N7—Fe1—N4 ⁱ	90.31(5)	N14 ^{iv} —Fe2—N13 ⁱⁱⁱ	88.97(5)
N7 ⁱ —Fe1—N4 ⁱ	89.69(5)	N14—Fe2—N13 ⁱⁱ	91.03(5)
N7—Fe1—N4	89.69(5)	N14 ^{iv} —Fe2—N13 ^v	91.03(5)
N7 ⁱ —Fe1—N7	180.00(6)	N14—Fe2—N14 ^{iv}	180.0

Symmetry transformations: i = 1-x, 1-y, 1-z; ii = 1-x, 1-y, -z; iii = 2-x, -y, 1-z; iv = 1-x, -y, -z;
v = x, -1+y, z; vi = 1-x, 1-y, -z; vii = x, 1+y, z; viii = x, y, -1+z.

Compound 6			
Bond lengths [Å]			
Co1—N1	2.1580(2)	Co2—N8	2.1288(2)
Co1—N1 ⁱ	2.1580(2)	Co2—N8 ^{vi}	2.1288(2)
Co1—N4	2.1289(2)	Co2—N13 ⁱⁱⁱ	2.1500(2)
Co1—N4 ⁱ	2.1289(2)	Co2—N13 ^v	2.1500(2)
Co1—N7	2.1105(2)	Co2—N14 ^{vi}	2.1304(2)
Co1—N7 ⁱ	2.1105(2)	Co2—N14	2.1305(2)
Bond angles [°]			
N4—Co1—N4 ⁱ	180.0	N13 ^v —Co2—N13 ⁱⁱⁱ	180.0
N4—Co1—N1 ⁱ	89.01(6)	N8—Co2—N13 ^v	86.93(6)
N4 ⁱ —Co1—N1	89.01(6)	N8 ^{iv} —Co2—N13 ⁱⁱⁱ	86.94(6)
N4 ⁱ —Co1—N1 ⁱ	90.99(6)	N8 ^{iv} —Co2—N13 ^v	93.06(6)
N4—Co1—N1	90.99(6)	N8—Co2—N13 ⁱⁱⁱ	93.07(6)
N1—Co1—N1 ⁱ	180.00(6)	N8—Co2—N8 ^{iv}	180.00(7)
N7—Co1—N4	89.81(6)	N8—Co2—N14	91.48(6)
N7 ⁱ —Co1—N4	90.19(6)	N8—Co2—N14 ^{iv}	88.52(6)
N7 ⁱ —Co1—N4 ⁱ	89.81(6)	N8 ^{iv} —Co2—N14 ^{iv}	91.48(6)
N7—Co1—N4 ⁱ	90.19(6)	N8 ^{iv} —Co2—N14	88.52(6)
N7—Co1—N1 ⁱ	90.92(6)	N14 ^{iv} —Co2—N13 ^v	89.80(6)
N7 ⁱ —Co1—N1	90.92(6)	N14—Co2—N13 ⁱⁱⁱ	89.81(6)
N7 ⁱ —Co1—N1 ⁱ	89.08(6)	N14—Co2—N13 ^v	90.19(6)
N7—Co1—N1	89.08(6)	N14 ^{iv} —Co2—N13 ⁱⁱⁱ	90.20(6)
N7 ⁱ —Co1—N7	180.0	N14 ^{iv} —Co2—N14	180.0

Symmetry transformations: i = 1-x, 1-y, -z; ii = -x, 2-y, -z; iii = 1-x, 1-y, 1-z; iv = 1-x, 2-y, 1-z;
v = x, 1+y, z; vi = 1-x, 2-y, 1-z; vii = 1-x, 1-y, 1-z; viii = x, -1+y, z.

Compound 7			
Bond lengths [Å]			
Fe1—O1	2.140(5)	Fe1—N1 ⁱⁱⁱ	2.177(3)
Fe1—O2	2.097(5)	Fe1—N6 ^{iv}	2.203(3)
Fe1—N1	2.177(3)	Fe1—N6 ⁱⁱ	2.203(3)
Bond angles [°]			
O1—Fe1—N1 ⁱⁱⁱ	84.08(1)	O2—Fe1—N6 ^{iv}	86.74(1)
O1—Fe1—N1	84.08(1)	N1 ⁱⁱⁱ —Fe1—N1	168.2(2)

O1—Fe1—N6 ^{iv}	93.26(1)	N1—Fe1—N6 ^{iv}	94.37(1)
O1—Fe1—N6 ⁱⁱ	93.26(1)	N1 ⁱⁱⁱ —Fe1—N6 ⁱⁱ	94.37(1)
O2—Fe1—O1	180.0	N1 ⁱⁱⁱ —Fe1—N6 ^{iv}	86.31(1)
O2—Fe1—N1 ⁱⁱⁱ	95.92(1)	N1—Fe1—N6 ⁱⁱ	86.30(1)
O2—Fe1—N1	95.92(1)	N6 ⁱⁱ —Fe1—N6 ^{iv}	173.5(2)
O2—Fe1—N6 ⁱⁱ	86.74(1)		

Symmetry transformations: i = x, 1/2+y, 1/2+z; ii = x, -1/2+y, -1/2+z; iii = 1-x, 1-y, z; iv = 1-x, 3/2-y, -1/2+z.

Table S5. Hydrogen-bond geometry for compounds 1–7.

Compound 1				
<i>D</i> —H... <i>A</i>	<i>D</i> —H [Å]	H... <i>A</i> [Å]	<i>D</i> ... <i>A</i> [Å]	<i>D</i> —H... <i>A</i> [Å]
C1—H1...F2	0.95	2.27	3.127(4)	149
Compound 2				
<i>D</i> —H... <i>A</i>	<i>D</i> —H [Å]	H... <i>A</i> [Å]	<i>D</i> ... <i>A</i> [Å]	<i>D</i> —H... <i>A</i> [Å]
C1—H1...N1 ⁱⁱⁱ	0.95	2.69	3.170(3)	112
C1—H1...F1 ^{ix}	0.95	2.27	3.121(8)	149
C1—H1...F1A ^{ix}	0.95	2.39	3.12(2)	133
C3—H3A...F2A ^x	0.99	2.48	3.19(2)	129
Symmetry transformations: iii = y, -x+y+1, -z+1. ix = 1-y, x-y, z; x = 2-x, 1-y, 1-z				
Compound 3				
<i>D</i> —H... <i>A</i>	<i>D</i> —H [Å]	H... <i>A</i> [Å]	<i>D</i> ... <i>A</i> [Å]	<i>D</i> —H... <i>A</i> [Å]
C1—H1...O1	0.95	2.37	3.201(4)	146
C1—H1...O1A ^{ix}	0.95	2.58	3.149(6)	119
C3—H3A...O1A ^{viii}	0.99	2.60	3.478(7)	147
C3—H3B...O2A ⁱⁱ	0.99	2.63	3.251(8)	121
Symmetry transformations: ii = -x+1, -y+1, -z+1; viii = -y+1, x-y+1, z; ix = -x+y, -x+1, z.				
Compound 4				
<i>D</i> —H... <i>A</i>	<i>D</i> —H [Å]	H... <i>A</i> [Å]	<i>D</i> ... <i>A</i> [Å]	<i>D</i> —H... <i>A</i> [Å]
C1—H1...N1 ^{vi}	0.95	2.69	3.172(3)	112
C1—H1...O1 ^{vi}	0.95	2.60	3.164(6)	119
C1—H1...O1A ^{ix}	0.95	2.37	3.199(8)	146
C3—H3A...O2	0.99	2.65	3.265(1)	120
C3—H3B...O1 ^{ix}	0.99	2.58	3.442(8)	145
Symmetry transformations: vi = y, -x+y, -z+1; ix = -x+1, -y, -z+1.				
Compound 5				
<i>D</i> —H... <i>A</i>	<i>D</i> —H [Å]	H... <i>A</i> [Å]	<i>D</i> ... <i>A</i> [Å]	<i>D</i> —H... <i>A</i> [Å]
C1—H1...N7 ⁱ	0.95	2.69	3.145(2)	110
C5—H5...S2	0.95	2.93	3.7418(2)	144
C7—H7A...S1 ^{viii}	0.99	2.72	3.6888(2)	165
C7—H7B...S2	0.99	2.82	3.7645(2)	160
C10—H10...N11 ^{ix}	0.95	2.58	3.366(2)	141
C12—H12B...S1 ^{viii}	0.99	3.01	3.5452(2)	115
C15—H15B...S1 ^x	0.99	3.00	3.5177(2)	114
C15—H15B...S2 ^{xi}	0.99	2.74	3.5798(2)	143

C16—H16...S1 ^{xii}	0.95	2.71	3.5713(2)	152
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Symmetry transformations: i = -x+1, -y+1, -z+1; viii = -x+2, -y+1, -z+1; ix = -x+2, -y+1, -z; x = -x+2, -y+2, -z+1; xi = x+1, y+1, z; xii = x, y, z-1.

Compound 6				
<i>D</i> —H... <i>A</i>	<i>D</i> —H [Å]	H... <i>A</i> [Å]	<i>D</i> ... <i>A</i> [Å]	<i>D</i> —H... <i>A</i> [Å]
C1—H1...S2 ^{iv}	0.95	2.94	3.7500(2)	144
C11—H11...N12 ^{vii}	0.95	2.58	3.370(2)	141
C17—H17...S1 ^{viii}	0.95	2.70	3.5616(2)	152
C15—H15A...S2 ^{vii}	0.99	2.74	3.5819(2)	143
C15—H15A...S1 ^{ix}	0.99	2.98	3.5111(2)	115
C3—H3A...S2 ^{iv}	0.99	2.81	3.7601(2)	161
C3—H3B...S1 ^x	0.99	2.72	3.6850(2)	164
C12—H12A...S1 ^x	0.99	2.98	3.523(2)	115

Symmetry transformations: iv = -x+1, -y+2, -z+1; vii = -x, -y+1, -z+1; viii = x, y, z+1; ix = -x, -y, -z; x = -x, -y+1, -z.

Compound 7				
<i>D</i> —H... <i>A</i>	<i>D</i> —H [Å]	H... <i>A</i> [Å]	<i>D</i> ... <i>A</i> [Å]	<i>D</i> —H... <i>A</i> [Å]
O1—H1...Br1	0.74(5)	2.58(5)	3.281(2)	159(6)
O2—H2...O3 ⁱ	0.77(5)	1.95(5)	2.714(4)	171(6)
C1—H1A...Br1 ⁱⁱ	0.95	2.86	3.721(4)	151
C2—H2A...N3 ^v	0.95	2.67	3.442(6)	139
C3—H3A...N3 ^v	0.99	2.62	3.510(5)	149
C4—H4...Br1	0.95	3.07	3.918(4)	150
C5—H5...Br1 ^{vi}	0.95	3.10	3.701(4)	123
C6—H6A...Br1 ^{vi}	0.99	3.13	3.818(4)	128
C8—H8...Br1 ^{vii}	0.95	2.83	3.737(4)	160

Symmetry transformations: i = -x+1, -y+1, z; ii = -x+1, -y+3/2, z-1/2; v = -x+3/4, y-1/4, z+1/4; vi = -x+3/4, y+1/4, z-1/4; vii = -x+1, -y+3/2, z+1/2.

S7. Distortion of the coordination polyhedra of 1–7

The stabilization of the LS state can depend on the distortion of the metal atom coordination sphere, such that a low distortion in the HS favors the LS state [**Error! Reference source not found.**]. Unfortunately, this behavior is different for different groups (e.g. results of octahedrally-coordinated metal atoms in nitroprussides [2] cannot be extrapolated to tetrahedrally-coordinated metal atoms in tetracyanido metal complexes due to different geometry and electronic structure [1]).

The indices for distortion were calculated using the OctaDist software [3]. The distortion parameters were calculated as follows and are listed in Table S6:

1. ζ parameter [4]: $\zeta = \sum_{i=1}^6 |d_i - d_{mean}|$
 - a. d_i : individual M–L bond distance
 - b. d_{mean} : mean metal-ligand bond distance
2. Σ parameter [5]: $\Sigma = \sum_{i=1}^{12} |90 - \phi_i|$
 - a. ϕ_i : individual cis angle
3. θ parameter [6]: $\theta = \sum_{i=1}^{24} |60 - \theta_i|$
 - a. θ_i : individual angle between two vectors of two twisting faces

The values Σ and θ are derived by summation over the absolute values of all 12 differences $90 - \phi_i$ and 24 differences $60 - \theta_i$, respectively, in the octahedron. The angles ϕ_i and θ_i are 90° and 60° , respectively, giving the parameters Σ and θ as zero for a perfect octahedron [1]. However, a very small deviation in ϕ_i and θ_i by only 1° will already result in $\Sigma = 12^\circ$ and $\theta = 24^\circ$.

The angle distortion Σ for the metal atoms in **1–4** and those for the metal atoms in the layers of **5** and **6** is smaller than 13° , the torsional distortion smaller than 29° (Table S6). Only for the metal atoms in the chains of **5** and **6** and in **7** is the angle and torsional distortion somewhat larger. Thus, the metal environments in **1–4** and those in the layers of **5** and **6** are close to a perfect octahedron.

In the literature an SCO effect is correlated to a not too high distortion.

The distortion indices in **1–4** are not as high as in $[\text{Fe}(\mu\text{-atrz})_3](\text{X})_2 \cdot 2\text{H}_2\text{O}$ ($\text{X} = \text{BF}_4, \text{ClO}_4$) ($\text{atrz} = \text{trans-4,4'-azo-1,2,4-triazole}$), where SCO can be observed [7]. In case of **5** the distortion in the environment of Fe2 may be too high in comparison to $[\text{Fe}(\text{bntrz})_3][\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$ ($\text{bntrz} = 4\text{-(benzyl)-1,2,4-triazole}$), a compounds where SCO is present. The parameters Σ and θ for Fe1 in **5** are, however, in a good range [8]. In $[\text{Fe}_3(\text{bntrz})_6(\text{tcnset})_6]$ ($\text{tcnset} = 1,1,3,3\text{-tetracyano-2-thioethylpropenide}$) both Fe1 and Fe2 atoms give an SCO and its Fe2 atom also has distortion parameters not far from those for Fe2 in **5** [9]. Therefore, there should be more than just the distortion for the missing spin transition in **1–6**. Only in **7** the distortion may be too high to expect the stabilization of a low-spin state.

Table S6. Mean M–L distance and values for distortion indices of the metal atom coordination environment in compounds 1–7.

Compound	M	Mean distance <D> [Å]	Distance distortion ζ [Å]	Angle distortion Σ [°]	Torsional distortion θ [°]
1	Fe1	2.19	0.00	9.54	21.84
2	Co1	2.15	0.00	9.12	20.87
3	Fe1	2.19	0.00	12.52	28.57
4	Co1	2.15	0.00	10.45	23.89
5	Fe1	2.17	0.13	5.84	19.49
	Fe2	2.18	0.07	20.63	56.43
6	Co1	2.13	0.10	8.43	23.77
	Co2	2.14	0.05	18.96	57.88
7	Fe1	2.17	0.19	52.89	145.78
Comparative compounds with SCO effect					
[Fe(μ -atrz) ₃](BF ₄) ₂ ·2H ₂ O [Ref. 7]	Fe1	2.18	0.04	12.83	41.30
[Fe(μ -atrz) ₃](ClO ₄) ₂ ·2H ₂ O [Ref. 7]	Fe1	2.18	0.03	13.13	34.13
[Fe(bntrz) ₃][Pt(CN) ₄]·H ₂ O [Ref. 8]	Fe1 (HS)	2.19	–	10	23
	Fe2 (HS)	2.19	–	10	26
[Fe ₃ (bntrz) ₆ (tcnset) ₆] [Ref. 9]	Fe1 (HS)	2.18	–	8	9
	Fe2(HS)	2.16	–	24	39

S8 Additional structure images

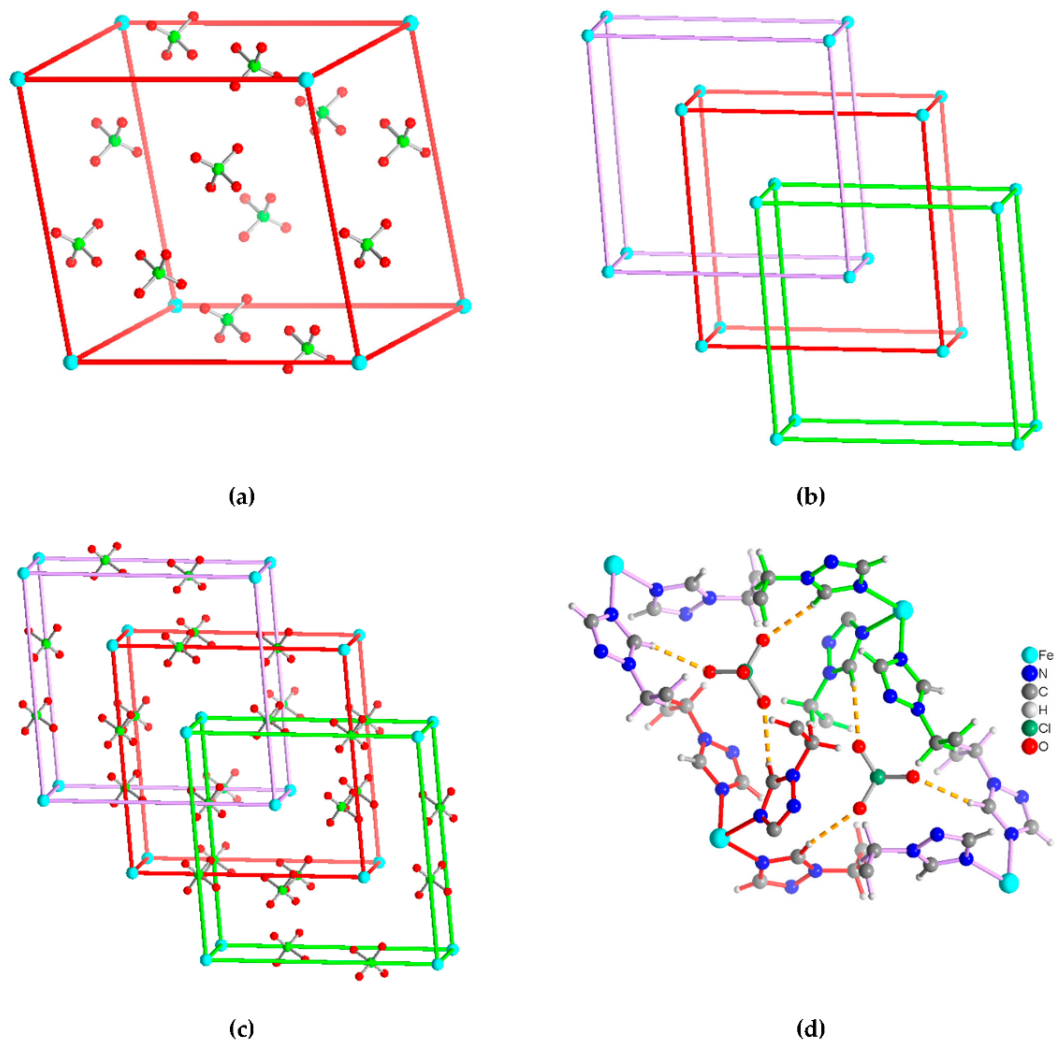


Figure S26. (a) Schematic presentation of the primitive lattice metal-linker topology in **3** (identical to **1**, **2**, **4**) with the positions of the anions on the faces of the primitive lattice. (b) Threefold interpenetration of three symmetry-related primitive lattices, differentiated by color. (c) Threefold interpenetrated lattices similar to (b) shown with ClO_4^- anions, indicating no present voids. (d) Template-effect of the ClO_4^- (and similarly of the BF_4^-) anions through (triazole) $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds (orange dashed lines) to triazole moieties from three different networks of **3**.

S9. Powder X-ray diffraction patterns of 1-7

The increasing baseline below 5° 2Theta stems from the PXRD device measurement method with the low-background silicon holder.

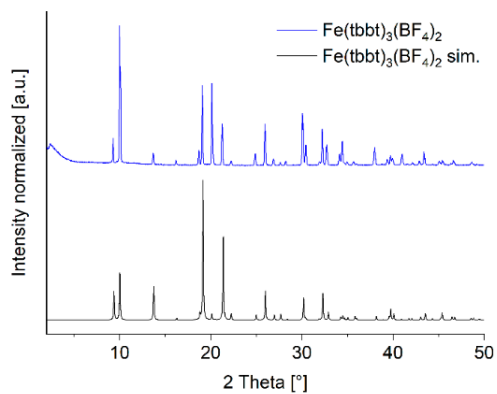


Figure S27. Comparison of diffraction pattern of 1 with its simulation.

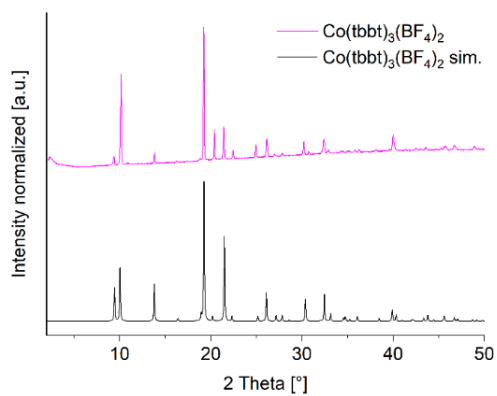


Figure S28. Comparison of diffraction pattern of 2 with its simulation.

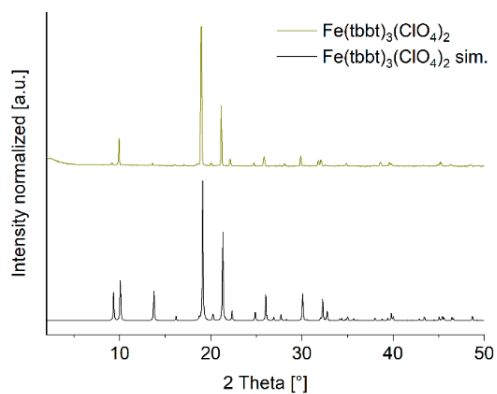


Figure S29. Comparison of diffraction pattern of 3 with its simulation.

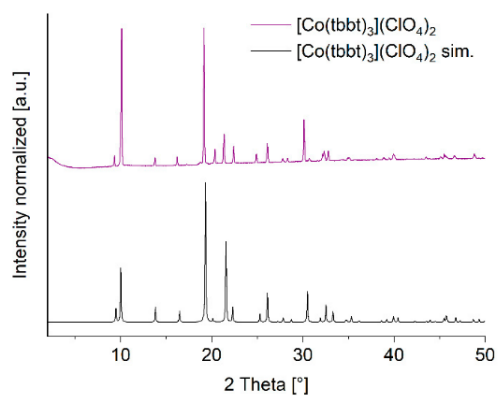


Figure S30. Comparison of diffraction pattern of 4 with its simulation.

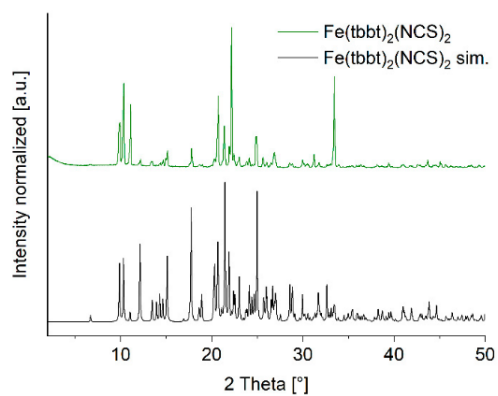


Figure S31. Comparison of diffraction pattern of 5 with its simulation.

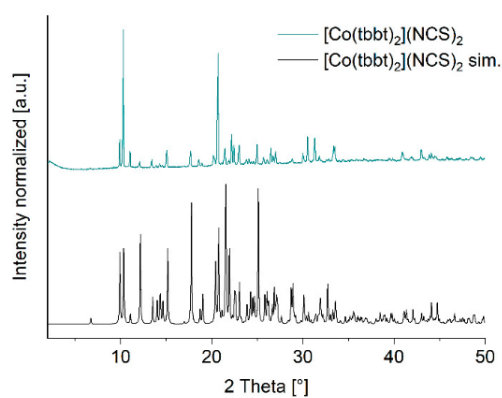


Figure S32. Comparison of diffraction pattern of 6 with its simulation.

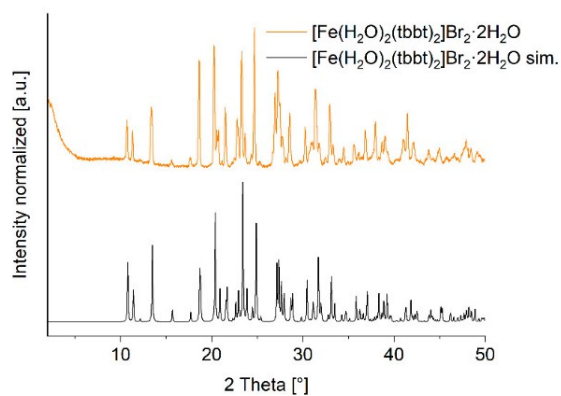


Figure S33. Comparison of diffraction pattern of 7 with its simulation.

S10. Pressure experiments of 5

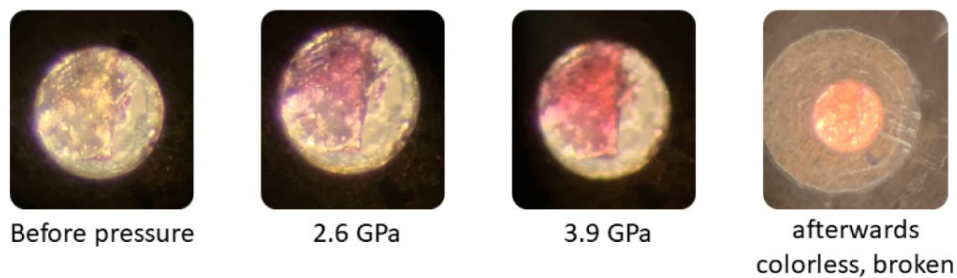


Figure S34. SC of 5 in a diamond anvil cell at different pressures.



Figure S35. Powder of 5 before (left) and after (right) pressure (9 t, 10 min).

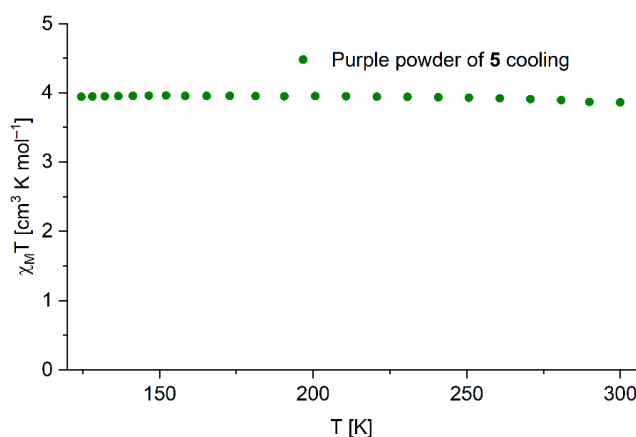


Figure S36. Magnetic properties of the purple phase of **5** measured in cooling mode. A paramagnetic ground state is present.

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3.2 Metal-organic Azolate Frameworks with an Acetylene-bis-pyrazolate Linker: Assessing the Role of the Triple-bond Spacer in Gas and Vapor Sorption

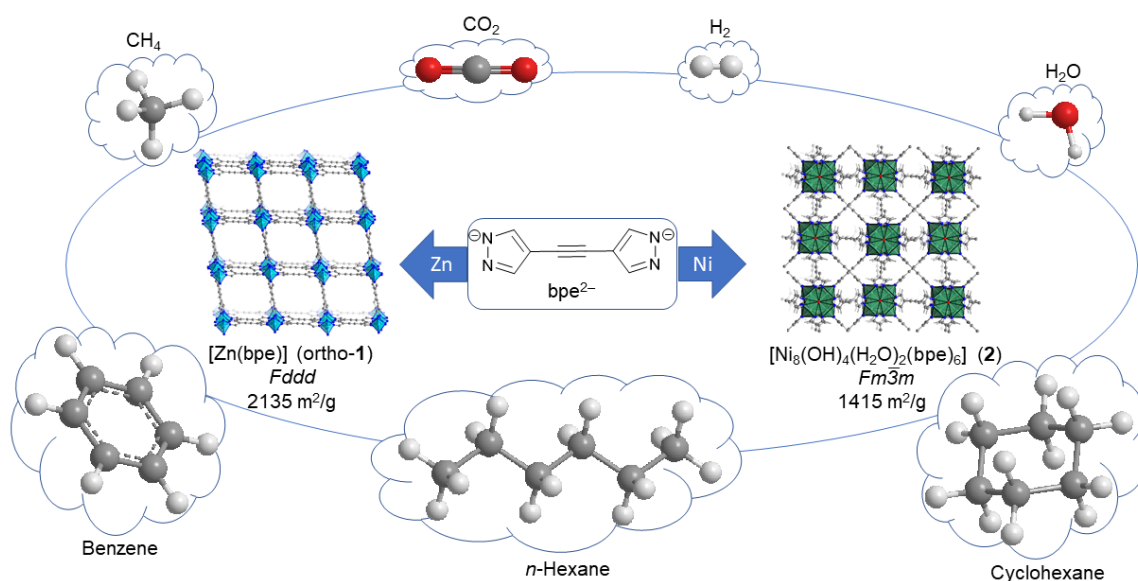
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Dustin N. Jordan, Tim Müller, Robert Oestreich, Till Strothmann, Istvan Boldog, Christoph Janiak:

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Kurzzusammenfassung:



Die Reaktion von [H₄bpe²⁺](TFA⁻)₂ (H₂bpe = 1,2-bis(1*H*-pyrazol-4-yl)ethin; HTFA = Trifluoressigsäure) mit Zn(NO₃)₂·4H₂O in DMF bei 75 °C für neun Tage führte zu der metall-organischen Gerüstverbindung [Zn(bpe)]·1.8DMF (ortho-1·1.8DMF) (HHUD-5). Die Einkristall-Strukturanalyse hat ergeben, dass ortho-1·1.8DMF in der orthorhombischen Raumgruppe *Fddd* mit rhombischen Kanälen kristallisiert und somit ein Polymorph des zuvor veröffentlichten [Zn(bpe)]·1.2DMF (tetra-1·1.2DMF) darstellt, welches gemäß der Rietveld-Verfeinerung in der tetragonalen Raumgruppe *P4₂/mmc* mit quadratischen Kanälen kristallisiert. Ortho-1 und Tetra-1 besitzen ähnliche BET-Oberflächen mit 2135 m²/g (totales Porenvolumen von 0.77 cm³/g bei p/p₀ = 0.95) für ortho-1 und 1904 m²/g (totales Porenvolumen von 0.73 cm³/g bei p/p₀ = 0.95) für tetra-1, wenn eine optimierte Aktivierung verwendet wird (vorher wurde eine BET-Oberfläche von 1380 m²/g veröffentlicht). Die Reaktion des boc-geschützten Linkers Boc₂bpe mit Ni(OAc)₂·4H₂O in DMF/Wasser unter Rückfluss führte zu dem MOF [Ni₈(OH)₄(H₂O)₂(bpe)₆]·nSolv (2·nSolv) (HHUD-6), welches in der kubischen Raumgruppe *Fm3m* kristallisiert und ein neues Mitglied der isoretikulären [Ni₈(OH)₄(H₂O)₂L₆]-Serie (L = Bis-pyrazolat oder Carboxylat-pyrazolat) ist. Verbindung 2 besitzt eine Oberfläche von 1415 m²/g und ein totales Porenvolumen von 0.78 cm³/g bei p/p₀ = 0.80. Die CO₂-Aufnahme bei 273 K und 1 bar ist 3.99 mmol/g für ortho-1 und 5.84 mmol/g für 2; die CH₄-Aufnahme lag bei 1.11 mmol/g für ortho-1 und bei 1.64 mmol/g für 2. Dies ist im Einklang mit den höheren Sorptionsenthalpien in 2, wobei *open metal sites* nach Aktivierung möglich sind. Über 2 bar für CO₂ und über 6 bar für CH₄ übersteigt die Aufnahme von ortho-1 die Aufnahme von 2 aufgrund der höheren Oberfläche von ortho-1.

Beide MOFs zeigen hohe H₂-Aufnahmen mit 11.6 mmol/g für ortho-**1** und 8.7 mmol/g für **2** bei 77 K und 1 bar. Der Vergleich mit den CO₂-, CH₄- und H₂-Aufnahmen in den analogen MOFs mit dem leicht längeren 4,4'-(1,4-phenylen)bis(pyrazolat) Linker, welcher eine Phenylen-Einheit anstelle der Acetylen-Einheit aufweist, zeigt einen vermeintlichen Vorteil der -C≡C- Dreifachbindung. Dampfsorptionsexperimente mit volatilen organischen Verbindungen bei 293 K ergaben Typ I Isotherme für ortho-**1** mit Aufnahmen von 8.2 mmol/g für Benzol, 6.6 mmol/g für Cyclohexan und 5.7 mmol/g für *n*-Hexan. Typ II Isothermen im Fall von **2** ergaben Aufnahmen von 10.4 mmol/g für Benzol, 10.7 mmol/g für Cyclohexan und 8.8 mmol/g für *n*-Hexan. Aus der Wasserdampfsorption und anderen Stabilitätstests geht hervor, dass beide MOFs stabil gegenüber Wasser sind. Zusätzlich zeigen diese Ergebnisse die Hydrophobie des bpe²⁻ Linkers.

Anteil an der Publikation:

- Dustin N. Jordan: Idee und Konzeptualisierung, Synthese der Liganden und MOFs, Lösung und Verfeinerung von [Zn(bpe)]·1.8DMF (ortho-**1**·1.8DMF), Strukturelle Analyse beider Verbindungen, Charakterisierung der Materialien, Auswertung und Interpretation der Ergebnisse, Verschriftlichung und Revision des Manuskripts.
- Tim Müller: Unterstützung bei den Dampf-Sorptionsmessungen.
- Robert Oestreich: Unterstützung bei den Gas-Sorptionsmessungen am Microtrac Belsorp MAX II.
- Till Strothmann. Durchführung der thermogravimetrischen Analysen.
- István Boldog: Idee und Konzeptualisierung, Rietveld-Verfeinerung für [Ni₈(OH)₄(H₂O)₂(bpe)₆] (**2**), Revision des Manuskriptes.
- Christoph Janiak: Idee und Konzeptualisierung, Verschriftlichung und Revision des Manuskriptes.

Metal–Organic Azolate Frameworks with an Acetylene-bis-pyrazolate Linker: Assessing the Role of the Triple-Bond Spacer in Gas and Vapor Sorption

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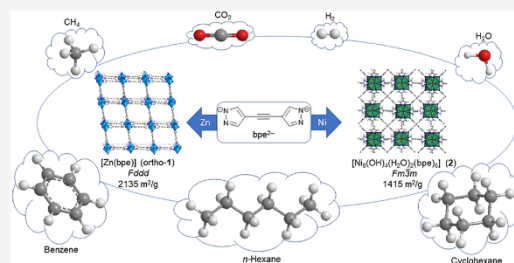
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ABSTRACT: The reaction of the diprotonated linker precursor in the form of the salt $[H_4bpe^{2+}](TFA^-)_2$ ($H_2bpe = 1,2$ -bis(1*H*-pyrazol-4-yl)ethyne; HTFA = trifluoroacetic acid) with $Zn(NO_3)_2 \cdot 4H_2O$ in DMF at 75 °C for 9 days led to single crystals of the metal–organic framework (MOF) $[Zn(bpe)] \cdot 1.8DMF$ (ortho-1, $Fddd$) (HHUD-5). The compounds crystallize in the orthorhombic space group $Fddd$ with rhombic channels, and is a polymorph of the previously reported structure of $[Zn(bpe)] \cdot 1.2DMF$ (tetra-1, $P4_2/mmc$) that crystallizes in the tetragonal space group $P4_2/mmc$ and features square channels as established from powder X-ray diffraction (PXRD) data. Microporous ortho-1 and tetra-1 demonstrate similar porosities with surface areas (pore volumes) of 2135 m^2/g (0.77 cm^3/g at $p/p_0 = 0.95$) and 1904 m^2/g (0.73 cm^3/g at $p/p_0 = 0.95$) when an optimized activation is employed (1380 m^2/g was reported previously for tetra-1). Reaction of the boc-protected linker precursor Boc₂bpe with $Ni(OAc)_2 \cdot 4H_2O$ in DMF/water under reflux yielded the MOF $[Ni_3(OH)_4(H_2O)_2(bpe)_6] \cdot nSolv$ (2, $Fm\bar{3}m$) (HHUD-6), which crystallized in the cubic space group $Fm\bar{3}m$ established from PXRD. Compound 2 is the newest member of the isorecticular series of $[Ni_3(OH)_4(H_2O)_2L_6]$ ($L =$ bis-pyrazolate or carboxylate-pyrazolate) and exhibits a surface area of 1415 m^2/g and a pore volume of 0.78 cm^3/g at $p/p_0 = 0.80$. The CO_2 uptake at 273 K and 1 bar was 3.99 mmol/g for ortho-1 and 5.84 mmol/g for 2; the CH_4 uptake was 1.11 mmol/g for ortho-1 and 1.64 mmol/g for 2, all in line with the higher heat of adsorption of the gases in 2, where open metal sites are possible after activation. Above 2 bar for CO_2 , and above 6 bar for CH_4 , the uptake in ortho-1 surpasses that in 2 due to the higher surface area of ortho-1. Both MOFs show high H_2 uptakes of 11.6 mmol/g for ortho-1 and 8.7 mmol/g for 2 at 77 K and 1 bar. Comparison to the CO_2 , CH_4 , and H_2 uptake in the analogous MOFs with the slightly longer 4,4'-(1,4-phenylene)bis(pyrazolate) linker (having phenylene instead of acetylene spacer) suggests an advantage of the $-C\equiv C-$ triple bond. Vapor adsorption experiments with volatile organic compounds at 293 K for ortho-1 yielded uptakes of 8.2 mmol/g for benzene, 6.6 mmol/g for cyclohexane, and 5.7 mmol/g for *n*-hexane with type I isotherms. Compound 2 gave uptakes of 10.4 mmol/g for benzene, 10.7 mmol/g for cyclohexane, and 8.8 mmol/g for *n*-hexane with type II isotherms. Both MOFs are water stable as indicated by water vapor sorption and stability tests which also show a hydrophobicity of the bpe^{2-} linker.



INTRODUCTION

The removal and minimization of anthropogenic emissions of greenhouse gases like CO_2 or CH_4 by reversible physisorption processes is of high interest.^{1–4} Physisorption processes could also be applied to the removal of vapors of volatile organic compounds (VOCs) such as benzene, most of which enter the environment through the emissions from gasoline- or diesel-powered vehicles.^{5,6} These VOCs cause damage to the environment and the health of living species even at trace concentrations.^{7–9}

Metal–organic frameworks (MOFs) are a promising material class for gas and vapor physisorption.^{2,3,10–16} MOFs

are composed of metal ions or metal (coordination) clusters as nodes connected through multidentate organic linker molecules, thereby forming two- or three-dimensional coordination networks with potential porosity.^{2,17–19} The

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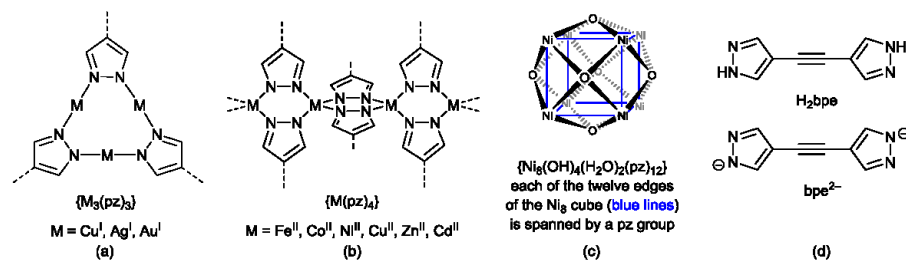


Figure 1. Examples of secondary building units (SBUs) in metal-pyrazolate frameworks: (a) $\{M_3(pz)_3\}$ (pz = pyrazolate), (b) $\{M(pz)_4\}$ dual-strand chains of four-coordinated, divalent metal ions, (c) $\{Ni_8(OH)_4(H_2O)_2(pz)_{12}\}$ (pz groups not shown for clarity), (d) the neutral acetylene-bis(pyrazole) ligand and the deprotonated acetylene-bis(pyrazolate) linker used in this work.

large number of possible combinations of metals and linkers and the possibility of ligand size and functionality tailoring allows to adjust the properties and the structure of the MOFs in a controllable manner via the pore size and the functionalization of the pore.^{10,11,20–22} The pore size is an important MOF design factor regarding the optimization of the gas or vapor uptake at very low partial pressure, since this trace-level uptake can be increased through very small micropores with a narrow pore size distribution.^{10,15,23–28}

MOFs are prone to degrade upon exposure to water or even to atmospheric moisture, and hence the development of robust MOFs is important for applications.^{26,29–31} Polytopic carboxylates are among the most studied ligands. Based on the HSAB principle high-valent metal atoms, which are hard acids (e.g., Zr^{4+} , Cr^{3+} , Fe^{3+} , Al^{3+}), form strong coordination bonds with O-donor ligands (hard bases) leading to MOFs with a certain level of stability against hydrolysis.^{32,33} Lower valent metal ions (e.g., Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Fe^{2+}) are softer acids and give more stable MOFs with N-donor linkers (softer bases) as, for example, metal-azolate frameworks (MAFs). MAFs are the second most important MOF subclass after the carboxylate MOFs. MAFs exhibit not only great thermal stability, often above 400 °C in air, but also an exceptional chemical resistance e.g. toward boiling alkaline water or other solvents for a certain time.^{3,31,34,35} The stability of MAFs can be ascribed to the high basicity of the azolate linker, a rather covalent metal–nitrogen bond, and an often hydrophobic inner surface.^{31,34–38} When all N-donor atoms are deprotonated and involved in metal coordination and a nonfunctionalized carbon backbone is present, the inert and hydrophobic surface is less prone to the attack of polar species, such as water, which could replace the linker.^{34,35}

For pyrazolates, there are several characteristic secondary building units (SBUs) such as trigonal-planar $\{M_3(pz)_3\}$ (pz = pyrazolate) clusters for linear, monovalent metal ions (M = Cu^I , Ag^I , Au^I) (Figure 1a) and different varieties of (typically dual-strand) chains for four-coordinating, divalent metal ions (Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II}) (Figure 1b).³⁴ Bitopic linear or slightly angular ligands give thereby rise to 3D frameworks, e.g., for Zn with *pts* topology.^{35,39,40} Besides pyrazolate-bridged metal atoms, there are also polynuclear clusters in which the metal atoms are bridged by pyrazolate groups and also oxide, hydroxide or aqua ligands resulting in, e.g., octahedral, cubic, triangular, or even crown ether-like SBUs. In the cubic SBU $\{Ni_8(OH)_4(H_2O)_2(pz)_{12}\}$, the Ni^{2+} cations are located at the corners of a cube, Ni-bridging μ_4-OH^- or μ_4-H_2O groups above the center of the faces and 12 Ni-bridging pyrazolate groups on the edges (Figure 1c). Besides a high

stability due to strong Ni–N coordination bonds, the cubic nature of this SBU makes it an ideal candidate for highly porous *fcu* structures offering many potential applications in several fields.^{41–53} An isoreticular series of MOFs with formula $[Ni_8(\mu_4-X)_4(\mu_4-L)_6]$ and such a cubic SBU connected by linear linkers was first presented by Masciocchi et al.,⁴¹ expanded by Padial et al.⁴³ and studied further by Freund et al.,⁴⁷ Zhang et al.⁴⁸ and others.^{49–53} In this series the cubic SBUs form (12)-connected 3D-networks with *fcu* topology, resulting in octahedral and tetrahedral pores.

In this work, we investigate two MOFs with the linker 1,2-bis(1*H*-pyrazol-4-yl)ethyne (H_2bpe) (Figure 1d), which adds to the topical subject of MOFs with acetylene-units in the linker backbone.^{16,40,43,54–58} The $-C\equiv C-$ triple bond spacer in the acetylene-dicarboxylate linker was said to result in the HHUD MOFs⁵⁹ in high hydrophilicity, high CO_2 adsorption capacity, and enthalpy compared to aliphatic or aromatic spacer moieties.^{54,55,57,58} Based on the structural similarity of carboxylates and pyrazolates regarding the bridging action of adjacent metal atoms in metal-cluster SBUs,^{62–64} we investigate here the shortest acetylene-bis-pyrazolate linker 4,4'-(ethyne-1,2-diyl)bis(pyrazolate) (bpe^{2-}) (Figure 1d) in a Zn- and in a Ni-MOF. We introduce the single-crystal structure of $[Zn(bpe)] \cdot 1.8DMF$ (ortho-1.1.8DMF, HHUD-5),^{59–61} which crystallizes in an orthorhombic space group. For this MOF $[Zn(bpe)] \cdot 1.2DMF$, Moroni et al. recently published a Rietveld-refined structure in a tetragonal space group (tetra-1.1.2DMF), which had been the only publication of a *bpe*-MOF, so far.⁴⁰ The novel MOF $[Ni_8(OH)_4(H_2O)_2(bpe)_6] \cdot nSolv$ ($2nSolv$, HHUD-6)⁵⁹ is isoreticular to the $[Ni_8(\mu_4-X)_4(\mu_4-L)_6]$ series.^{41–43,47,48} For both MOFs, gas, and vapor sorption properties were studied in this work, which leads to a reassessment of the role of the triple bond toward CO_2 , CH_4 , H_2 , and H_2O uptake.

EXPERIMENTAL SECTION

Materials. All chemicals were obtained from commercial suppliers and used without further purification if not stated otherwise (Section S1, Supporting Information). For the Sonogashira reaction, triethylamine and tetrahydrofuran (THF) were dried over molecular sieves (3 Å). The used water was deionized.

Instrumentation. *Single Crystal X-ray Diffraction (SCXRD).* Suitable single crystals of $[Zn(bpe)] \cdot 1.8DMF$ (ortho-1.1.8DMF) were selected with a polarized-light microscope and mounted in an oil drop on a cryo-loop. The data were collected using a Rigaku XtaLAB Synergy S diffractometer 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 carried out with CRYSLISPRO.⁶⁶ The structure was solved

using SHELXT and refined by SHELXL using OLEX2 as a shell.^{67–69} Figures were drawn with the DIAMOND 4.0 software.⁷⁰ Additional crystal data can be found in Section S3, Supporting Information. The void volume was calculated with the software Mercury 2023.3.0 (Build 392256) (contact surface model; grid spacing: 0.2 Å; probe radius: 1.8 Å).⁷¹

Powder X-ray Diffractograms (PXRD). PXRD patterns were obtained with a Rigaku MiniFlex diffractometer (600 W, 40 kV, 15 mA) using Cu-K α radiation ($\lambda_{\text{mean}} = 1.54184$ Å) at ambient temperature. The increasing baseline before 5° is attributed to the PXRD device measurement method with the low-background silicon holder in Bragg–Brentano geometry. The strongest reflex was normalized to 1. Simulated powder patterns were calculated from the single crystal data with the Mercury 2023.3.0 (Build 392256) software.⁷¹

Rietveld Refinement for [Ni₆(OH)₄(H₂O)₂(bpe)₆] $\cdot$ nSolv (2-nSolv, HHUD-6). The structural model for 2-nSolv was constructed in accordance with the known analog based on the 1,4-bis(1H-pyrazol-4-yl)benzene linker.⁴³ The refinements were performed using the Jana 2006 software.⁷² The peak shapes were fitted by the pseudo-Voigt function (four parameters were refined during all refinement cycles except the very last, to ensure convergence). Due to the not easily correctable distortions of the first two strongest peaks, the latter were excluded from the refinement (the exclusion of the two peaks in the $2\theta = 10$ – 70° range is not critical for refinement, but improves the indices due to correction of the strong asymmetry; see Figure S13, Supporting Information).

The experimental PXRD data were collected using a Rigaku MiniFlex diffractometer (600 W, 40 kV, 15 mA) using a Cu X-ray source, with an assumed K α_1 ($\lambda = 1.54051$) to K α_2 ($\lambda = 1.54433$) ratio of 2.00, in the angular range of $2\theta = 10$ – 72° . Using two or more K α -values increases the precision of the refinement if narrow reflexes are present. The peak asymmetry was corrected using Simpson's model with one parameter refined (111 and 002 reflexes were excluded due to strong asymmetry, which was not expedient to correct). Focusing correction for Bragg–Brentano geometry was applied and the sample shift was refined freely. The background was defined manually and fixed during the refinement.

The Rietveld refinement (Figure S13, Table S3, Supporting Information) could be successfully concluded for the whole data set, albeit a sufficiently good fit (Bragg R = 4.8% and GoF = 2.7) was only reached, when the first two peaks were excluded, and the atoms belonging to the guest molecules, located in the voids of the framework are explicitly modeled using the Fourier difference map (carbon atoms were used for this purpose).

The atomic displacement parameters (ADPs) for all the atoms of the framework and all the atoms belonging to the guests were fixed to be equal to each other within the given groups. The occupancy factors of the guest atoms were refined freely in most cases (except for a few cases, where symmetry considerations were taken into account). Unlike for the framework atoms with typical ADPs (0.08), the guest atoms were refined with very large ADP values (~ 0.5). The positions of the guests (but not the framework atoms) are also strongly dependent on fine differences in the choice of the refined data range and parameters. Hence, the location of the guest atoms with the large ADP parameters could be viewed as a simple analog of the SQUEEZE procedure employed for single crystal data: the guest atoms modeled diffusely cover the areas with the highest probability of the solvent molecule localization. The precision of the guest atom placement is, evidently, very low. Additional crystal data can be found in Section S4, Supporting Information.

Thermogravimetric Analyses (TGA). Thermogravimetric analyses were performed using a Netzsch TG209 F3 Tarsus under a nitrogen atmosphere or under synthetic air with a heating ramp of 5 K min^{–1} up to 600 or 1000 °C.

FT-IR Spectra. FT-IR spectra were collected using a Bruker TENSOR 37 IR spectrometer in ATR mode (Platinum ATR-QL, Diamond) in the range 4000–500 cm^{–1}.

NMR Spectra. NMR-spectra were measured with a Bruker Avance III—300 (¹H: 300 MHz); (¹³C{¹H}: 75 MHz); (¹⁹F{¹H}: 282.4 MHz) or a Bruker Avance III—600 (¹³C{¹H}: 150 MHz).

Elemental Analyses. Elemental analyses were carried out using an Elemental Vario MICRO Cube analyzer. During weighing and handling the samples could not be protected from the ambient moisture due to technical reasons, hence, there are deviations, *inter alia*, due to the uptake of atmospheric moisture.

Sorption Measurements. Activation of both MOFs was performed directly at the outgassing/measurement ports of the Microtrac Belsorp MAX II and Quantachrome Autosorb iQ MP gas adsorption analyzers. [Zn(bpe)] $\cdot$ 1.8DMF (ortho-1-1.8DMF) was activated for 3 h at 120 °C in vacuum (10^{-7} mbar). For activation of 2, the as-synthesized MOF was soaked in chloroform (25 mL) overnight and activated for 7 h at 130 °C in vacuum (10^{-7} mbar). Both MOFs were reactivated for 1 h at 60 °C in vacuum between the adsorption measurements.

The nitrogen sorption measurements at 77 K were performed using a Microtrac Belsorp MAX II. Adsorption data for carbon dioxide, methane (273 K, 293 K), and hydrogen (77 K, 87 K) were collected on a Quantachrome Autosorb iQ MP. Vapor sorption measurements were carried out with a Quantachrome VStar4 instrument. Each sample was degassed under vacuum similar to gas sorption experiments prior to the measurement. The isotherms were only collected up to $p/p_0 = 0.9$ to avoid vapor condensation. Gravimetric high-pressure sorption measurements were performed on a Rubotherm IsoSORB Static (G-HP) at 293 K and up to 20 bar. Blank measurements were made with helium and the mass change was measured with a magnetic suspension balance (resolution 0.01 mg; reproducibility, i.e. standard deviation 0.03 mg).

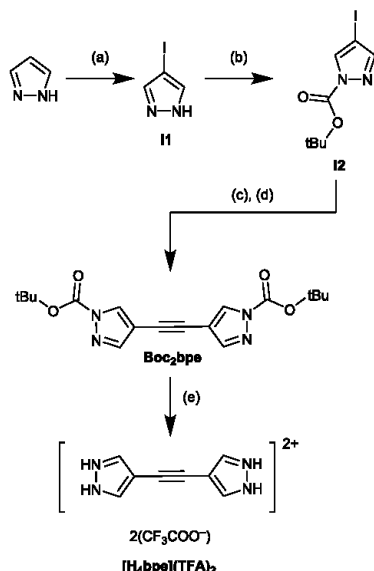
Isotherm fits were calculated using the 3Psim software,⁷³ which is a tool for the interpretation and evaluation of experimental isotherms containing several adsorption models: Henry, Langmuir adsorption isotherm (LAI), Toth, Sips, Freundlich, Dual Site Langmuir, DS Langmuir Sips (DSLAI Sips) and uniform distribution and Langmuir local isotherm (UNILAN). Fits were always performed with the best model possible. For IAST (ideal adsorbed solution theory) selectivity calculations only Langmuir, Toth, DS Langmuir, and DSLAI Sips models can be used.

Synthesis. Synthesis of 1,2-Bis(1-boc-pyrazol-4-yl)ethyne (Boc₂bpe) and 4,4'-(Ethyne-1,2-diyl)bis(1H-pyrazol-2-ium)-bis(trifluoroacetate) ([H₂bpe](TFA))₂. The boc-protected linker precursor was synthesized by a three-step reaction. The pyrazolium trifluoroacetate salt was synthesized with an additional step (Scheme 1). The intermediates 4-iodo-1H-pyrazole (II) and 1-boc-4-iodopyrazole (I2) were synthesized according to Padial et al.⁴³

NaOAc $\cdot$ 3H₂O (19.27 g, 141.6 mmol) was added to a suspension of 1H-pyrazole (4.8 g, 70.5 mmol) in H₂O (35 mL), and the suspension was heated to 60 °C until complete dissolution. Subsequently, an aqueous solution of I₂ (11.28 g, 44.4 mmol) and KI (22.08 g, 133 mmol) was added over a period of 30 min. Finally, H₂O₂ (4 mL, 39.2 mmol, 30%) was added and the solution was refluxed overnight. After cooling to room temperature, the resulting precipitate II was washed with H₂O and dried at 60 °C under vacuum. Yield: 7.2 g (52%, Lit.⁴³ 74%). ¹H NMR (300 MHz, DMSO-*d*₆): δ [ppm]: 7.74 (s) (Figure S1, Supporting Information). ¹³C{¹H}-NMR (75 MHz, DMSO-*d*₆): δ [ppm]: 56.7, 133.1, 143.5 (the assignments are in Figure S2, Supporting Information).

4-Iodo-1H-pyrazole (II, 6.0 g, 30.9 mmol), *tert*-butyl dicarbonate (10.2 g, 46.7 mmol) and 4-(dimethylamino)pyridine (0.3 g, 2.5 mmol) were dissolved in a mixture of dichloromethane (80 mL) and triethylamine (15 mL) and stirred at room temperature for 30 min. The solvent of the yellow solution was removed in a rotary evaporator and the product I2 was purified via column chromatography (silica gel, cyclohexane/ethyl acetate 4:1). Yield: 8.0 g (88%, Lit.⁴³ 98%). ¹H NMR (300 MHz, CDCl₃): δ [ppm]: 1.65 (s, 9H), 7.70 (s, 1H), 8.14 (s, 1H) (Figure S3, Supporting Information). ¹³C{¹H}-NMR (75 MHz, CDCl₃): δ [ppm]: 28.0, 61.4, 86.3, 135.1, 146.5, 148.5 (the assignments are in Figure S4, Supporting Information).

Scheme 1. Synthetic Route to Boc₂bpe and [H₄bpe](TFA)₂; (a) KI, I₂, NaOAc·3H₂O, H₂O₂, H₂O; (b) Di-*tert*-butyl dicarbonate, 4-(dimethylamino)pyridine, NEt₃, DCM; (c) [Pd(PPh₃)₂Cl₂], CuI, trimethylsilylacetylene, THF (dry), NEt₃ (dry), N₂; (d) Bu₄NF·H₂O, I₂; (e) HTEA, DCM



To synthesize the boc-protected linker 1,2-bis(1-boc-pyrazol-4-yl)ethyne (Boc₂bpe), a two-step Sonogashira reaction was performed as a one-pot reaction. In an oven-dried Schlenk flask, the first half of 1-boc-4-iodopyrazole (I₂, 1.3 g, 4.4 mmol) was combined with [Pd(PPh₃)₂Cl₂] (72 mg, 0.10 mmol, 2 mol %) and CuI (26 mg, 0.14 mmol, 3 mol %) and degassed at room temperature. Under the N₂ atmosphere a dried and deoxygenated mixture of THF (20 mL) and NEt₃ (5 mL) was added. After 15 min of stirring, trimethylsilylacetylene (0.56 mL, 4 mmol) was added, which resulted in a color change of the mixture from orange to yellow. While stirring for 24 h a triethylammonium iodide precipitate formed. Afterward, tetrabutylammonium fluoride hydrate (1.23 g, 4.4 mmol) was added and the mixture was stirred for 15 min. Then, the second half of 1-boc-4-iodopyrazole (I₂, 1.3 g, 4.4 mmol) was added. After 24 h the orange-brownish suspension was filtered. H₂O (15 mL) was added to the filtrate which was then extracted four times with ethyl acetate (4 × 10 mL). The organic phase was dried over MgSO₄, the solvent removed in a rotary evaporator and the resulting red-brown oil was purified by column chromatography (silica gel, cyclohexane/ethyl acetate 2:1) to afford pure 1,2-bis(1-boc-pyrazol-4-yl)ethyne (Boc₂bpe) as an off-white powder. Yield: 0.6 g (43%). C₁₈H₂₂N₄O₄: calc. C 60.32, H 6.19, N 15.63, found C 60.35, H 6.19, N 15.35%. IR $\tilde{\nu}$ [cm⁻¹]: 3143 (w), 3093 (w), 2984 (w), 1778 (s), 1746 (s), 1594 (w), 1551 (w), 1476 (w), 1429 (m), 1390 (s), 1372 (s), 1333 (m), 1280 (s), 1255 (s), 1228 (m), 1147 (s), 1017 (m), 984 (w), 954 (s), 878 (m), 840 (s), 825 (s), 763 (s), 722 (m), 657 (s), 603 (m) (see Figure S10, Supporting Information). ¹H NMR (300 MHz, DMSO-*d*₆): δ [ppm]: 1.58 (s, 9H), 8.01 (s, 1H), 8.60 (s, 1H) (Figure S5, Supporting Information). ¹³C{¹H}-NMR (75 MHz, DMSO-*d*₆): δ [ppm]: 27.4, 81.7, 85.7, 105.2, 133.8, 145.2, 146.3 (assignment in Figure S6, Supporting Information).

The last step is a deprotection, which leads to the formation of the desired linker precursor 4,4'-(ethyne-1,2-diyl)bis(1H-pyrazol-2-ium)-bis(trifluoroacetate) ([H₄bpe](TFA)₂). Boc₂bpe (0.5 g, 1.4 mmol) was dissolved in DCM (35 mL). After the addition of trifluoroacetic

acid (1 mL, 13.1 mmol), the solution was stirred for 24 h. The resulting white solid was filtered, washed with DCM, and dried at 40 °C in vacuum. Yield: 0.35 g (0.9 mmol, 64%). C₈H₆N₄·C₂F₃O₄H₂: calc. C 37.32, H 2.09, N 14.51, found C 37.77, H 2.59, N 14.76%. IR $\tilde{\nu}$ [cm⁻¹]: 3148 (br), 3106 (m), 1678 (m), 1475 (m), 1437 (m), 1378 (m), 1208 (s), 1180 (s), 1126 (s), 1066 (s), 907 (m), 791 (s), 723 (s), 639 (s), 610 (m) (see Figure S10, Supporting Information). ¹H NMR (300 MHz, DMSO-*d*₆): δ [ppm]: 7.85 (s, 2H), 13.94 (s, 1H) (Figure S7, Supporting Information). ¹³C{¹H}-NMR (75 MHz, DMSO-*d*₆): δ [ppm]: 81.8, 101.8, 136.1, 158.3 (assignment in Figure S8, Supporting Information). ¹⁹F{¹H}-NMR (282.4 MHz, DMSO-*d*₆): δ [ppm]: -75.35 (Figure S9, Supporting Information).

Synthesis of [Zn(bpe)]·1.8DMF (ortho-1-1.8DMF, HHUD-5) and Activated [Zn(bpe)] as Ortho-1 and Tetra-1. Zn(NO₃)₂·4H₂O (209 mg, 0.76 mmol) and [H₄bpe](TFA)₂ (63 mg, 0.16 mmol) were dissolved in DMF (9 mL) and heated at 75 °C for 9 days. The resulting colorless crystals of ortho-1-1.8DMF were washed with DMF (3 × 9 mL) and stored in DMF. Activation to [Zn(bpe)] (ortho-1) was carried out by heating [Zn(bpe)]·1.8DMF for 3 h at 130 °C in vacuum (10⁻⁷ mbar). The resulting microcrystalline powder of activated ortho-1 was stored under an inert atmosphere to prevent moisture adsorption from ambient air. Yield: 24 mg (68%, activated MOF). C₆H₄N₄Zn·0.5H₂O calc. C 41.68, H 2.19, N 24.30, found C 42.12, H 2.16, N 24.58. IR $\tilde{\nu}$ [cm⁻¹]: 1670 (w), 1589 (w), 1382 (s), 1246 (m), 1160 (m), 1084 (s), 1031 (s), 847 (s), 772 (w), 736 (s), 639 (s) (see Figure S16, Supporting Information). We name this MOF HHUD-5 in our sequence but in this publication, we refer to it as ortho-1 for comparison with tetra-1.

The synthesis and activation of the tetragonal polymorph tetra-1 was carried out as previously described in the publication of Moroni et al.⁴⁰ Yield: 44 mg (70%, activated MOF). C₆H₄N₄Zn·0.25H₂O calc. C 42.51, H 2.01, N 24.79, found C 42.81, H 2.06, N 24.01. IR $\tilde{\nu}$ [cm⁻¹]: 1670 (w), 1588 (w), 1383 (s), 1245 (m), 1160 (m), 1084 (s), 1032 (s), 849 (s), 736 (s), 639 (s) (see Figure S16, Supporting Information).

Synthesis of [Ni₆(OH)₄(H₂O)₂(bpe)₃·nSolv (2-nSolv, HHUD-6). Compound 2-nSolv was synthesized after the procedure of Padial et al. with the boc-protected linker Boc₂bpe.⁴³ Ni(OAc)₂·4H₂O (148 mg, 0.6 mmol) and Boc₂bpe (144 mg, 0.4 mmol) were dissolved in a mixture of DMF (32 mL) and H₂O (8 mL) and refluxed overnight. The blue microcrystalline powder was washed with DMF (2 × 30 mL), methanol (2 × 30 mL), and chloroform (1 × 30 mL) before being soaked in chloroform (30 mL) overnight. On the next day, the sample was dried in vacuum at 60 °C. During drying the powder turned dark green, but no changes in the diffraction pattern were observable (see Figure S15, Supporting Information). Activation was carried out for 7 h at 130 °C in vacuum (10⁻⁷ mbar). The green powder was stored under an inert atmosphere to prevent moisture adsorption from ambient air. Yield: 87 mg, (87%, activated MOF). C₄₈H₃₃N₂₄Ni₆O₈·5H₂O calc. C 36.02, H 2.65, N 21.00, exp.: C 36.87, H 3.57, N 18.18. (We note that acetate or hydroxide in place of the linker and residual DMF affect the CHN analysis.) IR $\tilde{\nu}$ [cm⁻¹]: 3387 (br), 1653 (s), 1570 (m), 1520 (m), 1437 (w), 1384 (s), 1238 (s), 1164 (w), 1103 (w), 1076 (m), 1034 (s), 995 (w), 952 (w), 837 (s), 776 (m), 739 (s), 643 (s) (see Figure S16, Supporting Information). We name this MOF as HHUD-6 in our sequence but in this publication, we refer to it mostly as 2 for comparison with ortho- and tetra-1.

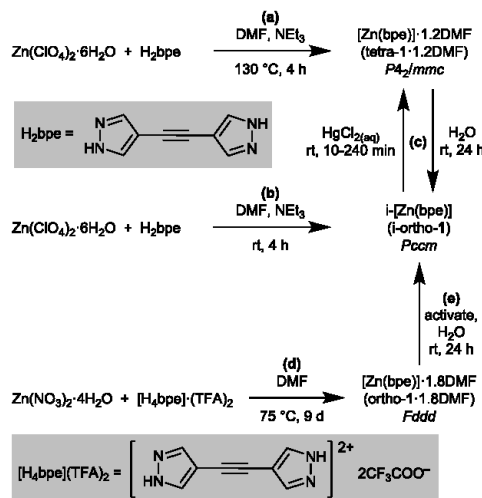
RESULTS AND DISCUSSION

The synthesis of the linker started with an iodination reaction of 1H-pyrazole, followed by a protection using di-*tert*-butyl dicarbonate (Di-Boc) to give 1-boc-4-iodopyrazole from which in a one-pot, two-step Sonogashira reaction the boc-protected linker Boc₂bpe was synthesized and transformed into the deprotected bis-pyrazolium salt [H₄bpe](TFA)₂. Since metal-azolate frameworks tend to form and precipitate rather quickly when the nonprotected pyrazole ligand is used, protected ligands like Boc₂bpe prevent rapid precipitation of the product

and yield a better crystallinity of the sample.⁴³ Here, the bis-pyrazolium salt $[\text{H}_4\text{bpe}](\text{TFA})_2$ of the linker is used due to a possible modulating effect of trifluoroacetic acid (HTFA) or trifluoroacetate (TFA^-), which could increase the crystallinity of MOFs.^{65,74}

Moroni et al. synthesized a noninterpenetrated tetragonal polymorph $[\text{Zn}(\text{bpe})]\cdot 1.2\text{DMF}$ (tetra-1·1.2DMF) as a microcrystalline powder using $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ and H_2bpe in a DMF/triethylamine mixture at 130 °C within 4 h (Scheme 2a). At room temperature under the same conditions an

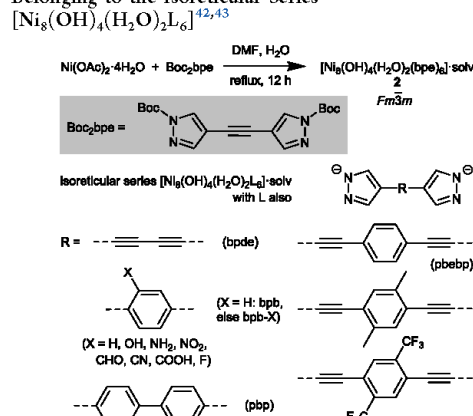
Scheme 2. Schematic Representation of the Synthetic Path and Interconversion of Tetra-1 and the Interpenetrated i-Ortho-1 Published by Moroni et al.⁴⁰ and the Herein-Presented Noninterpenetrated Ortho-1



orthorhombic, 2-fold interpenetrated (i) version of $[\text{Zn}(\text{bpe})]$ (i-ortho-1) was formed (Scheme 2b). After 24 h in water tetra-1 also converted into i-ortho-1, which could be transformed back with HgCl_2 in an aqueous dispersion to the noninterpenetrated, albeit HgCl_2 -clathrated, tetragonal form $\text{HgCl}_2\text{@tetra-1}$ (Scheme 2c).⁴⁰ Here, we grew colorless single crystals of an orthorhombic, albeit noninterpenetrated $[\text{Zn}(\text{bpe})]$ polymorph (ortho-1·1.8DMF) using $\text{Zn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ and $[\text{H}_4\text{bpe}](\text{TFA})_2$ in neat DMF at 75 °C over 9 days (Scheme 2d). Again, an interconversion from noninterpenetrated (activated) ortho-1 to i-ortho-1 can be observed after 24 h in water (Scheme 2e). Thus, it is conceivable to assign tetra-1 as the kinetic and ortho-1 as a more stable, albeit still intermediate product, and i-ortho-1 as the final thermodynamic product under the given conditions. The better quality in crystallinity of ortho-1 might be ascribed to the longer reaction time and/or to a modulating effect of trifluoroacetic acid or rather trifluoroacetate, which was present in the reaction in the form of the linker salt $[\text{H}_4\text{bpe}](\text{TFA})_2$.^{46,65,74}

$[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]\cdot n\text{Solv}$ (2·nSolv) was synthesized similar to the other representatives of the same isoreticular series using a synthesis procedure by Padial et al., according to which $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ and the bis-pyrazole or boc-protected linker precursor were refluxed overnight in a DMF/water-mixture (Scheme 3).⁴³

Scheme 3. Schematic Overview over the Synthesis Conditions for 2·nSolv and the Bis-pyrazolate MOFs Belonging to the Isoreticular Series



The structure of the MOFs was elucidated by single-crystal X-ray analysis for ortho-1·1.8DMF and Rietveld refinement for 2·nSolv, as presented below. The phase purity of the MOFs was proven through a positive match between the simulated and experimental powder X-ray diffraction (PXRD) pattern (Section S5, Supporting Information).

Crystal Structure of $[\text{Zn}(\text{bpe})]\cdot 1.8\text{DMF}$ (Ortho-1·1.8DMF, HHUD-5). Zinc bis-pyrazolate MOFs tend to crystallize either in tetragonal or in orthorhombic space groups, with a difference in the exact location of guest molecules. The structural motif of tetrahedrally coordinated zinc ions, which are doubly bridged by pyrazolate groups giving parallel chains, is the same. The chains are connected by the $-\text{C}\equiv\text{C}-$ spacer of the linkers to either square or rhombic cross sections of the main channels, which run along the chains.^{39,40,75} Moroni et al. reported a structure of the noninterpenetrated MOF $[\text{Zn}(\text{bpe})]\cdot 1.2\text{DMF}$ (tetra-1·1.2DMF) from Rietveld refinement in the tetragonal space group $P4_2/mmc$ (Figure 2). By variation of the synthesis procedure, we were able to grow single crystals of a polymorph $[\text{Zn}(\text{bpe})]\cdot 1.8\text{DMF}$ (ortho-1·1.8DMF), which crystallized in the orthorhombic space group $Fddd$.

The asymmetric unit of tetra-1·1.2DMF contains one $\text{Zn}(\text{II})$ atom, a quarter of a bpe^{2-} molecule (on special positions with a multiplicity of 2, 4, or 8 for the atoms), and a partially occupied DMF molecule (site occupation factor 0.15 on a general position, multiplicity 16) (Figure 2a). The asymmetric unit of the newly found polymorph $[\text{Zn}(\text{bpe})]\cdot 1.8\text{DMF}$ (ortho-1·1.8DMF) consists of two equivalent $\text{Zn}(\text{II})$ ions, one linker, and about two DMF solvent molecules (Figure 3a). In both polymorphs, the coordination sphere of each zinc(II) ion is composed of four pyrazolate rings from four bpe^{2-} molecules in a tetrahedral fashion (Figures 2b and 3b) with $\text{Zn}-\text{N}$ bond lengths between 1.950(5) Å and 1.999(6) Å. The acetylene bond length ($\text{C4}\equiv\text{C5}$) with 1.187(1) Å is consistent with the expected length of a triple bond.⁷⁶

Both tetra-1 and ortho-1 present three-dimensional 4-connected networks with *pts* topology.⁴⁰ Tetra-1 has square channel cross sections (Figure 2c),⁴⁰ while ortho-1 has rhombic channels with approximately the same 8×8 Å width (Figure 3c,e). The networks display also smaller

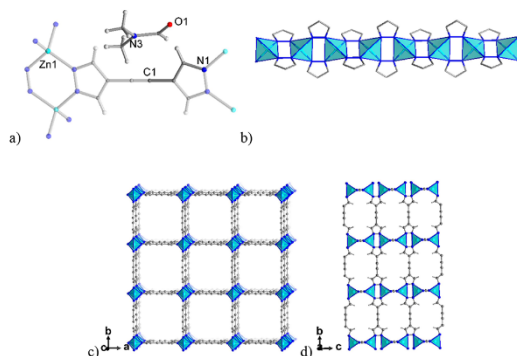


Figure 2. (a) Expanded asymmetric unit of $[\text{Zn}(\text{bpe})]\cdot 1.2\text{DMF}$ (tetra-1·1.2DMF) reported by Moroni et al.⁴⁰ (50% thermal ellipsoids, H atoms with arbitrary radii). Symmetry-related atoms are displayed semitransparent. (b) 1D Zn-SBU chain. (c, d) Sections of the packing diagram of tetra-1·1.2DMF; viewed along the larger (c) and smaller (d) channels (DMF molecules not shown). The structure corresponds to the deposited cif file with ref. code: BIMXEE.⁴⁰

channels perpendicular to the main one. These smaller-sized channels have roughly oval-shaped $4 \times 8 \text{ \AA}$ cross sections (Figures 2d and 3d,f).

Crystal Structure of $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]\cdot n\text{Solv}$ (2·nSolv, HHUD-6). $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]\cdot n\text{Solv}$ (2·nSolv) is a new member of the isoreticular $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2\text{L}_6]$ series with the first representative reported by Masciocchi et al. and continued by others.^{41–43,46–53} The new MOF 2·nSolv crystallizes as expected in the cubic space group $Fm\bar{3}m$. The asymmetric unit contains one Ni(II) atom, a quarter of a bpe^{2-} molecule and a Ni-bridging $\mu_4\text{-OH}^-$ or $\mu_4\text{-H}_2\text{O}$ group treated as sharing O atoms of the respective ligands in a statistical occupation ratio of 2:1, leading to the formation of $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2]^{12+}$ clusters as part of a highly symmetric $\{\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{pz})_{12}\}$ -SBU (Figure 4a,b) of cubic symmetry. The Ni(II) atoms occupy the vertices of the cube, and $\mu_4\text{-Ni-bridging OH}^-$ or H_2O groups reside over the center of the faces (O1) (Figure 4c). The N–N bonds of the pyrazolates are located along the edges (Figure 4c). Furthermore, there is an inversion center in the middle of the acetylene bond. Due to the high cubic symmetry, only the atoms Ni1, N1, O1, C1–C3 are crystallographically unique. Each nickel(II) atom is octahedrally coordinated in a *facial* configuration by three symmetry-related N-donor atoms from three pyrazolates of

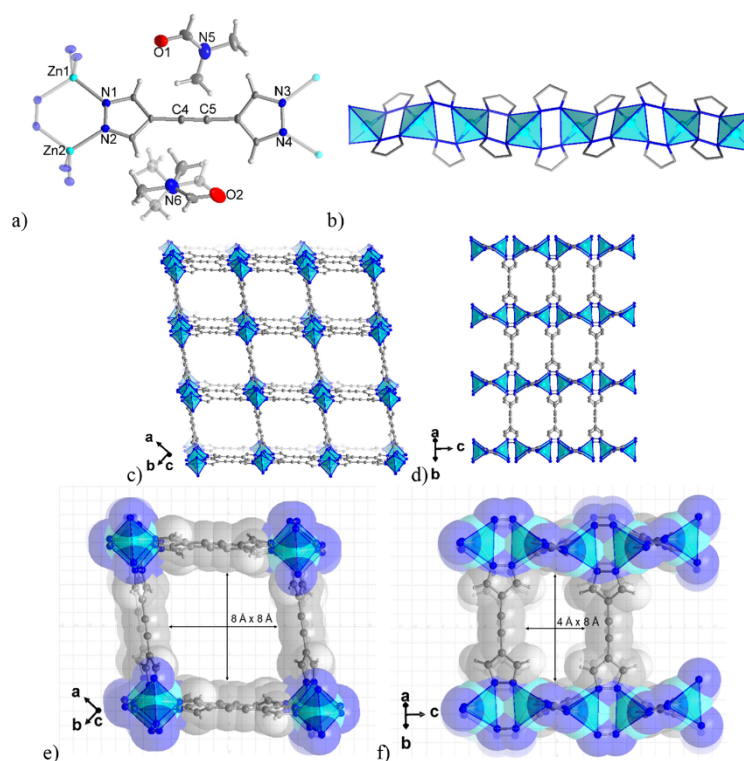


Figure 3. (a) Expanded asymmetric unit of ortho-1·1.8DMF (HHUD-5) (50% thermal ellipsoids, H atoms with arbitrary radii). Symmetry-related atoms and one of the disorder components of the DMF molecule is displayed with semitransparent atoms. (b) 1D Zn-SBU chain. (c, d) Sections of the packing diagram of ortho-1; viewed along the larger (c) and smaller (d) channel. (e, f) Determination of the channel sizes using the space-filling model and an underlying $1 \times 1 \text{ \AA}$ grid. DMF molecules were not shown in (c–f).

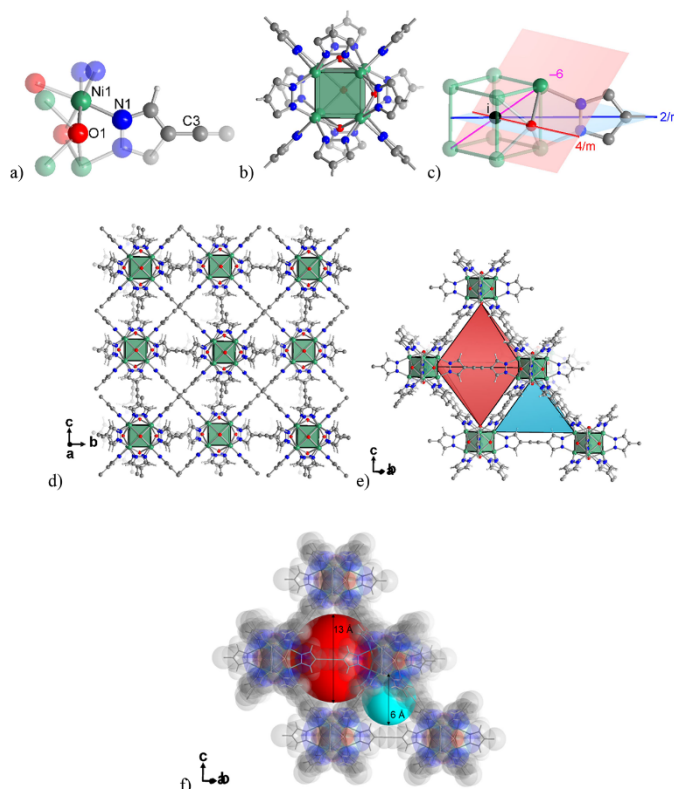


Figure 4. (a) Expanded asymmetric unit of 2-nSolv (HHUD-6) (50% thermal ellipsoids, H atoms with arbitrary radii). Symmetry-related atoms are shown semitransparent. (b) $\{Ni_8(OH)_4(H_2O)_2(pz)_{12}\}$ -SBU (pz = pyrazolate) (H atoms are not shown for clarity). (c) $\{Ni_8\}$ cube with selected symmetry elements and Hermann–Mauguin notation. (d) Section of the packing diagram of **2**. (e) Octahedral (red) and tetrahedral (blue) pores of **2**. (f) Determination of the octahedral and tetrahedral pore size with a space-filling model and spheres inside of the pores. Graphics were prepared with the software Diamond.⁷⁰

three different linker molecules with a Ni–N bond length of 2.044(9) Å and three symmetry-related μ_4 -bridging oxygen atoms with a Ni–O bond length of 2.234(5) Å. The acetylene bond length (C3≡C3') with 1.204(1) Å is consistent with the expected length of a triple bond.⁷⁶

The cubic Ni-SBUs have Ni⋯Ni distances of 2.952(1) Å and N/O–Ni–N/O bond angles of 90°. The SBUs form a (12)-connected 3D network with *fcu* topology (Figure 4d), as the other isorecticular nickel bis-pyrazolate MOFs with a larger octahedral and a smaller tetrahedral pore (Figure 4e), and akin to other *fcu*-topology MOFs, e.g. UiO-66.^{41,43,45,77,78} The larger octahedral pore has diagonal corner–corner distances of around 14 Å, while the smaller, tetrahedral pore has corner–face separations of 8 Å. If a sphere is inscribed in the octahedral and tetrahedral pores, such that its surface touches the space-filling outline of the framework (Figure 4f), then the sphere in the octahedral pore has a diameter of ~13 and ~6 Å in the tetrahedral pore, giving sphere (pore) volumes of ~1150 and ~113 Å³, respectively.

Gas Sorption Measurements. $[Zn(bpe)] \cdot 1.8DMF$ (ortho-1·1.8DMF) could be fully activated after 3 h at 120 °C in vacuum (10^{-7} mbar), and $[Ni_8(OH)_4(H_2O)_2(bpe)_6] \cdot nSolv$ (2-nSolv) after 7 h at 130 °C in vacuum (10^{-7} mbar)

without decomposition as evidenced by unchanged PXRD traces (Section S5, Supporting Information). No mass loss due to solvent was visible for the activated samples in the thermogravimetric trace (Section S7, Supporting Information). Thermogravimetric analyses (TGA) also indicated a thermal stability of up to 500 °C for **1** and to around 330 °C for **2** under a nitrogen atmosphere (under synthetic air: 480 °C for ortho-1 and 250 °C for **2**). The steady mass loss of 2–3 wt % observed for **2** around 250 °C (under N₂) and 150 °C (under air) (Figure S18, Supporting Information) is assigned to dehydration of the four hydroxido ligands (giving $2(\mu_4-O^{2-}) + 2H_2O$, theor. 2.5%) akin to UiO-66.⁷⁹ The activated samples exhibited permanent porosity as shown by the physisorption of various gases and vapors. After gas sorption experiments, both materials retain crystallinity and porosity (Section S16, Supporting Information).

Prior to each gas sorption measurement, ortho-1·1.8DMF was activated for 3 h at 120 °C and **2** for 7 h at 130 °C in vacuum (10^{-7} mbar). For reactivation between sorption measurements, only 60 °C for 1 h in vacuum was applied.

Volumetric nitrogen adsorption experiments at 77 K yielded an ideal type I(a) isotherm for ortho-1, typical for microporous materials having mainly narrow micropores of a width of

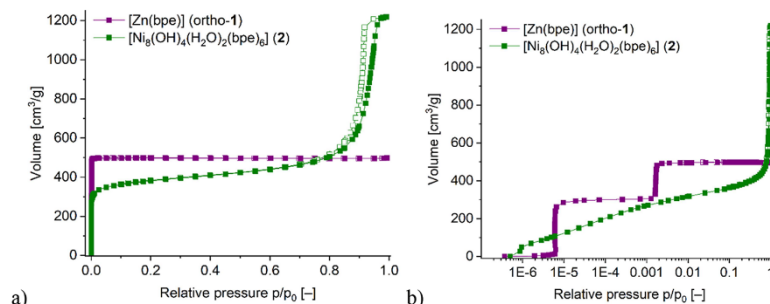


Figure 5. Volumetric nitrogen adsorption isotherms at 77 K of [Zn(bpe)] (ortho-1) and [Ni₆(OH)₄(H₂O)₂(bpe)₆] (2) (a) using a linear pressure scale and (b) using a logarithmic pressure scale (filled symbols for adsorption, empty symbols for desorption). The desorption isotherm was measured until a relative pressure of 0.01 for ortho-1 and 0.1 for 2 and is hardly visible as it exactly traces (coincides with) the adsorption isotherms for ortho-1 over the full range and for 2 in the lower pressure range.

Table 1. Comparison of the BET Surface Areas, Void Volumes (V_{void}), and the Total Pore Volume (V_{pore}) ($p/p_0 = 0.95$) of 1 (Tetra and Ortho) and 2 with Selected Isorecticular Metal Bis-pyrazolate (M = Zn, Ni) MOFs from the Literature

Linker	Length [Å] ^a	Zn-MOFs			Ni-MOFs		
		BET [m ² /g]	V_{void} [%] ^b (V_{pore} [cm ³ /g])	Ref.	BET [m ² /g]	V_{void} [%] ^b (V_{pore} [cm ³ /g])	Ref.
	5.9	778	43	35	—	—	—
	8.4	1380	62	40	1415	63 (0.78) ^d	this work (2)
		1904	62 (0.73)	this work (tetra-1)			
	9.9	2135	62 (0.77)	this work (ortho-1)	1770	65	43
	10.9	—	—	—	1920	74	43
	15.4	1214	48 ^f (0.64)	87	2225 3020	81 (1.48)	43 88

^aBased on N...N distances in the single-crystal structures (for bpde²⁻: ref. code: HAFTOZ).⁴² ^bCalculated with mercury as percent of unit cell volume (contact surface model; grid spacing: 0.2 Å; probe radius: 1.8 Å).⁷¹ ^cTotal pore volume (V_{pore}) experimentally obtained from N₂ adsorption isotherms. ^dTotal pore volume at $p/p_0 = 0.8$. ^eValue was given with no further details in ref 35. ^fValue was reported in ref 87 and calculated with PLATON (contact surface model and a probe radius of 1.2 Å).^{89,90}

around 10 Å (Figure 5a).⁸⁰ As Thommes et al. noted, the BET theory reaches its limits in connection with type I isotherms, so that the surface area of 2135 m²/g only represents an apparent surface area instead of a realistic probe-accessible surface area.⁸⁰ A porosity analysis for ortho-1 with the program Mercury 2023.3.0 yielded a specific surface area of 1990 m²/g and a specific pore volume of 0.79 cm³/g (experimental value: 0.77 cm³/g) (Table S6, Supporting Information) in good agreement with the experimental values.⁷¹ Interestingly, after the initial steep uptake at a very low relative pressure of less than 5×10^{-4} , further uptake follows between 5.5×10^{-4} and 1.6×10^{-3} , forming a plateau, followed by a second uptake step (Figure 5b), which is an indication of bimodal distribution of the pore sizes with a low size dispersion (cf. Figure 3c–f). Pronounced framework flexibility, which is sometimes registered in microporous materials as a response to gas adsorption, seems to be unlikely for ortho-1 since the desorption branch exactly traces the adsorption branch of the isotherm.^{12,81,82} Because neither nonlocal density functional theory (NLDF) nor grand canonical Monte Carlo

simulation (GCMC) led to a good isotherm fit, pore size analysis was performed using the Saito-Foley (SF) method, which is widely used to determine the pore size of microporous materials even though it underestimates pore sizes.⁸³ In our case the calculated pore sizes of 5.5 and 8 Å (Figure S19, Supporting Information) seem to fit very well with the channel sizes in Figure 3d,f (4×8 and 8×8 Å). The ideal isotherm shape, visibility of the plateau, and the good fit for the pore size calculation could be ascribed to an exceptionally uniform crystallinity of ortho-1.

For 2, the isotherm starts as type I(a) (for microporous) and then continues as a type IV(a) isotherm (for mesoporous materials) with its characteristic final saturation plateau (BET surface area: 1415 m²/g). For the type IV branch, a hysteresis of type H1 was observed, which indicates a material with a narrow size range of uniform mesopores (Figure 5a). Again, it has to be taken into account, that the BET surface might only represent an apparent surface.⁸⁰ For 2, the isotherm on the logarithmic pressure scale gives a smooth increase in adsorbed volume up to $p/p_0 = 0.1$ and does not show different uptake

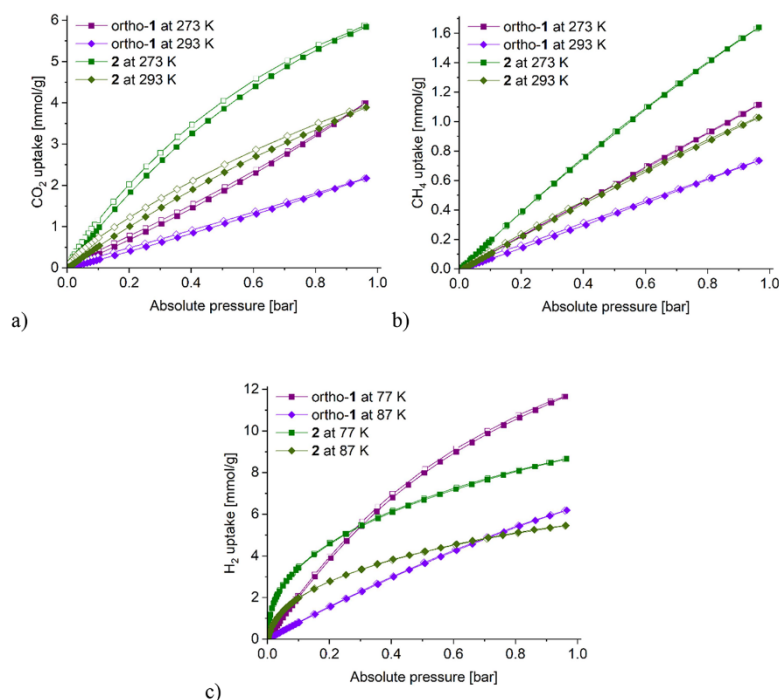


Figure 6. Gas sorption isotherms of [Zn(bpe)] (ortho-1) and $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ (**2**) for (a) CO_2 at 273 and 293 K, (b) CH_4 at 273 and 293 K and (c) H_2 at 77 and 87 K (filled symbols for adsorption, empty symbols for desorption).

steps for the tetrahedral and octahedral pores (Figure 5b). A geometric porosity analysis for the idealized structure of **2** with the program Mercury 2023.3.0 gives a specific surface area of $2301 \text{ m}^2/\text{g}$ and a specific pore volume of $0.78 \text{ cm}^3/\text{g}$ (Table S7, Supporting Information).⁷¹ This value is in accordance with the total pore volume of $0.78 \text{ cm}^3/\text{g}$ calculated using Gurvich's rule at $p/p_0 = 0.80$, the relative pressure value just before the large uptake step, which is ascribed to textural effects, i.e., primarily to condensation in the mesoporous interparticle space.⁸⁴ The contact surface is derived by a probe with a given diameter rolling over the surface and represents the profile of the pore surface but can overestimate the surface area and porosity, compared to the experimental values, as it does not take into account a simultaneous overlap with neighboring surfaces in narrow pores.⁸⁵ In the latter, the opposite contact surfaces are at a distance of the length of the adsorbate molecule, which then interacts with the surfaces at their opposite sides. From the theoretical calculation, the surface area is counted twice, while the experimental determination gives only the surface area contribution for one adsorbed molecule.

GCMC calculations for the pore size distribution analysis provided a good fit giving micropores in the range between 6 and 8 Å (Figure S20, Supporting Information), again in agreement with the pore sizes in Figure 4f). A sizable contribution of mesopores with a broader size distribution is present between 100 and 280 Å due to the textural effects (Figure S20, Supporting Information). Using the t-plot method, a surface area of $1535 \text{ m}^2/\text{g}$ with micropores of 6 Å was calculated (Figure S21, Supporting Information). While

the t-plot method is imprecise in the absence of nonporous reference material, the qualitative analysis of the plot confirms the insignificant content of small mesopores. The t-plot-based values are in reasonably good correspondence with the BET surface and the pore size distribution according to the GCMC method.

With BET surface areas of $2135 \text{ m}^2/\text{g}$ for ortho-1 and $1415 \text{ m}^2/\text{g}$ for **2**, a comparison with the published data of other zinc- and nickel bis-pyrazolate MOFs of isorecticular structure is consistent regarding the expected trend of surface area increase with the linker length (Table 1). The shortest linker 4,4'-bis-pyrazolate (bpz^{2-}) leads to a surface area of $778 \text{ m}^2/\text{g}$ for the Zn-MOF. For 4,4'-(ethyne-1,2-diyl)bis(pyrazolate) (bpe^{2-}), the Zn-MOF tetra-1 published by Moroni et al. shows a surface area of $1380 \text{ m}^2/\text{g}$.⁴⁰ We have checked the BET surface area of tetra-1, which we resynthesized according to the procedure of Moroni et al., and have obtained a surface area of $1904 \text{ m}^2/\text{g}$ with the same plateau in the low relative pressure range as for ortho-1 (Section S10, Supporting Information).⁴⁰ The polymorph of tetra-1 was verified by PXRD (Figure S14, Supporting Information). We assume, that the increase of the BET surface area for tetra-1, which is now as expected similar to ortho-1, can be ascribed to the activation in a very high vacuum (10^{-7} mbar using a turbomolecular vacuum pump), which freed the smaller channels of [Zn(bpe)] from residual DMF and thus made them accessible for the nitrogen molecules. This shows that such porosity data strongly depend on the activation procedure and that a comparison of surface area and pore volume values from literature can only be a rough trend analysis, which must be treated with care and not

overinterpreted. The longer 4,4'-(1,4-phenylene)bis(pyrazolate) (bpb²⁻) linker results in slightly larger surface areas (2288 m²/g for the Zn-analog and 1770 m²/g for the Ni-analog).^{39,43} For 4,4'-(buta-1,3-diyne-1,4-diyl)bis(pyrazolate) (bpde²⁻) only a nickel-analog is known, which has the highest BET surface area with 1920 m²/g.⁴³ For the longest presented ligand 4,4'-(1,4-phenylenebis(ethyne-2,1-diyl))bis(pyrazolate) (pbebp²⁻) the Zn-MOF only has a surface area of 1214 m²/g, possibly due to partial structure collapse during activation, which demonstrates the objective limits of the possibility to increase the surface area with elongation of the linker.⁸⁷ For the Ni-MOF the correlation remains valid since the surface area of this analog is 2225 m²/g.⁴³ Tarnowicz-Ligus et al. reported an even higher surface area (3020 m²/g), which was ascribed to less DMF inside the pores.⁸⁸ Evidently, replacing the phenylene spacer in bpb²⁻ with an about 1.5 Å shorter single $\text{—C}\equiv\text{C—}$ triple bond to give the bpe²⁻ linker or by about 1 Å longer two $\text{—C}\equiv\text{C—}$ triple bonds to give the bpde²⁻ linker does not boost the specific surface area of the derived MOFs beyond expectation from the linker length as was suggested before.¹⁶

For ortho-1, the CO₂ uptake of 3.99 mmol/g (273 K, Figure 6a, Table 2) slightly exceeds the adsorption capacity of the

Table 2. Gas Adsorption Uptakes for Ortho-1 and 2 for CO₂, CH₄ and H₂ at Different Temperatures and Pressures

MOF	P [bar]	CO ₂ uptake [mmol/g]		CH ₄ uptake [mmol/g]		H ₂ uptake [mmol/g]	
		273 K	293 K	273 K	293 K	77 K	87 K
ortho-1	1	3.99	2.17	1.11	0.74	11.6	6.2
	20		14.1		6.8		
2	1	5.84	3.89	1.64	1.03	8.7	5.5
	20		7.6		4.97		

[Zn(bpb)] analog with the longer bpb²⁻ linker (~3 mmol/g, Table S8, Supporting Information). Further, with a type I(b) isotherm, ortho-1 reaches a CO₂ uptake of 14.1 mmol/g at 293 K and 20 bar (Figure S23, Supporting Information) compared to only 9.1 mmol/g for [Zn(bpb)] at even lower temperature of 273 K and higher pressure of 30 bar.⁸⁶ The CO₂ adsorption capacity of 2 at 1 bar and 273 K (5.84 mmol/g, Figure 6a, Table 2) exceeds the uptake of the isoreticular bpb-X²⁻ analogs [Ni₆(OH)₄(H₂O)₂(bpb-X)₆] (~2.5 to 3.44 mmol/g) (Table S8, Supporting Information). This could be interpreted as an advantage of a $\text{—C}\equiv\text{C—}$ triple bond over a phenylene spacer in the linker for CO₂ adsorption.^{16,39,53,56} However, comparison of adsorption data from different sources must be done with care and can be misleading, for example, in view of different activation protocols and the thereby achieved porosity.

The CO₂ uptake of 2 at 1 bar also exceeds that of ortho-1 (Figure 6a, Table 2), albeit above 2 bar ortho-1 surpasses 2 (Table 2, Figure S23, Supporting Information). The higher CO₂ uptake of 2 over ortho-1 at low pressure is in line with the higher heat of adsorption (see below) in 2 at the comparative gas loadings (Figures S25 and S27, Supporting Information). The higher uptake in ortho-1 over 2 above 2 bar is correlated with the higher surface area of the former in the presence of a weak adsorbent–adsorbate interaction. Evidence of the relatively weak adsorbent–adsorbate interaction in ortho-1, together with a low surface coverage (far from saturation), is given by the near linearity of the adsorption isotherms in the

low-pressure range at 273 and 293 K (Figure 6a, Figure S21a,b). Moreover, there is a slight deviation from linearity toward an unfavorable convex instead of the usual concave shape between 0 and 1 bar. This deviation has a minor influence on the absolute uptake but limits the utility of heat of adsorption calculations at low pressures, as discussed below). It is worth mentioning, that at very low relative pressures the Henry law, as additionally discussed below, dictates a nearly linear isotherm (the relative pressure for CO₂ at 1 bar and 273 or 293 K is 0.018 and therefore this region is only the beginning of a complete isotherm over the whole relative pressure range up to $p/p_0 = 1$, which would then correspond to 56.6 bar at 293 K). The nonexpected convex deflection from linearity at low pressures is visible, but relatively small (it is not impossible that minor deformations of the framework might contribute to this deviation or kinetic effects due to not long enough equilibration times), however, the high-pressure isotherm is of the common concave shape (Figure S23, Supporting Information). At 293 K the CO₂ adsorption of ortho-1 isotherm is almost linear until ~4 bar when the slope decreases to give the concave shape (Figure S23, Supporting Information).

The CO₂ adsorption isotherm is also close to linear for 2 at <0.4 bar pressure. Such close linearity in this pressure range is also visible for the CO₂ isotherms of [Zn(bpb)] and other MOFs.^{39,91–95} However, the discussed small deflections from a typical adsorption isotherm, particularly for 1, make a physically meaningful fitting problematic. No model among the available ones (see the Experimental section) other than the Freundlich model was applicable for fitting and subsequent heat of adsorption (HoA) determination, indicating the limitations of simple adsorption models for ultramicroporous materials (deviations might be caused, for example, by the flexibility of the framework, which could be local enough to be hardly detectable by diffraction methods or unaccounted kinetic effects).^{80,81,96–99} The large fitting error at low pressures, which is in part caused and in part amplified by larger-than-average experimental errors of measured uptakes, makes the determination of HoA nonreliable (or rather, with such a large error that it is simply not informative). The use of only two isotherms for HoA calculation with a temperature difference of 20 K does not increase the error associated with fitting *per se*, but it assumes an uncertainty regarding the precise temperature, to which the calculated values should be ascribed.^{100,101} Therefore, the calculated HoA values for CO₂ in the very low-pressure range are excluded from the discussion (for the sake of symmetry it was done also for 2, even if the data for ortho-1 is particularly affected). As for 1, the heat of adsorption for CO₂ at a loading of 1 mmol/g is 16 kJ/mol and continues to rise to 18 kJ/mol at 2.2 mmol/g (Figure S25, Supporting Information) and is therefore in the same range as [Zn(bpb)] with the heat of adsorption of 20 kJ/mol.³⁹ For 2, the HoA is 21 kJ/mol at 1 mmol/g and remains constant up to 3.9 mmol/g (Figure S27, Supporting Information).

The CH₄ uptake of ortho-1 with 6.8 mmol/g at 293 K and 20 bar also exceeds the methane uptake of 2.4 mmol/g for [Zn(bpb)] at even lower temperature of 273 K and higher pressure of 30 bar (Table S9, Supporting Information).¹⁰¹ Again, 2 has a higher CH₄ uptake at 1 bar than its bpb-X²⁻ analogs (Table S9, Supporting Information)⁴⁹ and ortho-1 (Figure 6b), but above 6 bar the CH₄ uptake of ortho-1 surpasses that of 2 (Table S9, Figure S23, Supporting Information). The higher CH₄ uptake of 2 over ortho-1 at

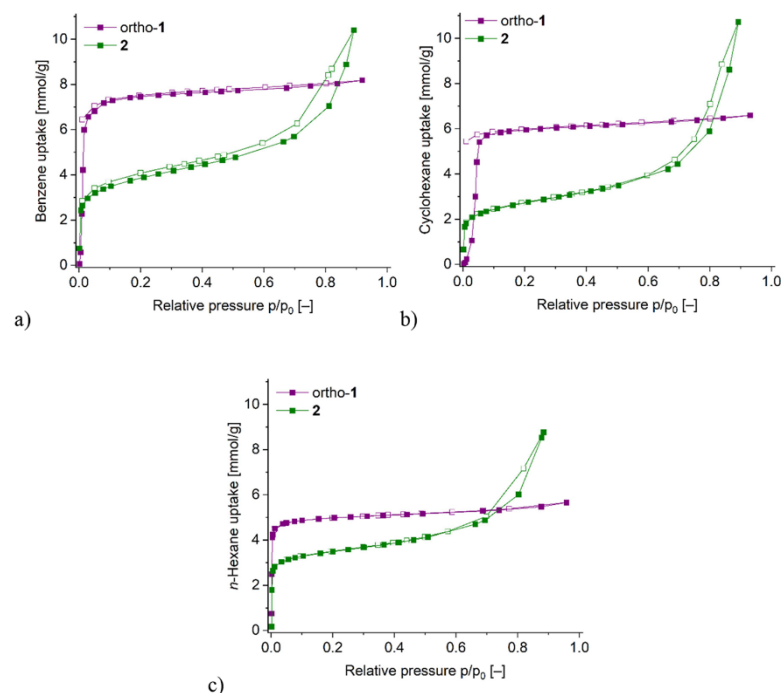


Figure 7. Vapor sorption isotherm of $[\text{Zn}(\text{bpe})]$ (ortho-1) and $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ (2) at 293 K for (a) benzene, (b) cyclohexane, and (c) *n*-hexane (filled symbols for adsorption, empty symbols for desorption).

low pressure is in line with the higher heat of adsorption (see below) in 2 for the same gas loadings (Figures S25 and S27, Supporting Information). As seen for CO_2 , the higher CH_4 uptake in ortho-1 over 2 above 6 bar is explained by the higher surface area of ortho-1.

The CH_4 adsorption isotherm for ortho-1 up to 1 bar is almost linear, as can be found for other MOFs in the literature.^{93,102} After fitting the isotherm with the Freundlich model a zero-coverage heat of adsorption Q_{st}^0 for CH_4 in ortho-1 of around 15 kJ/mol was determined. A slight decrease for the HoA-value with increasing amount adsorbed is apparent (13 kJ/mol at 0.74 mmol/g; Figure S25, Supporting Information), implying that CH_4 molecules are adsorbed at energetically slightly more favorable sites first before less favorable sites are occupied.^{100,101} CO_2/CH_4 selectivity for ortho-1 could not be calculated as none of the common fitting models, e.g., Langmuir or Toth were applicable for these types of isotherms of ortho-1. The latter models were derived for adsorption on fixed sites, but since microporous materials can be influenced by various adsorbate-induced rearrangements, this assumption is not valid. Even though the Langmuir or Toth fitting equations are valid to describe the adsorption in many microporous solids, they fail to describe a strictly linear or a slightly convex isotherm in the case of ortho-1 without an assumption of a very large error.^{81,98}

The zero-coverage heat of adsorption Q_{st}^0 of 2 for CH_4 is 26 kJ/mol. The HoA then decreases to 18 kJ/mol at a loading of 0.72 mmol/g (Figure S27, Supporting Information).^{100,101} The IAST selectivity for CO_2/CH_4 mixtures at 273 or 293 K and 1 bar for 2 were calculated using the 3Psim software (for further

details, see Section S14, Supporting Information).⁷³ Toth-fitted isotherms yielded selectivities of 5.8 at 273 K and 6.3 at 293 K (Figure S29, Supporting Information).

The almost linear CO_2 and CH_4 isotherms of ortho-1 in Figures 6a,b and S23 (Supporting Information) indicate that the linear limit, i.e., Henry's law region extends to the pressure of about 4 and 6 bar, respectively. An initial linear, i.e., Henry adsorption isotherm means that the amount of adsorbate is proportional to the partial pressure of the adsorptive gas, coinciding with low surface coverage (far from saturation) and adsorption energy, which is independent of surface coverage as the surface has no inhomogeneities. With such an initial low slope of the isotherm, that is, a small Henry constant, the thermal energy at 293 K is comparable to the rather small heat of adsorption due to weak attractive forces between adsorbent and adsorbate so that the surface coverage is low. Only at higher pressures above 4 and 6 bar, respectively, CO_2 and CH_4 molecular clustering is induced, followed by pore filling.⁸⁰

With a hydrogen adsorption capacity of 11.6 mmol/g, ortho-1 shows a significantly higher H_2 uptake than 2 with 8.7 mmol/g at 1 bar and 77 K (Figure 6c, Table 2). A reason for this high uptake of ortho-1 could be the uniform crystallinity since the combination of a small pore size with a rather narrow pore size distribution is known to improve the hydrogen adsorption capacity of carbon materials.^{23,27,28,103,104} However, below ~ 0.3 bar at 77 K and ~ 0.7 bar at 87 K, compound 2 adsorbs more H_2 than ortho-1. Compound 2 has a significantly higher HoA (Figures S25 and S27, Supporting Information). At higher loading the higher surface area of ortho-1 over 2 then dominates as seen for CO_2 and CH_4 adsorption.

The heat of adsorption for H₂ in ortho-1 is around 5–6 kJ/mol (Figure S25, Supporting Information), which is in line with values measured for many other MOFs, but far below the requirements for hydrogen storage (15 kJ/mol).^{100,103–105} The heat of adsorption for H₂ in 2 surpasses the requirement of 15 kJ/mol with a value of 20 kJ/mol at zero coverage,^{104–107} however, the HoA-value decreases rapidly and is already below the requirement at an uptake of 0.1 mmol/g. With 6 kJ/mol at a gas loading of 3.82 mmol/g, the HoA for H₂ in 2 is in the range of many other MOFs and close to the value in ortho-1 (Figure S27, Supporting Information).^{100,103–105}

Compared to the only other available zinc bis-pyrazolate MOF [Zn(bpb)], ortho-1 shows again a higher uptake as for CO₂ and CH₄ (Table S10, Supporting Information).^{16,31,56} The highest hydrogen uptake among Zn-MOFs was reported for UPC-S01 (14.8 mmol/g at 1 bar, 77 K).¹⁰³

The consistently higher gas uptake of CO₂, CH₄, and H₂ in 2 versus 1 at lower pressures is explained by the formation of open metal sites from activation.¹⁰⁶ The two μ_4 aqua ligands in [Ni₈(OH)₄(H₂O)₂(bpe)₆], 2 can be removed leaving coordinatively unsaturated sites at each nickel atom in the cluster. Theoretical investigations suggest higher heats of adsorption at the open metal sites, especially on Ni²⁺ with the appropriate models.¹⁰⁸ The emphasized CO₂ adsorption properties with high Q_{st}^0 in Zr-, Hf- and Ce-MOFs with the acetylenedicarboxylate linker and UiO-66 topology^{54,55,57,58} can very well be due to the open metal sites from linker defects for which UiO-66 structures types are prone to.^{77,109,110} The gas uptakes of 2 are contrasted with the ones of UiO-66 in Table S11 (Supporting Information) and appear to be similar to UiO-66 with low defects when adjusting for the different temperatures and pressures.

Vapor Sorption Measurements. Toxic volatile organic compounds (VOCs) like benzene, cyclohexane, and *n*-hexane in the air, both indoors and outdoors, are of general concern due to their health risks, also since the oxidative degradation of benzene, the most toxic indoor VOC,⁵⁶ generates secondary pollutants.^{7–10,56} The adsorptive removal of VOCs using MOFs,^{6,9,10,56,111} among other adsorbents, is of particular interest due to low energy for recyclability. The removal of *n*-hexane is relevant because of its metabolization to 2,5-hexanedione, which is a nerve-damaging and toxic compound.^{10,56,112}

Furthermore, benzene and cyclohexane have similar physical properties such as boiling point and vapor pressure. Consequently, the petrochemical industry has to rely on cost-intensive devices and energy-intensive distillation processes to obtain phase-pure products and is looking for better alternatives, such as using MOFs for physisorptive separation.^{56,111,113} MOFs with triple bonds, as in ortho-1 and 2, are interesting candidates for separation since double or triple bonds could interact with benzene through $\pi \cdots \pi$ interactions.^{56,93}

Similar to the gas sorption measurements, ortho-1 was activated for 3 h at 120 °C in vacuum (10^{−7} mbar) and 2 for 7 h at 130 °C in vacuum (10^{−7} mbar). For reactivation between sorption measurements, only 60 °C for 1 h in vacuum was applied. For benzene, cyclohexane, and *n*-hexane, vapor sorption measurements at 293 K yielded a slightly S-shaped type I isotherm without a hysteresis for ortho-1 and a type II isotherm with a small hysteresis of type H3 for 2 (Figure 7). The absence of significant hysteresis in ortho-1 indicates that

there are no kinetic restrictions for the guest molecule desorption.^{12,56,114}

The vapor uptake for ortho-1 is in the lower relative pressure regions significantly higher than for 2, which we trace to the presence of the small channels in ortho-1. The small channels in ortho-1 with a cross-section of 4 Å × 8 Å can provide good interactions with both ends of the adsorbed molecule to opposite surfaces of the adsorbent. Gaseous benzene has a kinetic diameter of 5.85 Å, cyclohexane of 6 Å, and linear *n*-hexane of 4.3 Å.¹¹⁵ As none of these molecules is spherical, the van-der-Waals dimensions along the *x*, *y* and *z* axis are *x* = 6.628 (MIN2), *y* = 7.337, *z* = 3.277 Å for benzene, *x* = 7.168, *y* = 6.580 (MIN2), *z* = 4.982 Å for cyclohexane, and *x* = 10.344, *y* = 4.536 (MIN2), *z* = 4.014 Å for *n*-hexane.¹¹⁶ The MIN2 values are the critical molecular dimensions for diffusion through cylindrical pore cross-sections. The two shorter dimensions of each of these VOCs indicate that the molecules will fit into the 4 Å × 8 Å cross-section in ortho-1, with multiple dispersive interactions with the channel surface. The small channel in ortho-1 will become well accessible if it adapts to the guest molecules, which is a known phenomenon for microporous materials.^{12,81,82}

The adsorbate–adsorbent interaction energy and hence the affinity at low partial pressure is higher if the adsorbent structure has Connolly surfaces, i.e., pore-limiting diameters, at the dimension of the adsorbed molecule.^{117–119} The latter can then interact with several points on the adsorbent surface.⁸⁰ The Connolly surface of an adsorbent is the surface that is accessible for the adsorbate.

The maximum uptake for ortho-1 is 8.2 mmol/g for benzene, 6.6 mmol/g for cyclohexane, and 5.7 mmol/g for *n*-hexane. The uptake for 2 at a relative pressure of 0.7 is 5.7 mmol/g for benzene, 4.4 mmol/g for cyclohexane, and 4.9 mmol/g for *n*-hexane. The large uptake step for 2 starting at a relative pressure of 0.7 results in uptakes of 10.4 mmol/g for benzene, 10.7 mmol/g for cyclohexane, and 8.8 mmol/g for *n*-hexane at *p/p*₀ = 0.9 and is likely due to textural effects, i.e., condensation in interparticle voids (Figure 7).¹² After vapor sorption experiments, both MOFs retain crystallinity and porosity (Section S16, Supporting Information).

IAST (ideal adsorbed solution theory) selectivities at 293 K and variable vapor pressure for 1:1 (v/v) mixtures of *n*-hexane/cyclohexane, *n*-hexane/benzene, and benzene/cyclohexane were calculated using the 3Psim software (Section S15, Supporting Information).⁷³ Similar to the above gas sorption experiments, the attempted data fitting with the standard adsorption isotherm equations was not successful, reflecting the limited utility of the standard models in this case.^{80,81,96–99}

For 2, a dual site Langmuir fit was applicable up to a relative pressure of 0.5 or an absolute pressure of 0.052 bar. For higher pressures, the large uptake step could not be fitted in a satisfying way. The selectivities for all mixtures are below 5. For *n*-hexane/cyclohexane mixtures the selectivity is highest with up to 5 at 0.013 bar and then decreases to 3.9 at 0.050 bar (Figure S31, Table S12, Supporting Information). This modest selectivity between the smallest and largest adsorbate, *n*-hexane, and cyclohexane is in line with their kinetic diameters. The smaller *n*-hexane can, for example, enter the regions with acute angles of the tetrahedral pores (cf. Figure 4f), which are inaccessible for the bulkier cyclohexane. Thus, 2 has a certain potential for the industrial separation of *n*-hexane and cyclohexane, where selectivities above 3 are desired.^{115,120}

For *n*-hexane/benzene and benzene/cyclohexane, their kinetic diameters or molecular dimensions are apparently not

different enough to give a selectivity above 2.1 with **2** (Figure S31, Table S12, Supporting Information). In the absence of differentiating adsorbate–adsorbent interactions, the low selectivity of **2** is in agreement with the expectations.^{12,56,114,116}

Furthermore, we have measured the adsorption capacities of water vapor, which is interesting for potential applications in adsorption heat pumps, water-driven adsorption chillers, or water harvesting.^{121–124} The hydrophobic [Zn(bpe)] (ortho-1) has an uptake of 0.02 g/g, whereas for the more hydrophilic [Ni₈(OH)₄(H₂O)₂(bpe)₆] (**2**) a maximum uptake of 0.19 g/g was obtained (Figure 8). Both MOFs show a large hysteresis

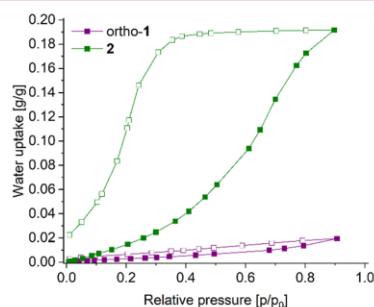


Figure 8. Water vapor sorption isotherm of [Zn(bpe)] (ortho-1) and [Ni₈(OH)₄(H₂O)₂(bpe)₆] (**2**) at 293 K (filled symbols for adsorption, empty symbols for desorption).

and neither reaches the typical requirements for cyclic water sorption applications, where a steep and high uptake (>0.3 g/g) in the relative pressure range of 0.05 to 0.35 with a small hysteresis is desirable.¹²² Stability tests via PXRD and N₂ sorption showed that both, ortho-1 and **2**, remain crystalline and porous after water vapor sorption (Figures S32–S36). By comparison, the Zr-, Hf- and Ce-MOFs with the acetylenedicarboxylate linker and UiO-66 topology^{54,55,57,58} were rather hydrophilic with type I(b) isotherms and small hystereses. Their respective water uptakes were about 0.2 g/g at $p/p_0 = 1$ with 80% of the uptake completed at $p/p_0 \approx 0.4$. The high hydrophilicity was suggested to be due to the $\text{—C}\equiv\text{C—}$ triple bond in the linker. At the same time, these UiO-66 analogs feature a myriad of hydrophilic $\mu_3\text{—OH}$, $\mu_3\text{—O}$, and $\mu\text{—O}_2\text{C}$ sites in the $\{\text{M}_6(\mu_3\text{—OH})_4(\mu_3\text{—O})_4(\text{O}_2\text{C—})_{12}\}$ -SBUs ($\text{M} = \text{Zr, Hf, Ce}$), amplified by the missing linker defects, where terminal M—OH and M—OH_2 at least partially replace the carboxylate group. In [Zn(bpe)] (ortho-1) such hydrophilic groups are completely missing. In [Ni₈(OH)₄(H₂O)₂(bpe)₆] (**2**) the hydrophilic $\mu_4\text{—OH/OH}_2$ ligands are present in the same number per SBU as the $\mu_3\text{—O/OH}$ ligands in UiO-66,⁷⁷ but it is evident that the bpe^{2−} linker is rather hydrophobic and counteracts and dominates the hydrophilic $\mu_4\text{—OH}$ and $\mu_4\text{—OH}_2$ influence. This is due to the much less hydrophilic nature of the pyrazolate moiety compared to carboxylate, and, to some extent, due to the partial shielding of the more hydrophilic areas.

Stability Toward Water, Acids, and Bases. Since metal-azolate frameworks tend to be stable at various pH conditions in aqueous dispersions, we have tested the stability of (activated) ortho-1 and **2** over 24 h in water (pH = 7), 1 h in 1 mol/L NaOH (pH = 14) and 1 h in 1 mol/L HCl (pH = 1) (Section S17, Supporting Information).^{3,31–35} After 24 h in

water, Moroni et al. reported a conversion of the non-interpenetrated [Zn(bpe)] (tetra-1) to an interpenetrated orthorhombic polymorph (i-ortho-1). This interconversion also occurs for (activated) ortho-1. Already after 1 h in 1 mol/L NaOH the conversion to i-ortho-1 appears to be complete and i-ortho-1 is stable against bases. In 1 mol/L HCl, ortho-1 decomposes. The more hydrophilic MOF **2** shows no significant deterioration in water and 1 mol/L NaOH. Similar to ortho-1, also **2** almost completely dissolved in 1 mol/L HCl.

CONCLUSIONS

The porous coordination polymers of the simplest acetylene-augmented bis-pyrazolate ligand, 4,4'-(ethyne-1,2-diyl)bis-pyrazolate (bpe^{2−}) were revisited regarding their structural chemistry, thereby strengthening the foundations for the subsequent structure–property relations. The structure of [Zn(bpe)]·1.2DMF (tetra-1·1.2DMF) was previously reported by Moroni et al. via Rietveld refinement.⁴⁰ Here, we were able to grow single crystals of [Zn(bpe)]·1.8DMF (ortho-1·1.8DMF, HHUD-5) and report the structure of this polymorph from single crystal data. There are three polymorphs established at the moment, namely tetra-1, ortho-1, and i-ortho-1, the latter being the interpenetrated variant of the former. Depending on the disposition of the guest molecules, zinc bis-pyrazolates tend to crystallize either in tetragonal space groups (tetra-1) or orthorhombic space groups (ortho-1).^{39,40,75} Due to an improved activation method, we were able to demonstrate BET surface areas at 2135 m²/g for ortho-1 and 1904 m²/g for tetra-1 instead of the formerly reported 1380 m²/g for tetra-1. An excellent crystallinity of the activated ortho-1 led to an ideal type I(a) isotherm reflecting the exclusively microporous character and the narrow pore size distribution. The second MOF, reported here, [Ni₈(OH)₄(H₂O)₂(bpe)₆]·nSolv (2·nSolv, HHUD-6), was synthesized and structurally analyzed for the first time and is a new representative of the known isoreticular [Ni₈(OH)₄(H₂O)₂L₆] series, which all crystallize in the cubic space group $Fm\bar{3}m$.^{41–43} Compound **2** has a surface area of 1415 m²/g.

The higher affinities to CO₂, CH₄, and H₂ gases, reflected by higher heats of adsorption at near zero coverages, expressed by **2** compared to ortho-1 at low pressure can be explained primarily by the open metal sites of the activated {Ni₈(OH)₄(pz)₁₂}-SBU. At higher pressures above 2 bar for CO₂, 6 bar for CH₄ (at 293 K) above ~0.3 bar at 77 K, and ~0.7 bar at 87 K for H₂, the uptake in ortho-1 surpasses that in **2** due to the higher surface area of ortho-1 compared to **2**. For both MOFs, the CO₂, CH₄, and H₂ uptake exceeded the values for the respective bpb^{2−} analogs, where the ligand contains phenylene instead of an acetylene spacer between the pyrazolate rings. This observation implies a beneficial character of the acetylene over the phenylene moiety regarding specific adsorption characteristics.^{16,39,53,56,86}

For the volatile organic compounds (VOCs), benzene, cyclohexane, and *n*-hexane, ortho-1 showed high uptakes at lower relative pressure regions with close-to-type I isotherms, characteristic of microporous compounds only. For **2**, the adsorption isotherms have at least in part a type II character (added meso- and macroporous features) partially reflecting the textural effects, namely the filling of large interparticle voids. The absence of wide hystereses in both MOFs for VOC adsorption implies the absence of significant $\pi\cdots\pi$ or $\text{C—H}\cdots\pi$ interactions between the adsorbent and the adsorbate.^{12,56,114}

Water vapor sorption experiments showed a clear hydrophobic nature in ortho-1, preventing water molecules from entering the channels. Compound **2** showed higher hydrophilicity because of its bridging hydroxido and aqua ligands in the $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{pz})_{12}]$ -SBU. The much higher experimental water uptakes of MOFs based on the related acetylenedicarboxylate linker reflect the much lower hydrophilicity of the bis-pyrazolate linker, conditioned by the carboxylate/pyrazolate difference. The bis-pyrazolate bpe^{2-} linker is hydrophobic at large as it lacks the carboxylate groups and little hydrophilicity is evident from the $-\text{C}\equiv\text{C}-$ triple bond.

Both MOFs demonstrate permanent porosity, which does not deteriorate upon repeated adsorption measurement and degassing cycles, as well as in aqueous medium at pH = 7 (>24 h) and pH = 14 (>1 h), confirming the expectations regarding the enhanced stabilities of 3d-metal-pyrazolate MOFs in aqueous medium.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.cgd.4c00165>.

Section S1: Used chemicals; Section S2: Ligand analyses; Section S3: Crystal data of $[\text{Zn}(\text{bpe})]\cdot 1.8\text{DMF}$ (ortho-1·1.8DMF, HHUD-5); Section S4: Rietveld refinement for $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]\cdot n\text{Solv}$ (2·nSolv, HHUD-6); Section S5: Powder X-ray diffraction patterns of ortho-1, tetra-1 and **2**; Section S6: IR measurements of ortho-1, tetra-1 and **2**; Section S7: Thermogravimetric analyses of ortho-1 and **2**; Section S8: Porosity analysis for ortho-1 and **2** with the program Mercury. Section S9: Pore size distribution for ortho-1 and **2**; Section S10: Comparison of nitrogen adsorption isotherms for ortho-1 and tetra-1; Section S11: High-pressure sorption experiments for ortho-1 and **2**; Section S12: Comparison of CO_2 , CH_4 , H_2 uptakes for ortho-1, **2** and different isoreticular MOFs from the literature; Section S13: Calculations and fitting for the isosteric heat of adsorption of CO_2 , CH_4 , and H_2 ; Section S14: Calculations and fitting for the IAST selectivity of CO_2 and CH_4 for **2**; Section S15: Calculations and fitting for the IAST selectivity of VOCs for **2**; Section S15: Stability after gas and vapor sorption experiments of ortho-1 and **2**; Section S16: Stability of ortho-1 and **2** toward water, 1 mol/L NaOH and 1 mol/L HCl; and Section S17: References (PDF)

AIFF files (ZIP)

Accession Codes

CCDC 2330470 and 2281888 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: + 44 1223 336033.

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Notes

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Supplementary Information

Metal-organic Azolate Frameworks with an Acetylene-bis-pyrazolate Linker: Assessing the Role of the Triple-bond Spacer in Gas and Vapor Sorption

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Content

- S1 Used chemicals
- S2 Ligand analyses
- S3 Crystal data of [Zn(bpe)]·1.8DMF (ortho-**1**·1.8DMF, HHUD-5)
- S4 Rietveld refinement for [Ni₈(OH)₄(H₂O)₂(bpe)₆]·nSolv (**2**·nSolv, HHUD-6)
- S5 Powder X-ray diffraction patterns of ortho-**1**, tetra-**1** and **2**
- S6 IR measurements of ortho-**1**, tetra-**1** and **2**
- S7 Thermogravimetric analyses of ortho-**1** and **2**
- S8 Porosity analysis for ortho-**1** and **2** with the program Mercury
- S9 Pore size distribution for ortho-**1** and **2**
- S10 Comparison of nitrogen adsorption isotherms for ortho-**1** and tetra-**1**
- S11 High-pressure sorption experiments for ortho-**1** and **2**
- S12 Comparison of CO₂, CH₄, H₂ uptakes for ortho-**1**, **2** and different isorecticular MOFs from the literature
- S13 Calculations and fitting for the isosteric heat of adsorption of CO₂, CH₄ and H₂
- S14 Calculations and fitting for the IAST selectivity of CO₂ and CH₄ for **2**
- S15 Calculations and fitting for the IAST selectivity of VOCs for **2**
- S16 Stability after gas and vapor sorption experiments of ortho-**1** and **2**
- S17 Stability of ortho-**1** and **2** towards water, 1M NaOH and 1M HCl
- S18 References

S1 Used chemicals

Chemical	Supplier	Purity
[Pd(PPh ₃) ₂ Cl ₂]	BLDpharm	98.3%
1,4-Dioxane	Fisher	99.8%
4-(Dimethylamino)pyridine	Aldrich	99%
Benzene	VWR	99.9%
Copper iodide	Alfa Aesar	98%
Cyclohexane	VWR	99.5%
Dichloromethane	Fisher	99.8%
Di- <i>tert</i> -butyl dicarbonate	Apollo Scientific	99%
Ethyl acetate	Fisher	99.8%
HCl (37%)	Sigma-Aldrich	37%
Hydrogen peroxide	Roth	30%
Iodine	Grüssing	99.5%
Methanol	Merck	99.8%
MgSO ₄	VWR	99.4%
<i>N,N</i> -Dimethylformamide	Fisher	99.5%
NaOAc·3H ₂ O	Riedel-de Haën	p. a.
<i>n</i> -Hexane	VWR	97%
Ni(OAc) ₂ ·4H ₂ O	Aldrich	98%
Potassium hydroxide	Supelco	p. a.
Potassium iodide	Merck	p. a.
Pyrazole	Aldrich	98%
Silica gel, 35-70 µm, 60A	Thermo scientific	Ultra pure
Sodium hydroxide	Chemsolute	99.5%
Tetrabutylammonium fluoride hydrate	Aldrich	98%
Tetrahydrofuran	Merck	99.9%
Triethylamine	Fisher	99.5%
Trifluoroacetic acid	Acros Organics	99.5%
Trimethylsilylacetylene	BLDpharm	98.94%
Zn(ClO ₄)·6H ₂ O	Johnson Matthey Alfa Products	98.9%
Zn(NO ₃) ₂ ·4H ₂ O	Lab inventory	—

S2 Ligand analyses

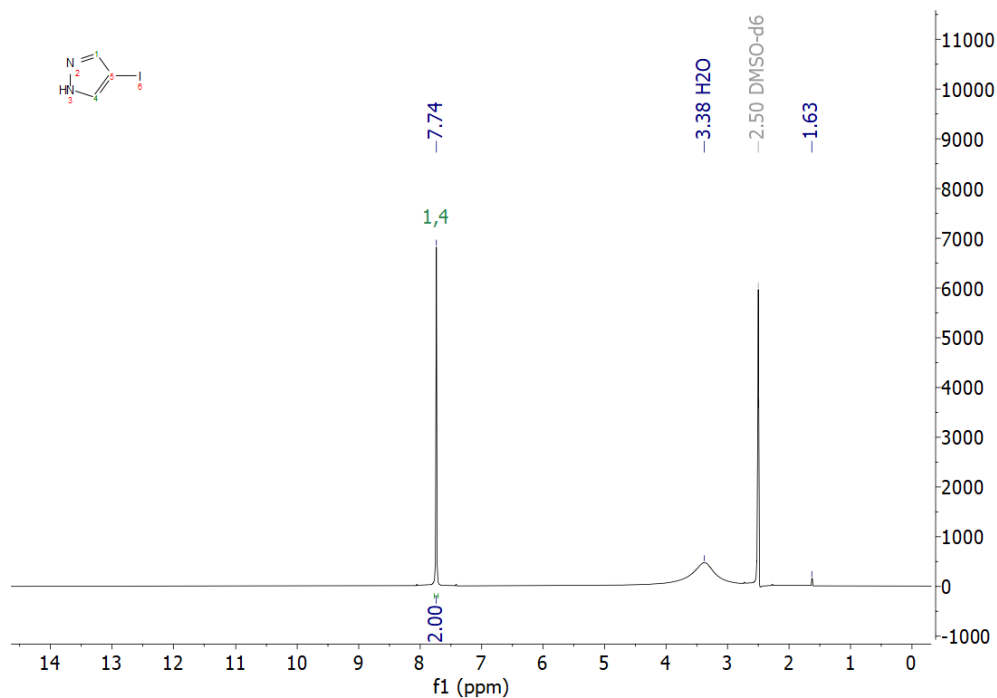


Figure S1. ¹H-NMR spectrum (300 MHz, DMSO-d₆) of 4-iodo-1H-pyrazole (II).

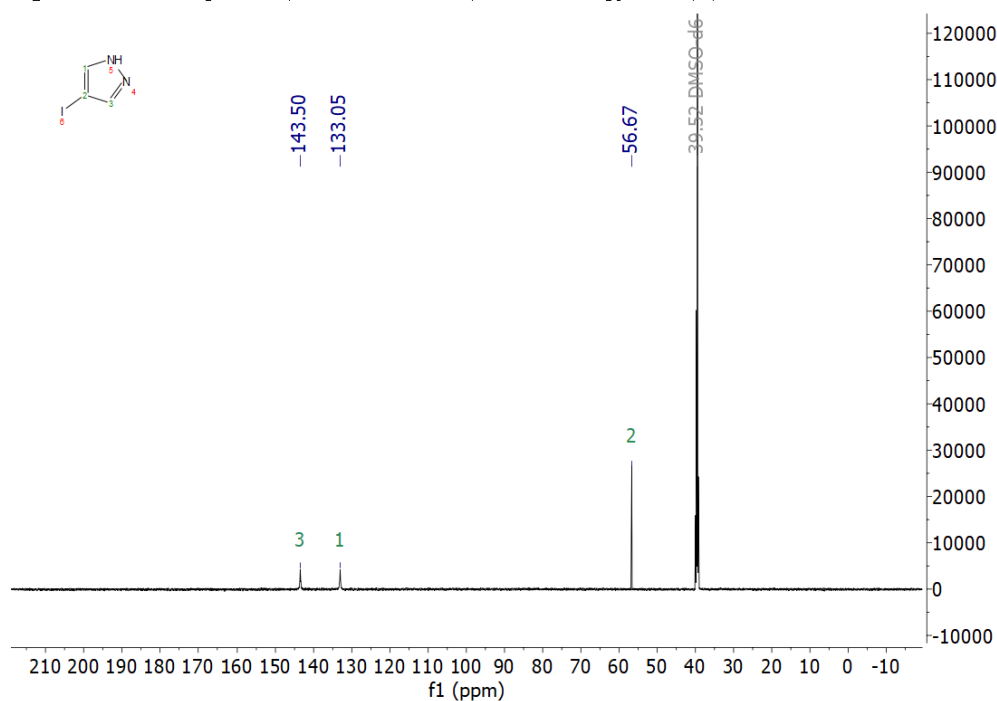


Figure S2. ¹³C{¹H}-NMR spectrum (150 MHz, DMSO-d₆) of 4-iodo-1H-pyrazole (II). The chemical shifts correspond to the values reported in the literature.^{1,2}

S3

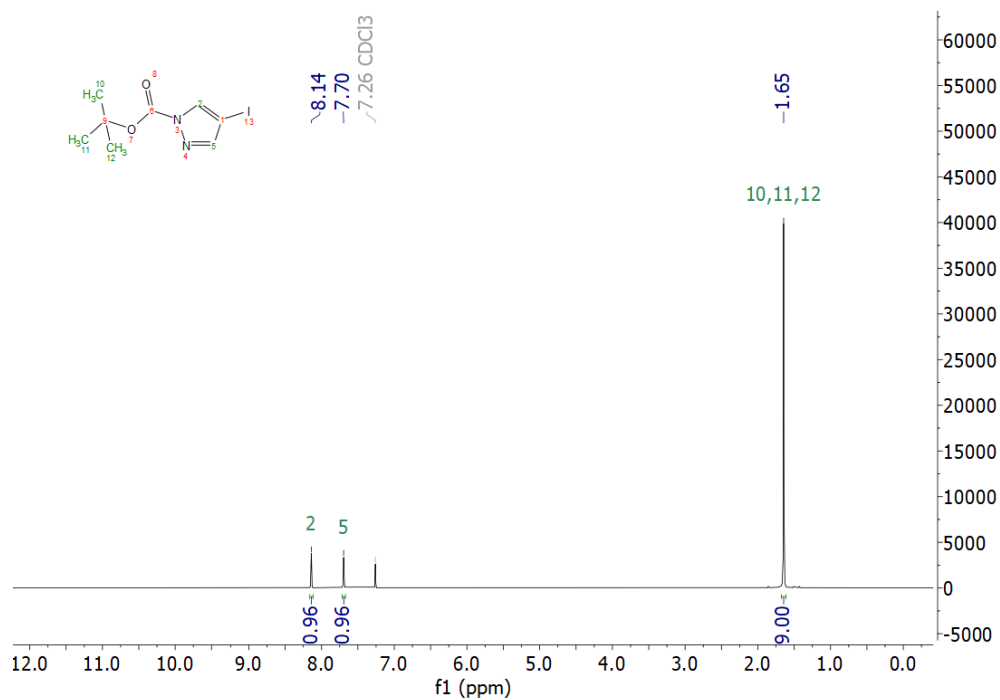


Figure S3. ¹H-NMR spectrum (300 MHz, CDCl₃) of 1-boc-4-iodopyrazole (**12**).

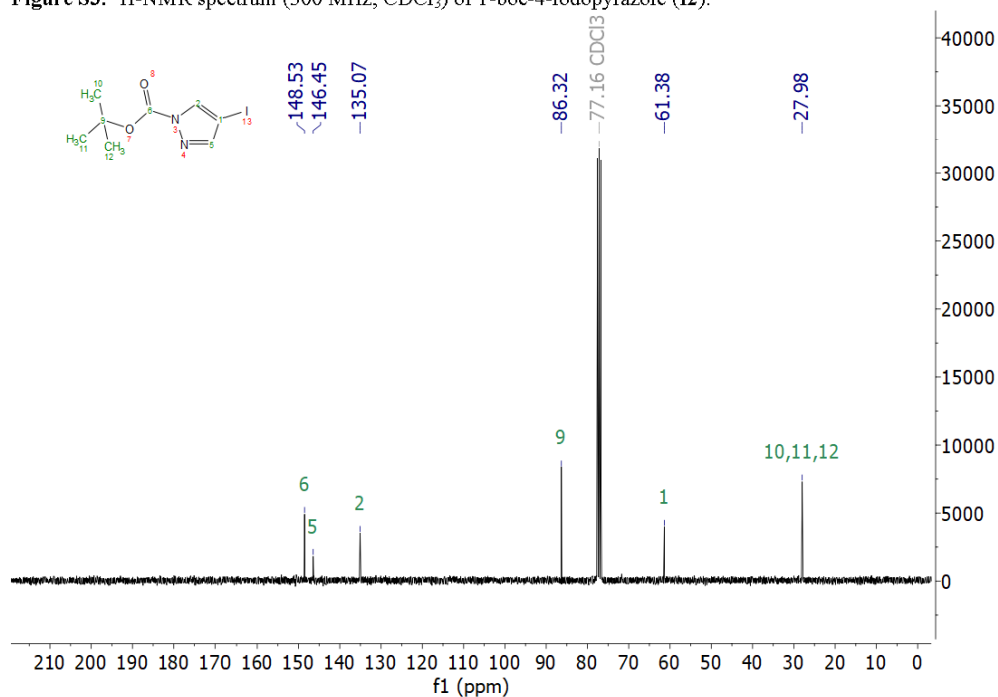


Figure S4. ¹³C(¹H)-NMR spectrum (75 MHz, CDCl₃) of 1-boc-4-iodopyrazole (**12**).

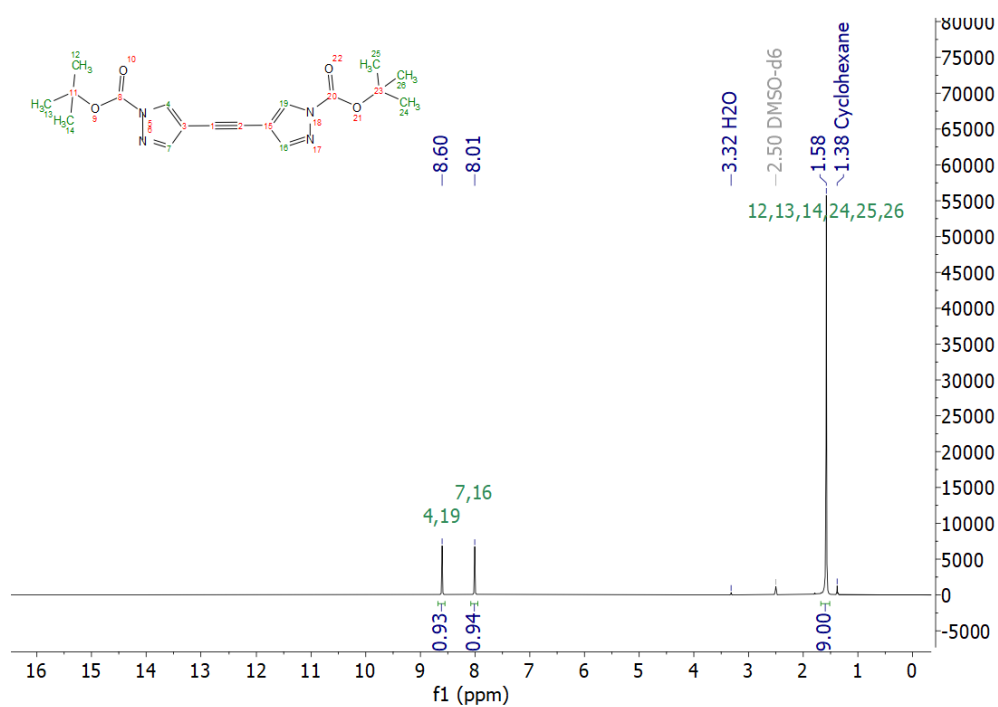


Figure S5. ¹H-NMR spectrum (300 MHz, DMSO-d₆) of 1,2-bis(1-boc-pyrazol-4-yl)ethyne (Boc₂bpe).

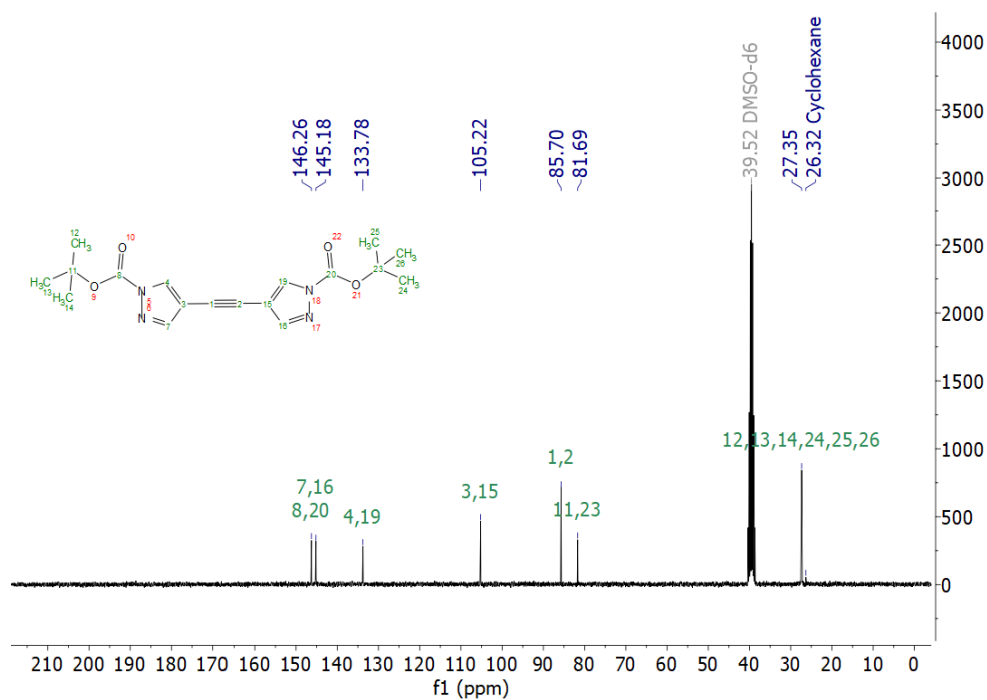


Figure S6. ¹³C{¹H}-NMR spectrum (75 MHz, DMSO-d₆) of 1,2-bis(1-boc-pyrazol-4-yl)ethyne (Boc₂bpe).

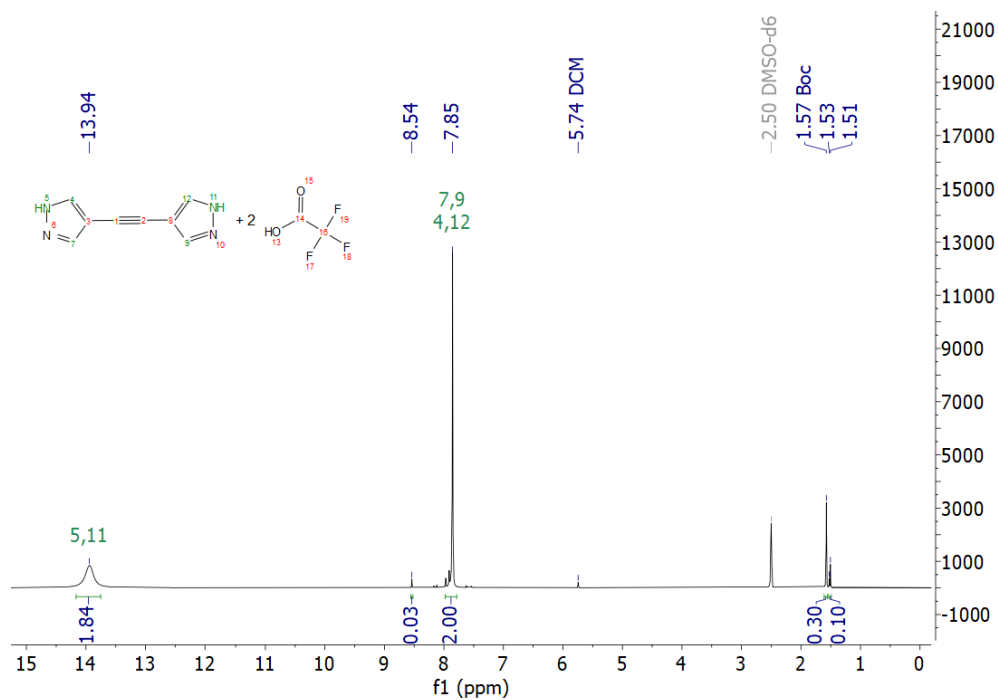


Figure S7. ¹H-NMR spectrum (300 MHz, DMSO-d₆) of 4,4'-(ethyne-1,2-diyl)bis(1*H*-pyrazol-2-ium)-bis(trifluoroacetate) ([H₄bpe](TFA)₂).

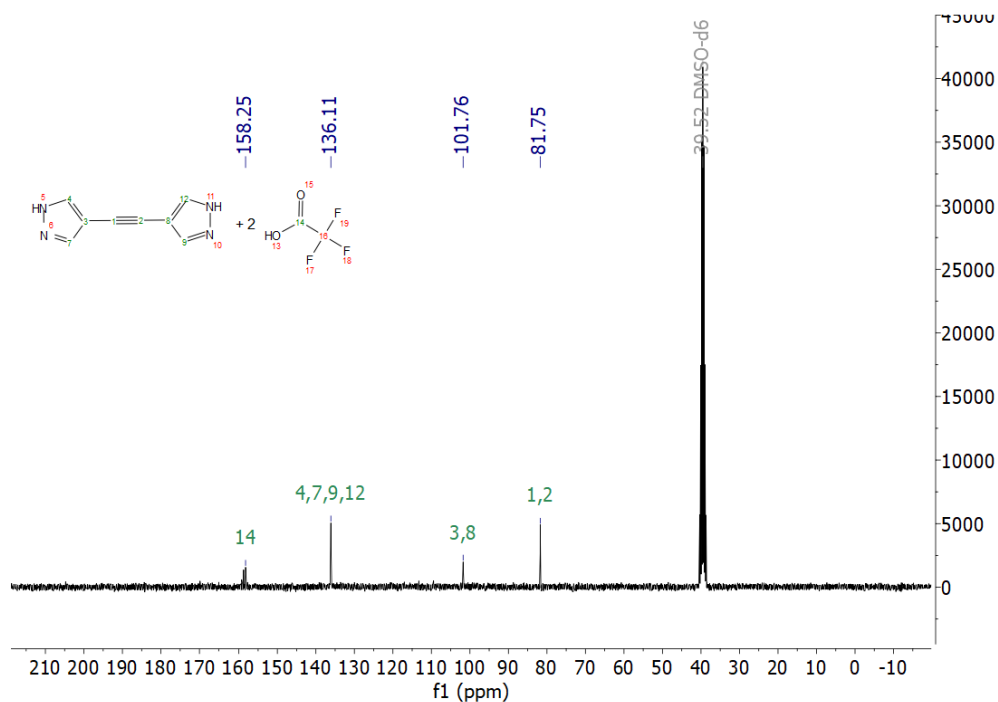


Figure S8. ¹³C{¹H}-NMR spectrum (75 MHz, DMSO-d₆) of 4,4'-(ethyne-1,2-diyl)bis(1*H*-pyrazol-2-ium)-bis(trifluoroacetate) ([H₄bpe](TFA)₂).

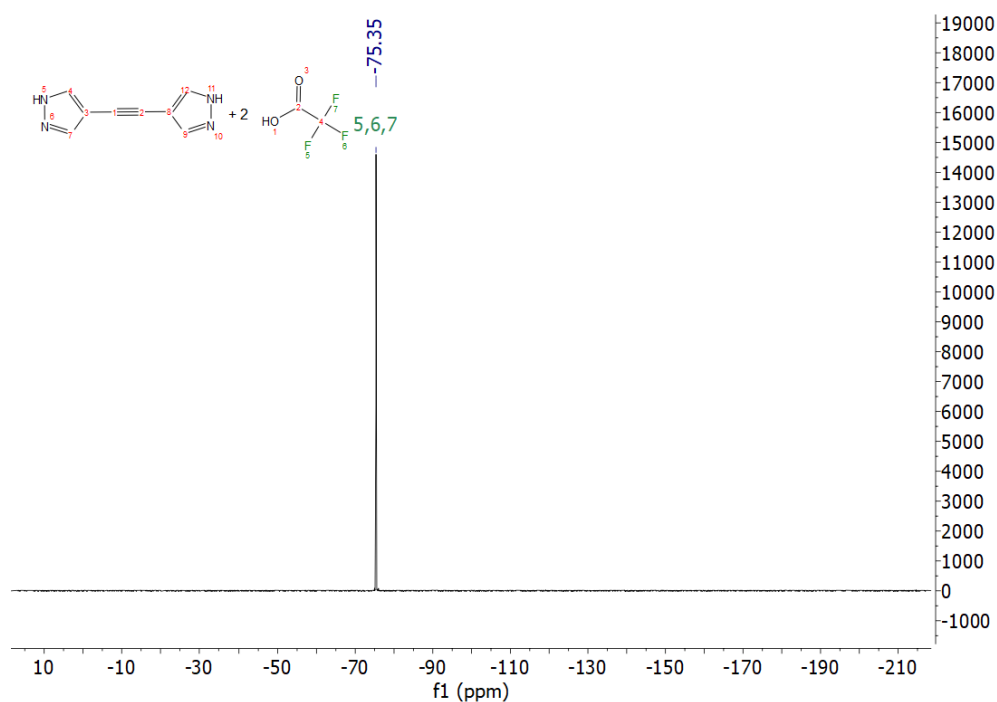


Figure S9. ^{19}F $\{^1\text{H}\}$ -NMR spectrum (282.4 MHz, DMSO-d_6) of 4,4'-(ethyne-1,2-diyl)bis(1*H*-pyrazol-2-ium)-bis(trifluoroacetate) ($[\text{H}_4\text{bpe}](\text{TFA})_2$).

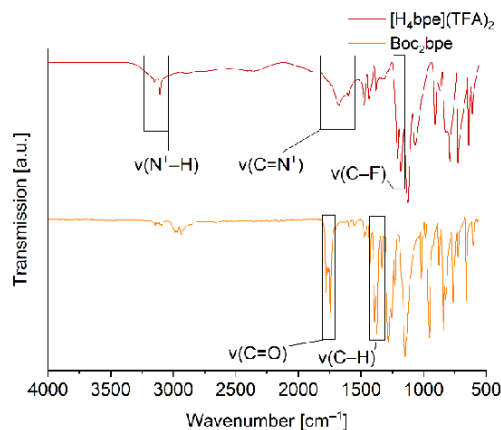


Figure S10. IR spectra (ATR) of Boc_2bpe and $[\text{H}_4\text{bpe}](\text{TFA})_2$. In the IR spectrum of Boc_2bpe characteristic bands of the boc-group are visible ($\nu(\text{C}=\text{O})$: 1778 cm^{-1} , $\nu(\text{C}-\text{H})$: 1372 cm^{-1}). In the upper spectrum of $[\text{H}_4\text{bpe}](\text{TFA})_2$, the salt character becomes clear through a $\nu(\text{N}^+-\text{H})$ band at 3106 cm^{-1} and a $\nu(\text{C}=\text{N}^+)$ band at 1678 cm^{-1} . At 1208 cm^{-1} the presence of the trifluoroacetate is confirmed through $\nu(\text{C}-\text{F})$ bands.

S3 Crystal data of [Zn(bpe)] (ortho-1·1.8DMF, HHUD-5)

Table S1. Crystal data for [Zn(bpe)] (ortho-1·1.8DMF).

CCDC Depositon no.	2330470
Empirical formula	$C_8H_4N_4Zn \cdot C_3H_7NO \cdot C_{2.34}H_7N_{0.891}O_{0.891}$
<i>M</i> [g/mol]	356.67
<i>T</i> [K]	120
Crystal system	Orthorhombic
Space group	<i>Fddd</i>
<i>a</i> [Å]	34.5706(5)
<i>b</i> [Å]	30.3896(4)
<i>c</i> [Å]	14.2844(2)
<i>V</i> [Å ³]	15007.0(4)
<i>Z</i>	32
ρ_{calc} [g/cm ³]	1.263
μ [mm ⁻¹]	1.94
<i>F</i> (000)	5903
Crystal size [mm ³]	0.12 × 0.08 × 0.07
λ (Cu <i>K</i> α) [Å]	1.54184
No. of unique reflections	3361
No. of reflections	26979
<i>R</i> _{int}	0.041
<i>R</i> [<i>F</i> ² > 2 <i>s</i> (<i>F</i> ²)]	0.075
<i>wR</i> (<i>F</i> ²)	0.188

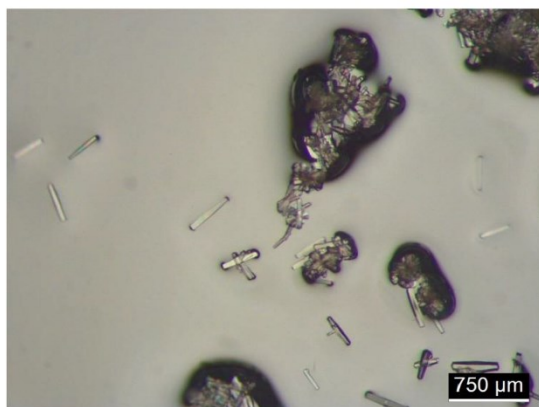


Figure S11. Image of crystals of [Zn(bpe)]·1.8DMF.

Table S2. Selected bond lengths and angles for [Zn(bpe)]·1.8DMF (ortho-**1**·1.8DMF).

Bond lengths [Å]			
Zn1—N1 ⁱ	1.958(5)	C1—C3	1.367(10)
Zn1—N1	1.958(5)	C2—C3	1.437(9)
Zn1—N4 ⁱⁱ	1.999(6)	C3—C4	1.430(10)
Zn1—N4 ⁱⁱⁱ	1.999(6)	C4—C5	1.187(11)
Zn2—N2 ^{iv}	1.950(5)	C5—C6	1.433(10)
Zn2—N2	1.950(5)	C7—C6	1.446(10)
Zn2—N3 ^v	1.987(5)	C8—C6	1.325(11)
Zn2—N3 ⁱⁱ	1.987(5)		
Bond angles [°]			
N1 ⁱ —Zn1—N1	110.8(3)	N2 ^{iv} —Zn2—N2	114.0(3)
N1—Zn1—N4 ⁱⁱ	108.6(2)	N2—Zn2—N3 ⁱⁱ	110.1(2)
N1 ⁱ —Zn1—N4 ⁱⁱ	112.3(2)	N2 ^{iv} —Zn2—N3 ⁱⁱ	108.2(2)
N1 ⁱ —Zn1—N4 ⁱⁱⁱ	108.6(2)	N2 ^{iv} —Zn2—N3 ^v	110.1(2)
N1—Zn1—N4 ⁱⁱⁱ	112.3(2)	N2—Zn2—N3 ^v	108.2(2)
N4 ⁱⁱⁱ —Zn1—N4 ⁱⁱ	104.0(3)	N3 ^v —Zn2—N3 ⁱⁱ	105.9(3)
Symmetry transformations: i = x, -y+3/4, -z+7/4; ii = x+1/4, y-1/4, -z+3/2; iii = x+1/4, -y+1, z+1/4; iv = -x+5/4, y, -z+5/4; v = -x+1, y-1/4, z-1/4.			

S4 Rietveld refinement for $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6] \cdot n\text{Solv}$ ($2 \cdot n\text{Solv}$, HHUD-6)

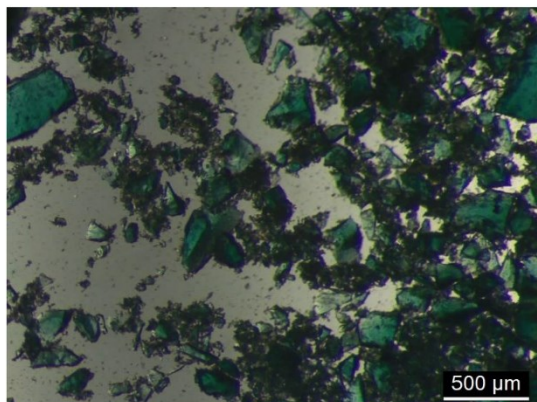


Figure S12. Image of crystals of $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6] \cdot n\text{Solv}$ ($2 \cdot n\text{Solv}$). Several attempts to collect single crystal data on the diffractometer failed as the crystals were not single crystals. No diffraction spots could be seen, only circular diffraction patterns were observed.

The structural model for $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6] \cdot n\text{Solv}$ ($2 \cdot n\text{Solv}$) was constructed in accordance with the known analog based on the 1,4-bis(1*H*-pyrazol-4-yl)benzene linker.³ The refinements were performed using the Jana 2006 software.⁴ The peak shapes were fitted by the pseudo-Voigt function (four parameters were refined during all refinement cycles except the very last, to ensure convergence). Due to the not easily correctible distortions of the first two strongest peaks, the latter were excluded from the refinement (the exclusion of the two peaks in the $2\theta = 10\text{--}70^\circ$ range is not critical for refinement, but improves the indices due to correction of the strong asymmetry; see Figure S13).

The experimental PXRD data were collected using a Rigaku MiniFlex (600 W, 40 kV, 15 mA) with Cu X-ray source, with assumed $K\alpha_1$ ($\lambda = 1.54051$) to $K\alpha_2$ ($\lambda = 1.54433$) ratio of 2.00, in the angular range of $2\theta = 10\text{--}72^\circ$. The peak asymmetry was corrected using Simpson's model with one parameter refined (111 and 002 reflexes were excluded due to strong asymmetry, which was not expedient to correct). Focusing correction for Bragg-Brentano geometry was applied and the sample shift was refined freely. The background was defined manually and fixed during the refinement.

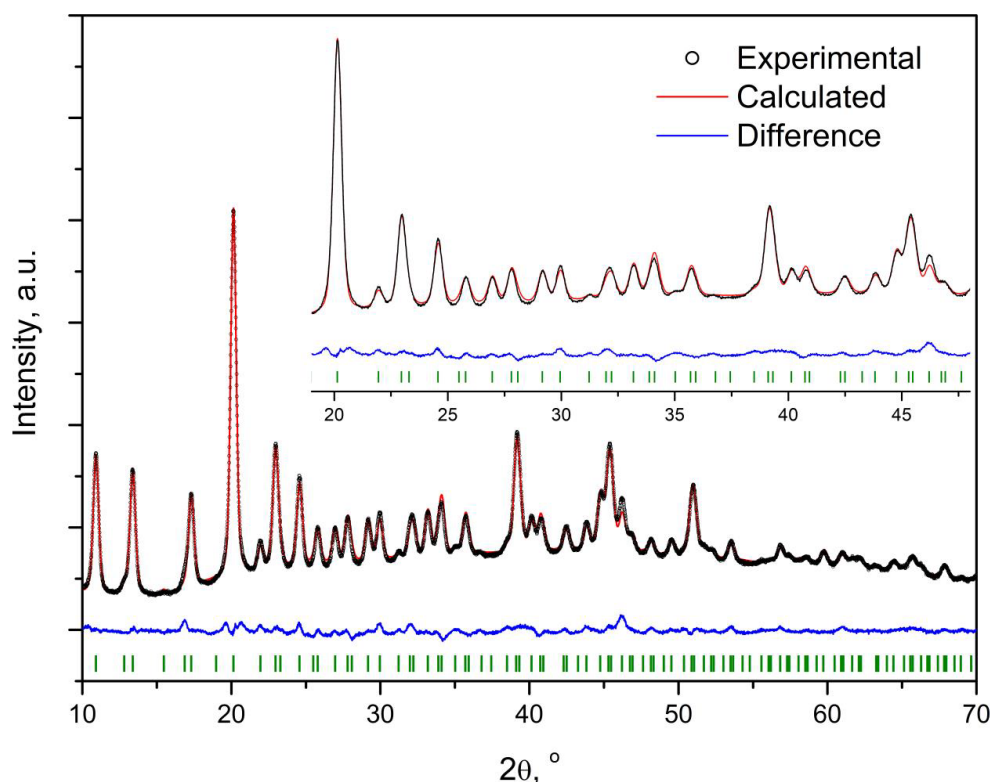


Figure S13. Rietveld refinement of the structure of $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6] \cdot n\text{Solv}$ ($2 \cdot n\text{Solv}$) (the bars represent the calculated values of the peak positions).

The Rietveld refinement (Figure S13, Table S3) could be successfully concluded for the whole data set, albeit a sufficiently good fit (Bragg $R = 4.8\%$ and $\text{GoF} = 2.7$) was only reached, when the first two peaks were excluded, and the atoms belonging to the guest molecules, located in the voids of the framework are explicitly modeled using the Fourier difference map (carbon atoms were used for this purpose).

The atomic displacement parameters (ADPs) for all the atoms of the framework and all the atoms belonging to the guests were fixed to be equal to each other within the given groups. The occupancy factors of the guest atoms were refined freely in most cases (except for a few cases, where symmetry considerations were taken into account). Unlike for the framework atoms with typical ADPs (0.08), the guest atoms were refined with very large ADP values (~ 0.5). The positions of the guests (but not the framework atoms) are also strongly dependent on fine differences in the choice of the refined data range and parameters. Hence, the location of the guest atoms with the large ADP parameters could be viewed as a simple analog to the SQUEEZE procedure employed for single crystal data: the guest atoms modeled diffusely

covers the areas with the highest probability of the solvent molecule localization. The precision of the guest atom placement is, evidently, very low.

Table S3. Crystal data and Rietveld refinement for $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6] \cdot n\text{Solv}$ (**2** · nSolv).

CCDC Deposit no.	2281888
Empirical formula	$\text{C}_{48}\text{H}_{32}\text{N}_{24}\text{Ni}_8\text{O}_6 \cdot [\text{C}_{50}]^{\text{a)}$
M_r [g/mol]	2111.9 ^{a)}
T [K]	293
Diffractionmeter	Rigaku MiniFlex
Wavelength [Å] ^{a)}	Cu $K\alpha_1$, Cu $K\alpha_2$; 1.54051, 1.54433; $I(\text{Cu } K\alpha_1)/I(\text{Cu } K\alpha_2) = 2.00$
Crystal system	Cubic
Space group	$Fm\bar{3}m$ (ITC No.225)
a [Å]	22.8943(16)
V [Å ³]	12000.0(14)
Z	4
Calc. density [g/cm ³]	1.169
μ [mm ⁻¹]	1.765
$F(000)$	4226
θ range (refinement) [°]	10.01 to 69.99°
θ step [°]	0.01
Parameters / restraints/constraints	18 / 1 / 23
R_p , wR_p	0.0096, 0.0127
$R[F > 2\sigma(F)]$, $wR^{\text{b)}$	0.0480, 0.0613
R , wR (all data) ^{b)}	0.0492, 0.0614
Largest diff. peak and hole, eÅ ⁻³	0.20, -0.18
Goodness of fit, χ^2 ^{c)}	2.72

^{a)} The hydrogen atoms of the OH and H₂O ligands were not refined (*i.e.* there are 8 more hydrogen atoms given in the empirical formula than it was refined). The atoms in square brackets belong to the refined guest molecules, refined as carbon atoms with variable occupancies, but ADP fixed to be equal. The molecular weight of the $\text{C}_{48}\text{H}_{32}\text{N}_{24}\text{Ni}_8\text{O}_6$ framework is 1510.49.

^{b)} Based on extracted structure factors (synonyms: R_{Bragg} , R_F).

^{c)} The goodness of fit or χ^2 in PXRD refinement is $\chi^2 = \frac{\sum_{i=1}^n w_i (Y_i^{\text{obs}} - Y_i^{\text{calc}})^2}{n - p}$, where n is the total number of measured data points; p is the number of free least squares parameters; Y_i^{obs} is the observed intensity of the i -th data point; Y_i^{calc} is the calculated intensity of the i -th data point; w_i is the weight of the i -th data point, which is usually taken as $w_i = 1/\sigma^2 = 1/Y_i^{\text{obs}}$.⁵

Table S4. The structure of **2**·nSolv, referred to in a form of a SHELX res-file (in the section featuring the atoms, columns 3-5 correspond to fractional x,y,z coordinates, while columns 4 and 5 to occupancies and U_{iso} -s respectively.)

```
CELL 1.5478 22.8943 22.8943 22.8943 90.0000 90.0000 90.0000
ZERR 0.0000 0.0016 0.0016 0.0016 0.0000 0.0000 0.0000
LATT 4
SYMM -y, x, z
SYMM -x, -y, z
SYMM y, -x, z
SYMM x, -z, y
SYMM x, -y, -z
SYMM x, z, -y
SYMM z, y, -x
SYMM -x, y, -z
SYMM -z, y, x
SYMM z, x, y
SYMM y, z, x
SYMM -y, -z, x
SYMM z, -x, -y
SYMM -y, z, -x
SYMM -z, -x, y
SYMM -z, x, -y
SYMM y, -z, -x
SYMM y, x, -z
SYMM -y, -x, -z
SYMM -x, z, y
SYMM -x, -z, -y
SYMM z, -y, x
SYMM -z, -y, -x
SFAC Ni O N C H
Ni1 1 0.43551 0.43551 -0.06448 0.1667 0.08910
O1 2 0.50000 0.40080 0.00000 0.1250 0.08910
N1 3 0.37806 0.37806 -0.02751 0.5000 0.08910
C1 4 0.33816 0.33816 -0.04585 0.5000 0.08910
C2 4 0.31331 0.31331 0.00000 0.2500 0.08910
C3 4 0.26859 0.26859 0.00000 0.2500 0.08910
H1 5 0.32881 0.32881 -0.08840 0.5000 0.10690
G1 4 0.50000 0.21950 0.00000 0.1250 0.51800
G2 4 0.50000 0.00000 0.00000 0.0208 0.51800
G3 4 0.25000 0.25000 -0.25000 0.0042 0.51800
G4 4 0.37030 0.18180 -0.12970 0.4820 0.51800
G5 4 0.50000 0.15630 0.00000 0.1250 0.51800
G6 4 0.31060 0.23000 -0.18940 0.2980 0.51800
```

Table S5. Selected bond lengths and bond angles of $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6] \cdot \text{nSolv}$ (**2**·nSolv).

Bond lengths [Å]			
Ni1—N1	2.044(9)	C1—C2	1.323(1)
Ni1—N1 ⁱ	2.044(9)	C2—C3	1.448(1)
Ni1—N1 ⁱⁱ	2.044(9)	C3—C3 ^{iv}	1.204(1)
N1—N1 ⁱⁱⁱ	1.260(2)		
Bond angles [°]			
N1—Ni1—N1 ⁱ	96.83(4)	N1 ⁱ —Ni1—N1 ⁱⁱ	96.83(4)
N1—Ni1—N1 ⁱⁱ	96.83(4)	Ni1—N1—N1 ⁱⁱⁱ	114.47(3)
C2—C3—C3 ^{iv}	180.0(5)		
Symmetry transformations: i = z+1/2, x, y-1/2; ii = y, z+1/2, x-1/2; iii = y, x, -z; iv = -x+1/2, -y+1/2, z.			

S5 Powder X-ray diffraction patterns of ortho-1, tetra-1 and 2

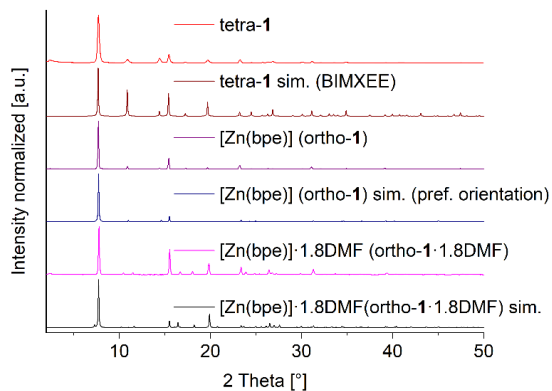


Figure S14. Comparison of simulated and experimental powder X-ray diffraction pattern of ortho-1·1.8DMF, activated ortho-1 and tetra-1, the latter synthesized according to Moroni *et al.* (Ref. code: BIMXEE).⁶ The simulated pattern for activated ortho-1 was derived by omitting the DMF atom positions in ortho-1·1.8DMF and assuming a preferred orientation: $h = 2$, $k = 2$, $l = 1$, March-Dollase = 7).

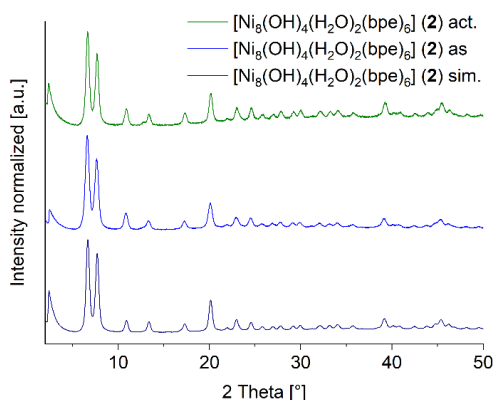


Figure S15. Comparison of the simulated powder X-ray pattern of $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ (2) with the experimental pattern before and after activation. The increasing baseline before 5° is attributed to the PXRD device measurement method with the low-background silicon holder.

S6 IR measurements of ortho-1, tetra-1 and 2

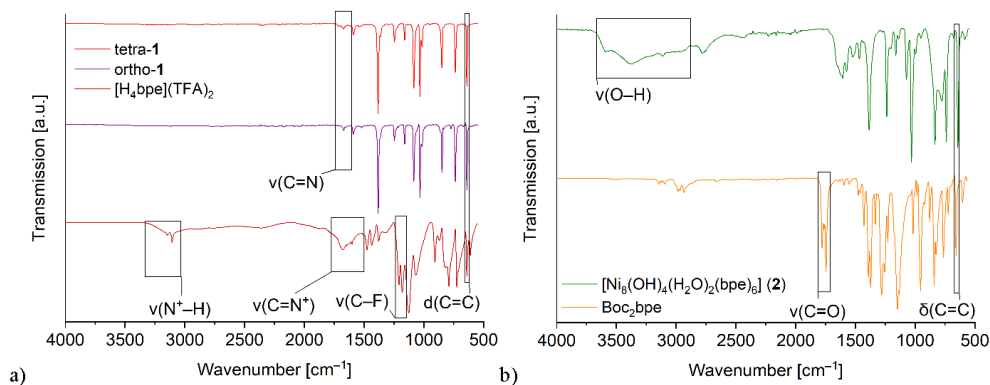


Figure S16. a) IR spectra (ATR) of $[\text{H}_4\text{bpe}](\text{TFA})_2$, activated ortho-1 and tetra-1. b) IR spectra (ATR) of Boc_2bpe and activated $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ (**2**).

The spectrum of the linker precursor salt $[\text{H}_4\text{bpe}](\text{TFA})_2$ (Figure S16a) shows bands for $\nu(\text{N}^+-\text{H})$ at 3106 cm^{-1} , $\nu(\text{C}=\text{N}^+)$ at 1678 cm^{-1} and $\nu(\text{C}-\text{F})$ at 1208 cm^{-1} . The $\nu(\text{N}^+-\text{H})$ and $\nu(\text{C}-\text{F})$ bands cannot be found in the spectra of ortho-1 and tetra-1. Both MOFs feature a $\nu(\text{C}=\text{N})$ band at around 1670 cm^{-1} . In all three IRs a $\delta(\text{C}=\text{C})$ band at around 639 cm^{-1} is visible.

In the IR spectrum (ATR) of the linker precursor Boc_2bpe (Figure S16b) the boc-group is discernable through the $\nu(\text{C}=\text{O})$ band at 1778 cm^{-1} . This band cannot be seen in the spectrum of **2** indicating a complete removal of the boc-group. In **2**, a broad characteristic $\nu(\text{O}-\text{H})$ band is present due to hydrogen bonding involving the H_2O , OH^- ligands of the coordination cluster and water guest molecules from adsorbed atmospheric moisture during the sample preparation.

S7 Thermogravimetric analyses of ortho-1 and 2

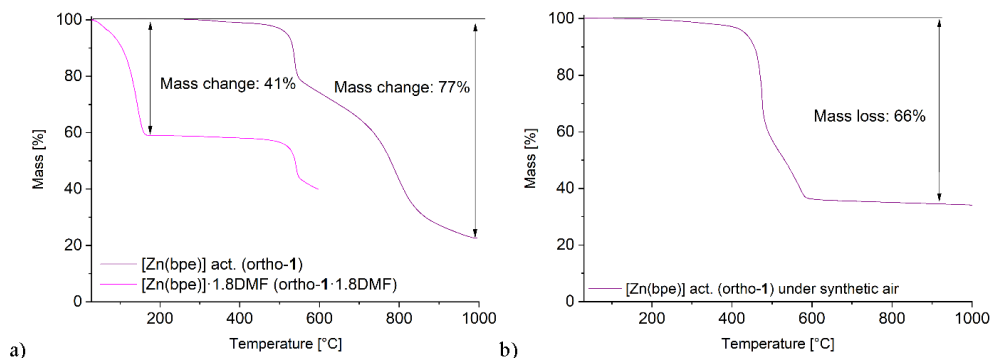


Figure S16.

- a) Thermogravimetric analysis of [Zn(bpe)]·1.8DMF (ortho-1·1.8DMF) and activated [Zn(bpe)] (ortho-1) under nitrogen atmosphere (heating rate 5 K min⁻¹). For [Zn(bpe)]·1.8DMF the loss of DMF with an experimental mass change of 41% is close theoretical weight loss of 37.3% for 1.8 DMF molecules. The theoretical weight loss of the bpe²⁻ in the activated sample [Zn(bpe)] would be 70.5%, the theoretical residue of Zn 29.5%. The higher mass loss of 77% (less Zn residue) could be ascribed to the beginning evaporation of Zn (boiling point 907 °C) below 1000 °C.⁷
- b) Thermogravimetric analysis of activated [Zn(bpe)] (ortho-1) under synthetic air atmosphere (heating rate 5 K min⁻¹). Compared to the nitrogen atmosphere, ortho-1 decomposes around 20 °C earlier (480 °C instead of 500 °C). The mass loss of 66% or residual mass of 34% correlates with the decomposition of the linker (theor. 70.5%), compensated by the oxidation of Zn to ZnO (theor. 36.7 wt%) as a residue.

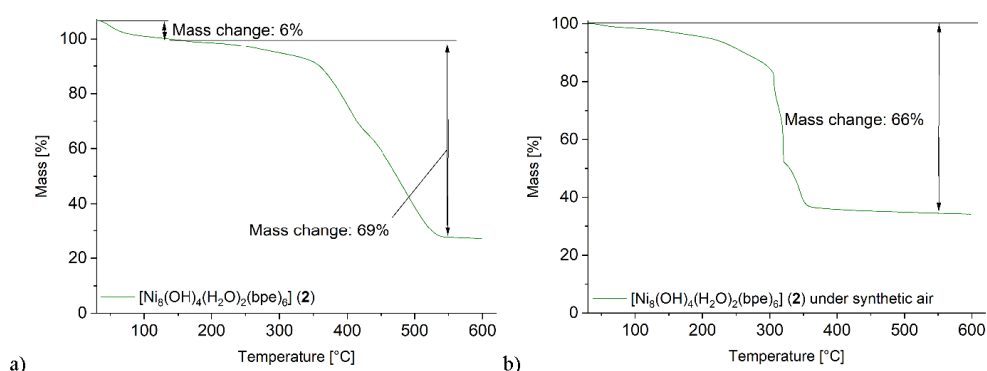


Figure S17.

- a) Thermogravimetric analysis of activated [Ni₈(OH)₄(H₂O)₂(bpe)₆] (2) under nitrogen atmosphere (heating rate 5 K min⁻¹). The theoretical mass loss of the ligands [(OH)₄(H₂O)₂(bpe)₆] would be 68.9 wt% leaving a theoretical residual mass of 31.1 wt% of nickel, which is in good agreement with the experimental values. The mass loss of 6 wt% in the beginning of the TGA is ascribed to adsorbed moisture from the atmosphere during TGA preparation, which could not be done under inert conditions.
- b) Thermogravimetric analysis of activated [Ni₈(OH)₄(H₂O)₂(bpe)₆] (2) under synthetic air atmosphere (heating rate 5 K min⁻¹). Compared to the nitrogen atmosphere, 2 decomposes around 80 °C earlier (250 °C instead of 330 °C). The mass loss of 66 wt% correlates with the decomposition of the ligands [(OH)₄(H₂O)₂(bpe)₆] (theor. 68.9 wt%) leaving a mixture of Ni and NiO as a residue. Neat Ni would result in theoretical residue of 31.1 wt%; NiO in a theoretical residual mass of 39.6 wt%, (based on the starting compound [Ni₈(OH)₄(H₂O)₂(bpe)₆].

S8 Porosity analysis for ortho-1 and 2 with the program Mercury

The porosity analysis for both compounds was performed with the program Mercury 2023.3.0.⁸

Table S6. Porosity analysis for [Zn(bpe)] (ortho-1).

Parameter	Result
System Volume [Å ³]	15007
System Mass [g/mol]	7089.696
System Density [g/cm ³]	0.784
Total surface area [Å ²]	2343
Total surface area per volume [m ² /cm ³]	1561
Total surface area per mass [m ² /g]	1990
Network-accessible surface area [Å ²]	2343
Network-accessible surface area per volume [m ² /cm ³]	1561
Network-accessible surface area per mass [m²/g]	1990
Total helium volume [Å ³]	10118
Total helium volume [cm ³ /g]	0.859
Total geometric volume [Å ³]	10511
Total geometric volume [cm ³ /g]	0.893
Network-accessible helium volume [Å ³]	10118
Network-accessible helium volume [cm ³ /g]	0.859
Network-accessible geometric volume [Å ³]	10510
Network-accessible geometric volume [cm ³ /g]	0.893
Pore limiting diameter [Å]	7.65
Maximum pore diameter [Å]	8.29
Number of percolated dimensions	1
Compound	[Zn(bpe)] (ortho-1)
Empirical formula	C ₈ H ₄ N ₂ Zn
<i>M</i> [g/mol]	221.52
<i>V</i> [Å ³]	15007.6(3)
<i>Z</i>	32
Mercury 'Void' calculation	using contact surface ^b
(probe radius 1.8 Å, grid spacing 0.2 Å)	
void volume, <i>V</i> _{unit cell} (Å ³)	9264
(% of unit cell volume)	(62)
- specific (cm ³ g ⁻¹) ^a	0.787

^a specific pore volume calculated according to $(V_{\text{unit cell}} \times N_A) / (Z \times M_{\text{asym unit}})$; N_A = Avogadro's constant, $6.022 \cdot 10^{23} \text{ mol}^{-1}$, Z = number of asymmetric formula units, $M_{\text{asym unit}}$ = molecular weight of asymmetric formula unit (in g/mol). As a help to reproduce the specific number the values for Z and $M_{\text{asym unit}}$ from the X-ray structures are included.

^b In Mercury voids can be calculated using two different methods:

- Calculate voids using Solvent Accessible Surface gives the volume which can be occupied by the center of a probe of a given radius.
- Calculate voids using Contact Surface maps the volume that can be occupied by the full probe (including its radius) and thus gives a better estimate of the volume that could be filled by solvent or guest molecules.
- A full description of these two different surfaces and the ways in which they can be used is given in: L. J. Barbour, *Chem. Commun.* **2006**, 1163–1168.⁹

Table S7. Porosity analysis for $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ (**2**).

Parameter	Result
System Volume [$\text{\AA}^3$]	12000
System Mass [g/mol]	6009.630
System Density [g/cm ³]	0.832
Total surface area [$\text{\AA}^2$]	2296
Total surface area per volume [m^2/cm^3]	1914
Total surface area per mass [m^2/g]	2301
Network-accessible surface area [$\text{\AA}^2$]	2296
Network-accessible surface area per volume [m^2/cm^3]	1914
Network-accessible surface area per mass [m^2/g]	2301
Total helium volume [$\text{\AA}^3$]	8661
Total helium volume [cm^3/g]	0.868
Total geometric volume [$\text{\AA}^3$]	8255
Total geometric volume [cm^3/g]	0.827
Network-accessible helium volume [$\text{\AA}^3$]	8661
Network-accessible helium volume [cm^3/g]	0.868
Network-accessible geometric volume [$\text{\AA}^3$]	8224
Network-accessible geometric volume [cm^3/g]	0.824
Pore limiting diameter [$\text{\AA}$]	5.08
Maximum pore diameter [$\text{\AA}$]	12.80
Number of percolated dimensions	3
Compound	$[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ (2)
Empirical formula	$\text{C}_{48}\text{H}_{32}\text{N}_{24}\text{Ni}_8\text{O}_6$
M [g/mol]	1510.49
V [$\text{\AA}^3$]	12000.0(14)
Z	4
Mercury 'Void' calculation	using contact surface ^b
(probe radius 1.8 $\text{\AA}$, grid spacing 0.2 $\text{\AA}$)	
void volume, $V_{\text{unit cell}}$ ($\text{\AA}^3$)	7819
(% of unit cell volume)	(63)
- specific ($\text{cm}^3 \text{ g}^{-1}$) ^a	0.779

^a specific pore volume calculated according to $(V_{\text{unit cell}} \times N_A)/(Z \times M_{\text{asym unit}})$; N_A = Avogadro's constant, $6.022 \times 10^{23} \text{ mol}^{-1}$, Z = number of asymmetric formula units, $M_{\text{asym unit}}$ = molecular weight of asymmetric formula unit (in g/mol). As a help to reproduce the specific number the values for Z and $M_{\text{asym unit}}$ from the X-ray structures are included.

^b In Mercury voids can be calculated using two different methods:

- Calculate voids using Solvent Accessible Surface gives the volume which can be occupied by the center of a probe of a given radius.
- Calculate voids using Contact Surface maps the volume that can be occupied by the full probe (including its radius) and thus gives a better estimate of the volume that could be filled by solvent or guest molecules.
- A full description of these two different surfaces and the ways in which they can be used is given in: L. J. Barbour, *Chem. Commun.* **2006**, 1163–1168.⁹

S9 Pore size distribution analysis for ortho-1 and 2

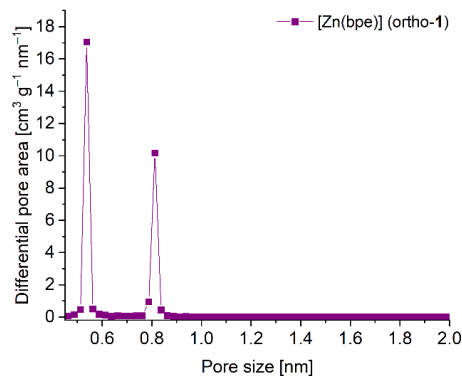


Figure S18. Pore size distribution analysis of ortho-1 performed using Saito-Foley (SF) method giving micropore sizes of 5.5 Å and 8 Å.

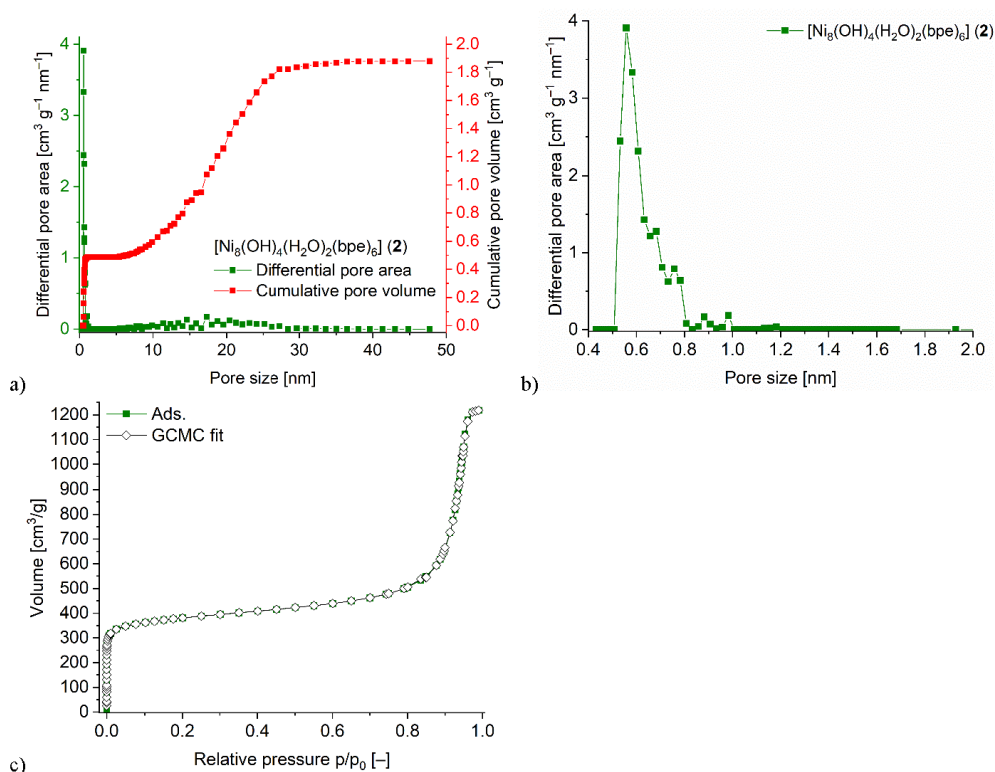


Figure S20. a) Pore size distribution analysis of 2 performed using GCMC calculations over the whole range of 0.4 to 50 nm, giving micropore sizes in the range between 0.6 to 0.8 nm (6 Å to 8 Å). The red curve gives the cumulative pore volume. A contribution of mesopores with broader size distribution is present between ~10 nm and ~28 nm and associated with the pore volume from ~0.5 to 1.88 cm³/g. The pore volume from ~0.5 to 0.78 cm³/g is responsible for the gas uptake in the relative pressure range from ~0.2 to 0.8, the pore volume from 0.78 to 1.88 cm³/g with the large uptake step from 0.8 to 1.0. We had chosen the relative pressure of 0.8 to determine the pore volume which is inherent in the MOF structure. The pore volume of 0.78 cm³/g at p/p₀ = 0.80 agreed with the specific pore volume of 0.78 cm³/g from a geometric porosity analysis for the idealized structure of 2 with the program Mercury. b) Enlarged diagram between 0.4 nm and 2 nm. c) Comparison of experimental adsorption isotherm and GCMC fit (Interpolate curve: 3D spline curve; Model: Cylinder; Adsorbent: Metal oxide; PSD fitting parameter: Tikhonov regularization; Definition of pore width: solid definition).

S19

The GCMC method could be imprecise for MOFs regarding exact values, because there is no universal MOF-reference for a proper kernel. Hence, the results of the GCMC calculations are not viewed as a precise method here and the provided results are rather indicative. In any case, it is possible to see three pore sizes (Figure S20b), centered at 6 Å, 7 Å, and 8 Å, however the pore size at 7 Å is not very distinct and partially coalesces with the size centred at 6 Å (the fine details do depend on the kernel, so it is not worth to proceed with the analysis further).

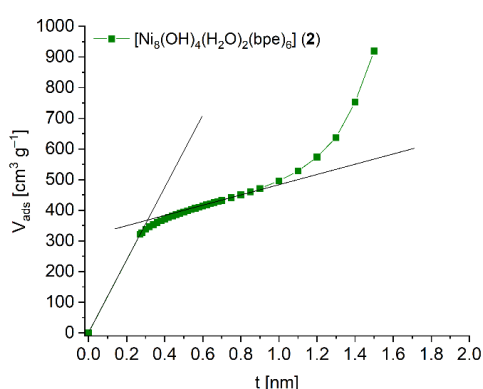


Figure S19. Analysis of **2** according to the t-plot method (where the adsorbed volume V_{ads} is expressed by the thickness of adsorption layer t) giving a surface area of 1535 m²/g and micropores of 6 Å.

S10 Comparison of nitrogen adsorption isotherms for ortho-1 and tetra-1

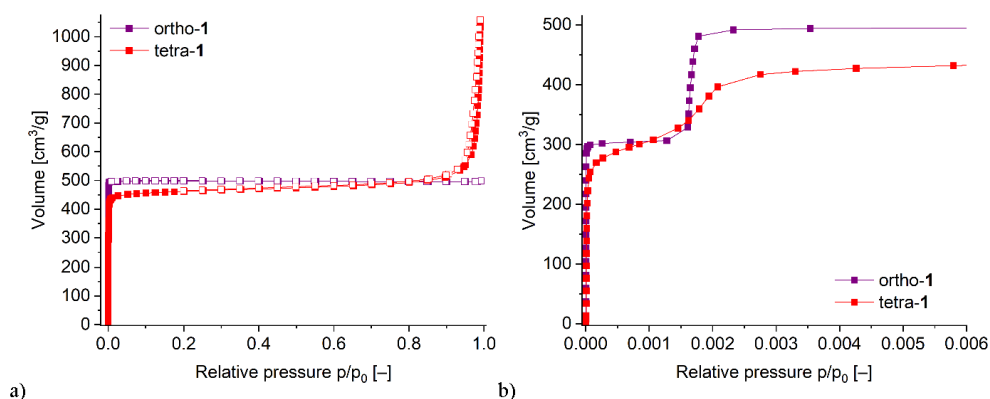


Figure S20. Comparison of the N₂ isotherms of ortho-1 (BET surface area: 2135 m²/g) and tetra-1 synthesized according to Moroni *et al.* (BET surface area: 1904 m²/g) over a) the full relative pressure range and b) between a relative pressure of 0 to 0.006.⁶

S11 High-pressure sorption experiments for ortho-1 and 2

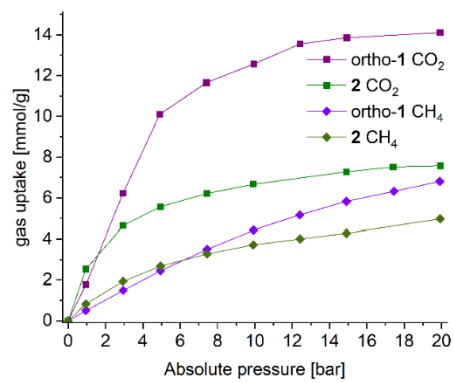


Figure S21. Gravimetric high-pressure isotherms for ortho-1 and 2 with CO₂ and CH₄ at 293 K.

S12 Comparison of CO₂, CH₄, H₂ uptakes for ortho-1, 2 and different isorecticular MOFs from the literature

The following linkers and their respective abbreviations are used in the following tables:

Linker	Abbreviation
	bpe ²⁻
	X = H: bpb ²⁻ , else bpb-X ²⁻
(X = H, OH, NH ₂ , NO ₂ , CHO, CN, COOH, F)	
	bpde ²⁻
	pbp ²⁻
	pbebp ²⁻
	bdc ²⁻
	adc ²⁻

Table S8. Comparison of the CO₂ uptake at different temperatures and pressures of ortho-1, 2 and other isorecticular MOFs from the literature (the table does not claim to be complete).

Linker	MOF	Temp. [K]	CO ₂ uptake [mmol/g]	P [bar]	Ref.
bpe ²⁻	ortho-1 (HHUD-5)	273 293 293	3.99 2.17 11.4	1 20	this work
bpb-X ²⁻	[Zn(bpb)]	273	~3	1	10
	[Zn(bpb-OH)]	273	9.1	30	11
	[Zn(bpb-NH ₂)]	273	~4.5	1	10
	[Zn(bpb-NH ₂)]	273	~2.7	1	10
	[Zn(bpb-NO ₂)]	273	~2.9	1	10
	[Co(bpb)]	298	~0.5 ~17	1 50	12 12
	[Co(bpb-F)]	298	~1.6	1	12
bpe ²⁻	2 (HHUD-6)	273 293 293	5.84 3.89 7.6	1 20	this work
bpb-X ²⁻	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpb) ₆]	273 298	~3.2 ~2.1	1	13
	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpb-OH) ₆]	273 298	~3 ~2.1	1	13
	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpb-NH ₂) ₆]	273 298	~2.5 ~1.7	1	13
	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpb-CHO) ₆]	293 303	3.44 ~2.5	1	14
	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpb-CN) ₆]	293 303	3.04 ~2.1	1	14
	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpb-COOH) ₆]	293 303	2.65 ~2	1	14
bpde ²⁻	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpde) ₆]	298	~2.5	1	15
pbebp ²⁻	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (pbebp) ₆]	298	~2	1	15

Table S9. Comparison of the CH₄ uptake at different temperatures and pressures of ortho-**1**, **2** and other isorecticular MOFs from the literature (the table does not claim to be complete).

Linker	MOF	Temp. [K]	CH ₄ uptake [mmol/g]	P [bar]	Ref.
bpe ²⁻	ortho-1 (HHUD-5)	273 293 293	1.11 0.74 6.8	1 20	this work
bpb ²⁻	[Zn(bpb)]	273	2.4	30	11
	[Co(bpb)]	298	~9.2	60	12
bpe ²⁻	2 (HHUD-6)	273 293 293	1.64 1.03 4.97	1 20	this work
bpb-X ²⁻	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpb-CHO) ₆]	293 303	1.04 ~0.8	1	14
	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpb-CN) ₆]	293 303	0.84 ~0.6	1	14
	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpb-COOH) ₆]	293 303	0.74 ~0.5	1	14

Table S10. Comparison of the H₂ uptake at different temperatures and pressures of ortho-**1**, **2** and other isorecticular MOFs from the literature (the table does not claim to be complete).

Linker	MOF	Temp. [K]	H ₂ uptake [mmol/g]	P [bar]	Ref.
bpe ²⁻	ortho-1 (HHUD-5)	77 87	11.6 6.2	1	this work
bpb ²⁻	[Zn(bpb)]	77 87	7.9 5	1	16
	[Co(bpb)]	298	~1.5	95	12
		77	15.4	30	17
bpe ²⁻	2	77 87	8.7 5.5	1	this work
pbp ²⁻	[Ni ₈ (OH) ₄ (H ₂ O) ₂ (pbp) ₆]	77	14.9	34.5	18

Table S11. Comparison of the gas uptakes of **2** with UiO-66 and HHUD-MOFs.

Linker	MOF	Temp. [K]	Gas uptake [mmol/g]	P [bar]	Ref.
CO ₂					
bpe ²⁻	2 (HHUD-6)	273 293 293	5.84 3.89 7.6	1 20	this work
bdc ²⁻	UiO-66 (low defects)	298	7.3	30	19
	UiO-66 (high defects)	298	5.63	1	20
adc ²⁻	HHUD-1 (Zr)	293	0.9	1	21
	HHUD-4	273 293	3.77 2.74	1	22
CH ₄					
bpe ²⁻	2 (HHUD-6)	273 293 293	1.64 1.03 4.97	1 20	this work
bdc ²⁻	UiO-66 (low defects)	298	6.3	80	19
adc ²⁻	HHUD-4	273 293	1.25 0.72	1	22
H ₂					
bpe ²⁻	2 (HHUD-6)	77 87	8.7 5.5	1	this work
bdc ²⁻	UiO-66 (low defects)	77	8.5	1	23
	UiO-66 (high defects)	77	6.5	1	23
adc ²⁻	HHUD-1 (Zr)	77	4.1	1	21
	HHUD-4	77	6.36	1	22

S13 Calculations and fitting for the isosteric heat of adsorption of CO₂, CH₄ and H₂

Since no other fit was applicable, CO₂ and CH₄ adsorption isotherms of ortho-1 were fitted using the Freundlich model:

$$q = (b \cdot p)^c$$

q = amount absorbed [mmol/g]

b = affinity constant [1/bar]

c = heterogeneity exponent

p = pressure [bar]

The adsorption isotherms for H₂ (77 K and 87 K) of ortho-1 and all isotherms of **2** were fitted using the Freundlich-Langmuir model:

$$q = \frac{a \cdot b \cdot p^c}{1 + b \cdot p^c}$$

q = amount absorbed [mmol/g]

a = maximal loading [mmol/g]

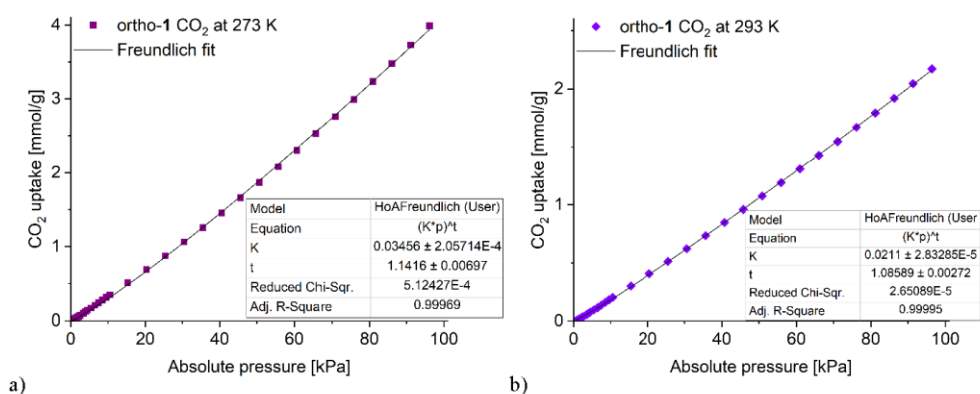
b = affinity constant [1/bar]

c = heterogeneity exponent

p = pressure [bar]

The isosteric heat of adsorption was calculated according to Clausius-Clapeyron:

$$Q_{st} = -R \left(\frac{T_2 \cdot T_1}{T_2 - T_1} \right) \ln \frac{p_2}{p_1}$$



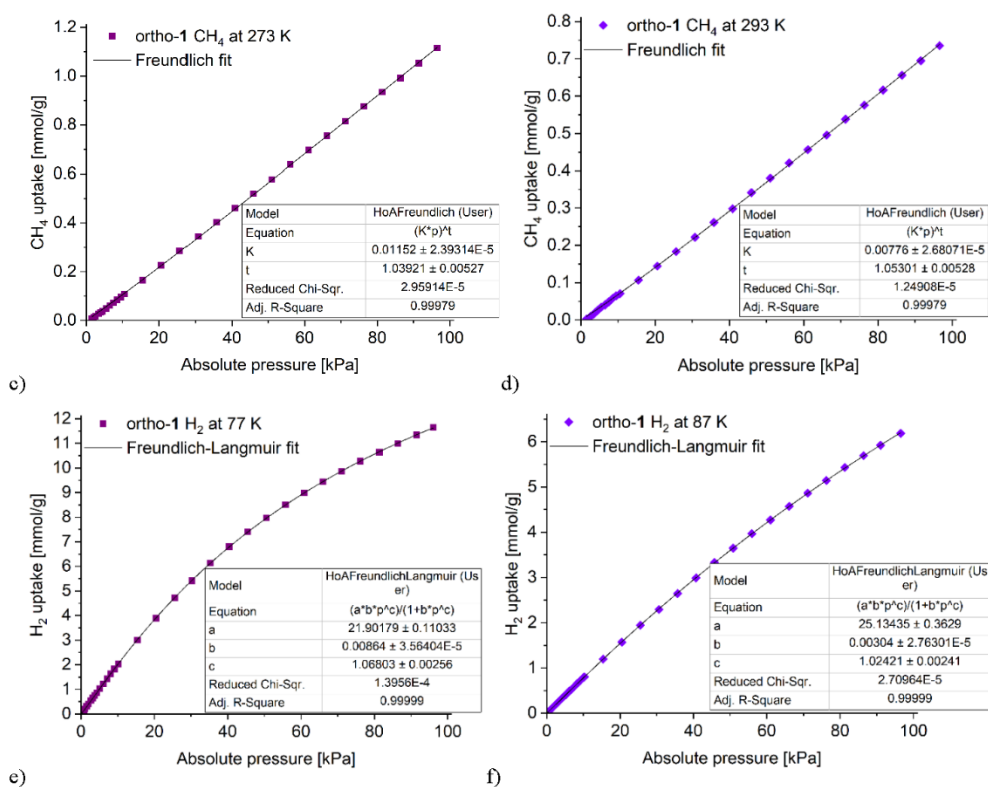


Figure S22. Experimental adsorption isotherms of ortho-1, their model fits (Freundlich for CO₂, CH₄ and Freundlich-Langmuir for H₂) and fitting parameters for CO₂ at a) 273 K and b) 293 K, for CH₄ at c) 273 K and d) 293 K, for H₂ at e) 77 K and f) 87 K.

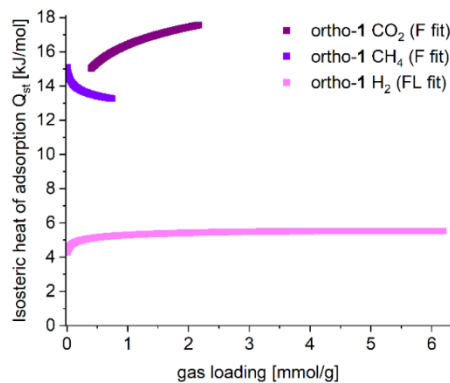


Figure S23. Isosteric heat of adsorption of ortho-1 for CO₂, CH₄ and H₂. For CO₂ and CH₄ Freundlich fit was used, while for H₂ Freundlich-Langmuir was used. Please note, that the increasing HoA for CO₂ can be ascribed to larger errors regarding calculated value. For that reason, we have not displayed the HoA below 0.4 mmol/g.

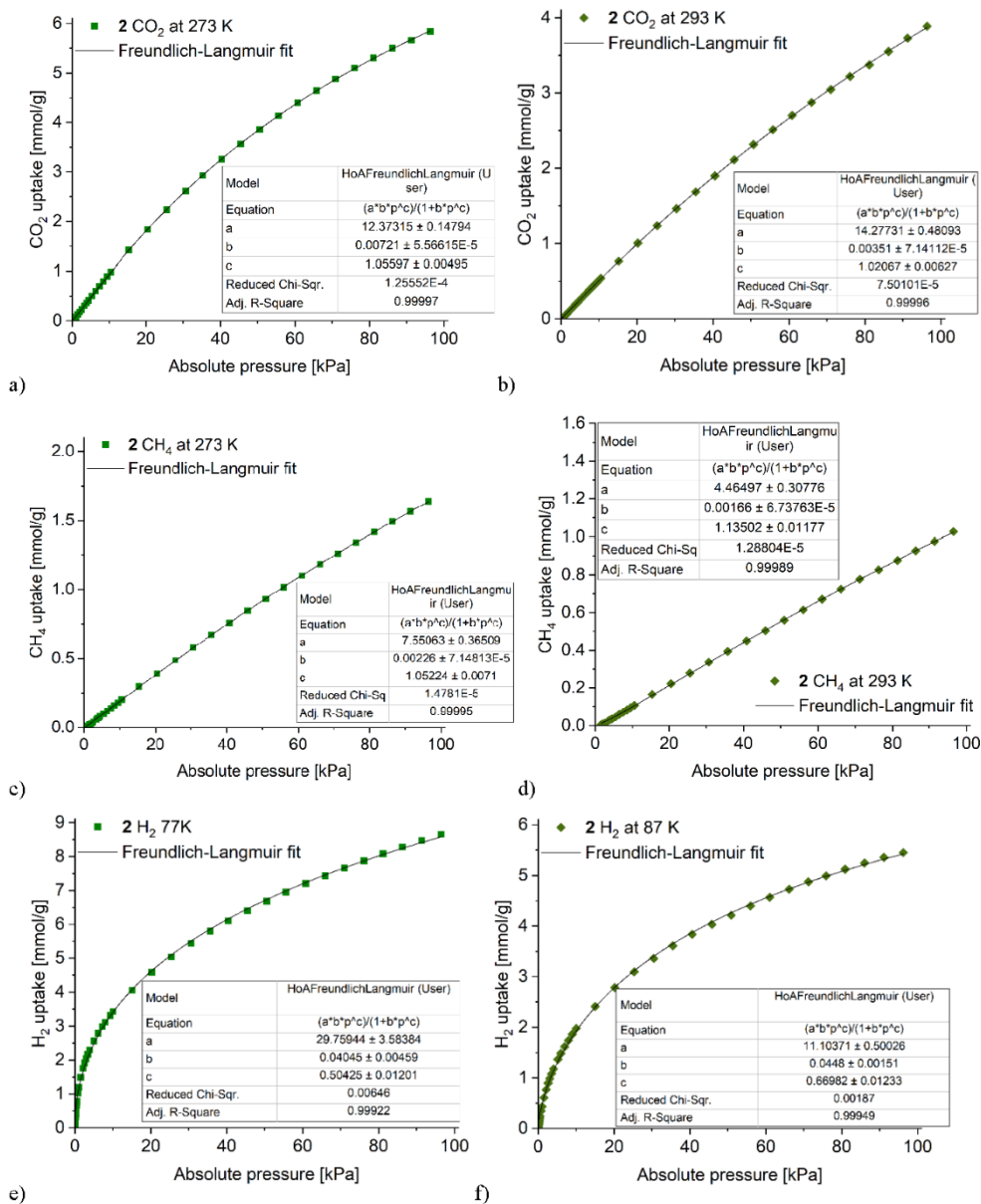


Figure S24. Experimental adsorption isotherms of **2**, their model fits (Freundlich-Langmuir) and fitting parameters for CO₂ at a) 273 K and b) 293 K, for CH₄ at c) 273 K and d) 293 K, for H₂ at e) 77 K and f) 87 K.

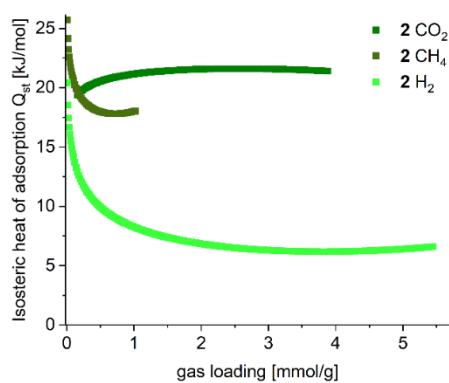


Figure S25. Isosteric heat of adsorption of **2** for CO₂, CH₄ and H₂.

S14 Calculation and fitting for the IAST selectivity of CO₂ and CH₄ for **2**

The CO₂ and CH₄ adsorption isotherm were fitted using the 3Psim software.²⁴ 3Psim is a tool for the interpretation and evaluation of experimental adsorption data containing several adsorption models: Henry, Langmuir adsorption isotherm (LAI), Toth, Sips, Freundlich, Dual Site Langmuir, DS Langmuir Sips (DSLAI Sips) and uniform distribution and Langmuir local isotherm (UNILAN). Fits were always performed with the best model possible. For ortho-**1**, no model gave a good fit. A possible explanation could be that the common adsorption theories were derived for adsorption on fixed sites, but since microporous materials are influenced by various adsorbate-induced rearrangements, this assumption is not valid. Even though these equations are sufficient enough to describe adsorption in many microporous solids, they are not sufficient enough to describe it in the case of ortho-**1**.²⁵⁻³⁰ In the case of the IAST selectivity calculations Toth model gave the best fit for **2** (Freundlich-Langmuir fit cannot be used for IAST calculation in this software):

$$q = q_{max} \cdot \frac{K \cdot p}{[1 + (k \cdot p)^t]^{\frac{1}{t}}}$$

q = amount absorbed [mmol/g]

q_{max} = maximal loading [mmol/g]

K = Toth constant/ affinity constant [1/bar]

t = heterogeneity exponent

p = pressure [bar]

The IAST (ideal adsorbed solution theory) selectivity was calculated using “IAST with Toth” isotherm model with two components. Selectivities were calculated with a constant molar composition of 50:50 and the total pressure was set to 1 bar. The formula used is:

$$S = \frac{x_1/x_2}{y_1/y_2}$$

x_i = adsorbed vapor amount

y_i = molar fractions of the CO₂ and CH₄, respectively.

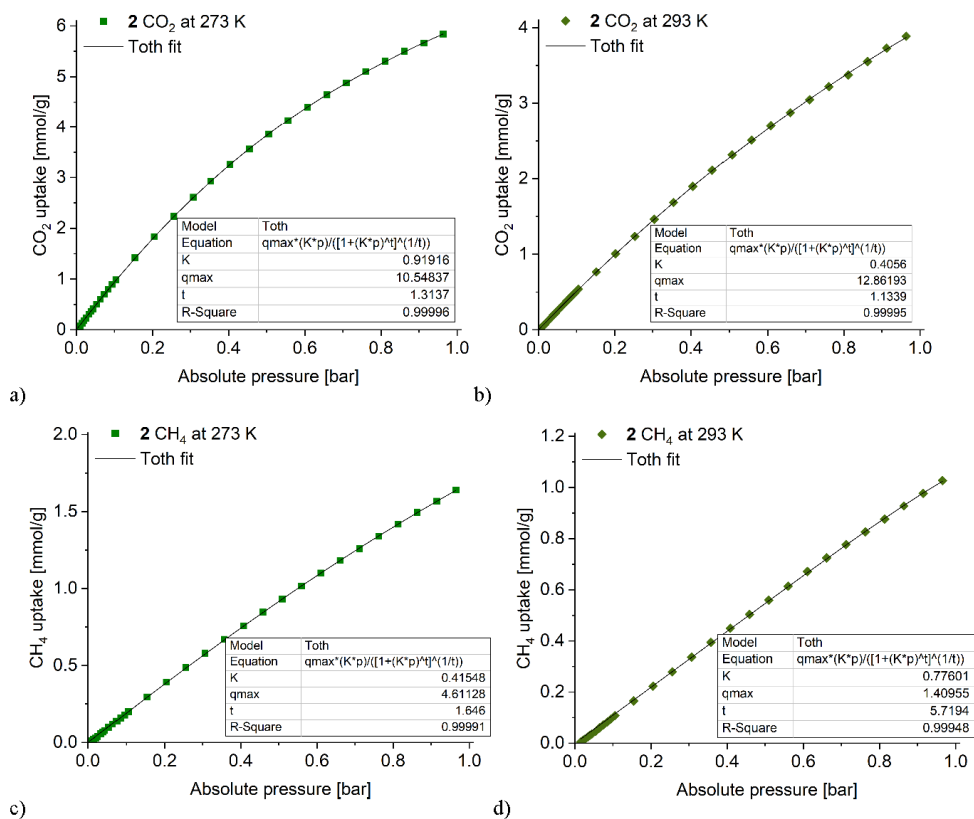


Figure S26. Experimental adsorption isotherms of **2**, their model fits (Toth) and fitting parameters for CO₂ at a) 273 K, b) 293 K and CH₄ at c) 273 K and d) 293 K.

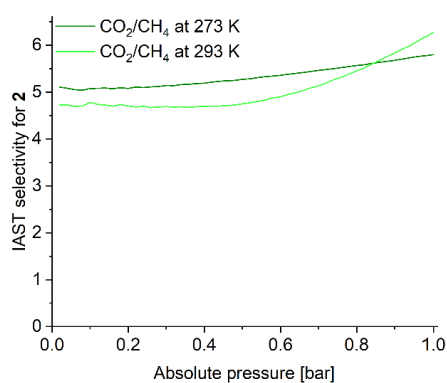


Figure S27. IAST selectivity of **2** for CO₂/CH₄ mixtures at 273 K and 293 K.

S15 Calculations and fitting for the IAST selectivity of VOCs for **2**

The adsorption isotherms for *n*-hexane, cyclohexane and benzene for **2** were fitted with the 3PSim software using Dual Site Langmuir fitting (No fit for ortho-**1** was applicable for the same reasons as in Section S11).²⁴ The fits were performed in a specific pressure range to reduce the fitting error.

$$q = q_1 \cdot \frac{K_1 p}{1 + K_1 p} + q_2 \cdot \frac{K_2 p}{1 + K_2 p}$$

q = amount absorbed [mmol/g]

q₁ = maximal loading 1 [mmol/g]

K₁ = affinity constant 1 [1/bar]

q₂ = maximal loading 2 [mmol/g]

K₂ = affinity constant 2 [1/bar]

p = pressure [bar]

The IAST (ideal adsorbed solution theory) selectivity was calculated with the 3PSim software using “IAST with DS Langmuir” isotherm model with two components.²⁴ Selectivities were calculated with a constant vapor composition of 50:50 of both VOCs over a pressure range from 0 bar to 0.052 bar due to fitting problems of the uptake step at higher pressures. The formula used is:

$$S = \frac{x_1/x_2}{y_1/y_2}$$

x_i = adsorbed vapor amount

y_i = molar fractions of the corresponding VOC

Table S12. IAST selectivities for different VOC-mixtures for [Ni₈(OH)₄(H₂O)₂(bpe)₆] (**2**) at selected pressures.

Compound	VOC (x ₁ and x ₂)	IAST selectivity		
		0.010 bar	0.025 bar	0.050 bar
[Ni ₈ (OH) ₄ (H ₂ O) ₂ (bpe) ₆] (2)	benzene and cyclohexane	2.1	1.7	1.0
	<i>n</i> -hexane and benzene	1.4	1.2	1.0
	<i>n</i> -hexane and cyclohexane	5.0	4.7	3.9

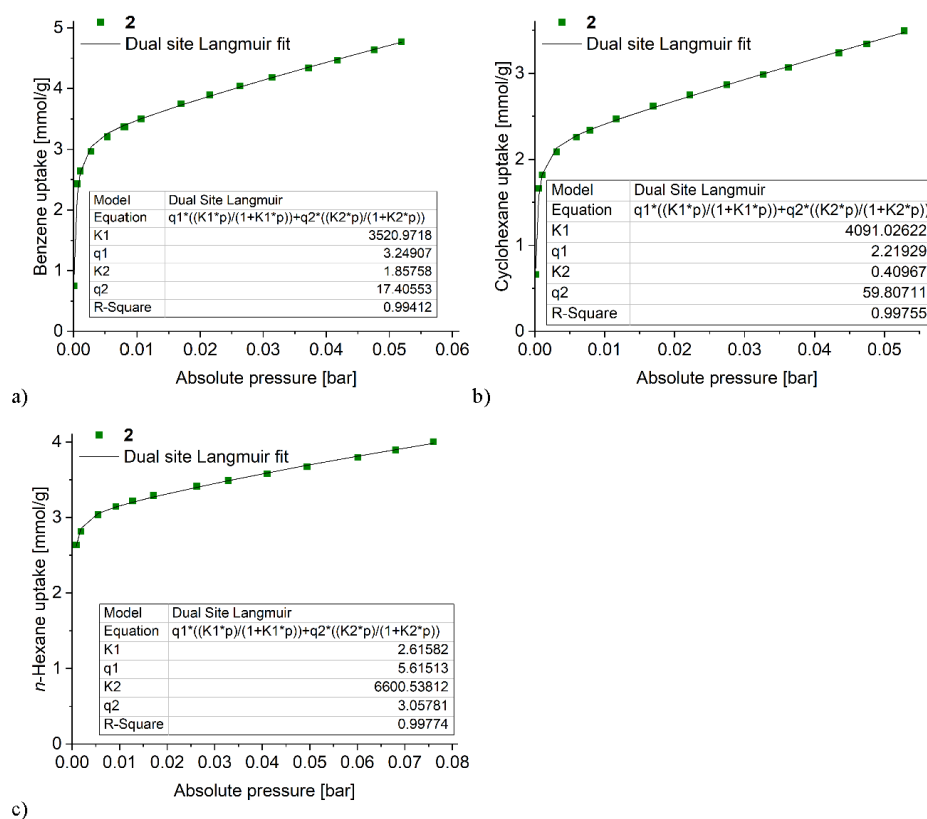


Figure S28. Experimental adsorption isotherms of **2** at 293 K, their model fits (Dual Site Langmuir) and fitting parameters for a) benzene, for b) cyclohexane and for c) *n*-hexane.

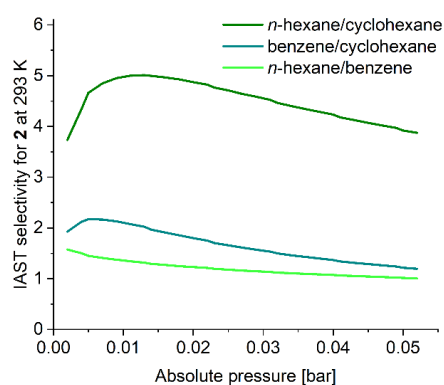


Figure S29. IAST selectivity of **2** for VOC mixtures at 293 K.

S16 Stability after gas and vapor sorption experiments of ortho-1 and 2

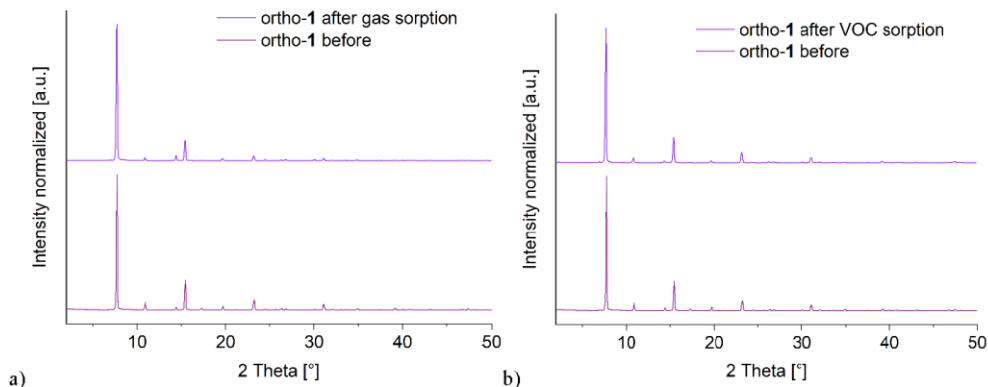


Figure S30. Powder pattern of ortho-1 a) before sorption experiments and after CO₂, CH₄, H₂ sorption experiments and b) before and after VOC sorption experiments.

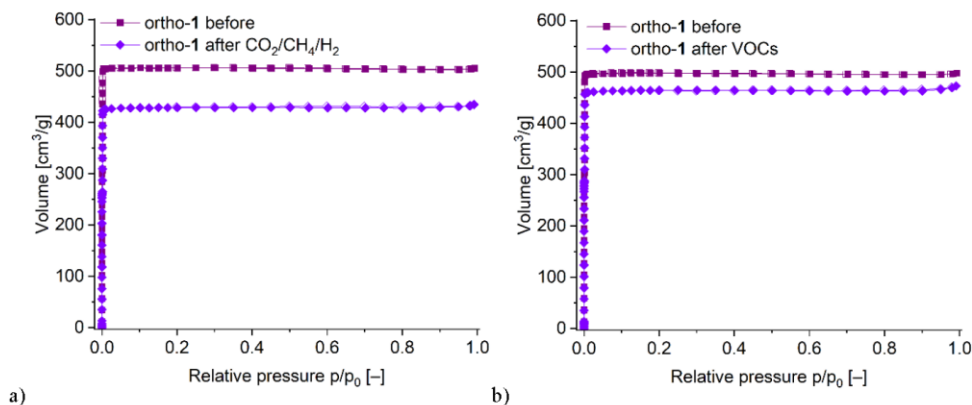


Figure S31. Volumetric nitrogen sorption of ortho-1 at 77 K (a) before gas sorption experiments (squares) (BET: 2180 m²/g) and after CO₂, CH₄ and H₂ sorption (diamonds) (BET: 1837 m²/g) and (b) before VOC sorption experiments (squares) (BET: 2135 m²/g) and after benzene, cyclohexane and *n*-hexane sorption experiments (diamonds) (BET: 1992 m²/g).

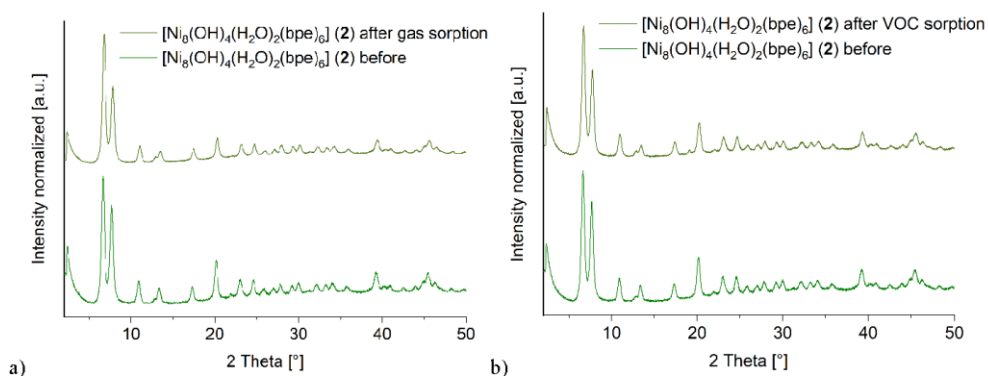


Figure S32. Powder pattern of 2 a) before sorption experiments and after CO₂, CH₄, H₂ sorption experiments and b) before and after VOC sorption experiments. The increasing baseline before 5° is attributed to the PXRD device measurement method with the low-background silicon holder.

S32

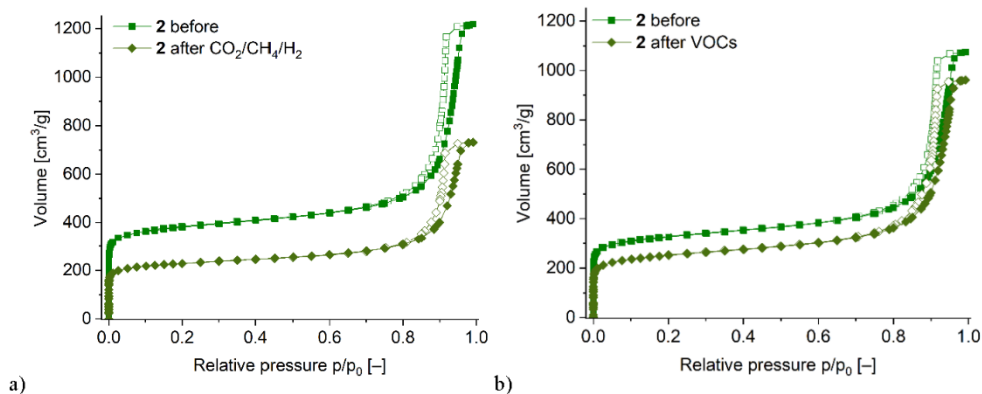


Figure S33. Volumetric nitrogen sorption of **2** at 77 K (a) before gas sorption experiments (squares) (BET: 1415 m²/g) and after CO₂, CH₄ and H₂ sorption (diamonds) (BET: 840 m²/g) and (b) before VOC sorption experiments (squares) (BET: 1193 m²/g) and after benzene, cyclohexane and *n*-hexane sorption experiments (diamonds) (BET: 906 m²/g).

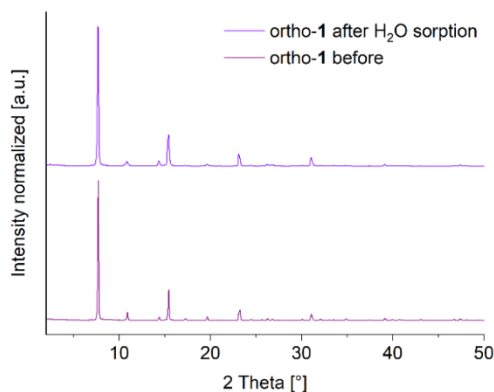


Figure S34. Powder pattern of ortho-1 before and after water vapor sorption experiment.

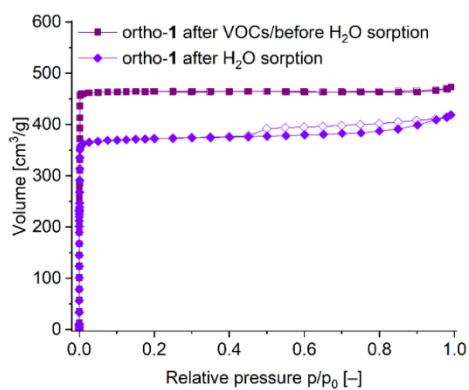


Figure S35. Volumetric nitrogen sorption of ortho-1 at 77 K after VOC (and before H₂O) sorption experiments (squares) (BET: 1992 m²/g) and after H₂O sorption (diamonds) (BET: 1552 m²/g).

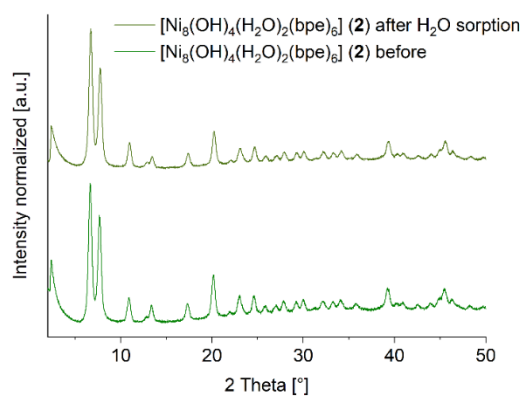


Figure S36. Powder pattern of **2** before and after water vapor sorption experiment. The increasing baseline before 5° is attributed to the PXRD device measurement method with the low-background silicon holder.

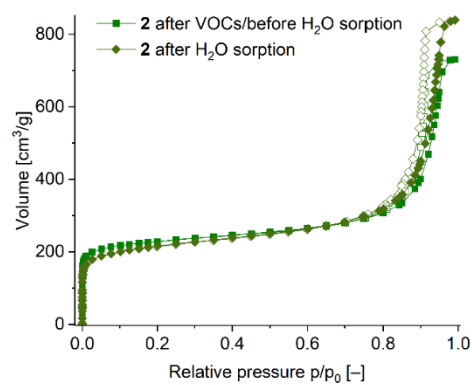


Figure S37. Volumetric nitrogen sorption of **2** at 77 K after VOC (and before H₂O) sorption experiments (squares) (BET: 906 m²/g) and after H₂O sorption (diamonds) (BET: 766 m²/g).

S17 Stability of ortho-1 and 2 towards water, 1 mol/L NaOH and 1 mol/L HCl

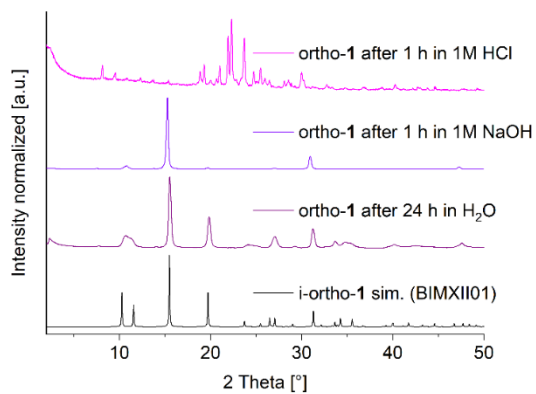


Figure S38. Comparison of the powder pattern of activated ortho-1 after 24 h in water, 1 h in 1 mol/L NaOH and 1 h in 1 mol/L HCl against the interpenetrated orthorhombic polymorph i-ortho-1 (Ref. code: BIMXII01) published by Moroni *et al.*⁶

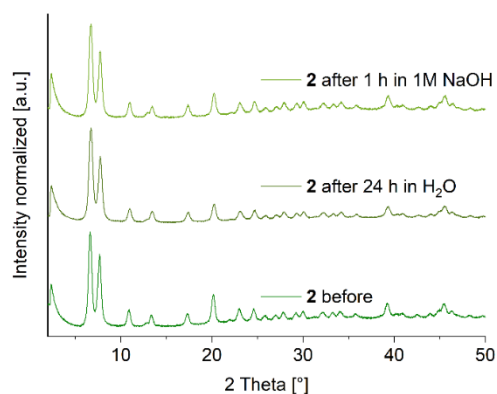


Figure S39. Powder pattern of **2** after 24 h in water and 1 h in 1 mol/L NaOH. After 1 h in 1 mol/L HCl the MOF completely decomposed.

S18 References

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3.3 Beiträge an weiteren Veröffentlichungen

In diesem Kapitel werden alle bis zu diesem Zeitpunkt veröffentlichte Publikationen in der Rolle als Co-Autor vorgestellt. Die Co-Autorschaften wurden im Rahmen von Service-Messungen, insbesondere für die Auswahl und Messung von Einkristallen mittels *single crystal X-ray diffraction* (SCXRD, dt. Einkristall-Röntgendiffraktometrie) und der anschließenden Strukturverfeinerung, erhalten. Eine weitere Co-Autorschaft wurde für Hochdrucksorptionsmessungen erhalten.

Die Veröffentlichungen werden in chronologischer Reihenfolge beginnend mit den neusten Publikationen vorgestellt. Hierfür wurden die Kurzzusammenfassungen übersetzt und der Anteil an der entsprechenden Publikation nochmals hervorgehoben.

“Novel Re(I) complexes as potential selective theranostic agents in cancer cells and in vivo in *Caenorhabditis elegans* tumoral strains”

Alicia Marco, Pezhman Ashoo, Samanta Hernández-García, Pedro Martínez-Rodríguez, Natalia Cutillas, Annette Vollrath, Dustin Jordan, Christoph Janiak, Fernando Gandía-Herrero, José Ruiz, *J. Med. Chem.* **2024**, DOI: 10.1021/acs.jmedchem.3c01869

Es wurde eine Reihe von Rhenium(I)-Komplexen des Typs $\text{fac}[\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{N})\text{L}]^{0/+}$, **Re1-Re9**, synthetisiert ($\text{N}^{\wedge}\text{N}$ = zweizähniger Benzimidazol-Ligand mit Esterfunktionalität, L = Chlorid oder Pyridintyp-Ligand). Die neuen Verbindungen zeigten eine starke Aktivität gegenüber A2780-Ovarialkrebszellen. Die aktivsten Komplexe, **Re7-Re9**, welche 4-NMe₂py beinhalten, zeigten eine bemerkenswerte Aktivität in 3D-HeLa-Sphäroiden. Die Emission im Rotbereich von **Re9**, welches einen elektronenarmen Benzothiazol-Bestandteil enthält, ermöglichte die Verwendung als Bioimaging-Tool für die *in vitro* und *in vivo* Visualisierung. Die Wirksamkeit von **Re9** wurde in zwei verschiedenen *C. elegans* Tumorstämmen, JK1466 und MT2124, getestet, um die untersuchten onkogenen Pfade zu erweitern. Die Ergebnisse zeigten, dass **Re9** in der Lage war, das Tumorwachstum in beiden Stämmen zu reduzieren, indem es die ROS-Produktion innerhalb der Zellen erhöhte. Außerdem war die Selektivität der Verbindung gegenüber Krebszellen bemerkenswert, da sie weder die Entwicklung noch die Nachkommenschaft der Nematoden beeinträchtigte.

Eigenanteile an der Veröffentlichung:

- Messung und Auswertung der Einkristall-Strukturanalyse für **Re3**·CHCl₃.

“Single-Crystal Structure Analysis of Three Novel Iron(II) Coordination Polymers with Bridging 1,3,5-Tris((1*H*-1,2,4-triazol-1-yl)methyl)benzene”

Aysenur Limon, Dustin N. Jordan, Till Strothmann, Laure P. Cuignet, Yann Garcia, Christoph Janiak, *Crystals* **2023**, *13*, 1574. DOI: 10.3390/cryst13111574

Drei neuartige Eisen(II)-Koordinationspolymere $[\text{Fe}(\text{H}_2\text{O})_2(\text{ttmb})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (**1**), $[\text{Fe}(\text{H}_2\text{O})_2(\text{ttmb})_2](\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$ (**2**) und $[\text{Fe}(\text{NCS})_2(\text{ttmb})_2]$ (**3**) wurden mit dem Linker 1,3,5-Tris((1*H*-1,2,4-triazol-1-yl)methyl)benzol (ttmb) synthetisiert. Die Einkristall-Strukturen zeigen, dass alle drei Verbindungen eine Doppelketten-Struktur bilden, wobei die benachbarten Eisenatome durch zwei ttmb-Linker verbrückt sind. Die Eisen(II)-Ionen sind oktaedrisch von vier N4-Donoratomen aus den 1,2,4-Triazol-1-yl-Gruppen von vier verschiedenen ttmb-Linkern umgeben, die eine Ebene bilden und zwei *trans*-koordinierte Aqua-Liganden in **1** und **2** oder Isothiocyanat-Liganden in **3** in den axialen Positionen besitzen. In Anbetracht des neutralen verbrückenden ttmb-Linkers gibt es in **1** und **2** ein nicht-koordiniertes Gegenanion (ClO_4 bzw. BF_4) und in **3** ein koordiniertes NCS-Anion. Die Verbindungen **1** und **2** sind isostrukturell. Interessanterweise nutzt der ttmb-Linker nur zwei seiner drei potenziell koordinierenden Triazol-Gruppen. Alle Eisen(II)-Koordinationsnetzwerke sind farblos oder haben eine hellgelbe Farbe, was auf den *high-spin*-Zustand hinweist.

Eigenanteile an der Veröffentlichung:

- Synthese des ttmb-Liganden.
- Messungen und Auswertung der Einkristall-Strukturanalysen.

“Unravelling gas sorption in the aluminum metal-organic framework CAU-23: CO₂, H₂, CH₄, SO₂ sorption isotherms, enthalpy of adsorption and mixed-adsorptive calculations”

Christian Jansen, Niels Tannert, Dirk Lenzen, Marco Bengsch, Simon Millan, Anna Goldman, Dustin N. Jordan, Linda Sondermann, Norbert Stock, Christoph Janiak, *Z. Anorg. Allg. Chem.* **2022**, *648*, e202200170. DOI: 10.1002/zaac.202200170

Dieser Bericht umfasst die erste größere Evaluation der Gas-Sorptionseigenschaften von CAU-23 für die Adsorptive CO₂, H₂, CH₄ und SO₂. Die Porosität von CAU-23 liegt im Mittelfeld der Al-MOFs bezogen auf die spezifischen BET-Oberflächen (MIL-100 > MIL-53 > CAU-23 > MIL-160 > MIL-53-TDC > Al₂Fu₃ > CAU-10-H) und dem totalen Porenvolumen

(MIL-100 > MIL-53 > CAU-23 > Al₂O₃ = MIL-160 > MIL-53-TDC > CAU-10-H). Die Aufnahmen von CO₂ (3.97 mmol/g, 293 K) und H₂ (10.25 mmol/g, 77 K) von CAU-23 liegen an zweiter Stelle in der Serie und sind nur geringfügig niedriger als die für MIL-160. Die CH₄-Aufnahme von CAU-23 (0.89 mmol/g, 293 K) ist im Vergleich mit den anderen Al-MOFs gering. Die SO₂-Aufnahme (8.4 mmol/g, 293 K) folgt der Porosität. Höhere SO₂-Aufnahmen wurden nur für MIL-53 und MIL-100 beobachtet. CAU-23 ist eines der besten Al-MOFs für die CO₂-Hochdrucksorption mit einer Aufnahme von 33 Gew.-% bei 20 bar, 293 K. Gas-Sorptionsmessungen bei zwei unterschiedlichen Temperaturen ergaben nahezu Null-Deckungs-Adsorptionseenthalpien ΔH_{ads}^0 von –22 kJ/mol für CO₂ und –38 kJ/mol für SO₂, welche im unteren Bereich der Al-MOFs (–22 kJ/mol bis –39 kJ/mol für CO₂; –41 kJ/mol bis –51 kJ/mol für SO₂) liegen. Die ΔH_{ads} für CAU-23 für CO₂ und SO₂ steigt mit steigender Gasaufnahme auf –25 kJ/mol bzw. –57 kJ/mol. Für CO₂/CH₄- und SO₂/CO₂-Trennung liegen die IAST-Selektivitäten bei 5 und 27–50 (abhängig von dem molaren Anteil und dem Modell) in Einklang mit den Bereichen 4.5–6.3 und 17–50 der meisten anderen Al-MOFs, bei denen nur MIL-53-TDC mit 83 und MIL-160 mit 126 für die SO₂/CO₂-Selektivität bei einem molaren Anteil von 0.5 hervorstechen.

Eigenanteile an der Veröffentlichung:

- Durchführung und Auswertung der Hochdruckadsorptionsmessungen.

4. Zusammenfassung

Im ersten Teil dieser Arbeit wurden 1,2,4-Triazol-basierte Koordinationspolymere synthetisiert, strukturell aufgeklärt und hinsichtlich der Einflussfaktoren der unterschiedlichen Gegenionen auf die Struktur und den SCO-Eigenschaften untersucht.

Hierfür wurden mit dem Linker 1,1'-(*trans*-2-buten-1,4-diyl)bis-1,2,4-triazol (tbbt) sieben neue Koordinationsnetzwerke mit den Summenformeln $[\text{Fe}(\text{tbbt})_3](\text{BF}_4)_2$ (**1**), $[\text{Co}(\text{tbbt})_3](\text{BF}_4)_2$ (**2**), $[\text{Fe}(\text{tbbt})_3](\text{ClO}_4)_2$ (**3**), $[\text{Co}(\text{tbbt})_3](\text{ClO}_4)_2$ (**4**), $[\text{Fe}(\text{NCS})_2(\text{tbbt})_2]$ (**5**), $[\text{Co}(\text{NCS})_2(\text{tbbt})_2]$ (**6**) und $[\text{Fe}(\text{H}_2\text{O})_2(\text{tbbt})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (**7**) synthetisiert (Abbildung 18).

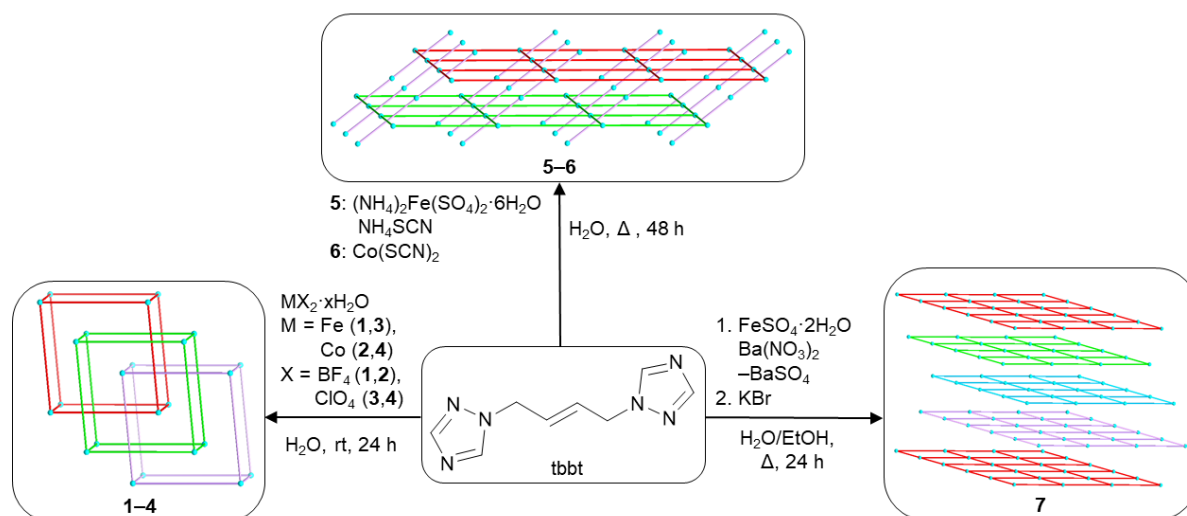


Abbildung 18. Überblick über die Synthesen der Verbindungen **1–7** und deren ausgebildeten topologischen Strukturen. Die blauen Kugeln repräsentieren die Metallatome und werden durch tbbt-Liganden verknüpft. Die Abbildung wurde mit Genehmigung von Ref. 140 reproduziert. Copyright ©2023 von den Autoren, Lizenznehmer MDPI.

Die Kristallstrukturanalyse haben ergeben, dass die Verbindungen **1–4** isostrukturell sind und in der trigonalen Raumgruppe $P\bar{3}$ kristallisieren (Abbildung 19).

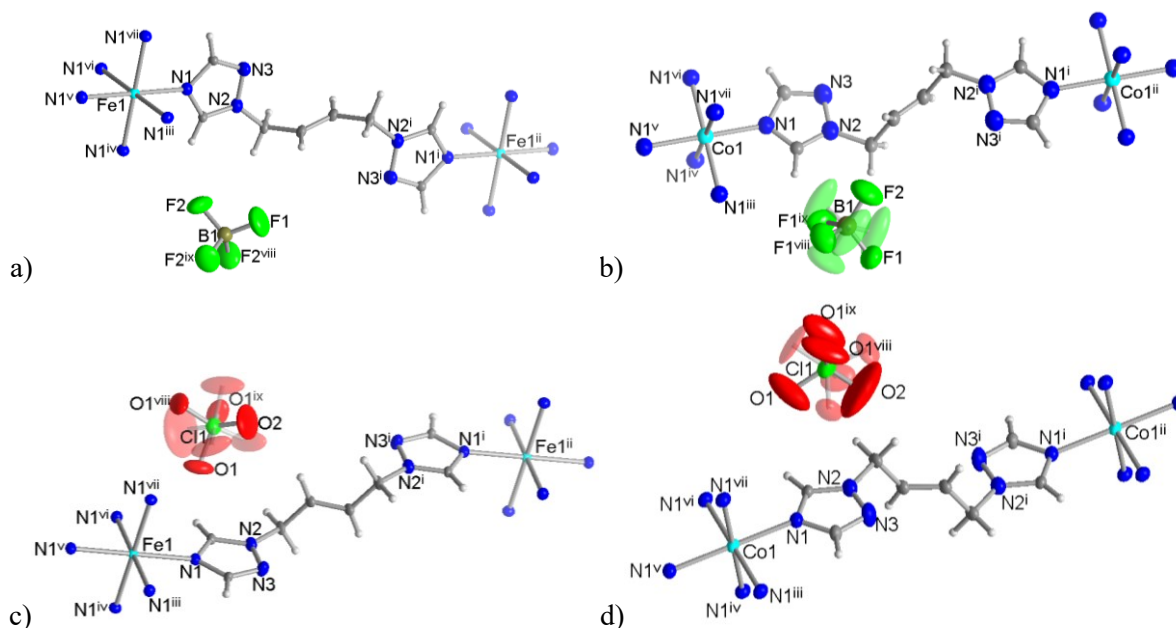


Abbildung 19. Erweiterte asymmetrische Einheiten von a) **1**, b) **2**, c) **3** und d) **4** (thermische Ellipsoide entsprechen einer Wahrscheinlichkeit von 50%). Die Fehlordnung der Anionen wurde semi-transparent dargestellt. Die Symmetrietransformationen lauten wie folgt: a) i = $1 - x, 2 - y, 2 - z$; ii = $1 + x, y, 1 + z$; iii = $-1 - x + y, 1 - x, z$; iv = $-1 + y, -x + y, 1 - z$; v = $-x, 2 - y, 1 - z$; vi = $1 + x - y, 1 + x, 1 - z$; vii = $1 - y, 2 + x - y, z$; viii = $-x + y, 1 - x, z$; ix = $1 - y, 1 + x - y, z$. b) i = $2 - x, 1 - y, 2 - z$; ii = $x, -1 + y, 1 + z$; iii = $1 - x + y, 1 - x, z$; iv = $1 - y, x - y, z$; v = $2 - x, 2 - y, 1 - z$; vi = $2 - y, 1 + x - y, z$; vii = $1 - x + y, 2 - x, z$; viii = $1 - x + y, 1 - x, z$; ix = $1 - y, x - y, z$. c) i = $1 - x, 1 - y, -z$; ii = $-1 + x, -1 + y, -1 + z$; iii = $2 - y, 1 + x - y, z$; iv = $1 + x - y, x, 1 - z$; v = $2 - x, 2 - y, 1 - z$; vi = $y, 1 - x + y, 1 - z$; vii = $1 - x + y, 2 - x, z$; viii = $1 - y, 1 + x, z$; ix = $-x + y, 1 - x, z$. d) i = $1 - x, -y, 2 - z$; ii = $1 + x, y, 1 + z$; iii = $-y, x - y, z$; iv = $-x + y, -x, z$; v = $-x, -y, 1 - z$; vi = $x - y, x, 1 - z$; vii = $y, -x + y, 1 - z$; viii = $1 - x + y, 1 - x, z$; ix = $1 - y, x - y, z$. Die Abbildungen wurden mit Genehmigung von Ref. 140 übernommen. Copyright ©2023 von den Autoren, Lizenznehmer MDPI.

Die Struktur der Komplexe **1–4** besteht aus drei sich gegenseitig durchdringenden, symmetriebezogenen 3D-Netzwerken, in welchen der Linker jeweils in der *anti*-Konformation vorliegt. Jedes einzelne 3D-Netzwerk bildet ein primitives, nahezu kubisches Gitter (**pcu**) mit nicht-koordinierenden BF₄⁻ oder ClO₄⁻ Anionen in den Zwischenräumen, welche über Wasserstoffbrückenbindungen die Interpenetration kontrollieren (Abbildung 20).

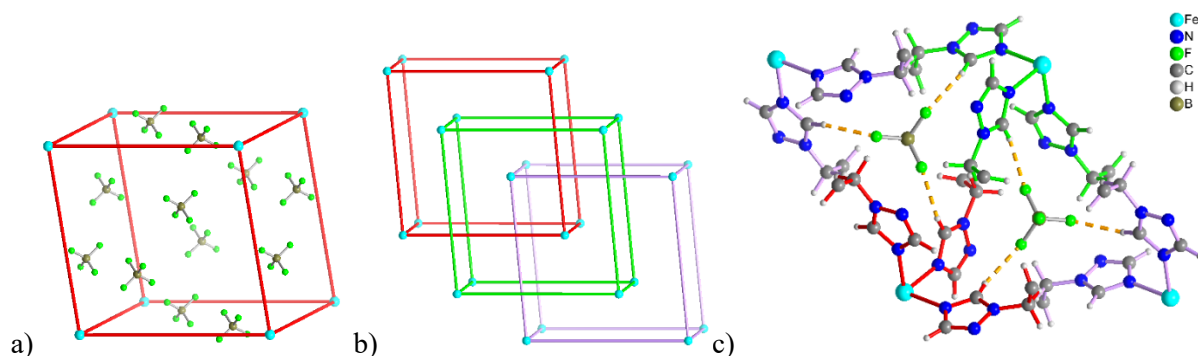


Abbildung 20. a) Übersicht der **pcu**-Topologie in **1** (vergleichbar für **2–4**) mit den Positionen der Anionen auf den Flächen des kubischen Gitters. b) Dreifache Interpenetration von drei symmetrie-bezogenen kubischen Gittern. c) Templat-Effekt der BF_4^- Anionen (vergleichbar für ClO_4^-), welche Wasserstoffbrückenbindungen mit den Triazol-Einheiten der tbbt-Linker ausbilden. Die Abbildungen wurden mit Genehmigung von Ref. 140 reproduziert. Copyright ©2023 von den Autoren, Lizenznehmer MDPI.

Die beiden isostrukturellen Verbindungen **5** und **6** kristallisieren in der triklinen Raumgruppe $P\bar{1}$. Die Isothiocyanat-Anionen sind im Gegensatz zu den anderen Verbindungen direkt an das Metallzentrum koordiniert (Abbildung 21). Die Strukturen von **5** und **6** setzen sich aus zweidimensionalen **sql**-Schichten, die parallel zueinander im AB-Schichttyp stehen und in denen der tbbt-Linker jeweils in der *anti*-Konformation vorliegt, zusammen. Diese Schichten sind von eindimensionalen Ketten, in welchen die Linker in der *syn*-Konformation vorliegen, durchdrungen und haben beide die gleiche Summenformel $[\text{M}(\text{NCS})_2(\text{tbbt})_2]$ ($\text{M} = \text{Fe}, \text{Co}$). Wasserstoffbrückenbindungen zwischen den Isothiocyanat-Anionen und den tbbt-Linkern steuern auch hier den Aufbau und die Interpenetration (Abbildung 22).

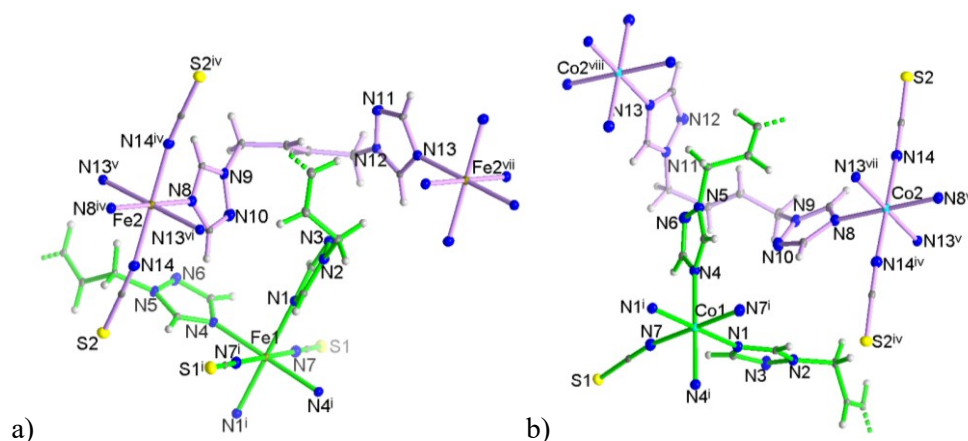


Abbildung 21. Erweiterte asymmetrische Einheiten von a) **5** und b) **6**. Die Schichten sind in grün und die Ketten in lila dargestellt (thermische Ellipsoide entsprechen einer Wahrscheinlichkeit von 50%). Die Symmetrietransformationen lauten: a): i = $1 - x$, $1 - y$, $1 - z$; ii = $1 - x$, $1 - y$, $-z$; iii = $2 - x$, $-y$, $1 - z$; iv = $1 - x$, $-y$, $-z$; v = x , $-1 + y$, z ; vi = $1 - x$, $1 - y$, $-z$; vii = x , $1 + y$, z ; in b): i = $1 - x$, $1 - y$, $-z$; ii = $-x$, $2 - y$, $-z$; iii = $1 - x$, $1 - y$, $1 - z$; iv = $1 - x$, $2 - y$, $1 - z$; v = x , $1 + y$, z ; vi = $1 - x$, $2 - y$, $1 - z$; vii = $1 - x$, $1 - y$, $1 - z$; viii = x , $-1 + y$, z . Die Abbildungen wurden mit Genehmigung von Ref. 140 übernommen. Copyright ©2023 von den Autoren, Lizenznehmer MDPI.

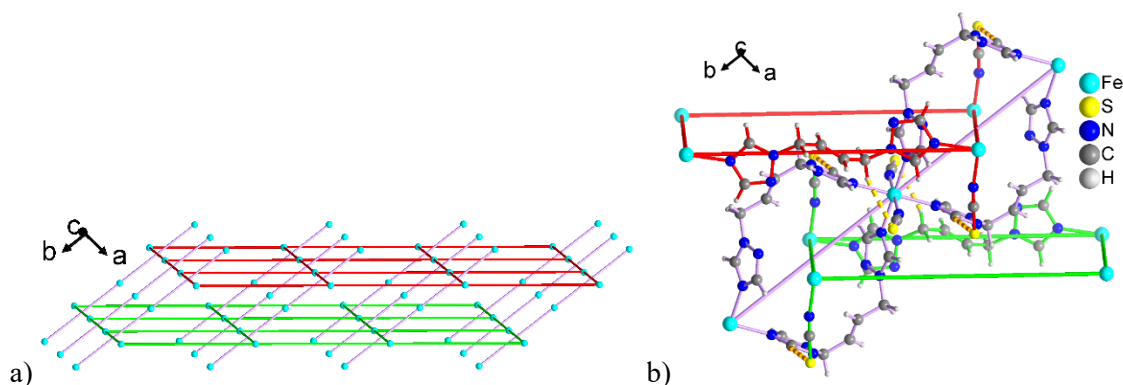


Abbildung 22. a) Schematische Darstellung der **sql**-Schichten in **5** (vergleichbar für **6**), welche von eindimensionalen Ketten durchdrungen werden. b) Darstellung der Wasserstoffbrückenbindungen zwischen den Ketten und Schichten. Die Abbildungen wurden mit Genehmigung von Ref. 140 reproduziert. Copyright ©2023 von den Autoren, Lizenznehmer MDPI.

Ein anderes Strukturmotiv konnte durch die Verwendung von Bromid als Gegenion erhalten werden. Verbindung **7** kristallisiert in der orthorhombischen Raumgruppe *Fdd2* (Abbildung 23).

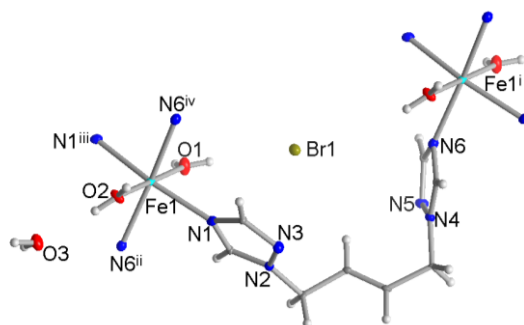


Abbildung 23. Erweiterte asymmetrische Einheit von **7** (thermische Ellipsoide entsprechen einer Wahrscheinlichkeit von 50%). Die Symmetrietransformationen lauten: i = x, 1/2 + y, 1/2 + z; ii = x, -1/2 + y, -1/2 + z; iii = 1 - x, 1 - y, z; iv = 1 - x, 3/2 - y, -1/2 + z. Die Abbildung wurde mit Genehmigung von Ref. 140 übernommen. Copyright ©2023 von den Autoren, Lizenznehmer MDPI.

Die Struktur von Verbindung **7** besteht aus parallelen, zweidimensionalen **sql**-Schichten im ABCD-Schichttyp. Dadurch, dass die Linker in den Schichten in der *syn*-Konformation vorliegen, kommt es in **7** anders als in den anderen Strukturen zu keiner Interpenetration. Stattdessen ist jede Pore sowohl mit Wassermolekülen als auch mit Bromid-Ionen gefüllt, welche beide jeweils durch die Bildung von Wasserstoffbrückenbindungen zur Stabilisierung der Struktur beitragen (Abbildung 24).

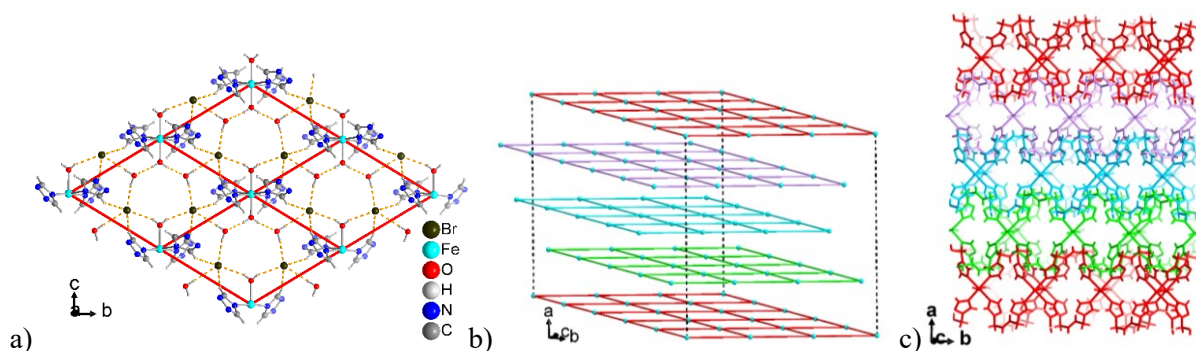


Abbildung 24. a) Darstellung der Wasserstoffbrückenbindungen in den Poren von **7**. b) ABCD-Schichtstruktur der **sql**-Schichten (inkl. schwarzer Hilfslinie). c) ABCD-Struktur, welche die Interdigitierung der einzelnen Schichten veranschaulicht. Die Abbildung wurde mit Genehmigung von Ref. 140 reproduziert. Copyright ©2023 von den Autoren, Lizenznehmer MDPI.

Im Rahmen dieser Forschung konnte gezeigt werden, dass die Interpenetration der Verbindungen **1–6** nicht über π - π -Wechselwirkungen zwischen den Triazol-Ringen oder den C=C-Doppelbindungen, sondern über die ausgebildeten (Triazol)C-H $\cdots$ F₄B⁻, C-H $\cdots$ O₄Cl⁻ und C-H $\cdots$ SCN⁻ Wasserstoffbrückenbindungen, kontrolliert wird. Dies lässt auf einen Templat-Effekt der entsprechenden nicht-kordinierten oder koordinierten Anionen als Grund für die Interpenetration schließen. In **7** werden die (Triazol)C-H $\cdots$ Br⁻ Wechselwirkungen durch die O-H $\cdots$ O und O-H $\cdots$ Br Wasserstoffbrückenbindungen unter Beteiligung der Aqua-Liganden und der Kristallwassermoleküle unterstützt. Es ist offensichtlich, dass die koordinierten und nicht-kordinierten Anionen eine wesentliche Rolle bei der Bildung der Netzwerke spielen und die Interpenetration steuern. Alle Eisen(II) Koordinationsnetzwerke sind farblos, cremefarben bis gelb-orange und liegen bis zu 77 K im *high-spin*-Zustand vor. Verbindung **5** verweilt sogar bei Temperaturen bis zu 10 K im *high-spin*-Zustand.

Im zweiten Teil der Arbeit wurde der Einfluss der -C $\equiv$ C- Dreifachbindung auf die Sorptionseigenschaften Pyrazolat-basierter MOFs anhand zweier neuer MOFs mit dem Linker 1,2-bis(1*H*-pyrazol-4-yl)ethin (H₂bpe) untersucht.

Das erste MOF [Zn(bpe)]·1.8DMF (HHUD-5) kristallisiert in der orthorhombischen Raumgruppe *Fddd* (Abbildung 25a) und stellt somit ein Polymorph des bereits veröffentlichten [Zn(bpe)]·1.2DMF, welches in der tetragonalen Raumgruppe *P4₂/mmc* auskristallisiert, dar (Abbildung 26a). Dieser literaturbekannte Polymorphismus führt zur Ausbildung rhombischer anstelle von quadratischen Kanälen (8 Å × 8 Å und 4 Å × 8 Å), während das Grundgerüst bestehend aus einem 4-c Netzwerk mit **pts**-Topologie erhalten bleibt (Abbildung 25, Abbildung 26).

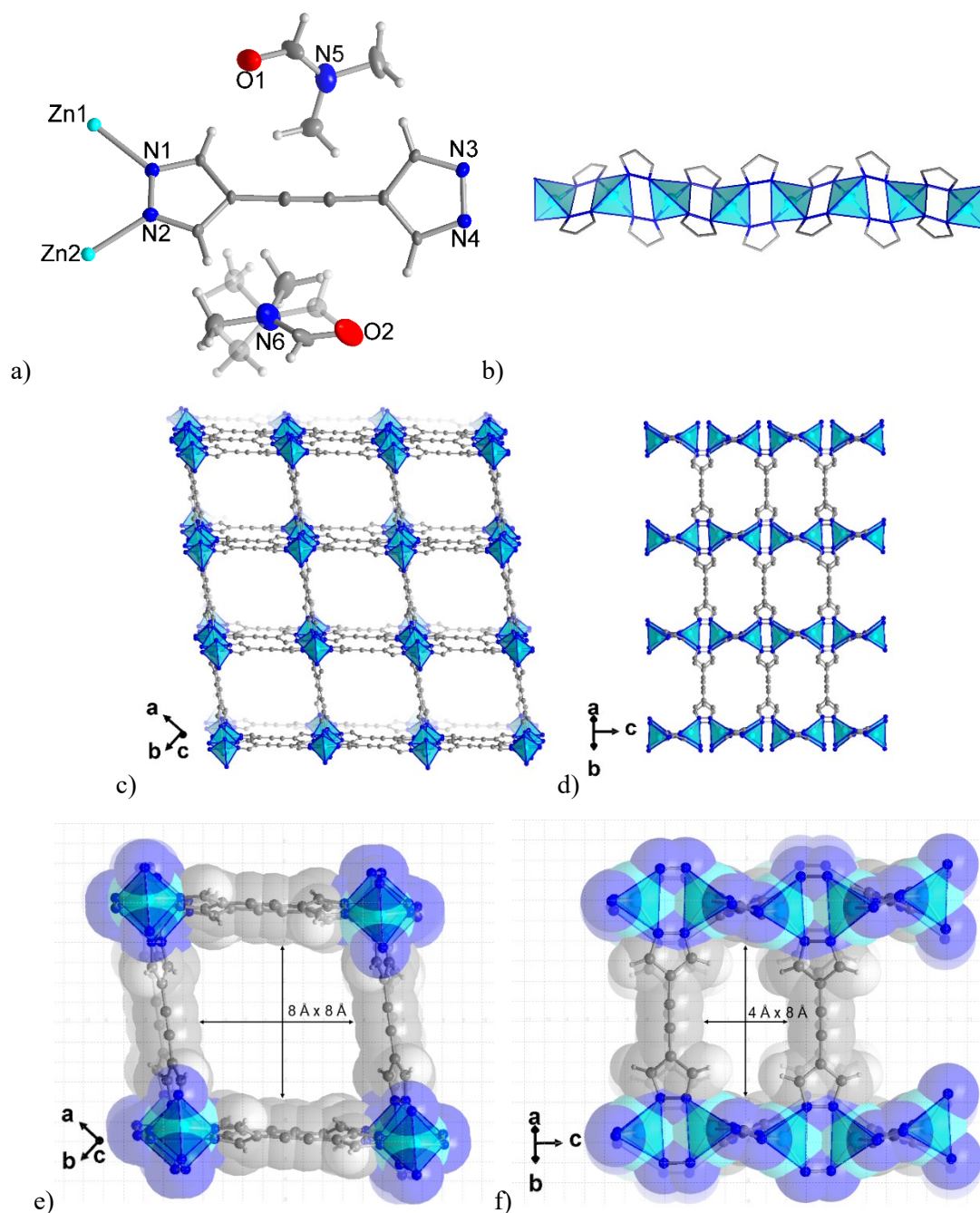


Abbildung 25. a) Erweiterte asymmetrische Einheit des orthorhombischen Polymorphs $[\text{Zn}(\text{bpe})] \cdot 1.8\text{DMF}$ (HHUD-5) (thermische Ellipsoide entsprechen einer Wahrscheinlichkeit von 50%). Symmetriebezogene Atome und die Fehlordnung des DMF-Moleküls sind semi-transparent dargestellt. b) Zn-SBU-Kette. c, d) Ausschnitt des Netzwerkes betrachtet in Richtung der größeren (c) und kleineren (d) Kanäle. e, f) Bestimmung der Kanalgrößen über die Verwendung des Raumfüllungsmodell und einem $1 \text{ \AA} \times 1 \text{ \AA}$ -Raster. Die Abbildung wurde mit Genehmigung von Ref. 125 übernommen. Copyright ©2024, American Chemical Society.

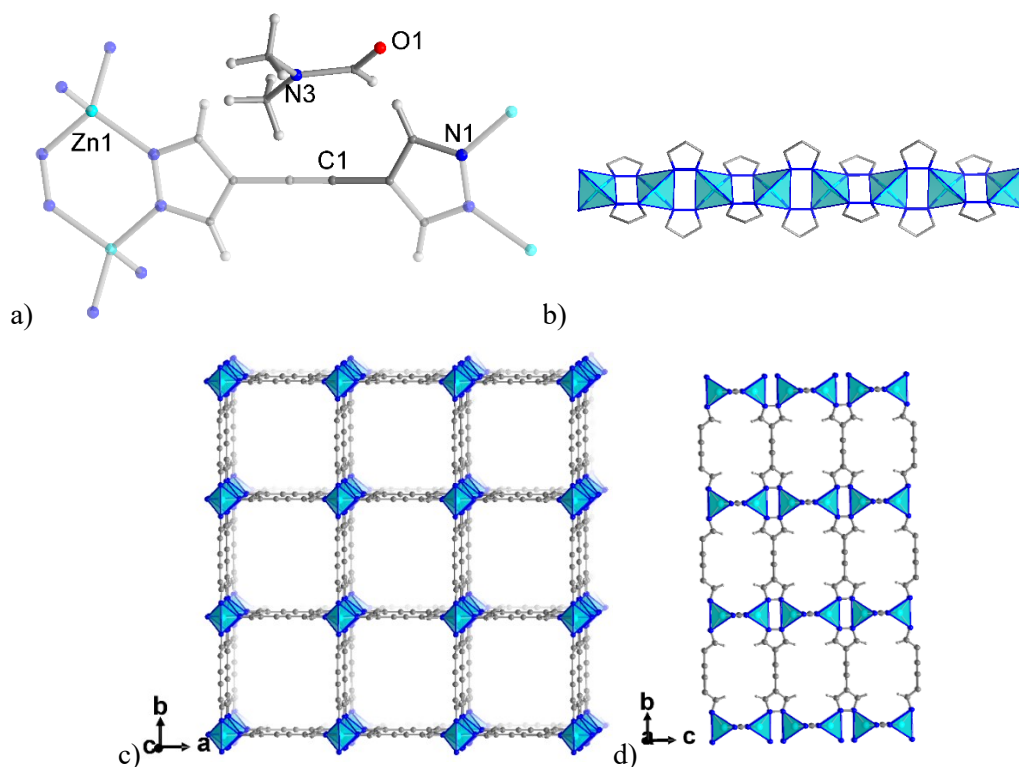


Abbildung 26. a) Erweiterte asymmetrische Einheit des tetragonalen Polymorphs $[\text{Zn}(\text{bpe})]\cdot 1.2\text{DMF}$ (thermische Ellipsoide entsprechen einer Wahrscheinlichkeit von 50%). Symmetriebezogene Atome sind semi-transparent dargestellt. b) Zn-SBU-Kette. c, d) Ausschnitt des Netzwerkes betrachtet in Richtung der größeren (c) und kleineren (d) Kanäle. Die Abbildung wurde mit Genehmigung von Ref. 125 übernommen. Copyright ©2024, American Chemical Society.

Bei dem zweiten MOF $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]\cdot n\text{Solv}$ (HHUD-6) handelt es sich um ein neues Mitglied der isoretikulären $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2\text{L}_6]$ -Serie. Die Verbindung kristallisiert in der kubischen Raumgruppe $Fm\bar{3}m$ aus und bildet $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2]^{12+}$ -Cluster als Teil der hoch symmetrischen $\{\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{pz})_{12}\}$ -SBU aus. Das hieraus resultierende 12-c 3D-Netzwerk mit **fcu**-Topologie beinhaltet größere, oktaedrische Poren (13 Å) und kleinere, tetraedrische Poren (6 Å) (Abbildung 27).

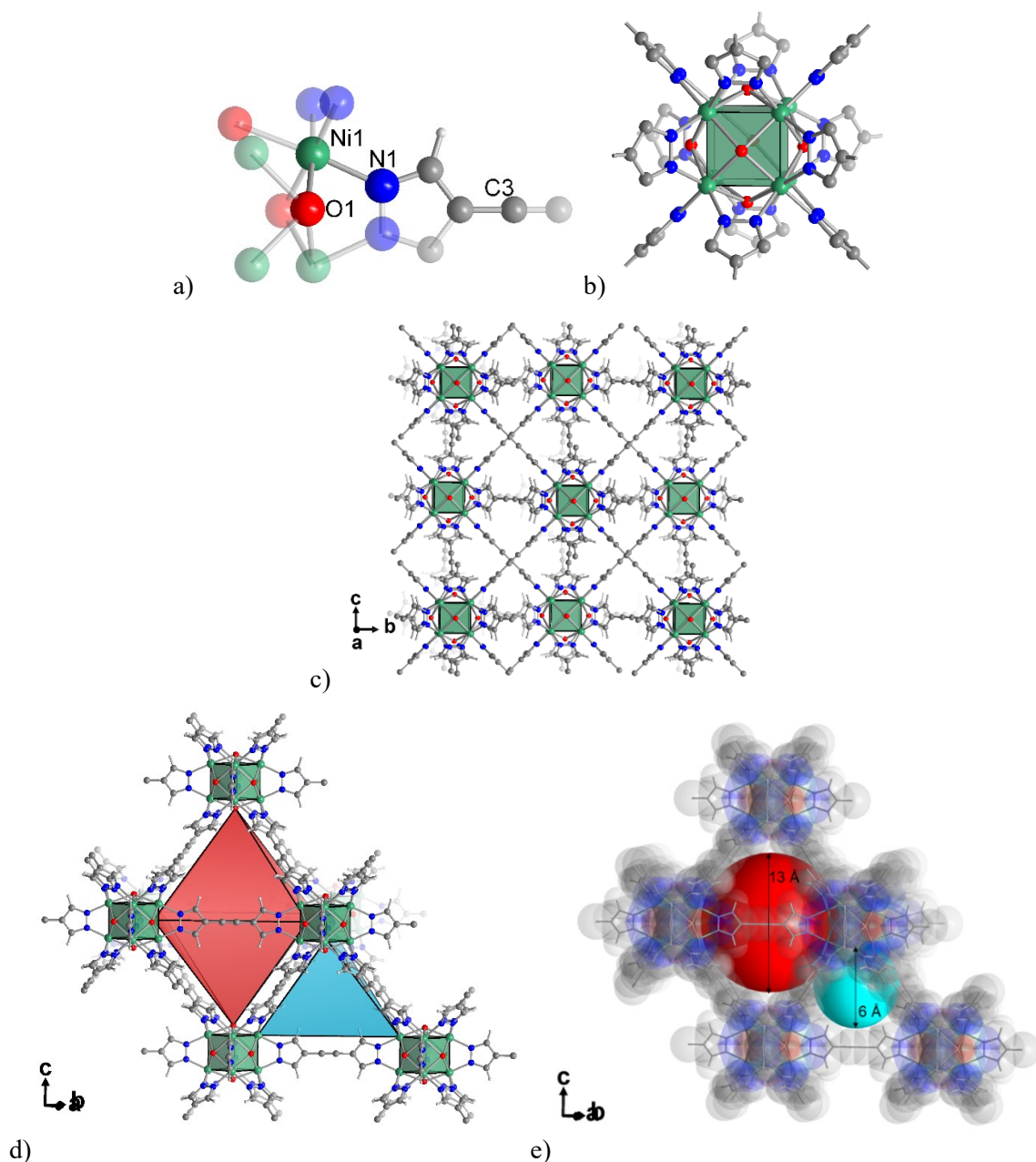


Abbildung 27. a) Erweiterte asymmetrische Einheit von $[Ni_8(OH)_4(H_2O)_2(bpe)_6] \cdot nSolv$ (HHUD-6) (thermische Ellipsoide entsprechen einer Wahrscheinlichkeit von 50%). Symmetriebezogene Atome sind semi-transparent dargestellt. b) $\{Ni_8(OH)_4(H_2O)_2(pz)_{12}\}$ -SBU. c) Ausschnitt des Netzwerkes. d) Oktaedrische (rot) und tetraedrische (blau) Pore. e) Bestimmung der Porengrößen mit dem Raumfüllungsmodell und Kugeln innerhalb der Poren. Die Abbildung wurde mit Genehmigung von Ref. 125 übernommen. Copyright ©2024, American Chemical Society.

Nach vollständiger Aktivierung beider MOFs wurden Stickstoff-Sorptionsisothermen zur Bestimmung der BET-Oberfläche aufgenommen. Für ortho-[Zn(bpe)] wurde hierbei eine ideale Typ I-Isotherme, welche charakteristisch für Materialien mit kleinen Mikroporen und einer schmalen Porenverteilung ist, erhalten. Die Oberfläche von ortho-[Zn(bpe)] liegt bei $2135 \text{ m}^2/\text{g}$ (Porenvolumen: $0.77 \text{ cm}^3/\text{g}$) (Abbildung 28a). Die Oberfläche für tetra-[Zn(bpe)] konnte durch

entsprechende Aktivierung im Vergleich zur Literatur auf $1990 \text{ m}^2/\text{g}$ erhöht werden. Für beide Polymorphe konnte in einem relativen Druckbereich zwischen $5.5 \cdot 10^{-4}$ und $1.6 \cdot 10^{-3}$ ein Plateau beobachtet werden, welches für zwei unterschiedliche Größen der Kanäle/Poren oder die für mikroporöse Materialien typischen Netzwerkanpassungen an die Stickstoffmoleküle spricht (Abbildung 28b). Die Porenanalyse ergab Porengrößen von $5.5 \text{ \AA}$ und $8 \text{ \AA}$ und ist demnach im Einklang mit den aus der Kristallstruktur vorhergesagten Werten.

Die Isotherme von $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ beginnt als Typ I-Isotherme und endet als Typ IV-Isotherme in dessen Bereich eine Typ H1-Hysterese vorliegt. Die hohe Aufnahme in dem relativen Druckbereich von 0.8 bis 0.99 ist vermutlich unter anderem auf texturale Effekte, wie Kondensation im interpartikulären Raum zurückzuführen (Abbildung 28b). Die Oberfläche liegt bei $1415 \text{ m}^2/\text{g}$ (Abbildung 28a). Die Porenverteilung ergab Mikroporen im Bereich von $6 \text{ \AA}$ bis $8 \text{ \AA}$. Das Porenvolumen bei $p/p_0 = 0.8$ liegt bei $0.78 \text{ cm}^3/\text{g}$.

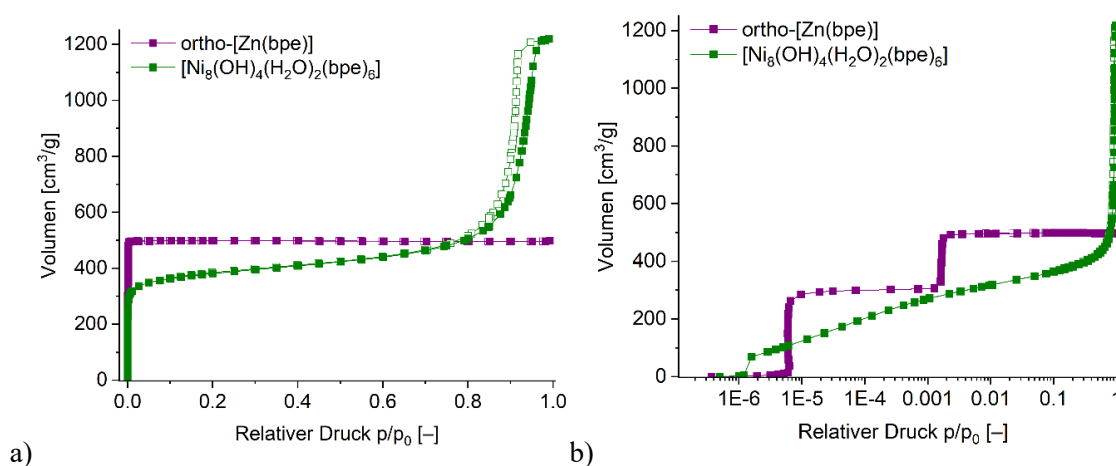


Abbildung 28. Volumetrische Stickstoff-Sorptionsisothermen bei 77 K von ortho-[Zn(bpe)] und $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ a) mit linearer x-Achse und b) auf logarithmischer x-Achse (ausgefüllte Symbole symbolisieren die Adsorption, leere Symbole stehen für die Desorption). Die Abbildung wurde mit Genehmigung von Ref. 125 reproduziert und ins Deutsche übersetzt. Copyright ©2024, American Chemical Society.

Nach der Bestimmung der BET-Oberflächen wurden die Aufnahmefähigkeiten beider MOFs bezüglich CO_2 , CH_4 und H_2 untersucht (Abbildung 29). Im niedrigen Druckbereich besitzt $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ eine höhere Aufnahme als ortho-[Zn(bpe)]. Dies kann womöglich auf die durch die Aktivierung entstandenen *open metal sites* zurückgeführt werden. Bei höherem Druck folgt die Aufnahme dann den BET-Oberflächen, sodass ortho-[Zn(bpe)] eine höhere Aufnahme besitzt. Die nahezu linearen Isothermen für ortho-[Zn(bpe)] können über das Gesetz von Henry, welches einen linearen Zusammenhang zwischen der Aufnahme und dem Partialdruck bei niedrigem relativem Druck beschreibt, erklärt werden (für CO_2 bei 1 bar: $p/p_0 = 0.018$).

Beim Vergleich mit Literaturwerten von isoretikulären MOFs mit Phenylen-Einheiten anstelle der Dreifachbindung, wie z.B. MOFs mit dem Linker H_2bpb , ist zu erkennen, dass die hier vorgestellten MOFs höhere Gasaufnahmen besitzen. Dies kann als positiver Einfluss der $-\text{C}\equiv\text{C}-$ Dreifachbindung auf die Sorptionseigenschaften, wie auch bereits in anderen Publikationen erfolgt, verstanden werden. Allerdings müssen hierbei auch andere Faktoren, wie die Aktivierungsprozedur und das vorhandene Porenvolumen berücksichtigt werden, sodass diese Literaturvergleiche stets mit Vorsicht zu betrachten sind.

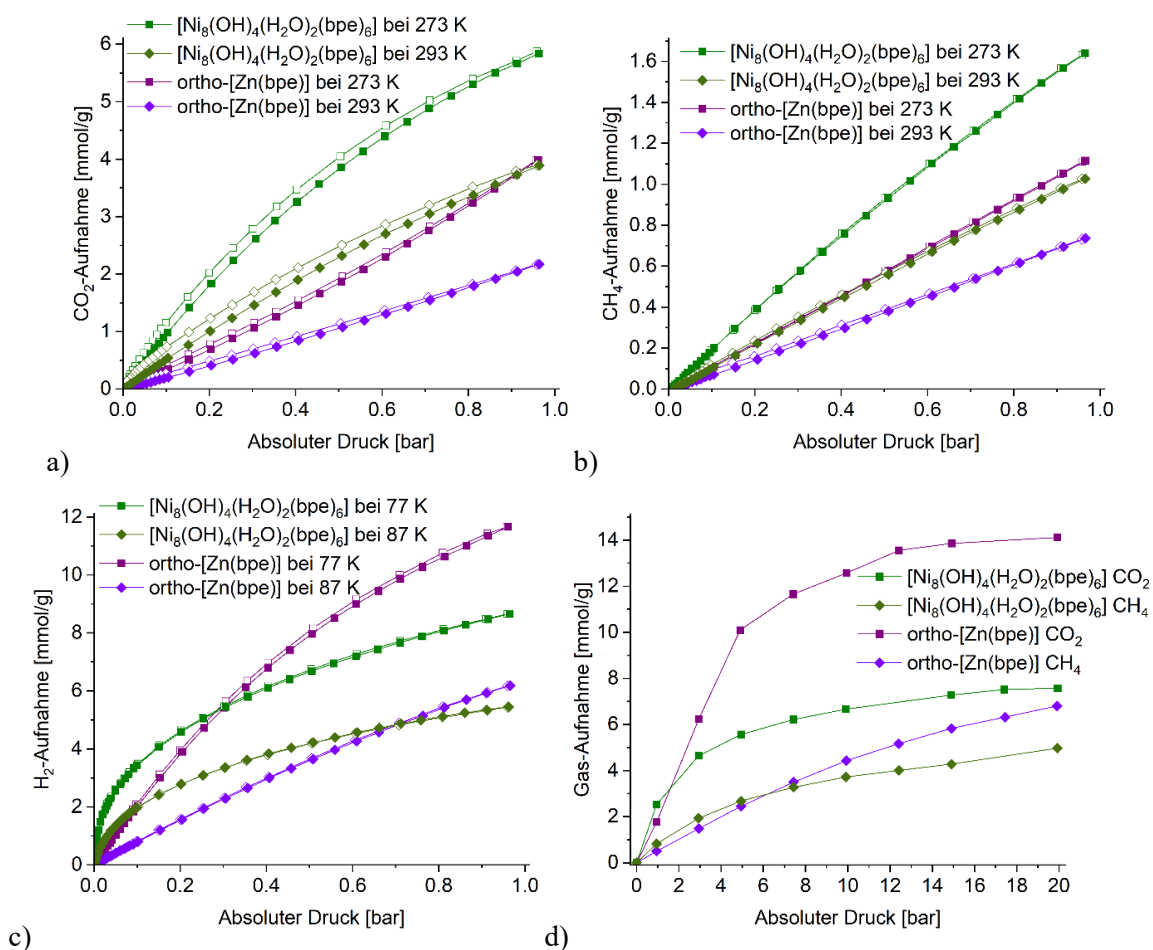


Abbildung 29. Gas-Sorptionsisotherme von $\text{ortho-}[\text{Zn}(\text{bpe})]$ und $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ für a) CO_2 bei 273 K und 293 K (volumetrisch), b) für CH_4 bei 273 K und 293 K (volumetrisch), c) für H_2 bei 77 K und 87 K (volumetrisch) und d) für CO_2 und CH_4 bei 293 K bis zu 20 bar (gravimetrisch). Die Abbildung wurde mit Genehmigung von Ref. 125 reproduziert und ins Deutsche übersetzt. Copyright ©2024, American Chemical Society.

Weiterhin wurden Dampf-Sorptionsisothermen sowohl für die *volatile organic compounds* (VOCs, dt. volatile organische Verbindungen) Benzol, Cyclohexan und *n*-Hexan als auch für Wasser aufgenommen (Abbildung 30). Die Isothermen für die VOCs zeigen, dass $\text{ortho-}[\text{Zn}(\text{bpe})]$ bei niedrigem relativem Druck eine deutlich höhere Aufnahme besitzt. Dies könnte auf die kleinen Kanäle, welche Wechselwirkungen zwischen den adsorbierten

Molekülen und der Oberfläche des Adsorbens begünstigen, zurückgeführt werden. Die höhere Aufnahme für $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ bei höherem relativem Druck könnte auf Kondensationseffekte zurückgeführt werden.

Für die Wasser-Sorptionen zeigen sich deutlich unterschiedlichere Isothermen bzw. Eigenschaften. Ortho- $[\text{Zn}(\text{bpe})]$ hat eine deutlich niedrigere Wasser-Aufnahme als $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$. In beiden Fällen sind große Hysteresen zu erkennen. Im Vergleich hierzu, wurde in den MOFs, welche auf dem Acetylendicarboxylat-Linker basieren, deutlich hydrophileres Verhalten mit schmalen Hysteresen beobachtet. In diesen Arbeiten wurde das Aufnahmeverhalten der hohen Hydrophilie der $-\text{C}\equiv\text{C}-$ Dreifachbindung zugeschrieben. Gleichzeitig besitzen diese MOFs eine Vielzahl an hydrophilen Gruppen in deren $\{\text{M}_6(\mu_3\text{-OH})_4(\mu_3\text{-O})_4(\text{O}_2\text{C-})_{12}\}$ -SBUs ($\text{M} = \text{Zr}, \text{Hf}, \text{Ce}$). Während die hydrophilen Stellen in ortho- $[\text{Zn}(\text{bpe})]$ vollständig fehlen, sind diese in $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ vorhanden. Dennoch ist zu sehen, dass der verwendete Bis-Pyrazolat-Linker eher hydrophob ist und dem Einfluss der hydrophilen Gruppen in $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ entgegenwirkt.

Sowohl nach der Wasser-Sorption als auch nach weiteren Stabilitätstest zeigte sich, dass beide MOFs in Wasser und in wässriger ein-molarer Kaliumhydroxid-Lösung stabil sind.

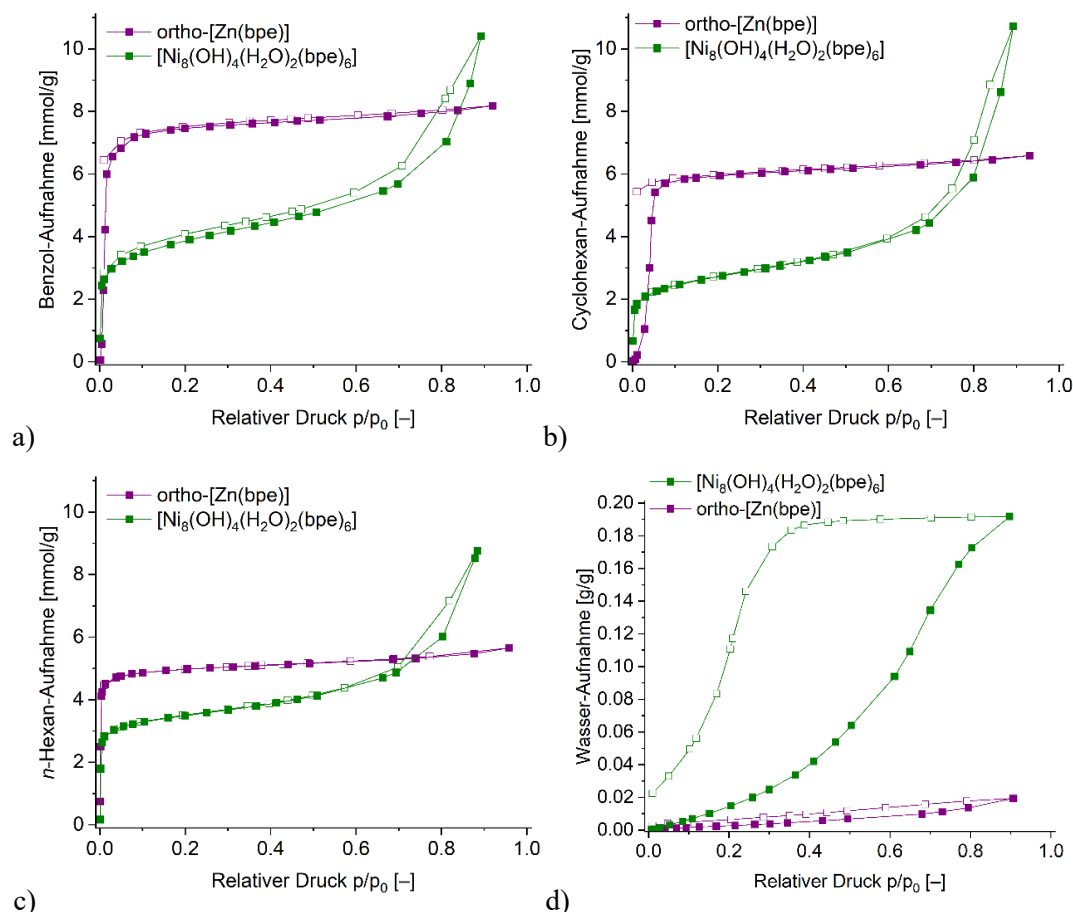


Abbildung 30. Dampf-Sorptionsisotherme für ortho-[Zn(bpe)] und $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ bei 293 K für a) Benzol, b) Cyclohexan, c) *n*-Hexan und d) Wasser. Die Abbildung wurde mit Genehmigung von Ref. 125 reproduziert und ins Deutsche übersetzt. Copyright ©2024, American Chemical Society.

Zusammenfassend wurden in dem zweiten Teil dieser Arbeit zwei neue MOFs, ortho-[Zn(bpe)] (HHUD-5) und $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6]$ (HHUD-6), sowohl strukturell als auch hinsichtlich des Sorptionsverhaltens vorgestellt. Hierbei konnte ein vermeintlicher Vorteil der $\text{-C}\equiv\text{C-}$ -Dreifachbindung gegenüber einer Phenylen-Einheit beim Vergleich mit der Literatur sowie der Hydrophilie-Unterschied zwischen den auf Acetylen-Einheiten basierenden Bis-Pyrazolat- und Bis-Carboxylat-Linker herausgestellt werden.

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