

**Phosphonate-Based Coordination Polymers: Advancing
Stability and Performance for Electrochemical Energy
Storage in Aqueous Media**

Inaugural Dissertation

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submitted by

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Ich, Tim Müller, 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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LLMs in Form von ChatGPT (Model GPT 5.2 Thinking), sowie DeepL Pro wurden in dieser Dissertation ausschließlich zur sprachlichen Glättung und stilistischen Überarbeitung verwendet. Inhaltliche Aussagen, Interpretationen, Schlussfolgerungen und Literaturangaben wurden vor und nach der KI gestützten sprachlichen Überarbeitung sorgfältig geprüft. Ich übernehme die volle Verantwortung für sämtliche Inhalte dieser Arbeit.

Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt. Es wurden keine früheren erfolglosen Promotionsversuche unternommen.

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Kurzzusammenfassung

Die vorliegende Arbeit adressiert die begrenzte Langzeitstabilität vieler etablierter Elektrodenmaterialien in wässrigen Superkondensatoren. Besonders unter stark sauren oder stark alkalischen Bedingungen sowie in konzentrierten Salzlösungen begünstigen Auflösung, Oxidation, Quellung und strukturelle Degradation einen Leistungsabfall und erschweren die Interpretation von Alterungsmechanismen. Insbesondere konventionelle MOFs auf Basis von Carboxylat Linkern sind durch geringe intrinsische Leitfähigkeit und häufig unzureichende Hydrolysestabilität limitiert. Dadurch werden Ligandenaustausch, die Auflösung der Knotenpunkte und ein Kollabieren des Netzwerkes begünstigt.

Vor diesem Hintergrund verfolgt die Dissertation das Ziel, die Rolle phosphonatbasierter Koordinationsnetzwerke als hydrolytisch robuste und zugleich elektrochemisch abstimmbare Elektrodenmaterialien für die Energiespeicherung in wässrigen Elektrolyten weiter zu schärfen und durch belastbare Struktur-Eigenschafts-Beziehung zu untermauern. Der Ansatz beruht auf dem HSAB Konzept, das für harte und mittelharte Metalle starke Metall Sauerstoff Phosphor Bindungen mit Phosphonsäuren als Linkern vorhersagt. Dadurch können Hydrolyse, Ligandenaustausch und Metallauslösung im Vergleich zu vielen Carboxylat Netzwerken reduziert werden.

Im Rahmen dieser Arbeit wurden mehrere Projekte durchgeführt. Zunächst wurden Lanthanoid-Phosphonate mit Diamantane-4,9-Diphosphonsäure als Materialien für Sensorik und potenziell protonenleitfähige Materialien synthetisiert. Da Reproduzierbarkeit und isolierte Ausbeuten nicht ausreichend waren, wurde dieser Strang nicht weiterverfolgt. Im Fokus standen anschließend redoxaktive Cu/V sowie Ni/V basierte Metallphosphonate. Beide wurden als hochkristalline Feststoffe unter hydrothermalen Bedingungen hergestellt und hinsichtlich chemischer Stabilität und elektrochemischer Aktivität untersucht.

[Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] zeigt, dass robuste Phosphonat-Netzwerke in neutralen, wässrigen Elektrolyten elektrochemisch aktiv bleiben, ohne auf stark konzentrierte Säuren oder Basen angewiesen zu sein. Unter mild sauren und mild alkalischen Bedingungen werden spezifische Kapazitäten von etwa 140 F g⁻¹ bei 1 mV s⁻¹ erreicht, während die Kinetik in neutralen Salzelektrolyten stärker limitiert ist und die reversible Redoxreaktion entsprechend langsamer verläuft. Gleichzeitig wurde die Bedeutung belastbarer Post-Cycling Charakterisierung hervorgehoben, da Aussagen zur Phasenstabilität deutlich belastbarer sind, wenn sie nicht nur über Morphologie, sondern zusätzlich über phasensensitive Methoden wie Pulver-Röntgendiffraktometrie und Spektroskopie gestützt werden.

Im letzten Projekt wurde ein anionisches Vanadiumphosphonat-MOF, [Ni(2,2'-bpy)₃]²⁺[(VO(H₂O))₂(VO)₄(μ-O)₂(C₆H₅PO₃)₆]²⁻·2H₂O, synthetisiert, das redoxaktive Kationenkomplexe vom Typ [Ni(2,2'-bpy)₃]²⁺ enthält. Dadurch ließ sich die Dichte an redoxaktiven Stellen erhöhen, während die chemische Robustheit des Phosphonatrückgrats erhalten blieb. In 1 M Na₂SO₄ erreicht das Material in galvanostatischen Messungen 79 F g⁻¹ bei 1 A g⁻¹, während zyklische Voltammetrie bei 1 mV s⁻¹ eine deutlich höhere integrierte Kapazität von etwa 300 F g⁻¹ ergibt, was den starken Einfluss der Scan-Rate und der zugänglichen Redoxprozesse auf die scheinbare Kapazität unterstreicht. Nach einer kurzen Aktivierungsphase von etwa 200 Zyklen, in der der Kapazitätserhalt kontinuierlich ansteigt, erreicht er etwa 98% und bleibt über 10000 Zyklen im Wesentlichen konstant, ohne einen erkennbaren Abfall. Dies

weist auf eine sehr hohe Zyklenstabilität in 1 M Na₂SO₄ bei pH 7 hin. Darüber hinaus zeigt sich eine hohe chemische Stabilität in einem moderaten pH Bereich von 2 bis 10 über einen Zeitraum von mindestens einer Woche unter konstantem Rühren, bestätigt durch sowohl PXRD Messungen als auch REM Bilder mit EDX-Mapping. Damit wird demonstriert, dass mehrere redoxaktive Zentren in phosphonatbasierte Koordinationsnetzwerke integrierbar sind, ohne die Hydrolysestabilität zu verlieren. Die vorliegende Arbeit zeigt damit, dass Phosphonat-Koordinationspolymeren und Phosphonat-MOFs vielversprechende, noch unzureichend untersuchte Materialien zur Energiespeicherung in wässrigen Medien darstellen.

Abstract

This thesis addresses the limited long-term stability of many established electrode materials in aqueous supercapacitors. Particularly under strongly acidic or strongly alkaline conditions and in concentrated salt solutions, dissolution, oxidation, swelling and structural degradation promote a drop in performance and make it difficult to interpret ageing mechanisms. Conventional MOFs based on carboxylate linkers are particularly limited by low intrinsic conductivity and often insufficient hydrolysis stability. This promotes ligand exchange, dissolution of the nodes and collapse of the network.

Against this background, the dissertation aims to further refine the role of phosphonate-based coordination networks as hydrolytically robust and simultaneously electrochemically tunable electrode materials for energy storage in aqueous electrolytes and to underpin this with robust structure-property relationships. The approach is based on the HSAB concept, which predicts strong metal-oxygen-phosphorus bonds with phosphonic acids as linkers for hard and medium-hard metals. This reduces hydrolysis, ligand exchange and metal leaching compared to many carboxylate networks.

Several projects were carried out as part of this work. First, lanthanide phosphonates with diamantane-4,9-diphosphonic acid were synthesized as materials for sensor technology and potentially proton-conductive materials. As reproducibility and isolated yields were insufficient, this strand was not pursued further. The focus then shifted to redox-active Cu/V and Ni/V-based metal phosphonates. Both were produced as highly crystalline solids under hydrothermal conditions and investigated in terms of chemical stability and electrochemical activity.

[Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] shows that robust phosphonate networks remain electrochemically active in neutral aqueous electrolytes without relying on highly concentrated acids or bases. Under mildly acidic and mildly alkaline conditions, specific capacitances of about 140 F g⁻¹ at 1 mV s⁻¹ are achieved, whereas kinetics in neutral salt electrolytes are more strongly limited and the reversible redox response is correspondingly slower. At the same time, the importance of robust post cycling characterisation was emphasized, as statements on phase stability are significantly more reliable when they are supported not only by morphology but also by phase sensitive methods such as powder X ray diffraction and spectroscopy.

In the last project, an anionic vanadium phosphonate MOF, [Ni(2,2'-bpy)₃]²⁺ [(VO(H₂O))₂(VO)₄(μ-O)₂(C₆H₅PO₃)₆]²⁻·2H₂O, was synthesized, which contains redox-active cation complexes of the type [Ni(2,2'-bpy)₃]²⁺. This increased the density of redox-active sites while maintaining the chemical robustness of the phosphonate backbone. In 1 M Na₂SO₄, the material achieves 79 F g⁻¹ at 1 A g⁻¹ in galvanostatic measurements, while cyclic voltammetry at 1 mV s⁻¹ yields a significantly higher integrated capacitance of approximately 300 F g⁻¹,

underscoring the strong influence of the scan rate and accessible redox processes on the apparent capacity. After a short activation phase of about 200 cycles, during which the capacity retention increases continuously, it reaches about 98% and remains essentially constant over 10000 cycles without any noticeable decline. This indicates very high cycle stability in 1 M Na₂SO₄ at pH 7. In addition, high chemical stability is demonstrated in a moderate pH range of 2 to 10 over a period of at least one week under constant stirring, confirmed by both PXRD measurements and SEM images with EDX mapping. This demonstrates that multiple redox-active centres can be integrated into phosphonate-based coordination networks without losing hydrolysis stability. The present work thus shows that phosphonate coordination polymers and phosphonate MOFs are promising yet insufficiently investigated materials for energy storage in aqueous media.

List of publications

This cumulative dissertation was completed between July 2022 and February 2026 at the Institute of Inorganic Chemistry and Structural Chemistry I at Heinrich Heine University Düsseldorf under the supervision of Dr Gündoğ Yücesan and Prof. Dr Christoph Janiak. This work resulted from the following publications:

First author publications:

- (1) T. Müller, P. Ferber, P. M. Roos, N. Assahub, C. Janiak: „Lanthanide Coordination Networks Based on Diamantane-4,9-Diphosphonic Acid”.

Z. Anorg. Allg. Chem. **2025**, e202500158. DOI: 10.1002/zaac.202500158

- (2) T. Müller, J. G. A. Ruthes, B. Batacharya, D. Silbernagl, P. Tholen, A. Limon, G. Kinik, C. Janiak, M. Suta, F. Emmerling, V. Presser, G. Yücesan: „Where Most Frameworks Degrade: Flexible Bimetallic Phosphonate Crystals as pH-Universal Supercapacitor Electrodes”.

Adv. Funct. Mater. **2026**, 0:e00026. DOI: 10.1002/adfm.202600026

- (3) T. Müller, J. G. A. Ruthes, L. Wagner, A. Quade, Y. Zorlu, J. C. Goldschmidt, O. Janka, R. Feyerherm, G. Hanna, V. Presser, G. Yücesan: „A pH-Tolerant Nickel–Vanadium Phosphonate Metal-Organic Framework for Stable Aqueous Supercapacitor Cycling”.

Submitted manuscript.

Co-author publications:

- (4) D. N. Jordan, T. Müller, R. Oestreich, T. Strothmann, I. Boldog, C. 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

List of abbreviations

Abbreviation	Definition
1D, 2D, 3D	One-, two-, three-dimensional
2,2'-bpy	2,2'-bipyridine
AAS	Atomic absorption spectroscopy
AC	Activated carbon
AFM	Atomic force microscopy
AI	Artificial intelligence
ASCs	Asymmetric supercapacitors
BET	Brunauer, Emmett, Teller
BDC	1,4-benzenedicarboxylate
BPDC	4,4'-biphenyldicarboxylate
CN	Coordination network
CNT(s)	Carbon nanotube(s)
COF	Covalent organic framework
CP	Coordination polymer
C _{sp}	Specific capacitance
CV	Cyclic voltammogram
CVD	Chemical vapor deposition
DABCO	1,4,diazabicyclo[2.2.2]octane
Diam	Diamantane
DMF	N,N-dimethylformamide
DMSO	Dimethyl sulfoxide
e. g.	for example (exempli gratia)
EDL	Electric double layer
EDLC	Electric double layer capacitor
EIS	Electrochemical impedance spectroscopy
ESS	Energy storage system
GCD	Galvanostatic charge/discharge
GO	Graphene oxide
H ₄ HEDP	1-hydroxyethane-1,1-diphosphonic acid
HER	Hydrogen evolution reaction
HF	Hydrofluoric acid
HHTP	2,3,6,7,10,11-hexahydroxytriphenylene
HITP	2,3,6,7,10,11-hexaaminotriphenylene
HKUST	Hong Kong University of Science and Technology
HSAB	Hard and Soft Acids and Bases
HSCs	Hybrid supercapacitors
HTFA	Trifluoroacetic acid
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IR	Infrared spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
L	Linker (ligand)
Ln	Lanthanide

M	Molar concentration (mol L^{-1})
MIL	Materials Institute Lavoisier
MOF	Metal-organic framework
MWCNTs	Multi-walled carbon nanotubes
OER	Oxygen evolution reaction
OFG	Oxygen functional groups
PANI	Polyaniline
PCN	Porous Coordination Network
PEDOT	Poly(3,4-ethylenedioxythiophene)
PPA	Phenylphosphonic acid
PXRD	Powder X-ray diffraction
PVA	Poly(vinyl alcohol)
rGO	Reduced graphene oxide
SBU	Secondary building unit
SC	Supercapacitor
SEM-EDX	Scanning electron microscopy with energy dispersive X-ray spectroscopy
SSA	Specific surface area
STA	St. Andrews
SWCNTs	Single-walled carbon nanotubes
TEABF ₄	Tetraethylammonium tetrafluoroborate
TGA	Thermogravimetric analysis
TPDC	4,4''-terphenyldicarboxylate
TUB	Technische Universität Berlin
UiO	Universitetet i Oslo
VdW	Van der Waals
VOC	Volatile organic compound
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZIF	Zeolitic Imidazolate Framework

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Chapter 1: Introduction

1.1 The increasing demand for advanced energy storage systems

Global energy demand keeps increasing, primarily due to population growth and because industrial production continues to rise. At the same time, anthropogenic climate change is linked to high greenhouse gas emissions from burning fossil fuels [1]. This makes a higher share of renewable energies in the energy supply necessary [1, 2, 3, 4]. In 2024, the global energy demand increased by 2.2%, nearly double the ten year average. A major part of this came from the electricity sector, where demand increased by 4.3%, reflecting the particularly strong growth in the power sector [2]. Important drivers were the increased use of air conditioning systems, the electrification of industry and transportation, and the fast growth of data centres and artificial intelligence (AI) related infrastructure [2, 4, 5, 6]. As a result, investment in clean energy systems as an alternative to fossil fuels has become a strategic priority, supported by policy frameworks such as the European Green Deal [3, 7, 8].

One problem of many renewable power sources is their intermittency. This leads to a temporal mismatch between energy generation and demand and therefore requires a significant energy storage capacity [9]. If the storage is not sufficient, fluctuations in supply can disturb stable grid operation, causing voltage deviations and inefficient balancing done by conventional power plants [10, 11]. That is why energy storage systems (ESS) play an important role in bridging this gap, and contribute to enhanced flexibility, resilience, and reliability of modern electricity grids [12, 13, 14]. In practice, integrating renewables in an efficient way usually needs a portfolio of different storage technologies, so that overall system efficiency improves [15]. **Table 1** gives a comprehensive classification of ESS. In addition, the increasing electrification of industrial processes, heating, and transportation significantly amplifies the demand for rapidly available electrical energy [16].

Table 1. Classification of energy storage systems (ESS) [17].

Mechanical	Thermal	Electrochemical	Electrical	Chemical
– Pumped Hydro Storage – Compressed Air Energy Storage – Flywheels	– Sensible Molten Salt – Phase Change Materials – Latent Heat	– Lithium Ion – Sodium Ion – Lead Acid – Sodium Sulphur – Nickel Cadmium – Redox Flow – Solid-State	– Capacitors – Supercapacitors – Superconductive Magnetic Energy Storage	– Power-to-X – Fuel Cells

As a result, research on advanced energy storage systems has increased strongly. Currently, rechargeable batteries are in a leading position because they offer relatively high energy density, they can easily be scaled from single cells to large packs, and industrial manufacturing lines already exist. Lithium ion (Li-ion) batteries have become the default choice in portable electronics and electric vehicles and are also becoming more important in stationary energy storage [18]. Even with their high energy density, the achievable power density is often restricted when long cycle life and safe operation are required. This is because high current rates increase polarization, side reactions, and heat generation, which speeds up ageing [19, 20]. In grid applications, frequent

deep cycling, high current peaks, and elevated temperatures can accelerate battery degradation [21].

These limitations show that energy storage technologies, that offer rapid charge/discharge capabilities, high power density, and superior long term stability are needed. Batteries are good for applications requiring charge/discharge cycles ranging from minutes to hours, while conventional capacitors are optimised for very short cycles in the millisecond (ms) to microsecond (μ s) range [22, 23]. Supercapacitors (SCs), also referred to as ultracapacitors, are designed to bridge this gap [24]. In many applications, SCs can be charged and discharged very fast, typically within few seconds to around a minute [25]. This makes them suitable for short term high power tasks, such as regenerative braking or car starters, peak power buffering and power quality support. Some SCs can reach very long cycle life between 10000 and 1000000 charge/discharge cycles, which is important for devices that need to last for a long time and that are cycled very often [26, 27]. The Ragone plot (**Figure 1a**) shows that the power density of SCs can approach, or even overlap with, conventional electrolytic capacitors, while offering energy densities closer to those of batteries at the same time [22]. Although SCs remain more expensive than batteries, the demand for high power storage devices has strongly increased research activities in this area. This development is also connected to the search for electrode materials and new electrolytes that combine high performance with improved durability and cost efficiency [22, 28, 29].

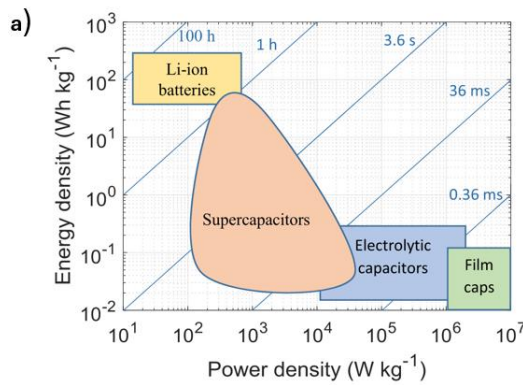


Figure 1. a) Ragone plot of electrical energy storage systems. Characteristic times correspond to lines with unity slope. Modified from Berrueta *et al.*, IEEE Access **2019**, 7, 50869–50896, licensed under CC BY 4.0 [22].

The position of supercapacitors between capacitors and batteries reflects their underlying charge storage mechanisms. Depending on device type, charge storage can happen by electric double layer formation, fast surface redox processes in pseudocapacitors, or by combining both in hybrid supercapacitors [30]. These mechanisms and their implications for materials design are discussed in the following section.

1.2 From Classical Capacitors to Electrochemical Supercapacitors

In a simple capacitor, energy is stored in the electric field between two metal plates. These plates are separated by a dielectric that prevents charge from flowing directly. When a voltage is applied, equal and opposite charges build up on the plate surfaces, so energy is stored purely physical (non-Faradaic) [31]. Batteries, on the other hand, store energy through Faradaic reactions. Charge storage is linked to electrochemical redox processes and goes together with chemical changes in the electrode materials. Dielectric capacitors rely on dielectric polarization to store electrical energy. Because they can provide very high power density and extremely fast discharge, they are widely used in pulsed power electronics. Still, their practical energy density remains limited [23]. Research on dielectric materials, including ceramic films, tries to improve energy density and

efficiency, but the limits of planar electrodes and finite dielectric thickness remain [31, 32, 33, 34, 35]. The basic concept is shown in **Figure 2**.

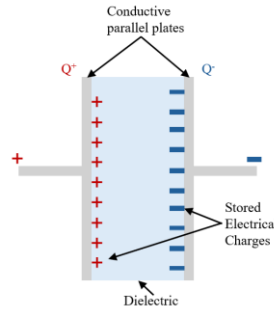


Figure 2. Schematic representation of a dielectric capacitor.

To avoid these geometric limits, supercapacitors (SCs) store charge at the electrode/electrolyte interface and can additionally use fast, near surface Faradaic processes, depending on the electrode chemistry [36, 37]. Depending on the device design, charge storage is reached either by mainly non-Faradaic electric double layer formation (EDL), in which ions are physically adsorbed at the electrode surface, or by mainly Faradaic surface redox processes in pseudocapacitors, or by a combination of both mechanisms in hybrid supercapacitors [37]. This combination places SCs between traditional capacitors and batteries, offering higher energy densities than dielectric capacitors while maintaining high power density and excellent cycling stability [38]. An overview of the most important supercapacitor types, their charge storage mechanisms and representative electrode materials is presented in **Figure 3**.

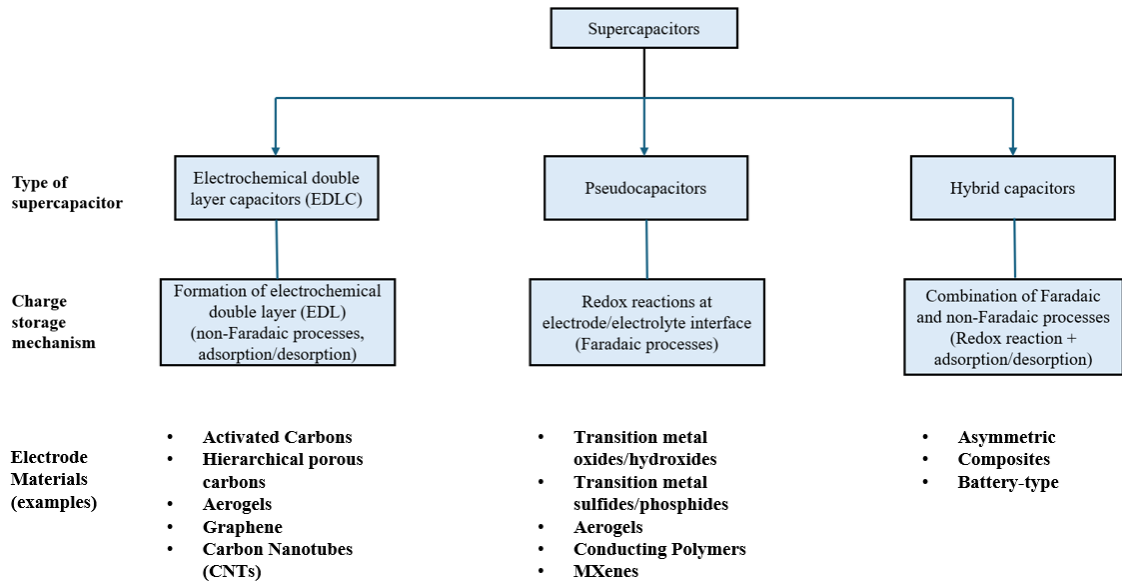


Figure 3. Classification of supercapacitor types, charge storage mechanisms, and examples of electrode materials.

Structurally, a supercapacitor has the same basic design as a conventional electrochemical cell. It consists of a positive and a negative electrode with an ion permeable separator between them. The separator prevents electrical short circuits while enabling ionic transport. In symmetric SCs, the same active material is used at both electrodes, whereas asymmetric SCs employ different materials on the positive and negative sides to enlarge the operating voltage window and enhance energy density. In all cases, the active materials are typically coated onto metallic current collectors, which provide efficient electronic conduction to the external circuit [39]. In

electrochemical double layer capacitors, porous carbon materials are used to provide a large accessible surface area for charge storage, while pseudocapacitors typically use redox-active materials. In these materials, fast and reversible Faradaic redox reactions at or near the surface make an important contribution to the measured capacitance. Hybrid capacitors combine both types of electrodes to integrate double layer and pseudocapacitive contributions within a single device and thereby push the trade-off between energy and power to more favourable regimes [40, 41]. The electrolyte is another critical design parameter, as it controls ionic conductivity, the accessible potential window and interfacial stability. The electrolyte thus influences the achievable specific capacitance (C_{sp}), the performance at high discharge rates, the electrochemical stability window, and the long term performance of supercapacitors [29, 42]. Electrolytes are generally categorized into liquid types, including aqueous (acidic, neutral, and alkaline), organic, and ionic liquids, as well as solid state and redox-active electrolytes [43]. Each class comes with their own trade-offs, for example, aqueous electrolytes are limited by a narrow potential window, while organic electrolytes often suffer from volatility and flammability concerns [41, 43, 44, 45].

Since both the electrolyte and electrode materials determine how ions and electrons are stored, the resulting charge storage mechanisms vary significantly depending on the device type [46]. These fundamental mechanisms are illustrated schematically in **Figure 4**.

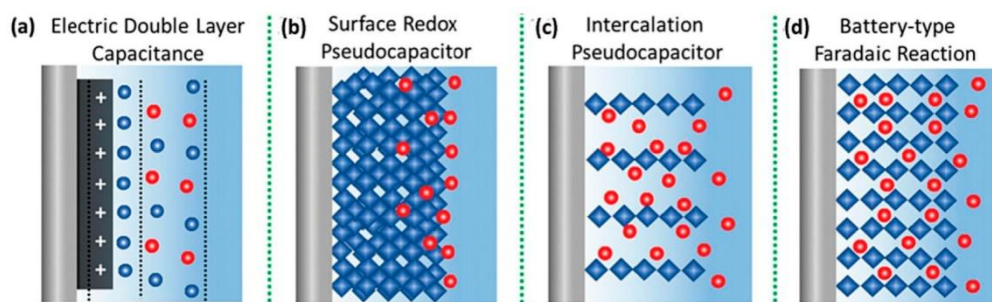


Figure 4. Schematic illustration of the energy storage mechanisms of (a) EDLC, (b) Surface Redox Pseudocapacitor, (c) Intercalation Pseudocapacitor, (d) Battery-type Faradaic Reaction (Hybrid SC). Reproduced from Gao et al., *Inorganics* **2025**, *13*, 49, licensed under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>) [46].

1.2.1 Electric Double layer Capacitors (EDLCs)

EDLCs store electrical energy by electrostatic ion accumulation at the interface between the electrolyte and the electrode surface. When a voltage is applied, ions rearrange. Cations move to the negatively polarised electrode, and anions move to the positively polarised electrode. This forms two charge separated layers at the interface, one at the charged electrode surface and the other made of counter ions from the electrolyte [47, 48]. In ideal EDLCs, no charge transfer takes place across the interface. Instead, energy is stored and released by physical adsorption and desorption of ions. Because adsorption and desorption are much faster than Faradaic redox reactions, EDLCs can charge and discharge fast and they also show excellent long term cycling stability [49]. Over the past decades, several models have been developed to describe the formation and structure of the electric double layer (EDL) at the electrode/electrolyte interface [50].

As a simple way to describe electric double layer charge storage in capacitors and supercapacitors, the Stern model is often used as a practical baseline [51]. It assumes a compact layer of counter ions close to the electrode, in series with a diffuse ion layer in the electrolyte, and it treats the interface in a simplified continuum picture with a mean field ion distribution [52, 53]. In this model, the double layer capacitance is mainly influenced by the accessible surface area, the effective ion electrode separation and dielectric properties in the compact layer, and the ionic

strength that sets the diffuse layer thickness. At the same time, specific adsorption and pore confinement can lead to deviations in real porous electrodes [52, 54].

Beyond the interfacial structure itself, the specific capacitance is also influenced by the nature and conductivity of the electrode material, the size and valence of the ions, and the pore structure and accessibility of the electrode [55]. When pore dimensions get close to the diameter of solvated ions, partial desolvation can occur when ions enter the confined pore space. This allows counter ions to approach the carbon surface more closely and can increase the local electric field. As a result, capacitance in sub nanometre pores can exceed values predicted by idealised Helmholtz Stern behaviour [54, 56, 57]. This pore and solvation dependence provides a natural bridge to redox-active charge storage mechanisms, which can further increase the apparent capacitance beyond purely electrostatic double layer formation.

1.2.2 Pseudocapacitors

Unlike EDLCs, which store charge primarily through electrostatic ion adsorption at the electrolyte/electrode interface, pseudocapacitors store energy via fast and reversible Faradaic reactions. These processes take place at or near the electrode surface and, in some cases, within accessible lattice sites of the active material. By exploiting electron transfer reactions rather than purely dielectric polarization, pseudocapacitors can achieve specific capacitances significantly higher than those of typical carbon-based EDLCs.

It is important to note that despite the Faradaic nature of the underlying charge-storage mechanism, the electrochemical response of an ideal pseudocapacitor remains capacitive. The potential varies approximately linearly with the stored charge. Cyclic voltammograms (CV curves) display a quasi-rectangular shape, and galvanostatic charge-discharge curves are nearly linear in time. This is different from diffusion controlled battery-type behaviour, where phase transformations or slow solid state diffusion lead to clear plateaus and sharp redox features [58, 59, 60]. Depending on the material and the physical process involved, pseudocapacitance is typically categorized into two main mechanisms, as shown schematically in **Figure 4b** and **c** [61].

1. Surface Redox Pseudocapacitance: In surface redox pseudocapacitors, ions from the electrolyte are electrochemically adsorbed on the electrode surface or within a near surface region, together with a Faradaic charge transfer step. Typical examples include the surface protonation/deprotonation or cation adsorption at transition metal oxides such as RuO₂ or NiO or conducting polymers, such as polyaniline [61, 62, 63]. Because these reactions are mainly limited to the surface (or a thin surface layer) and proceed without a clear bulk phase transformation, the electrode can show a capacitive-like response. The CV curves remain nearly rectangular, and the charge-discharge profiles are close to linear, even though the stored charge is associated with redox processes rather than pure double layer formation [64].

2. Intercalation Pseudocapacitance: Intercalation pseudocapacitance occurs when ions insert into crystallographic tunnels, interlayers, or other accessible lattice sites of a redox-active host, again together with electron transfer but without a two phase transition of the host structure [59, 65]. In contrast to classical battery type intercalation, the insertion process is fast enough and sufficiently uniform that the electrode keeps a pseudocapacitive electrochemical signature. The potential varies roughly linearly with the state of charge, and the CV shows broad, featureless capacitive currents rather than sharp redox peaks. Importantly, distinct redox peaks do not automatically exclude pseudocapacitive charge storage. In many real materials, especially when multiple redox couples contribute or when insertion steps are limited to narrower potential

intervals, peak shaped CV features can coexist with mainly capacitive kinetics. The classification therefore depends on the rate determining kinetics and the absence of a diffusion limited two phase transformation, rather than on the complete absence of peaks [63, 66, 67]. Prototypical materials include Nb₂O₅-based systems and several MXenes, in which cations can intercalate into layered or tunnel structures over a wide potential range at high rates [68, 69].

These mechanistic archetypes are directly relevant for this thesis. Many coordination networks (CNs) and metal phosphonate frameworks combine redox-active metal centres with accessible channels, tunnels, or interlayer spaces. Such architectures can, hypothetically, support both surface confined redox pseudocapacitance and shallow intercalation type storage in aqueous electrolytes [70]. Establishing and using this behaviour in structurally robust, hydrolytically stable phosphonate-based networks is therefore a key motivation for the material developments presented in the later chapters of this work.

1.2.3 Hybrid Supercapacitors and Asymmetric Supercapacitors

Hybrid supercapacitors (HSCs) consist of two different electrodes, resulting in an asymmetric configuration. A typical example is the combination of an EDLC-type electrode, such as a porous carbon material serving as the negative electrode, with a battery-type positive electrode such as PbO₂ or Ni(OH)₂ [71]. This can allow a higher cell voltage and therefore a wider operating potential window of the device, which can increase device level energy density within the stability limits of aqueous electrolytes [72, 73]. The term HSC is often used when the two electrodes operate by different charge storage mechanisms, while asymmetric supercapacitors (ASCs) are a broader descriptor that can also refer to cells with unequal mass loadings or different materials that do not necessarily combine distinct mechanisms. Following Brousse et al., ASC can be limited to systems in which at least one electrode shows capacitive or pseudocapacitive behaviour [71, 74]. The main goal of hybrid and asymmetric configurations is to combine high power capability and long cycling stability of EDLC electrodes with the higher energy density of battery-type materials [75].

It is worth noting that phosphate and phosphonate-based electrodes are evaluated in asymmetric or hybrid configurations, where a pseudocapacitive positive electrode is paired with a carbonaceous negative electrode to exploit a wider cell voltage in aqueous electrolytes [76, 77]. Reports on nickel phosphate or nickel organophosphonate positive electrodes combined with activated carbon can show higher device level energy density while maintaining good cycle stability, highlighting phosphonate derived frameworks as practical candidates for robust positive electrodes [78]. Metal phosphonate frameworks can link these design ideas in one material. Many of them have pores, channels, or layered spaces, so ions can move through the structure and reach more accessible surface area for charge storage. At the same time, the metal centres in the inorganic units, preferably transition metals, can act as redox sites and enable fast surface, or near surface, reactions, which adds a pseudocapacitive contribution on top of double layer charging [79, 80, 81]. Accordingly, both electrode roles are important with porous carbons as the EDLC benchmark and robust redox-active frameworks as pseudocapacitive positives, which motivates the broad material overview in the following section.

1.3 Electrode Materials for Supercapacitors

The electrochemical performance of supercapacitors is largely determined by the type and structure of their electrode materials. Current research distinguishes several main classes, including carbon materials, transition metal oxides and hydroxides, conducting polymers,

MXenes, and coordination network materials such as MOFs and phosphonate frameworks. Each class shows its own characteristic charge storage behaviour and a specific ratio of accessible surface area, redox site density, electronic transport, ion transport, and processability. Together, these factors determine specific capacitance, rate capability, and device level energy and power.

For established electrode families, the main limitation in aqueous supercapacitors rarely lies in a single parameter, but rather in the way in which chemistry, structure and interfaces change during long term cycling. Typical failure mechanisms include hydrolysis or ligand exchange for coordination-based solids, metal leaching and phase reconstruction in redox-active oxides, carbon oxidation, gas evolution and wettability changes at positive potentials, and loss of contact due to swelling, restacking, delamination, or mechanical fatigue [82, 83]. The following sections therefore discuss each material class with a focus on performance limiting degradation pathways under aqueous conditions, as the primary motivation for chemically robust phosphonate-based coordination networks.

1.3.1 Porous Carbon Materials

Porous carbon materials are among the most mature and widely used family of electrode materials for electric double layer capacitors (EDLCs) and hybrid supercapacitors, because they are low cost, have established processing routes, and tunable pore structure. Carbon-based electrodes store charge by the reversible adsorption of ions at the electrode/electrolyte interface rather than by Faradaic redox processes, showing an EDLC type behaviour. This charge storage mechanism enables excellent rate performance and long term cycling stability [84, 85, 86, 87]. Still, the use of porous carbons is not without limitations, which must be considered when comparing them to emerging electrode material classes. In aqueous electrolytes, carbon electrodes are typically limited by the narrow thermodynamic stability window of water and by parasitic surface reactions that become increasingly relevant at elevated polarisation. This limits the usable cell voltage and therefore energy density even when rate capability and cycle life are excellent [82, 88]. Therefore, purely non-Faradaic EDLC carbons are a robust benchmark, but they do not directly solve the need for higher energy storage under aqueous cycling, which motivates the exploration of chemically robust, redox-active materials, including framework type materials [89]. Within this material class, activated carbon (AC), carbon nanotubes (CNTs, including multi-walled CNTs), and graphene (including graphene-based composites) are the three most representative materials used in commercial and research scale supercapacitors. Other carbon materials, such as carbon aerogels, carbide derived or onion like carbon materials are briefly mentioned here only for completeness [84, 90].

1.3.2 Activated Carbon

Activated carbons have long served as a benchmark electrode material for commercial EDLCs. Their high specific surface area (SSA), availability of cheap starting materials such as bio waste or plants, and mature activation technologies (chemical or physical) make them attractive materials for applications [90, 91]. Activated carbon is typically obtained by carbonisation of suitable precursors, followed by physical or chemical activation to generate micro and mesoporous structures. Chemical activation is widely used to maximise porosity and is commonly carried out with agents such as KOH, ZnCl_2 , or H_3PO_4 , with the specific pore architecture depending on reagent choice and process conditions [92, 93]. An overview of common production routes is shown in **Figure 5**.

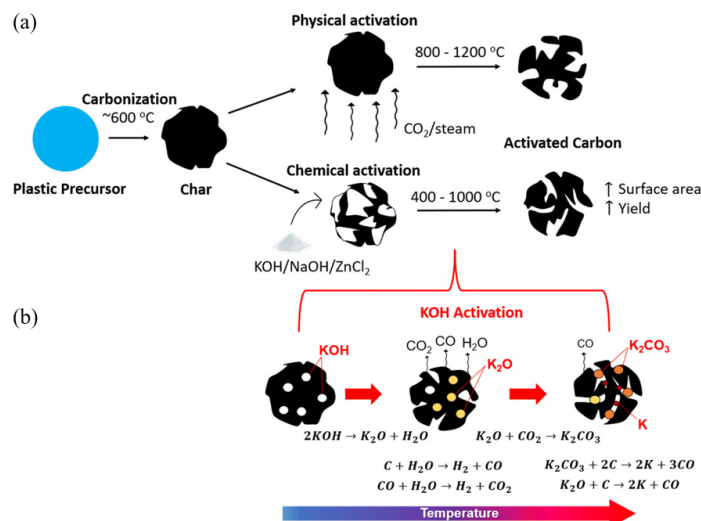


Figure 5. (a) Illustration of activated carbon production through physical versus chemical activation; (b) KOH activation mechanism. Reproduced from R. Blanchard and T. H. Mekonnen, RSC Appl. Polym., 2024, 2, 557 DOI: 10.1039/D4LP00016A, under the terms of the Creative Commons Attribution 3.0 Unported License (<https://creativecommons.org/licenses/by/3.0/>) [93].

Literature comparisons shows that ZnCl₂ or H₃PO₄ activation can provide higher carbon yields, whereas strong base activation, especially KOH, can yield among the reported highest SSA values, with reported values up to 4200 m² g⁻¹ [94, 95, 96, 97, 98]. Besides the total surface area, pore size distribution is also important. Narrow micropores, especially below 1 nm, can show a stronger than expected increase in capacitance when their size becomes similar to the size of the bare ion, which fits with partial desolvation effects discussed in Section 1.2.1 [54, 99]. In common electrolytes such as 6 M KOH, an almost linear correlation between capacitance and SSA is observed. For this, the narrow micropores of many ACs are especially helpful [99, 100].

A schematic comparison of the most important degradation processes is shown in **Figure 6**.

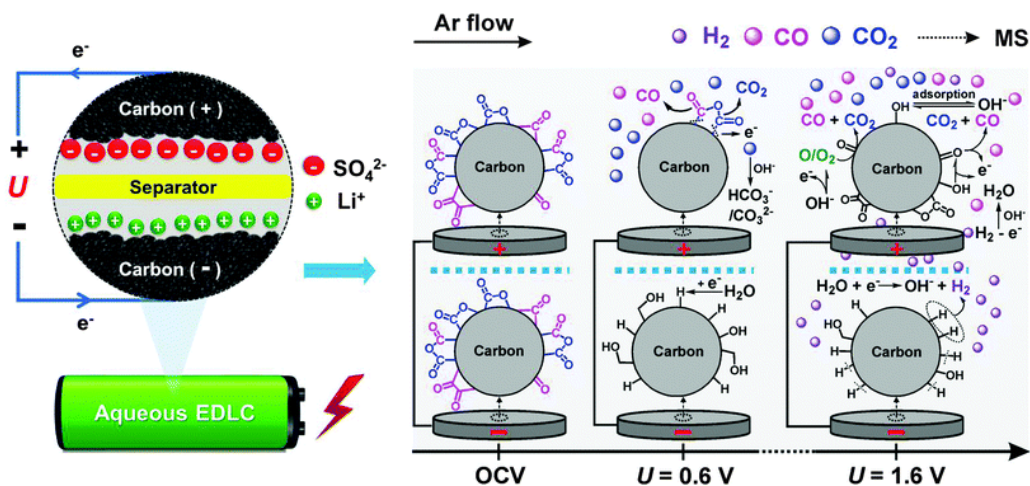


Figure 6. Gas evolution and electrochemical processes occurring on the activated carbon surface at different cell voltages in EDLCs with 1 mol L⁻¹ Li₂SO₄ electrolyte (positively polarized electrode on the top). Reproduced from M. He et al., Energy Environ. Sci., 2016, 9, 623, DOI: 10.1039/C5EE02875B, under the terms of the Creative Commons Attribution–NonCommercial 3.0 License (<https://creativecommons.org/licenses/by-nc/3.0/>) [82].

Several limitations arise in practical electrochemical environments. The inherently hydrophobic surface of many carbons hinders electrolyte wetting and ion transport, particularly in aqueous systems, thereby reducing effective capacitance [84, 90, 101]. In addition, aggressive activation chemistries and high processing temperatures can increase environmental burden, and overactivation may introduce defects or surface functionalities that compromise long term

electrochemical stability [100, 102]. He et al. investigated the behaviour of carbon-based EDLCs in high-voltage aqueous supercapacitors by *in situ* gas analysis using different neutral salt solutions (pH 6–7) [82].

They identified four categories of degradation processes. These are the decomposition of functional groups on the carbon surface, water splitting (HER and OER), carbon corrosion, and chemical or electrochemical gas consumption. These processes are central to long term performance and safety [82, 83]. Despite these limiting factors, carbon electrodes still have a good sustainability profile, because they can be produced from renewable or waste precursors and rely on comparatively scalable processing, while delivering excellent cycling stability [103, 104].

In summary, activated carbon is a very successful and robust electrode material for commercial supercapacitors, but its performance in aqueous electrolytes is still constrained by surface reactions and gas formation at elevated cell voltages [83]. Accelerated ageing studies under high-voltage floating and cycling further show that electrolyte decomposition, irreversible gas evolution, pore blocking and progressive resistance increase can be main factors for long term performance limits in aqueous carbon/carbon devices [83, 105]. These limitations motivate the development of redox-active electrode materials that remain stable at the electrode-electrolyte interface in aqueous media and additionally enable pseudocapacitive charge storage, rather than relying solely on non-Faraday electric double layer capacitors (EDLCs). This draws attention to metal-phosphonate coordination networks, as strong metal-oxygen-phosphorus bonds can improve chemical stability in water, and transition metal centres provide redox sites for rapid and largely reversible charge storage, often supported by nanostructures or conductive composites [106, 107, 108].

1.3.3 Graphene-based derivatives

Carbon nanotubes (CNTs) and graphene-based carbons, including graphene oxide (GO) and reduced graphene oxide (rGO) (**Figure 7**), are widely studied electrode materials for supercapacitors because they combine high electrical conductivity with a large, potentially accessible surface area [50, 89, 109, 110, 111].

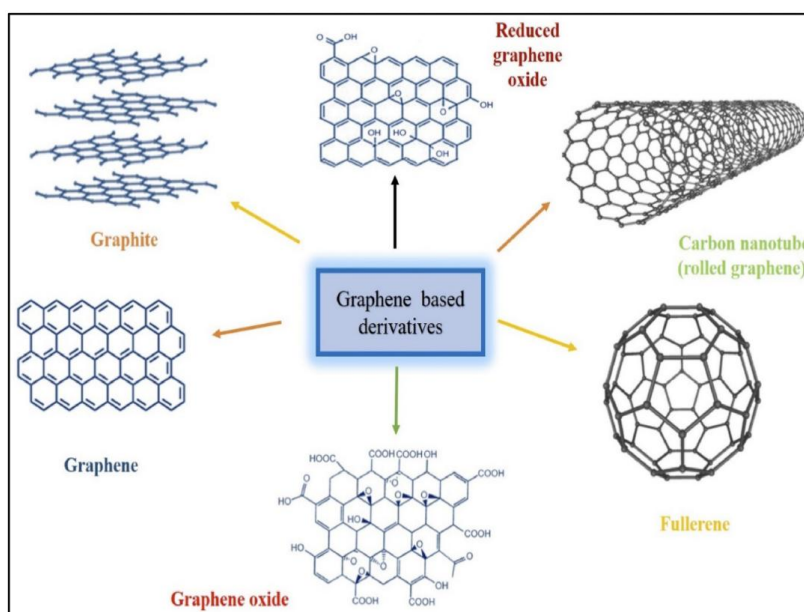


Figure 7. Graphene and its derivatives. Reproduced from S. Kumar et al., *Catalysts* **2023**, *13*, 111, under the terms of the Creative Commons Attribution (CC BY 4.0) [112].

Graphene is a single layer of sp^2 -hybridised carbon atoms arranged in a two-dimensional (2D) hexagonal network. Strong in plane σ -bonding provides a rigid scaffold, while delocalised π -electrons enable high electronic conductivity [113, 114]. Graphene exhibits an high thermal conductivity, an electrical conductivity around $1 \times 10^5 \text{ S m}^{-1}$ and theoretical SSA of about $2630 \text{ m}^2 \text{ g}^{-1}$ [109, 113, 115, 116]. Due to π - π and VdW interactions between its layers and poor solubility of graphene in most solvents, restacking of graphene sheets into graphite like stacks is a common problem, and can drastically reduce the effective SSA [117, 118]. Restacking also reduces ion mobility, which decreases the theoretical maximum capacitance [118, 119, 120]. Because pristine graphene and graphene derivatives such as GO and rGO, as well as carbon nanotubes, remain difficult and expensive to produce at scale, rGO, heteroatom doped graphene, and other readily processable carbon architectures are more practical for real supercapacitor applications [110, 121, 122].

A key advantage of rGO, especially in engineered three-dimensional (3D) structures and composites, is reduced sheet restacking. This helps to preserve electrochemically accessible surface area and improves ion transport, often yielding specific capacitances around 200 to about 350 F g^{-1} [129, 123, 124, 125]. A practical advantage of GO and rGO is their scalable synthesis from abundant graphite via oxidative exfoliation, followed by controlled reduction of GO to rGO [114, 126, 127]. Conventional oxidation often relies on concentrated acids and strong oxidants, which can generate hazardous byproducts and raises safety and sustainability concerns. In addition, carbon electrode processing may involve hazardous activating agents and potential nanomaterial toxicity, so modified and greener protocols have been developed to improve safety and reduce harmful byproducts [128, 129, 130]. In supercapacitors, graphene derived carbons typically provide EDLC charge storage at the electrode/electrolyte interface. In composite systems, the rGO framework, which shows EDLC-type behaviour, ensures good electrical conductivity and structural integrity, while the secondary component contributes pseudocapacitance, prevents aggregation, and supplies additional redox-active sites [131, 132, 133]. This synergistic design can significantly enhance both, energy and power density, and improve cycling stability, making rGO composite electrodes among the most widely used and often competitive carbon-based materials for supercapacitor applications [123, 134, 135]. Still, rGO is not ideal in isolation. Residual oxygen functionalities and structural defects lower conductivity compared with pristine graphene, and higher defect density and oxygen functionalisation can increase resistance. This becomes increasingly important at high current densities, because partial restacking can occur again during cycling, thereby reducing surface accessibility and ion transport [118, 119, 123, 136]. For this reason, many high performance composites employ rGO as a conductive and flexible matrix to improve transport and stabilise the electrode architecture [55, 123, 131, 137].

Carbon nanotubes, CNTs, are one-dimensional (1D) sp^2 -carbon nanostructures. They have the same graphitic bonding as graphene, but they form tubes that can connect sheet-based scaffolds [138, 139]. SWCNTs can be described as rolled graphene sheets, whereas MWCNTs consist of several concentric cylinders. SWCNTs show a relatively high surface area of up to roughly $1600 \text{ m}^2 \text{ g}^{-1}$ and well-defined electronic properties as well as high chemical stability due to the nature of the covalent sp^2 bonds within the graphitic lattice [111, 140, 141, 142]. MWCNTs show lower porosity up to approximately $430 \text{ m}^2 \text{ g}^{-1}$, and the mechanical stability is additionally influenced by the number of sidewalls [143, 144]. When used as the sole active material, CNT electrodes store charge mainly like electric double layer capacitor (EDLC), through reversible, non-Faradaic adsorption of electrolyte ions on the accessible surface area [144]. Reported capacitance values depend strongly on nanotube type, packing density, alignment, and surface

functionalisation, and modest pseudocapacitive contributions may arise from heteroatom groups introduced during purification or oxidation [144, 145, 146]. In practice, the electrochemically accessible surface area is frequently reduced by CNT bundling and entanglement, which increase tortuosity and limit ion access to internal surfaces, so that neat CNT electrodes often deliver only moderate EDLC capacitance despite excellent conductivity [144, 147, 148]. In addition, CNT materials and their processing typically remain costly relative to activated carbon, which limits their attractiveness as a scalable standalone active material [122, 149].

In summary, activated carbon remains a leading commercial choice due to its low cost and scalable production, while graphene derivatives are most valuable as conductive scaffolds in composite electrodes, but also come at a higher cost [89, 150, 151]. In modern supercapacitor design, graphene and its derivatives are therefore mainly used in hybrid and composite electrodes as a conductive and mechanically stable scaffold [152, 153]. A redox-active phase is then deposited on this scaffold, for example transition metal oxides or hydroxides such as MnO_2 or Ni(OH)_2 , or conducting polymers [154, 155, 156]. In such composites, the carbon scaffold provides EDLC type charge storage and efficient electron transport, while the coating adds Faradaic redox reactions. This mixed EDLC and pseudocapacitive behaviour can lead to higher specific capacitances than neat carbon electrodes. Values of up to around 950 F g^{-1} have been reported for MnO_2/CNT , $\text{RuO}_2/\text{graphene foam}$ and RuO_2/CNT composites under the reported conditions [156, 157, 158, 159]. The conductive backbone also buffers mechanical strain and improves rate capability and cycling stability compared with the corresponding pure oxide or polymer electrodes [155, 160, 161]. During long term cycling, performance loss is often linked to changes in the redox-active phase, such as dissolution, cracking, or loss of electrical contact, whereas the carbon framework is usually more stable [83, 162, 163, 164]. Consequently, CNTs are most relevant as supporting components in composite architectures that target higher performance and improved long term stability [165]. Accordingly, carbon scaffolds mainly address electronic transport, whereas higher energy storage under aqueous cycling requires intrinsically redox-active and chemically robust active phases, which motivates metal phosphonate coordination networks as pseudocapacitive components with high structural stability and electrochemical reversibility in supercapacitor electrodes [107, 166].

In many composite electrodes, a carbon additive is used to form conductive pathways and lower the internal resistance, especially when the active material is poorly conductive [167, 168]. In this thesis, the metal phosphonate network is the main redox-active cathode material, and carbon is used mainly as a conductive additive. MXenes similarly show how high conductivity and tuneable surface chemistry can expand the design possibilities for high performance supercapacitor electrodes. Therefore, these are introduced beforehand.

1.3.4 MXenes

MXenes are two-dimensional early transition metal carbides and carbonitrides that have attracted interest as supercapacitor electrodes because they combine high electronic conductivity with redox-active, termination rich surfaces [169, 170]. The first member of this class, $\text{Ti}_3\text{C}_2\text{T}_x$, was reported by Naguib et al. in 2011 [171]. They have the general formula $\text{M}_{n+1}\text{X}_n\text{T}_x$ (**Figure 8**), where M is an early transition metal, such as Ti, Zr, V or Mo, X is carbon and/or nitrogen, T_x represent terminal surface groups such as O-, OH-, F- or Cl-, and n typically takes values between 1 and 3 and can reach 4 in some systems [172]. MXenes originate from layered ternary carbides and nitrides that are known as MAX phases ($\text{M}_{n+1}\text{AX}_n$), by selective removal of the A element from the parent MAX phase with fluorine containing etchants. Commonly used etchants are

hydrofluoric acid or LiF and HCl that generate HF in situ and favour intercalation and delamination [170, 171, 173]. MXenes consist of close packed layers of transition metal atoms with X atoms occupying the octahedral sites between adjacent M layers, forming a hexagonal lattice [171, 174]. The resulting nanosheets show high conductivity and tunable surface chemistry, but their stability in humid air and aqueous media can be limited due to progressive oxidation [175, 176, 177, 178].

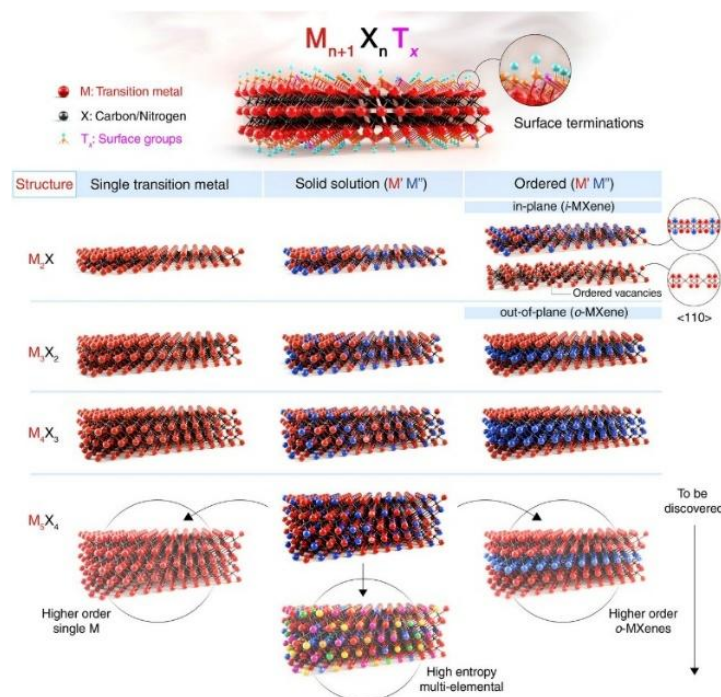


Figure 8. Schematic illustration of the MXene structures and compositional variants. MXenes follow a general formula $M_{n+1}X_nT_x$, where M is an early transition metal, X is C and/or N, and T_x denotes surface terminations, with n typically 1–3 (in some systems up to 4). The M sublattice can form solid solutions or ordered variants, including in plane ordered i-MXenes, vacancy ordered phases, and out of plane ordered o-MXenes. Adapted from A. VahidMohammadi *et al.*, *Science* **2021**, 372, eabf1581. DOI:10.1126/science.abf1581. Reprinted with permission from AAAS [179].

Their two-dimensional morphology enables short ion diffusion paths and good electrolyte access, while the tunable surface chemistry allows control of hydrophilicity and electrochemical activity. MXenes, and $Ti_3C_2T_x$ in particular, show an unusual combination of double layer and pseudocapacitive charge storage, which leads to high gravimetric and also volumetric capacitances [175, 176]. Delaminated $Ti_3C_2T_x$ films typically deliver around 100–350 F g⁻¹ at low current densities in aqueous electrolytes, while volumetric capacitances above 1000 F cm⁻³ have been reported, exceeding conventional porous carbons that often show 100–200 F g⁻¹ and often suffer from lower packing densities [180]. However, as with 2D carbons, restacking and aggregation can reduce the accessible surface area and hinder ion transport, so keeping open architectures is essential [181].

MXene composites with porous carbons can combine MXene conductivity and redox activity with the surface accessibility and structural stability of the carbon host, and specific capacitances above 500 F g⁻¹ with excellent rate performance have been reported for $Ti_3C_2T_x$, carbon nanofiber and related architectures (**Figure 9**) [180]. Compared with transition metal oxides such as MnO_2 or $NiCo_2O_4$, which can show very high gravimetric capacitances but often suffer from poor electrical conductivity and limited rate capability, MXene/oxide hybrids use the MXene sheets as highly conductive current collectors and mechanical buffers, enabling synergistic capacitances a broad range of 300–1600 F g⁻¹ depending on composition and test conditions [182, 183].

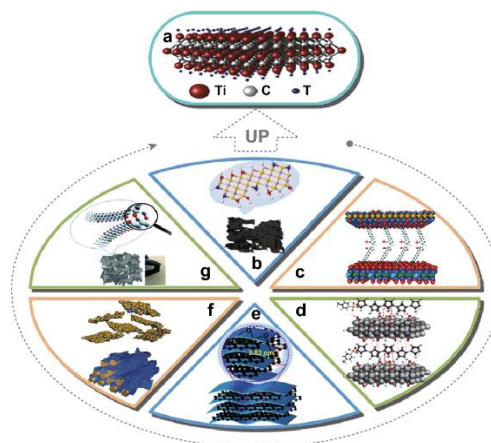


Figure 9. Enhancing the capacitance of $\text{Ti}_3\text{C}_2\text{T}_x$ as electrode materials of supercapacitors. **a** Structure of $\text{Ti}_3\text{C}_2\text{T}_x$. **b** N-doped $\text{Ti}_3\text{C}_2\text{T}_x$. **c** $\text{Ti}_3\text{C}_2\text{T}_x$ /layered metallic double hydroxides. **d** $\text{Ti}_3\text{C}_2\text{T}_x$ /conductive polymers. **e** Carbon-intercalated $\text{Ti}_3\text{C}_2\text{T}_x$ composite paper. **f** $\text{WO}_3/\text{Ti}_3\text{C}_2\text{T}_x$ composite paper. **g** 3D $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels. Reproduced from X. Zang *et al.*, *Nano-Micro Lett.* **2020**, *12*, 77. DOI: 10.1007/s40820-020-0415-5, licensed under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>) [180].

MXene performance can be limited by processing and stability issues. Fluorine etching raises safety and environmental concerns and often yields O-, OH-, F- terminations that are difficult to control. This can influence electrochemical behaviour and reproducibility, motivating fluorine free and scalable routes [184, 185]. MXenes such as $\text{Ti}_3\text{C}_2\text{T}_x$ are sensitive to oxidation in humid air and aqueous media. Oxidation gradually lowers capacitance and changes the structure of the material [186]. Strategies such as surface functionalisation, protective coatings, or non aqueous electrolytes can slow oxidation, but they may also reduce ion mobility and usable capacity [187]. Doo et al. reported that oxidation of aqueous $\text{Ti}_3\text{C}_2\text{T}_x$ suspensions is accelerated under acidic conditions and retarded under basic conditions (**Figure 10**) [188, 189]. Finally, the restacking tendency of MXene sheets, mentioned above, continues to restrict ion accessibility and active surface area. The development of three-dimensional or composite architectures helps to reduce this problem and maintain high performance [184, 190].

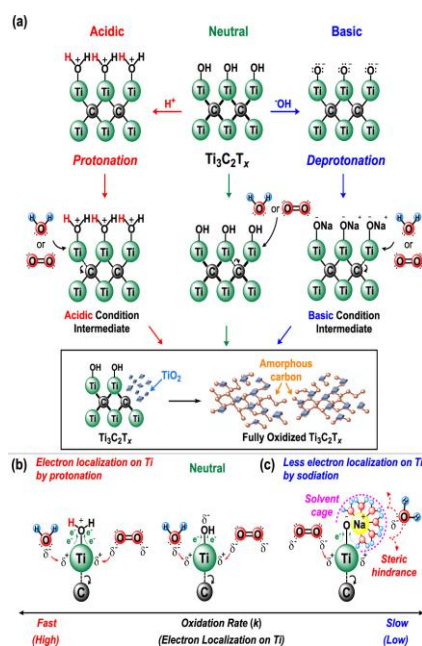


Figure 10. (a) Proposed Mechanism of the Oxidation Reaction of $\text{Ti}_3\text{C}_2\text{T}_x$ Colloids under (b) Acidic and (c) Basic Conditions. Reproduced with permission from S. Doo et al., *ACS Appl. Mater. Interfaces* **2021**, *13* (19). Copyright © 2021, American Chemical Society [188].

For aqueous cathodes, these limits show that high conductivity alone is not enough if the active material changes during cycling, for example by termination drift, oxidation, or structural reconstruction. The key requirement is therefore chemical and structural stability in water, in addition to electronic transport. The following section summarises transition metal oxides as benchmark pseudocapacitive cathodes and outlines their main degradation mechanisms in aqueous electrolytes.

1.3.5 Metal Oxides

Transition metal oxides and hydroxides are widely investigated for supercapacitor electrodes as pseudocapacitive materials, because their multivalent cations enable fast, reversible surface or near surface redox reactions in aqueous electrolytes [59, 191, 192]. Their practical behaviour is determined by the oxide structure and oxidation state, which control electronic transport and ion access at the electrode/electrolyte interface [192, 193].

In aqueous supercapacitors, multivalent oxides and hydroxides, for example based on Mn, Ni, Co, V, Fe, or Ru, can provide pseudocapacitive charge storage via rapid and reversible surface or near surface redox [191]. $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ established an early benchmark for high pseudocapacitance (around 1000 F g^{-1}), whereas MnO_2 (theoretically up to 1370 F g^{-1}) became a widely used prototype due to low cost and favourable environmental considerations relative to Ru-based materials [194, 195, 196, 197, 198, 199]. Mixed metal oxides, such as NiCo_2O_4 , ZnCo_2O_4 , and MnCo_2O_4 have attracted growing attention because multiple redox-active centres can improve capacitance and conductivity compared with binary analogues and sometimes even the stability [200, 201, 202].

The performance of metal oxides in supercapacitor electrodes is strongly influenced by their crystal structure because it defines the available pathways for electronic transport and ion movement. Spinel type (transition) metal oxides with the general composition AB_2O_4 (e.g. $\text{A} = \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}$; $\text{B} = \text{Co}^{3+}, \text{Fe}^{3+}$) are widely studied, because their three-dimensional (3D) networks of corner-sharing octahedra and tetrahedra enables efficient electron conduction and mechanical robustness during redox cycling [203, 204]. The ternary spinel NiCo_2O_4 is a well-studied example of this family, as it allows for multiple redox states, resulting in higher electrical conductivity and specific capacitance compared to those of the corresponding binary oxides NiO or Co_3O_4 [200, 203, 205]. Perovskite type oxides (ABO_3) combine tunable electronic structure with intrinsic conductivity and redox-active B-site cations, making them attractive pseudocapacitor electrodes, especially in nanostructured or composite architectures [206, 207, 208, 209]. Layered and tunnel structured MnO_2 polymorphs allow ion diffusion through tunnels or interlayer galleries. In $\delta\text{-MnO}_2$, interlayer water or preinserted cations can widen the layer spacing and make ion insertion easier. This can improve rate capability and cycling stability in aqueous electrolytes compared with denser polymorphs [210, 211]. **Figure 11** shows the crystal structures of these common transition metal oxides.

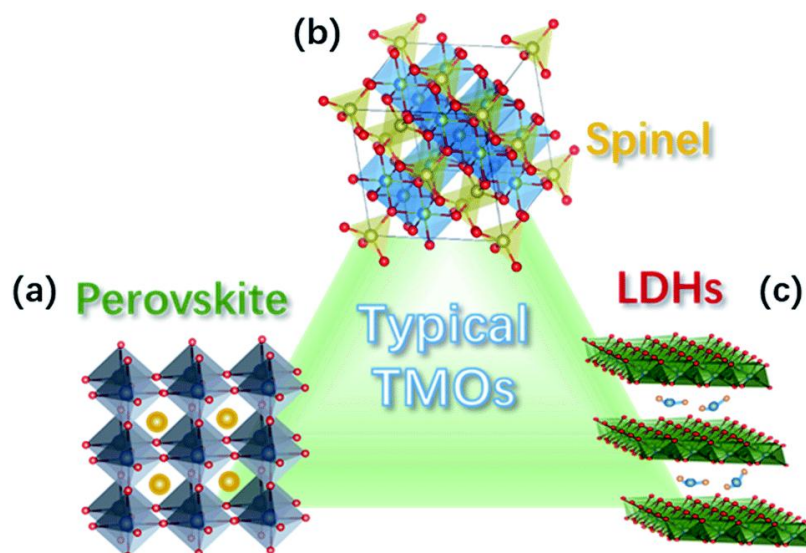


Figure 11. Crystal structure of common transition metal oxides used in electrochemical applications: (a) perovskite, (b) spinel, and (c) layered double hydroxides. Reproduced with permission [212]. Copyright © The Royal Society of Chemistry 2021.

Charge storage in many transition metal oxides comes from fast and reversible redox reactions at, or close to, the surface. This results in more pseudocapacitive behaviour rather than purely diffusion controlled storage [58]. Among transition metal oxides, RuO_2 and MnO_2 are established pseudocapacitive references, showing highly reversible proton or cation coupled surface redox. Beyond these classical systems, intercalation type pseudocapacitance has been reported for oxides such as Nb_2O_5 and MoO_2 , where cations insert into near surface lattice sites without a phase transformation [65, 213, 214, 215, 216]. In real electrodes, most transition metal oxides show mixed charge storage behaviour combining EDLC, pseudocapacitive and diffusion controlled processes [217]. The distinction between true pseudocapacitance and double layer charging on redox activated surfaces requires kinetic analysis [63, 71]. Understanding these mechanistic differences is important for correctly interpreting the electrochemical response of redox-active frameworks such as phosphonate-based coordination networks discussed in later sections.

Composite structures are often used to overcome the limitations of oxides, especially their poor conductivity and mechanical degradation. To accomplish this, pseudocapacitive oxides are combined with conductive or structurally supportive components such as porous carbons, conductive polymers, or Mxenes [218, 219, 220, 221, 222].

Despite high redox activity, many metal oxides are limited by poor intrinsic electrical conductivity and by degradation during cycling, so conductive additives and careful electrode design are usually needed [223]. Under aqueous cycling, repeated ion insertion and extraction can cause structural strain, volume changes, and loss of electrical contact, while chemical instability can lead to dissolution or conversion into hydroxide like species, causing progressive capacity fading [83, 223, 224]. Especially Mn and Ru-based oxides can undergo metal dissolution and hydroxide like phase reconstruction, which reduces active sites and increases internal resistance. At high potentials, oxygen evolution and proton insertion can further destabilize the lattice, for example $\text{MnO}_2 \rightarrow \gamma\text{-H}_x\text{MnO}_2 \rightarrow \text{MnOOH} + \text{Mn}(\text{OH})_2$ and $\text{RuO}_2 \rightarrow \text{Ru}(\text{OH})_3$ transformations [83, 225]. Additional degradation can involve reduction to soluble cations, followed by re oxidation and surface deposition at high anodic potentials [225, 226].

Practical use of some oxide electrodes is additionally limited by cost, scarcity, and supply chain considerations, especially for Ru-based systems and for Co and Ni-based materials [59, 227, 228,

229]. Taken together, limited long term stability in water, poor intrinsic conductivity, and materials availability restrict the use of many metal oxides in practical supercapacitor devices [230, 231]. These limitations motivate coordination networks, where multidentate ligands can immobilise redox-active metal centres and, in principle, mitigate dissolution and reconstruction in aqueous electrolytes, which forms the basis for the concepts discussed in the following sections.

Activated carbon remains the most robust commercial EDLC benchmark, but in aqueous electrolytes its usable cell voltage and energy density are constrained by surface reactions and gas evolution, while hydrophobic surfaces and pore accessibility effects can limit wetting and rate performance in practice [82, 83, 84, 88, 105]. Graphene, GO and rGO offer high theoretical specific surface area, but practical electrodes often suffer from sheet restacking, low packing density and contact resistances that reduce electrochemically accessible area and ion transport, while GO is intrinsically insulating and rGO can retain defects and oxygen functionalities that compromise conductivity and stability at high rates [110, 114, 117, 118, 119]. CNTs primarily improve electronic transport and mechanical integrity as conductive scaffolds, yet bundling and limited intrinsic charge storage mean that overall performance is often governed by the stability and utilisation of the coupled redox-active phase rather than the carbon backbone itself [83, 160, 161, 165]. MXenes combine high conductivity with termination rich surfaces and mixed double layer and pseudocapacitive storage, but fluorine-based etching and termination control complicate processing, and restacking plus progressive oxidation can reduce accessible active sites and long term stability [170, 171, 175, 178, 181]. Metal oxides can reach high pseudocapacitance but are often limited by poor intrinsic conductivity and by dissolution or hydroxide like reconstruction under aqueous cycling. This motivates the construction of composites using conductive materials and more chemically robust redox-active frameworks [83, 217, 223, 224, 231]. In this context, MOFs are viewed as a possible next generation supercapacitor material, because their modular node and linker design enables tunable surface area, pore size, pore geometry and pore polarity, as well as tuneable surface functionality via linker choice, defects and post-synthetic modification [232, 233, 234]. This way wetting and ion mobility can be optimised in ordered pores or channels while enabling a rational balance of EDLC and fast Faradaic charge storage [70]. Special framework designs even allow for intrinsically conductive MOF electrodes [235, 236, 237].

1.3.6 Metal-organic frameworks (MOFs)

Coordination polymers (CPs) comprise a broad and structurally diverse class of solid state materials. The term is commonly traced back to Bailar in 1964 [238]. Intentionally designed three-dimensional coordination polymers were reported by Hoskins and Robson in 1989, and the concept of crystal “tectonics” in metal-organic systems was further developed by Mann in 1993 [239, 240]. In 1995, Yaghi and co-workers introduced the term “Metal-organic framework” (MOF) for open 3D metal-organic structures [241]. In 1997, Kitagawa and co-workers showed reversible gas adsorption in porous coordination polymers, establishing MOFs as relevant materials for gas adsorption and separation [242, 243].

According to IUPAC (International Union of Pure and Applied Chemistry), coordination networks are a subclass of coordination polymers in which coordination entities extend periodically in two or three dimensions to form a crosslinked framework [244, 245]. Metal-organic frameworks are coordination networks with organic ligands containing potential voids [246]. They are built from metal ions or metal oxo clusters, termed secondary building units (SBUs), that are connected by polytopic organic linkers, as shown in **Figure 12** [247].

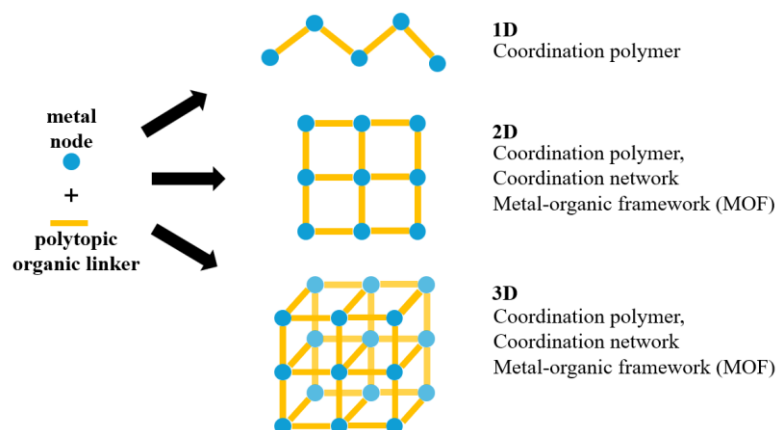


Figure 12. Scheme of coordination polymers based on metal centres (connectors) and linear ditopic ligands (linkers) featuring different structural dimensionalities. Illustration created based on Janiak et al. [247].

The properties of MOFs can be tailored to applications by selecting a suitable combination of secondary building unit and organic linker, and by adjusting synthesis conditions that control connectivity and porosity [243, 248, 249]. This structural diversity is also important for creating optimizable surfaces for electrochemical applications [70, 235]. Even with the same linker, changes in reaction conditions and SBUs can yield different topologies and pore architectures, as illustrated in **Figure 13** [107, 248, 250].

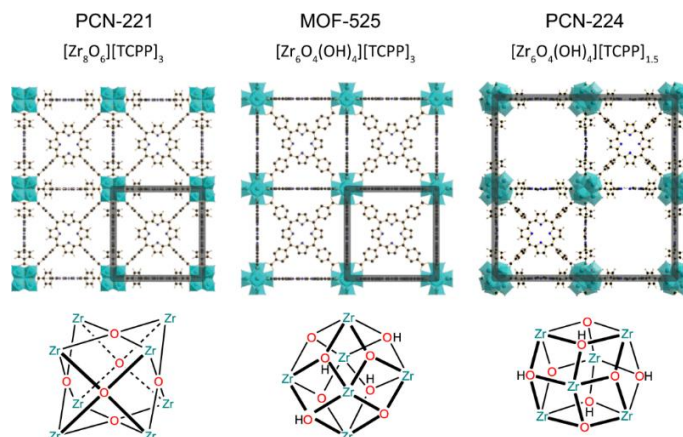


Figure 13. PCN-221, MOF-525, and PCN-224 built of Tetrakis(4-carboxyphenyl)porphyrin (TCPP) linkers and Zr-cluster (teal) with unit cells highlighted, viewed along the c-axis, and their corresponding Zr_6O_6 , straight $Zr_6O_4(OH)_4$, and tilted $Zr_6O_4(OH)_4$ cluster, respectively. Reproduced from C. Koschnick et al., *Nat. Commun.* **2021**, 12, 3099, licensed under CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/> [251].

Isorecticular chemistry, on the other hand, allows systematic variation of linker length or non-coordinating functionality while retaining topology [248]. A typical example is provided by the Zr-based UiO (UiO = Universitetet i Oslo) series, in which terephthalate (1,4-benzenedicarboxylate, BDC), 4,4'-biphenyldicarboxylate (BPDC) and 4,4''-terphenyldicarboxylate (TPDC) construct the isorecticular frameworks UiO-66, UiO-67 and UiO-68, respectively. All these materials adopt the same *fcu* topology while exhibiting progressively larger pores [252]. By adjusting the linker length, the distance between SBUs and thus the pore size can be controlled. According to IUPAC, porous solids are classified by pore width into microporous (pore widths < 2 nm), mesoporous (2–50 nm) and macroporous (> 50 nm) materials [253]. While some MOFs are purely microporous, many also exhibit a mixture of micro and mesopores, so that they are hierarchically porous [254, 255]. Such variability can also affect chemical stability in water, because defects in the crystal and extremely high surface areas, making the labile coordination sites available to ligand exchange and metal leaching [256, 257,

258]. Again, the UiO series is a good example for this. While UiO-66 shows water stability for several weeks, UiO-67 and UiO-68 dissolve in pure water in a shorter time period [259]. The stability in aqueous buffers is even worse than in plain water as studies of Demel et al. showed. UiO-66 was systematically studied in different buffers (0.1 to 1M) and 1 M sodium hydroxide solution. The compound dissolved within less than 30 minutes in many of these medias while not being long term stable in any buffer that was tested, primarily to release of the terephthalate linker [260].

The pore size has a big impact on the accessible surface area and adsorption behaviour. The surface area is usually determined by nitrogen or argon physisorption at their cryogenic boiling points of 77 K and 87 K, respectively. Subsequently, a Brunauer-Emmett-Teller (BET) analysis is performed for microporous materials. Pore size distributions, total pore volume and information about the pore shape can be calculated from the same data, with advanced models giving additional structural information [254, 261, 262]. These properties enable their use in adsorption and separation applications. They also affect electrochemical performance, because accessible pores improve ion transport and can increase the usable capacitance [65, 263, 264, 265]. Beyond adsorption and energy storage, coordination polymers and MOFs have been explored in water treatment, catalysis, sensing and biomedical applications [266, 267, 268, 269]. In electrodes, microporosity increases the density of accessible surface sites and can enhance surface redox-based pseudocapacitance when these sites are ion accessible, while mesopores and interconnected channels minimise transport limitations and improve rate performance [270]. Longer ligands typically enlarge MOF pores without changing topology, improving ion access and double layer contributions, but they lower the volumetric and often gravimetric density of redox-active sites, so smaller ligands generally give higher capacity when those sites remain accessible [70].

Most reported MOFs rely on aryl carboxylates or azolates, whereas phosphonate and phosphinate linkers form a smaller but growing class. These linkers are attractive because stronger metal-oxygen-phosphorus coordination can improve chemical and hydrolytic stability by reducing the rate of hydrolysis and ligand exchange [249, 271]. Representative examples of common linker families are shown in **Figure 14**.

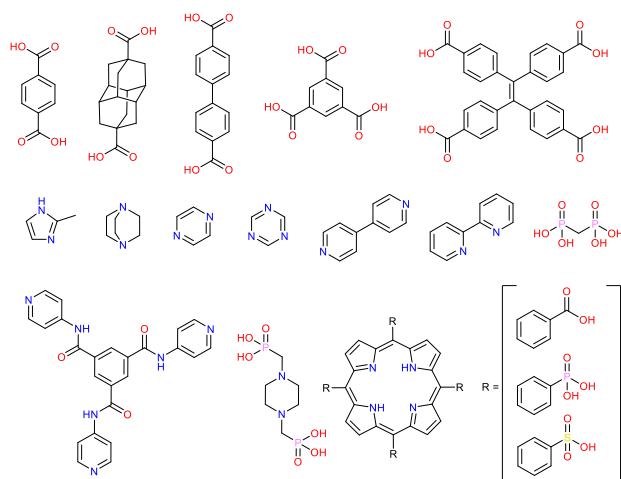


Figure 14. Common organic linker molecules used for MOF synthesis in their protonated forms.

Carboxylate MOFs remain the most widely studied framework class, yet their applicability in electrochemical energy storage faces intrinsic limitations due to the hydrolysis susceptibility of the M-O-C(O) linkage. Many carboxylate representatives lose their crystallinity and porosity in acidic or basic aqueous media due to ligand protonation, competitive coordination of H₂O or OH⁻

and gradual metal or linker leaching [272, 273]. Even frameworks with high valent metal clusters can decompose under strongly acidic or basic conditions or during prolonged electrochemical cycling [273, 274]. Under alkaline operations, redox-active frameworks often transform into mixed metal (oxy)hydroxides, so the MOF acts as a sacrificial precursor rather than a long term electrode material [275, 276, 277].

Imidazolate MOFs, e. g. ZIFs (ZIF = Zeolitic imidazolate frameworks), and related azolate frameworks were developed to enhance chemical stability through strong M-N coordination and zeolite-like topologies [278]. They are generally more resistant to short term exposure to water and basic solutions than carboxylate MOFs, although detailed studies reveal pronounced pH dependent degradation. Zn-based ZIFs often gradually dissolve in neutral water and rapidly decompose under acidic conditions, whereas Co-based ZIFs frequently reconstruct into mixed metal (oxy)hydroxides under alkaline electrochemical operation [277, 278, 279, 280, 281]. Consequently, intact imidazolate frameworks only rarely serve as stable, long term electrode materials and are more commonly employed as precursors for N-doped carbons or nanostructured metal (oxy)hydroxides rather than as active MOFs in energy storage devices [282, 283, 284].

Pyrazolate MOFs occupy an intermediate position between carboxylate and imidazolate systems. Their chelating M–N bonds can yield frameworks that retain crystallinity and porosity across a broad pH range, including strongly basic conditions relevant for harsh aqueous electrolytes [285, 286, 287]. However, their intrinsic electronic conductivity remains low and only a limited number of pyrazolate frameworks have been evaluated as supercapacitor electrodes, typically requiring conductive additives to achieve competitive rate performance [282, 288].

Taken together, carboxylate, imidazolate and pyrazolate MOFs illustrate the versatility of coordination networks, but they also highlight two recurring limitations for direct use as supercapacitor electrodes. Insufficient stability in strongly acidic or basic aqueous media, and low intrinsic electronic conductivity remain dominant constraints [272, 273, 274]. Consequently, many MOFs are primarily employed as precursors for MOF derived carbons or metal oxyhydroxides, or as porous scaffolds in composite electrodes. This reflects a central trade-off between chemical robustness, accessible porosity, and electronic conductivity in MOF-based electrodes. Conductive MOF electrodes show that, in selected designs, electronic transport can be integrated into the framework itself, enabling supercapacitor electrodes without conductive additives, and motivating industrial translation including a joint patent granted and assigned to Massachusetts Institute of Technology and Automobili Lamborghini S.p.A [289]. Ji et al. report that 2D MOFs based on transition metals, such as Ni and Cu, can show favourable properties for electrochemical energy storage applications. They state that 2D MOFs offer superior electrochemical performance compared to their 3D counterparts because their ultrathin structure maximizes the exposure of active sites and facilitates ion transport, thereby reducing the energy barriers for redox reactions [235]. $[\text{Ni}_3(\text{HITP})_2]$ shows a very high bulk conductivity of 5000 S m^{-1} , surpassing many carbon materials, while maintaining a substantial surface area of $630 \text{ m}^2 \text{ g}^{-1}$. This performance is attributed to its π -conjugated 2D layers permeated by 1D cylindrical channels ($\sim 1.5 \text{ nm}$), an architecture that simultaneously ensures high conductivity and a large accessible surface area for electric double layer capacitance [290]. However, these examples do not remove the broader need to demonstrate long term structural persistence under aqueous polarisation, because many coordination frameworks remain susceptible to hydrolysis, ligand exchange, and node dissolution in water. This motivates alternative linker chemistries, most notably phosphonates, that retain MOF designability while strengthening metal ligand bonding, thereby improving hydrolytic stability and reducing metal leaching in water, consistent

with hard acid, hard base considerations and the strong metal-oxygen-phosphorus bonding motif [291, 292].

1.3.7 Metal phosphonates and phosphonate MOFs

Metal phosphonates and phosphonate MOFs form the central materials class of this thesis. In the following, their historical development, structural chemistry, and bonding characteristics are explained, with emphasis on features that underpin hydrolytic and chemical robustness and make them promising candidates for electrochemical energy storage. Although phosphonates are known to be exceptionally stable, limited long term studies have been conducted. Also, the synthesis of microporous phosphonates is very limited in the literature [107].

Crystalline metal phosphonates as a distinct class can be traced to Clearfield's work in the 1960s on layered zirconium phosphates such as α -Zr(HPO₄)₂·H₂O, focused on ion exchange and intercalation [293, 294]. In 1969, the crystal structure of Zr(HPO₄)₂·H₂O was elucidated and has since served as a prototype for layered architectures in zirconium phosphates and many metal phosphonates [295]. These insights enabled synthetic protocols for high valent metal phosphates, primarily based on Zr⁴⁺, Ti⁴⁺, and Sn⁴⁺, with tunable interlayer chemistry, which later inspired analogous strategies for organophosphonate derived metal phosphonates [296, 297].

In 1978, Alberti and co-workers reported the first genuine metal-organophosphonate frameworks, Zr(HOCH₂PO₃)₂·H₂O, Zr(C₆H₅PO₃)₂ and Zr(C₂H₅OPO₃)₂, which adopt layered structures closely related to the zirconium phosphate prototype [298]. These materials were initially regarded as non-porous inorganic organic hybrids but were later recognized as precursors to open-framework and microporous materials [299, 300]. Despite the early work on phosphonates in the 1980s and 1990s, not much progress in the synthesis of phosphonate-based frameworks has been made. This is largely because phosphonates often form dense, non porous layered solids and tend to precipitate as poorly crystalline phases due to their low solubility. In addition, their flexible coordination and deprotonation behaviour limits the formation of well defined SBUs, which makes rational design and single crystal structure determination difficult, so many studies rely on PXRD [107, 291]. Early porous phosphonates derived from phosphonic and diphosphonic acids were subsequently reported by several groups [298, 300, 301, 302]. A schematic representation of layered metal phosphonate motifs can be found in **Figure 15**.

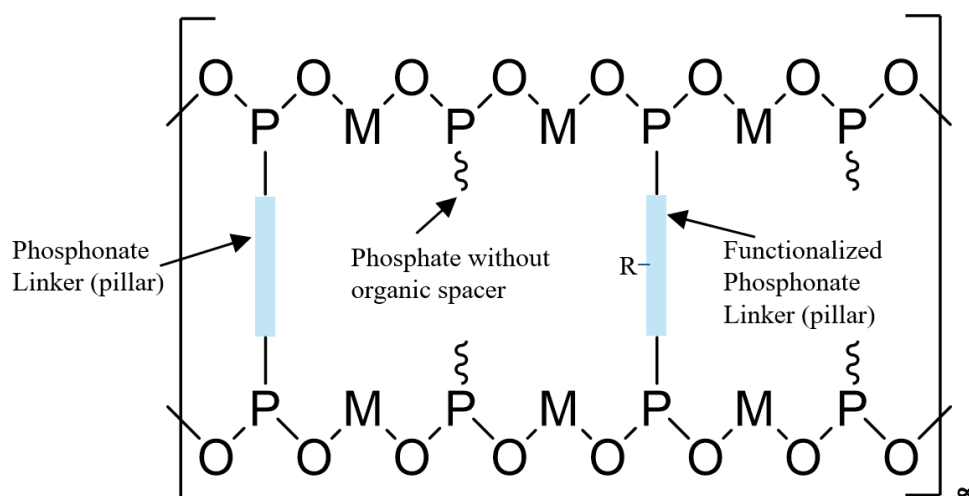


Figure 15. Scheme of layered metal phosphonates. The first traditional layered phosphates (e. g. Clearfield et al.) were synthesized without an organic spacer (“pillar”) between P-functionalities [294]. Later, organophosphonates were used to introduce “pillars” between the inorganic layers to introduce porosity [298]. In advanced materials, functional groups attached to the organic portion of the pillar can further tune the properties of the framework [303].

Extension of these concepts to permanently microporous frameworks and MOF like architectures occurred later than for carboxylate MOFs. Early porous phosphonate MOFs include MIL-58 (MIL = Materials Institute Lavoisier), MIL-91(Ti and Al) and STA-12(Ni) (STA = St. Andrews). Their structures are built from edge- or corner-sharing chains of metal polyhedra that are linked by organodiphosphonate linker, thereby forming microporous channels below 2 nm in diameter [304, 305, 306]. In 2011, isorecticular expansion of STA-12 by elongating the organic linker yielded STA-16. It was one of the first phosphonate networks to approach the mesoporous regime, with a pore diameter ranging from 1.8 nm (STA-16(Ni)) up to 2.15 nm for (STA-16(Co)) [307]. Since then, MOF design strategies such as isorecticular or mixed linkers, and higher linker connectivity (including tritopic up to hexatopic) have been transferred to phosphonate systems [308, 309, 310, 311, 312]. Notably, CAU-29(Mn, Co, Ni, Cd) (CAU = Christian-Albrechts-Universität zu Kiel) and CAU-30(Zr, Hf) based on tetrakis(4-phosphonophenyl)porphyrin combine high porosity with stability from pH 2–12, supporting their potential as future candidates for aqueous supercapacitor electrodes [313, 314].

The phosphonic acid group, $R-P(=O)(OH)_2$, is highly versatile and occurs in structurally diverse molecules, including metal phosphonate frameworks [291, 315, 316]. Phenylphosphonic acid is a simple representative of aromatic phosphonic acids and illustrates the distorted tetrahedral geometry at phosphorus, in contrast to the near trigonal planar geometry of carboxylate groups in benzene 1,4 dicarboxylic acid [317, 318]. This geometric difference between tetrahedral phosphonate and planar carboxylate units has important consequences for framework connectivity and dimensionality.

Phosphonic acids ($R-PO_3H_2$) are phosphorus(V) oxoacids that behave as diprotic Brønsted acids, undergoing stepwise deprotonation to give the monoanionic hydrogen phosphonate $R-PO_3H^-$ and the dianionic phosphonate $R-PO_3^{2-}$ species in aqueous solution. For most aromatic phosphonic acids, literature values for the first pK_a lies between 1.1 and 2.3, whereas the second pK_a is usually found between about 5.3 and 7.2, with the exact values depending on the substituents on the aromatic ring [316]. Electron withdrawing groups lower both pK_a values, whereas electron donating groups increase them [316, 319, 320]. This behaviour is highly relevant for solvothermal synthesis of metal phosphonates and phosphonate MOFs, because the building species can span neutral $R-PO_3H_2$, mono deprotonated $R-PO_3H^-$ and fully deprotonated $R-PO_3^{2-}$, depending on solution pH and modulators [291]. In addition, phosphonic acids often show lower logP values and increased polarity which is often accompanied with higher water solubility compared to the corresponding carboxylic acids, facilitating solution-based synthesis [320].

According to Pearson's hard-soft acid-base (HSAB) concept, phosphonate ligands act as hard bases. Their donor atoms are oxygen atoms bound to a high-valent P(V) centre, resulting in a highly localized negative charge and low polarizability [321, 322, 323]. Consequently, they preferentially coordinate to hard or borderline hard metal cations with high formal charge and significant oxophilicity, such as Zr^{4+} , Ti^{4+} , Al^{3+} , Fe^{3+} , V^{5+} and many rare-earth ions, as well as to some borderline first row transition metals including Ni^{2+} or Co^{2+} [305, 310, 314, 324]. In contrast, carboxylate linkers ($R-COO^-$) are typically less acidic with slightly softer oxygen donors, whereas azolate linkers provide nitrogen donor sites that are more polarizable and therefore better matched to borderline or softer late transition metals such as Zn^{2+} , Cu^{2+} , Co^{2+} or Ni^{2+} [279, 291, 325, 326].

The higher acidity and charge density of phosphonate ligands generally translate into stronger and more ionic metal-oxygen bonds than those formed by analogous carboxylates [327]. In fully deprotonated phosphonate groups (PO_3^{2-}), the -2 charge is delocalized over three oxygen donors,

whereas in carboxylates (CO_2^-) it is shared between only two O atoms. According to HSAB, deprotonation of the more acidic $\text{R-PO}_3\text{H}_2$ group therefore produces harder and more strongly binding oxygen donors than deprotonation of $\text{R-CO}_2\text{H}$ [321]. Consistent with this, comparisons of isostructural structures show that M-O(P) bonds are often shorter than the corresponding M-O(COO) bonds for a given metal ion and coordination number, which is in line with stronger, more electrostatic metal-ligand interactions and higher bond dissociation energies [107, 291, 328, 329]. This effect is particularly pronounced for early transition metals and high valent main group cations such as Zr^{4+} , Ti^{4+} , Sn^{4+} and Hf^{4+} , where hard/hard matching, combined with the higher charge and the larger number of oxygen donors on the phosphonate, results in strong and often directional M-O(P) linkages [330]. In phosphonate MOFs and related frameworks based on Zr^{4+} , Hf^{4+} or trivalent rare earth nodes, these connections frequently assemble into characteristic eight-membered $\text{M}_2\text{P}_2\text{O}_4$ rings (M-O-P-O-)₂ that propagate into one-dimensional inorganic building units. Such chains (sometimes double chains) can act as persistent SBUs that underpin both rigidity and designability [271, 314, 324]. As a result, phosphonate frameworks can remain intact under conditions that readily cleave analogous M-O(COO) bonds in carboxylate MOFs [331].

Despite their favourable bonding characteristics, phosphonate MOFs still face significant challenges. Crystallisation often occurs by rapid precipitation and produces nanocrystalline powders or poorly crystallised solids, which makes reliable structure determination and topological analysis difficult [106, 291, 332]. In addition, phase control and predictable framework formation remain challenging in metal-organophosphonates, because diverse phosphonate binding modes can lead to competing connectivities and low synthetic designability [333]. Additionally, most MOFs are intrinsically insulating, so electrochemical operation often requires conductive composites or post-synthetic modification to enable efficient charge transport [334]. At the same time, phosphonate MOFs often have high lattice charge density and frequently show hydrolytic stability across broad pH ranges and at high ionic strength which distinguishes phosphonate frameworks from carboxylate, imidazolate and pyrazolate MOFs. This makes them interesting candidates for electrochemical applications that need to have long term stability in harsh, often aqueous environments [166, 272, 325, 331].

1.3.8 Phosphonate coordination networks and their derivatives as supercapacitor electrodes

As outlined in Section 1.3.7, metal phosphonates and phosphonate MOFs combine strong M-O-P- bonds with high anionic lattice charge density in chain and layer type architectures, often featuring eight-membered $\text{M}_2\text{P}_2\text{O}_4$ ring motifs. An increasing number of three-dimensional frameworks has been reported in the past years [271, 291, 335]. These bonding patterns can translate into exceptional hydrolytic robustness across a wide pH range and high ionic strength, in sharp contrast to many archetypal carboxylate MOFs that often degrade rapidly in aqueous electrolytes [273, 313, 335, 336]. In this work, this robustness motivates phosphonate-based coordination networks as a platform for long term stable supercapacitor electrodes in aqueous media.

From an electrochemical design perspective, the stepwise deprotonation of phosphonic acids fixes the framework charge and distribution and density of anionic sites, thereby tuning the interaction with charge compensating ions [331, 337]. In layered metal phosphonates this ranges from charge neutral, hydrogen bonded layers to negatively charged sheets separated by counter cations or polar molecules, whereas phosphonate-based coordination networks, such as MOFs, can provide interconnected micro- and/or mesopores that reduce tortuosity and facilitate ion access [331, 338, 339]. Charge storage is commonly governed by fast Faradaic redox at transition metal centres coupled to uptake and release of H^+ , OH^- or other ions. In many layered phosphonates this appears

as surface redox plus shallow interlayer insertion (intercalation pseudocapacitance), kinetically distinct from the slow bulk intercalation of classical battery electrodes [340, 341, 342]. Because most phosphonate frameworks are only moderately conductive, electrodes typically require intrinsic semiconductivity in selected phosphonate MOFs or composites with conductive scaffolds that provide percolation and additional double layer capacitance [70, 343, 344, 345]. In contrast, phosphonate-derived metal phosphates obtained by thermal treatment can store charge via deeper, diffusion-controlled ion insertion and multielectron redox reactions, which leads to more battery-like or “supercapattery” behaviour. This shows that phosphonate coordination networks can be tuned from predominantly pseudocapacitive to more intercalation-type electrodes [346, 347].

Phosphonate coordination networks and phosphonate MOFs have therefore been proposed as a chemically resilient platform for aqueous supercapacitor electrodes, but translating this general promise into reproducible device-level performance is not straightforward [331]. In aqueous media, reported capacitances and cycling stabilities can depend strongly on the potential window, the electrolyte composition and on electrode formulation parameters such as conductive additive fraction and mass loading. Mechanistic interpretation therefore requires evidence that the intact phosphonate framework remains the dominant electrochemically addressed phase, rather than being masked by reconstructed surface layers or leached species [29, 348].

Electronic transport is a second practical constraint. Many phosphonate frameworks are insulating or only weakly semiconducting, so composites are often required to achieve high rate performance and reduce ohmic losses [331, 343, 349]. Conductive phosphonate MOFs have nevertheless been reported, including Cu phosphonate systems such as TUB75 and TUB40, indicating that charge transport can in selected motifs be improved within the phosphonate MOF family itself [344, 350]. This motivates two complementary strategies that guide the following overview, first, identifying phosphonate networks that remain intact and electrochemically addressable in different media, especially in aqueous media, and second, discussing how composite electrode design compensates for insufficient intrinsic electronic conductivity [331, 351].

The following subsection therefore focuses on supercapacitor studies in which phosphonate coordination networks or phosphonate MOFs are employed as the uncalcined electrode material, either as a standalone phase or as the defined redox-active component in a composite. These are separated from reports that mainly use phosphonate solids as precursors for conversion into other inorganic phases [346, 352].

Many studies on uncalcined metal phosphonate electrodes in aqueous electrolytes investigate materials with layer motifs and, less frequently, frameworks with microporous channels, as ion-accessible pathways such as interlayer galleries or channels can shorten transport distances compared to dense bulk phases. In these systems, the response is often interpreted as mainly surface controlled redox processes with possible shallow insertion into near surface interlayer regions, while more diffusion limited contributions may arise when transport proceeds through narrower channels, defects, or poorly wetted domains. These motifs are commonly realised in Ni, Co, Mn-based structures where fast metal centred redox can enable faster uptake and release of charge compensating ions [78, 341, 342, 353]. Electrolyte choice also strongly influences supercapacitor performance [55, 354]. Alkaline electrolytes, typically KOH-based, often increase apparent capacitance because metal redox couples are more accessible and hydroxide can participate in charge compensation, whereas neutral salts can reduce driving forces and narrow the usable window, but can simplify stability interpretation by reducing corrosion and parasitic

reactions [29, 355]. Meaningful comparisons therefore require explicit reporting of potential windows, reference electrodes, and electrode formulation parameters such as mass loading and conductive additive fraction [341, 356].

Many transition metal phosphonates crystallise in layered motifs, where inorganic metal, oxygen, phosphorus sheets alternate with organic groups at surfaces or in interlayers. Such lamellar architectures are attractive for aqueous supercapacitors because redox-active sites are near the electrode electrolyte interface and ion transport distances to accessible galleries can be short [357]. For example, nickel phenylphosphonate-based hierarchical microspheres in 3 M KOH deliver 500.8 F g^{-1} at low current density (0.5 A g^{-1}), and retain 305.5 F g^{-1} (61%) after 1000 cycles under the reported conditions [78]. Even higher capacitance and cycle stability was achieved with spherical Ni phosphonate particles based on Ni^{2+} and the linker 1,1'-binaphthyl-2,2'-diyl hydrogenphosphate [343]. Mohanty et al. investigated layered monometallic and bimetallic Ni and Co phosphonate networks based on the linker 1,1'-binaphthyl-2,2'-diyl hydrogenphosphate in 6 M KOH at 2 A g^{-1} [341]. A strong composition dependent effect was observed, with 883 F g^{-1} for the Co framework, 2119 F g^{-1} for the Ni framework, and 3537 F g^{-1} for the mixed metal analogue. This enhancement was attributed to synergistic Ni and Co redox chemistry and improved charge transport in thin layered morphologies with accessible porosity. Importantly, the bimetallic framework retained 87.6% of its capacitance after 2000 cycles and still delivered 574 F g^{-1} in a coin cell configuration, supporting relevance beyond idealised three-electrode testing [341].

A layered Mn phosphonate is built from a mixed linker system comprising [1,4-phenylenebis(hydroxymethylene)]bis(phosphonic acid) and 1,10-phenanthroline. The structure contains two crystallographically independent Mn(II) centres, which are coordinated by phosphonate groups in different protonation states together with the 1,10-phenanthroline co-ligand [358]. These coordination units form zig zag one-dimensional chains that further assemble into a three-dimensional supramolecular architecture and is reported to be stable between pH 2 and 12. Although evaluated as an oxygen evolution reaction catalyst rather than a supercapacitor electrode, it illustrates that phosphonate lattices can combine ion accessible motifs with broad pH robustness, while electrode design must still address limited intrinsic conductivity [358].

Besides layered motifs, an increasingly important subset of metal phosphonates and phosphonate-based frameworks exhibits permanent micro or mesoporosity that can, in principle, be accessible to electrolyte ions. Such porosity is difficult to realise because strong M-O-P bonding and high connectivity favour dense, charge rich lattices. Advances in the design of multitopic ligands and in structure controlling synthesis have expanded the accessible open architectures at the interface between coordination polymers and porous MOFs [79, 350, 359].

Rom et al. reported three zinc phosphonate compounds based on 1-hydroxyethane-1,1-diphosphonic acid (H_4HEDP) together with different co-ligands and evaluated their electrochemical behaviour. The network connectivities are shown in **Figure 16** [360].

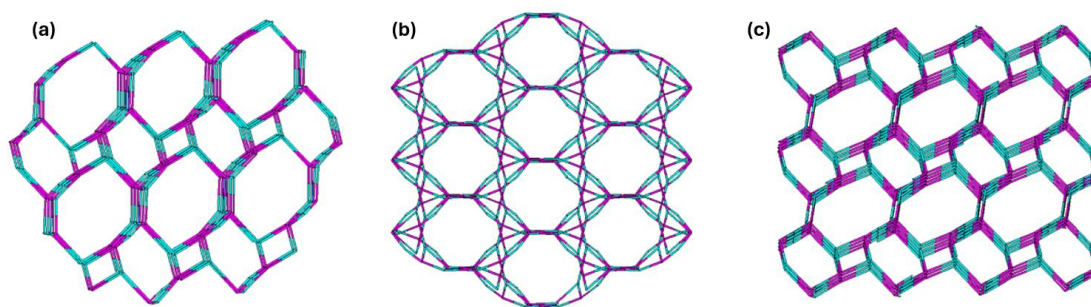


Figure 16. Node connectivity of the three zinc and diphosphonate units in (a) compound 1, (b) compound 2 and (c) compound 3. Cyan colour represents zinc atoms and violet colour represents the diphosphonate units. Adapted from Ref. [360], with permission from Elsevier, Copyright © 2022.

Notably, compound 3 (**Figure 16c**), which consists of interconnected zig zag chains, shows the highest specific capacitance within this series at 216 F g^{-1} and a cycle stability of 79.6% over 5000 cycles in 6 M KOH at a current density of 1 A g^{-1} . Both the capacitance and the cycle stability exceed those of compound 1 and 2 (**Figure 16a and b**) under same test conditions. This has been attributed to its interconnected zig zag chain motif with multiple accessible channels, which increases the density of electrochemically addressable sites and can reduce hydroxide driven structural degradation during cycling [360].

A permanently porous Ti-phosphonate MOF with a BET surface area of $382 \text{ m}^2 \text{ g}^{-1}$ was investigated for sensing and supercapacitor performance by Chakraborty et al. In an asymmetric device configuration, an areal capacitance of 14.96 F cm^{-2} was reported at 1 mA cm^{-2} using 1 M TEABF₄ in DMSO as the electrolyte, with about 75% capacitance retention after 5000 cycles [351]. Notably, an initial decrease of roughly 10% occurred early in cycling, consistent with a gradual activation and concurrent evolution of the electrode surface. The authors attributed this behaviour to slow framework degradation accompanied by TiO₂ formation, which was suggested to contribute only marginally to the measured capacitance [351, 361]. Although this example uses a non-aqueous electrolyte, it shows that metal phosphonate frameworks can achieve device relevant areal performance and maintain long term cycling stability. At the same time, it highlights degradation processes that could also become important in aqueous electrolytes. **Table 2** provides an overview of selected electrode materials tested in aqueous electrolytes. To enable a meaningful comparison across material classes, the benchmark table includes only literature reports that clearly specify the electrolyte composition, the applied rate metric, and the cycling protocol. Gravimetric capacitance values are interpreted cautiously when mass loading, electrode formulation, or the fraction of conductive additive and binder are not reported, since these parameters can dominate the apparent performance. If key details are unavailable, the entry is retained and flagged as not reported to minimise selection bias.

Table 2. Comparison of the electrochemical performances of various supercapacitor electrodes in aqueous electrolytes.

Electrode material	Electrolyte	Specific capacitance (F g^{-1})	Performance retention (%)	Reference
Traditional MOFs				
$[\text{Ni}(\text{C}_4\text{H}_4\text{N}_2)(\text{CHO}_2)_2]_n/\text{rGO}$	5 M KOH	125 @ 0.2 A g^{-1}	96 after 5000 cycles	[362]
$\text{Ni}_3(\text{HITP}^{*1})_2$	0.5 M Na_2SO_4	170 @ 0.1 mA cm^{-2}	84 after 100000 cycles	[363]
$\text{Cu}_3(\text{HHTP}^{*2})_2$	1 M KCl	206.7 @ 1 A g^{-1}	79.7 after 5000 cycles	[364]
ZIF-67	6 M KOH	65.5 @ 5 mV s^{-1}	not reported	[365]
$\text{NiC}_2\text{O}_4/\text{ZIF-67}$	6 M KOH	1019.7 @ 5 mV s^{-1}	73 after 2000 cycles	[365]
HKUST/PANI*3	6 M KOH	270 @ 1 A g^{-1}	not reported	[366]

Electrode material	Electrolyte	Specific capacitance (F g ⁻¹)	Performance retention (%)	Reference
HKUST/PEDOT ^{*4} /rGO	KCl/PVA	360 @ 5 mV s ⁻¹	95.5 after 4000 cycles	[367]
Co-V-MOF	1M KOH	1711 @ 1 A g ⁻¹	92.1 after 10000 cycles	[368]
Metal-phosphonate frameworks				
Ni phenylphosphonate/AC	3 M KOH	500.8 @ 0.5 A g ⁻¹	61 after 1000 cycles	[78]
NiCoBPA	1 M KOH	911.11 @ 2 A g ⁻¹	84.6 after 2000 cycles	[341]
Zn phosphonate MOF/AC	6 M KOH	216 @ 1 A g ⁻¹	79.6 after 5000 cycles	[360]
Cu/V phosphonate	1 mM H ₃ PO ₄	140 @ 1 mV s ⁻¹	60 after 10000 cycles ^{*5}	Chapter 3.2
Ni/V phosphonate MOF	1 M Na ₂ SO ₄	80 @ 1 A g ⁻¹	96 after 10000 cycles	Chapter 3.3
Transition metal nanoparticles				
NiO/AC	2 M KOH	568.7 @ 0.5 A g ⁻¹	90.6 after 5000 cycles	[369]
NiWO ₄ /AC	2 M KOH	586.2 @ 0.5 A g ⁻¹	91.4 after 5000 cycles	[370]
NiO/graphene aerogel	6 M KOH	587.3 @ 1 A g ⁻¹	98.5 after 1000 cycles	[371]
ZrO ₂ /carbon nanofibers	6 M KOH	140 @ 1 A g ⁻¹	82.6 after 10000 cycles	[372]
NiO/MnO ₂ /MWCNT	2 M KOH	1320 @ 1 A g ⁻¹	93.5 after 3000 cycles	[373]
MXenes				
MXene/lignosulfate/GO-aerogel	3 M H ₂ SO ₄	386 @ 2 mV s ⁻¹	96.3 after 10000 cycles	[374]
TiN nanosheet	0.5 M Na ₂ SO ₄	165 @ 5 mV s ⁻¹	100 after 200000 cycles	[375]
TiN nanosheet	1 M KOH	205 @ 5 mV s ⁻¹	42.4 after 200000 cycles	[375]
ε-MnO ₂ /MXenes	6 M KOH	210.9 @ 10 mV s ⁻¹	88% after 10000 cycles	[376]
Activated Carbon				
N-doped AC	6 M KOH	319 @ 0.2 A g ⁻¹	92.6 after 10000 cycles	[377]
AC-OFG ^{*6} (41%)	6 M KOH	142 @ 1 A g ⁻¹	95 after 10000 cycles	[378]
S-doped AC (9% S)	1 M H ₂ SO ₄	293 @ 1 A g ⁻¹	99.3 after 12500 cycles	[379]
P-doped AC	6 M KOH	141 @ 5 A g ⁻¹	95 after 10000 cycles	[380]

^{*1} HTP = 2,3,6,7,10,11-hexaaminotriphenylene, ^{*2} HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene, ^{*3} PANI = Polyaniline, ^{*4} PEDOT = poly(3,4-ethylenedioxythiophene), ^{*5} The structure remained intact, ^{*6} OFG = oxygen functional groups: -OH, =O, CHO.

Direct benchmarking remains difficult because performance metrics and test protocols are not uniformly specified, and incomplete reporting of cell configuration, two-electrode versus three-electrode testing, mass loading, electrode composition, and rate definitions can distort apparent performance [66, 356]. In addition, many metal phosphonates, especially phosphonate-based coordination networks, are obtained only as microcrystalline or nanocrystalline solids, so single crystal structures are often unavailable [331]. Without a clear structural model, it becomes difficult to assign ion transport pathways, redox environments, and storage mechanisms, and structure-performance relationships can remain speculative unless supported by post-mortem, in situ, or operando characterisation [381]. Another critical problem is that the materials used (the active phase) are often only checked to a limited extent after the electrochemical measurements. In many studies, structural and chemical analysis after cycling is restricted to morphology, whereas diffraction and spectroscopy-based checks of phase integrity are less frequently reported. As a result, apparent stability and performance in concentrated electrolytes can be overestimated, because many electrode materials can reconstruct under operation and should be regarded as precursors to the true electrochemically active phase [382, 383]. Community guidelines therefore emphasise transparent reporting of metrics, test configurations, and calculation methods to enable meaningful comparison [66, 356]. Overall, these findings highlight metal phosphonate networks as a promising but still underexplored platform that combines chemical robustness and structural diversity with competitive electrochemical performance. In practice, limited intrinsic conductivity is typically addressed by conductive additives that establish a percolating electron transport network, while selected phosphonate motifs can also offer intrinsic conductivity.

2. Motivation

Established electrode families exhibit characteristic failure modes in aqueous supercapacitors, particularly under strongly acidic or strongly alkaline conditions or in concentrated salt solutions, where dissolution, oxidation, swelling, and structural degradation determine long term behaviour. Activated carbon is relatively robust, but surface reactions can drive carbon oxidation, self-discharge, and wettability drift. Graphene, CNTs, and MXenes provide high conductivity, yet electrode architectures can evolve during processing and cycling through restacking, swelling, and contact loss, reducing accessible surface area and compromising electron pathways. Transition metal oxides and hydroxides often deliver high initial pseudocapacitance, but cycling can induce metal leaching, phase reconstruction, and loss of electrical contact. Conventional MOFs face further limitations because they are usually poorly conductive and often not stable against hydrolysis, so ligand exchange, node dissolution, and framework collapse can occur. Together, these constraints motivate phosphonate coordination networks, where hard oxygen donor ligands can form strong bonds to hard metal centres and thereby reduce the rate of hydrolysis and metal leaching while retaining tunable redox chemistry.

The motivation behind this work is to establish phosphonate coordination polymers and phosphonate MOFs as hydrolytically robust yet electrochemically tunable electrode materials for energy storage in aqueous electrolytes. This choice follows HSAB considerations and the typically strong M-O-P bonding motif, which can reduce hydrolysis, ligand exchange, and metal leaching compared with many carboxylate-based frameworks under harsh aqueous conditions. The central goal is to derive design principles that connect i) framework chemistry and hydrolytic robustness, ii) mixed valence and redox site density as the origin of pseudocapacitance, iii) pore and channel accessibility as the kinetic constraint, and iv) electrode architecture and conductive networking as the prerequisite for practical rate capability and long lifetime. This includes distinguishing intrinsic framework related charge storage from surface reconstruction by combining electrochemical analysis with phase sensitive, post-mortem characterisation, and by critically benchmarking two-electrode versus three-electrode configurations where relevant. This also includes translating chemical robustness into functional electrodes by integrating phosphonate phases into electronically percolated carbon scaffolds where required.

In order to establish phosphonate coordination networks as stable and functional materials, this work pursues a multi-stage strategy. It separates structural chemistry and electrochemical applications. In the first project, lanthanide-based coordination networks are being developed with diamantane-4,9-bis(hydrogenphosphonate) as the linker and Eu^{3+} , Er^{3+} and Gd^{3+} as metal centres. Phosphonate ligands enable potentially robust metal-oxygen-phosphorus bonds. Lanthanide ions also offer a variety of coordination modes. This allows the creation of networks with well defined connectivity that may be relevant for sensor technology and good proton transport, among other things. The linker is produced in situ from a dichlorophosphoryl precursor under hydrothermal conditions. Smaller amounts of other monophosphonic acids, such as p-ethylphosphonic acid, and base additives, such as DABCO or bipyridine derivatives, serve as modulators. They control phosphonate deprotonation and help to build the coordination network. Controlling the synthesis is a key challenge in the production of phosphonate frameworks. The initial project also highlights a practical bottleneck. The purity of the precursor and batch variability influence phase purity and isolated yield. This makes scaling of the desired product difficult and can lead to fluctuating test results between batches or the selection of test methods based on the material available within a batch. These limitations directly led to a subsequent focus on redox-active Cu, Ni and V phosphonate frameworks. Here, the stability of the networks in

aqueous electrolytes can be directly linked to capacitive and pseudocapacitive charge storage. This shift enables a direct correlation between structure, stability and performance under electrochemical bias in aqueous media. The materials are systematically evaluated under defined aqueous electrolyte conditions.

In the second project, mechanically flexible Cu/V phosphonate single crystals were obtained under solvothermal conditions using a slightly modified method from Yücesan et al. [384]. The material class was chosen to test whether strong M-O-P binding motifs can suppress hydrolysis and metal leaching while maintaining accessible redox-active sites for pseudocapacitive charge storage. A further objective was to examine whether structural stability and crystal flexibility can mitigate mechanical stress during cycling and support long term electrochemical stability. Finally, the project aimed to translate intrinsic framework robustness into functional composite electrodes by ensuring electronic percolation through conductive carbon scaffolds where required.

The aim of the final project of this thesis was to increase the density of redox-active sites in a hydrolytically robust phosphonate framework by combining a layered anionic vanadium phosphonate scaffold with an additional, well defined redox active cationic complex. By embedding $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}$ species within the vanadium phosphonate layers, the work targeted a hybrid electrode concept in which chemical robustness, mixed valence redox chemistry, and ion accessible charge storage sites can be addressed simultaneously under aqueous conditions. A central objective was to demonstrate operation in practically relevant, mild aqueous electrolytes, including neutral salt electrolytes, while maintaining phase integrity during long term cycling. In addition, the project was designed to separate intrinsic framework related charge storage from electrolyte driven surface reconstruction by pairing electrochemical testing with phase sensitive post-mortem verification.

3. Cumulative part

Sections 3.1 to 3.3 present three publications for which I am first author. These articles have either been published in peer reviewed journals or are currently under review. Each publication is listed separately and in chronological order by publication date. Each article is accompanied by a brief summary and a description of the contributions of all authors.

3.1 Lanthanide Coordination Networks Based on Diamantane-4,9-Diphosphonic Acid

Tim Müller, Peter Ferber, Philipp M. Roos, Nabil Assahub, Christoph Janiak

Z. Anorg. Allg. Chem. **2025**, 00, e202500158. DOI: 10.1002/zaac.202500158, Ref. [324].

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Abstract:

Four new Ln-based (Ln = Eu, Gd, Er) coordination networks, $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$ and $\{[\text{LnL}_{1.5}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (Ln = Eu, Gd, Er), were synthesized using the precursor diamantane-4,9-bis(dichlorophosphoryl) ($\text{Diam}(\text{POCl}_2)_2$) to form in situ the linker diamantane-4,9-bis(hydrogenphosphonate) ($\text{L} = \text{Diam}(\text{PO}_3\text{H})_2^{2-}$) with singly deprotonated phosphonate groups. These coordination networks represent the first reported examples of diamantane-phosphonate networks. The combination of Ln^{3+} ions and $\text{Diam}(\text{PO}_3\text{H})_2^{2-}$ resulted in the formation of doubly $-\text{PO}_3\text{H}^-$ bridged Ln chains. These chains are interconnected by the diamantane moiety of the diamantane-4,9-bis(hydrogenphosphonate) linker, forming 2D (Eu) or 3D (Eu, Gd, Er) networks. In the 3D networks, Eu^{3+} , Gd^{3+} , and Er^{3+} exhibit an uncommon coordination number of 6, from five phosphonate groups and one aqua ligand. This may be due to the constraints of the 3D network but at the same time shows the adaptability of Ln^{3+} ions to coordination constraints crucial for the formation of the 3D phosphonate frameworks.

Author's contribution to the publication:

- Dr. István Boldog provided the first batch of the linker precursor $\text{Diam}(\text{POCl}_2)_2$.
- Tim Müller was responsible for literature research and planning of the research project.
- Method transfer to other Ln^{3+} ions with experimental support of Philipp M. Roos.
- Synthesis of $\text{Diam}(\text{POCl}_2)_2$ and hydrolysis study with the support of Philipp M. Roos.
- Measurement of all single crystals using single crystal X-Ray diffraction (SCXRD) and determination of single crystal structures by Peter Ferber.
- Resynthesis, upscaling and characterization of the Ln coordination networks using powder X-Ray diffraction (PXRD) with the support of Philipp M. Roos.
- Thermogravimetric analysis, measured by Nabil Assahub and evaluated by Tim Müller.
- Illustrations of the structures and the structural descriptions were provided by Prof. Dr. Christoph Janiak.
- Tim Müller was responsible for revising the manuscript and supporting information with the support from Peter Ferber and Prof. Dr. Christoph Janiak.

DOI: 10.1002/zaac.202500158

Lanthanide Coordination Networks Based on Diamantane-4,9-Diphosphonic Acid

Tim Müller, Peter Ferber, Philipp M. Roos, Nabil Assahub, and Christoph Janiak*

Dedicated to Prof. Dr. Mathias Wickleder on the occasion of his 60th Birthday

Four new Ln-based (Ln = Eu, Gd, Er) coordination networks, $\{[Eu_{1.5}(H_2O)_4(H_2O)]_n\}$ and $\{[Ln_{1.5}(H_2O)]_n\}$ (Ln = Eu, Gd, Er), were synthesized using the precursor diamantane-4,9-bis(dichlorophosphoryl) ($\text{Diam}(\text{POCl}_2)_2$) to form in situ the linker diamantane-4,9-bis(hydrogenphosphonate) ($\text{L} = \text{Diam}(\text{PO}_3\text{H})_2^{2-}$) with singly deprotonated phosphonate groups. These coordination networks represent the first reported examples of diamantane-phosphonate networks. The combination of Ln^{3+} ions and $\text{Diam}(\text{PO}_3\text{H})_2^{2-}$ resulted in the formation of doubly $-\text{PO}_3\text{H}^-$

bridged Ln chains. These chains are interconnected by the diamantane moiety of the diamantane-4,9-bis(hydrogenphosphonate) linker, forming 2D (Eu) or 3D (Eu, Gd, Er) networks. In the 3D networks, Eu^{3+} , Gd^{3+} , and Er^{3+} exhibit an uncommon coordination number of 6, from five phosphonate groups and one aqua ligand. This may be due to the constraints of the 3D network but at the same time shows the adaptability of Ln^{3+} ions to coordination constraints crucial for the formation of the 3D phosphonate frameworks.

1. Introduction

Organophosphonate ligands R-PO_3^{2-} or $\text{R-PO}_3\text{H}^-$ are highly valued in coordination chemistry for their versatility and robust binding capabilities, leading to a steady growth in their research. Phosphonate groups can bind to metal ions through up to three oxygen atoms.^[1,2] The strong $\text{M}-\text{O}-\text{P}$ bonds enhance the thermal and chemical stability of the resulting structures.^[3,4] Their structural characteristics enable the formation of chemically and thermally stable coordination networks. Yet, the synthesis of porous metal-phosphonate framework structures remains challenging due to the flexibility in the metal-oxygen binding.^[5,6] Both, the number of phosphonic acid groups in the linker^[7] and the selected metal ion^[8] are key factors in the synthesis of phosphonate-based coordination networks, together with the pH value of the synthesis medium which governs the (de)protonation state of the phosphonic acid ($\text{pK}_1 = 2-4$, $\text{pK}_2 = 4-9$).^[9] One route to predictable structures could be the use of bidentate phosphonate monoesters, as they have a similar binding mode to carboxylate linkers, leaving an alkoxy group that can be modified further.^[10]

Diamantane ($\text{C}_{14}\text{H}_{20}$) consists of two fused adamantane cages and can be a linear linker in metal coordination networks with

donor groups at the axial bridge-head 4,9-positions (Figure 1). The use of diamantane-containing linkers is very limited so far, with a series of molybdenum oxide diamantane-4,9-bis(triazol-4-yl) coordination polymers^[11] and a diamantane-4,9-dicarboxylate based UiO-66 analog (HHUD-3).^[12] The rigid and hydrophobic structure of diamondoid cage molecules can improve the stability of materials.^[13,14]

Compared to other phosphonate ligands,^[15] bulky diamantane-based phosphonates offer unique structural features that could influence lanthanide coordination and could possibly introduce porosity, while the addition of phosphonate groups further broadens their chemical versatility.^[12,16] Diamantanes are highly functionalizable, making them attractive for coordination chemistry application,^[17,18] in catalysis, sensing, drugs, and advanced materials science.^[19,20] When combined with lanthanides, some phosphonate linkers may also exhibit interesting luminescent or magnetic properties.

Lanthanide coordination networks owe a remarkable structural diversity due to the high coordination number and flexible coordination environment of the lanthanide ion.^[21-23] Coordination geometry flexibility and high coordination numbers make lanthanide-based networks a promising class of materials with properties such as luminescence,^[24,25] thermal stability,^[26] magnetism,^[27,28] and catalytic behavior.^[29-31]

Lanthanide-containing materials are well known for their narrow emission bands and high color purity in both the visible (VIS) and near-infrared (NIR) regions. Among them, Eu^{3+} and Tb^{3+} are the most used lanthanide ions in luminescence applications.^[32] For example, the Müller-Buschbaum group fine-tuned the luminescence color of $[\text{Gd}_2\text{Cl}_6(\text{bipy})_3] \cdot 2\text{bipy}$ from green to red by varying the amounts of Eu^{3+} or Tb^{3+} .^[33] Additionally, they synthesized the porous MOF $[\text{Ce}(\text{Im})_3\text{ImH}] \cdot \text{ImH}$ ($\text{ImH} = 1\text{-Himidazole}$), which exhibits blue luminescence and serves as a highly responsive detector for H_2O , O_2 , CH_2Cl_2 and MeCN .^[34]

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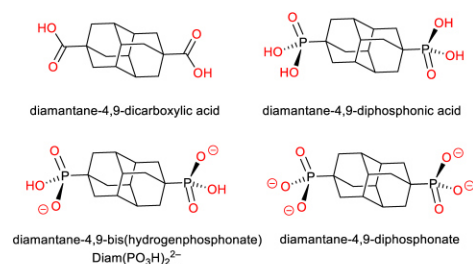


Figure 1. Structures of diamantane-4,9-dicarboxylic acid and -diphosphonic acid with the mono- and bis-deprotonated phosphonates.

Lanthanide coordination-networks have also been explored for their proton conductivity. Bazaga-García et al. reported a series of Ln[H(O₃PCH₂)₂-NH-(CH₂)₂-SO₃]₂·2H₂O networks (Ln = La, Pr, Nd, Sm, Eu, Gd, and Tb) which have been investigated as proton-conductive materials for membrane electrode assemblies.^[35] Layered Ln-oxalatophosphonates [Ln(H₂L)(C₂O₄)]·H₂O [Ln = La, Ce, Pr, H₂L = H(O₃PCH₂)₂-NH-(CH₂)₂-SO₃] and [Ln₂(H₃L)(C₂O₄)₃(H₂O)₄]₂·2H₂O [Ln = Eu and Dy, H₃L = H(O₃PCH₂)₂-NH-(CH₂)₂-SO₃H] exhibit both characteristic luminescence and intriguing magnetic properties, such as temperature-dependent magnet behavior and antiferromagnetic interaction between Dy^{III} ions at low temperatures.

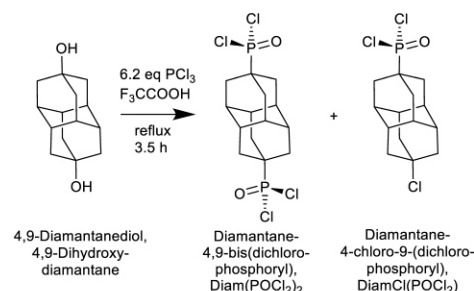
This study introduces four novel coordination networks synthesized using diamantane-4,9-bis(hydrogenphosphonate) as the linker with the lanthanides Eu³⁺, Gd³⁺, and Er³⁺.

The structural similarity of the diphosphonates to dicarboxylates allows for reticular chemistry,^[36–38] while the stronger M—O—P bonds may enhance thermal and chemical stability.^[39,40]

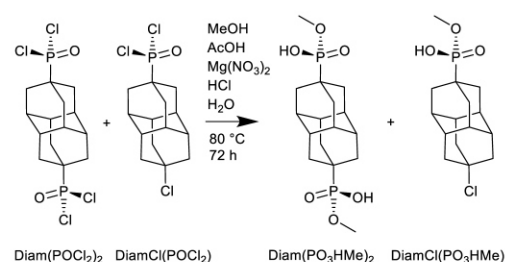
2. Results and Discussion

The reaction of 4,9-dihydroxydiamantane with PCl₃ in trifluoroacetic acid as described by Fokin et al.^[41] afforded in our hands a mixture of the desired product diamantane-4,9-bis(dichlorophosphoryl) (Diam(POCl₂)₂) and of diamantane-4-chloro-9-(dichlorophosphoryl), DiamCl(POCl₂) as a byproduct (Scheme 1). DiamCl(POCl₂) probably forms with hydrochloric acid from the hydrolysis of PCl₃ with traces of water. Attempts to separate the two compounds via column chromatography were unsuccessful.

To try to separate the mixture of Diam(POCl₂)₂ and DiamCl(POCl₂) through formation of a magnesium phosphonate network with only the hydrolysis product of Diam(POCl₂)₂, we reacted the mixture with methanol, Mg(NO₃)₂·6H₂O, water, and acetic acid in the presence of catalytic amounts of hydrochloric acid (Scheme 2). However, the reaction afforded no magnesium compound, but instead the product mixture contained crystals of diamantane-4,9-bis(methyl hydrogenphosphonate) (Diam(PO₃HMe)₂, Figure 2), which is the dimethyl ester of



Scheme 1. Synthesis of Diam(POCl₂)₂ and the DiamCl(POCl₂) byproduct.



Scheme 2. Synthesis of diamantane-4,9-bis(methyl hydrogenphosphonate), (Diam(PO₃HMe)₂), and diamantane-4-chloro-9-(methyl hydrogenphosphonate) (DiamCl(PO₃HMe)).

diamantane-4,9-diphosphonic acid (Diam(PO₃H₂)₂), and of diamantane-4-chloro-9-(methyl hydrogenphosphonate) (DiamCl(PO₃HMe), Figure 3) as a monohydrate. The latter is the monomethyl ester of diamantane-4-chloro-9-phosphonic acid. Both esters derive from the hydrolysis of the respective dichlorophosphoryl compounds Diam(POCl₂)₂ and DiamCl(POCl₂) (Scheme 2).

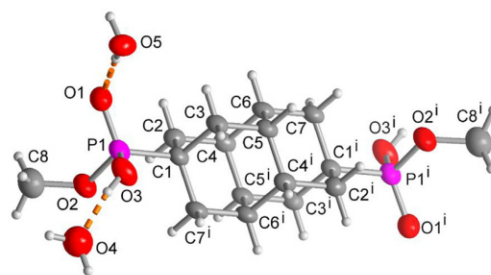


Figure 2. Molecular structure of diamantane-4,9-bis(methyl hydrogenphosphonate) (Diam(PO₃HMe)₂) trihydrate with two hydrogen-bonded crystal water molecules (orange dashed lines). A detailed description of the structure can be found in the Section S5, Supporting Information.

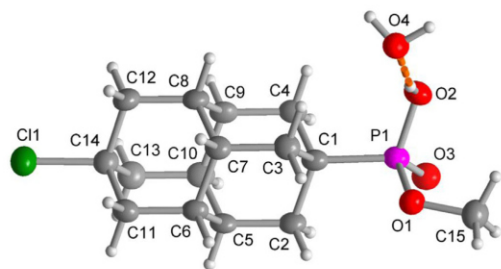
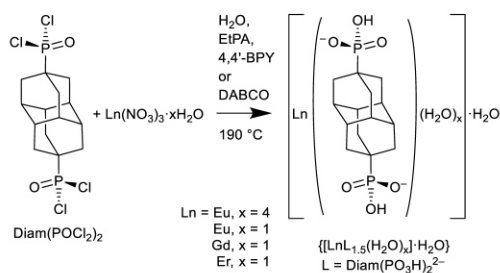


Figure 3. Molecular structure of diamantane-4-chloro-9-(methyl hydrogenphosphonate) (DiamCl(PO₃HMe)) monohydrate with the hydrogen-bonded crystal water molecule (orange dashed line). A detailed description of the structure can be found in the Section S6, Supporting Information.

Commercial Diam(POCl₂)₂, supplied by TransMIT, served as a precursor for the in situ generation of diamantane-4,9-bis(hydrogenphosphonate) (Diam(PO₃H)₂²⁻) by hydrolysis of the P–Cl bonds under hydrothermal conditions. The slowly formed phosphonate then acted as a linker in the synthesis of four novel lanthanide-based coordination networks as well-crystallized reaction products (Figure S1, Supporting Information, Scheme 3). The synthesis was only successful when using p-ethylphosphonic acid (EtPA) and 4,4'-bipyridine (4,4'-BPY) or 1,4-diazabicyclo [2.2.2]octane (DABCO). EtPA served both as a well-soluble monophosphonic acid to lower the pH and as a modulator. Modulators like EtPA can influence crystallization kinetics by controlling the deprotonation of linker molecules and regulating coordination to the metal centers, in order to improve crystallinity and for morphology control. This approach is well established in the synthesis of carboxylate MOFs, where monocarboxylic acids are routinely used as modulators to control crystal growth and improve crystallinity.^[42,43] 4,4'-Bipyridine and DABCO can act as a weak ligand that temporarily coordinates to the metal centers, thereby acting as a template. As a base, it can modulate the pH value and deprotonate the phosphonic acid with formation



Scheme 3. In situ formation of lanthanide networks with diamantane-4,9-bis(hydrogenphosphonate), Diam(PO₃H)₂²⁻ from the hydrolysis of Diam(POCl₂)₂. Ln = Eu, Gd, Er, EtPA = p-ethylphosphonic acid, 4,4'-BPY = 4,4'-bipyridine, DABCO = 1,4-diazabicyclo [2.2.2]octane.

of bipyridinium cations. Eventually, the EtPA modulator and 4,4'-BPY or DABCO will be displaced by the phosphonate linker, enabling the formation of the desired coordination network.^[44]

The four networks were orthorhombic {[EuL_{1.5}(H₂O)₄]·H₂O}_n (1-o), monoclinic {[EuL_{1.5}(H₂O)]·H₂O}_n (1-m), {[GdL_{1.5}(H₂O)]·H₂O}_n (2) and {[ErL_{1.5}(H₂O)]·H₂O}_n (3) with L = Diam(PO₃H)₂²⁻ and with the latter three networks being isostructural.

The tetraaqua europium compound {[EuL_{1.5}(H₂O)₄]·H₂O}_n (1-o) crystallizes in the orthorhombic crystal system with the space group Pbca. The asymmetric unit contains one Eu atom, a fully and a half-occupied diamantane-4,9-bis(hydrogenphosphonate) linker, four aqua ligands, and a crystal water molecule (Figure 4). Each phosphonate group in the linker is only singly deprotonated, forming a hydrogenphosphonate (–PO₃H) group.

The unique Eu atom is eight-coordinated by four O atoms from four different hydrogenphosphonate (–PO₃H) groups and four aqua ligands (Figure 4b,c). The coordination environment around Eu adopts a distorted dodecahedral or square antiprismatic geometry. The shape of the coordination polyhedron in {[EuL_{1.5}(H₂O)₄]·H₂O}_n (1-o) is very close to square antiprism (SAPR-8) with a CShM value of 0.770 (the values of the CShM, which is the minimal mean square deviation of the vertex

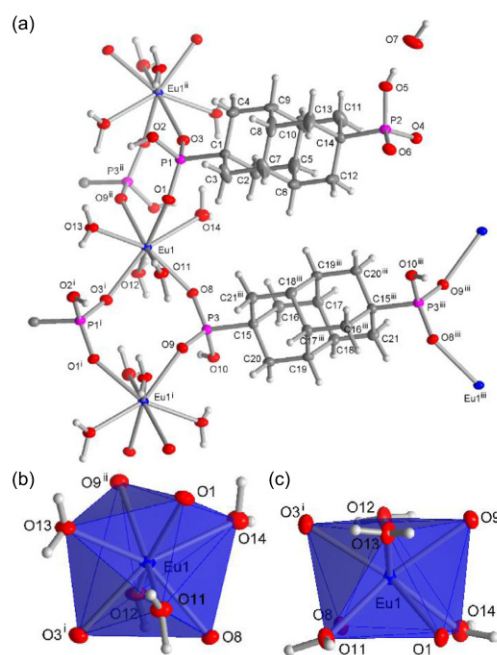


Figure 4. The extended asymmetric unit a) in {[EuL_{1.5}(H₂O)₄]·H₂O}_n (1-o), and the coordination sphere around europium emphasizing the coordination as dodecahedral b) or as square-antiprismatic c) (50% thermal ellipsoids), symmetry codes: (i) $x + 1/2, y, -z + 1/2$; (ii) $x - 1/2, y, -z + 1/2$; (iii) $-x + 2, -y + 1, -z + 1$. A selection of bond distances and angles in 1-o can be found in Table S7b, Supporting Information.

coordinates from the ideal polyhedron, were computed by the SHAPE 2.1 program,^[45] and the shorthand codes of the polyhedra in the brackets follow the ones used in the program). In comparison, the triangular dodecahedron (TDD-8) is the second most corresponding among typical symmetric idealized polyhedra with a CShM value of 1.83 compared to the much more different cube (CU-8) at 6.93. It is interesting to note that while the observed shape of the $\{\text{EuO}_8\}$ is not very far from the triangular dodecahedron, it is not lying on the minimal distortion path from the square antiprism to the latter (the deviation from the path is 31.9 and generalized coordinate of 51.8 in the range of 0–100%, as calculated by SHAPE 2.1). On the other hand, the observed geometry could be viewed as lying on the minimal distortion path from the square antiprism to a cube (the deviation from the path is 4.8, while the generalized coordinate is 26.0). Thus, the actual configuration could be represented as a modest rotation of the bottom part of the prism around the original C_4 axis towards the cubic shape.

The phosphonate linker with P1 and P2 is only a bridging group at P1, coordinating two Eu atoms. The phosphonate group at P2 is not coordinated to a metal atom and is solely involved in hydrogen bonding (Figure 4a). In the linker containing P3, which sits on a special position, each phosphonate group bridges between two Eu atoms, resulting in the linker as a whole connecting four Eu atoms. Out of the four $-\text{PO}_3\text{H}^-$ groups around Eu, two with P1 and two with P3, each bridge to a neighboring Eu atom, resulting in each Eu atom being in total connected to 6 other Eu atoms (Figure 5).

The direct phosphonate P1 and P3 bridging action between the Eu atoms leads to a slightly corrugated doubly bridged Eu

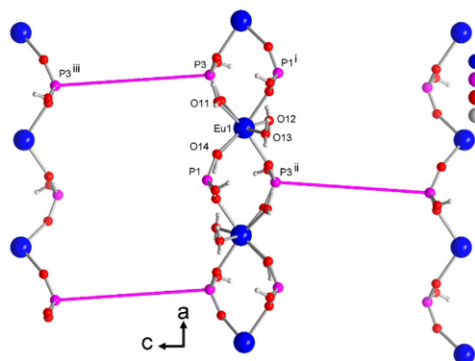


Figure 5. Schematic connectivity around Eu in **1-o** showing the connectivity to 6 neighboring Eu atoms from which two are connected directly through the P1 and P3 phosphonate groups and four across the P3-P3' diamantane linker. The diamantane unit is replaced by a direct P–P connector in magenta for clarity (the crystal water molecules are not shown). Also, for clarity, the diamantane moiety in the P1-P2 linker, which is only metal-coordinating at P1, has been removed together with the non-coordinating P2 group (cf. Figure S15, Supporting Information). Symmetry codes: (i) $x + 1/2, y, -z + 1/2$; (ii) $x - 1/2, y, -z + 1/2$; (iii) $-x + 2, -y + 1, -z + 1$.

chain parallel to the crystallographic a -direction. Each Eu chain is “left-and-right” connected through the P3-P3' linker to two adjacent strands (Figure 5), forming a layered 2D 6-c uninodal network with the point symbol $3^6.4^2.5^6.6$ as analyzed by ToposPro (details in Supporting Information).^[46]

The hydrogen bonding scheme in **1-o** is illustrated in Figure S16, Supporting Information. The H-atoms of the hydrogenphosphonate groups ($-\text{PO}_3\text{H}^-$) are all involved in hydrogen bonding, either to other phosphonate groups or to the crystal water molecule.

The monoaqua lanthanide compounds $\{[\text{LnL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ ($\text{Ln} = \text{Eu}$ (**1-m**), Gd (**2**), Er (**3**)) crystallize isostructurally in the monoclinic crystal system with the space group $P2_1/n$. Their asymmetric unit consists of one Ln^{3+} atom, a fully and half-occupied diamantane-4,9-bis(hydrogenphosphonate) linker, one aqua ligand, and a crystal water molecule. The crystal water molecule is split over two nearby positions with 0.75 and 0.25 occupancy in **1-m**, two partially occupied crystal water molecules in **2** and two half-occupied crystal water molecules in **3**. As before, each phosphonate group is only singly deprotonated, presenting a hydrogenphosphonate (PO_3H^-) group.

In the structure of **1-m** and of **2**, the Eu^{3+} and Gd^{3+} atom are six- to seven-coordinated by five to six O atoms from five different hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) groups and the aqua ligand. The sixfold coordination around Eu^{3+} and Gd^{3+} is a distorted octahedron (Figure 6a,b). A coordination from a long $\text{Eu1}-\text{O4}^i$ bond of

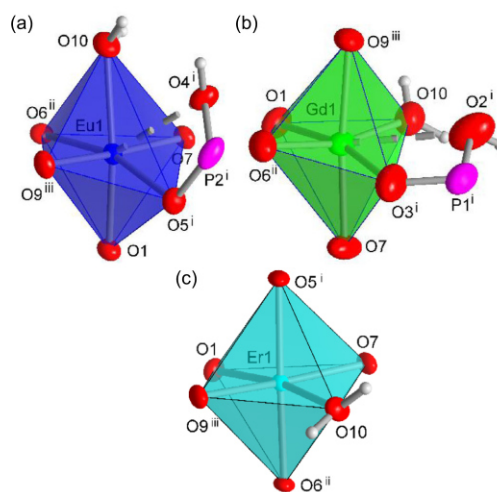


Figure 6. The coordination sphere around a) Eu^{3+} in **1-m**, b) Gd^{3+} in **2**, and c) Er^{3+} in **3** in the isostructural networks $\{[\text{LnL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (50% thermal ellipsoids). Symmetry codes in **1-m**: (i) $-x + 1/2, y + 1/2, -z + 1/2$; (ii) $x + 1, y, z$; (iii) $-x + 3/2, y + 1/2, -z + 1/2$; in **2**: (i) $-x + 1/2, y - 1/2, -z + 3/2$; (ii) $x - 1, y, z$; (iii) $-x + 1/2, y + 1/2, -z + 3/2$; in **3**: (i) $-x + 1/2, y + 1/2, -z + 3/2$; (ii) $x + 1, y, z$; (iii) $-x + 3/2, y - 1/2, -z + 3/2$. A selection of bond distances and angles in **1-m**, **2**, and **3** can be found in Table S9b, S11b, S13b, Supporting Information, respectively.

2.823 Å may be taken into account from a then chelating O—P—OH group (Figure 6a). The other Eu1—O bond lengths lie between 2.090 and 2.399 Å (Table S9b, Supporting Information).

The possibly sevenfold coordination of Gd³⁺ derives from a long Gd1—O2ⁱ bond of 2.900 Å from a chelating O—P—OH group (Figure 6b). The other Gd1—O bond lengths lie between 2.228 and 2.401 Å (Table S11b, Supporting Information). The sevenfold coordination of Eu³⁺ and Gd³⁺ would be capped octahedrons (Figure 6a,b).

In the Er structure of **3**, the Er³⁺ atom is clearly only six-coordinated by five O atoms from five different hydrogenphosphonate (PO₃H[−]) groups and an aqua ligand (Figure 6c). The Er1—O bond lengths lie between 2.178 and 2.336 Å (Table S13b, Supporting Information). The next nearest Er—O distance is over 3.7 Å. The coordination around Er is a distorted octahedron. The tendency towards sevenfold coordination of Eu³⁺ and Gd³⁺ versus the clearly sixfold coordination of Er³⁺ in the isostructural networks is evidence of the larger ionic radii of Eu³⁺ (0.947 Å) and Gd³⁺ (0.935 Å) versus Er³⁺ (0.89 Å). At the same time, it can be noted that in the structure of **1-o** Eu³⁺ was eightfold coordinated.

The lanthanide contraction leads to a systematic decrease in ionic radii from La³⁺ to Lu³⁺, decreasing also the coordination number (CN) and influencing the ligand preferences.^[47–49] The coordination number of lanthanides ranges from 6 to 12, depending on ligand size, charge, and steric effects.^[50,51] Lanthanides with larger ionic radii, such as La³⁺, Ce³⁺, and Pr³⁺, tend to adopt nine-coordination, whereas smaller lanthanides like Eu³⁺ and Dy³⁺ show nine- and eight-coordination.^[52,53] Gadolinium(III) and erbium(III) also display CN = 8 or 9 in many complexes, though CN = 6 is observed in structures with sterically demanding ligands or strong chelating effects.^[54–56]

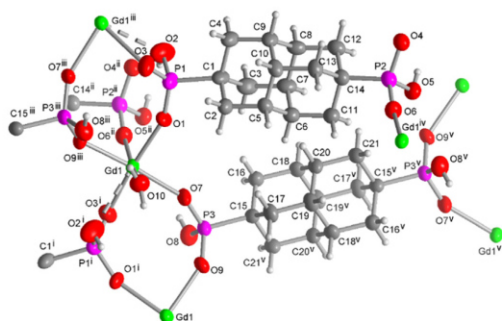


Figure 7. The extended asymmetric unit in $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$, not showing the minor contribution of the disordered atoms of the phosphonate group at P1. The linker containing P1 and P2 acts as a bridging group only at P1, coordinating to two Gd atoms. At P2, it is terminally coordinated to only one Gd atom. The linker with P3, which occupies a special position, connects four Gd atoms (50% thermal ellipsoids). Symmetry codes: (i) $-x + 1/2, y - 1/2, -z + 3/2$; (ii) $x - 1, y, z$; (iii) $-x + 1/2, y + 1/2, -z + 3/2$; (iv) $x + 1, y, z$; (v) $-x + 1, -y, -z + 1$. See Figure S17 and S24, Supporting Information for the structure images of **1-m** and **3**, respectively.

In the Ln-phosphonate structures described here, only in **1-o** does Eu³⁺ display the common CN of 8 with four phosphonate groups and four water molecules, while in **1-m**, **2**, and **3**, Eu³⁺, Gd³⁺, and Er³⁺ each exhibit an uncommon CN of 6, comprising five phosphonate groups and one water molecule. This may be due to the constraints of the 3D network architecture (see below) on coordination behavior.^[57] Conversely, the adaptability of Ln³⁺ ions to coordination constraints is crucial for the structural diversity of their complexes and for the formation of the 3D phosphonate frameworks.^[32]

We will visualize the following general network structure description with the Gd compound **2**. In the three isostructural compounds $\{[\text{LnL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (Ln = Eu (**1-m**), Gd (**2**), Er (**3**)), the fully occupied linker bridges only between three Ln atoms as with one of its ends it functions as a monodentate group and is terminally coordinated to only one Ln atom (Figure 7).

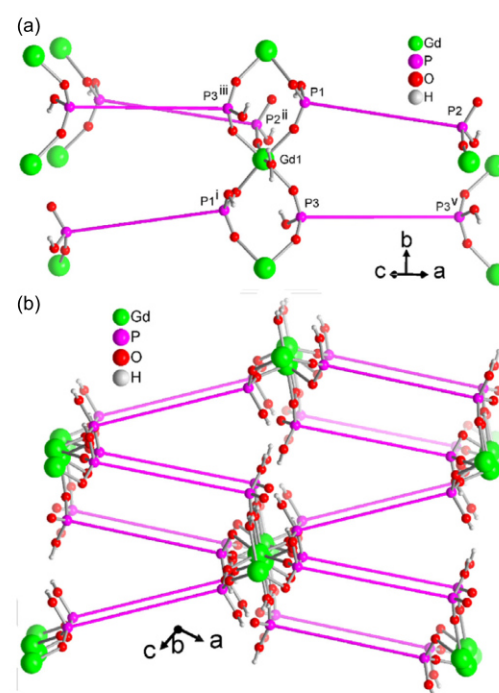


Figure 8. Schematic connectivity around Gd in **2** showing the connectivity to 10 neighboring Gd atoms from which two are connected directly through the P1 and P3 phosphonate groups and eight across the diamantane moiety of the linker. The doubly bridged Gd chains run parallel to the *b*-direction and are up-and-down connected to four parallel chains. a) View perpendicular to the *b*-direction, b) view approximately along the *b*-direction depicting the extended 3D network. The diamantane unit is replaced by a direct P—P connector in magenta for clarity (the crystal water molecules are not shown). Symmetry codes: (i) $-x + 1/2, y - 1/2, -z + 3/2$; (ii) $x - 1, y, z$; (iii) $-x + 1/2, y + 1/2, -z + 3/2$; (iv) $x + 1, y, z$; (v) $-x + 1, -y, -z + 1$. See Figure S18 and S25, Supporting Information for the corresponding images of **1-m** and **3**.

In the half-occupied linker, which sits on a special position, each phosphonate bridges between two Ln atoms, and the linker as a whole then connects four Ln atoms. Each Ln atom is in total connected to 10 other Ln atoms, with two through the direct phosphonate P1 and P3 bridging action and eight connected across the diamantane moiety of the linker (Figure 7, 8a).

The direct phosphonate bridging action between two adjacent Ln atoms leads to a corrugated doubly bridged Ln-phosphonate chain (Figure 8a) which is "left-and-right" connected to four adjacent strands giving 3D 10-c uni-nodal networks (Figure 8b) with the point symbol $3^{12}4^{22}5^{10}6$ as analyzed by ToposPro.^[45,58]

As seen in 1-o, and also in 1-m, 2, and 3, the H-atoms of the hydrogenphosphonate groups ($-\text{PO}_3\text{H}^-$) are all involved in hydrogen bonding, either to other phosphonate groups or to the crystal water molecules. The hydrogen bonding schemes for 1-m, 2, and 3 are shown in Figures S20, S23, and S27, Supporting Information, respectively; a small graph set analysis is given in Section S11, Supporting Information, with Figure S28, Supporting Information.

At last, the hydrophobic interactions between the diamantane moieties within the hydrophobic layers deserve a mention. The weak C—H—H—C contacts could play a role in stabilizing hydrophobic structures, when present in large numbers (the "sticky finger interactions"). In the presented structures their role is secondary, and the contact length tends to be quite long, suggesting mere dispersion/vdW interactions. This is expected, because the primary structure-defining forces are the metal-phosphonate coordination and H—bonding, and the residual-space filling water molecules with other constituents of the polar layers play a role in defining the overall density of the structure rather than the interaction between the diamantane moieties.

3. Conclusions

The structural investigations of the presented lanthanide hydrogenphosphonate frameworks reveal distinct coordination environments depending on the ionic radii of the respective metal centers and the dimensionality of the network. In the 2D network, the largest Ln^{3+} ion in the series here, Eu^{3+} adopts the expected eightfold coordination. In the isostructural 3D networks, Eu^{3+} , Gd^{3+} , and Er^{3+} all tend to a more unusual sixfold coordination in a distorted octahedron. While Eu^{3+} and Gd^{3+} in these 3D networks still have a long Ln—O bond, Er^{3+} has an unequivocal coordination number (CN) of six. This finding emphasizes the critical role of constraints of a coordination network which apparently overrules typical CN preferences of eight to nine of Ln^{3+} ions. Simultaneously, the Ln ions need to be adaptable in their coordination number for the formation of the phosphonate-based frameworks. Further studies will expand the range of Ln ions to verify the above hypothesis about CN and network dimensionality.

4. Experimental Section

Chemicals: All chemicals were used as received from suppliers in reagent grade quality (full list in Table S1, Supporting Information).

Single-Crystal X-Ray Crystallography: Data collection was carried out on a Rigaku XtaLAB Synergy (Rigaku, Tokyo, Japan), Dualflex, HyPix diffractometer with a micro-focus X-ray tube with Cu-K α radiation ($\lambda = 1.54182 \text{ \AA}$). A polarized-light Leica M80 microscope (Leica, Wetzlar, Germany) was used to choose suitable single crystals which were covered with oil on a cryo-loop. Temperature for data collection was 150 K. CRYSLISPRO was used for cell refinement, data reduction, and absorption correction.^[59] The crystal structures were solved using OLEX2—1.5 with SHELXT and refined with SHELXL.^[60–62] All nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms on C were positioned geometrically. Hydrogen atoms on O were found and refined with Uiso(H) = 1.5 Ueq(O). Crystal and structure refinement data of diamantane-4,9-bis(methyl hydrogenphosphonate) ($\text{Diam}(\text{PO}_3\text{HMe})_2$) and diamantane-4-chloro-9-(methyl hydrogenphosphonate) ($\text{DiamCl}(\text{PO}_3\text{HMe})$) are summarized in Table 1, for the lanthanide diamantane-phosphonate networks in Table 2. The crystallographic data (excluding structure factors) for the structures were deposited with the Cambridge Crystallographic Data Centre (CCDC deposition numbers 2,455,260–2,455,265) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.^[63]

Powder X-Ray Diffraction (PXRD): PXRD patterns were measured over the 2θ range of $5\text{--}50^\circ$ in reflective mode using a Rigaku MiniFlex600 or a Bruker D2 Phaser diffractometer with graphite monochromated Cu-K α irradiation ($\lambda = 1.54182 \text{ \AA}$) at room temperature. The Rigaku MiniFlex600 was operated using a 600 W source (40 kV, 15 mA) and equipped with a HyPix-400 MF 2D hybrid pixel array detector (HPAD); the measurements were performed with a 0.01° step size. The Bruker D2 Phaser diffractometer was operated with a 300 W source (30 kV, 10 mA) and equipped with a Lynxeye detector.

Thermogravimetric Analysis (TGA): Thermogravimetric analyses were performed using a Netzsch TG209 F3 Tarsus under synthetic air with a heating ramp of 10 K min^{-1} up to 1000°C .

NMR Spectra: NMR-spectra were measured with a Bruker Avance NEO evo—600 (^1H : 600 MHz, ^{31}P : 242.9 MHz). ^1H -NMR chemical shifts are referenced to the residual solvent signal versus TMS ($\delta\text{CHCl}_3 = 7.26 \text{ ppm}$). $^{31}\text{P}\{^1\text{H}\}$ -NMR chemical shifts are externally referenced to H_3PO_4 .

Synthesis of Diamantane-4,9-Bis(Dichlorophosphoryl), $\text{Diam}(\text{POCl}_2)_2$: Procedure a: Diamantane-4,9-bis(dichlorophosphoryl) was synthesized according to a modified version of a method developed by Fokin et al. (Scheme 1).^[41] The amount of 597 mg (2.7 mmol) of 4,9-dihydroxydiamantane was added to a 100 mL two-necked round bottom flask, followed by the addition of 15 mL of trifluoroacetic acid and 1.5 mL (17.1 mmol) of PCl_3 . The reaction mixture was refluxed for 3.5 h and subsequently quenched with water. A solid product was isolated by filtration and dried in a vacuum oven at 60°C overnight. While the literature reports a yield of $\approx 90\%$, consistent reproducibility proved challenging across multiple batches. Notably, product precipitation occurred inconsistently, with some reactions yielding immediate precipitates within 30 min, while others remained in solution until quenching with cold water. The ^1H and ^{31}P NMR analysis (see Figures S7 and S8, Supporting Information) revealed the presence of at least $\text{DiamCl}(\text{POCl}_2)$ and $\text{Diam}(\text{POCl}_2)_2$ (cf. Scheme 1) in a ratio of $\approx 2.6:1$ which could not be separated by column chromatography in our hands.

Procedure b: To explore alternative reaction conditions, a solvothermal approach was investigated. For this, 55 mg (0.25 mmol) of 4,9-dihydroxydiamantane, 3 mL of trifluoroacetic acid, and 0.2 mL (2.3 mmol) of PCl_3 were combined in a 10 mL Teflon-lined steel autoclave. The reaction mixture was heated to 95°C within 1.5 h, maintained at this temperature for 6 h, and then gradually cooled to room temperature. A solid product was isolated in about 10% yield

Table 1. Crystal and structure refinement data for Diam(PO₃HMe)₂ and DiamCl(PO₃HMe).

	Diam(PO ₃ HMe) ₂	DiamCl(PO ₃ HMe)
Empirical formula	C ₁₆ H ₂₆ O ₆ P ₂ ·3(H ₂ O)	C ₁₅ H ₂₂ ClO ₃ P·H ₂ O
M/g mol ⁻¹	430.35	334.76
T/K	150	150
Wavelength/Å ^{a)}	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2 ₁ /c
a/Å	6.84902(12)	16.7708(2)
b/Å	11.2619(2)	7.3404(1)
c/Å	25.2013(5)	12.6215(2)
β/deg	95.9935(16)	92.134(1)
V/Å ³	1933.22(6)	1552.68(4)
Z	4	4
Calcd. Density/g cm ⁻³	1.479	1.432
μ/mm ⁻¹	2.47	3.27
F(000)/e	920	712
Crystal size/mm ³	0.65 × 0.31 × 0.18	0.15 × 0.08 × 0.05
θ Range/deg	3.5–78.4	2.6–79.7
Reflections collected	25,193	29,195
Independent reflections; R _{int}	1966; 0.079	3274; 0.036
Completeness to θ _{max} /%	1.000	1.000
R1; wR2 (I > 2 σ(I)) ^{a)}	0.1016; 0.2726	0.0448; 0.1198
R1; wR2 (all data) ^{b)}	0.1010; 0.2736	0.0406; 0.1167
Goodness-of-fit ^{c)}	1.14	1.12
Δρ _{fin} (max; min)/e Å ^{-3d)}	1.12; -0.72	0.45; -0.45
CCDC no.	2,455,260	2,455,261

^{a)}R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$; ^{b)}wR2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$, a and b are constants adjusted by the program; ^{c)}GoF = $S = [\sum w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters; ^{d)}Largest peak and hole in final difference map.

Table 2. Crystal and structure refinement data for 1-o, 1-m, 2, and 3.

	{[EuL _{1.5} (H ₂ O) ₄]·H ₂ O} _{nr} (1-o)	{[EuL _{1.5} (H ₂ O)]·H ₂ O} _{nr} (1-m)	{[GdL _{1.5} (H ₂ O)]·H ₂ O} _{nr} (2)	{[ErL _{1.5} (H ₂ O)]·H ₂ O} _{nr} (3)
Empirical formula	C ₂₁ H ₃₈ EuO ₁₃ P ₃ ·H ₂ O	C ₂₁ H ₃₂ EuO ₁₀ P ₃ ·H ₂ O	C ₂₁ H ₃₂ GdO ₁₀ P ₃ ·H ₂ O	C ₂₁ H ₃₂ ErO ₁₀ P ₃ ·H ₂ O
M/g mol ⁻¹	761.40	707.35	712.64	722.65
T/K	150	150	150	150
Wavelength/Å ^{a)}	1.54184	1.54184	1.54184	1.54184
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	Pbca	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
a/Å	11.4048(2)	11.8043(2)	11.9044(2)	11.9973(1)
b/Å	19.9120(2)	11.1236(2)	11.0888(2)	10.9778(1)
c/Å	23.4321(3)	19.8966(4)	19.9039(3)	19.7560(1)
β/deg	90	104.673(2)	103.737(2)	102.836(1)
V/Å ³	5321.25(13)	2527.35(8)	2552.27(8)	2536.92(4)
Z	8	4	4	4
Calcd. density/g cm ⁻³	1.901	1.859	1.855	1.892
μ/mm ⁻¹	19.22	20.22	19.10	8.45
F(000)/e	3088	1424	1428	1444
Crystal size/mm ³	0.22 × 0.12 × 0.06	0.25 × 0.2 × 0.05	0.15 × 0.12 × 0.08	0.44 × 0.08 × 0.04
θ Range/deg	3.8–77.4	4.0–79.5	4.0–77.1	4.0–78.1
Reflections collected	33,907	25,766	78,115	81,749
Independent reflections; R _{int}	5374; 0.052	5331; 0.052	5314; 0.078	5187; 0.062
Completeness to θ _{max} /%	0.999	0.9998	1.000	1.000
R1; wR2 (I > 2 σ(I)) ^{a)}	0.0359; 0.0973	0.0498; 0.1415	0.0490; 0.1383	0.0357; 0.993
R1; wR2 (all data) ^{b)}	0.0339; 0.0957	0.0527; 0.1447	0.0459; 0.1350	0.0343; 0.0978
Goodness-of-fit ^{c)}	1.045	1.13	1.143	1.087
Δρ _{fin} (max; min)/e Å ^{-3d)}	1.04; -1.26	1.73; -1.29	0.978; -2.01	1.49; -1.39
CCDC no.	2,455,262	2,455,263	2,455,264	2,455,265

^{a)}R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$; ^{b)}wR2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$, a and b are constants adjusted by the program; ^{c)}GoF = $S = [\sum w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters; ^{d)}Largest peak and hole in final difference map.

by filtration, washed with cold ultrapure water, and dried in a vacuum oven at 60 °C for 1 day. The ^1H and ^{31}P NMR analysis (see Figures S9 and S10, Supporting Information) revealed again the presence of $\text{DiamCl}(\text{POCl}_2)_2$ and $\text{Diam}(\text{POCl}_2)_2$ (cf. Scheme 1) in a ratio of about 0.8:1. Elevating the temperature or extending the reaction time did not significantly improve the yield or selectivity of the reaction towards $\text{Diam}(\text{POCl}_2)_2$.

Synthesis of Diamantane-4,9-Bis(Methyl Hydrogenphosphonate, $\text{Diam}(\text{PO}_3\text{HMe})_2$, and Diamantane-4-Chloro-9-(Methyl Hydrogenphosphonate) ($\text{DiamCl}(\text{PO}_3\text{HMe})$) Monohydrate: The amount of 5.4 mg (0.01 mmol) of the above mixture from procedure b which contained diamantane-4,9-bis(dichlorophosphoryl) and diamantane-4-chloro-9-(dichloro-phosphoryl) together with 5.8 mg (0.02 mmol) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was placed in a Pyrex glass tube. Subsequently, 2 mL of methanol, 100 μL of ultrapure water, and 250 μL of glacial acetic acid were added sequentially. The Pyrex tube was sealed and subjected to ultrasonic homogenization for 10 min. The tube was then transferred to a synthesis oven and heated at 80 °C for 72 h. From the product mixture crystals of $\text{Diam}(\text{PO}_3\text{HMe})_2$, diamantane-4-chloro-9-(methyl hydrogenphosphonate) ($\text{DiamCl}(\text{PO}_3\text{HMe})$) and of unreacted $\text{Diam}(\text{POCl}_2)_2$ were obtained as thin, colorless rods and thin plates and only identified from single-crystal X-ray analysis (no further analyses were performed).

Synthesis of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$ 1-o: In a typical procedure, 18.7 mg (0.044 mmol) of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 5.5 mg (0.013 mmol) of commercial diamantane-4,9-bis(dichlorophosphoryl), 3.1 mg (0.02 mmol) of 4,4'-bipyridine, and 11.2 mg (0.10 mmol) of p-ethylphosphonic acid (EtPA) were combined in a 10 mL Teflon liner. Ultrapure water (5 mL) was added, and the mixture was stirred for ≈ 3 min with a small stirring bar on a stirring plate. The Teflon liner was then sealed in a stainless-steel autoclave and heated to 190 °C within 8 h. The reaction was maintained at 190 °C for 5 days before being gradually cooled to room temperature over 16 h. The resulting product was transferred to a centrifuge tube and washed several times with ultrapure water. The product consisted of a mixture of white microcrystalline powder and thin, colorless needles. As it was not possible to further purify the compound (see Figure S1A, Supporting Information), no further analyses such as PXRD or TGA could be performed.

Synthesis of $\{[\text{Eu}(\text{L}_{1.5}(\text{H}_2\text{O})) \cdot \text{H}_2\text{O}\}_n$ 1-m: The hydrothermal synthesis was carried out as for 1-o, combining $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (124.1 mg, 0.29 mmol), 42.2 mg (0.10 mmol) of commercial diamantane-4,9-bis(dichlorophosphoryl), 23.4 mg (0.15 mmol) of 4,4'-bipyridine, 37.4 mg (0.34 mmol) p-ethylphosphonic acid, and 10 mL of water. The resulting product was thoroughly washed with ultrapure water and methanol and obtained as colorless needles/rods (see Figure S1B, Supporting Information). The product was dried overnight in a vacuum oven at 60 °C for further analysis. The powder X-ray diffractogram and thermogravimetric analysis are given in Figures S2 and S4, Supporting Information, respectively. Compound 1-m could also be obtained without 4,4'-bpy.

Yield: 35.4 mg, 75% based on linker.

Synthesis of $\{[\text{Gd}(\text{L}_{1.5}(\text{H}_2\text{O})) \cdot \text{H}_2\text{O}\}_n$ 2: The hydrothermal synthesis was carried out as for 1-o, from 130.9 mg (0.29 mmol) of $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 42.1 mg (0.10 mmol) of commercial diamantane-4,9-bis(dichlorophosphoryl), 23.4 mg (0.15 mmol) of 4,4'-bipyridine, 37.4 mg (0.34 mmol) p-ethylphosphonic acid, and 10 mL of water with heating to 180 °C. Washing and drying were carried out analogously to 1-m. The resulting product was isolated as thin, colorless needles (see Figure S1C, Supporting Information). To further characterize compound 2, PXRD and TGA are shown in Figure S3 and S5, Supporting Information, respectively.

Yield: 42.8 mg, 88% based on linker.

Synthesis of $\{[\text{Er}(\text{L}_{1.5}(\text{H}_2\text{O})) \cdot \text{H}_2\text{O}\}_n$ 3: The hydrothermal synthesis was carried out as for 1-o, from 128.6 mg (0.29 mmol) of $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 42.0 mg (0.10 mmol) of diamantane-4,9-bis(dichlorophosphoryl), and 15.7 mg (0.14 mmol) of 1,4-diazabicyclo[2.2.2]octane, 37.3 mg (0.34 mmol) p-ethylphosphonic acid, and 5 mL of water. Washing and drying were carried out analogously to 1-m. The resulting product was isolated as thin, colorless needles (see Figure S1D, Supporting Information), with some powdery by-product which could not be removed by washing. PXRD and TGA are displayed in Figure S3 and S6, Supporting Information, respectively.

Yield: 50.6 mg, 76% based on linker.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

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Supporting Information

Lanthanide coordination networks based on diamantane-4,9-diphosphonic acid.

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Section S1. List of chemicals**Table S1.** Overview of chemicals used.

Chemical	Supplier	Purity
4,4'-Bipyridine	J&K Scientific	99%
4,9-Diamantanediol	TransMIT	95%
Diamantane-4,9-bis(dichlorophosphoryl)	TransMIT	95%
1,4-Diazabicyclo[2.2.2]octane	Alfa Aesar	98%
P-Ethylphosphonic acid	Alfa Aesar	98%
Europium(III) nitrate pentahydrate	Sigma-Aldrich	99.9%
Erbium(III) nitrate pentahydrate	chemPUR	99.9%
Gadolinium(III) nitrate hexahydrate	Alfa Aesar	99.9%
Hydrochlorid acid	VWR	35%
Acetone	VWR	100%
Chloroform	Fischer Sci.	99.8%
Ethanol	Merck	p.a.
Methanol	Fisher	99,9%
Trifluoroacetic acid	CARLO ERBA	p.a.

Section S2. Crystal images and powder X-ray diffraction

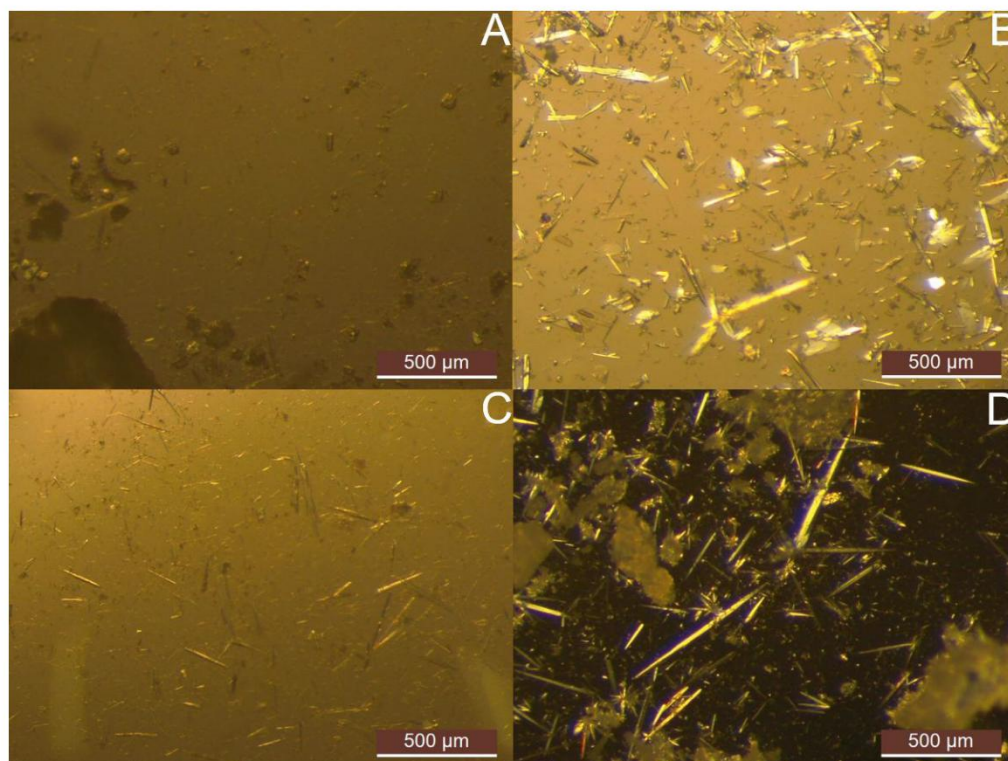


Figure S1. Optical microscope images of A $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}$ (**1-o**), B $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**1-m**), C $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**2**) and D $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**3**) ($\text{L} = \text{Diam}(\text{PO}_3\text{H})_2^{2-}$).

The powder patterns (Figure S2, left) of wet and dried forms of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**) demonstrate that crystallinity is retained upon drying. The pattern of the dried sample shows a similar pattern to the simulation derived from single-crystal data, whereas the wet sample shows diminished peak intensity but matches the dried sample. This could be due to the presence of water, which could result in a preferred orientation. Both samples also show additional an experimental peak at 7.2° , which does not match the simulated pattern. The synthesis was reproduced seven times. All resulting samples showed consistent PXRD patterns in both wet and dry states. Despite extensive X-ray analysis through cell-checking on several crystals, no other phase has been identified that could account for the extra reflections.

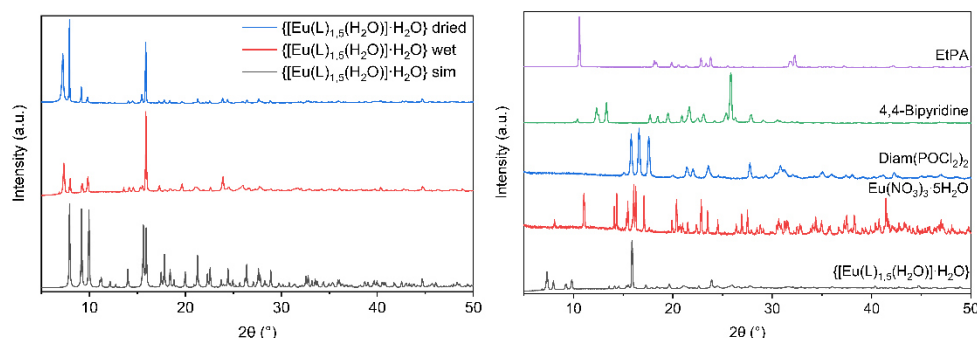


Figure S2. Powder diffractograms of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**) ($\text{L} = \text{Diam}(\text{PO}_3\text{H})_2^{2-}$). Left: Comparison of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ wet (crystals in water droplet), crystals after drying and the simulation from the single crystal structure. Right: Comparison of dried $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ with all used starting materials to verify the proper washing procedure.

Figure S3 shows the powder patterns of $\{[\text{LnL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ ($\text{Ln} = \text{Gd}, \text{Er}$) (**2, 3**) after washing with water and methanol. The experimental PXRD patterns of both compounds show very good agreement with the simulated patterns derived from the corresponding single-crystal structures. All major reflections are preserved in the experimental data, and no additional or missing peaks are found, confirming the crystalline phase purity and structural integrity of the bulk samples.

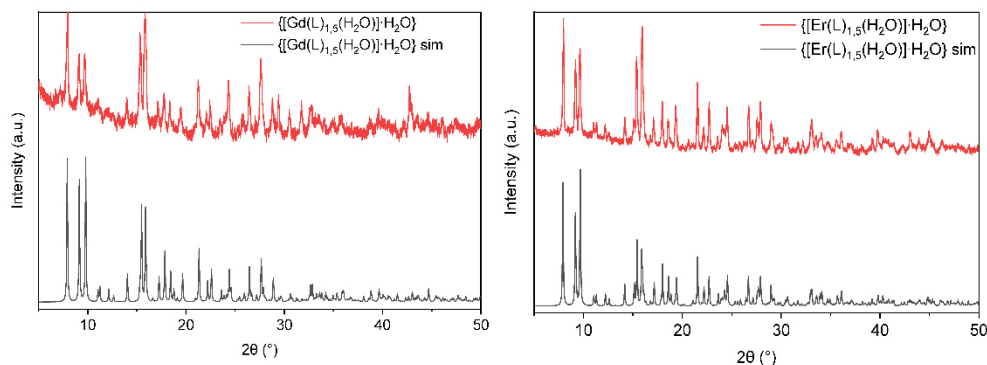


Figure S3. Powder diffractograms of $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**, left) and $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**, right) ($\text{L} = \text{Diam}(\text{PO}_3\text{H})_2^{2-}$) in comparison to powder patterns simulated from the single crystal structures.

Section S3. Thermogravimetric analysis (TGA)

The TG curves in Figures S4-S6 depict the thermal decomposition of $\{[\text{LnL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (Ln = Eu, Gd and Er, L = Diam(PO_3H) $_2^{2-}$) under synthetic air in the temperature range from 30 °C to 1000 °C at a heating rate of 5 K/min.

All coordination networks exhibit similar, well-defined decomposition profiles. In a first step, between 30 °C to around 180 °C the networks sequentially lose their water of crystallization followed by the coordinated water ligand. In a second step, the linker is degraded and the frameworks collapses. This happens between 400 and 1000 °C.

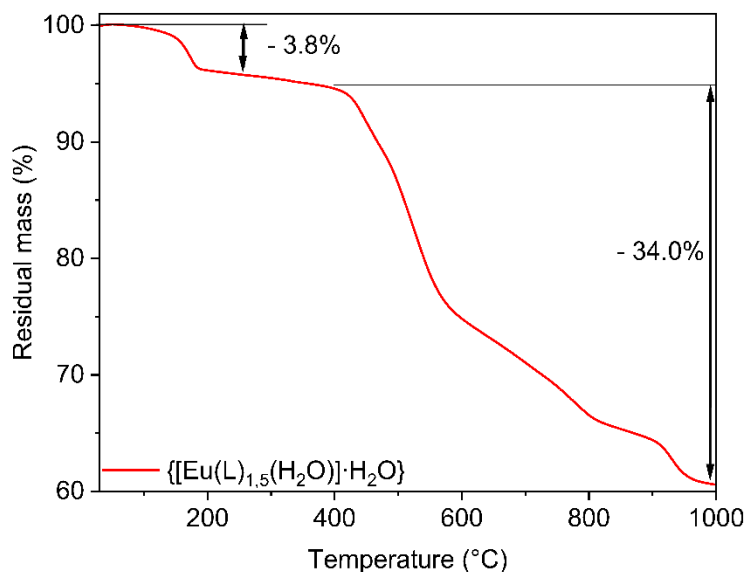


Figure S4. TG curve of $[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}_n$ (1-m) under air.

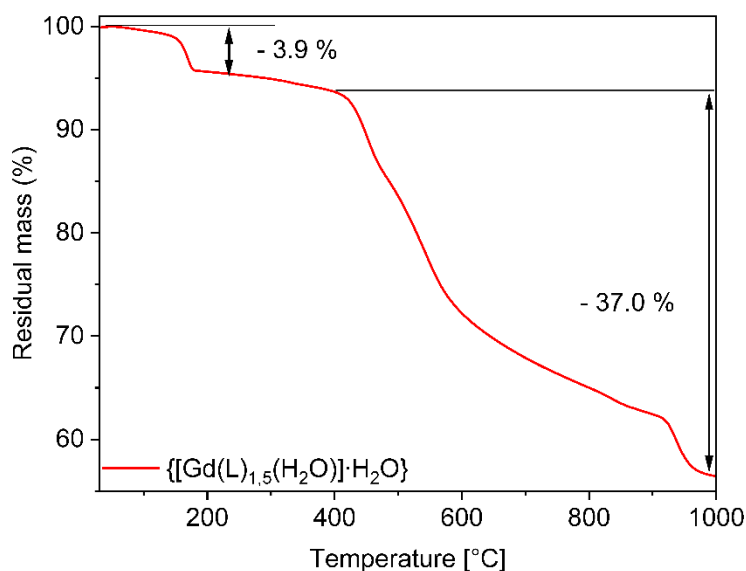


Figure S5. TG curve of $[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}_n$ (2) under air.

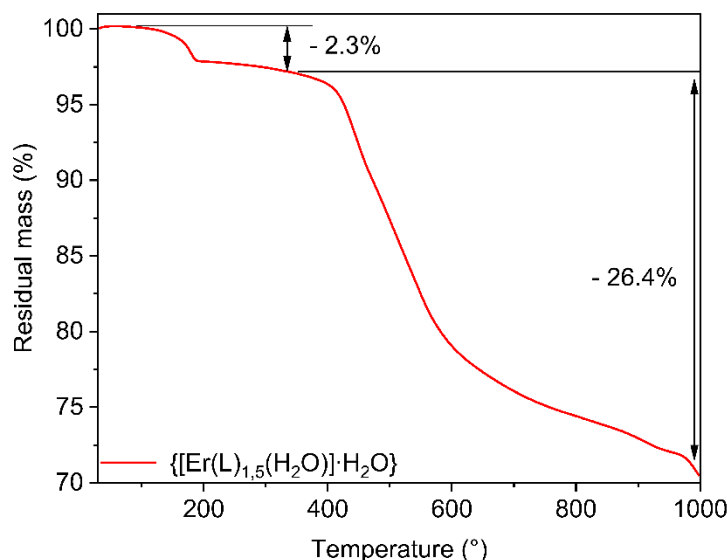


Figure S6. TG curve of $\{[\text{Er}(\text{L})_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**) under air.

Table S2. Comparison of theoretical and experimental mass loss and residual mass for $\{[\text{LnL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (Ln = Eu, Gd and Er, L = Diam(PO_3H) $_2^{2-}$).

		(1-m)	(2)	(3)
		1st region 30–180 °C		
mass loss exp (%)		- 3.8	- 3.9	- 2.3
mass loss theo (%)	– H ₂ O	- 2.5	- 2.5	- 2.5
	–2 H ₂ O	- 5.1	- 5.1	- 5.0
		2nd region 400–1000 °C		
mass loss exp (%)		- 34.0	- 37.0	- 26.4
mass loss theo (%)	–1.5 Diam = –C ₂₁ H ₂₇ (279.44 g/mol) (Diam = C ₁₄ H ₁₈)	- 39.5	- 39.2	- 38.7

The Δ -values in Table S2 indicate minor deviations between theoretical and experimental mass losses.

In the first step, the Er compound **3** shows a significantly lower mass loss (–2.3%) compared to Gd (**2**) and Eu (**1-m**) (–3.8%, –3.9%), likely due to retention of coordinated water or slower dehydration kinetics, which are typical for smaller lanthanides with higher Lewis acidity.

The second decomposition step shows lower experimental mass losses for all components especially for compound (**3**). The expected residue consists of a mixture of LnPO₄, LnP₂O₇, or condensed phosphates such as Ln(PO₃)₃, depending on temperature and oxygen availability. Variations in the residual mass can be attributed to the partial retention of carbonaceous or phosphate-rich intermediates in the sample of (**3**). Additionally, the higher residual mass observed for this sample is likely due to the presence of insoluble, powdery by-products that could not be fully characterized. These are presumed to be lanthanide oxides, which would reduce the proportion of decomposable organic components. The lower mass loss of (**1-m**) can be attributed to the presence of an additional phase (see Figure S2) which could not be completely removed or characterized further.

Section S4. NMR spectra of diamantane-4,9-bis(dichlorophosphoryl), Diam(POCl_2)₂ and diamantane-4,9-bis(methyl hydrogenphosphate, Diam(PO_3HMe)₂

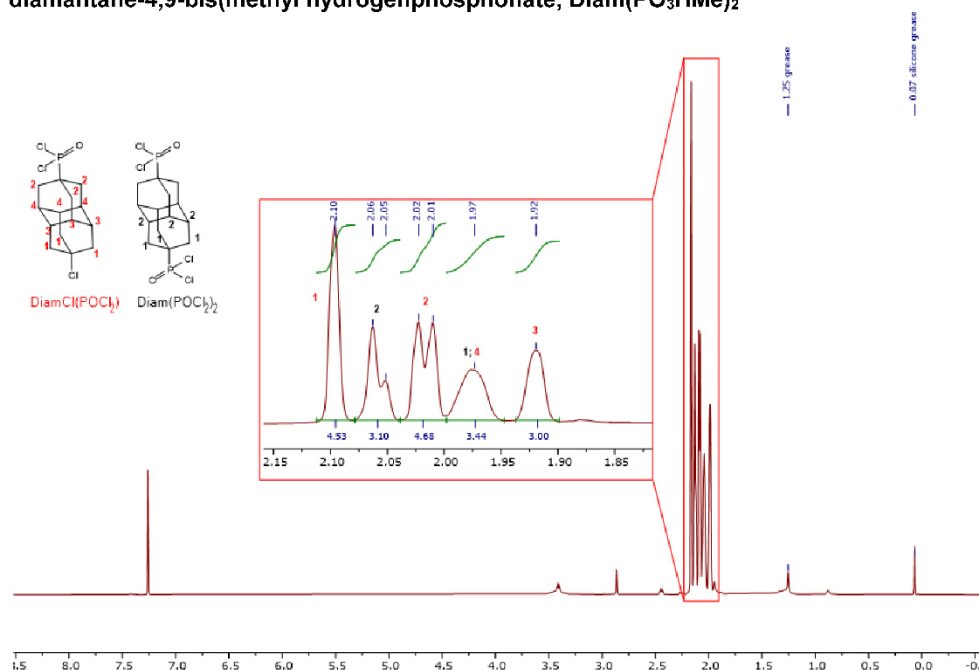


Figure S7. ^1H -NMR (600 MHz, CDCl_3) of the product mixture from procedure a, showing the presence of DiamCl(POCl_2) and Diam(POCl_2)₂ (NMR assignment in line with ref. 1,2). The ratio of 1:2:3 = 4.53:4.68:3 is lower than the expected 6:6:3 which indicates additional diamantane-based byproducts.

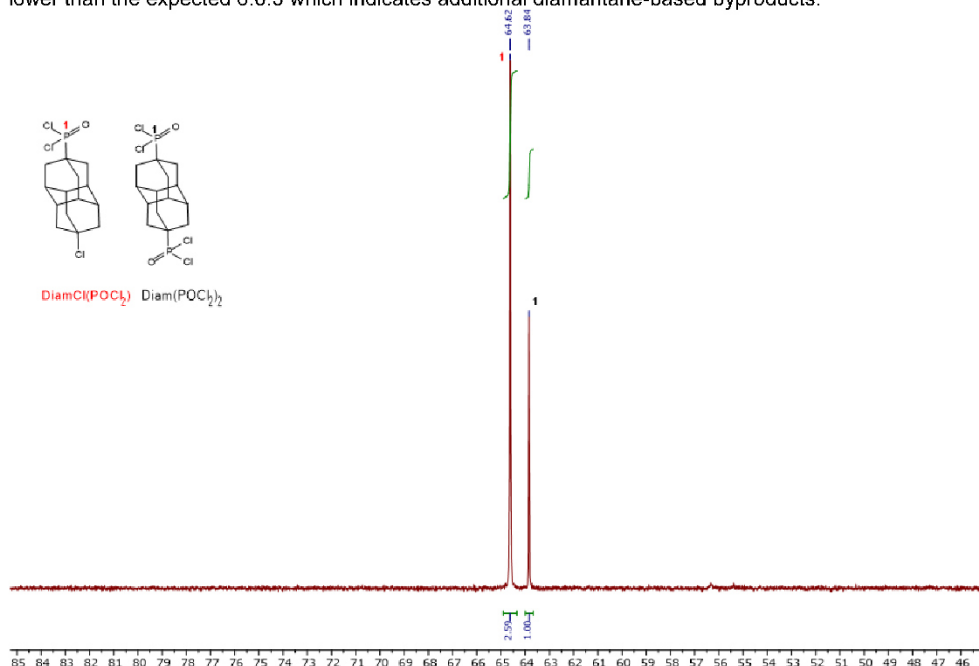


Figure S8. ^{31}P -NMR (242.9 MHz, CDCl_3) of the product mixture from procedure a, showing the presence of DiamCl(POCl_2) and Diam(POCl_2)₂ (NMR assignment in line with ref. 1,2).

S7

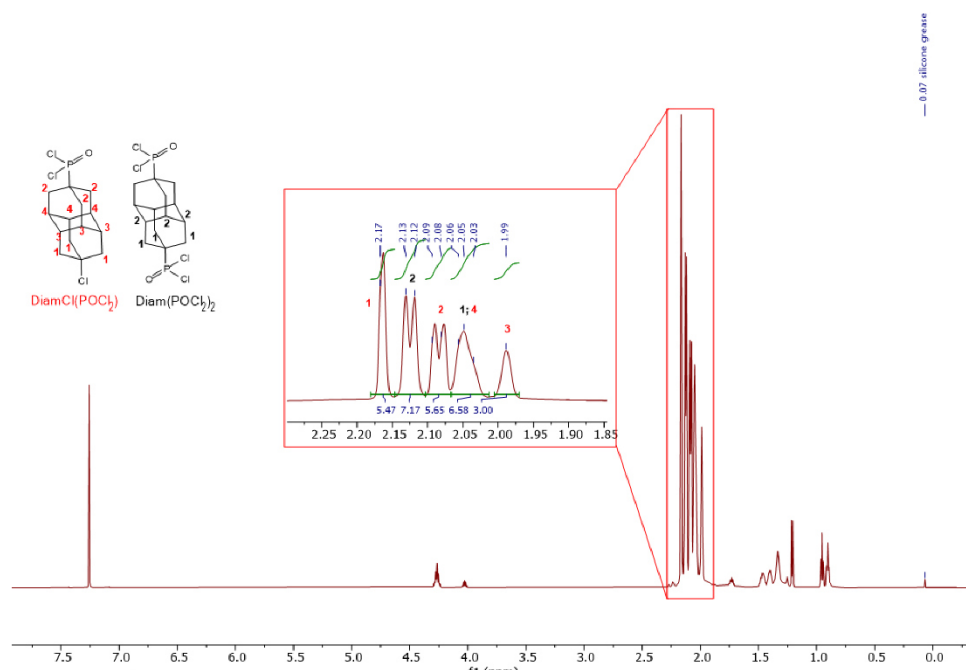


Figure S9. ^1H -NMR (600 MHz, CDCl_3) of the product mixture from procedure b, showing the presence of $\text{DiamCl}(\text{POCl}_2)$ and $\text{Diam}(\text{POCl}_2)_2$ (NMR assignment in line with ref. 1,2). The ratio of 1:2:3 = 5.47:5.65:3 is about 6:6:3 as expected.

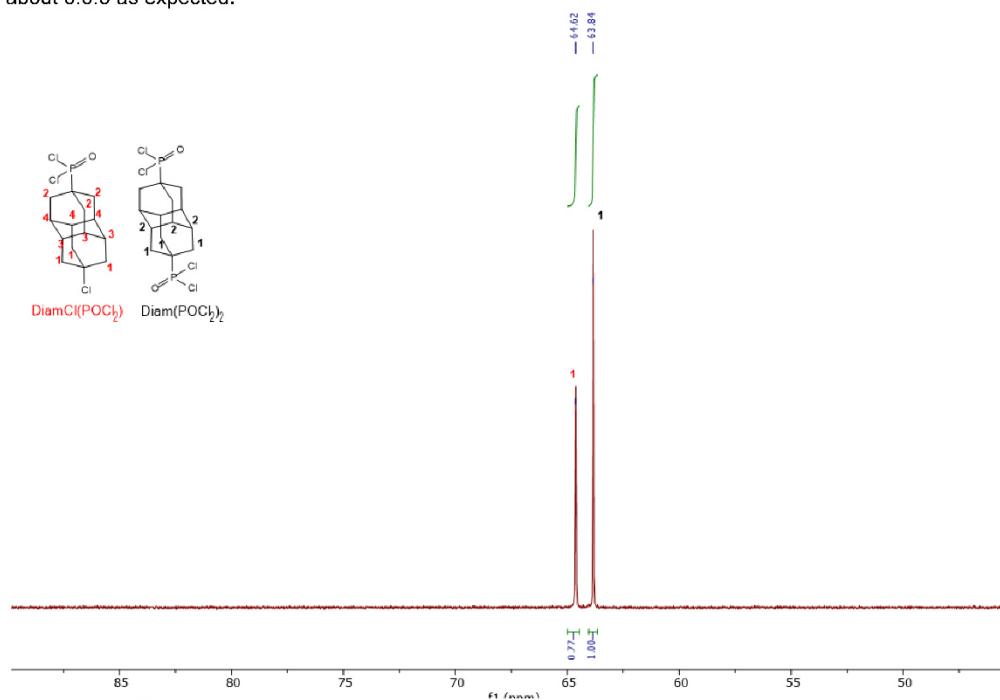


Figure S10. ^{31}P -NMR (242.9 MHz, CDCl_3) of the product mixture from procedure b, showing the presence of $\text{DiamCl}(\text{POCl}_2)$ and $\text{Diam}(\text{POCl}_2)_2$ (NMR assignment in line with ref. 1,2).

S8

Section S5. X-ray structure of diamantane-4,9-bis(methyl hydrogenphosphonate), Diam(PO₃HMe)₂

CCDC reference number is 2455260.

Table S3a. Crystal data and structure refinement details for Diam(PO₃HMe)₂.

Crystal data

C ₁₆ H ₂₆ O ₆ P ₂ · 3(H ₂ O)	<i>F</i> (000) = 920
<i>M_r</i> = 430.35	<i>D_x</i> = 1.479 Mg m ⁻³
Monoclinic, <i>C2/c</i>	Cu Kα radiation, λ = 1.54184 Å
<i>a</i> = 6.84902 (12) Å	Cell parameters from 18955 reflections
<i>b</i> = 11.2619 (2) Å	θ = 3.5–78.2°
<i>c</i> = 25.2013 (5) Å	μ = 2.47 mm ⁻¹
β = 95.9935 (16)°	<i>T</i> = 150 K
<i>V</i> = 1933.22 (6) Å ³	Block, clear colorless
<i>Z</i> = 4	0.65 × 0.31 × 0.18 mm

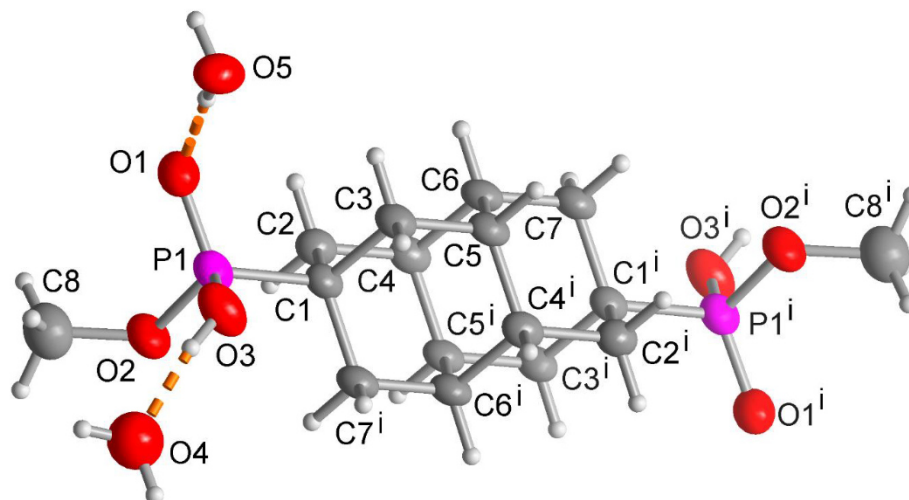
Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	1966 independent reflections
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	1939 reflections with <i>I</i> > 2σ(<i>I</i>)
Mirror monochromator	<i>R</i> _{int} = 0.079
Detector resolution: 10.0000 pixels mm ⁻¹	θ _{max} = 78.4°, θ _{min} = 3.5°
ω scans	<i>h</i> = -8→8
Absorption correction: gaussian <i>CrysAlis PRO</i> 1.171.41.90a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	<i>k</i> = -14→12
<i>T</i> _{min} = 0.022, <i>T</i> _{max} = 0.899	<i>l</i> = -30→30
25193 measured reflections	

Refinement

Refinement on <i>F</i> ²	21 restraints
Least-squares matrix: full	Hydrogen site location: mixed
<i>R</i> [<i>F</i> ² > 2σ (<i>F</i> ²)] = 0.1010 <i>R</i> [<i>F</i> ² , all data] = 0.1016	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> [<i>F</i> ² > 2σ (<i>F</i> ²)] = 0.2726 <i>wR</i> (<i>F</i> ² , all data) = 0.2736	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.1246 <i>P</i>) ² + 15.3999 <i>P</i>] where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>S</i> = 1.14	(Δ/σ) _{max} < 0.001
1966 reflections	Δ _{max} = 1.12 e Å ⁻³
133 parameters	Δ _{min} = -0.72 e Å ⁻³

Table S3b. Selected bond distances (Å) and bond angles (°) for **Diam(PO₃HMe)₂** referring to the atom numbering in the image below:



P1—O1	1.492 (4)		
P1—O2	1.584 (4)		
P1—O3	1.536 (4)		
P1—C1	1.808 (5)		
O1—P1—O2	111.5 (2)	C8—O2—P1	120.8 (4)
O1—P1—O3	111.7 (2)	P1—O3—H3	134 (6)
O1—P1—C1	112.2 (2)		
O2—P1—C1	103.4 (2)		
O3—P1—O2	109.7 (2)		
O3—P1—C1	108.1 (2)		

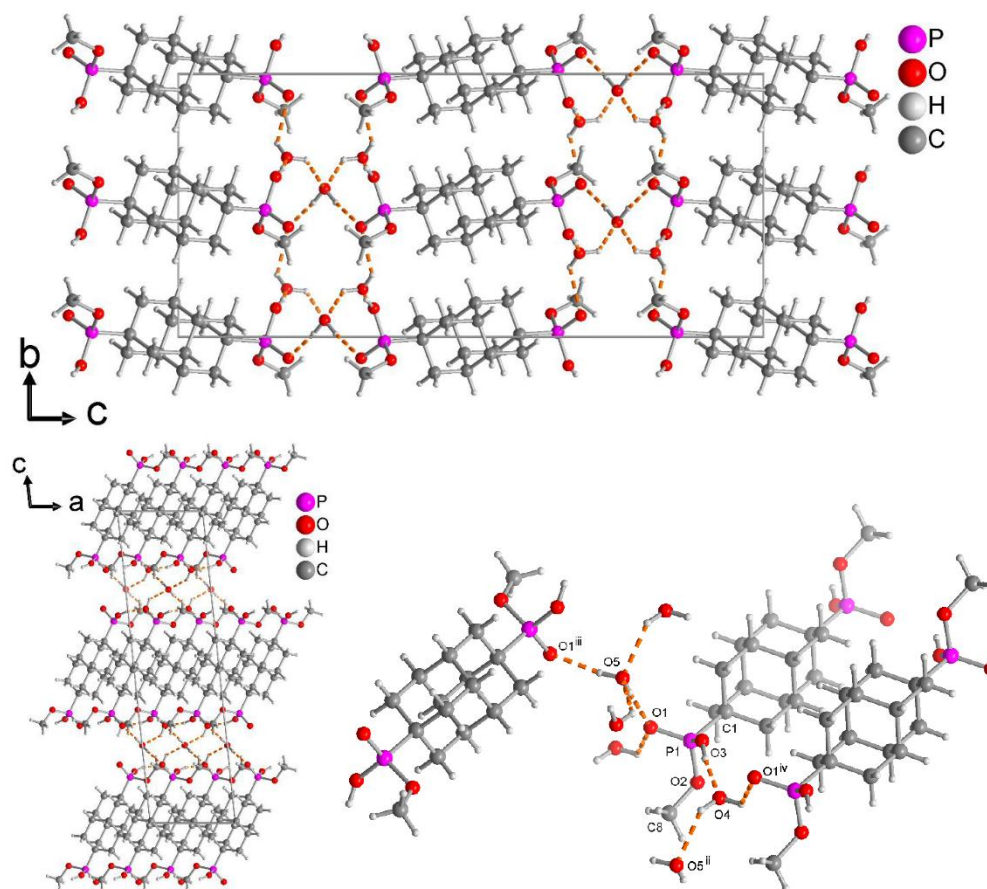


Figure S11. Projections of the unit cell packing and section of the packing diagram of **Diam(PO₃HMe)₂** with O-H $\cdots$ O interactions in the crystal, indicated as dashed orange lines. Further details of these O-H $\cdots$ O interactions, including the symmetry transformations are listed in Table S4. The projections of the unit cell show the expected separation between the hydrophilic phosphonate groups and the hydrophobic diamantane block in the packing.

Table S4. Hydrogen-bond geometry (Å, °) for **Diam(PO₃HMe)₂**.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O4—H4A $\cdots$ O5 ⁱⁱ	0.87	2.12	2.775 (6)	131
O4—H4B $\cdots$ O1 ^{iv}	0.87	2.17	2.670 (6)	116
O3—H3 $\cdots$ O4	0.85 (2)	1.62 (3)	2.438 (7)	160 (8)
O5—H5A $\cdots$ O1 ⁱⁱⁱ	0.87 (2)	1.90 (2)	2.768 (5)	170 (8)

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

Section S6. X-ray structure of diamantane-4-chloro-9-(methyl hydrogenphosphonate), DiamCl(PO₃HMe)

CCDC reference number is 2455261.

Table S5a. Crystal data and structure refinement details for **DiamCl(PO₃HMe)**.

Crystal data

C ₁₅ H ₂₂ ClO ₃ P·H ₂ O	$F(000) = 712$
$M_r = 334.76$	$D_x = 1.432 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$a = 16.7708 (2) \text{ \AA}$	Cell parameters from 15488 reflections
$b = 7.3404 (1) \text{ \AA}$	$\theta = 2.6\text{--}77.8^\circ$
$c = 12.6215 (2) \text{ \AA}$	$\mu = 3.27 \text{ mm}^{-1}$
$\beta = 92.134 (1)^\circ$	$T = 150 \text{ K}$
$V = 1552.68 (4) \text{ \AA}^3$	Block, clear colorless
$Z = 4$	$0.15 \times 0.08 \times 0.05 \text{ mm}$

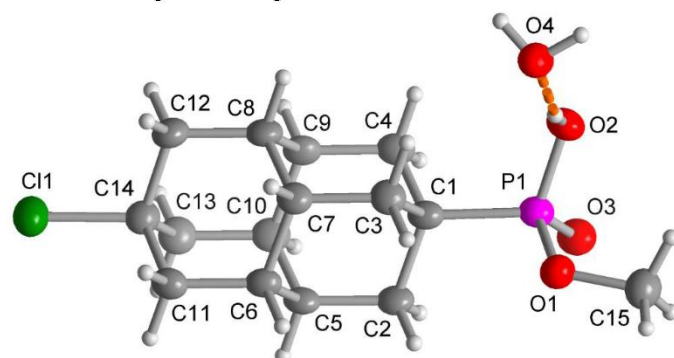
Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	3274 independ. reflect.
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	2917 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{\text{int}} = 0.036$
Detector resolution: $10.0000 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 79.7^\circ$, $\theta_{\text{min}} = 2.6^\circ$
ω scans	$h = -21 \rightarrow 21$
Absorption correction: gaussian <i>CrysAlis PRO</i> 1.171.41.90a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$k = -8 \rightarrow 8$
$T_{\text{min}} = 0.481$, $T_{\text{max}} = 0.922$	$l = -16 \rightarrow 15$
29195 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.0406$ $R[F^2, \text{all data}] = 0.0449$	H-atom parameters constrained
$wR[F^2 > 2\sigma(F^2)] = 0.1167$ $wR[F^2, \text{all data}] = 0.1198$	$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.6541P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.124$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3274 reflections	$\Delta_{\text{max}} = 0.45 \text{ e \AA}^{-3}$
195 parameters	$\Delta_{\text{min}} = -0.45 \text{ e \AA}^{-3}$
0 restraints	

Table S5b. Selected bond distances (Å) and bond angles (°) for **DiamCl(PO₃HMe)** referring to the atom numbering in the image below:



P1—O1	1.5809 (14)	P1—C1	1.8048 (19)
P1—O2	1.5486 (13)	Cl1—C14	1.8228 (19)
P1—O3	1.4895 (13)		
O1—P1—C1	103.10 (8)	C15—O1—P1	119.26 (12)
O2—P1—O1	108.63 (8)	P1—O2—H2	109.5
O2—P1—C1	110.00 (8)		
O3—P1—O1	112.45 (8)	C11—C14—Cl1	109.53 (13)
O3—P1—O2	108.92 (8)	C11—C14—C12	110.40 (16)
O3—P1—C1	113.56 (8)	C11—C14—C13	110.07 (15)

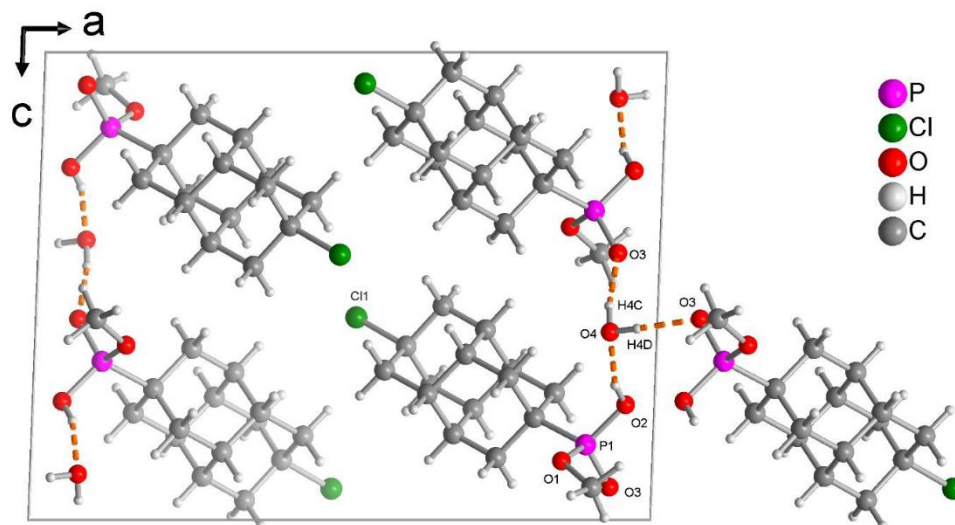


Figure S12. Section of the packing diagram of **DiamCl(PO₃HMe)** with O—H···O interactions in the crystal, indicated as dashed orange lines. Further details of these O—H···O interactions, including the symmetry transformations are listed in Table S6.

The strong hydrogen bonds occurring in **DiamCl(PO₃HMe)** are shown and described using the Etter graph-set notation in Figure S13. The graph-set notation depicts only the level 1 units with the shortest rings and chains as calculated by Mercury.³

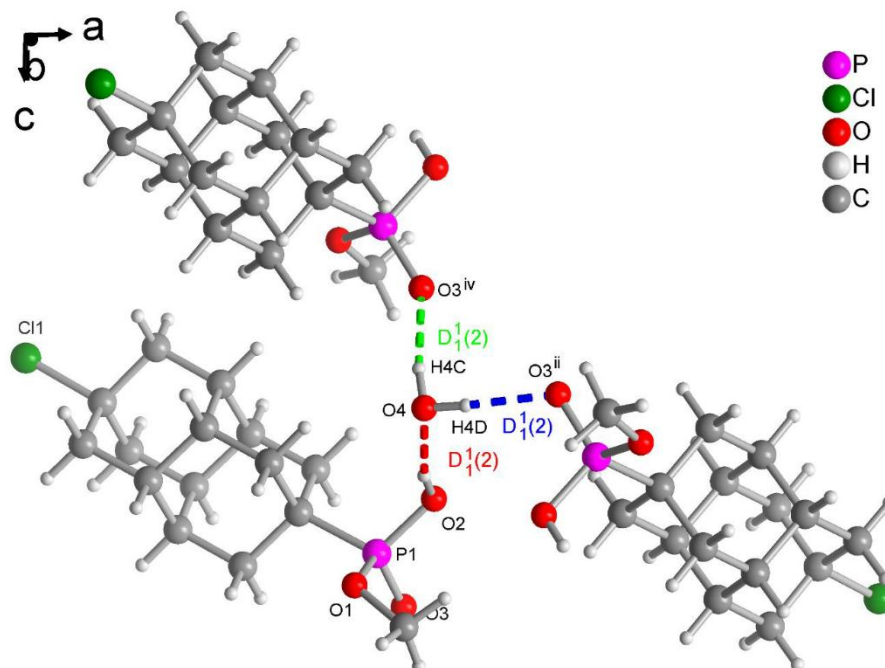


Figure S13. Section of the packing diagram of **DiamCl(PO₃HMe)** with level-1 graph-set calculated by Mercury,³ which consists of finite $D_1^1(2)$ patterns (differentiated as a, b, c in red, green and blue, respectively). The hydrogen bonds are depicted as colored dashed lines with the color according to their graph-set assignment. Symmetry codes: (ii) $2-x, 1/2+y, 3/2-z$; (iv) $x, 3/2-y, -1/2+z$.

Table S6. Hydrogen-bond geometry (Å, °) for **DiamCl(PO₃HMe)**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2\cdots O4$	0.84	1.70	2.5010 (19)	159
$O4-H4C\cdots O3^i$	0.87	1.83	2.6890 (19)	171
$O4-H4D\cdots O3^{ii}$	0.87	1.86	2.7234 (19)	170

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

Section S7. X-ray structure of orthorhombic $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$, $\text{L} = \text{Diam}(\text{PO}_3\text{H})_2^{2-}$ (1-o)

CCDC reference number is 2455262.

Table S7a. Crystal data and structure refinement details for $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$ (1-o).

Crystal data

$\text{C}_{21}\text{H}_{38}\text{EuO}_{13}\text{P}_3 \cdot \text{H}_2\text{O}$	$D_x = 1.901 \text{ Mg m}^{-3}$
$M_r = 761.40$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
Orthorhombic, $Pbca$	Cell parameters from 18693 reflections
$a = 11.4048 (2) \text{ \AA}$	$\theta = 3.8\text{--}77.4^\circ$
$b = 19.9120 (2) \text{ \AA}$	$\mu = 19.22 \text{ mm}^{-1}$
$c = 23.4321 (3) \text{ \AA}$	$T = 150 \text{ K}$
$V = 5321.25 (13) \text{ \AA}^3$	Block, clear orange
$Z = 8$	$0.22 \times 0.12 \times 0.06 \text{ mm}$
$F(000) = 3088$	

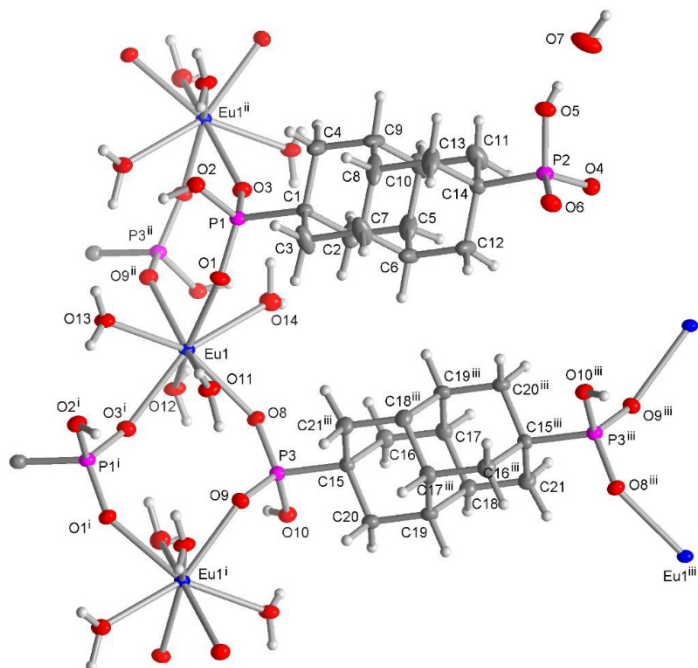
Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	5045 reflect. with $I > 2\sigma(I)$
Detector resolution: $10.0000 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.052$
ω scans	$\theta_{\text{max}} = 78.4^\circ$, $\theta_{\text{min}} = 3.8^\circ$
Absorption correction: gaussian <i>CrysAlis PRO</i> 1.171.41.90a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$h = -13 \rightarrow 13$
$T_{\text{min}} = 0.024$, $T_{\text{max}} = 0.523$	$k = -25 \rightarrow 17$
33907 measured reflections	$l = -29 \rightarrow 27$
5374 independent reflections	

Refinement

Refinement on F^2	1 restraint
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.0339$ $R[F^2, \text{all data}] = 0.0359$	Only H-atom coordinates refined
$wR[F^2 > 2\sigma(F^2)] = 0.0957$ $wR[F^2, \text{all data}] = 0.0973$	$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2 + 5.6111P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.045$	$(\Delta/\sigma)_{\text{max}} = 0.001$
5374 reflections	$\lambda_{\text{max}} = 1.04 \text{ e \AA}^{-3}$
472 parameters	$\Delta_{\text{min}} = -1.26 \text{ e \AA}^{-3}$

Table S7b. Selected bond distances (Å) and bond angles (°) for $[\{\text{EuL}_{1.5}(\text{H}_2\text{O})_4\} \cdot \text{H}_2\text{O}]_n$ (1-o) referring to the atom numbering in the image below:



50% thermal ellipsoids

Eu1—O1	2.354 (2)	O3—Eu1 ⁱⁱ	2.386 (2)
Eu1—O3 ⁱ	2.386 (2)	O9—Eu1 ⁱ	2.379 (2)
Eu1—O8	2.361 (2)		
Eu1—O9 ⁱⁱ	2.379 (2)		
Eu1—O11	2.426 (2)		
Eu1—O12	2.456 (2)		
Eu1—O13	2.449 (2)		
Eu1—O14	2.514 (2)		
P1—O1	1.505 (2)	P3—O8	1.512 (2)
P1—O2	1.590 (2)	P3—O9	1.513 (2)
P1—O3	1.515 (2)	P3—O10	1.592 (2)
P1—C1	1.822 (3)	P3—C15	1.809 (3)
P2—O4	1.516 (2)		
P2—O5	1.578 (2)		
P2—O6	1.508 (2)		
P2—C14	1.819 (3)		
O1—Eu1—O3 ⁱ	137.34 (7)	O1—P1—O2	109.38 (13)

O1—Eu1—O8	110.99 (8)	O1—P1—O3	113.63 (12)
O1—Eu1—O9 ⁱⁱ	85.77 (7)	O1—P1—C1	112.34 (13)
O1—Eu1—O11	71.01 (8)	O2—P1—C1	103.32 (13)
O1—Eu1—O12	149.36 (8)	O3—P1—O2	109.49 (12)
O1—Eu1—O13	75.60 (8)	O3—P1—C1	108.16 (13)
O1—Eu1—O14	68.07 (8)	O4—P2—O5	109.62 (13)
O3 ⁱ —Eu1—O11	76.04 (8)	O4—P2—C14	109.59 (13)
O3 ⁱ —Eu1—O12	72.79 (8)	O5—P2—C14	105.05 (13)
O3 ⁱ —Eu1—O13	72.56 (8)	O6—P2—O4	113.61 (13)
O3 ⁱ —Eu1—O14	151.53 (8)	O6—P2—O5	105.62 (12)
O8—Eu1—O3 ⁱ	83.53 (7)	O6—P2—C14	112.88 (13)
O8—Eu1—O9 ⁱⁱ	134.39 (7)	O8—P3—O9	115.21 (12)
O8—Eu1—O11	72.95 (8)	O8—P3—O10	108.19 (12)
O8—Eu1—O12	71.60 (8)	O8—P3—C15	110.43 (13)
O8—Eu1—O13	147.42 (8)	O9—P3—O10	110.23 (12)
O8—Eu1—O14	72.81 (8)	O9—P3—C15	109.62 (13)
O9 ⁱ —Eu1—O3 ⁱ	113.03 (8)	O10—P3—C15	102.39 (13)
O9 ⁱ —Eu1—O11	150.40 (7)		
O9 ⁱ —Eu1—O12	73.63 (8)	P1—O1—Eu1	145.84 (13)
O9 ⁱ —Eu1—O13	76.62 (8)	P1—O3—Eu1 ⁱⁱⁱ	144.45 (13)
O9 ⁱ —Eu1—O14	75.46 (8)	P3—O8—Eu1	142.10 (12)
O11—Eu1—O12	134.69 (8)	P3—O9—Eu1 ⁱ	137.82 (12)
O11—Eu1—O13	79.91 (8)		
O11—Eu1—O14	110.59 (8)		
O12—Eu1—O14	84.66 (8)		
O13—Eu1—O12	119.56 (8)		
O13—Eu1—O14	135.21 (8)		

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

The asymmetric unit of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ (**1-o**) consists of one Eu atom, a fully and a half-occupied diamantane-bis(hydrogenphosphonate) linker, four aqua ligands and a crystal water molecule (see above image) to give a formula unit of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ with $\text{L} = \text{Diam}(\text{PO}_3\text{H})_2^{2-}$. Each phosphonate group in the diamantane-bis(phosphonate) linker is only singly deprotonated, that is it presents a hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) group.

In the structure of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ (**1-o**) the single unique Eu atom is eight-coordinated by four O atoms from four different hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) groups and four aqua ligands.

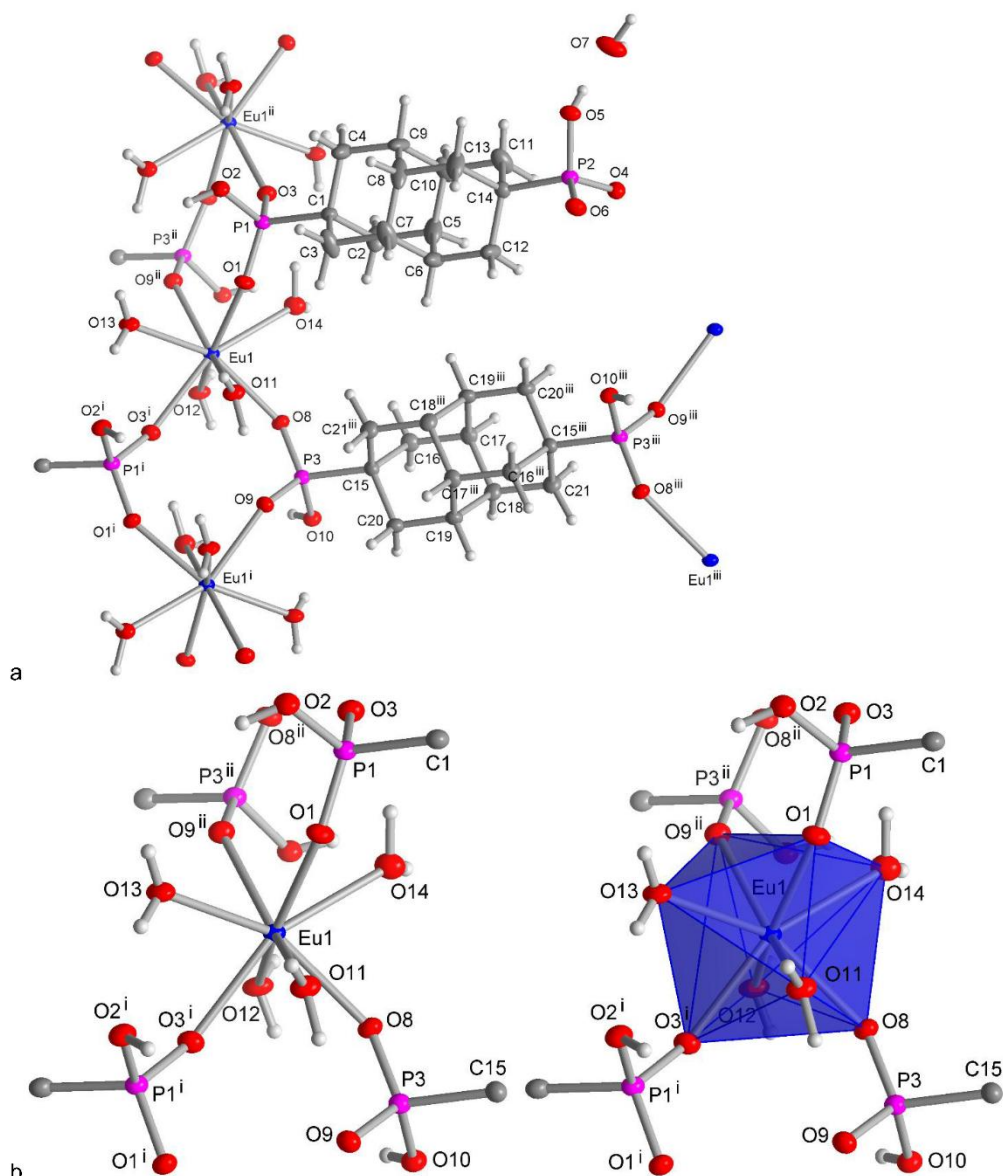


Figure S14. The extended asymmetric unit (a) and the coordination sphere around europium (b) in $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$ (**1-o**) (50% thermal ellipsoids), symmetry codes: (i) $x+1/2, y, -z+1/2$; (ii) $x-1/2, y, -z+1/2$; (iii) $-x+2, -y+1, -z+1$.

The phosphonate linker with P1 and P2 is only a bridging group at P1 and coordinates to two Eu atoms. The group at P2 is not coordinated to a metal atom and is only involved in hydrogen bonding. In the linker with P3, which sits on a special position, each phosphonate group bridges between two Eu atoms and the linker as a whole then connects four Eu atoms. Of the four $-\text{PO}_3\text{H}^-$ groups around Eu, two with P1 and two with P3, each bridge to a neighboring Eu atom. Consequently, each Eu atom is in total connected to 6 adjacent Eu atoms.

The direct phosphonate P1 and P3 bridging action between the Eu atoms leads to a slightly corrugated doubly-bridged Eu chain parallel to the crystallographic *a*-direction. Each Eu chain is "left-

and-right" connected to two adjacent strands giving a two-dimensional (2D) 6-c uninodal network with the point symbol $3^6.4^2.5^6.6$ as analyzed by ToposPro.^{4,5}

Topology for $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$ (1-o)

Atom Eu1 links by bridge ligands and has

Common vertex with		R(A-A)	f
Eu 1	0.7222 0.5887 0.7465 (1 1 0)	12.253A	1
Eu 1	0.7222 0.5887 -0.2535 (1 1 -1)	12.253A	1
Eu 1	1.2222 0.5887 0.7535 (2 1 1)	13.391A	1
Eu 1	0.2222 0.5887 -0.2465 (1 1 0)	13.640A	1
Common edge with		R(A-A)	
Eu 1	0.2778 0.4113 0.2535 (-1 0 0)	5.705A	2
Eu 1	1.2778 0.4113 0.2535 (0 0 0)	5.705A	2

Structural group analysis

Structural group No 1

Structure consists of layers (0 1 0) with EuP3O13C21H38

Num. groups=2; Thickness=7.53; Distances to Neighbors=9.956; 9.956

Coordination sequences

Eu1:	1 2 3 4 5 6 7 8 9 10
Num	6 16 24 32 40 48 56 64 72 80
Cum	7 23 47 79 119 167 223 287 359 439

TD10=439

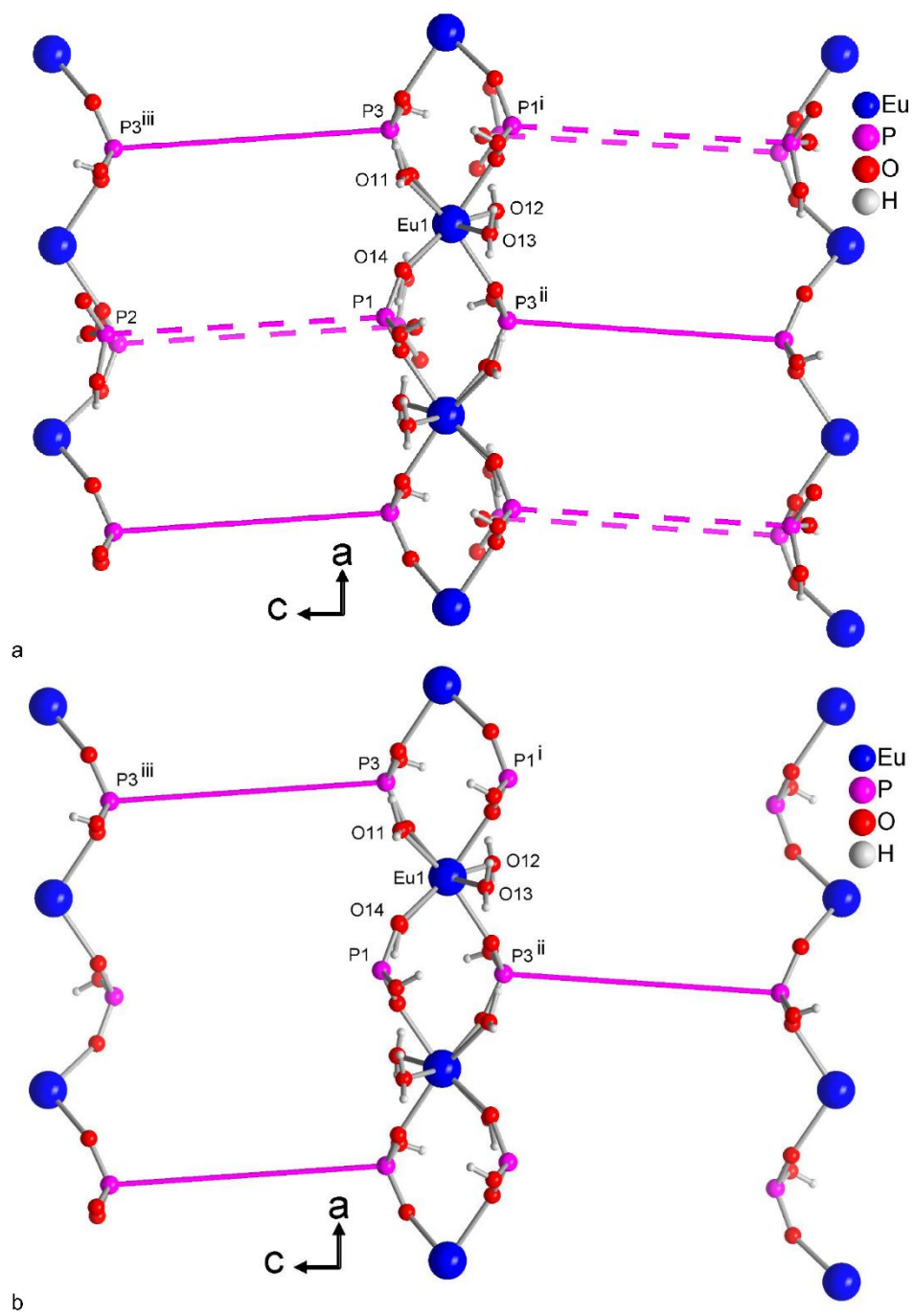
Vertex symbols for selected sublattice

Eu1 Point symbol: $\{3^6.4^2.5^6.6\}$

Extended point symbol: $[3.3.3.3.3.3.4.4.5.5.5.5.5(2).5(2).6(2)]$

Point symbol for net: $\{3^6.4^2.5^6.6\}$

6-c net; uninodal net



S20

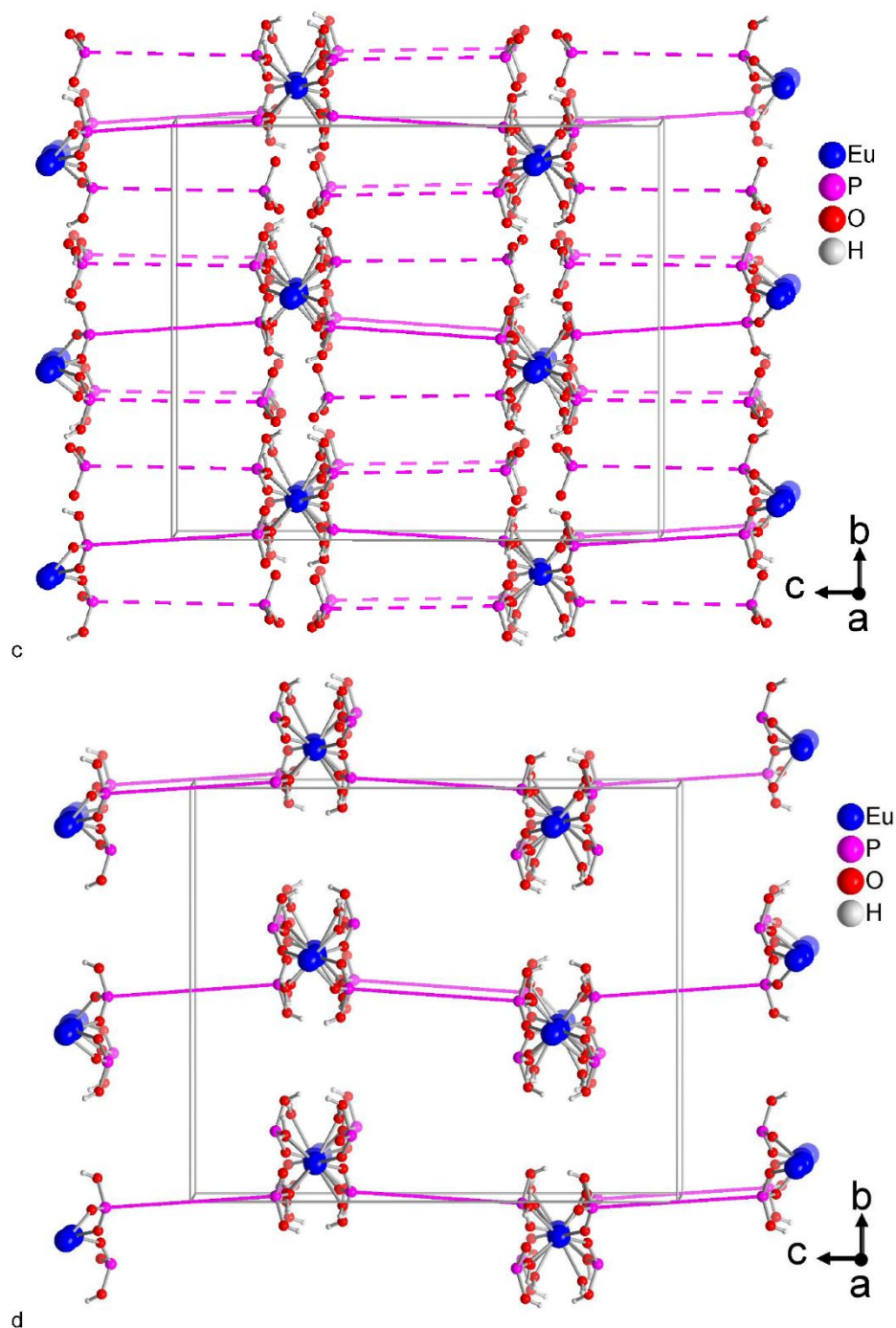


Figure S15. Schematic connectivity around Eu in $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$ (1-o) showing the connectivity to 6 neighboring Eu atoms from which two are connected directly through the P1 and P3 phosphonate groups and four across the diamantane linker. The doubly-bridged Eu chains run parallel to the *a*-direction and are "left-and-right" connected to two parallel chains. The diamantane unit is replaced by a direct P---P connector in magenta for clarity (the crystal water molecules are

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not shown). (a,b) View perpendicular to the *a*-direction. (c,d) View approximately along the *a*-direction (perpendicular to the *bc*-plane). For clarity the diamantane moiety in the P1-P2 linker, which is only metal-coordinating at P1, is shown as a dashed line (a,c) or has been removed together with the non-coordinating P2 group (b,d). Symmetry codes: (i) $x+1/2, y, -z+1/2$; (ii) $x-1/2, y, -z+1/2$; (iii) $-x+2, -y+1, -z+1$.

When viewing the 2D layers along the *a*-direction (perpendicular to the *bc*-plane) one gets the impression of a three-layer construction (above in c). However, the outer two layers are formed by the P1-P2 linkers where only the P1 group is metal-bridging (along *a*) and the P2 group is not metal-coordinated. When the diamantane moiety together with the non-coordinating P2 group is removed then the "single-linker layer" construction becomes apparent (above in d).

The crystal water molecule (O7) resides near two non-coordinated P2 group where it acts both as an acceptor and a donor to either one of them. The H-atoms of the hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) groups are all involved in hydrogen bonding, either to other phosphonate groups or to the crystal water molecule (from P2-O5-H). The non-coordinating phosphonate group with P2 and its O atoms O4, O5, and O6 is an H-bond acceptor with all of its three O atoms, such that O4 and O6 accept three H-bonds at each atom (Table S8).

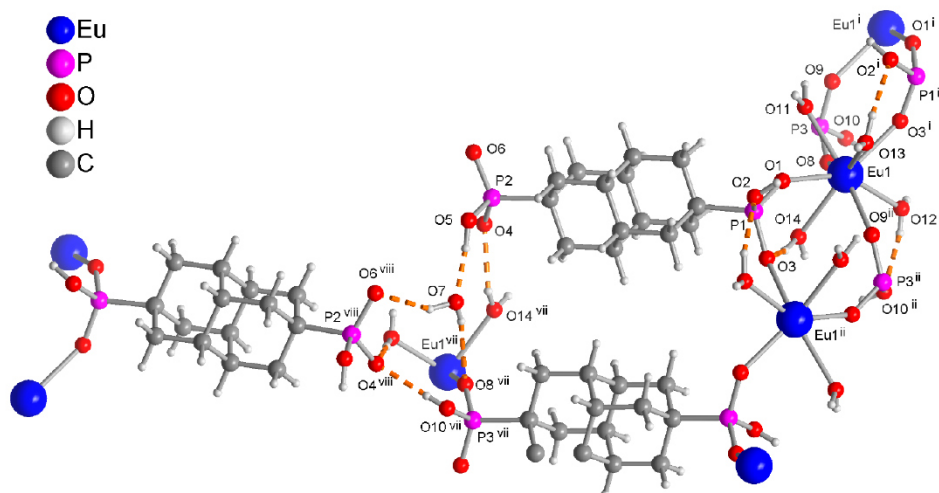


Figure S16. Hydrogen bonding scheme (dashed orange lines) around the crystal water molecule O7 and in part around the Eu atom in $[\text{EuL}_{1.5}(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (**1-o**). Further details of these O-H $\cdots$ O interactions, including the symmetry transformations are listed in Table S8.

The hydrogen bonding interactions exhibit a range of strengths, as indicated by the bond lengths and angles (Table S8). The shortest and most linear hydrogen bond is O5—H5A $\cdots$ O1, with a D $\cdots$ A distance of 2.768 Å and an angle of 170°, suggesting a strong and directional interaction. Similarly, O3—H3 $\cdots$ O4 forms a relatively strong hydrogen bond with a D $\cdots$ A distance of 2.438 Å and an angle of 160°, further stabilizing the crystal structure. In contrast, O4—H4A $\cdots$ O5 and O4—H4B $\cdots$ O1 display slightly weaker interactions, with D $\cdots$ A distances of 2.775 Å and 2.670 Å, respectively, and more bent geometries (131° and 116°). These variations in hydrogen bonding influence the overall packing and stability of the Eu compound, with the strongest interactions likely playing a key role in maintaining the integrity of the structure.

Table S8. Hydrogen-bond geometry (Å, °) for $[\text{EuL}_{1.5}(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (**1-o**).

D—H $\cdots$ A	D—H	H $\cdots$ A	D $\cdots$ A	D—H $\cdots$ A
O2—H2A $\cdots$ O6 ^{iv}	0.83 (5)	1.90 (5)	2.725 (3)	173 (4)
O5—H2 $\cdots$ O7	0.86 (5)	1.69 (5)	2.550 (3)	175 (4)
O10—H10 $\cdots$ O4 ^{vi}	0.75 (6)	1.88 (6)	2.635 (3)	174 (6)
O11—H11A $\cdots$ O5 ^v	0.83 (5)	2.02 (5)	2.824 (3)	165 (4)
O12—H12A $\cdots$ O4 ^{vi}	0.85 (5)	1.97 (5)	2.819 (3)	178 (4)
O12—H12B $\cdots$ O10 ⁱⁱ	0.77 (5)	2.06 (5)	2.737 (3)	147 (5)
O13—H13A $\cdots$ O6 ^{iv}	0.80 (5)	1.92 (5)	2.708 (3)	168 (5)
O13—H13B $\cdots$ O2 ⁱ	0.86 (5)	2.02 (5)	2.815 (3)	155 (4)
O14—H14A $\cdots$ O4 ^{vii}	0.78 (5)	2.09 (5)	2.746 (3)	144 (5)
O14—H14B $\cdots$ O3	0.95 (5)	2.07 (5)	2.978 (3)	155 (4)
O7—H7A $\cdots$ O8 ^{vii}	0.76 (5)	2.21 (5)	2.949 (4)	167 (6)
O7—H7B $\cdots$ O6 ^{viii}	0.90 (5)	2.14 (5)	2.957 (4)	150 (4)

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

Section S8. X-ray structure of compound $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$, L = Diam(PO_3H) $_2^{2-}$ (1-m)

CCDC reference number is 2455263.

Table S9a. Crystal data and structure refinement details for $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (1-m).

Crystal data

$\text{C}_{21}\text{H}_{32}\text{EuO}_{10}\text{P}_3 \cdot 0.188(\text{H}_8\text{O}_4) \cdot \text{H}_{0.50}\text{O}_{0.25}$	$F(000) = 1424$
$M_r = 707.35$	$D_x = 1.859 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$a = 11.8043 (2) \text{ \AA}$	Cell parameters from 15220 reflections
$b = 11.1236 (2) \text{ \AA}$	$\theta = 3.9\text{--}78.2^\circ$
$c = 19.8966 (4) \text{ \AA}$	$\mu = 20.22 \text{ mm}^{-1}$
$\beta = 104.673 (2)^\circ$	$T = 150 \text{ K}$
$V = 2527.35 (8) \text{ \AA}^3$	Plate, clear colourless
$Z = 4$	$0.25 \times 0.2 \times 0.05 \text{ mm}$

Data collection

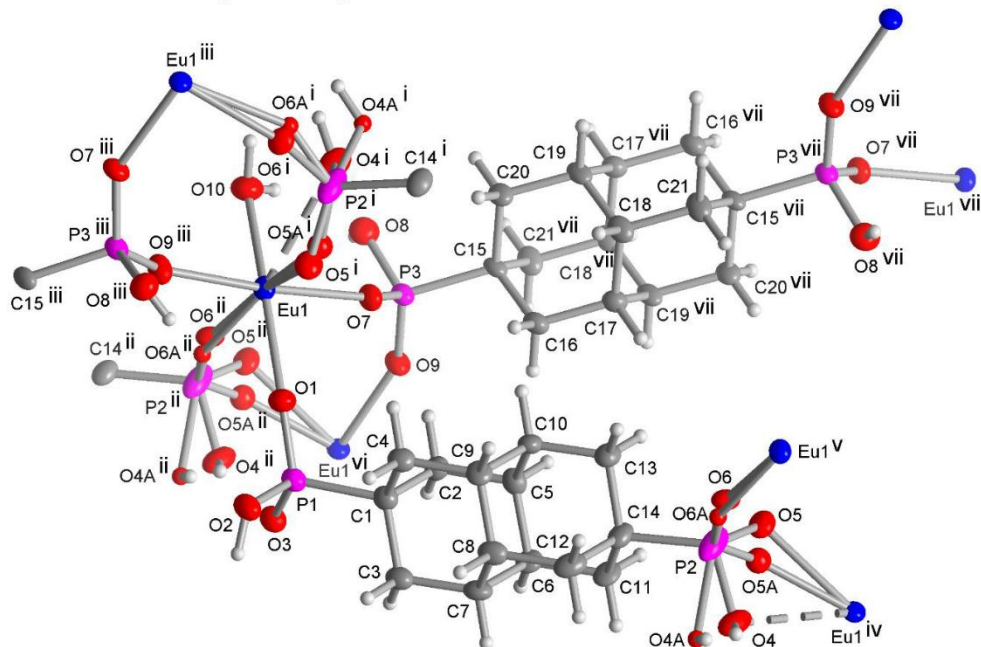
XtaLAB Synergy, Dualflex, HyPix diffractometer	5331 reflections	independ.
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	4898 reflections with $I > 2\sigma(I)$	
Mirror monochromator	$R_{\text{int}} = 0.052$	
Detector resolution: $10.0000 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 79.5^\circ$, $\theta_{\text{min}} = 4.0^\circ$	
ω scans	$h = -14 \rightarrow 15$	
Absorption correction: gaussian <i>CrysAlis PRO</i> 1.171.41.90a (Rigaku Oxford Diffraction, 2020) Numerical abs. correction based on gaussian integration over a multifaceted crystal model Empirical abs. correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$k = -13 \rightarrow 13$	
$T_{\text{min}} = 0.059$, $T_{\text{max}} = 0.815$	$l = -25 \rightarrow 24$	
25766 measured reflections		

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.0498$ $R[F^2, \text{all data}] = 0.0527$	$w = 1/[\sigma^2(F_o^2) + (0.0862P)^2 + 6.225P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR[F^2 > 2\sigma(F^2)] = 0.1415$ $wR(F^2, \text{all data}) = 0.1447$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.133$	$\Delta_{\text{max}} = 1.73 \text{ e \AA}^{-3}$
5331 reflections	$\Delta_{\text{min}} = -1.29 \text{ e \AA}^{-3}$
370 parameters	Extinction correction: <i>SHELXL2014/7</i> (Sheldrick 2014, $F_c' = kF_c[1 + 0.001 \times F_c^2/\sin(2\theta)]^{-1/4}$)
17 restraints	Extinction coefficient: 0.00027 (7)
Primary atom site location: dual	

The structures of $\{[\text{LnL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$, Ln = Eu, Gd, Er; L = Diam(PO_3H) $_2^{2-}$ are isostructural.

Table S9b. Selected bond distances (Å) and bond angles (°) for $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (1-m) referring to the atom numbering in the image below:



50% thermal ellipsoids. The phosphonate group at P2 is slightly disordered with the major contributing O atoms having a site occupation factor (SOF) of 0.79. The minor contribution of the disordered atoms is denoted with the suffix A, has an SOF of 0.21 and was only refined isotropically. The disordered crystal water molecule is not shown for clarity.

Eu1—O1	2.247 (3)	O5—Eu1 ^{iv}	2.399 (5)
Eu1—O5 ⁱ	2.399 (5)	O5A—Eu1 ^{iv}	2.090 (15)
Eu1—O5A ⁱ	2.090 (15)	O6—Eu1 ^v	2.269 (5)
Eu1—O6 ⁱⁱ	2.269 (5)	O6A—Eu1 ^v	2.350 (17)
Eu1—O6A ⁱⁱ	2.350 (17)	O9—Eu1 ^{vi}	2.299 (3)
Eu1—O7	2.293 (3)		
Eu1—O9 ⁱⁱⁱ	2.299 (3)	Eu1—O4 ^j	2.823 (6)
		O4—Eu1 ^{iv}	2.823 (6)
P1—O1	1.502 (4)	P2—O4	1.548 (5)
P1—O2	1.578 (4)	P2—O4A	1.941 (14)
P1—O3	1.522 (4)	P2—O5	1.548 (5)
P1—C1	1.806 (5)	P2—O5A	1.351 (13)
P3—O7	1.506 (4)	P2—O6	1.497 (5)
P3—O8	1.577 (4)	P2—O6A	1.496 (15)
P3—O9	1.512 (4)	P2—C14	1.820 (5)
P3—C15	1.816 (5)		

O1—Eu1—O5 ⁱ	79.99 (16)	O1—P1—O2	105.3 (2)
O1—Eu1—O6 ⁱⁱ	86.9 (2)	O1—P1—O3	114.6 (2)
O1—Eu1—O6A ⁱⁱ	78.8 (6)	O1—P1—C1	109.5 (2)
O1—Eu1—O7	87.55 (13)	O2—P1—C1	106.1 (2)
O1—Eu1—O9 ⁱⁱⁱ	96.51 (13)	O3—P1—O2	109.9 (2)
O1—Eu1—O10	160.09 (14)	O3—P1—C1	110.9 (2)
O5 ⁱ —Eu1—O10	118.53 (17)	O4—P2—O5	101.2 (3)
O5A ⁱ —Eu1—O1	91.7 (5)	O4—P2—C14	112.0 (3)
O5A ⁱ —Eu1—O6A ⁱⁱ	170.3 (7)	O5—P2—C14	109.0 (2)
O5A ⁱ —Eu1—O7	88.8 (6)	O5A—P2—O4A	99.8 (10)
O5A ⁱ —Eu1—O9 ⁱⁱⁱ	88.8 (6)	O5A—P2—O6A	137.9 (12)
O5A ⁱ —Eu1—O10	105.1 (6)	O5A—P2—C14	114.0 (7)
O6 ⁱ —Eu1—O5 ⁱ	164.5 (2)	O6—P2—O4	111.6 (3)
O6 ⁱ —Eu1—O7	88.0 (2)	O6—P2—O5	113.7 (4)
O6 ⁱ —Eu1—O9 ⁱⁱⁱ	94.49 (19)	O6—P2—C14	109.1 (3)
O6 ⁱ —Eu1—O10	75.7 (2)	O6A—P2—O4A	88.9 (9)
O7—Eu1—O5 ⁱ	99.50 (15)	O6A—P2—C14	106.8 (9)
O7—Eu1—O6A ⁱⁱ	92.7 (5)	O7—P3—O8	105.9 (2)
O7—Eu1—O9 ⁱⁱⁱ	175.32 (12)	O7—P3—O9	115.1 (2)
O7—Eu1—O10	82.38 (14)	O7—P3—C15	109.0 (2)
O9 ⁱⁱⁱ —Eu1—O5 ⁱ	78.99 (15)	O8—P3—C15	105.4 (2)
O9 ⁱⁱⁱ —Eu1—O6A ⁱⁱ	90.3 (6)	O9—P3—O8	111.4 (2)
O9 ⁱⁱⁱ —Eu1—O10	94.42 (15)	O9—P3—C15	109.5 (2)
P1—O1—Eu1	163.1 (2)	P3—O7—Eu1	142.8 (2)
P2—O5—Eu1 ^{iv}	110.4 (3)	P3—O9—Eu1 ^{vi}	154.1 (2)
P2—O5A—Eu1 ^{iv}	143.6 (13)		
P2—O6—Eu1 ^v	160.8 (4)		
P2—O6A—Eu1 ^v	149.3 (13)		

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

The asymmetric unit of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**) consists of one Eu atom, a fully and half-occupied diamantane-bis(hydrogenphosphonate) linker, one aqua ligand and a disordered crystal water molecule which is split over two nearby positions with 0.75 and 0.25 occupancy (see below) to give a formula unit of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ with $\text{L} = \text{Diam}(\text{PO}_3\text{H})_2^{2-}$. Each phosphonate group in the diamantane-bis(phosphonate) linker is only singly deprotonated, that is presents a hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) group.

In the structure of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**) the single unique Eu atom is six- to seven-coordinated by five to six O atoms from five different hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) groups and the aqua ligand. A coordination from a long Eu1—O4ⁱ bond of 2.823 Å from a then chelating P—OH group is depicted as a dashed bond in Figure S17. The other Eu1—O bond lengths lie between 2.090 and 2.399 Å (Table S9b). The six-fold coordination around Eu would be a clearly distorted octahedron, with the long bond to O4 it becomes a capped octahedron.

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The more likely seven-fold coordination of Eu versus the six- to seven-fold coordination of Gd and the clearly six-fold coordination of Er in the isostructural networks $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**) and $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**), respectively, is evidence of the larger ionic radius of Eu^{3+} (0.947 Å) versus Gd^{3+} (0.935 Å) and Er^{3+} (0.89 Å). In the orthorhombic structure in $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ (**1-o**) Eu^{3+} is clearly eight-fold coordinated with Eu-O bond lengths between 2.354 and 2.514 Å (Table S9b). Noteworthy, the long Ln---O bonds in the monoclinic structure of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**) and in $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**) involve the O atom of P-OH group.

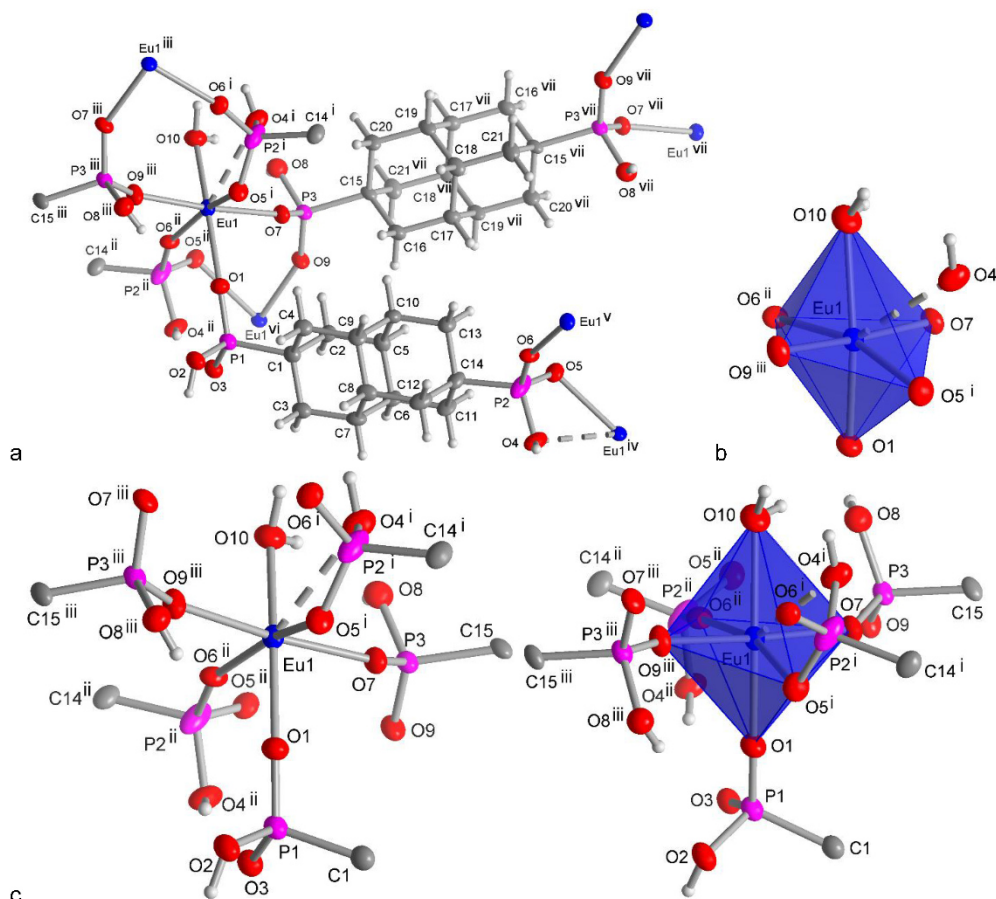


Figure S17. The extended asymmetric unit (a) and the coordination sphere around europium (b,c) in $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**), not showing the minor contribution of the disordered atoms of the phosphonate group at P2. The longer Eu1-O4 bond is shown as a dashed line. (50% thermal ellipsoids), symmetry codes: (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $x+1, y, z$; (iii) $-x+3/2, y+1/2, -z+1/2$; (iv) $-x+1/2, y-1/2, -z+1/2$; (v) $x-1, y, z$; (vi) $-x+3/2, y-1/2, -z+1/2$; (vii) $-x+1, -y+1, -z+1$.

The phosphonate linker with P1 and P2 is only a bridging group at P2 and coordinates to two Eu atoms. The group at P1 is terminally coordinated to only one Eu atom. In the linker containing P3, which sits on a special position, each phosphonate bridges between two Eu atoms so that the entire linker connects four Eu atoms. Out of the five $-\text{PO}_3\text{H}^-$ groups around Eu, the two with P2 and the two with P3 each bridge to a neighboring Eu atom. The group with P1 is only terminally coordinated. Each Eu atom is in total connected to 10 other Eu atoms, with eight of them connected through the bridging action of the diamantane moiety of the linker.

The direct phosphonate P2 and P3 bridging action between the Eu atoms leads to a corrugated doubly-bridged Eu chain parallel to the crystallographic *b*-direction. Each Eu chain is "left-and-right"

connected to two adjacent strands giving a three-dimensional (3D) 10-c uninodal network with the point symbol $3^{12}.4^{22}.5^{10}.6$ as analyzed by ToposPro.^{4,5}

Topology for $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (1-m)

Atom Eu1 links by bridge ligands and has

Common vertex with			R(A-A)		f
Eu 1	-0.2713	0.7437	0.2385	(-1 0 0)	11.804A 1
Eu 1	1.7287	0.7437	0.2385	(1 0 0)	11.804A 1
Eu 1	-0.2287	0.2437	0.2615	(0 -1 0)	12.708A 1
Eu 1	-0.2287	1.2437	0.2615	(0 0 0)	12.708A 1
Eu 1	0.2287	0.7563	0.7385	(-1 1 0)	12.789A 1
Eu 1	1.2287	0.7563	-0.2615	(0 1 -1)	12.789A 1
Eu 1	1.2713	1.2563	-0.2385	(2 2 0)	13.942A 1
Eu 1	0.2713	0.2563	0.7615	(1 1 1)	13.976A 1
Common edge with			R(A-A)		
Eu 1	0.7713	0.2437	0.2615	(1 -1 0)	5.593A 2
Eu 1	0.7713	1.2437	0.2615	(1 0 0)	5.593A 2

Structural group analysis

Structural group No 1

Structure consists of 3D framework with Eu1000P3000O9367C21000H31789

Coordination sequences

Eu1: 1 2 3 4 5 6 7 8 9 10
 Num 10 40 92 160 252 360 492 640 812 1000
 Cum 11 51 143 303 555 915 1407 2047 2859 3859

TD10=3859

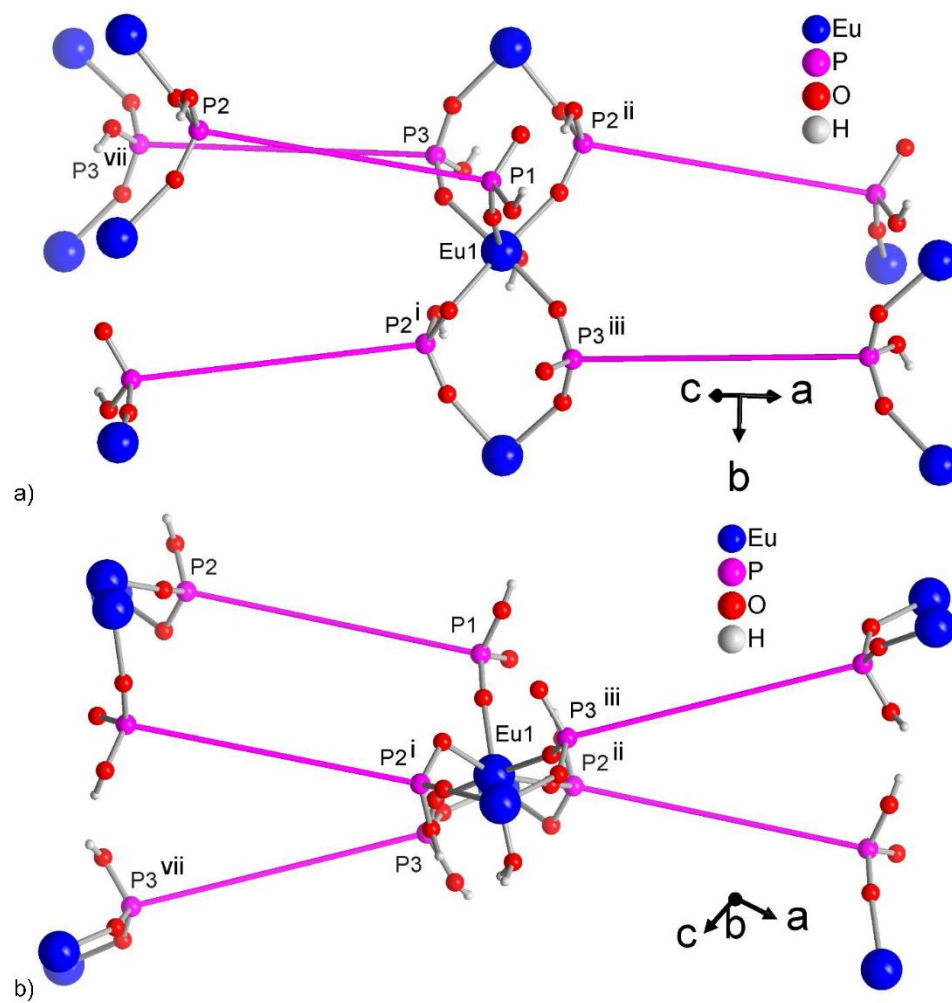
Vertex symbols for selected sublattice

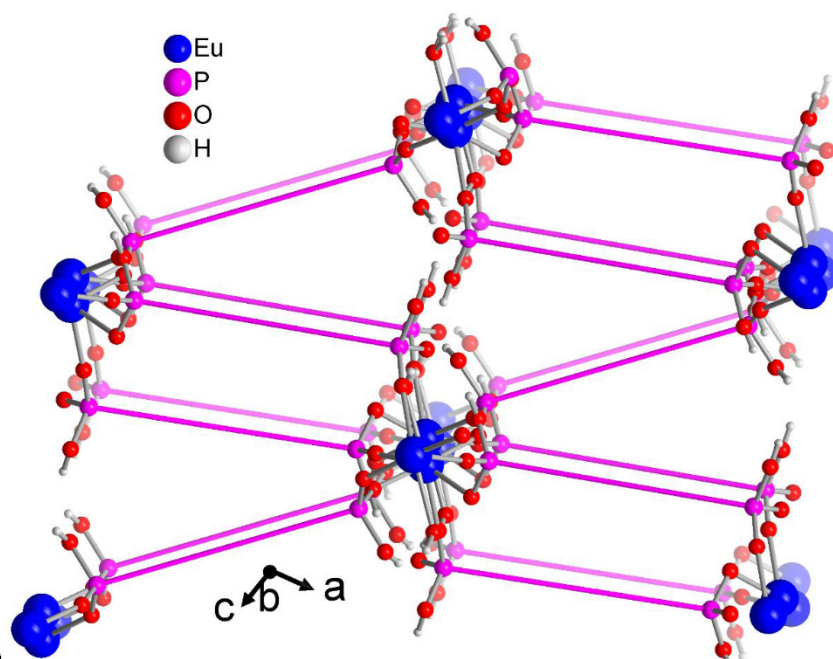
Eu1 Point symbol: $\{3^4 12.4^{22}.5^{10}.6\}$

Extended
 symbol: [3.3.3.3.3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4(2).4(2).4(2).4(2).4(2).4(2).4(3).4(3).4(3).4(3).5.5.5(2).5(2).5(2).5(2).5(3).5(3).5(5).5(5).6(14)] point

Point symbol for net: $\{3^4 12.4^{22}.5^{10}.6\}$

10-c net; uninodal net





c)
Figure S18. Schematic connectivity around Eu in $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**) showing the connectivity to 10 neighboring Eu atoms from which two are connected directly through the P2 and P3 phosphonate groups and eight across the diamantane linker. The doubly-bridged Eu chains run parallel to the *b*-direction and are up-and-down connected to four parallel chains. (a) View perpendicular to the *b*-direction, (b) approximately along the *b*-direction, (c) extended 3D network viewed along the *b*-direction. The diamantane unit is replaced by a direct P---P connector in magenta for clarity (the long Eu---O4 bond and the crystal water molecules are not shown). Symmetry codes: (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $x+1, y, z$; (iii) $-x+3/2, y+1/2, -z+1/2$; (vii) $-x+1, -y+1, -z+1$.

The two partially occupied crystal water molecules (O11 with 0.75, O12 with 0.25 site occupation factor) reside in voids in the 3D framework.

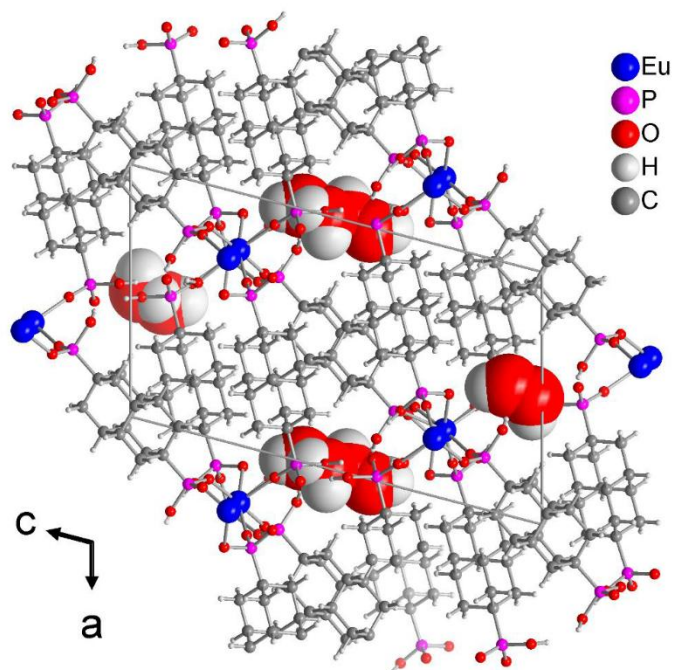


Figure S19. Section of the unit-cell packing diagram of $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**) with the half-occupied crystal water molecules shown in space-filling mode.

The H-atoms of the hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) groups are all involved in hydrogen bonding, either to other phosphonate groups (O2-H and O3-H) or to the crystal water molecule (from P3-O8-H). The O3 atom of the terminally coordinating phosphonate group with P1 accepts three H bonds (Table S10).

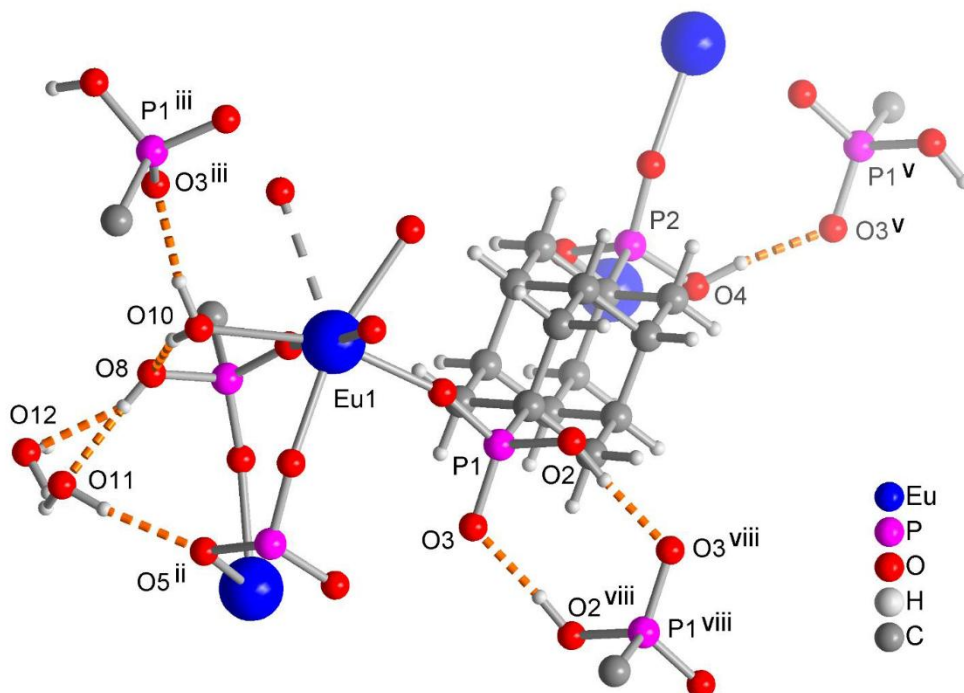


Figure S20. Hydrogen bonding scheme (dashed orange lines) in $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**). Further details of these O-H $\cdots$ O interactions, including the symmetry transformations are listed in Table S10.

Table S10. Hydrogen-bond geometry ($\text{\AA}$, $^\circ$) for $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O4}\cdots\text{H4}\cdots\text{O3}^v$	0.91 (1)	1.94 (5)	2.735 (6)	144 (8)
$\text{O4A}\cdots\text{H4A}\cdots\text{O3}^v$	0.84	2.01	2.630 (14)	130
$\text{O2}\cdots\text{H2}\cdots\text{O3}^{\text{viii}}$	0.89 (6)	1.70 (6)	2.584 (5)	174 (7)
$\text{O8}\cdots\text{H8}\cdots\text{O11}$	0.77 (4)	1.82 (5)	2.557 (7)	161 (7)
$\text{O8}\cdots\text{H8}\cdots\text{O12}$	0.77 (4)	1.92 (1)	2.63 (3)	153 (7)
$\text{O10}\cdots\text{H10A}\cdots\text{O3}^{\text{iii}}$	0.94 (6)	1.82 (6)	2.755 (5)	171 (6)
$\text{O10}\cdots\text{H10B}\cdots\text{O8}$	0.80 (6)	2.17 (6)	2.913 (6)	155 (7)
$\text{O11}\cdots\text{H11C}\cdots\text{O5}^{\text{ii}}$	0.87	1.96	2.825 (9)	173

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

Section S9. X-ray structure of compound $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$, L = Diam(PO₃H)₂²⁻ (2)

CCDC reference number is 2455264.

Table S11a. Crystal data and structure refinement details for $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (2).

Crystal data

C ₂₁ H ₃₂ GdO ₁₀ P ₃ ·H ₂ O	$F(000) = 1428$
$M_r = 712.64$	$D_x = 1.855 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$a = 11.9044 (2) \text{ \AA}$	Cell parameters from 44307 reflections
$b = 11.0888 (2) \text{ \AA}$	$\theta = 4.0\text{--}77.1^\circ$
$c = 19.9039 (3) \text{ \AA}$	$\mu = 19.10 \text{ mm}^{-1}$
$\beta = 103.737 (2)^\circ$	$T = 150 \text{ K}$
$V = 2552.27 (8) \text{ \AA}^3$	Block, clear colourless
$Z = 4$	$0.15 \times 0.12 \times 0.08 \text{ mm}$

Data collection

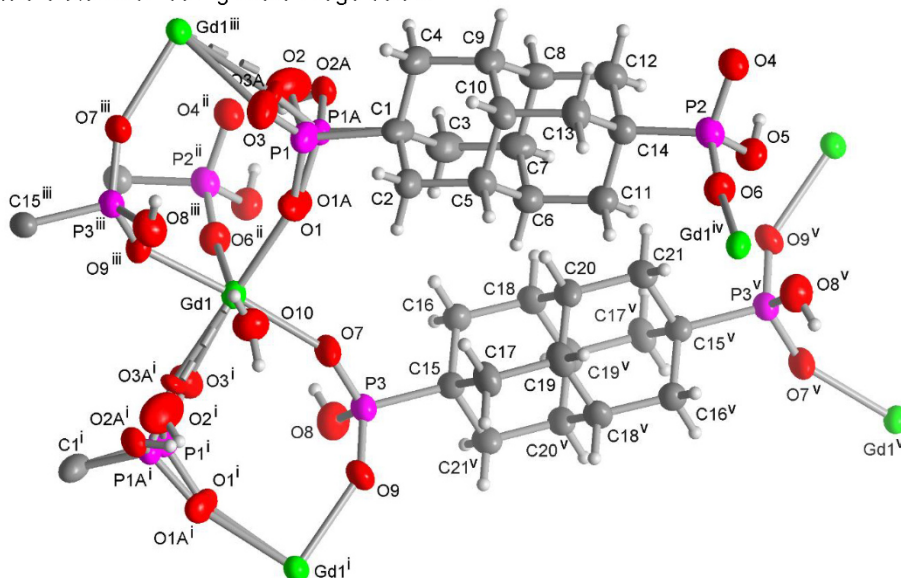
XtaLAB Synergy, Dualflex, HyPix diffractometer	4902 reflections with $I > 2\sigma(I)$
Detector resolution: $10.0000 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.078$
ω scans	$\theta_{\text{max}} = 80.0^\circ$, $\theta_{\text{min}} = 4.0^\circ$
Absorption correction: gaussian <i>CrysAlis PRO</i> 1.171.41.90a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$h = -15 \rightarrow 14$
$T_{\text{min}} = 0.087$, $T_{\text{max}} = 0.427$	$k = -14 \rightarrow 13$
78115 measured reflections	$l = -24 \rightarrow 24$
5314 independent reflections	

Refinement

Refinement on F^2	27 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.0459$ $R[F^2, \text{all data}] = 0.0490$	H atoms treated by a mixture of independent and constrained refinement
$wR[F^2 > 2\sigma(F^2)] = 0.1350$ $wR[F^2, \text{all data}] = 0.1383$	$w = 1/[\sigma^2(F_o^2) + (0.0853P)^2 + 3.106P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.143$	$(\Delta/\sigma)_{\text{max}} = 0.001$
5314 reflections	$\Delta_{\text{max}} = 0.98 \text{ e \AA}^{-3}$
393 parameters	$\Delta_{\text{min}} = -2.01 \text{ e \AA}^{-3}$

The structures of $\{[\text{LnL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$, Ln = Eu, Gd, Er; L = Diam(PO₃H)₂²⁻ are isostructural.

Table S11b. Selected bond distances (Å) and bond angles (°) for $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**) referring to the atom numbering in the image below:



The phosphonate group at P1 is slightly disordered with the major contributing atoms having a site occupation factor (SOF) of 0.58. The minor contribution of the disordered atoms has an SOF of 0.442 and are denoted with the suffix A (50% thermal ellipsoids). The crystal water molecule is not shown for clarity.

Gd1—O1	2.249 (8)	O3—Gd1 ⁱⁱⁱ	2.389 (11)
Gd1—O1A	2.268 (10)	O3A—Gd1 ⁱⁱⁱ	2.234 (8)
Gd1—O3 ⁱ	2.389 (11)	O6—Gd1 ^{iv}	2.228 (4)
Gd1—O3A ⁱ	2.233 (8)	O9—Gd1 ⁱ	2.276 (3)
Gd1—O6 ⁱⁱ	2.228 (4)		
Gd1—O7	2.280 (4)	Gd1—O2 ⁱ	2.900 (17)
Gd1—O9 ⁱⁱⁱ	2.276 (3)	O2—Gd1 ⁱⁱⁱ	2.900 (16)
Gd1—O10	2.401 (5)		
P1—O1	1.474 (8)	P2—O4	1.513 (4)
P1—O2	1.595 (9)	P2—O5	1.583 (4)
P1—O3	1.519 (9)	P2—O6	1.499 (4)
P1—C1	1.882 (8)	P2—C14	1.811 (5)
P1A—O1A	1.504 (10)	P3—O7	1.501 (4)
P1A—O2A	1.577 (8)	P3—O8	1.591 (4)
P1A—O3A	1.523 (8)	P3—O9	1.510 (4)
P1A—C1	1.747 (7)	P3—C15	1.812 (5)
O1—Gd1—O2 ⁱ	139.5 (5)	O1—P1—O2	110.2 (8)

O1—Gd1—O3 ⁱ	166.1 (5)	O1—P1—O3	118.1 (9)
O1—Gd1—O7	93.7 (5)	O1—P1—C1	106.3 (8)
O1—Gd1—O9 ⁱⁱⁱ	88.2 (5)	O2—P1—C1	106.8 (6)
O1—Gd1—O10	76.4 (5)	O3—P1—O2	102.5 (6)
O1A—Gd1—O7	90.4 (7)	O3—P1—C1	112.4 (5)
O1A—Gd1—O9 ⁱⁱⁱ	92.3 (7)	O1A—P1A—O2A	108.8 (10)
O1A—Gd1—O10	84.9 (6)	O1A—P1A—O3A	113.9 (11)
O3 ⁱ —Gd1—O2 ⁱ	53.6 (3)	O1A—P1A—C1	111.9 (10)
O3 ⁱ —Gd1—O10	115.0 (4)	O2A—P1A—C1	109.9 (5)
O3A ⁱ —Gd1—O1A	175.9 (7)	O3A—P1A—O2A	107.3 (6)
O3A ⁱ —Gd1—O7	88.0 (3)	O3A—P1A—C1	104.8 (5)
O3A ⁱ —Gd1—O9 ⁱⁱⁱ	89.7 (3)	O4—P2—O5	109.9 (2)
O3A ⁱ —Gd1—O10	98.9 (4)	O4—P2—C14	110.8 (2)
O6 ⁱⁱ —Gd1—O1	90.9 (5)	O5—P2—C14	106.3 (2)
O6 ⁱⁱ —Gd1—O1A	82.9 (6)	O6—P2—O4	114.4 (2)
O6 ⁱⁱ —Gd1—O2 ⁱ	126.59 (18)	O6—P2—O5	105.4 (2)
O6 ⁱⁱ —Gd1—O3 ⁱ	79.0 (3)	O6—P2—C14	109.5 (2)
O6 ⁱⁱ —Gd1—O3A ⁱ	93.5 (4)	O7—P3—O8	111.3 (3)
O6 ⁱⁱ —Gd1—O7	96.95 (16)	O7—P3—O9	115.4 (2)
O6 ⁱⁱ —Gd1—O9 ⁱⁱⁱ	88.58 (14)	O7—P3—C15	109.7 (2)
O6 ⁱⁱ —Gd1—O10	164.23 (15)	O8—P3—C15	105.1 (2)
O7—Gd1—O2 ⁱ	96.1 (2)	O9—P3—O8	105.4 (2)
O7—Gd1—O3 ⁱ	78.3 (3)	O9—P3—C15	109.4 (2)
O7—Gd1—O10	93.17 (17)		
O9 ⁱⁱⁱ —Gd1—O2 ⁱ	78.9 (2)	P1—O1—Gd1	157.0 (12)
O9 ⁱⁱⁱ —Gd1—O3 ⁱ	100.9 (3)	P1A—O1A—Gd1	163.7 (16)
O9 ⁱⁱⁱ —Gd1—O7	174.11 (15)	P1—O2—Gd1 ⁱⁱⁱ	89.1 (6)
O9 ⁱⁱⁱ —Gd1—O10	81.86 (16)	P1—O3—Gd1 ⁱⁱⁱ	112.6 (7)
O10—Gd1—O2 ⁱ	63.9 (2)	P1A—O3A—Gd1 ⁱⁱⁱ	139.9 (7)
		P2—O6—Gd1 ^{iv}	162.1 (3)
		P3—O7—Gd1	153.3 (2)
		P3—O9—Gd1 ⁱ	144.4 (2)

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

The asymmetric unit of $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**) consists of one Gd atom, a fully and half-occupied diamantane-bis(hydrogenphosphonate) linker, one aqua ligand and two partially occupied crystal water molecules (see below) to give a formula unit of $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ with $\text{L} = \text{Diam}(\text{PO}_3\text{H})_2^{2-}$. Each phosphonate group in the diamantane-bis(phosphonate) linker is only singly deprotonated, that is presents a hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) group.

In the structure of $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**) the single unique Gd atom is six-coordinated by five O atoms from five different hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) groups and the aqua ligand. A coordination from a long Gd1—O2ⁱ bond of 2.900 Å from a P—OH group is depicted as a dashed bond in Figure S21a,c but not taken into consideration for the octahedron in Figure S21b. The other Gd1—O bond lengths lie between 2.228 and 2.401 Å (Table S11b). The six-fold coordination around Gd is a

distorted octahedron. The still possibly seven-fold coordination of Gd versus the clearly six-fold coordination of Er in the isostructural network $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**) is evidence of the larger ionic radius of Gd^{3+} (0.935 Å) versus Er^{3+} (0.89 Å). At the same time, it can be noted that the only slightly larger Eu^{3+} (0.947 Å) is eight-fold coordinated in the orthorhombic structure in $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ (**1-o**) and six- to seven-fold coordinated in the monoclinic structure in $\{[\text{EuL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1-m**).

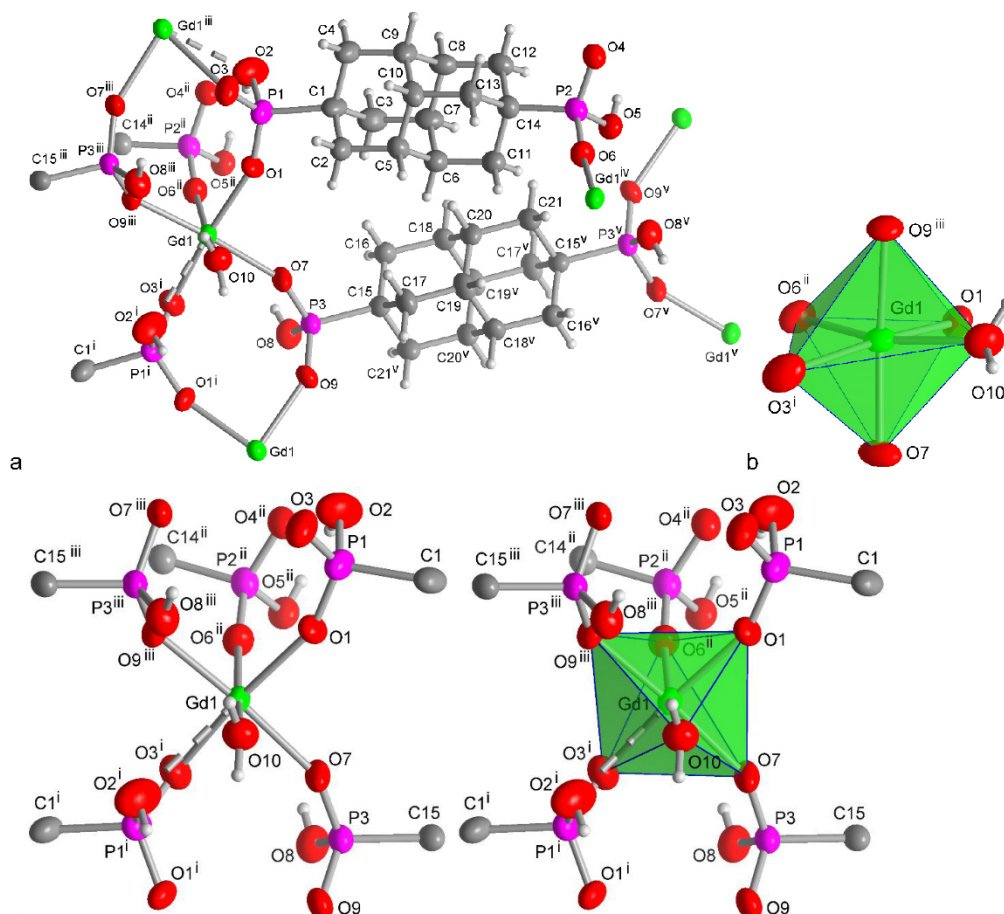
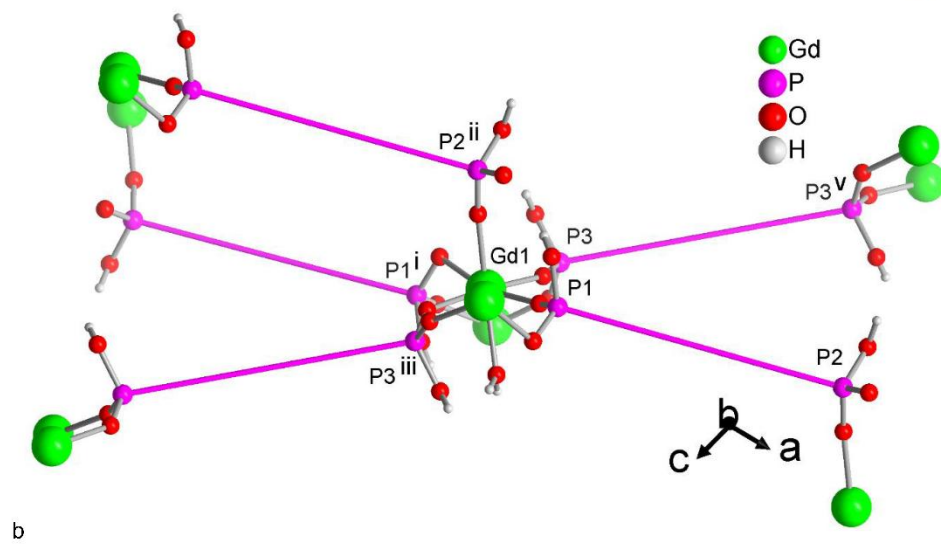
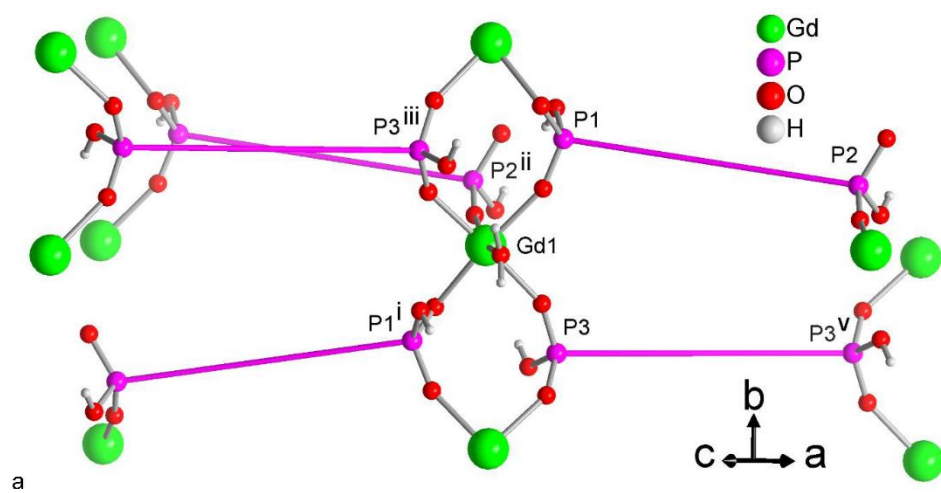
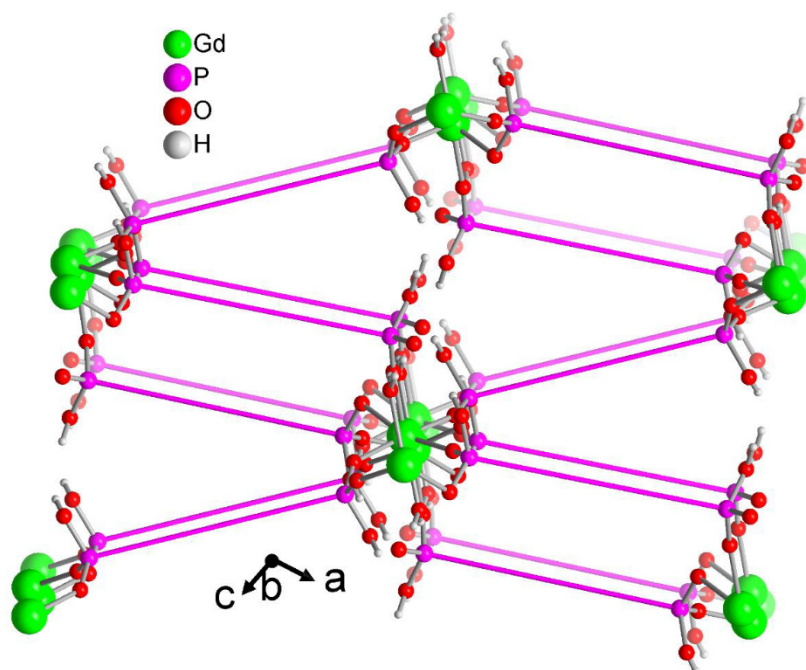


Figure S21. The extended asymmetric unit (a) and the coordination sphere around gadolinium (b,c) in $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**), not showing the minor contribution of the disordered atoms of the phosphonate group at P1. The longer Gd1-O2 bond is shown as a dashed line. (50% thermal ellipsoids), symmetry codes: (i) $-x+1/2, y-1/2, -z+3/2$; (ii) $x-1, y, z$; (iii) $-x+1/2, y+1/2, -z+3/2$; (iv) $x+1, y, z$; (v) $-x+1, -y, -z+1$.

The phosphonate linker with P1 and P2 is only a bridging group at P1 and coordinates to two Gd atoms. The group at P2 is terminally coordinated to only one Gd atom. In the linker containing P3, which sits on a special position, each phosphonate bridges between two Gd atoms and the entire linker connects four Gd atoms. Out of the five $-\text{PO}_3\text{H}^-$ groups around Gd, the two with P1 and the two with P3 each bridge to a neighboring Gd atom. The group with P2 is only terminally coordinated. Each Gd atom is in total connected to 10 other Gd atoms, with eight of them connected through the bridging action of the diamantane moiety of the linker.

The direct phosphonate P1 and P3 bridging action between the Gd atoms leads to a corrugated doubly-bridged Gd chain parallel to the crystallographic b -direction. Each Gd chain is "left-and-right"





^c
Figure S22. Schematic connectivity around Gd in $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**) showing the connectivity to 10 neighboring Gd atoms from which two are connected directly through the P1 and P3 phosphonate groups and eight across the diamantane linker. The doubly-bridged Gd chains run parallel to the *b*-direction and are up-and-down connected to four parallel chains. (a) View perpendicular to the *b*-direction, (b) approximately along the *b*-direction, (c) extended 3D network viewed along the *b*-direction. The diamantane unit is replaced by a direct P---P connector in magenta for clarity (the crystal water molecules are not shown). Symmetry codes: (i) $-x+1/2, y-1/2, -z+3/2$; (ii) $x-1, y, z$; (iii) $-x+1/2, y+1/2, -z+3/2$; (v) $-x+1, -y, -z+1$.

The two partially occupied crystal water molecules (O11 with 0.66, O11A with 0.38 site occupation factor) reside in voids in the 3D framework.

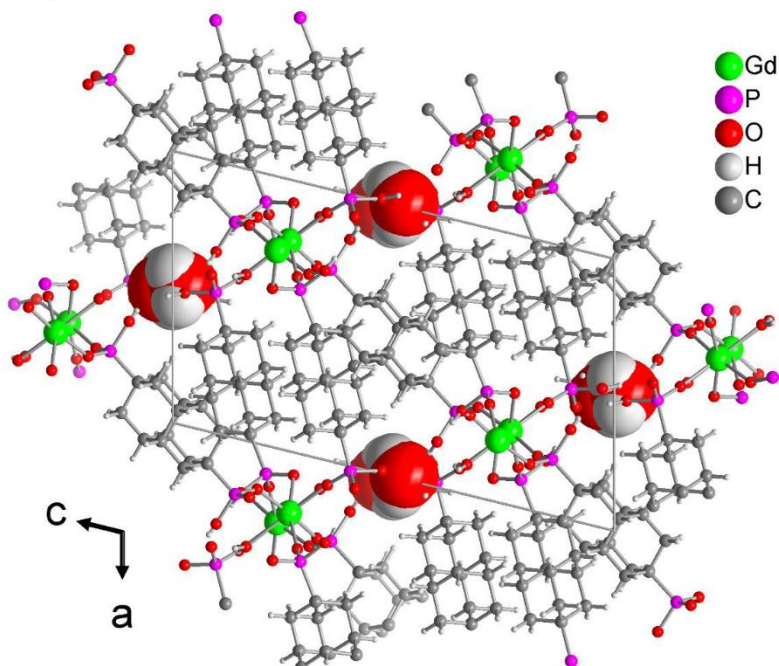


Figure S23. Section of the unit-cell packing diagram of $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**) with the half-occupied crystal water molecules shown in space-filling mode.

Table S12. Hydrogen-bond geometry ($\text{\AA}$, $^\circ$) for $\{[\text{GdL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**2**).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}\cdots\text{H2}\cdots\text{O4}^{\text{ii}}$	0.84	2.06	2.800 (10)	146
$\text{O2A}\cdots\text{H2A}\cdots\text{O4}^{\text{ii}}$	0.84	1.86	2.682 (9)	168
$\text{O5}\cdots\text{H5}\cdots\text{O4}^{\text{vi}}$	0.91 (9)	1.68 (9)	2.585 (5)	172 (9)
$\text{O8}\cdots\text{H8}\cdots\text{O11}$	0.83 (2)	1.81 (6)	2.534 (11)	146 (9)
$\text{O8}\cdots\text{H8}\cdots\text{O11A}$	0.83 (2)	1.79 (4)	2.601 (18)	164 (9)
$\text{O10}\cdots\text{H10B}\cdots\text{O4}^{\text{vii}}$	0.86 (2)	1.93 (4)	2.748 (6)	157 (9)
$\text{O11A}\cdots\text{H11F}\cdots\text{O5}^{\text{ii}}$	0.87	2.23	2.68 (2)	112

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

Section S10. X-ray structure of compound $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$, L = Diam(PO_3H) $_2^{2-}$ (3)

CCDC reference number is 2455265.

Table S13a. Crystal data and structure refinement details for $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (3).

Crystal data

$\text{C}_{21}\text{H}_{32}\text{ErO}_{10}\text{P}_3\cdot\text{H}_2\text{O}$	$F(000) = 1444$
$M_r = 722.65$	$D_x = 1.892 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$a = 11.9973 (1) \text{ \AA}$	Cell parameters from 62543 reflections
$b = 10.9778 (1) \text{ \AA}$	$\theta = 4.0\text{--}78.1^\circ$
$c = 19.7560 (1) \text{ \AA}$	$\mu = 8.45 \text{ mm}^{-1}$
$\beta = 102.836 (1)^\circ$	$T = 150 \text{ K}$
$V = 2536.92 (4) \text{ \AA}^3$	Block, clear orange
$Z = 4$	$0.44 \times 0.08 \times 0.04 \text{ mm}$

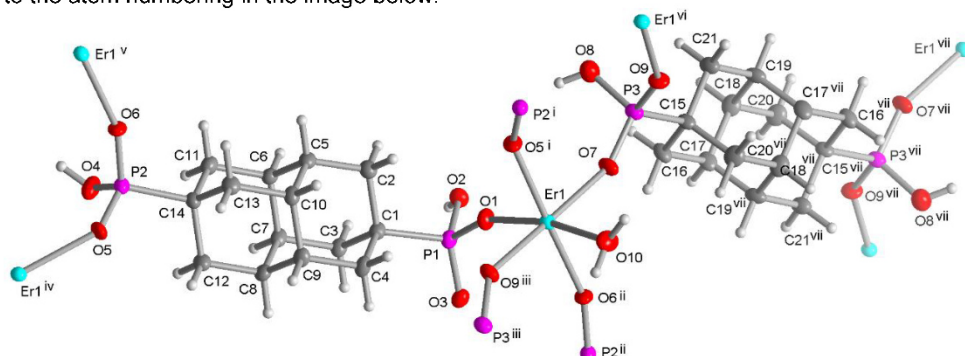
Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	5187 independent reflections
Radiation source: micro-focus sealed X-ray tube	4992 reflections with $I > 2\sigma(I)$
Detector resolution: $10.0000 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.062$
ω scans	$\theta_{\text{max}} = 78.4^\circ$, $\theta_{\text{min}} = 4.0^\circ$
Absorption correction: gaussian CrysAlis PRO 1.171.41.90a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$h = -15 \rightarrow 13$
$T_{\text{min}} = 0.071$, $T_{\text{max}} = 1.000$	$k = -13 \rightarrow 13$
81749 measured reflections	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.0343$ $R[F^2, \text{all data}] = 0.0355$	H atoms treated by a mixture of independent and constrained refinement
$wR[F^2 > 2\sigma(F^2)] = 0.0976$ $wR[F^2, \text{all data}] = 0.0991$	$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 7.498P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.087$	$(\Delta/\sigma)_{\text{max}} = 0.002$
5187 reflections	$\lambda_{\text{max}} = 1.49 \text{ e \AA}^{-3}$
361 parameters	$\Delta_{\text{min}} = -1.39 \text{ e \AA}^{-3}$
3 restraints	

Table S13b. Selected bond distances (Å) and bond angles (°) for $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**) referring to the atom numbering in the image below:



50% thermal ellipsoids, crystal water molecule not shown for clarity.

Er1—O1	2.178 (2)	O5—Er1 ^{iv}	2.229 (2)
Er1—O5 ⁱ	2.229 (2)	O6—Er1 ^v	2.195 (2)
Er1—O6 ⁱⁱ	2.195 (2)	O9—Er1 ^{vi}	2.235 (2)
Er1—O7	2.225 (2)		
Er1—O9 ⁱⁱⁱ	2.235 (2)		
Er1—O10	2.336 (3)		
P1—O1	1.495 (3)	P2—O6	1.499 (3)
P1—O2	1.579 (3)	P2—C14	1.805 (4)
P1—O3	1.519 (3)	P3—O7	1.505 (3)
P1—C1	1.808 (4)	P3—O8	1.591 (3)
P2—O4	1.583 (3)	P3—O9	1.507 (3)
P2—O5	1.504 (3)	P3—C15	1.811 (3)
O1—Er1—O5 ⁱ	89.16 (10)	O1—P1—O2	104.99 (16)
O1—Er1—O6 ⁱⁱ	90.02 (10)	O1—P1—O3	114.86 (15)
O1—Er1—O7	96.04 (10)	O1—P1—C1	109.58 (15)
O1—Er1—O9 ⁱⁱⁱ	88.89 (10)	O2—P1—C1	106.10 (15)
O1—Er1—O10	169.22 (11)	O3—P1—O2	109.98 (15)
O5 ⁱ —Er1—O9 ⁱⁱⁱ	91.66 (10)	O3—P1—C1	110.83 (16)
O5 ⁱ —Er1—O10	96.94 (11)	O4—P2—C14	104.34 (16)
O6 ⁱⁱ —Er1—O5 ⁱ	177.48 (10)	O5—P2—O4	108.92 (17)
O6 ⁱⁱ —Er1—O7	92.77 (10)	O5—P2—C14	109.64 (16)
O6 ⁱⁱ —Er1—O9 ⁱⁱⁱ	90.71 (10)	O6—P2—O4	109.64 (16)
O6 ⁱⁱ —Er1—O10	84.24 (11)	O6—P2—O5	114.35 (16)
O7—Er1—O5 ⁱ	84.95 (10)	O6—P2—C14	109.48 (16)
O7—Er1—O9 ⁱⁱⁱ	173.96 (10)	O7—P3—O8	110.75 (16)
O7—Er1—O10	93.36 (11)	O7—P3—O9	115.19 (16)
O9 ⁱⁱⁱ —Er1—O10	82.07 (11)	O7—P3—C15	109.42 (15)

		O8—P3—C15	105.44 (16)
P1—O1—Er1	158.96 (18)	O9—P3—O8	105.97 (16)
P2—O5—Er1 ^{iv}	137.94 (18)	O9—P3—C15	109.58 (16)
P2—O6—Er1 ^v	160.51 (17)		
P3—O7—Er1	154.73 (16)		
P3—O9—Er1 ^{vi}	145.26 (16)		

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

The asymmetric unit of $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**) consists of one Er atom, a fully and half-occupied diamantane-bis(hydrogenphosphonate) linker, one aqua ligand and two half-occupied crystal water molecules (see above image) to give a formula unit of $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ with $\text{L} = \text{Diam}(\text{PO}_3\text{H})_2^{2-}$. Each phosphonate group in the diamantane-bis(phosphonate) linker is only singly deprotonated, that is presents a hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) group.

In the structure of $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**) the single unique Er atom is only six-coordinated by five O atoms from five different hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) groups and an aqua ligand. The coordination around Er is a distorted octahedron with the angles involving the aqua ligand with O10, such as cis O9ⁱⁱⁱ-Er-O10 ($82.1(1)^\circ$) and trans O1-Er-O10 ($169.2(1)^\circ$) deviating most strongly from 90° and 180° .

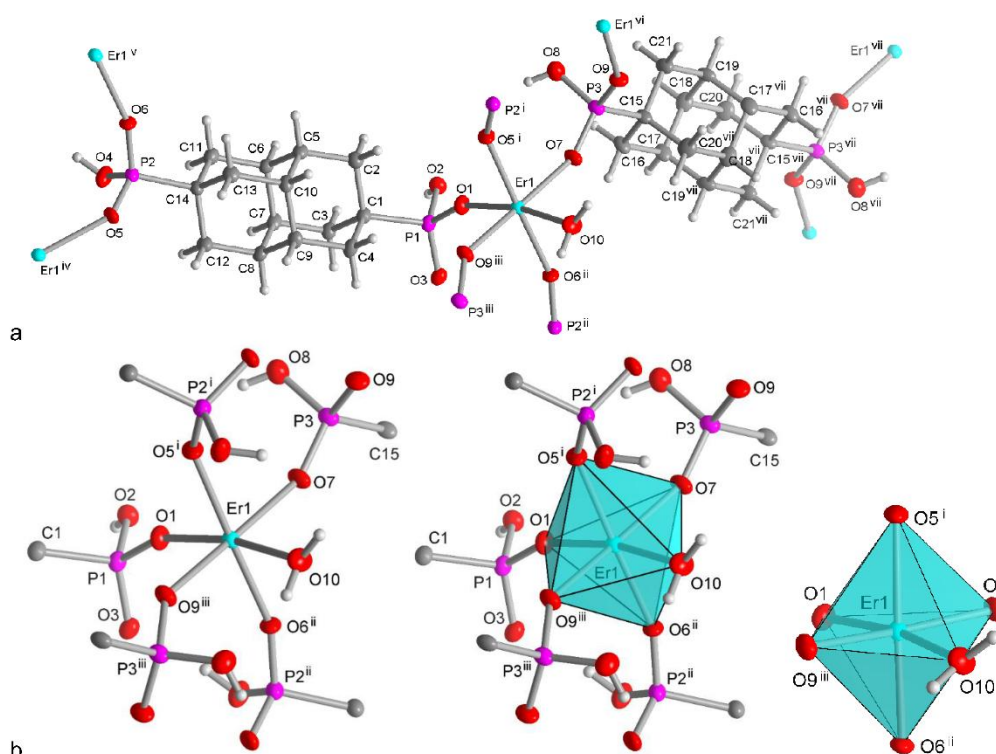


Figure S24. The extended asymmetric unit (a) and the coordination sphere around erbium (b) in $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**) (50% thermal ellipsoids), symmetry codes: (i) $-x+1/2, y+1/2, -z+3/2$; (ii) $x+1, y, z$; (iii) $-x+3/2, y-1/2, -z+3/2$; (iv) $-x+1/2, y-1/2, -z+3/2$; (v) $x-1, y, z$; (vi) $-x+3/2, y+1/2, -z+3/2$; (vii) $-x+2, -y+2, -z+1$.

Topology for $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (3)

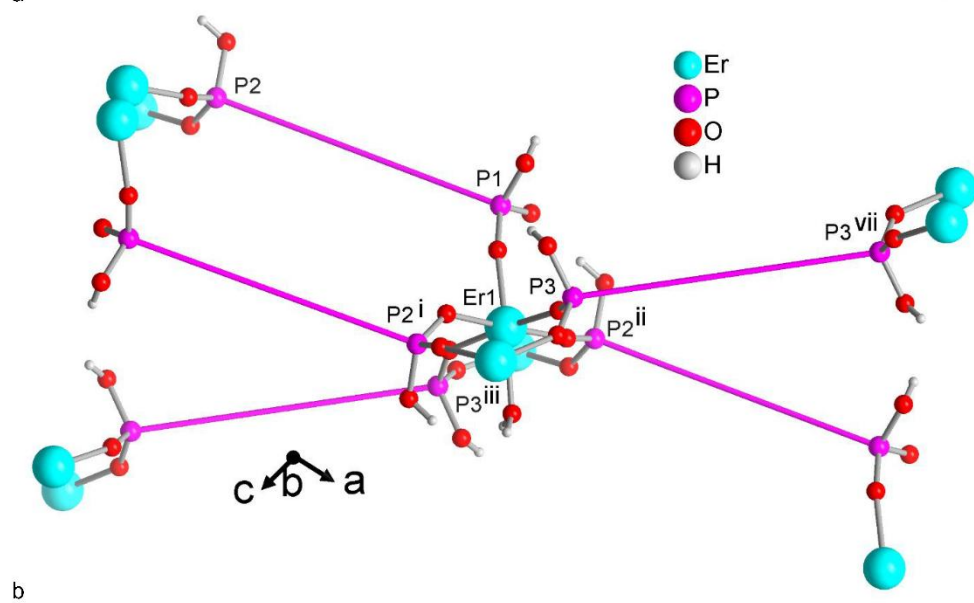
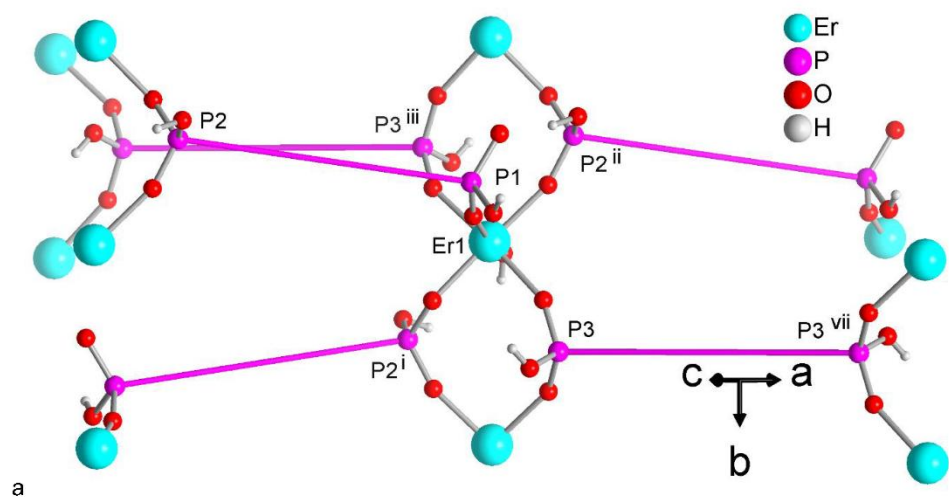
Structural group analysis

Structure consists of 3D framework with ErP3O10C21H32

Er1: 1 2 3 4 5 6 7 8 9 10
 Num 10 40 92 160 252 360 492 640 812 1000
 Cum 11 51 143 303 555 915 1407 2047 2859 3859

Er1 Point symbol:{3^12.4^22.5^10.6}

Point symbol for net: {3¹².4²².5¹⁰.6}



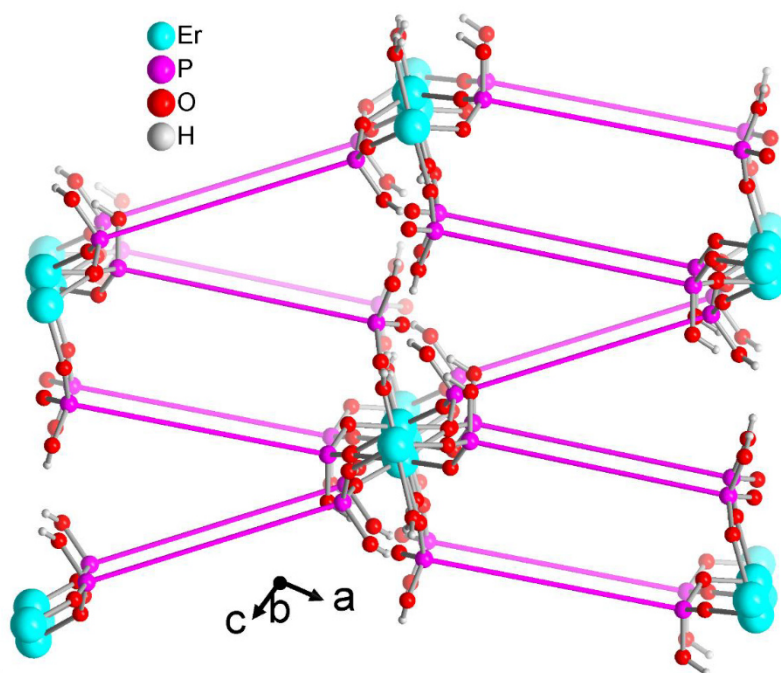


Figure S25. Schematic connectivity around Er in $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**) showing the connectivity to 10 neighboring Er atoms from which two are connected directly through the P2 and P3 phosphonate groups and eight across the diamantane linker. The doubly-bridged Er chains run parallel to the *b*-direction and are up-and-down connected to four parallel chains. (a) View perpendicular to the *b*-direction, (b) approximately along the *b*-direction, (c) extended 3D network viewed along the *b*-direction. The diamantane unit is replaced by a direct P---P connector in magenta for clarity (the crystal water molecules are not shown). Symmetry codes: (i) $-x+1/2, y+1/2, -z+3/2$; (ii) $x+1, y, z$; (iii) $-x+3/2, y-1/2, -z+3/2$.

The two half-occupied crystal water molecules reside in voids in the 3D framework.

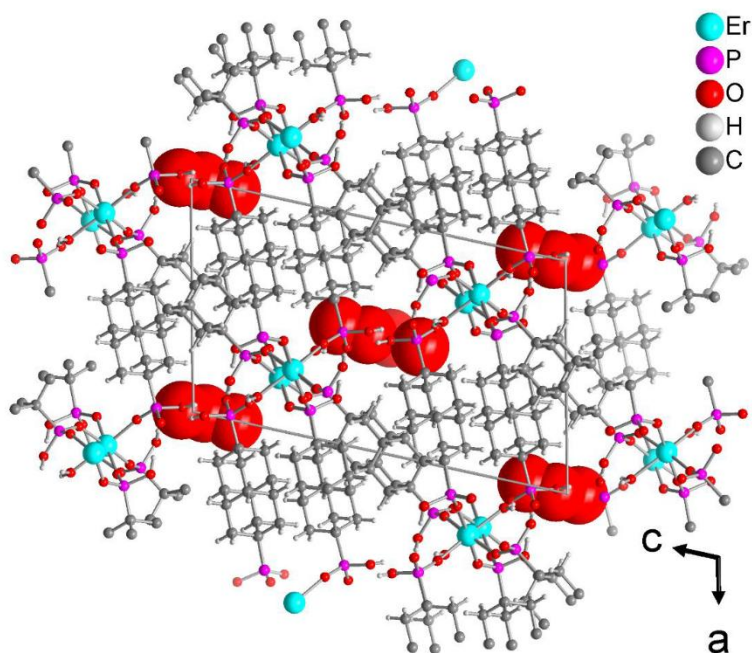


Figure S26. Section of the unit-cell packing diagram of $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**) with the half-occupied crystal water molecules shown in space-filling mode.

The H-atoms of the hydrogenphosphonate ($-\text{PO}_3\text{H}^-$) groups are all involved in hydrogen bonding, either to other phosphonate groups or to the crystal water molecules.

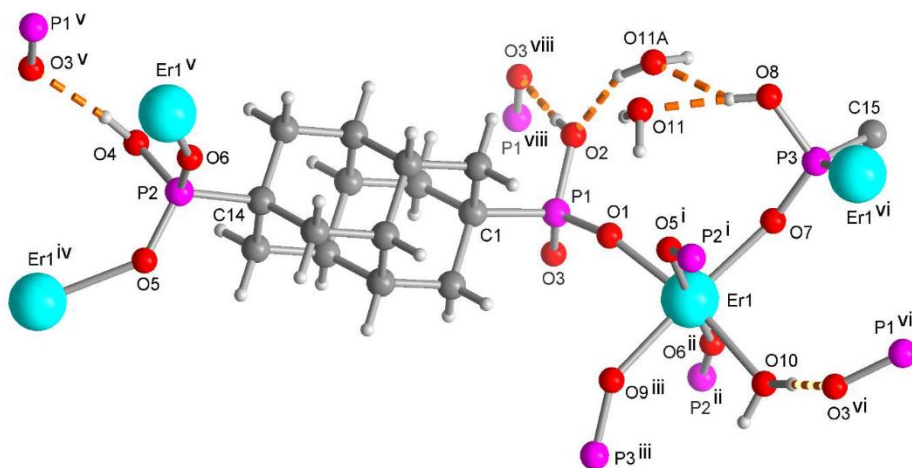


Figure S27. Hydrogen bonding scheme (dashed orange lines) in $\{[\text{ErL}_{1.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**3**). Further details of these O-H $\cdots$ O interactions, including the symmetry transformations are listed in Table S14.

Table S14. Hydrogen-bond geometry (Å, °) for {[ErL_{1.5}(H₂O)]·H₂O}_n (**3**).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2—H2···O3 ^{viii}	0.73 (6)	1.87 (6)	2.600 (4)	175 (6)
O4—H4···O3 ^v	0.90 (6)	1.85 (6)	2.739 (4)	170 (6)
O8—H8···O11	0.83 (2)	1.77 (3)	2.538 (7)	155 (6)
O8—H8···O11A	0.83 (2)	1.88 (4)	2.592 (10)	145 (5)
O10—H10B···O3 ^{vi}	0.87 (1)	1.87 (2)	2.725 (4)	168 (5)
O11A—H11F···O2	0.87	1.88	2.699 (10)	156

Symmetry codes: (v) *x*-1, *y*, *z*; (vi) -*x*+3/2, *y*+1/2, -*z*+3/2; (viii) -*x*+1, -*y*+1, -*z*+1.

Section S11. Graph-set analysis of hydrogen-bonding patterns

The graph-set analysis focused on general structural aspects and the rationalization of the structures, hence the analysis of the smallest ring patterns was prioritized.

All the structures of the symmetrically bifunctional diamantane compounds (except the monochlorodiamantane derivative) have a layered structure consisting of hydrophilic and hydrophobic layers. While the layered structure organization is very typical for the (hydrogen)phosphates/phosphonates, the presence of the large diamantane cores makes such organization particularly expected. The large hydrophobic cores packed in a layer define residual free space between the (hydrogen)phosphonate groups, which are filled by water, either coordinated or solvate molecules. The water molecules are efficiently associated with the (hydrogen)phosphonates, thereby constituting the hydrophilic layer, with a tendency to maximize the number of hydrogen bonds (i.e. the solvate water are often acts as 2/2 H-bond donor/acceptors).

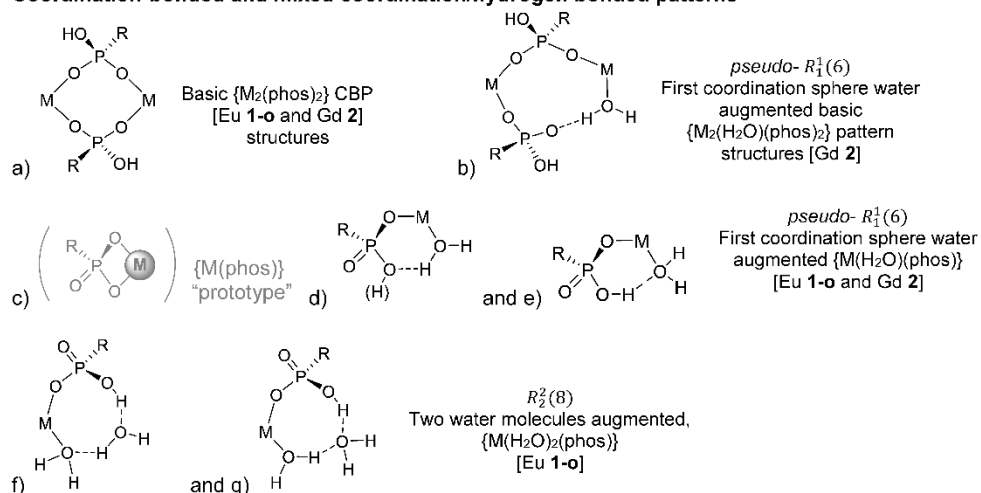
In diamantane-4,9-bis(methyl hydrogenphosphonate) trihydrate, the two crystallographically independent water, participate in four hydrogen bonds. The resulting H-bonded association form a 2D interconnected layer, which could be viewed as a stack of tubes, running along -110 direction. The adjacent phosphonates are not associated directly, but via H-bonding by means of H-bonded chains, consisting of one, two, or three water molecules. The smallest H-bonded ring in the structure, which is a specific assembly marker, is the centrosymmetric $\{(-O=P(OMe)OH\cdots O(H)H\cdots O(H)H\cdots O=P(OMe)OH\cdots)_2\}$, i.e. an $R_6^6(16)$ ring pattern according to the Etter's graph-set notation (Fig. S28l, see the short definition for the notation in the subscript to the table). The amount of water in the hydrophilic layer determined rather by steric demands, but the realization of that particular large ring pattern by the given composition is deemed probable, as it represents a two-water-molecules "augmented" version of the fundamental dicarboxylate/bis(monohydrogenphosphonate) patterns (Fig. S28h, i).

In both coordination compounds, **1-o** ($\{[EuL_{1.5}(H_2O)_4]\cdot H_2O\}_n$) and **2** ($\{[GdL_{1.5}(H_2O)]\cdot H_2O\}_n$) structures the hydrophilic layer is densely interconnected by H-bonds, particularly in the latter case. The dominant coordination bonded motif in both cases is a 1D chain composed of $\{(-M-OP(R)(OH)O\cdots)_2\}$ coordination bonded cycles (Fig. S28a) with shared metal ions, which constitute the coordination-bonded backbone. In the case of $\{[GdL_{1.5}(H_2O)]\cdot H_2O\}_n$ a third H-bonded small cycle, $\{(-M-OP(R)(OH)O\cdots M-O(H)O\cdots (OP(R)(OH)O)\cdots)_2\}$, which could be viewed as a water-augmented patterns given above (Fig. S28b), reinforces the connectivity within the chains. The latter are in turn associated by the smallest bis(hydrogenphosphonate) rings, $\{(-OP(R)(OMe)OH\cdots)_2\}$, $R_2^2(8)$ (Fig. S28f,g), and space-filling water molecules in H-bonded layers. On the other hand, the more water-rich $\{Eu(O_{water})_4(O_{phos})_4\}$ coordination environment of Eu in **1-o** with intermingled aqua- and mono(hydrogenphosphonic acid) ligands gives rise to numerous H-bonds leading in most cases to $\{-M-O(H)H\cdots O=P(OH)O\cdots\}$ cycles within the first coordination sphere (Fig S28d,e), which also reinforce the primary coordination-bonded cycles. The non-involved H-bond donors and acceptors densely interconnect those chains together to form a double-sheet layer morphology. Deeper graph-set analysis gives here little added value for the understanding of the structure as the various larger H-bonded cycles are of secondary importance in the context of structure rationalization.

The DiamCl(PO_3HMe) structure is different from the other reported structure, as the asymmetric functionalization does not prompt the molecules to form axially aligned hydrophobic layers. The density of donor and acceptor atoms is also lower due to the mono-functionalization resulting in lesser density of the formed H-bonded 2D layer of the methylphosphonate groups, connected via water molecules. The dominant ring pattern consists of $\{(-OP(R)(OH)(OMe)\cdots HOH\cdots)_2\}$, $R_4^2(8)$ (Fig. S28j), which acts as a square-shaped four-connected node for an H-bonded 4,4-net defining the H-bonded connectivity.

The most relevant structure-defining small-ring patterns, both coordination-bonded and mixed H-bonded, in the reported structures.

Coordination-bonded and mixed coordination/hydrogen bonded patterns



Hydrogen-bonded patterns

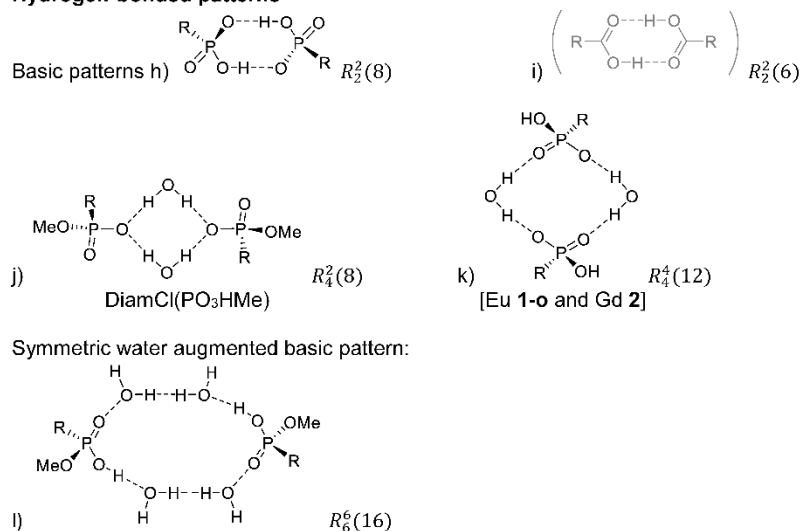


Figure S28. The most relevant structure-defining small-ring patterns, both coordination-bonded and mixed H-bonded, in the reported structures. The stereochemical designations for the phosphonate groups are given only to emphasize their tetrahedral shape and to suggest the attainable centrosymmetric geometry for some of the patterns. The grayed out prototypal patterns are not present in the structures but are given for comparison. Etter graph-set symbol definition: $G_d^a(n)$, where G indicates the pattern type, with R denoting rings, a the number of acceptors, and d the number of donors involved in the hydrogen-bonding network.

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3.2 Where Most Frameworks Degrade: Flexible Bimetallic Phosphonate Crystals as pH-Universal Supercapacitor Electrodes

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Abstract:

Herein, we report the charge storage and plastic properties of the redox-active, bimetallic metal phosphonate framework of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$. The flexible crystals of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ combine semiconducting behavior with mechanical flexibility on the same platform, which is an unusual and significant property that is not observed in traditional rigid layered electrode materials. In contrast to RuO_2 , graphene, or MXenes, which prefer concentrated acidic or basic electrolytes to operate effectively as electrodes, $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ works between sustainable pH values of 4 and 10 while reaching a specific capacitance of about 140 F/g in H_3PO_4 at pH 4 and in NaOH at pH 10 at 1 mV/s. It also demonstrates high chemical and electrochemical stability between pH 2 and pH 12 and in lithium hexafluorophosphate for extended periods. The use of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ as electrodes eliminates the need for harsh chemical environments, generating more sustainable and environmentally friendly energy storage solutions, and $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ can be synthesized in water at mild temperatures. The combination of chemical stability, mechanical flexibility of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$, and compatibility with mild electrolytes makes $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ a more sustainable alternative to conventional metal oxides, MXenes, and carbon-based electrodes in next-generation supercapacitors and battery technologies.

Author's contribution to the publication:

- T.M. reproduced the compound, optimized the synthesis, calculated the band gap measurements with the help of G.K. and M.S., and performed stability tests.
- J.G.A.R. performed the electrochemical characterization, Raman spectroscopy, SEM, and XRD characterization of the electrodes, and wrote the corresponding section.
- B.B. wrote the section about the mechanical properties and created the crystal structure pictures and videos.
- D.S. performed the AFM experiments and calculated the mechanical properties.
- A.L. performed SEM, and P. T. reproduced the compound for mechanical testing.
- F.E. supervised the mechanical flexibility work.
- V.P. supervised the supercapacitor and battery work, critically read and revised the manuscript.
- G.Y. synthesized the first batch of the compound, created the hypothesis, wrote the manuscript, and supervised the work.

RESEARCH ARTICLE OPEN ACCESS

Where Most Frameworks Degrade: Flexible Bimetallic Phosphonate Crystals as pH-Universal Supercapacitor Electrodes

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Keywords: batteries | bimetallic phosphonates | supercapacitors | sustainable energy storage

ABSTRACT

Herein, we report the charge storage and plastic properties of the redox-active, bimetallic metal phosphonate framework of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂]. The flexible crystals of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] combine high energy storage with mechanical flexibility on the same platform, which is an unusual and significant property that is not observed in traditional rigid layered electrode materials. In contrast to RuO₂, graphene, or MXenes, which prefer concentrated acidic or basic electrolytes to operate effectively as electrodes, [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] operates between pH values of 4 and 10 while reaching a specific capacitance of about 140 F/g in H₃PO₄ at pH 4 and in NaOH at pH 10 at 1 mV/s. It also demonstrates high chemical and electrochemical stability between pH 2 and 12 and in lithium hexafluorophosphate for extended periods. The use of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] as electrodes eliminates the need for harsh chemical environments, generating more sustainable and environmentally friendly energy storage solutions, and [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] can be synthesized in water at mild temperatures. The combination of chemical stability, mechanical flexibility of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂], and compatibility with mild electrolytes makes [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] a more sustainable alternative to conventional metal oxides, MXenes, and carbon-based electrodes in next-generation supercapacitors and battery technologies.

1 | Introduction

The current material landscape in supercapacitor and battery electrodes includes a diverse range of materials such as MXenes, graphene, carbon nanotubes, activated carbon, metal oxides, conductive polymers, and recently, metal-organic frameworks (MOFs) [1–6]. Each of these material types delivers advantages

and limitations in the form of variables such as energy density, power density, electrical conductivity, cycle life, and cost [1–6]. Additionally, structural diversity limitations hinder their further development for improved charge holding. For example, MXenes and graphene provide very high electrical conductivity [7–9]. Still, compared to MOFs, metal oxides, or coordination polymers, they offer very limited structural diversity for optimizing their surface

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areas to store electrical energy [10–12]. Despite their stability in various electrolytes, the covalent modifications on graphene and activated carbon are known to be difficult, providing limited structural diversity for further optimizations compared to MOFs or metal-organic solids [13]. MXenes or RuO₂ electrodes usually function under extremely acidic and basic aqueous electrolytes such as 3 M H₂SO₄ or 6 M KOH, while their charge storage is diminished in neutral electrolytes [14–17], and they are still very expensive, requiring high-temperature synthesis [13].

A plethora of electrode materials exists, offering diversity in dimensionality, sustainability, performance metrics, and synthesis-related costs. MXenes are an emerging and diverse 2D material family that enables plentiful applications for electrochemical energy storage and beyond [18, 19]. Yet, the MXene precursor, MAX-phases, typically requires high-temperature synthesis at or above 1000°C, and MXene synthesis involves etching, often involving toxic compounds such as hydrofluoric acid, which limits their sustainable synthesis [20–23]. Despite metal oxides providing high pseudocapacitance, the weaker stability of these materials in water, acids, bases, and aqueous electrolytes is problematic for their further optimization for long-term use [24, 25]. Metal oxides also have limited structural diversity compared to MOFs and coordination polymers [26]. Among other electrode materials, MOFs provide the largest structural diversity and well-established synthetic routes to optimize surface area and energy storage properties [26]. Still, MOFs are known to be insulators, with a very limited number of conductive unconventional MOFs in the literature [27, 28].

We have recently reported a new family of MOF semiconductors based on phosphonic acid linkers, which provide high stability in acids, bases, and electrolytes and offer potentially the richest structural diversity compared to conventional MOFs [29–32]. A few examples of phosphonate-MOFs have been reported to be very stable electrode materials for Li-ion batteries [31, 33]. We have recently reported the semiconducting properties of Cu/V-phosphonate systems. They exhibit large structural diversity, attributed to their wide range of coordination modes, protonation states, and metal oxide oligomerization patterns [34–36]. This structural versatility makes metal/phosphonate systems especially attractive for developing multifunctional, flexible conductive materials. Similarly, independent vanadium oxide moieties are also well-known conductors [37]. In this work, we wanted to study our previously reported organic-inorganic hybrid crystals of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂]. The Cu(II)/V(IV)/oxide chain is surrounded by π -stacked polyaromatic groups (2,2'-bipyridines and phenylphosphonic acids). Such structures hypothetically combine the redox properties of metal oxides and graphene on the same platform, plus improved stability through high-affinity metal phosphonate bonds that are generally resistant to hydrolysis in the presence of acids and bases [30, 38].

Hypothetically, semiconducting flexible crystalline materials would be an exciting class of material that combines mechanical adaptability with electronic functionality [39–41]. Embedding electrical conductivity into such crystals could enable new device architectures, particularly in flexible electronics and energy storage. While most existing flexible crystals rely on weak van der Waals interactions or labile coordination bonds with halogens to

achieve flexibility, these approaches often compromise structural integrity or functional performance. To the best of our knowledge, semiconducting behaviour has not been reported yet in flexible crystals [40, 41]. However, achieving a combination of flexibility, mechanical stability, and conducting properties is critical for advancing the design of energy storage devices. Also, again to the best of our knowledge, there are no bimetallic/organic hybrid flexible crystals in the literature with Tauc plots within the semiconducting regime. Herein, we report such crystals of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] separated and exfoliated into long crystalline sheets, which can be flexed to make a complete loop, as can be seen in Videos S1–S4. We previously reported the crystal structure and antiferromagnetic properties of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] [42]. Due to its unique flexibility and our recent findings about the electrically conductive behavior of Cu/V-phosphonates, we wanted to explore this organic/inorganic hybrid compound that combines aromatic moieties surrounding the redox-active bimetallic phosphonate chains and its application in Li-ion batteries and supercapacitors.

2 | Results

2.1 | Mechanical Flexibility of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂]

We previously reported the crystal structure and antiferromagnetic properties of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂], which was synthesized hydrothermally in water as a single-phase product above 180°C, and the mechanical properties have not yet been studied [42]. It crystallizes in the monoclinic P2₁/c and contains a rod-shaped chain constructed from corner-sharing of vanadium and copper square pyramids and phosphorus tetrahedra along the crystallographic *a*-axis. Crystals of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] exhibited complete mechanical flexibility, deforming easily when handled with a metal needle and retaining their deformed shape even after the removal of stress (Figure S1 and Video S1). As seen in Figure 1, face indexing from single-crystal X-ray diffractograms confirmed that the side faces correspond to (001)/(00 $\bar{1}$) and (010)/(0 $\bar{1}$ 0), whereas the top face was identified as (100)/(1 $\bar{0}$ 0), providing a precise determination of the bendable facets.

To gain deeper insight into this behavior, the crystals were examined under a microscope by applying mechanical stress using a pair of forceps and a metal needle in a three-point geometry. Crystals separated and exfoliated into long crystalline sheets, exhibiting remarkable reversible flexibility, even forming a complete loop and returning to their original shape upon stress removal when stressed perpendicular to the CP chains, specifically on the crystallographic face (001)/(00 $\bar{1}$), as seen in Video S2. Whereas in the case of thicker crystals, they easily surpassed the elastic limit and entered the plastic deformation regime, stressed upon the same crystallographic face. In contrast, when crystals were stressed along the (010)/(0 $\bar{1}$ 0) and (100)/(1 $\bar{0}$ 0) faces, brittle fracture was observed (Videos S3 and S4). This plastic bending behavior arises from the presence of a slip plane parallel to (00 $\bar{1}$) in the crystal structure. When a mechanical force is applied perpendicular to this slip plane, long-range molecular movement occurs, leading to plastic deformation [43, 44]. In thin crystals, however, the applied stress results only in short-range molecular movement, preventing plastic deformation and allowing the

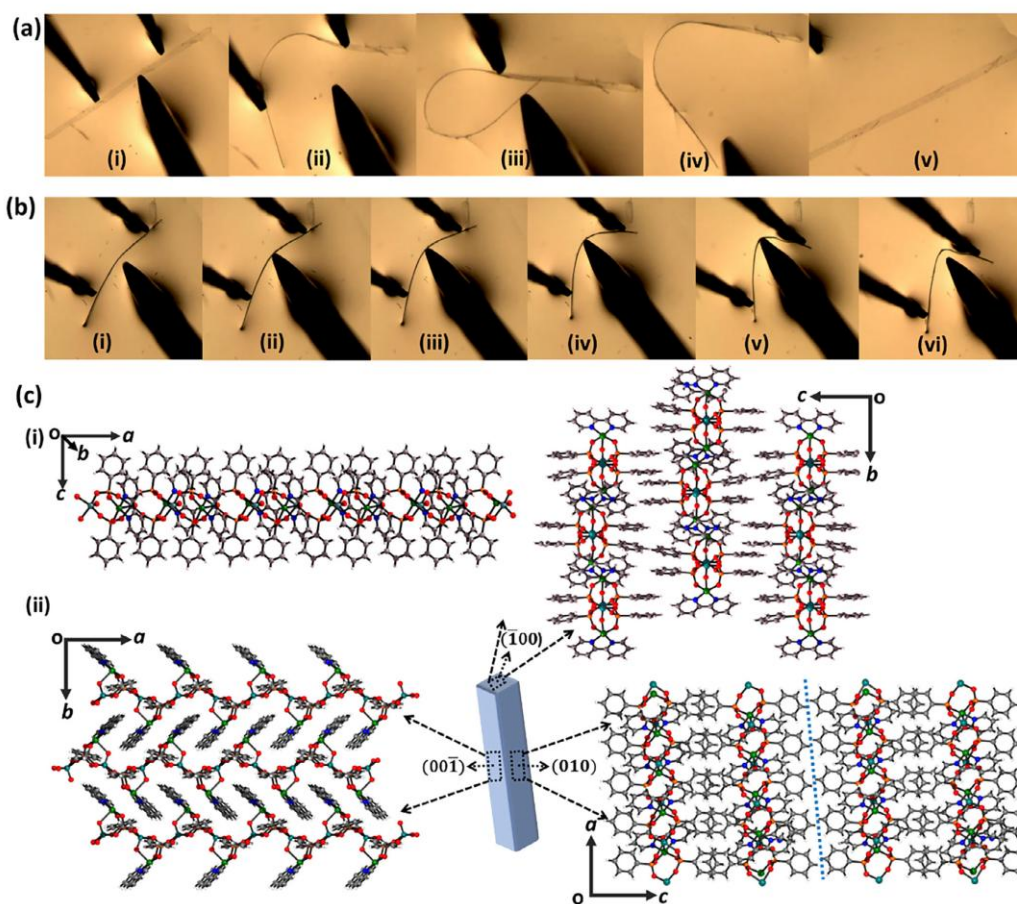


FIGURE 1 | Mechanical properties of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ single crystals. (a, b) Optical microscope images of three-point bending experiments performed on single crystals over the (001) crystallographic face: (a) thin and (b) thick crystals. The bending of the thin crystal is fully reversible (a, i–v), whereas the thicker crystal undergoes plastic deformation (b, i–vi). (c) Crystal packing in $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$. (i) Structure of the covalently bonded coordination polymer chain along the crystallographic *a*-axis. (ii) Crystal packing as viewed along the (100), (010), and (001) faces. Blue dotted lines show a potential slip plane.

crystals to recover their original form once the stress is released. Similar elastic reversible bending and irreversible plastic bending have been recently observed in metal halogen coordination polymers [39, 45]. However, the thickness-dependent flexibility of these systems remains unexplored. In contrast, such behavior is well-documented in molecular organic crystals, but to the best of our knowledge, $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ is the first metal-organic solid crystal generating such elastic behavior [46]. Atomic force microscopy (AFM) force distance curves were used to study the mechanical properties and elastic recovery of crystals with different thicknesses ($t_{\text{bulk}} > t_{\text{needle}} > t_{\text{sheet}}$), as shown in Figure S2. The elastic modulus increased with thickness, with values of 2.75 ± 0.09 GPa for bulk crystals, 2.03 ± 0.05 and 2.20 ± 0.04 GPa for needle-shaped crystals, and 1.79 ± 0.05 GPa for sheet-like crystals (Figure S3 and Table S1). Analysis of the retract curves showed that thinner structures experience less plastic deformation com-

pared to elastic deformation. As a result, the elastic recovery increased significantly as the crystal thickness decreased. This trend agrees well with the qualitative observations from our three-point bending experiments, confirming the superior flexibility and reversible deformation of thinner crystals.

2.2 | Band Gap

Direct and indirect band gaps of the material have been estimated by a Tauc plot generated from the diffuse reflectance spectra (Figure S4) [47, 48]. The compound has an optical band gap in the range between 1.75 and 2.50 eV, which clearly classifies this compound as semiconducting. Despite the low band gap, we were not able to measure electrical conductivity in the single crystals of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$, which is due to the difficulty

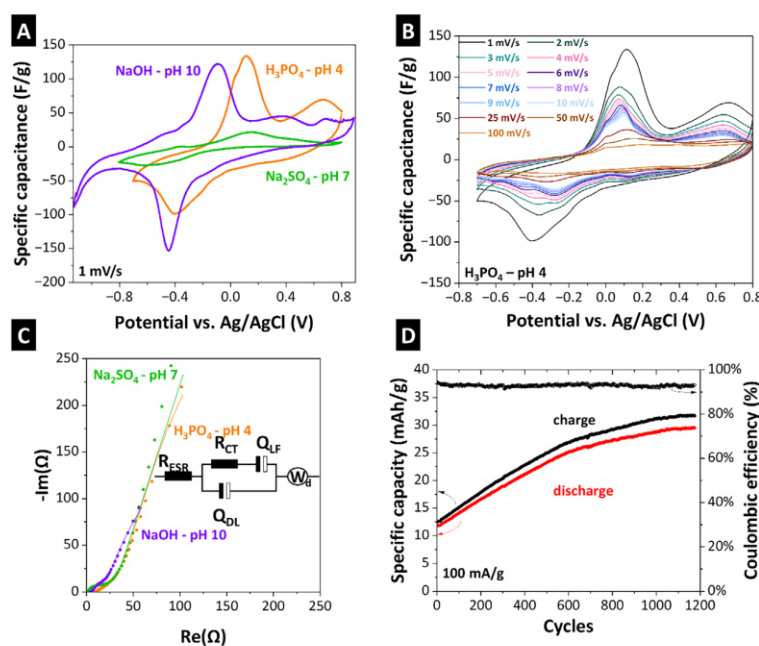


FIGURE 2 | A) Cyclic voltammograms of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ at different pH values. B) Cyclic voltammograms of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ at different scan rates. C) Electrochemical impedance spectra of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ at different pH values. D) Galvanostatic cycling with potential limitation at 100 mA/g for 1200 cycles of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ in organic electrolyte LiPF_6 1 M in EC:DMC (1:1 by volume) vs. Li^+/Li as reference and counter-electrode.

of measuring the electric conductivity in isolated rod-shaped structure of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$, and also due to the twinned crystal structure that can be cracked and exfoliated, which generate limited contact within the crystal.

2.3 | Electrochemical Stability and Energy Storage

The material was tested in different aqueous environments at pH 4, 7, and 10. Cyclic voltammograms shown in Figure 2A corroborate the preliminary observations about the chemical stability of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ along with reversible redox peaks, which decay in intensity in different scan rates, shown in Figure 2B. Given the presence of two electroactive metallic centers within the compound, potential shifts observed with increasing scan rates and varying pH suggest a strong correlation between reaction kinetics and ionic interactions in the electrolyte [49]. Moreover, this also suggests that the material is electrochemically active not only in the metallic center, as other structural groups directly impact diffusion kinetics, highlighting the versatility of the synthesized material [50]. Furthermore, there are slight deviations between environments, with a small difference from alkaline to acidic, further reinforcing the chemical stability of the material.

At neutral pH, slower reversible redox kinetics and lower specific capacitance indicate a shift toward diffusion-dominated charge storage over capacitive mechanisms. As seen in Figure 2A,B, the

specific capacitance for the electrodes in aqueous H_3PO_4 (pH 4) and aqueous NaOH (pH 10) electrolytes reaches approximately 140 F/g at a low scan rate of 1 mV/s, indicating efficient charge storage due to enhanced ion accessibility and Faradaic contributions under these conditions. MXenes and carbon-based electrodes usually require very concentrated acidic, aqueous 3 M H_2SO_4 and aqueous basic electrolytes 6 M KOH to provide similar capacitance values [15, 51, 52].

Complementary to the preliminary electrochemical analysis, the electrochemical impedance spectra shown in Figure 2C suggest that the system kinetics are directly associated with the electrolyte, as investigated with an equivalent circuit in the inset. At high frequencies, the material shows a partial semi-circle in the Nyquist plot, indicating a Faradaic reaction between electrode and electrolyte, with a charge transfer resistance value of 9.91 Ω at pH 4, 1.64 Ω at pH 7, and 2.53 Ω at pH 10, as observed in the redox peaks. At low frequencies, there is a combination of diffusional and capacitive behavior, with the presence of a second charge transfer resistance, which suggests charge intercalation into the inner electroactive sites of the material. This further supports the observation of reactive chemical groups occluded in the near-surface volume of the material. The fit of the Nyquist plots can be found in Table S2.

To better understand the energy storage process, in addition to using $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ as the working electrode and activated carbon as the counter electrode, we also prepared

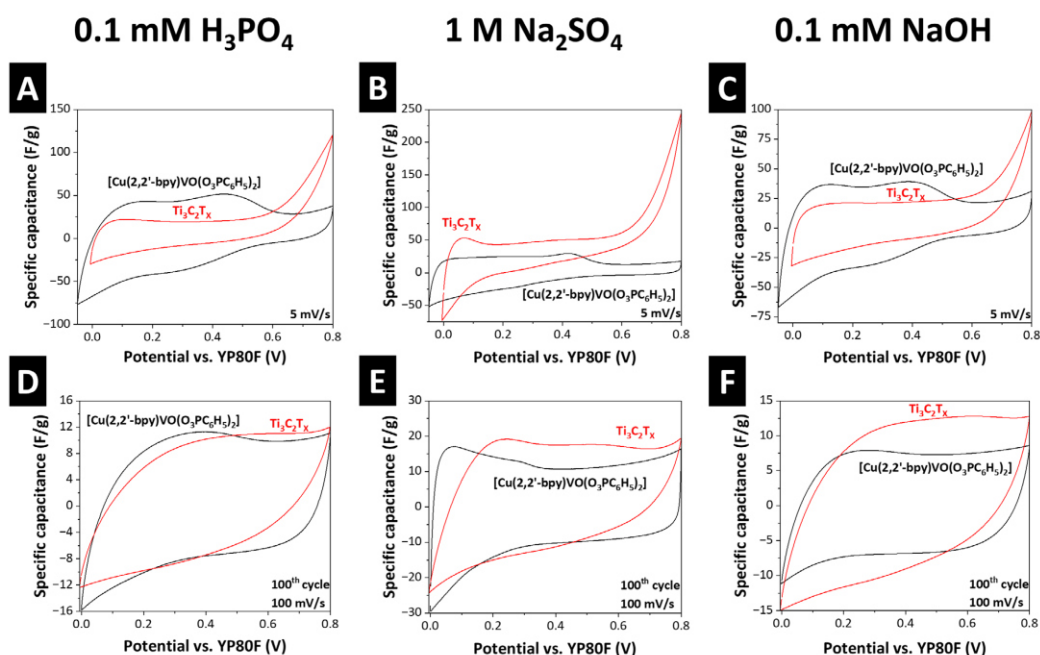


FIGURE 3 | Cyclic voltammograms for comparison of electrochemical behavior between [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] and Ti₃C₂T_x MXene at 5 mV/s in A) pH 4, B) pH 7, and C) pH 10. Comparison at 100 mV/s in D) pH 4, E) pH 7, and F) pH 10.

two-electrode cells with Ti₃C₂T_x. As seen in Figure 3A–C, the cyclic voltammograms at 5 mV/s and 100 mV/s display a quasi-rectangular shape in the different electrolytes, highlighting the pseudocapacitive behaviour of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂], as suggested by the EIS spectra of the electrodes. In comparison with MXene under the same conditions, [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] shows comparable values of specific capacitance in the used electrolyte conditions at pH 4, 7, and 10. Table S3 summarizes the specific capacitance of the known MOFs in the literature in different electrolyte conditions for comparison. As each of the MOFs reported in the literature was studied in a different electrolyte system, it was not possible to fully compare their capacitance values. [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] operates in a large pH range compared to the MOFs in the literature, which indicates its advantage, as it can be used under a variety of electrolyte conditions in a dynamic pH range.

The *b*-value analysis in the different electrolyte conditions was performed, indicating a significant diffusional contribution as the scan rate increases, as shown in Figure S5A–C [53, 54]. Using a high specific current of 1 A/g, we conducted extended galvanostatic charge/discharge cycling (Figure S5D–F). Overall, after an initial decrease, the performance was stable at a low amplitude. After 10 000 cycles, the structural integrity of the electrodes was investigated again by Raman spectroscopy, XRD, and SEM-EDX (Figure S6). The diffractograms shown in Figure S6A indicate the characterizing reflectance around 18°2θ, a characteristic signal of the pristine phosphonate [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] even after cycling in different electrolytes at pH 7 and 10, which is in alignment with Raman spectroscopy (Figure S6B). The

electron micrographs shown in Figure S6C–G further support the stability of the [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] as crystals are visible and intact. Due to the potential formation of extensive EEI at pH 4, it was not possible to obtain a reasonable X-ray diffractogram, although some crystals are visible in Figure S6E. The EDX mapping shown in Figures S7 and S8 indicates a homogenous distribution of elemental composition of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] in the prepared electrodes.

The electrochemical performance in an organic environment was also investigated in a lithium-ion battery system using a lithium hexafluorophosphate electrolyte (Figure 3D). The electrochemical stability of the material is once again highlighted, with the maintenance of operation after 1000 cycles of GCPL at 100 mA/g and an increase in capacity until a plateau is reached at 32 mAh/g. Although the charge storage of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] is limited when operated as a lithium-ion battery, the prolonged chemical stability and the structural versatility of metal phosphonates are significant indicators that they can be used to develop the next-generation long-lasting lithium-ion battery electrodes.

Figure S9A,B shows the cyclic voltammetry in LiPF₆ 1 M electrolyte that indicates a quasi-reversible diffusion-controlled mechanism, suggesting an intercalation mechanism, typical of battery-type materials. The sequential peaks suggest two one-electron redox reactions from distinct metallic centers. The first peak at 1.75 V vs. Li⁺/Li is associated with the oxidation of V^(IV) to V^(V), while the peak around 2.5 V vs. Li⁺/Li relates to the oxidation of Cu^(I) to Cu^(II) [55–57]. As for the reduction peaks at 1.5 and 0.5 V vs. Li⁺/Li, they correspond to the reduction

of Cu^(II) to Cu^(I) and V^(V) to V^(IV), respectively [57]. These redox reactions suggest a two-step process involving Cu and V redox couples with potential hysteresis due to possible structural changes and kinetic limitations during the Li⁺ insertion in the [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] framework, suggested by the galvanostatic charge-discharge pattern in 1,200 cycles, shown in Figure S9D [58]. Furthermore, there is no indication of an electrochemical contribution of the 2,2'-bipyridine ligand since it does not undergo redox reactions in this potential window, suggesting that it acts as a structural scaffold [42]. Still, the redox potential displacements may indicate that the electronic delocalization of the ligand impacts the diffusion kinetics.

The theoretical capacity of the [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] is 89 mAh/g, considering a two-electron transfer mechanism between Cu²⁺ ↔ Cu⁺ and between V⁵⁺ ↔ V⁴⁺. During galvanostatic cycling with potential limitation, although the specific capacity is relatively low, the increase within each cycle is highlighted. This could indicate that the material requires an activation step to allow more electroactive sites to undergo redox reactions, which would be related to the mechanical stress of the Li⁺ intercalation of each cycle. To put in perspective, Table S3 compares the specific capacity of our material with other reported MOF/phosphonates.

2.4 | Chemical Stability

Metal oxides are known for their high thermal stability but often exhibit limited chemical stability, especially in the presence of acids, bases, and aqueous electrolytes [59]. While transition metal phosphonates are known to be insoluble in water, a comprehensive study of their solubility constants has not been reported in the literature [38]. However, related copper phosphonates are employed as anticorrosion agents, such as protecting archeological sites from water and acid rain damage [60]. Phosphonates exhibit a very strong metal binding affinity; for example, the structurally analogous phosphonates demonstrate 4.5 orders of magnitude higher metal binding affinity compared to isostructural carboxylate ligands [61]. Furthermore, phosphates form insoluble copper salts with reported solubility product constants around 10⁻³⁷ [62]. This suggests the use of semiconducting phosphonates in electrochemical applications to improve the stability of Li-ion batteries or supercapacitors and limit the hydrolysis in the presence of an aqueous environment. This inherent stability of metal phosphonates is also important when employing a wide range of electrolytes to optimize charge storage potential. Therefore, in this work, we investigated the chemical stability of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] in acidic (HCl), basic (NaOH), and organic solvents. For this purpose, 15 mg of crystals of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] were weighed into sample vials and stirred rigorously in 10 mL of the respective medium for one week at room temperature. Subsequently, the samples were re-analyzed using X-ray diffraction (Figure S10A,B) after one week of rigorous stirring. As seen in Figure S10A,B, [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] crystals, after rigorously stirring between pH 2 and 12, retain their characteristic diffraction reflections, indicating high structural integrity within this pH range for one week. No new peaks have been observed within this pH range, suggesting that phase purity is retained after one week.

As can be seen in the scanning electron micrographs (Figure 4), despite vigorous stirring, the crystal edges remain sharp, suggesting there is no or very minimal dissolution between pH 2 and 12 after one week. At pH 1, the crystals were visually present after 3 h, with a slight blue coloring of the acid solution after stirring. After 24 h, the acid solution became blue-colored with a solid precipitate. After one week in 1 M HCl, a very limited presence of phosphorus element can be observed in SEM-EDX, indicating that the majority of the phenylphosphonic acid is protonated and released as a free acid (Figures S11–S25). As seen in Figure 4, at pH 14, some of the original structure is still present after one week of rigorous stirring in 10 mL of 1 M NaOH, indicating strong stability in the basic medium. Overall, the chemical stability tests in various pH values demonstrate that the material exhibits high stability across a broad range of conditions, except for significant degradation observed only at pH 1 after one day.

2.5 | Effect of pH on Crystal Structure and Morphology

As seen in Figures S11–S25, at low pH values, the scanning electron micrographs reveal some exfoliation while retaining the original X-ray diffractogram. At mild pH values of 4, the micrograph shows intact crystals and smooth surfaces. At higher pH values (10 and 12), the bulk structure is maintained, as confirmed by X-ray diffraction. Still, significant exfoliation into thin layers of crystals occurs at higher pH values while retaining the original crystal structure. Especially at pH 12, pronounced exfoliation results in the formation of thin rods peeling off the crystals. As the crystal edges remain sharp, no dissolution of the crystals at pH 12 is observed. These observations indicate that the material can withstand acidic and alkaline conditions without degradation after one week (and continuing) of rigorous stirring of 15 mg of crystals in 10 mL of corresponding acid and base concentrations.

2.6 | Effect of Organic Solvents on Structure and Morphology

As large sections of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] are composed of aromatic phenyl and bipyridine moieties, we wanted to further test the stability of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] in the presence of common organic solvents. Scanning electron micrographs (Figure 4) illustrate the exfoliation or peeling of [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] crystals after stirring for 1 week in 10 mL of a variety of organic solvents. The crystals still retain their characteristic diffraction reflections after exfoliation. In polar protic solvents such as methanol, ethanol, and 2-propanol, the crystals maintain their original crystal shape, which is confirmed by the sharp and well-defined X-ray reflections. Aprotic solvents such as DMF (N,N-dimethylformamide), DMAc (dimethylacetamide), and EtOAc (ethyl acetate) help the exfoliation of larger crystals form into a fibrous or fiber-like structure. The X-ray diffractograms indicate that the bulk crystal structure remains intact. Acetic acid (AcOH) also induces a significant exfoliation of the larger crystals, resulting in a fibrous appearance due to the flexibility of the crystals. Overall, [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] material is very robust under extreme chemical environments

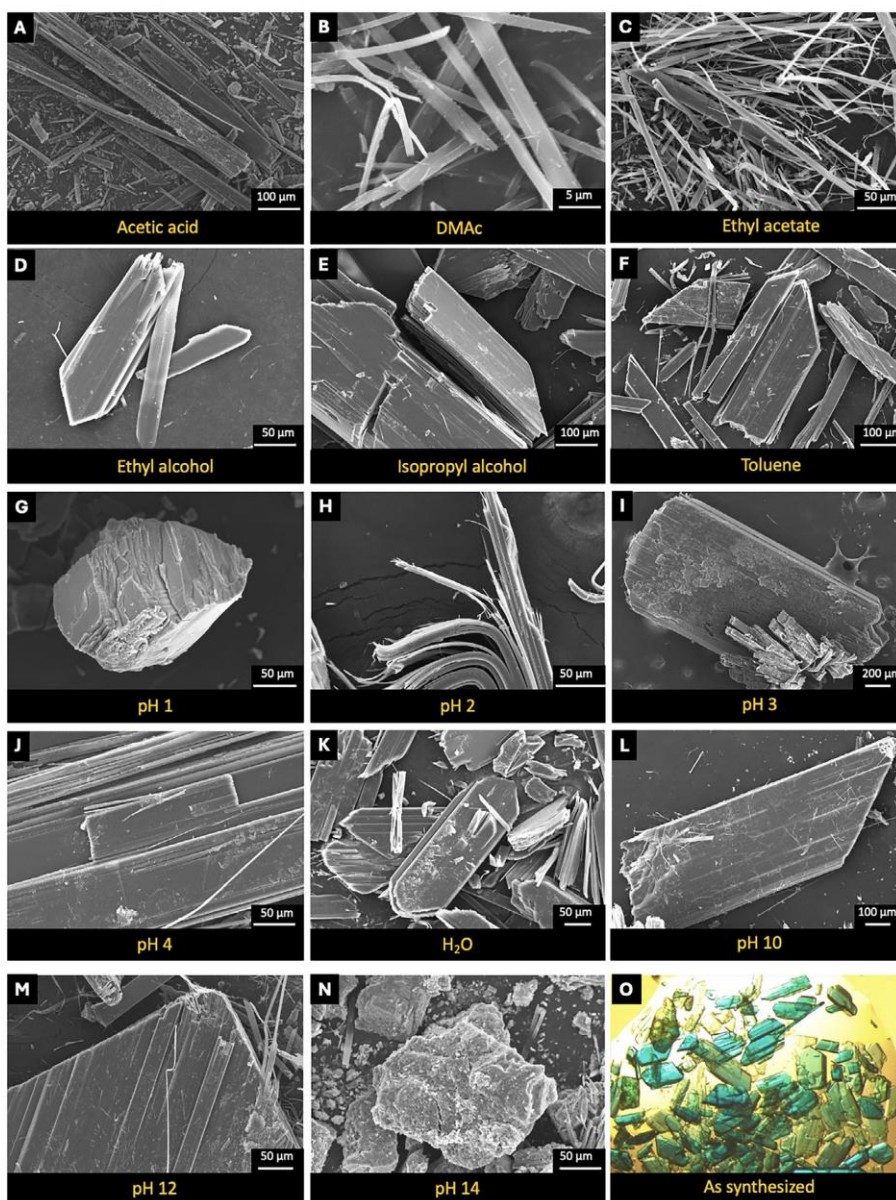


FIGURE 4 | Scanning electron micrographs of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ after stirring for 1 week under different pH conditions and in common organic solvents; a) acetic acid b) N,N-dimethylacetamide c) ethylacetate d) ethyl alcohol e) isopropyl alcohol f) toluene g) pH 1 h) pH 2 i) pH 3 j) pH 4 k) in water l) pH 10 m) pH 12 n) pH 14 and o) stereo microscope pictures of the crystals after synthesis.

and retains its structural integrity under a wide range of aqueous and organic conditions. Furthermore, crystals exfoliate at the brittle (010)/(0 $\bar{1}$ 0) and (100)/(1 $\bar{0}$ 0) faces while no deformation is observed in the flexible face of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$, generating hair-like exfoliated crystal bundles (Figure 4).

The exfoliation behavior observed at alkaline pH values is particularly interesting, as it increases the surface of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ crystals and potentially improves the interaction with electrolytes, leading to better charge storage capacity, which is a critical parameter for supercapacitors and batteries.

The stability of the material, even after exfoliation, is confirmed by consistent X-ray diffractograms (Figure S10), indicating that the core coordination framework remains intact. The observed structural stability in alkaline conditions could help increase the long-term performance and durability of batteries and supercapacitors.

2.7 | Thermal Stability

The thermal stability of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ was determined using thermogravimetric analysis (TGA), as shown in Figure S26. The compound exhibits high thermal stability, with only a minor mass loss of approximately 3.5% observed up to 410°C. This is attributed to the evaporation of the surface-adsorbed water vapor. Above 410°C, a significant weight loss occurs, corresponding to the decomposition of the 2,2'-bipyridine and phenylphosphonic acid (PPA) ligands of the coordination polymer. The decomposition associated with 2,2'-bipyridine loss is observed between 410°C and 460°C, although the steps may be overlapping. Subsequently, between 460°C and 610°C, further decomposition associated with the loss of PPA occurs, resulting in a residue of approximately 49.6 mass% at 610°C, which is nearly equivalent to the theoretical 51 mass% corresponding to the inorganic components of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$. Beyond 610°C, an additional minor loss of approximately 2 mass% is observed up to 1000°C, likely due to the gradual sublimation of P_4O_{10} or the loss of oxygen from CuO or VO_2 . These findings confirm that $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ exhibits high thermal stability, making it a promising candidate for applications requiring stability under elevated temperatures. The hydrothermal synthesis at 185°C–230°C is also indicative of the intrinsic stability of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ in an acidic aqueous environment.

3 | Conclusions

Herein, we report the first flexible bimetallic crystals for energy storage applications in the literature. The mechanically flexing crystals of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ have the potential to serve as a supercapacitor material due to their favorable electronic properties and chemical and structural stability. The crystals of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ could be exfoliated into thin, flexible sheets without losing the original crystal structure. The flexibility of single crystals can be utilized to manufacture supercapacitors in various shapes and forms. The chemical and thermal stability of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ is much better compared to the traditional electrode materials, as it can withstand harsh chemical conditions between pH 2 and 12 after vigorous stirring in 10 mL at room temperature. It slowly dissociates at pH 14 after one week and at pH 1 in one day. Intensive exfoliation of large crystals was observed due to rigorous stirring in a variety of chemical media. Still, no patterns of dissolving in acids and bases were observed, and the crystal structure remained intact. The organic–inorganic hybrid structure of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ combines the properties of organic materials and metal oxides on the same platform, where more than 50% of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ by mass is composed of polyaromatic moieties. In a pH-neutral environment, the electrochemical behavior differs from that observed

under acidic or alkaline conditions. Here, the reversible redox process proceeds more slowly, as indicated by the reduced specific capacitance values. This suggests that diffusional processes play a more dominant role than capacitive mechanisms, indicating that metal-binding phosphonate groups enhance chemical stability, thereby limiting hydrolysis at pH 2 and 12.

Furthermore, $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ provides a high specific capacitance of 140 F/g in H_3PO_4 at pH 4 and in NaOH at pH 10. The high capacitance at milder and environmentally friendlier electrolytes $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ is advantageous compared to other materials. For example, materials such as MXene or many carbon-based electrodes require extremely acidic and basic aqueous electrolytes such as 3 M H_2SO_4 or 6 M KOH to reach similar specific capacitance. Furthermore, $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ can be synthesized sustainably in water at 180°C. $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ remains stable over a total of 10000 charge and discharge cycles at pH 4 and 10, demonstrating its stability as a supercapacitor electrode material. These high capacitance values near neutral pH are also significant, as they provide more sustainable working conditions under mild pH values compared to aqueous 6 M KOH, where activated carbon electrodes generally operate. Considering conventional MOFs that are composed of water-soluble metal acetate clusters and metal oxides, instability in aqueous medium and electrolytes, these results are significant for further developing the next generation of electrode materials based on hybrid bimetallic Cu/V-phosphonates.

By combining structural flexibility, semi-conductivity, and chemical stability, $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ represents a novel class of hybrid materials and provides a framework for the design of durable and environmentally benign electrode architectures for future energy storage technologies.

4 | Methods

4.1 | Chemicals

All chemicals were purchased from standard commercial suppliers such as Fisher Scientific, Thermo Fisher, and Merck and were used without further purification. Deionized water (Type I, 18.2 MΩ·cm) for all syntheses and product washing was freshly prepared using an Arium Mini Ultrapure Water System.

4.2 | Synthesis

A mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.124 g, 0.50 mmol), Na_3VO_4 (0.059 g, 0.32 mmol), phenylphosphonic acid (0.448 g, 2.87 mmol), and 2,2'-bipyridine (0.071 g, 0.45 mmol) was added to a 23 mL polytetrafluoroethylene liner. Subsequently, 10 mL of ultrapure water was added to the liner, and the resulting orange suspension was stirred for two minutes before being placed in a stainless-steel container. The mixture was heated at 185°C for 48 h in a preheated oven and then removed using crucible tongs. Raising the reaction temperature from 180°C (the original procedure) to 185°C was crucial, as it suppressed the formation of trace amounts of $\text{Cu}(2,2'\text{-bpy})\text{SO}_4$ side product (less than 5 mass%), improving both the yield and purity of the target compound. The crystals can

also be synthesized at up to 230°C hydrothermally with complete phase purity. After cooling to room temperature, the reaction mixture was transferred to a 50 mL centrifuge tube and thoroughly washed with ultrapure water and acetone (approximately 100 mL each, in several aliquots). The resulting product, obtained as green rods or plates, was dried under vacuum at 60°C. The approximate yield was 90% based on vanadium at 185°C.

4.3 | X-Ray Diffraction

X-ray diffractograms were recorded on a Bruker D2 Phaser diffractometer (300 W, 30 kV, 10 mA) using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Measurements were performed at room temperature over a 2θ range of 2°–50° with a total scan time of 30 min. The data analysis was conducted using the software *Match!* (version 3.3.0, Crystal Impact). Diffractograms of the electrodes used in electrochemical characterization using a D8 Discover diffractometer (Bruker AXS) with a copper X-ray source (Cu-K α , $\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA), a Göbel mirror, and a 1 mm point focus. The samples were fixed to a glass sample holder at a desired amount for preparation. Another glass substrate was gently pressed onto the sample to ensure homogeneity, and the excess sample was removed from the glass substrate.

4.4 | Electrode Preparation

The electrodes used in the electrochemical testing were prepared using [Cu(2,2'-bpy)VO(O₃PC₆H₅)₂] as active material and carbon black (ACB, BP2000 from Cabot). For the preparation, 70 mass% of the active material and 20 mass% carbon black were mixed with 10 mass% of binder (polytetrafluoroethylene, 60 mass% dispersion in water, Merck) and ethanol in a mortar. Then, the materials were thoroughly triturated until a homogeneous mixture of dough was formed, and rolled and pressed with a calendaring machine (HR01 hot rolling machine, MTI) and dried at 100°C for 12 h under a vacuum of 6 kPa to form a sheet with a 430 μm thickness, measured using a C640 thickness tester from Labthink. The electrodes with a 10 mm diameter were punched out and characterized. For comparison, electrodes of few-layer Ti₃C₂T_x (Nanoplexus 99%) were prepared following the same methodology.

The electrode morphology was examined using SEM and X-ray diffraction before and after electrochemical testing. SEM was performed using a ZEISS GEMINI 500 microscope with an Xmax detector from Oxford Instruments at an acceleration voltage of 2 kV. Raman analysis was done using a Renishaw InVia microscope with an excitation laser of 532 nm and a power of 87 μW . The spectra were obtained from 10 points with a 10 s exposure time and accumulated five times, then treated for cosmic ray removal and normalization.

Three-electrode polyethylene-ether-ketone (PEEK) cells equipped with spring-loaded graphite pistons were used for electrochemical investigations [63]. The cells were assembled using a glass microfiber membrane (GF/A, Whatman) as a separator sandwiched between two electrodes: the working electrode of active material and the counter-electrode prepared using YP80F. The aqueous electrolytes consisted of phosphoric

acid 0.1 mM (Sigma–Aldrich 99%) with pH 4, sodium sulfate 1 M (Sigma–Aldrich 99%) with pH 7, and sodium hydroxide 0.1 mM (Sigma–Aldrich 99%) with pH 10. The electrochemical behavior of the active material was initially investigated using electrochemical impedance spectroscopy, performed from 100 kHz to 10 mHz at an open circuit potential of +0.02 V vs. Ag/AgCl (3 M) for 1 h. All tests were conducted at $25 \pm 1^\circ\text{C}$ in a climate chamber using a BioLogic VMP-300 potentiostat/galvanostat. Cyclic voltammetry was performed in different scan rates (1–100 mV/s) in a potential window of –0.8 to +0.8 V vs. Ag/AgCl (3 M). The electrochemical stability and specific capacitance of the active material were investigated using galvanostatic cycling with potential limitation (GCPL, at 1000 mA/g), where the specific capacitance (C_s in F/g) was calculated from each cycle discharge with constant current, following Equation (1):

$$C_s = \frac{i \cdot \Delta t}{m \cdot \Delta E} \quad (1)$$

where i (A) is the applied current, Δt (s) is the discharge time variation, m (g) is the total mass of the electrodes, and ΔE (V) is the potential vs. Ag/AgCl (V) corrected from the Ohmic drop. Furthermore, the stability of the material through the Coulombic efficiency of each cycle is assessed to identify parasitic reactions or degradation of the active material, along with electrolyte decomposition as well.

The morphology of the prepared electrodes was characterized prior to the electrochemical experiments to ensure a thorough characterization of the synthesized material Cu(2,2'-bpy)VO(O₃PC₆H₅)₂. The scanning electron micrographs displayed in Figure S27 indicate a homogenized distribution of the conductive carbon additive over the active material. However, it was possible to observe large smooth-surfaced crystals of the MOF active material, as seen in Figure S28B. At higher magnifications, Figure S28C,D, it is possible to observe layered stacked structures of the material synthesized in acidic conditions, as shown in the scanning micrographs presented in Figure S28, further corroborating the observation of the material stability during electrode preparation.

To further explore the effects of the electrode preparation on the morphology and structure of Cu(2,2'-bpy)VO(O₃PC₆H₅)₂, X-ray diffraction was performed, and the data are displayed in Figure S28E. The diffractogram displays the characteristic reflectance signals of the material at $6.7^\circ 2\theta$, $13.4^\circ 2\theta$, and $17.6^\circ 2\theta$, suggesting no significant changes in the material's structure.

Raman spectroscopy was used to investigate the electrode preparation over the chemical stability of the material, which is presented in Figure S28F. The faint Raman signal at 724 cm^{-1} is associated with a Cu–O stretching vibration of the copper metallic center [64]. The bands around 969 and 998 cm^{-1} are associated with the symmetric stretch of P–O bonds, which also display weaker bands from 405 to 471 cm^{-1} associated with asymmetric stretching and bending of the O–P–O bond deformation [65]. Moreover, it is also possible to observe the bands corresponding to the O–V–O bonds in the range of $338\text{--}472 \text{ cm}^{-1}$; symmetric stretching characteristic signals of O–V–O are present at 723 and 771 cm^{-1} , along with a stretching vibration with a frequency

of 855 cm⁻¹ [66]. These results further corroborate the presence of two electroactive metallic centers that can undergo redox reactions. At higher frequencies, the C–H and ring deformation of bipyridine molecules are much more prominent, with the characteristic sharp bands displaying at 1147, 1187, 3061, and 3080 cm⁻¹ [67, 68].

4.5 | Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measurements were performed under air using a TG Tarsus 209 F3 instrument (Netzsch). A gas flow rate of 10 cm³/min was applied. Samples were heated from 30°C to 1000°C at a heating rate of 10°C/min.

4.6 | Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy

Scanning electron micrographs of the samples were acquired using a JEOL JSM-6510 scanning electron microscope. Prior to imaging, the samples were sputter-coated with gold using a JEOL JFC-1200 Fine Coater. The electrode micrographs were collected with a ZEISS GEMINI 500 scanning electron microscope by applying an accelerating voltage of 2 kV at a working distance of 4.0 mm. Before the measurements, the samples were mounted on an aluminum stub, which was fixed with copper tape. Energy-dispersive X-ray spectra and elemental mapping were obtained using a Bruker XFlash Detector 410-M.

4.7 | Raman Spectroscopy

Raman analysis was done using a Renishaw InVia microscope with an excitation laser of 532 nm and a power of 87 μW. The spectra were obtained from 10 points with a 10 s exposure time and accumulated five times, then treated for cosmic ray removal and normalization.

4.8 | pH-Measurements

The pH of ultrapure water was adjusted to values between pH 1 and 14 using aqueous HCl (w = 0.37) and KOH (1 M). For pH = 1 or 14, pure aqueous HCL solution (0.1 M) or KOH solution (1 M) was used directly. All pH measurements were performed at room temperature (20°C) using a Metrohm 744 pH meter.

Author Contributions

T.M. reproduced the compound, optimized the synthesis, calculated the band gap measurements with the help of G.K. and M.S., and performed stability tests. J.G.A.R. performed the electrochemical characterization, Raman spectroscopy, SEM, and XRD characterization of the electrodes and wrote the corresponding section. B.B. wrote the section about the mechanical properties and created the crystal structure pictures and videos. D.S. performed the AFM experiments and calculated the mechanical properties. A.L. performed SEM, and P. T. reproduced the compound for mechanical testing. C.J. contributed to the data visualization. F.E. supervised the mechanical flexibility work. V.P. supervised the supercapacitor and battery work, critically read and revised the

manuscript. G.Y. synthesized the first batch of the compound, created the hypothesis, wrote the manuscript introduction, and supervised the work.

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Conflicts of Interest

Gündoğ Yücesan is listed as the inventor of a patent protecting the rights of metal phosphonate electrodes.

Data Availability Statement

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

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File 1: adfm74279-sup-0001-SuppMat.pdf.

Supporting File 2: adfm74279-sup-0002-VideoS1–S4.zip.

Supporting Information

Where Most Frameworks Degrade: Flexible Bimetallic Phosphonate Crystals as pH-Universal Supercapacitor Electrodes

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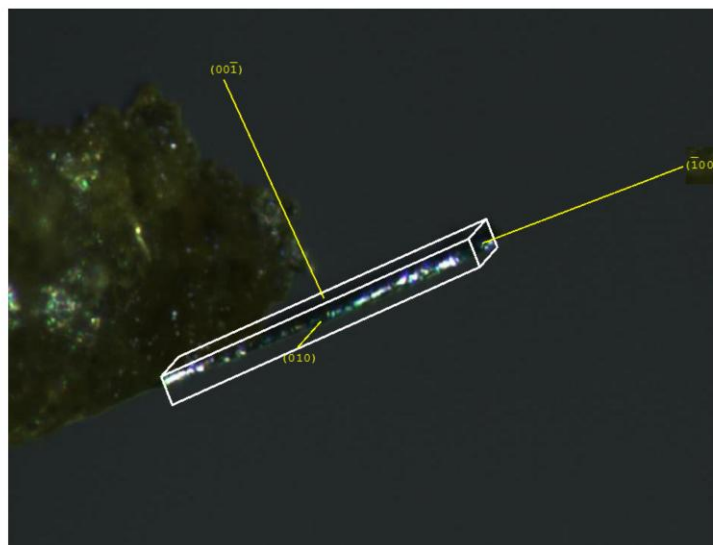


Figure S1. Face indexed image of pristine crystal of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$.

Atomic Force Microscopy.

To establish the mechanical properties of metal phosphonate framework, atomic force microscopy (AFM) force distance curves (FDC) was chosen a well-established method for such tasks. All AFM experiments were performed with an MFP-3D Asylum instrument (Oxford Instruments Asylum Research). The AFM was equipped with a biosphere B150-NCH (nanotools GmbH), with a tip radius of $R = 150 \text{ nm}$ and a spring constant of $k_c = 43.5 \text{ N/m}$. The tip's (EBD DLC) elastic modulus was assumed to be $E_t = 300 \text{ GPa}$ and the Poisson ratio was assumed to be $\nu_t = 0.25$.

Force spectroscopy measurements were performed using force distance curves (FDCs) with a maximum applied force of approximately $4.3 \text{ }\mu\text{N}$. Glass substrates ($E = 73 \text{ GPa}$, $\nu = 0.22$) served as reference materials. For each sample, a grid of 6×6 curves was recorded over a $5 \times 5 \text{ }\mu\text{m}^2$ area. The averaged curves and their standard deviations were analyzed to determine the elastic modulus (E , assuming a Poisson's ratio of $\nu = 0.3$ for the crystals), total deformation (D), plastic deformation (D_{pla}), and elastic recovery ($R = (D - D_{\text{pla}})/D$), including their respective uncertainties. Further details on the evaluation of FDCs using Hertzian contact mechanics and the determination of material elasticity are available in the.¹

Two different phenotypes of crystals were investigated, as shown in **Figure S2**.

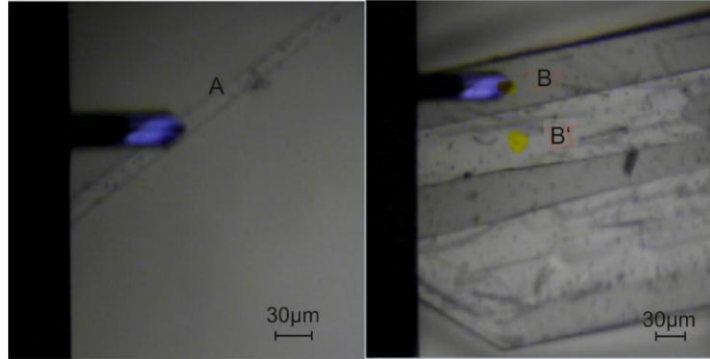


Figure S2. Optical micrograph of AFM/sample setup. The AFM's cantilever and chip are visible in the foreground. Left: needle-like crystal A. Right: crystal B, showing bulk-like (B) and sheet-like (B') geometries.

Each phenotype was measured at two different spots. The needlelike crystal A is uniform, and measurements were taken at arbitrary spots. Crystal B shows distinct regions, assigned B and B'. The slightly darker regions are expected to show the crystals bulk behavior (B) and the lighter regions - peeled off portions - are expected to show sheet-like behavior (B'). Crystals' cross section dimensions were estimated with A ($10 \times 10 \mu\text{m}^2$), B ($340 \times 30 \mu\text{m}^2$) and B' ($60 \times 1 \mu\text{m}^2$) to correlate crystal geometry with mechanical behavior.

In **Figure S3**, the resulting cross section areas are shown (red, right axis, open diamonds) together with the elastic modulus (black, left axis, squares). In **Figure S3**, deformation D at F_{max} is shown as green bars, confirming the inverse relationship of modulus and deformation, since materials with a higher modulus will deform less at the same applied force F_{max} . However, to assess elastic recovery - the capability to instantly recover from deformations upon removal of the applied force - plastic deformations need to be considered. Plastic deformations, shown in Figure S3b as yellow bars, are the residue deformation which is left after removing the applied force (F_0). The smaller the plastic deformation D_{pla} in relation to the overall deformations, the higher the elastic recovery, as shown in **Figure S3c** (black, filled circles).

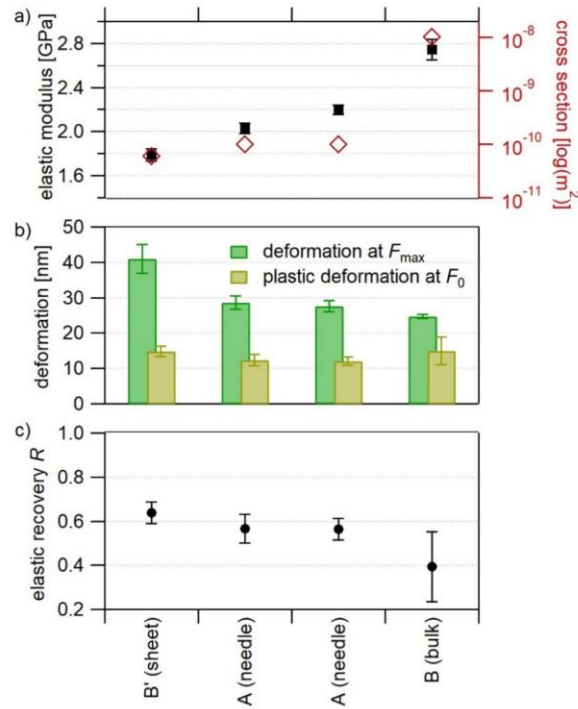


Figure S3. a) Elastic modulus E (black, filled squares) together with estimated cross section of crystal (red, empty diamonds). B) deformation at maximum applied force $F_{\max}$ (green bars) and residue (plastic) deformation upon removal of applied force F . c) elastic recovery $R = ((D - D_{\text{pla}})/D)$ in dependence of crystal geometry (black, filled circles).

Table S1. Elastic modulus E , deformations D and D_{pla} , and elastic recovery R .

measurement	E (GPa)	D (nm)	D_{pla} (nm)	R (%)
B' (sheet)	1.79±0.05	41±4	15±1	63.9±5.0
A (needle)	2.03±0.05	29±2	12±2	56.6±6.4
A (needle)	2.20±0.04	28±2	12±1	56.3±5.0
B (bulk)	2.75±0.09	25±1	15±4	39.4±15.9

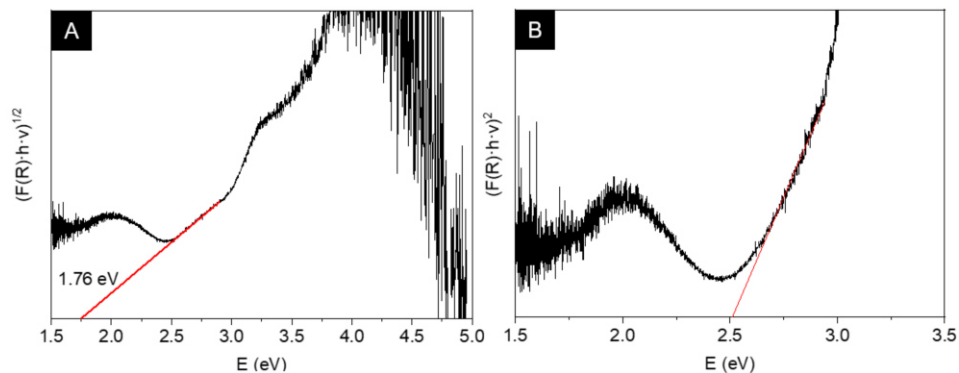


Figure S4. Tauc plots for an indirect (A) and direct (B) band gap estimation of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$.

Table S2: Fit of equivalent circuit of Nyquist plot.

	R_s Ω	R_{CT} Ω	Q_{DL} $F \cdot s^{(n-1)}$	n_{DL}	R'_{CT} Ω	Q_{LF} $F \cdot s^{(n-1)}$	n_{LF}	W_d Ω	t_d s
H_2SO_4 pH 2	1.16	1.56	$1.17 \cdot 10^{-2}$	0.565	5.39	$5.06 \cdot 10^{-2}$	0.883	31.93	18.28
H_3PO_4 pH 4	9.91	951.50	$7.58 \cdot 10^{-2}$	0.997	19.31	$2.19 \cdot 10^{-2}$	0.434	174.1	89.81
Na_2SO_4 pH 7	1.64	16.46	$9.44 \cdot 10^{-4}$	0.836	-	$3.70 \cdot 10^{-2}$	0.801	11.05	0.47
NaOH pH 10	2.53	6.95	$1.47 \cdot 10^{-1}$	0.120	659.00	$9.68 \cdot 10^{-2}$	0.832	13.81	0.92
LiPF_6 (EC:DMC)	2.79	24.59	$4.39 \cdot 10^{-6}$	1.00	139323.00	$9.59 \cdot 10^{-5}$	0.801	893.00	0.38

Table S3: Comparison of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ phosphonate framework with reported MOFs tested in aqueous capacitor systems.

MOF Material	Specific capacitance (F/g)	Electrolyte	Reference
$[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ Cu/V/Phosphonate	140 F/g at 1 mV/s 9 F/g at 1 A/g 140 F/g at 1 mV/s	0.1 mM H_3PO_4 1 M Na_2SO_4 0.1 M NaOH	This work
Graphene/Cu-MOF	190 F/g at 10 mV/s	6 M KOH	²
Co-MOF/Graphene	187 F/g at 0.25 A/g	1 M KOH	³
Cu-based MOF@1D carbon nanofibers	68 F/g at 1 A/g	1 M H_2SO_4	⁴
Cu-MOF@ δ - MnO_2	340 F/g at 1 A/g	1 M Na_2SO_4	⁵
rGO/Cu-MOF@PANI	276 F/g at 0.5 A/g	1 M H_2SO_4	⁶

Table S3: Comparison of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ phosphonate framework with reported MOFs tested in lithium-ion battery systems.

MOF Material	Specific capacity (mAh/g)	Potential window	Reference
$[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ Cu/V/Phosphonate	32 mAh/g at 100 mA/g	0.01-3 V	This work
MIL-53(Fe)	70 mAh/g at 50 mA/g	1.5-3.5 V	7
MIL-68(In)	32 mAh/g at 100 mA/g	1.5-3.5 V	8
PPL-IL gel polymer	63 mAh/g at 5 C	2.0-4.0 V	9
H ₈ L-Fe-MOF	319 mAh/g	1.0-3.5 V	10
Al-based phosphonate	238 mAh/g at 100 mA/g	0-4 V	11
Li ₂ CuPO ₄	188 mAh/g at C/60	2.5-4.5 V	12

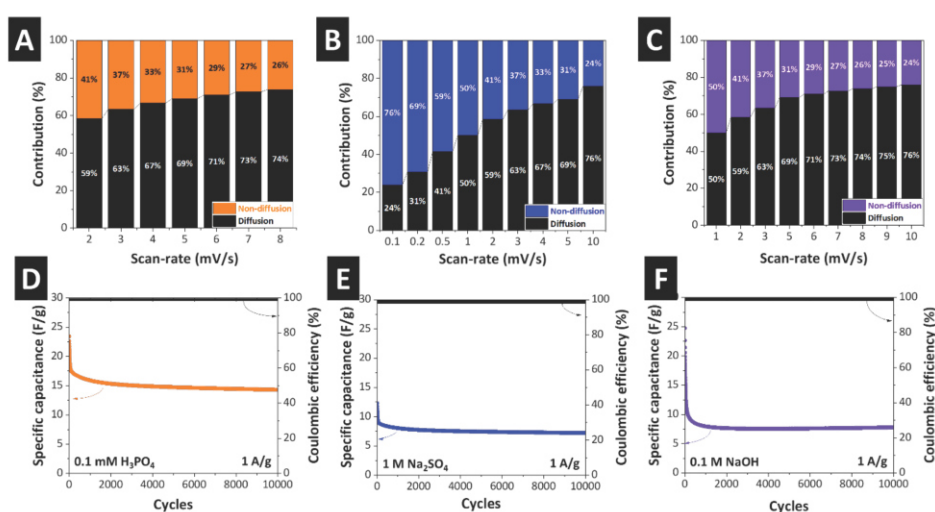


Figure S5. Diffusion- and non-diffusion-limited charge contribution of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ in A) pH 4, B) pH 7 and C) pH 10. D-F: Galvanostatic charge/discharge stability testing at 1 A/g.

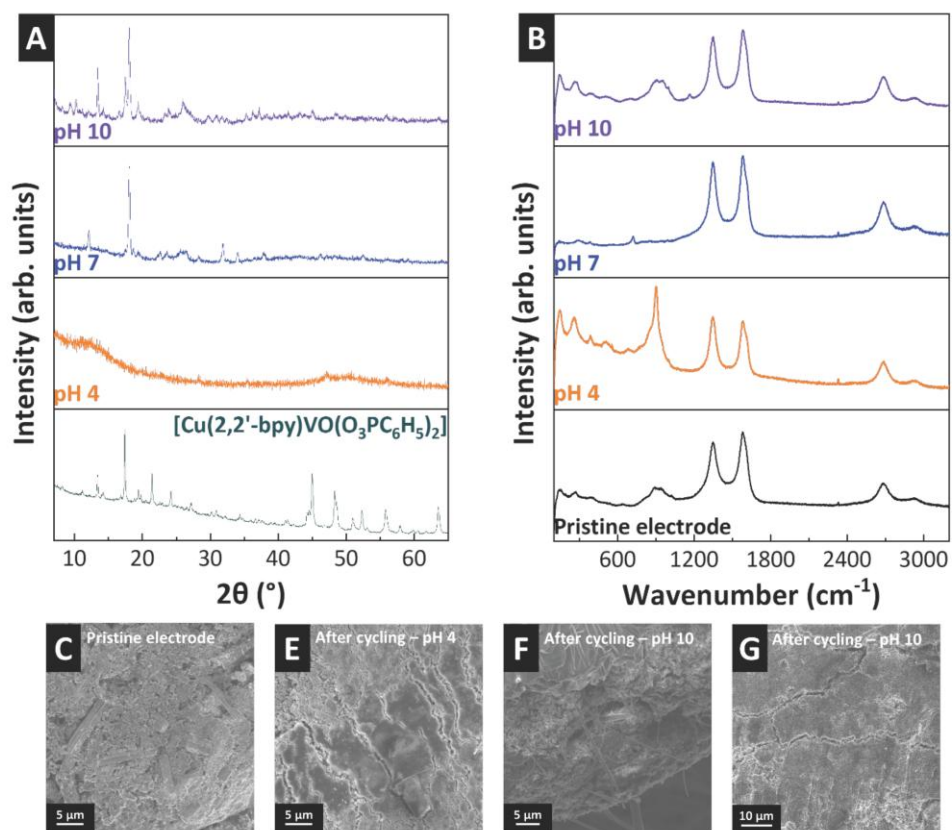


Figure S6. Ex-situ B) Raman spectra, A) X-ray diffractograms, and C) scanning electron micrographs of pristine, E) pH 4, F) pH 7, and G) pH 10 of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ electrodes before and after electrochemical cycling.

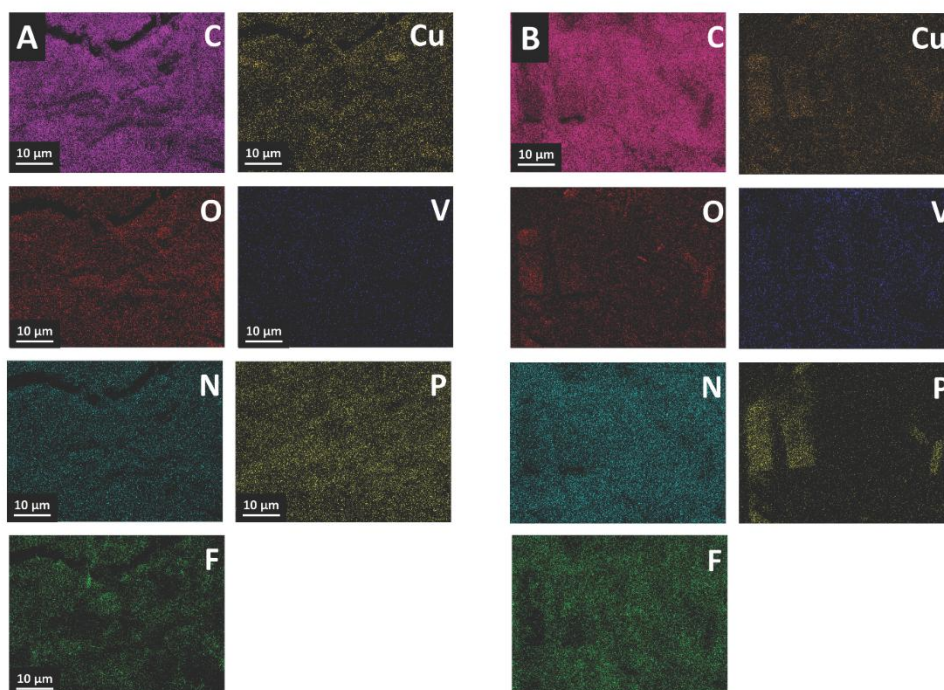


Figure S7. Elemental mappings (EDX) of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ electrodes at A) pristine and B) pH 4.

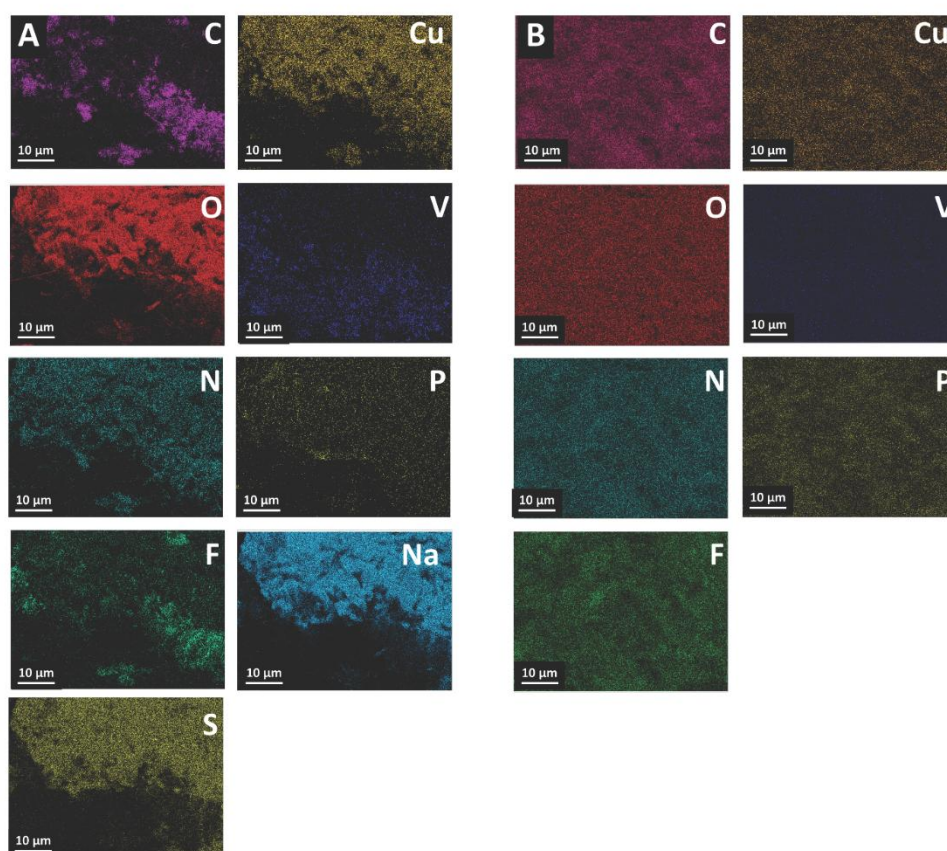


Figure S8. Elemental mappings (EDX) of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ electrodes at A) pH 7 and B) pH 10.

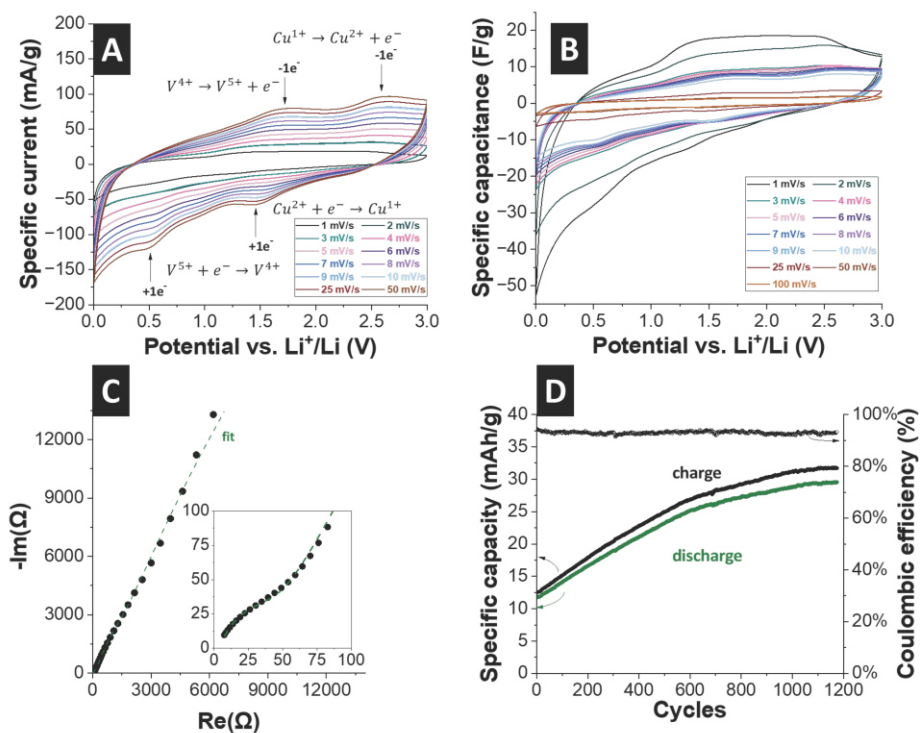


Figure S9. A-B) Cyclic voltammograms at different scan rates. C) Electrochemical impedance spectrum of $[Cu(2,2'-bpy)VO(O_3PC_6H_5)_2]$. D) Galvanostatic cycling with potential limitation at 100 mA/g for 1200 cycles of $[Cu(2,2'-bpy)VO(O_3PC_6H_5)_2]$ in organic electrolyte $LiPF_6$ 1 M in EC:DMC (1:1 by volume) vs. Li^+/Li as reference and counter-electrode.

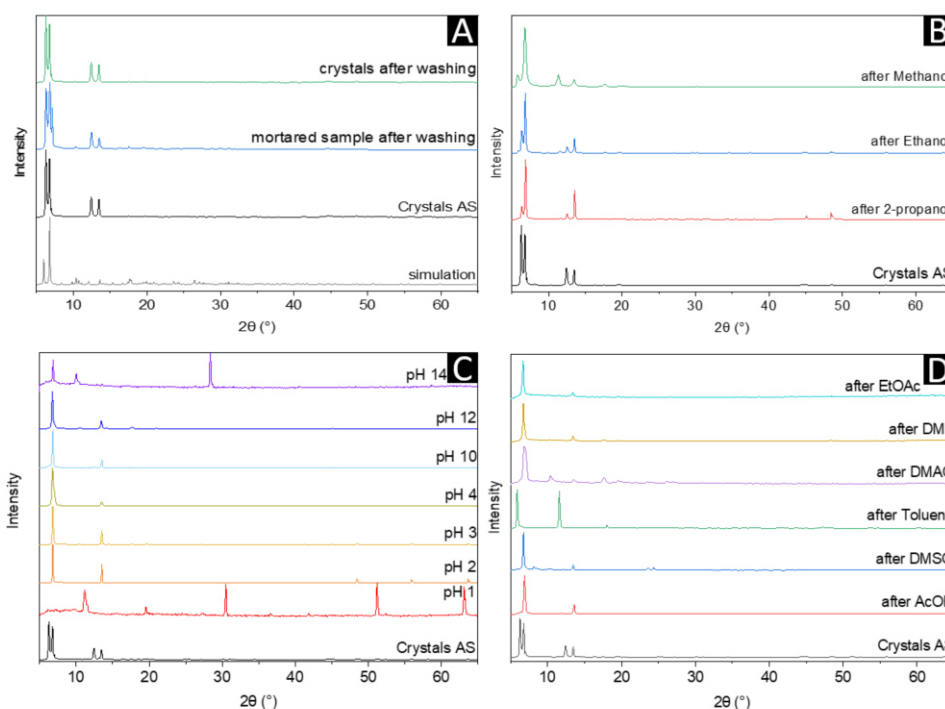


Figure S10: X-ray diffractograms of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$. **A:** Comparison of calculated pattern from single crystal structure (CCDC 255303; Code: XAKXUD) with the synthesized compound as synthesized, after grinding and crystals after washing with water/acetone several times for one day. **B:** Comparison of X-ray diffractogram of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ before and after stirring in common alcohols for 1 week. **C:** Comparison of X-ray diffractogram of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ before and after in solution of different pH-values between pH 1 and pH 14. **D:** Comparison of X-ray diffractogram of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ before and after stirring in several common organic solvents for one week.

Stability testing results (SEM-EDX)

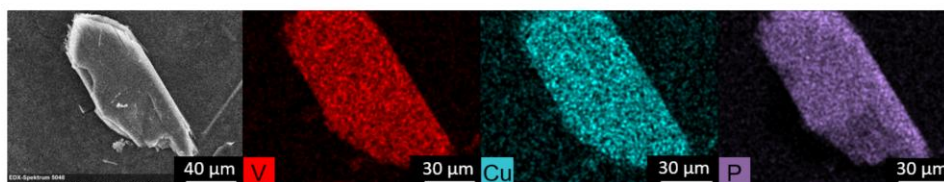


Figure S11. After washing with ultrapure water and isopropyl alcohol for 1 week.

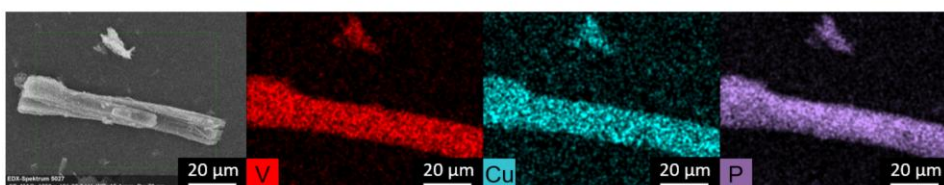


Figure S12. After stirring in glacial acetic acid for 1 week.

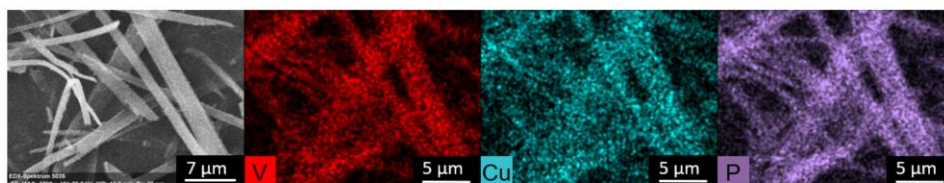


Figure S13. After stirring in N,N-dimethylacetamide for 1 week.

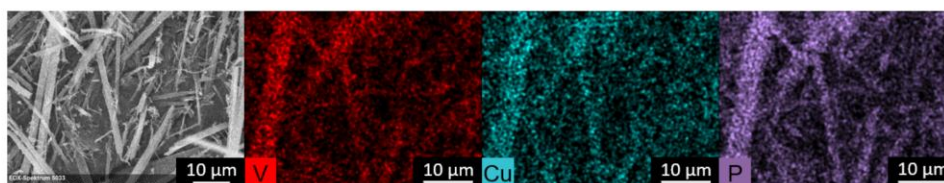


Figure S14. After stirring in N,N-dimethylformamide for 1 week.

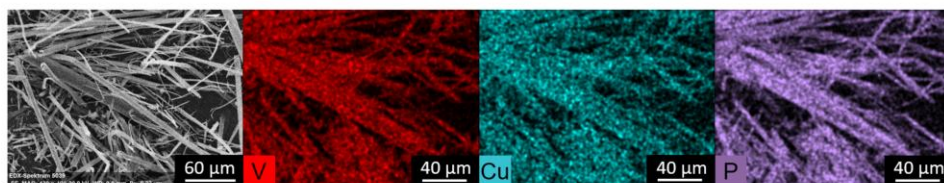


Figure S15. After stirring in ethyl acetate for 1 week.

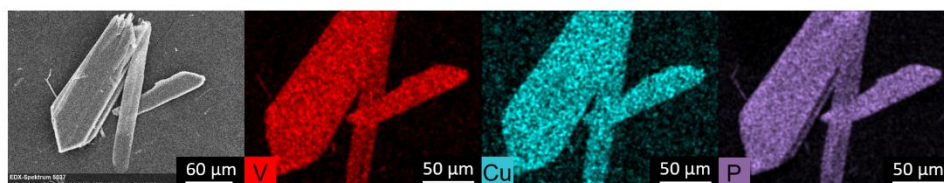


Figure S16. After stirring in Ethanol for 1 week.

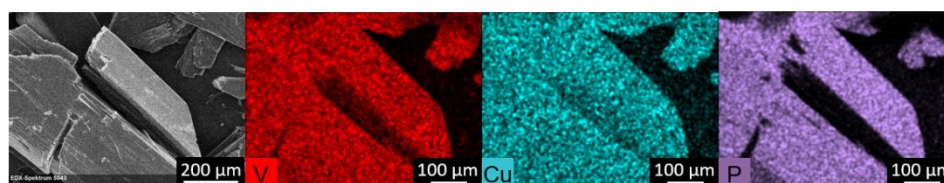


Figure S17. After stirring in isopropyl alcohol for 1 week.

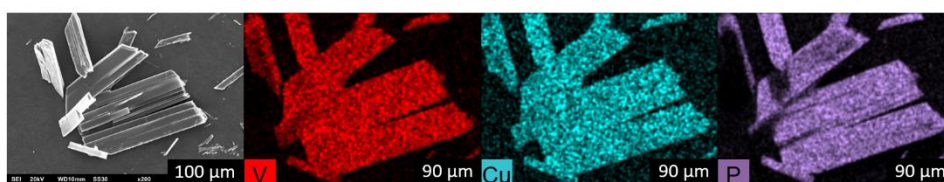


Figure S18. After stirring in toluene for 1 week.

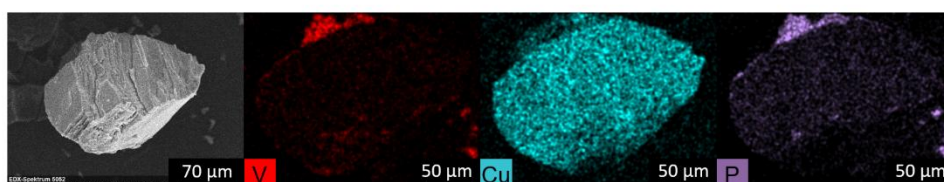


Figure S19. After stirring in aqueous solution (pH 1) for 1 week.

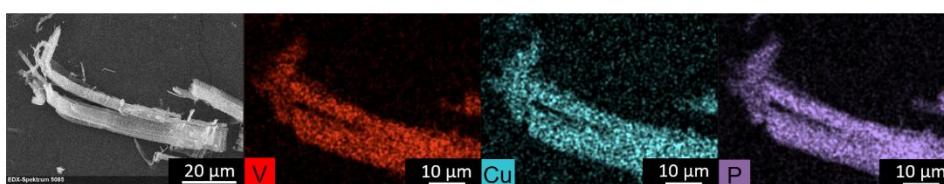


Figure S20. After stirring in aqueous solution (pH 2) for 1 week.

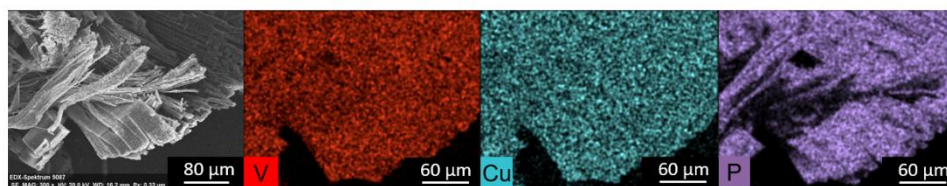


Figure S21. After stirring in aqueous solution (pH 3) for 1 week.

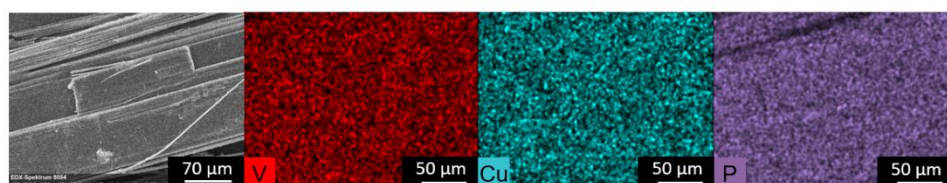


Figure S22. After stirring in aqueous solution (pH 4) for 1 week.

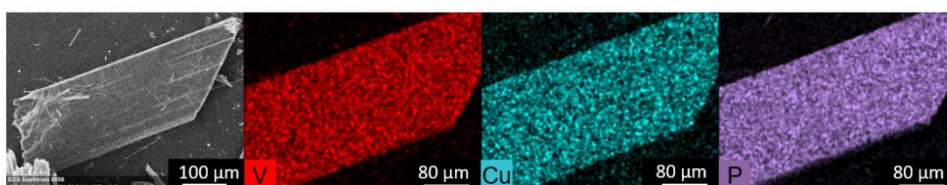


Figure S23. After stirring in aqueous solution (pH 10) for 1 week.

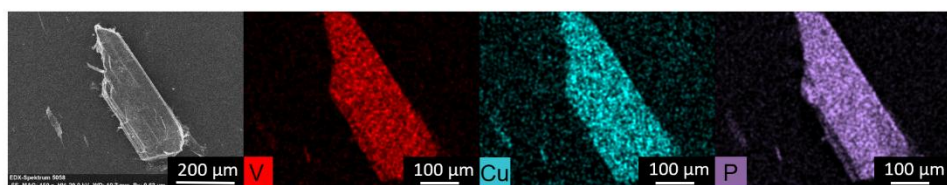


Figure S24. After stirring in aqueous solution (pH 12) for 1 week.

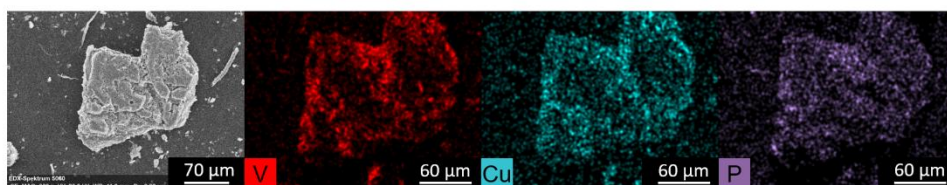


Figure S25. After stirring in aqueous solution (pH 14) for 1 week.

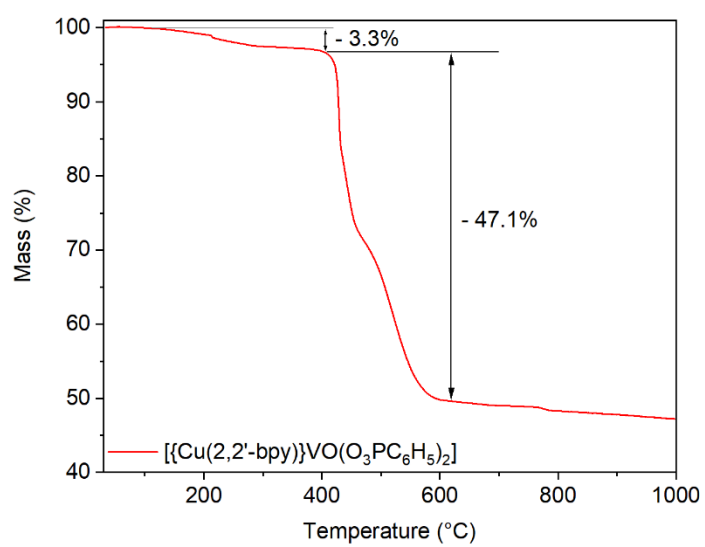


Figure S26. Thermogravimetric data of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ under air.

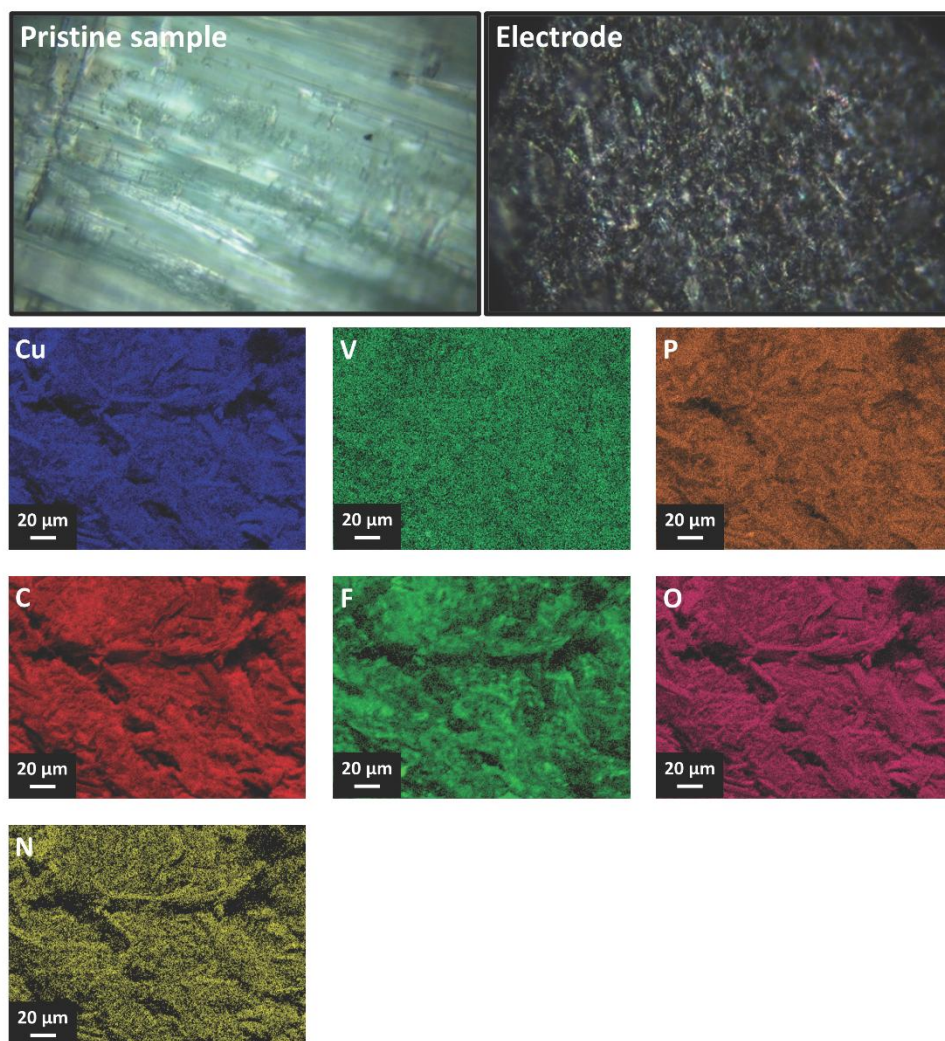


Figure S27. Scanning electron micrographs and elemental mappings (EDX) of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ electrodes.

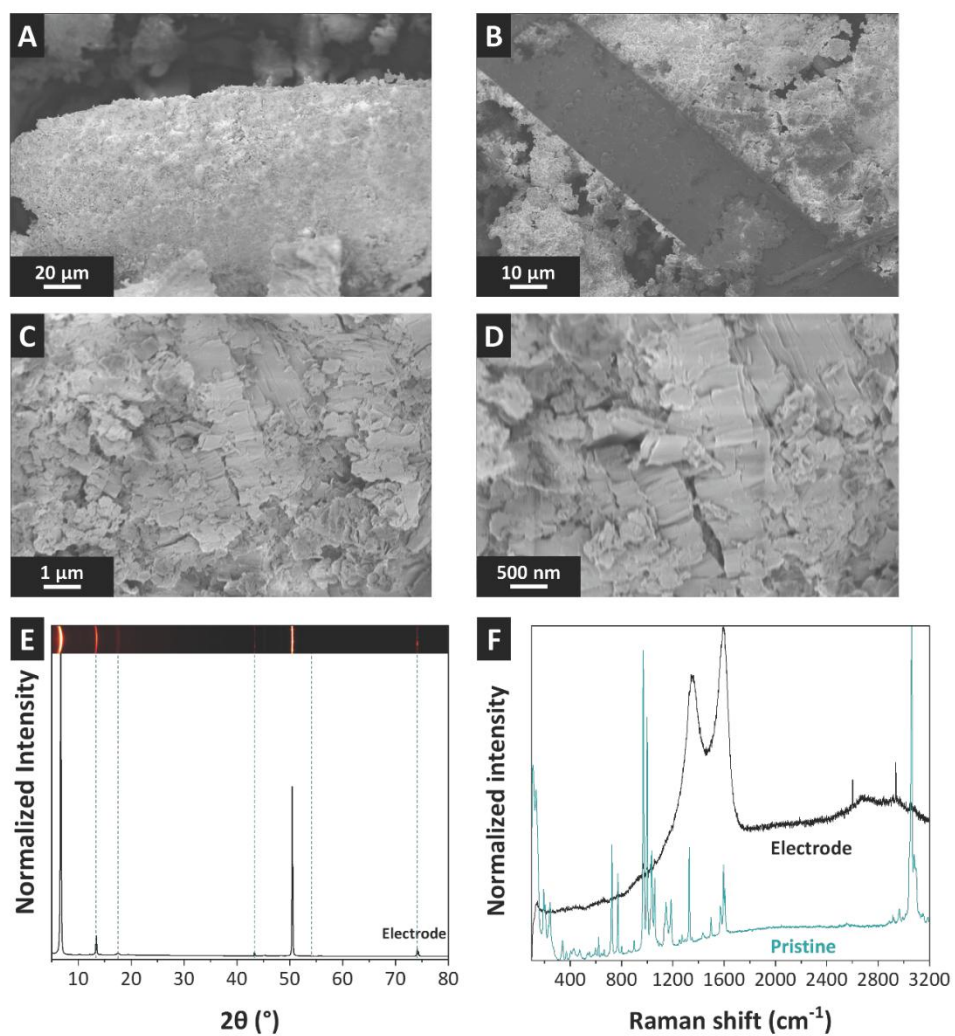


Figure S28. A,D) Scanning electron micrographs of the prepared electrodes at different magnifications, E) X-ray diffractogram of the prepared electrodes and F) Raman spectra of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ pristine sample and prepared electrode.

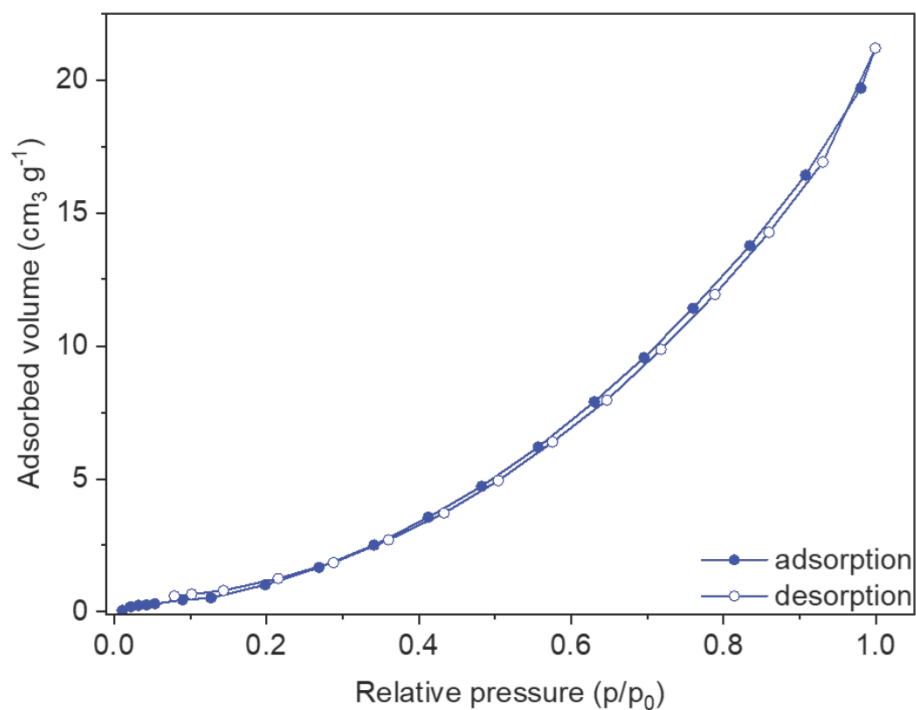


Figure S29. The N_2 adsorption-desorption isotherm of $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ recorded at 77 K displays a type III profile, characteristic of nonporous materials with weak adsorbate-surface interactions. The compound exhibits a BET surface area of $2.8 \text{ m}^2/\text{g}$. Analysis by the t-plot method indicates that the measured surface area originates entirely from the external particle surface, confirming the absence of measurable porosity accessible to nitrogen.

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3.3 A pH-Tolerant Nickel–Vanadium Phosphonate Metal-Organic Framework for Stable Aqueous Supercapacitor Cycling

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Abstract:

We report a hybrid layered luminescent metal-organic framework (MOF), $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$, in which redox-active $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}$ cations are embedded between anionic vanadium phosphonate layers $[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-}$ with 2,2'-bpy = 2,2'-bipyridine). X-ray photoelectron spectroscopy suggests coexisting Ni^{2+} , V^{2+} , V^{3+} , $\text{V}^{4+}/\text{V}^{5+}$ species on the surface of the crystals, indicating a highly dynamic redox system. The material exhibits photoluminescence peaks at 1.7 eV and 2.25 eV, respectively, consistent with semiconductor materials. Magnetic measurements reveal strong short-range antiferromagnetic interactions between the V^{4+} centers. Electrochemical characterization in aqueous media yields capacitances of 79 F/g in Na_2SO_4 (pH 7) and 43 F/g in H_3PO_4 (pH 4) at 1 A/g. In Na_2SO_4 (pH 7), the material reaches ≈ 300 F/g at a scan rate of 1 mV/s and retains its capacity for more than 10,000 cycles. The crystals remain chemically stable between pH 2 and pH 10 for at least one week. The combination of sustainable synthesis, robust redox activity, high capacitance, long cycle stability, and broad pH tolerance make these hybrid MOF crystals promising candidates for next-generation aqueous energy-storage applications.

Author contributions

- T.M. synthesized the compound, optimized the synthesis conditions for large-scale and single-phase production, obtained suitable crystals for structural analysis, and performed stability tests.
- J.G.A.R. performed the electrochemical characterization, Raman spectroscopy, and XRD characterization of the electrodes, and wrote the corresponding section.
- L.W. and J.C.G. carried out sample preparation, characterization, and analysis for optical measurements (reflectance/transmittance measurements for Tauc plots; photoluminescence spectra), conductivity measurements, created visualizations, and wrote the corresponding sections.
- O. J. performed the temperature-variable XRD studies.
- A.Q. performed the XPS experiments.
- Y.Z. performed the refinement of the crystal structure, prepared the crystallographic tables and wrote the corresponding section.
- A.L. took the SEM pictures
- R.F. performed magnetization measurements.

- G.H. critically read and revised the entire manuscript.
- V.P. supervised the supercapacitor and battery work, and critically read and revised the manuscript.
- G.Y. created the hypothesis, synthesized the first batch of the crystals, wrote the manuscript, supervised the work, arranged the collaborations, and provided the necessary funding, enabling the project to be hosted by the department.

A pH-Tolerant Nickel–Vanadium Phosphonate Metal-Organic Framework for Stable Aqueous Supercapacitor Cycling

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Abstract: We report a hybrid layered luminescing metal-organic framework (MOF), $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$, in which redox-active $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}$ cations are embedded between anionic vanadium phosphonate layers $[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-}$ with $2,2'\text{-bpy} = 2,2'\text{-bipyridine}$). X-ray photoelectron spectroscopy suggests coexisting Ni^{2+} , V^{2+} , V^{3+} , and $\text{V}^{4+}/\text{V}^{5+}$ species on the surface of the crystals, indicating a highly dynamic redox system. The material exhibits a main photoluminescence peak at 2.25 eV, consistent with semiconductor materials. Magnetic measurements reveal strong short-range antiferromagnetic interactions between the V^{4+} centers. Electrochemical characterization in aqueous media yields capacitances of 79 F/g in Na_2SO_4 (pH 7) and 43 F/g in H_3PO_4 (pH 4) at 1 A/g. In Na_2SO_4 (pH 7), the material reaches ≈ 300 F/g at a scan rate of 1 mV/s and retains capacity over more than 10,000 cycles. The crystals remain chemically stable between pH 2 and pH 10 for at least one week. Combined sustainable synthesis, robust redox activity, high capacitance, long cycle stability, and broad pH tolerance make these hybrid MOF crystals promising candidates for next-generation aqueous energy-storage applications.

Keywords:

chemically stable MOFs; magnetic materials; redox active complexes; sustainable energy storage

Introduction: Metal-organic frameworks (MOFs) and metal complexes are well-established classes of compounds, each offering tunable properties for diverse applications.^{1,2} Integrating metal complexes into bimetallic MOF platforms represents a promising hybrid strategy that combines the functionalities of both systems on a single scaffold. This approach has been explored in the development of novel microporous materials for sensing applications. For example, spin-active metallofullerene complexes have been incorporated into porous covalent-organic frameworks (COFs) to enable real-time monitoring of gas adsorption via spin-state switching.³ Similarly, spin crossover cages confined within MOF MIL-101 have been used to create colorimetric sensors for gas detection,⁴ while spin crossover complexes embedded in magnetic MOFs have shown potential for achieving long-range magnetic ordering.⁵

Hybrid systems that integrate MOFs with redox-active metal complexes can produce dynamic, multi-center redox activity and enable pseudocapacitive energy storage, features especially valuable for alkaline batteries and supercapacitors. However, to date, such redox-active complexes have typically been introduced into MOFs via post-synthetic modification. In this work, for the first time, we report a one-pot hydrothermal synthesis that directly incorporates redox-active complexes into anionic MOFs, and we characterize the resulting materials' electrochemical, luminescence, and magnetic properties.

We recently showed that bimetallic Cu-V phosphonates can form semiconducting materials with high structural diversity.⁶ Vanadium oxides are established semiconductors with notable pseudocapacitive behavior;⁷ but many metal-oxide electrodes suffer from limited chemical stability in aqueous environments.⁸ Durable electrodes that operate long-term in aqueous electrolytes remain non-existent, motivating the development of stable, water-compatible materials for sustainable supercapacitors. Phosphonate ligands differ from conventional metal-binding groups by their strong affinity for metal ions and by bearing a doubly negative charge per unit, which facilitates incorporation of additional metal centers, mixed-valence chemistry, and multiple redox sites.⁹⁻¹¹ We have previously shown that phosphonate oxygens also carry enhanced negative charge through P→O electron delocalization,^{12,13} contributing to improved hydrolytic stability of phosphonate-based MOFs in both acidic and basic media^{14,15}. These features make phosphonate MOFs attractive candidates for aqueous energy-storage applications.

A key advantage of phosphonic acid linkers in MOF chemistry is their ability to form water-insoluble secondary building units (SBUs) that resist hydrolysis in aqueous media.¹⁶ This contrasts with conventional MOFs, which often contain water-soluble metal carboxylate SBUs, and metal oxides that degrade in water and electrolytes due to interactions with strongly coordinating Lewis bases.^{17,18} Thus, integrating phosphonic acids into vanadium oxides could potentially enhance the chemical stability, surface area, and structural diversity of the resulting MOFs, while optimizing their semiconducting and energy storage properties. Prior work by Zubietta on hydrothermally synthesized vanadium phosphonates further supports the intrinsic thermal and chemical stability of these materials.¹⁹

Despite the high surface areas MOFs can provide, their application in supercapacitor electrodes has been limited due to their typically insulating nature and low chemical stability in aqueous media.²⁰⁻²² Alternative electrode materials such as MXenes, graphene, and RuO₂ often require harsh synthesis conditions, namely

extremely acidic/basic electrolytes (e.g., up to 6 M KOH or H₂SO₄) and high temperatures, limiting their scalability.²³⁻²⁵ In contrast, our approach focuses on the sustainable hydrothermal synthesis of vanadium phosphonate MOFs in water, incorporating redox-active complexes into their framework to create a redox-active, chemically robust, and thermally stable material. The resulting hybrid system enables tunable magnetic, electrocatalytic, and charge storage properties by modulating the oxidation states of the metal centers. Our prior unsuccessful attempts to synthesize Ni/V bimetallic MOFs revealed that nickel preferentially coordinates with nitrogen-donating ligands rather than participating in bimetallic oxide oligomerization with vanadium phosphonates.^{6,26} This observation guided our strategy to selectively incorporate redox-active nickel complexes into vanadium phosphonate MOFs instead of relying on direct bimetallic bonding.

In this study, for the first time, we report for the first time the synthesis of layered anionic vanadium phosphonate MOFs embedded with redox-active [Ni(2,2'-bpy)₃]²⁺ complexes. We developed reproducible hydrothermal synthesis conditions that sustainably generate the [Ni(2,2'-bpy)₃]²⁺ species during the synthesis. Electrochemical characterization confirms the presence of reversible redox behavior. Our measurements further demonstrate that [Ni(2,2'-bpy)₃]²⁺[(VO(H₂O))₂(VO)₄(μ-O)₂(C₆H₅PO₃)₆]²⁻ · 2H₂O can store energy through multiple mechanisms. The incorporation of phosphonate ligands significantly enhances chemical stability in acids and bases over 10000 cycles without compromising the chemical structure of the material, marking a promising step forward in the design of stable and semiconducting MOF-based energy storage platforms.

Synthesis and characterization: As shown in **Figure 1**, [Ni(2,2'-bpy)₃]²⁺[(VO(H₂O))₂(VO)₄(μ-O)₂(C₆H₅PO₃)₆]²⁻ · 2H₂O was synthesized hydrothermally by combining 93 mg (0.35 mmol) NiSO₄·6H₂O, 78 mg (0.42 mmol) Na₃VO₄, 99.8 mg (0.64 mmol) 2,2'-bipyridine, and 400 mg (2.53 mmol) phenylphosphonic acid in a 23 mL polytetrafluoroethylene-lined Parr acid digestion vessel. After adding 10 mL of ultrapure water, the mixture was stirred for 2 min and then placed in a synthesis oven. The temperature was gradually increased to 190 °C over 12 h (at a rate of ~14 K/h), held at this temperature for 48 h, and then cooled to room temperature over 2 h. After cooling, the resulting mixture was transferred to a 50 mL centrifuge tube, thoroughly washed with ultrapure water, and dried overnight at 60 °C in a vacuum drying oven.

Dark green, rod-shaped crystals up to 0.5 cm long were obtained in high visual purity, as seen in **Figure 1**. Single-crystal X-ray diffraction provided the crystal structure shown in **Figure 2**. Phase purity was confirmed by powder X-ray diffraction and inductively coupled plasma optical emission spectroscopy (ICP-OES), which together give a consistent molar ratio Ni:V = 1:(5.93 ± 0.06) across five measurements (*Supplementary Information, Table S1*). The chemical formula reported here is based on the single-crystal structure, the ICP-OES composition, and the electrochemical data, and assumes two V⁺⁵ ions coordinated to water and four V⁺⁴ ions; the magnetic measurements are consistent with this assignment. However, because the material exhibits dynamic redox behavior, alternative formulas with different vanadium oxidation state distributions may also be consistent. For example, one alternative formula could be based

on vanadium ions, V^{+4} ions, resulting in protonated water of crystallization and yielding the formula $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{4-} \cdot 2H_3O^+$. This formula also suggests the presence of additional redox pathways. We prefer the formula $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{2-} \cdot 2H_2O$, as $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{4-} \cdot 2H_3O^+$ has a more anionic framework with reactive H_3O^+ species and thus may be less stable. Another possible formula that assumes all V^{+4} ions is $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-OH)_2(C_6H_5PO_3)_6]^{2-} \cdot 2H_2O$. This formula suggests a potentially less stable form, as protonation of the bridging oxygen atoms across the network may reduce overall structural stability.

In addition to ICP-OES, we collected XPS data to confirm the elemental composition and surface oxidation states. The survey scan shows the expected elements (V, Ni, O, C, N, P). High-resolution V and Ni spectra indicate multiple vanadium oxidation states, predominantly V^{4+} , V^{3+} , V^{+2} and traces of V^{+5} (less than 2%), and Ni^{+2} . While XPS provides valuable information on surface speciation, it is inherently surface-sensitive and does not unambiguously report bulk oxidation states in these large crystals. X-ray irradiation can also induce redox changes that alter the observed vanadium speciation. Nonetheless, the XPS evidence for multiple vanadium valences, taken together with the crystal structure, ICP-OES stoichiometry, magnetic data, and electrochemistry, supports the assignment of a dynamic, mixed-valence redox system that distinguishes this material from typical MOFs.

The heating and cooling of the hydrothermal reaction vessels significantly influenced the final crystal morphology and structure. We hypothesize that placing the reaction vessel in a preheated oven suppressed the formation of the $[Ni(2,2'-bpy)_3]^{2+}$ complex at lower temperatures, resulting in alternative products. Likewise, rapid cooling led to the formation of a glassy-looking phase, reminiscent of Prince Rupert's drops, as illustrated in **Figure 1**. We hypothesize that the slow heating of the hydrothermal reaction mixture first forms the soluble $[Ni(2,2'-bpy)_3]^{2+}$ complex at lower temperatures, and that at higher temperatures $[Ni(2,2'-bpy)_3]^{2+}$ templates the assembly of the layered vanadium phosphonate $[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{2-}$ yielding the redox active hybrid MOF $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{2-} \cdot 2H_2O$.

Structure: The compound $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{2-} \cdot 2H_2O$ is composed of anionic layers of $[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{2-}$, within which the $[Ni(2,2'-bpy)_3]^{2+}$ complexes are located in the interlayer spaces. These cationic species both balance the framework charge and help template the structure during the hydrothermal synthesis, as illustrated in **Figure 2**. The anionic layers consist of mixed-valence vanadium oxide units, including two $[VO(H_2O)]_2$ moieties and four VO moieties. Vanadium centers adopt distorted square planar geometries. The cationic component, $[Ni(2,2'-bpy)_3]^{2+}$, features a Ni^{2+} ion octahedrally coordinated by six nitrogen atoms from three chelating 2,2'-bipyridine ligands (**Figure 2**). $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{2-} \cdot 2H_2O$ has large void channels with diameters of 16.1 Å and 9.2 Å accommodating the $[Ni(2,2'-bpy)_3]^{2+}$ cations and two additional waters of crystallization. Weaker non-covalent interactions between the alternating phenyl groups of

phenylphosphonic acids further stabilize the framework structure. A similar structural organization is also seen in phospholipid bilayers.

Tauc plots: To estimate the optical band gap of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$, diffuse reflectance spectroscopy was performed, followed by Tauc analysis.²⁷⁻²⁹ Transmission and reflection spectra of the powdered sample, clamped between two glass plates, were recorded using a PerkinElmer Lambda 1050 spectrophotometer. From these measurements, the absorbance spectrum was calculated and used to construct a Tauc plot (**Figure 3**). By applying a linear fit to the absorption edge of the Tauc plot, we obtain an optical band gap of 2.44 eV (508 nm), consistent with semiconducting behavior (band gaps that are narrower than 2.5 eV are generally considered to be semiconductors).

Photoluminescence spectrum: The photoluminescence (PL) spectrum of the sample was recorded using a Cicci Research photospectrometer with a 405 nm excitation laser. The spectrum revealed a prominent peak with a shoulder extending toward longer wavelengths (**Figure 4**). To analyze the emission features, the data were first background-corrected by subtracting a constant offset, calculated as the average signal intensity within 850-1100 nm. The corrected spectrum was then fitted using a sum of three Gaussian functions. The first Gaussian, fixed at 405 nm, corresponds to the excitation laser. The positions and widths of the remaining two Gaussians were optimized via non-linear least-squares fitting. After fitting, the background offset was re-added to the individual Gaussians and the combined fit for comparison with the measured data. This procedure yielded a major PL peak at 552 nm (2.25 eV) and a weaker, broader emission at 728 nm (1.70 eV) (*Supplementary Information*, **Figure S5**). In semiconductors, PL peaks typically reflect the electronic band structure, with emission energies approximating the band gap. The observed PL maximum is consistent with the optical band gap derived from the Tauc plot. However, it is red-shifted by approximately 50 nm, a common feature attributed to relaxation processes before recombination.

Conductivity measurements:

To evaluate the electrical conductivity along the long axis of the crystals, individual needle-shaped single crystals were mounted onto a glass plate using conductive silver paint (Plano) applied at both ends. Care was taken to prevent the silver paint from spreading along the crystal surface (*Supplementary Information*, **Figure S6**). Electrical contacts were then connected to the silver droplets, and current-voltage (I-V) characteristics were measured using a four-point probe configuration. The setup was validated using a control crystal thinly coated with silver paint to bridge the two contacts, which yielded an ohmic I-V response. Measurements on pristine crystals showed no detectable current even at the maximum applied voltage of 60 V. Given the instrument's current detection threshold of 0.1 nA (Cicci Research), the corresponding resistance along the crystal needle exceeds $6 \times 10^{11} \Omega$. With an electrode spacing of approximately 1.5 mm and a crystal diameter of approximately 0.1 mm, the calculated resistivity is greater than $3 \cdot 10^6 \Omega \text{ m}$, indicating a conductivity below $3 \cdot 10^{-7} \text{ S/m}$. This result only reflects the electrical

conductivity along the length of the needle-shaped crystal structure. The electrical conductivity can be different along the sides of the needle-shaped crystals.

Magnetization: Magnetization (M) measurements were conducted using a Quantum Design Magnetic Properties Measurement System (MPMS). A 2.37 mg sample was placed in a plastic capsule and mounted on a brass holder. Magnetic susceptibility, $\chi = M/H$, was recorded from 1.8 K to 320 K under an applied field of $\mu_0 H = 1$ T. Field-dependent magnetization was measured at 1.8 K up to 7 T. **Figure 5** displays the inverse susceptibility (χ^{-1}) as a function of temperature, along with a fit to the following function:

$$\chi(T) = C/(T - \theta) + \chi_o, \quad (1)$$

where χ_o is the temperature-independent diamagnetic contribution from the large number of nonmagnetic constituents, C is the Curie constant, and θ is the Curie-Weiss temperature. The fit results in $\chi_o = 1.68(1) \cdot 10^{-3}$ emu/mol, $C = 2.532(2)$ emu·K/mol, and $\theta = -9.8(1)$ K. **Figure 5** also shows the inverse susceptibility after subtraction of χ_o , together with a linear extrapolation corresponding to the Curie-Weiss law.

The negative value of θ indicates small antiferromagnetic interactions between the magnetic centers. From the value of C , we infer an effective moment of $\mu_{eff} = 4.50 \mu_B$. Note that, since $\chi \propto (\mu_{eff})^2$, for a mixture of different magnetic species with individual effective moments $\mu_{eff,i}$, we get $(\mu_{eff})^2 = \sum_i (\mu_{eff,i})^2$. With the spin-only values $\mu_{eff,Ni(II)} = 2.83 \mu_B$ and $\mu_{eff,V(IV)} = 1.73 \mu_B$ we expect $\mu_{eff} = 5.10 \mu_B$, assuming all six V ions to be tetravalent. Additional small orbital contributions would enhance this value. The discrepancy from the observed value suggests that a fraction of V ions is not contributing to the magnetic moment, hence being in the V^{5+} state. Assuming four V^{4+} per f.u., a total $\mu_{eff} = 4.47 \mu_B$ is calculated to be close to the observed value.

Below 50 K, $(\chi - \chi_o)^{-1}$ deviates from the high- T Curie-Weiss extrapolation, with a marked increase of the slope below ~ 12 K (inset in **Figure 5**). This feature can be explained assuming that the magnetic interaction between a pair of Ni^{2+} ions is very small, such that their susceptibility follows a Curie law $\chi_{Ni} \propto 1/T$, leading to a steep increase of χ at low T . Accordingly, we fitted a modified equation (**Eq. 2**) to the T dependence of the susceptibility:

$$\chi(T) = C_V/(T - \theta_V) + C_{Ni}/T + \chi_o \quad (2)$$

This fit is shown in the insert of **Figure 5A**. Given the limited validity of the Curie-Weiss extrapolation to the region $T < \theta_V$, we consider the agreement to be good. The fit gives $C_V = 1.564(2)$ emu·K/mol, $\theta_V = -22.5(5)$ K, and $C_{Ni} = 1.043(2)$ emu·K/mol. This results in $\mu_{eff,V} = 3.54 \mu_B$ and $\mu_{eff,Ni} = 2.89 \mu_B$, again consistent with four V^{4+} and one Ni^{2+} per formula unit. The large value of θ_V demonstrates significant antiferromagnetic interactions between the V^{4+} ions.

Figure 5B shows the magnetization curve measured at 1.8 K. We observe a magnetic moment of $2.76 \mu_B$ per formula unit at 7 T, where saturation is not yet reached. We assume that the Ni^{2+} moment is almost saturated at 7 T, and the residual moment stems from V^{4+} moments that are relatively weakly polarized due to their significant antiferromagnetic interactions. By modeling $M(H)$ for Ni^{2+} with an ideal Brillouin

function for $S = 1$, we can subtract the Ni^{2+} contribution from the measured values and thus estimate $M(\text{H})$ for the sum of the V^{4+} ions, as shown in **Figure 5B**.

Thermal stability: The thermal stability of $[\text{Ni}(\text{2,2'}\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ was examined by thermogravimetric analysis (TGA) under both synthetic air and nitrogen atmospheres (**Figure 6**). The compound exhibits high thermal stability up to approximately 400 °C, with a minor mass loss of ~1.2% between 190 °C and 290 °C, attributed to the release of water molecules. In air, a significant mass loss of ~21% occurs between 400 °C and 460 °C, corresponding to the decomposition of the 2,2'-bipyridine ligands. A second mass loss step of ~25% is observed between 470 °C and 610 °C, associated with the breakdown of the phenylphosphonic acid (PPA) linkers. Under a nitrogen atmosphere, the initial mass loss of ~1.7% between 150 °C and 290 °C is attributed to the loss of water of crystallization. Decomposition of the framework begins around 400 °C but proceeds more gradually and without distinct stepwise losses. The final residue stabilizes at ~50% under air and at ~48% under nitrogen, consistent with reduced oxidation under inert conditions.

Temperature-variable X-ray diffraction: We further assessed the thermal stability of the compound using temperature-variable in situ X-ray diffraction (XRD) up to 450 °C (*Supplementary Information, Figure S7*). The crystal structure remained stable up to 200 °C, after which the intensities of the observed Bragg reflections gradually decreased until 300 °C, indicating partial loss of order. Complete loss of crystallinity was observed around 350 °C. The presence of brown residues at 450 °C is consistent with thermal decomposition beginning around 400 °C. Temperature-variable XRD confirmed the absence of any phase transformation products, instead revealing a gradual loss of crystallinity while retaining the original diffraction positions. *Supplementary Information, Figure S7* shows X-ray diffractograms with increasing temperature.

Chemical stability: Although MOF research has grown into one of the largest areas in materials chemistry, only a limited number of MOFs exhibit sufficient stability to withstand aqueous environments. This limitation is primarily due to the widespread use of water-soluble metal-carboxylate SBUs, which often lead to structural decomposition under humid conditions. In contrast, phosphonate linkers offer significantly stronger metal-binding affinity than carboxylates, making them promising candidates for improving MOF stability. Thus, we tested the chemical stability of $[\text{Ni}(\text{2,2'}\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$. This compound was synthesized hydrothermally at 190 °C under strongly acidic conditions (pH 2), already suggesting a degree of intrinsic chemical stability.

We first investigated the effect of pH on the structure and morphology of the material. The compound was exposed to various chemical environments by dispersing small amounts of the material in 20 mL glass vials containing aqueous solutions of varying pH (adjusted using HCl and KOH), as well as in ethanol and glacial acetic acid. The suspensions were stirred for one week. XRD was then used to evaluate structural integrity. Afterward, the samples were dried under vacuum at 60 °C for 24 h and analyzed by scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (EDX) to investigate morphological and elemental changes. The micrographs in **Figure 7** show a homogeneous distribution of all elements in the

sample, localized exclusively to the areas where the sample is present. These results indicate that the structure remains fully intact after one week of stirring under the tested conditions. This is a promising finding, as $[(\text{Ni}(2,2'\text{-bpy})_3)]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-}\cdot 2\text{H}_2\text{O}$ appears to be a redox-active MOF with high chemical stability. Long-term stability studies are currently underway to assess the structural integrity of the crystals over the course of a year.

We also tested the stability in aqueous media at specific pH values. Solutions at pH 2, pH 3, and pH 4 were prepared by diluting 1 mol/L HCl and checking the pH with a pH electrode. Upon stirring, the material exhibited no visible changes in crystal size, color, or morphology. At pH 2, after stirring for 1 min, the crystals of $[(\text{Ni}(2,2'\text{-bpy})_3)]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-}\cdot 2\text{H}_2\text{O}$ settled at the bottom of the vial, leaving the supernatant clear. After one week of stirring, no signs of deformations or dissolution patterns were observed on the crystals, as seen in **Figure 8A**. Similar tests were conducted at pH 10 and pH 12 (by dilution with a 1 mol/L KOH solution, analogous to the previous procedure). While the material remained visually unchanged at pH 10 for one week, increasing the pH to 12 resulted in complete dissolution of the crystals, yielding a precipitate-free solution.

X-ray diffractograms (**Figure 9**) demonstrate that the structural integrity of the MOF is preserved upon exposure to mildly acidic and basic environments (pH 2 to pH 10) after one week, as indicated by the close match between the experimental and simulated diffraction patterns. Mechanical treatment by mortar grinding for one week and prolonged exposure to glacial acetic acid do not induce noticeable changes in the diffraction pattern, indicating that the framework retains its crystallinity under moderate mechanical and chemical stress. These results highlight the high stability of the material across a broad pH range, with only extreme acidic and basic conditions compromising its structural integrity. The material retains structural integrity after being mortared, indicating that $[(\text{Ni}(2,2'\text{-bpy})_3)]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-}\cdot 2\text{H}_2\text{O}$ can be processed into pellets, thin films, and membranes. It also forms slurries suitable for electrode fabrication, suggesting potential applicability in Li-ion battery electrodes.

Diffractograms of the electrodes used in the electrochemical characterization were recorded using a D8 Discover diffractometer (Bruker AXS) with a copper X-ray source (Cu-K α , $\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA), a Göbel mirror, and a 1 mm point focus. The samples were fixed to a glass sample holder in the desired amount for preparation. Another glass substrate was gently pressed onto the sample to ensure homogeneity, and the excess sample was removed from the glass substrate.

Electrochemistry: The electrodes used in the electrochemical testing were prepared using $[(\text{Ni}(2,2'\text{-bpy})_3)]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-}\cdot 2\text{H}_2\text{O}$ as active material, which was finely ground and mixed with conductive carbon black (C65, IMERYS Graphite&Carbon) and binder poly(vinylidene fluoride) (PVDF, Sigma-Aldrich) in a mass ratio of 7:2:1. PVDF was first dissolved in N-methyl-2-pyrrolidone (NMP) with a mass ratio of 1:9 and stirred until it became homogeneous, and then added to the mixture of active material and conductive carbon. The consistency of the slurry was controlled by adding NMP and mixing in a speed mixer (DAC150.1 FVZ Hauschild). Subsequently, a small volume of NMP was added to produce a thick paste, and the mixture was mixed at 1000 rpm for 2 min, followed by

2500 rpm for 2 min. A mixture of 10 mass% PVDF in NMP was added to the paste and stirred at 800 rpm for 6 min. A small amount of NMP was added and speed-mixed at 800 rpm for 2 min until a uniform mixture was achieved. The coating was applied using the doctor blade method with an automatic coater (MTI Mini Cast Coater MSK-AFA-HC100) to achieve a wet thickness of 200 μm over copper and graphite foil. The coated electrodes were dried overnight at 85 $^{\circ}\text{C}$ in a vacuum oven. The roll-pressed foil was then punched into circles with a diameter of 10 mm, ready to use. The electrodes were individually weighed with a precision of 0.01 mg. The mass was normalized by the active material content (i.e., 70%), and only electrodes containing more than 1 mg of active material were used in electrochemical testing to ensure reliable measurements.

To confirm that the active material did not degrade during electrode preparation, Raman analysis was done using a Renishaw InVia microscope with an excitation laser of 532 nm and a power of 87 μW . The spectra were obtained from 10 points with a 10 s exposure time and accumulated five times, then treated for cosmic ray removal and normalization.

For the electrochemical characterization experiments, three-electrode polyethylene-ether-ketone (PEEK) cells equipped with spring-loaded graphite pistons were used.³⁰ The electrochemical cells were assembled using a glass microfiber membrane (GF/A, Whatman) as a separator sandwiched between the working electrode of the active material and the counter-electrode prepared using YP-80F (Kuraray). The aqueous electrolytes consisted of phosphoric acid 0.1 mM (Sigma Aldrich 99%) with pH 4, sodium sulfate 1 M (Sigma Aldrich 99%) with pH 7, and sodium hydroxide 0.1 mM (Sigma Aldrich 99%) with pH 10. The electrochemical behavior of the active material was initially investigated using electrochemical impedance spectroscopy, performed from 100 kHz to 10 mHz at an open circuit potential of +0.406 V vs. Ag/AgCl (3 M) for pH 2, +0.350 V vs. Ag/AgCl (3 M) for pH 7, and -0.826 V vs. Ag/AgCl (3 M) for pH 10, all measured for 1 h prior to analysis. Next, cyclic voltammetry was performed at different scan rates (1-100 mV/s) in a potential window of -0.8 V to +0.8 V vs. Ag/AgCl (3 M). The electrochemical stability and specific capacitance of the active material were investigated using galvanostatic cycling with potential limitation (GCPL, at a high rate of 1 A/g) in a potential window of 0 V to +0.8 V vs. Ag/AgCl (3 M), where the specific capacitance (C_s in F/g) was calculated from each cycle discharge with constant current according to:

$$C_s = \frac{i \cdot \Delta t}{m \cdot \Delta E} \quad (3)$$

where i (A) is the applied current, Δt (s) is the discharge time variation, m (g) is the total mass of the electrodes, and ΔE (V) is the potential vs. Ag/AgCl (V) corrected from the Ohmic drop. Furthermore, the stability of the material was assessed through the Coulombic efficiency of each cycle to evaluate any parasitic reactions or degradation of the active material, as well as electrolyte decomposition. All tests were conducted at 25 ± 1 $^{\circ}\text{C}$ in a climate chamber using a BioLogic VMP-300 potentiostat/galvanostat.

The effects of the electrode preparation on the morphology and structure of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ were characterized by XRD, as shown in

Supplementary Information, Figure S8A-B. The diffractogram of the electrode displays the characteristic reflections of the material at $6.72^\circ 2\theta$, $13.54^\circ 2\theta$, and $20.38^\circ 2\theta$, suggesting no significant changes in the material's structure. However, the intensity is suppressed by the copper current collector $50.34^\circ 2\theta$, confirming the structural stability of the active material during electrode preparation.

Raman spectroscopy was used to investigate the electrode preparation and its impact on the chemical stability of the material, as presented in the *Supplementary Information, Figure S8C-D.* Overall, there are no significant changes in the spectra from the pristine material to the electrode, except for the contribution from the carbon additive. Moreover, the spectra further highlight the presence of a metallic center as shown by the shifts in 182 cm^{-1} related to the V-O-P lattice mode, the presence of two signals at 1028 and 1065 cm^{-1} , which can be associated with an $M^{(\text{Ni,V})}\text{-O-P}$ stretching vibration.^{31,32} The bands around 969 cm^{-1} and 998 cm^{-1} are associated with the symmetric and asymmetric stretches of P-O bonds.³³ Moreover, it is also possible to observe the bands corresponding to the O-V-O bonds in the range of 338 cm^{-1} to 472 cm^{-1} , symmetric stretching characteristic signals of O-V-O are present at 723 cm^{-1} and 771 cm^{-1} , along with a stretching vibration with a frequency of 855 cm^{-1} .³⁴ At higher frequencies, the C-H and ring deformation of bipyridine molecules are much more prominent, with the characteristic sharp bands displaying at 3061 cm^{-1} and 3080 cm^{-1} .^{35,36} These results further corroborate with the observation of chemical stability of the material during electrode preparation.

The electrochemical behavior of the $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ was investigated in different aqueous environments at pH 4, pH 7, and pH 10. Cyclic voltammograms at 1 mV/s , shown in **Figure 10A**, corroborate with the observations about the chemical stability of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ in different conditions. The voltammograms display a different behavior in each electrolyte. In acidic conditions, the active material displays a capacitor-like behavior with no distinctive redox reactions occurring.³⁷ In neutral pH, $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ displays a different behavior, where three redox pairs peaks are more evident at -0.45 V , -0.08 V , and 0.28 V vs. Ag/AgCl (V), where the last signal is related to the reversible oxidation of Ni(II) to Ni(III), suggesting a pseudocapacitive mechanism.^{38,39} In alkaline conditions, the active material displays only one distinct oxidation peak at -0.06 V vs. Ag/AgCl (V), suggesting the oxidation of the Ni(II) metallic center, hindering the electrochemical performance as observed by the relatively low values of specific capacitance.

To further study the electrochemical behavior $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ at pH 7, the electrodes were cycled at different scan rates. As shown in **Figure 10B**, increasing the scan rate leads to a decrease in specific capacitance, indicating that the material favors slower kinetic processes. The presence of three distinct redox pairs suggests the involvement of multiple electroactive metal centers. These centers are influenced by the scan rate, which causes potential shifts and a clear transition from pseudocapacitive to capacitor-like behavior. This indicates a strong correlation between reaction kinetics and ionic interactions within the electrolyte. At a scan rate of

1 mV/s in pH-neutral electrolyte, the material achieves a specific capacitance value of approximately 300 F/g in a pH-neutral electrolyte.^{37,40} Moreover, these observations suggest that the polymeric framework of $[\text{Ni}(\text{2,2'}\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ directly affects ion diffusion kinetics as the scan rate increases.⁴¹ Cyclic voltammograms recorded at scan rates from 0.1 mV/s to 10 mV/s (*Supplementary Information, Figure S9*) probe the kinetic effects on electrochemical response. As the scan rate increases, redox peaks broaden and shift, consistent with greater diffusion resistance.⁴²⁻⁴⁴ These trends support the presence of different electrochemical mechanisms of energy storage in the material.

To evaluate competing energy storage mechanisms, b -values were extracted from the scan rate dependence of the cyclic voltammogram peak currents ($i_{\text{peak}} = a \cdot \nu^b$);^{45,46} results are shown in *Supplementary Information, Figure S10A*. b -values ranging from 0.5 to 1 indicate a transition from diffusion-controlled processes (present in battery materials) to non-diffusion-controlled processes limited to electrode surfaces (present in capacitive/pseudocapacitive materials).⁴⁶⁻⁴⁸ The fitted b -values are 0.84 (pH 7), 0.64 (pH 4), and 0.52 (pH 10), indicating a higher non-diffusion-controlled contribution at neutral pH, a mixed mechanism at pH 4, and largely diffusion-limited behavior at pH 10. These results imply that electrochemical charge storage occurs primarily within the near-surface volume, with a stronger pseudocapacitive component under neutral conditions. An analysis of diffusion- and non-diffusion-controlled contributions (*Supplementary Information, Figure S10B-D*) shows that the relative diffusion contribution increases with scan rate and depends on electrolyte.

In addition to the electrodynamic analysis, the electrochemical impedance spectra (**Figure 10C**) further demonstrate that the system's mechanism and kinetics are closely linked to the interactions between $[\text{Ni}(\text{2,2'}\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ and the electrolyte. These interactions were examined using an equivalent circuit model shown in the inset. At high frequencies, the material shows a partial semi-circle in the Nyquist plot, indicating a Faradaic reaction between the electrode and electrolyte, with a charge transfer resistance value of 6.03 Ω at pH 4, 0.33 Ω at pH 7, and 12.51 Ω at pH 10, as observed in the redox peaks, which corroborate the previous observation of diffusion-limited redox reactions. At low frequencies, the system exhibits a combination of diffusional and capacitive behavior, characterized by the presence of diffusion resistance represented by a Warburg element. This reflects the charge diffusion into near-surface volume electroactive sites within the material, characteristic of a pseudocapacitive mechanism.^{49,50} This further supports the observation of reactive chemical groups occluded in the near-surface volume of the material. The fit values of the Nyquist plots are provided in *Supplementary Information, Table S2*.

The electrochemical stability of $[\text{Ni}(\text{2,2'}\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ was further investigated over 10,000 charge-discharge cycles using GCPL at a current density of 1000 mA/g

within a 0 to 0.8 V vs. Ag/AgCl potential window, under various electrolyte conditions, as shown in **Figure 10D**. The highest specific capacitance was observed under neutral conditions, reaching 79 F/g at a specific current of 1 A/g. This performance is comparable to values reported in the literature, which are typically achieved using more aggressive electrolytes.^{38,39,50} In the pH 4 electrolyte, the material exhibited a stable specific capacitance of 43 F/g, while at pH 10, it retained only a low and stable value of 0.1 F/g. This difference highlights the relationship between electrochemical stability and charge storage performance under different protonation conditions. The electrochemical stability was also investigated at slower specific currents to probe kinetic effects and handling robustness (*Supplementary Information, Figure S10E*, pH 7; *Supplementary Information, Figure S10F*, pH 4, 10-500 mA/g). Under pH-neutral conditions, the material showed good stability, delivering an initial specific capacity of 46 mAh/g (101 F/g), while under acidic conditions, the initial specific capacity dropped to 16 mAh/g (36 F/g) at 10 mA/g. Upon increasing the specific current to 500 mA/g, the capacity dropped to 10 mAh/g (23 F/g) at pH 7 and 2 mAh/g (5 F/g) at pH 4. When the current was returned to 10 mA/g, the capacity recovered, indicating reversible behavior. For comparison, considering the $\text{Ni(II)} \rightleftharpoons \text{Ni(III)}$ and $\text{V(IV)} \rightleftharpoons \text{V(V)}$ redox couples (seven electrons total) yields a theoretical capacity of 96 mAh/g.

A recent review by Walsh and Forse provides a comprehensive summary of the top-performing MOFs used as electrode materials for supercapacitors.⁵¹ Among them, $\text{Ni}_3(\text{HITP})_2$ stands out, achieving a specific capacitance of 84 F/g at a scan rate of 5 mV/s in a $[\text{BF}_4]$ ionic liquid electrolyte. Despite its high capacitance and use of a relatively mild electrolyte, $\text{Ni}_3(\text{HITP})_2$ suffers from limited long-term stability.⁵¹ Many MOF-based electrodes exhibit rapid degradation after the initial cycles and are generally less stable in water and aqueous environments. The review highlights several key challenges in the field, including narrow voltage stability windows, poor rate performance, and low cycling durability. As MOF-based supercapacitors remain an emerging research area, only a limited number of MOFs have been investigated for such applications.

To our knowledge, no previously reported MOFs combine long-term stability in aqueous electrolytes with sustained electrochemical performance. Our hybrid material, $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$, retains its capacitance after 10,000 cycles in pH 4, pH 7, and pH 10 electrolytes. Its retained charge-storage performance in these media is superior to benchmark materials such as MXenes under similar conditions.⁵² In terms of shelf stability, commonly cited robust MOFs (e.g., UiO-66) remain intact for only a few months in air; by contrast, the first batch of our material, synthesized a year ago, shows no visible degradation, indicating substantially improved long-term stability.

Surface area measurements: We measured surface area and water sorption to probe how water interacts with the framework and its ability to transport water into the lattice. As shown in *Supplementary Information, Figure S11*, water of crystallization can be removed and subsequently re-adsorbed without loss of the $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}$ complexes, confirming an ultramicroporous structure. The reversible uptake (12 mg/g) agrees well with the theoretical value (16 mg/g).

Conclusions: Unlike many conventional MOF electrodes, the nickel-vanadium phosphonate MOF reported here exhibits exceptional hydrolytic stability in both acidic and basic media. In neutral Na₂SO₄ (pH 7) at a scan rate of 1 mV/s, the material attains a specific capacitance of 300 F/g. Under practical current loading (1 A/g), it delivers stable specific capacitances of $\approx$ 80 F/g in neutral Na₂SO₄ and $\approx$ 43 F/g in acidic H₃PO₄, retaining performance over 10,000 cycles without measurable degradation (**Figure 10D**). Although the absolute capacitance is lower than some alkaline-optimized systems, the combination of broad pH stability (pH 2-10) and robust charge storage in environmentally benign electrolytes is exceptional.

These properties arise from the strong phosphonate backbone and layered vanadium phosphonate architecture, which confer enhanced hydrolytic resistance relative to carboxylate- or imidazolate-based MOFs.^{53,54} The one-pot, aqueous, low-temperature hydrothermal synthesis is in line with efforts toward more sustainable MOF preparation strategies.⁵⁵ Structural and spectroscopic characterization indicate a mixed-valence vanadium network (V⁴⁺/V⁵⁺) with embedded redox-active [Ni(2,2'-bpy)₃]²⁺ complexes, producing dynamic redox behavior. Magnetic data support the proposed V⁴⁺/V⁵⁺ and Ni²⁺ assignments, and temperature-variable XRD shows the primary diffraction features persist to 300 °C. Electrical conductivity along the needle axis is low ($<3 \times 10^{-7}$ S/m), indicating charge storage proceeds via surface and redox processes rather than bulk electrical conduction.

Overall, this vanadium phosphonate MOF expands the scope of MOF-based electrode materials by demonstrating stable, high-performance charge storage in aqueous environments. Its durable chemistry, sustainable synthesis, and demonstrated electrochemical resilience make it a promising candidate for next-generation aqueous energy-storage applications and motivate further exploration of phosphonate-based frameworks for practical devices.

Author contributions

T.M. synthesized the compound, optimized the synthesis conditions for large-scale and single-phase production, obtained suitable crystals for structural analysis, and performed stability tests.

J.G.A.R. performed the electrochemical characterization, Raman spectroscopy, and XRD characterization of the electrodes, and wrote the corresponding section.

L.W. and J.C.G. carried out sample preparation, characterization, and analysis for optical measurements (reflectance/transmittance measurements for Tauc plots; photoluminescence spectra), conductivity measurements, created visualizations, and wrote the corresponding sections.

O. J. performed the temperature-variable XRD studies.

A.Q. performed the XPS experiments.

Y.Z. performed the refinement of the crystal structure, prepared the crystallographic tables and wrote the corresponding section

A.L. took the SEM pictures

R.F. performed magnetization measurements.

G.H. critically read and revised the entire manuscript.

V.P. supervised the supercapacitor and battery work, and critically read and revised the manuscript.

G.Y. created the hypothesis, synthesized the first batch of the crystals, wrote the manuscript, supervised the work, arranged the collaborations, and provided the necessary funding, enabling the project to be hosted by the department.

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Data availability statement

The Supplementary Information includes crystal structure refinement information, Nyquist plots, X-ray diffractograms, XPS spectra, and Raman spectra. The corresponding CIF has been submitted to the CCDC under the reference number 2479918.

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Figures

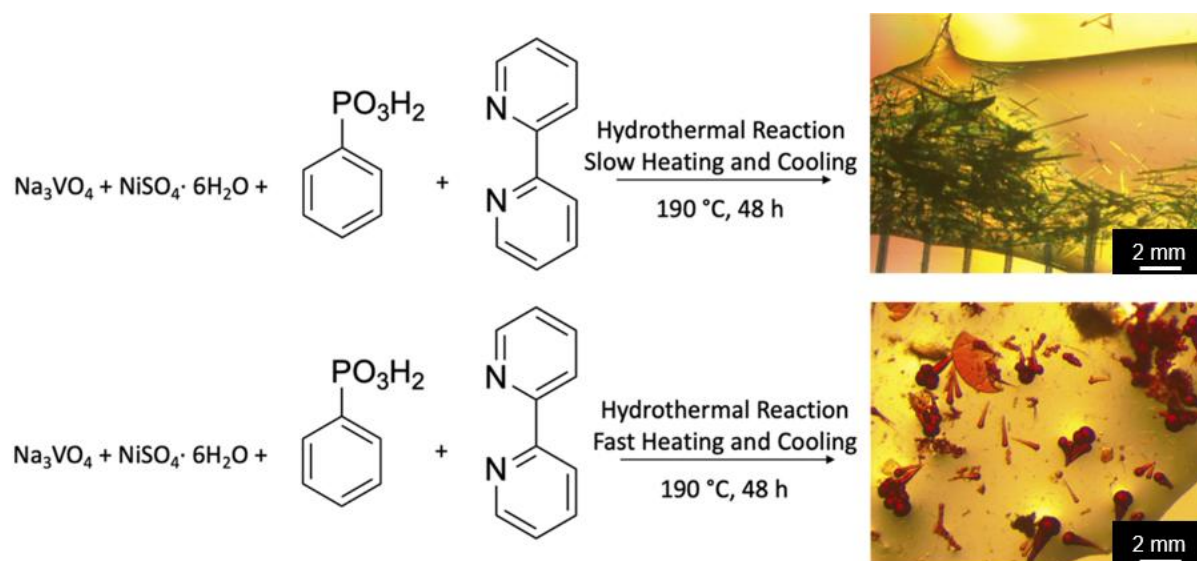


Figure 1. Synthesis of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ (top) and production of non-crystalline material during fast heating and cooling (bottom).

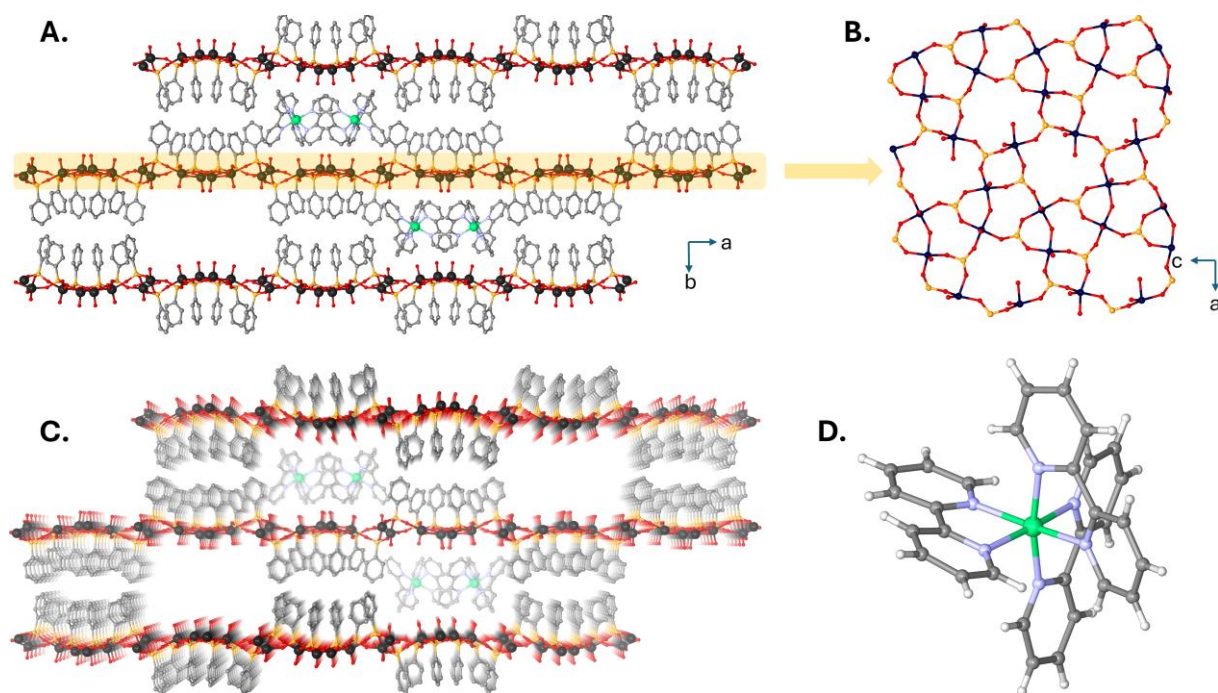


Figure 2. a) Representation of crystal structure of $[\text{Ni}(\text{2,2'}\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ b) representation of the layered $[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-}$ motif. c) Visualization of pore channels showing the embedding of $[\text{Ni}(\text{2,2'}\text{-bpy})_3]^{2+}$ complexes within the interlayer spaces of the anionic $[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-}$ layers, highlighting potential pore sites. D) Visualization of the $[\text{Ni}(\text{2,2'}\text{-bpy})_3]^{2+}$ complexes within the pores of $[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-}$.

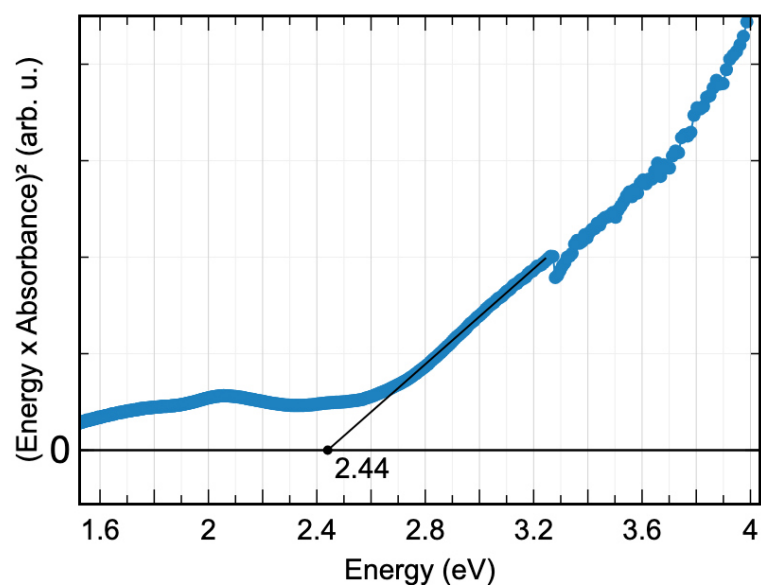


Figure 3. Tauc plot derived from reflection and transmission spectra measured on a sample of crystal powder clamped between two glass plates.

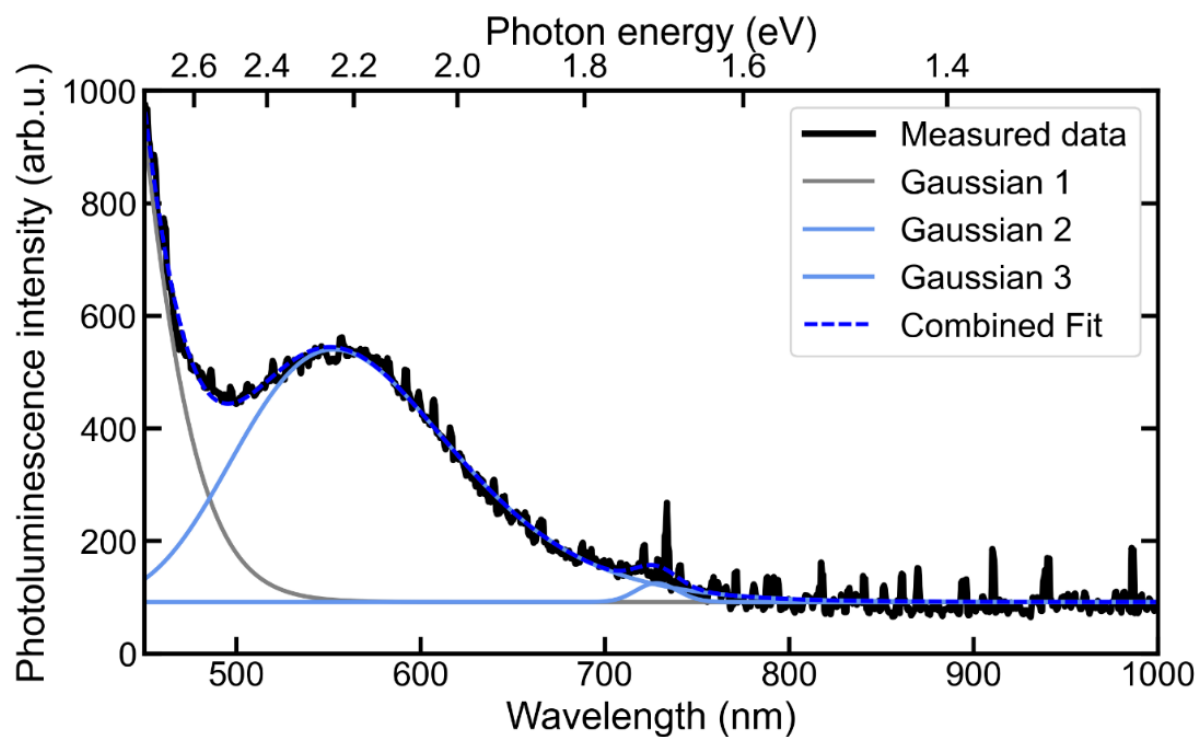


Figure 4. Photoluminescence spectrum of the crystal powder (black), cleaved between two glass plates. The sample was excited with a 405 nm laser. The grey Gaussian function indicates the traces of the excitation light source. The two blue Gaussian curves were fitted to the data, optimized to yield a maximum agreement between the sum of the three Gaussians (blue dashed line) and the measured data points.

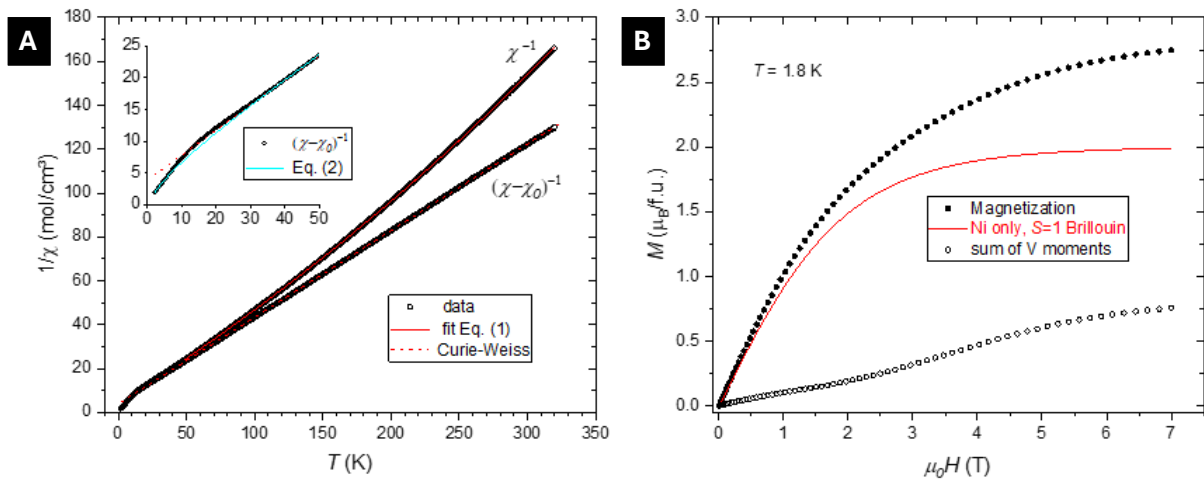


Figure 5. A) Inverse magnetic susceptibility as a function of temperature. Raw data (upper curve) together with a fit (red line) to Eq. (1) and the same data corrected for the diamagnetic contribution (lower curve) together with the Curie-Weiss extrapolation (red dotted line). The insert shows a blow-up of the low- T region, highlighting a marked increase of slope below ~ 12 K. Here, the blue line shows the fit to Eq. (2) that ascribes the increased slope to the Curie term from Ni^{2+} ions. B) Field dependence of the magnetization measured at 1.8 K, suggesting a saturation magnetization of $\sim 3 \mu_B$ at this temperature. Modelling $M(H)$ for Ni^{2+} with an ideal Brillouin function for $S = 1$ (red line), the Ni^{2+} contribution is subtracted from the measured values (full circles), resulting in an estimate of $M(H)$ for the sum of the V^{4+} ions (open circles).

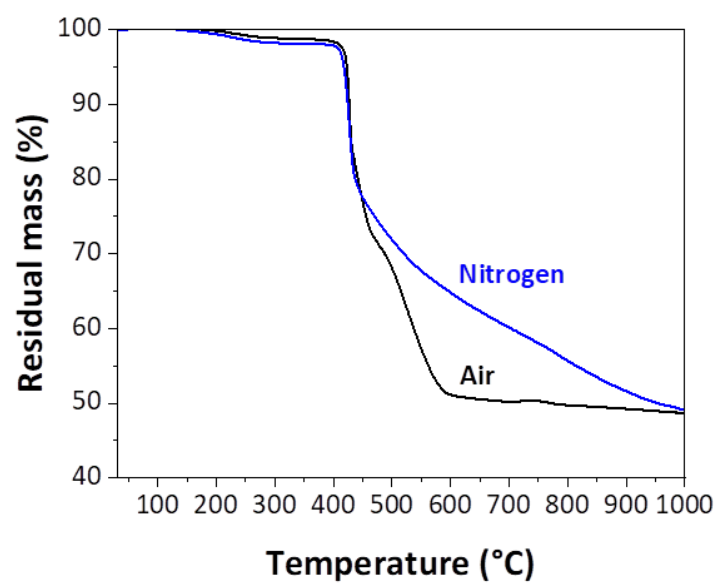


Figure 6. Thermogravimetric analysis of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ under nitrogen (blue curve) and synthetic air (black curve).

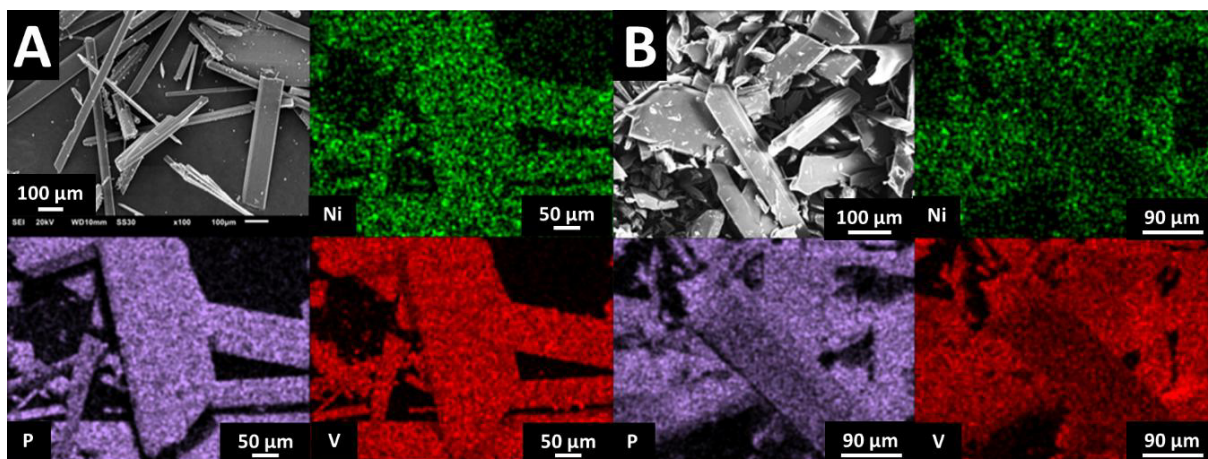


Figure 7: Scanning electron micrographs of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ after stirring in ethanol (**A**) or glacial acetic acid (**B**) for one week (green = nickel, purple = vanadium, red = phosphorus).

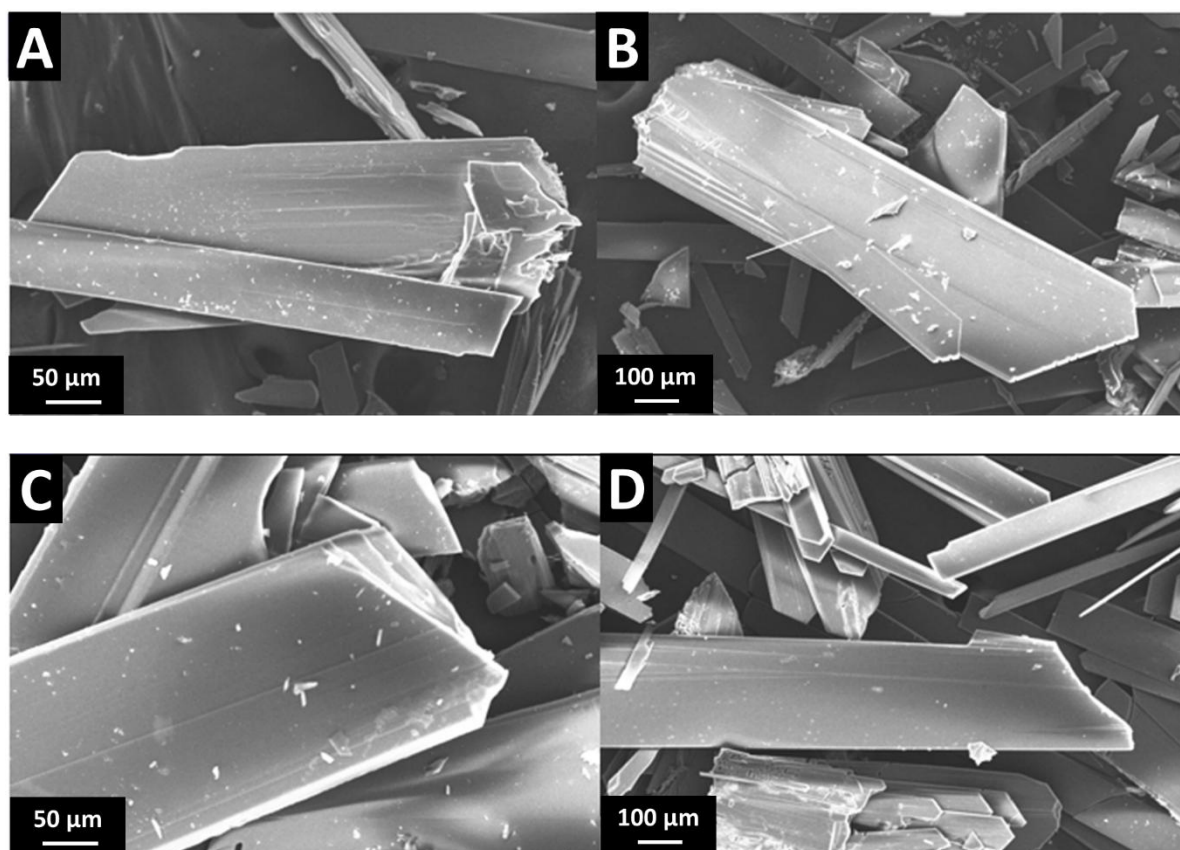


Figure 8. Scanning electron micrographs of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ after stirring for one week in aqueous solution at pH 2 (A), pH 3 (B), pH 4 (C), and pH 10 (D).

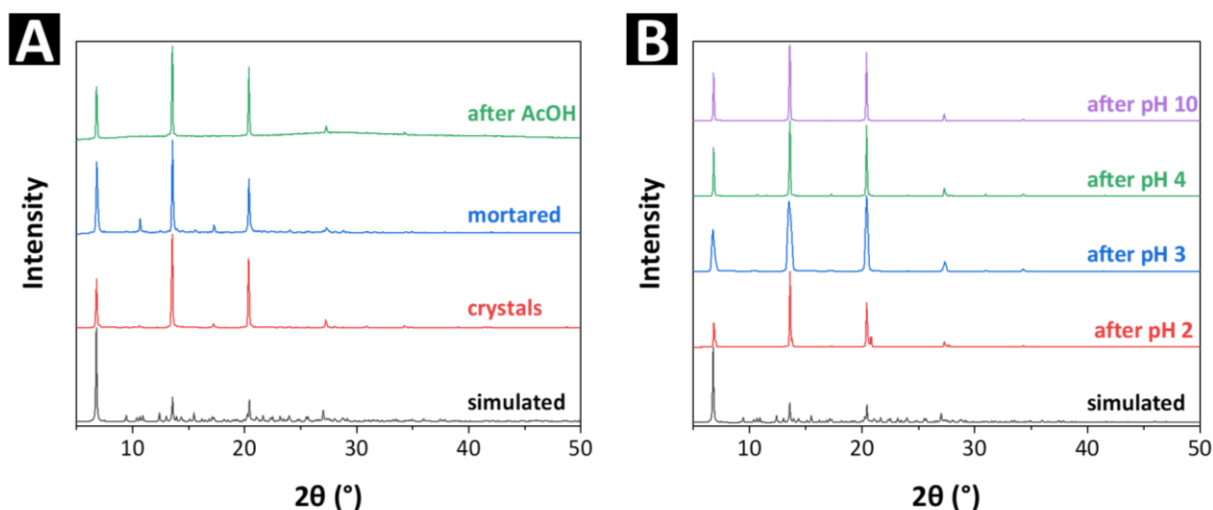


Figure 9: X-ray diffractograms of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$. (A) Comparison of the simulated pattern (based on the single-crystal structure) with experimental patterns of crystals after washing with water and ethanol, both before and after mortaring, as well as after stirring in concentrated acetic acid for one week. (B) Comparison of the simulated pattern with experimental patterns of samples stirred in aqueous solutions at pH 2, pH 3, pH 4, and pH 10 for one week. All samples were measured in transmission mode without further treatment.

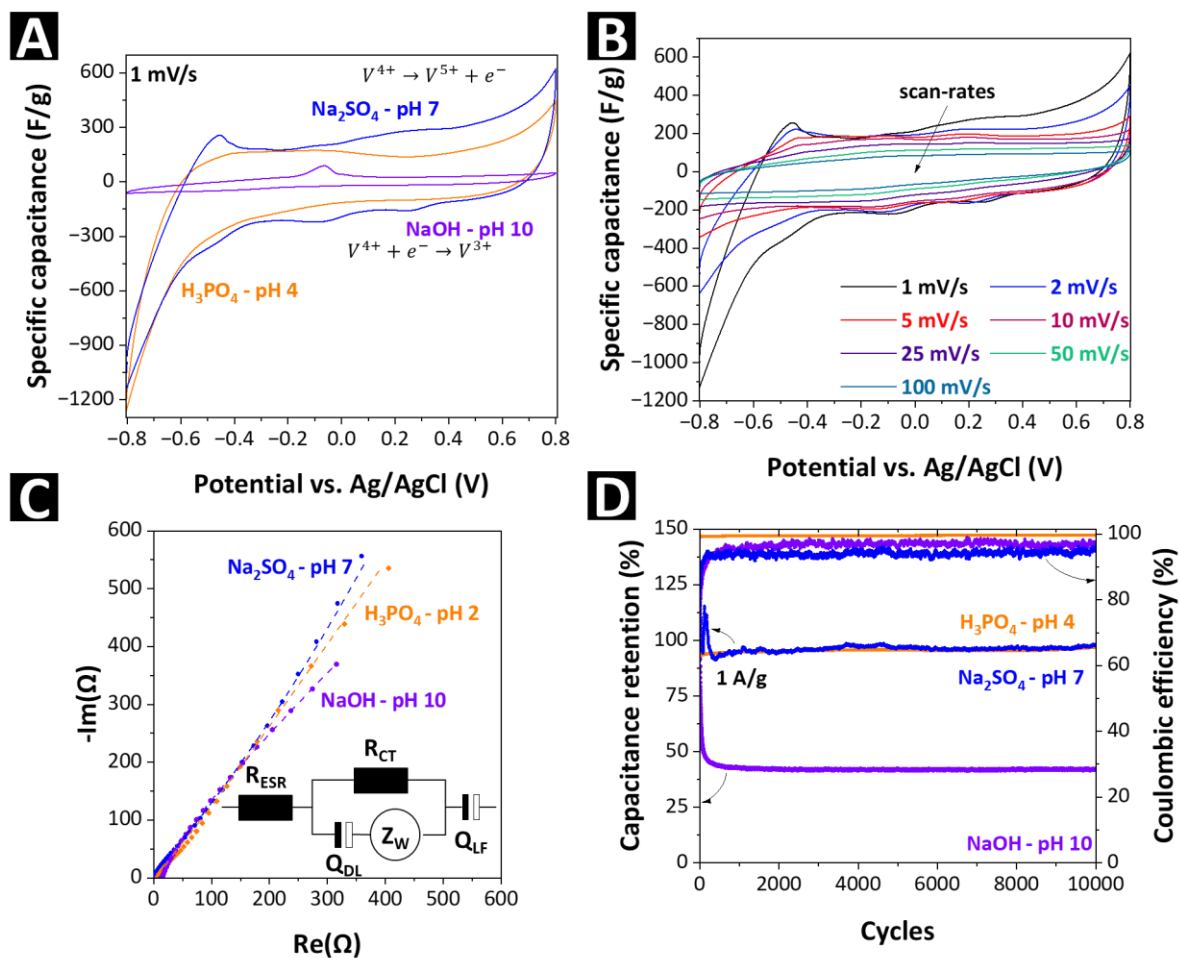


Figure 10. A) Cyclic voltammograms of $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{2-} \cdot 2H_2O$ in different pH electrolytes. B) Cyclic voltammograms of $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{2-} \cdot 2H_2O$ at different scan rates in pH 7. C) Electrochemical impedance spectra of $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{2-} \cdot 2H_2O$ at different pH values. Inset: Equivalent circuit used for data analysis. D) Capacitance retention analysis at 1 A/g for 10000 cycles of $[Ni(2,2'-bpy)_3]^{2+}[(VO(H_2O))_2(VO)_4(\mu-O)_2(C_6H_5PO_3)_6]^{2-} \cdot 2H_2O$ in different pH electrolytes.

A pH-Tolerant Nickel–Vanadium Phosphonate Metal-Organic Framework for Stable Aqueous Supercapacitor Cycling

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Inductively coupled plasma optical emission spectroscopy (ICP-OES): Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed to confirm the molar ratio of Ni and V in the crystal structure.

Approximately 1 mg of the solid compound was weighed onto a PTFE weighing boat and transferred to a digestion tube before 2 mL of ultrapure nitric acid ($w = 0.67$) was added to it. The samples were digested using the MARSXpress 2.0 microwave (CEM). For this purpose, the samples were heated to 200 °C within 25 min at 7.2 °C/min and the temperature was held at 200 °C for 30 min. The clear solution was made up to a volume of 50 mL in a volumetric flask and measured using an Agilent ICP-OES 5800 connected to an Agilent SPS 4 Autosampler. For the measurement of the nickel content the wavelengths 222 nm and 232 nm were used while 292 nm, 309 nm, and 313 nm were used to determine the vanadium content.

Table S1. ICP–OES-derived Ni and V contents and calculated Ni:V ratios for $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$.

Sample	Ni ($\mu\text{g}/\text{mg}$)	V ($\mu\text{g}/\text{mg}$)	Ni:V (molar)	Ratio (calc.)
1	28.9	147.3	0.17	1:5.85
2	27.6	139.8	0.17	1:5.88
3	29.3	149.7	0.17	1:5.92
4	27.9	142.4	0.17	1:6.02
5	28.2	143.3	0.17	1:5.99

Elemental analysis of nickel and vanadium was performed in five independent ICP-OES measurements after external calibration for each element with R-values of 0.9999 to 1.000. The results were normalized to the sample mass and converted to molar amounts to determine the metal stoichiometry. The five measurements yield a consistent molar ratio of $\text{Ni}:\text{V} = 1 : (5.93 \pm 0.06)$. The small standard deviation demonstrates the high reproducibility of the analysis and confirms the expected stoichiometry of the compound.

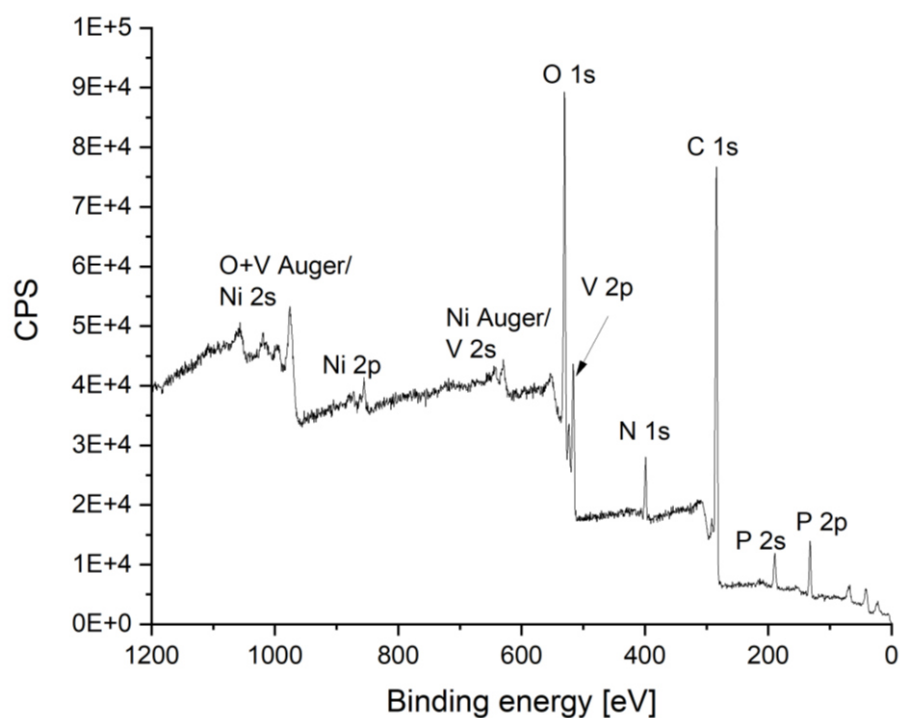


Figure S1. X-ray photoelectron survey scan of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$.

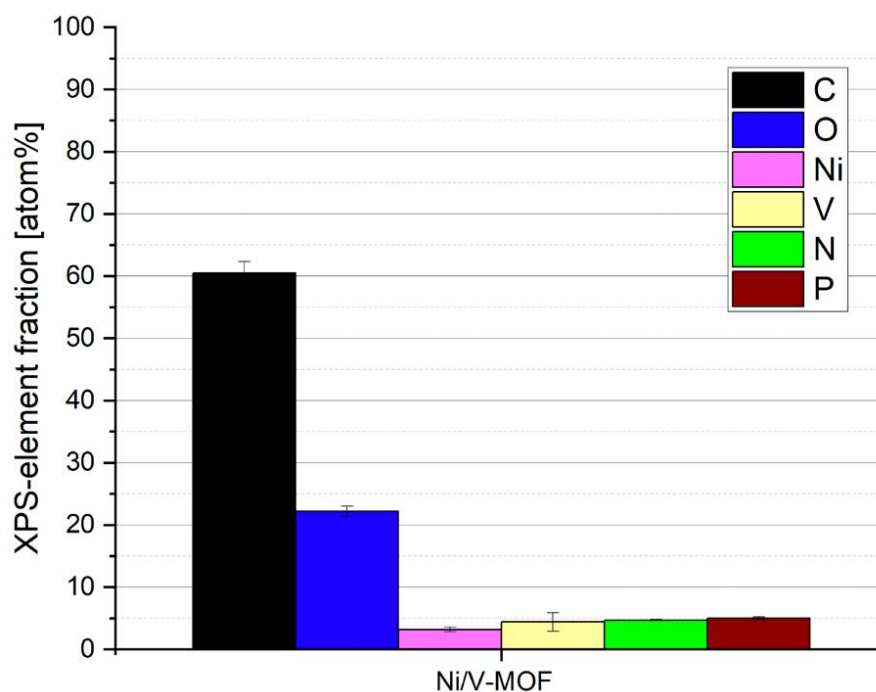


Figure S2. X-ray photoelectron elemental fractions.

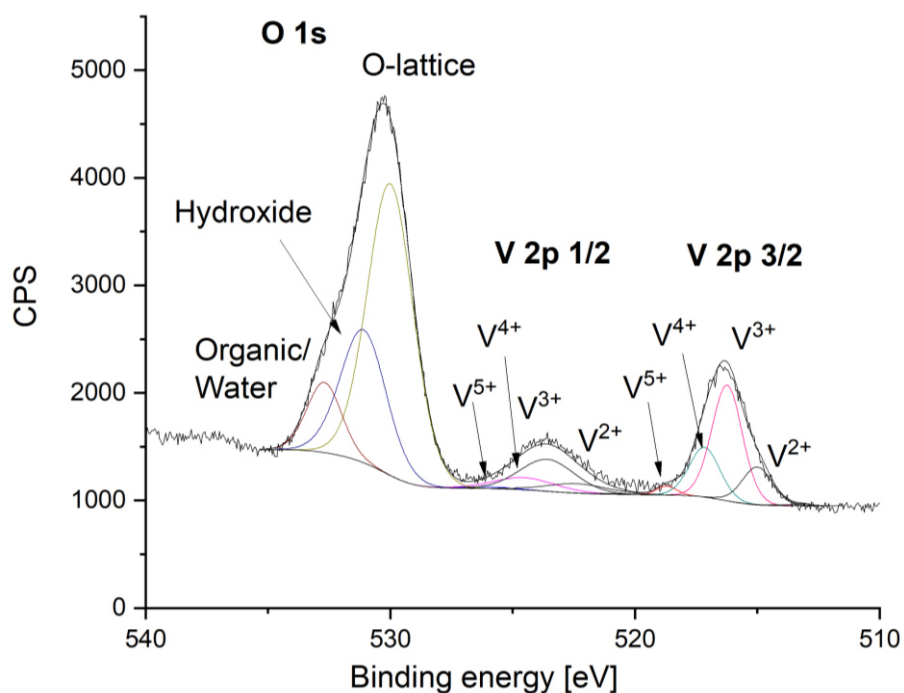


Figure S3. X-ray photoelectron O 1s - V 2p spectrum including the combined fitting of the V 2p and the O 1s signal and indicates the presence of several oxidized vanadium species.

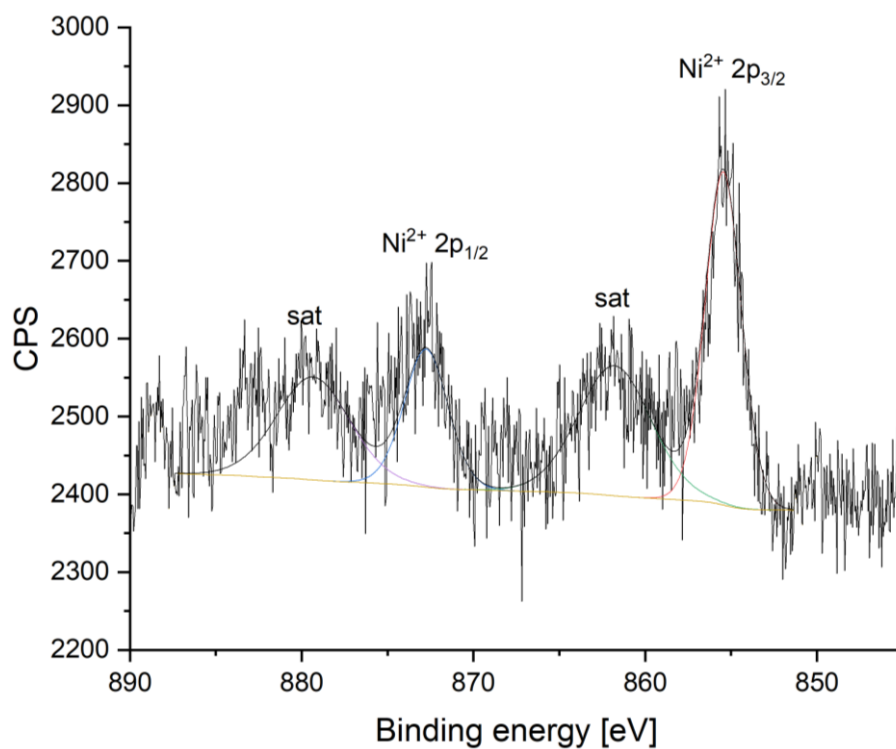


Figure S4. X-ray photoelectron spectrum. The shape of the highly resolved measured Ni 2p peak indicates the presence of Ni²⁺.

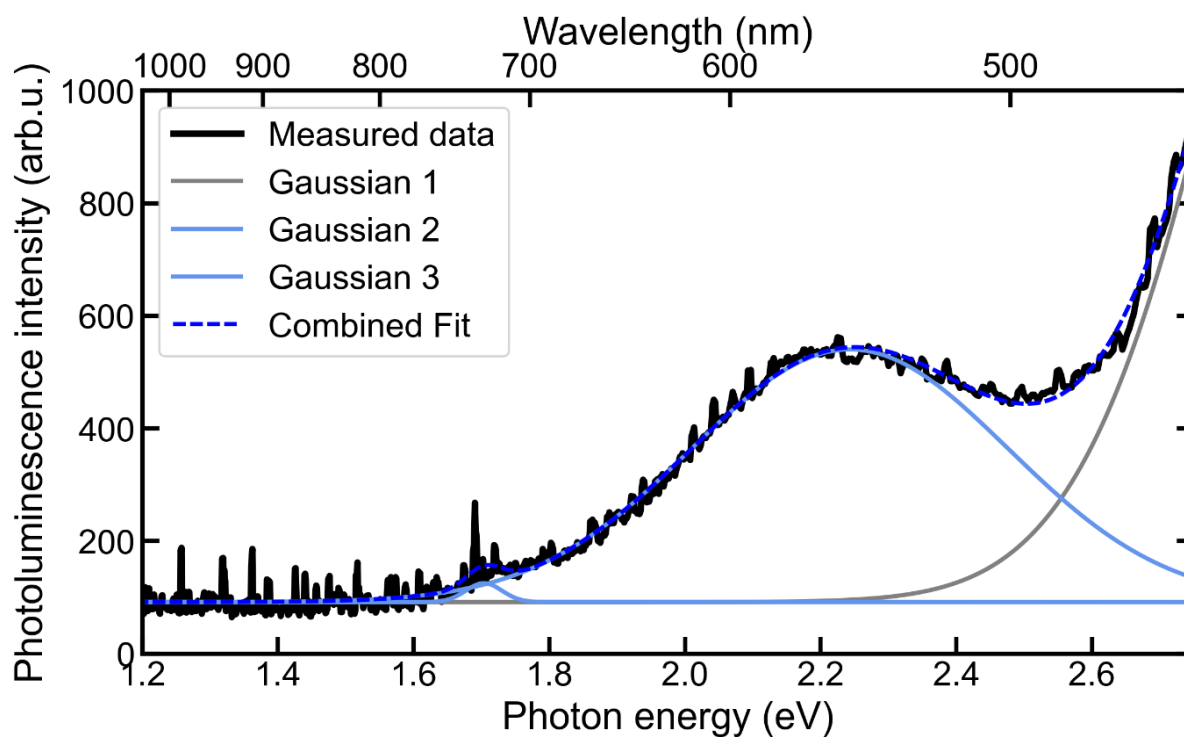


Figure S5. Photoluminescence spectrum of the crystal powder (black), as displayed in **Figure 4** in the manuscript, but plotted as a function of photon energy instead of wavelength.

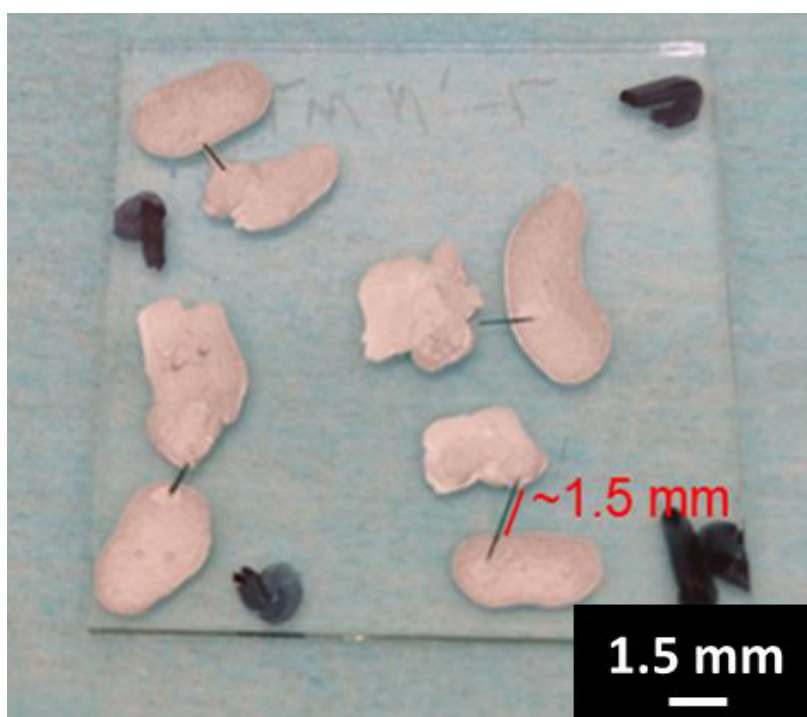


Figure S6. Four crystal needles fixed with conductive silver paint on both ends onto a glass substrate paint. Glass dimensions are approximately 25x25 mm². The red scale bar indicates a length of approximately 1.5 mm.

Sample preparation for PL spectrum: To fix the crystals in a plane, crystal powder was spread on the center of a glass slide (25x25 mm²). The edge of the glass slide was coated with ultraviolet (UV) curable glue (Delo), onto which a second glass slide was applied. The glue was then cured with UV light, avoiding exposure of the powder to UV light.

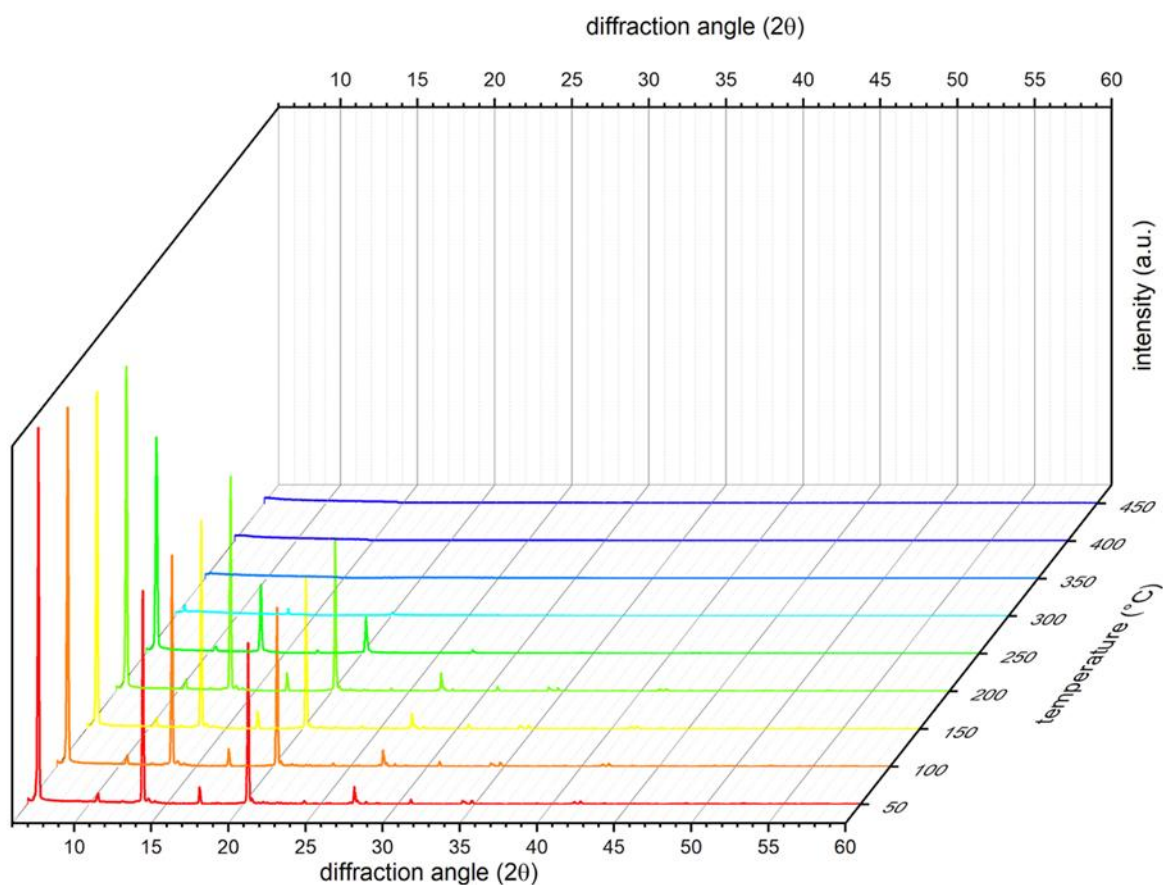


Figure S7. Temperature dependent X-ray diffraction data of $[\text{Ni}(\text{2,2'}\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ (a.u. is arbitrary units).

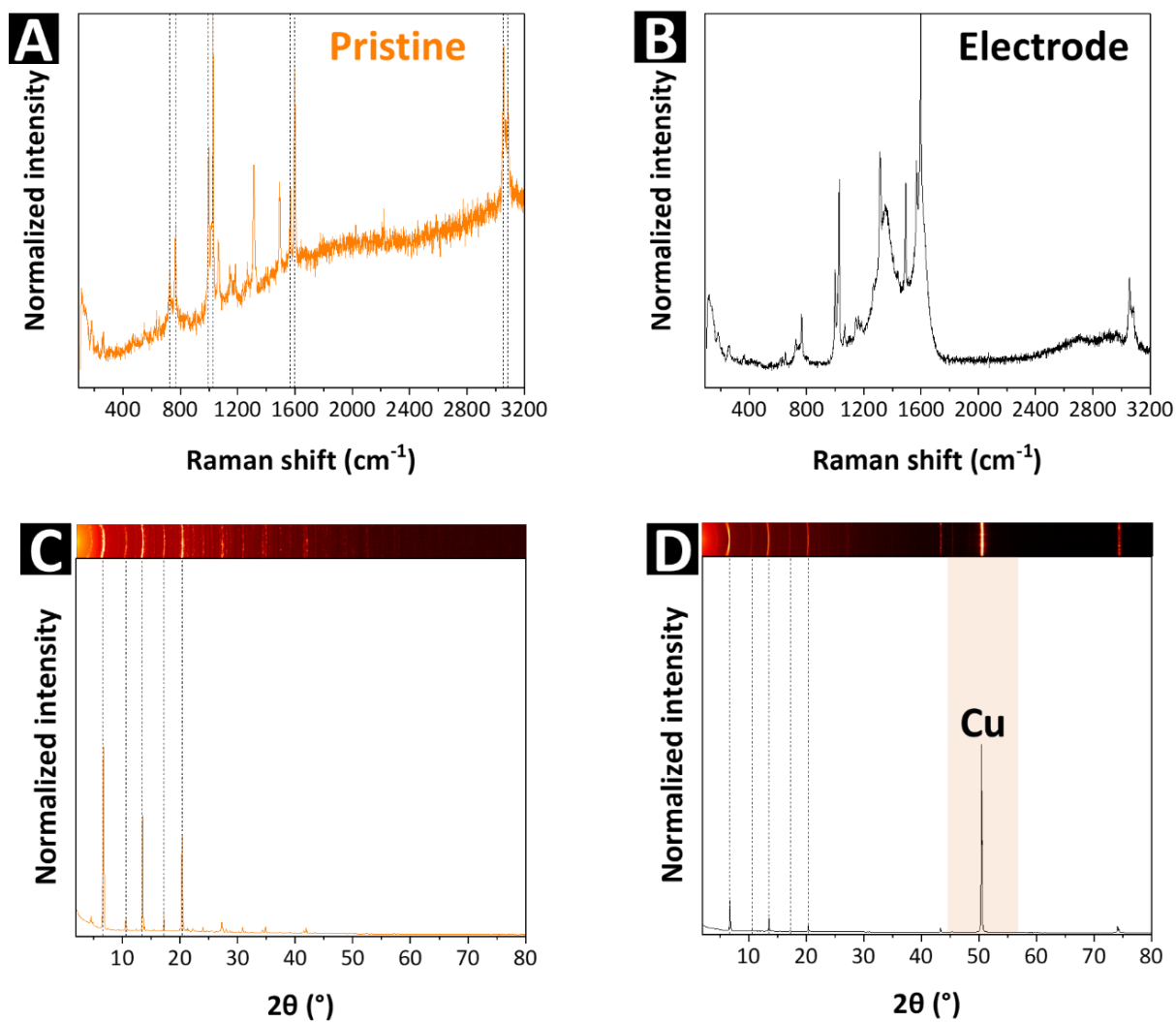


Figure S8. A-B) Raman spectra and C-D) X-ray diffractograms of $[(\text{Ni}(2,2'\text{-bpy})_3)]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ pristine sample and prepared electrode, respectively.

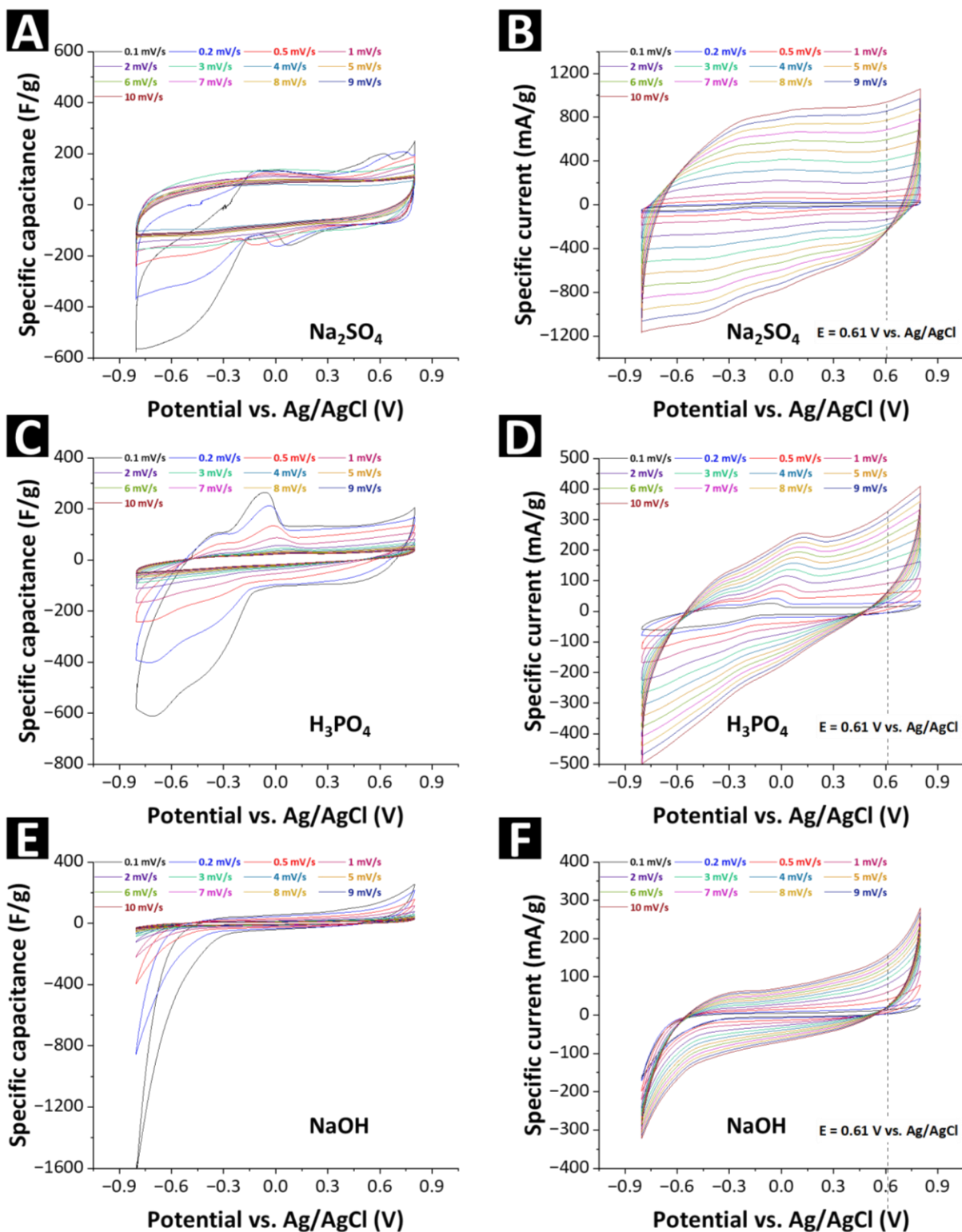


Figure S9. Cyclic voltammetry of $[\text{Ni}(\text{2,2'-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O})_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6)]^{2-} \cdot 2\text{H}_2\text{O}$ for different scan rates from 0.1 mV/s to 10 mV/s in A-B) pH 7 electrolyte (1 M Na_2SO_4), C-D) pH 4 electrolyte (0.001 M H_3PO_4) and E-F) pH 10 electrolyte (0.1 mM NaOH).

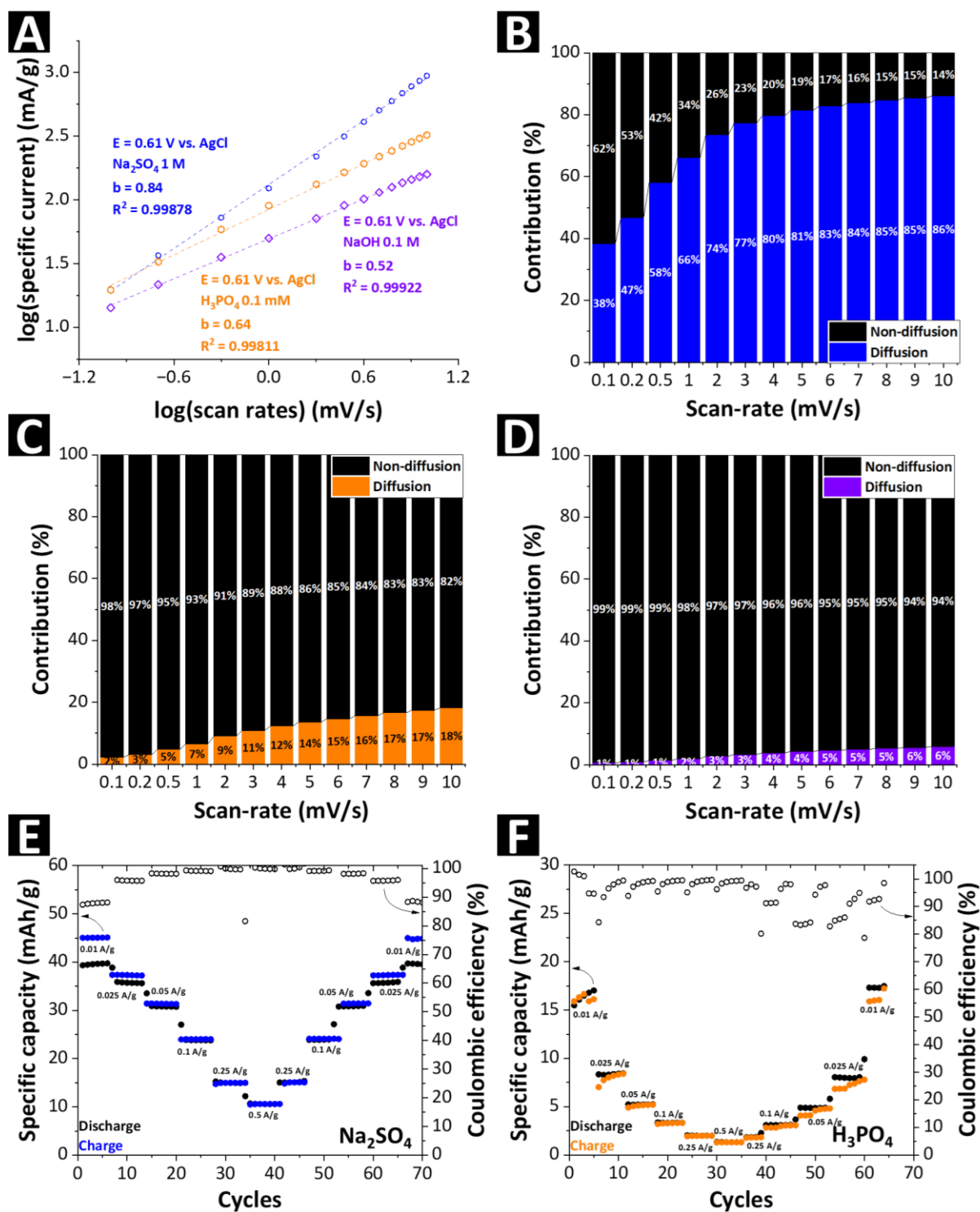


Figure S10. A) b-value analysis of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ in different electrolytes. B) Current contribution at pH 7 electrolyte (1 M Na_2SO_4). C) Current contribution at pH 4 electrolyte (0.001 M H_3PO_4). D) Current contribution at pH 10 electrolyte (0.1 mM NaOH). Rate handling experiments at E) pH 7 electrolyte (1 M Na_2SO_4) and F) pH 4 electrolyte (0.001 M H_3PO_4).

XPS analyses: XPS analyses were carried out using a Kratos Axis Supra (Kratos Analytical Ltd., Manchester, UK) spectrometer with a monochromatic Al K α source (10 mA, 15 kV). The Kratos charge neutralization system was applied during the acquisition. The survey scan was performed with an analysis area of 300 x 700 μ m and a pass energy of 160 eV. The high-resolution analyses of Ni 2p and O 1s/V 2p regions were performed at 15 mA and 15 kV and with a pass energy of 10 eV. All spectra were charge-corrected to the O-lattice component in the O 1s signal to 530.0 eV. A standard Shirley background was used for all spectra. The spectra were analyzed using CasaXPS software (version 2.3.15).

Table S2. Nyquist equivalent circuit fitting

	R_{ESR} (Ω)	Q_{DL} (s)	n_{DL}	R_{CT} (Ω)	W (Ω)	Q_{LF} (s)	n_{LF}
Na₂SO₄	0.33	$2.48 \cdot 10^{-3}$	0.876	28.22	101.60	$1.03 \cdot 10^{-1}$	0.997
NaOH	12.51	$8.67 \cdot 10^{-4}$	0.999	25.34	275.50	$2.22 \cdot 10^{-2}$	0.395
H₃PO₄	6.03	$7.55 \cdot 10^{-3}$	0.882	12.56	1.43	$2.37 \cdot 10^{-3}$	0.612

Single-crystal X-ray crystallography: Intensity data of [Ni(2,2'-bpy)₃]²⁺[(VO(H₂O))₂(VO)₄(μ -O)₂(C₆H₅PO₃)₆]²⁻ · 2H₂O were collected at 100 K on a Bruker Venture D8 diffractometer with graphite-monochromated Mo-K α (0.7107 Å) radiation. All structures were solved by direct methods and refined based on F² by use of the SHELX program package as implemented in OLEX 2 version 1.5.[1-3] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Graphics were drawn with the program Mercury 2025.3.3 [4]. Crystal data and structure refinement for Vanadium-Phosphonate-MOF are given in **Table S3**. The CCDC number is 2479918 respectively, and contain the supplementary crystallographic data reported in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Table S3. Crystal data and structure refinement.

Compound	$[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$
Empirical formula	$\text{C}_{66}\text{H}_{62}\text{N}_6\text{NiO}_{30}\text{P}_6\text{V}_6$
Formula weight	1969.38
Temperature/K	100
Crystal system	orthorhombic
Space group	$\text{Pca}2_1$
a/Å	27.8667(9)
b/Å	25.9876(9)
c/Å	10.7193(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å³	7762.8(4)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.685
μ/mm^{-1}	1.140
F(000)	3984
Crystal size/mm³	$0.4 \times 0.09 \times 0.01$
Radiation	$\text{MoK}\alpha$ ($\lambda=0.71073$ Å)
2θ range for data collection/$^\circ$	4.286 to 50
Index ranges	$-33 \leq h \leq 33, -28 \leq k \leq 30, -12 \leq l \leq 10$
Reflections collected	89782
Independent reflections	12704 [$R_{\text{int}} = 0.0538$, $R_{\text{sigma}} = 0.0380$]
Data/restraints/parameters	12704/2/1057
Goodness-of-fit on F^2	1.038
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0272$, $wR_2 = 0.0618$
Final R indexes [all data]	$R_1 = 0.0306$, $wR_2 = 0.0632$
Largest diff. peak/hole / e Å⁻³	0.38/-0.32
Flack parameter	-0.003(6)

X-ray diffractograms of $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})_2(\text{C}_6\text{H}_5\text{PO}_3)_6]^{2-} \cdot 2\text{H}_2\text{O}$ elevated temperatures were recorded on a D8-A25-Advance diffractometer (Bruker AXS) in Bragg-Brentano θ - θ -geometry (goniometer radius 280 mm) with $\text{Cu K}\alpha$ -radiation ($\lambda = 154.0596$ pm) using a XRK 900 (Anton Paar GmbH) reactor chamber. The samples were prepared on Si zero-background sample holders and investigated in air in the temperature range of 50 °C to 450 °C with intervals of 100 °C with heating rates of 10 K/min, respectively. A 12 μm Ni foil working as K_β filter and a variable divergence slit were mounted at the primary beam side. The secondary beam side was equipped with a LYNXEYE detector (192 channels). Diffraction patterns were recorded between 6° and 60° 2 θ with a step size of 0.013° and a total scan time of 1 h for each temperature. The thermal expansion of the reaction chamber and sample holder was determined using elemental Si (NIST Standard reference material 640f, $a = 5.4311(1)$ nm). The obtained data was refined using the Bruker TOPAS 5.0 software package,[5] keeping the lattice parameter of Si fixed while refining the height displacement. This was conducted for different temperatures from which a linear regression was determined. For the subsequent measurements, the z-height was modified by the previously determined values as a function of the temperature used.

Water Adsorption: All sorption measurements were done on the BELSorp-max II by MicrotracBEL Corporation.

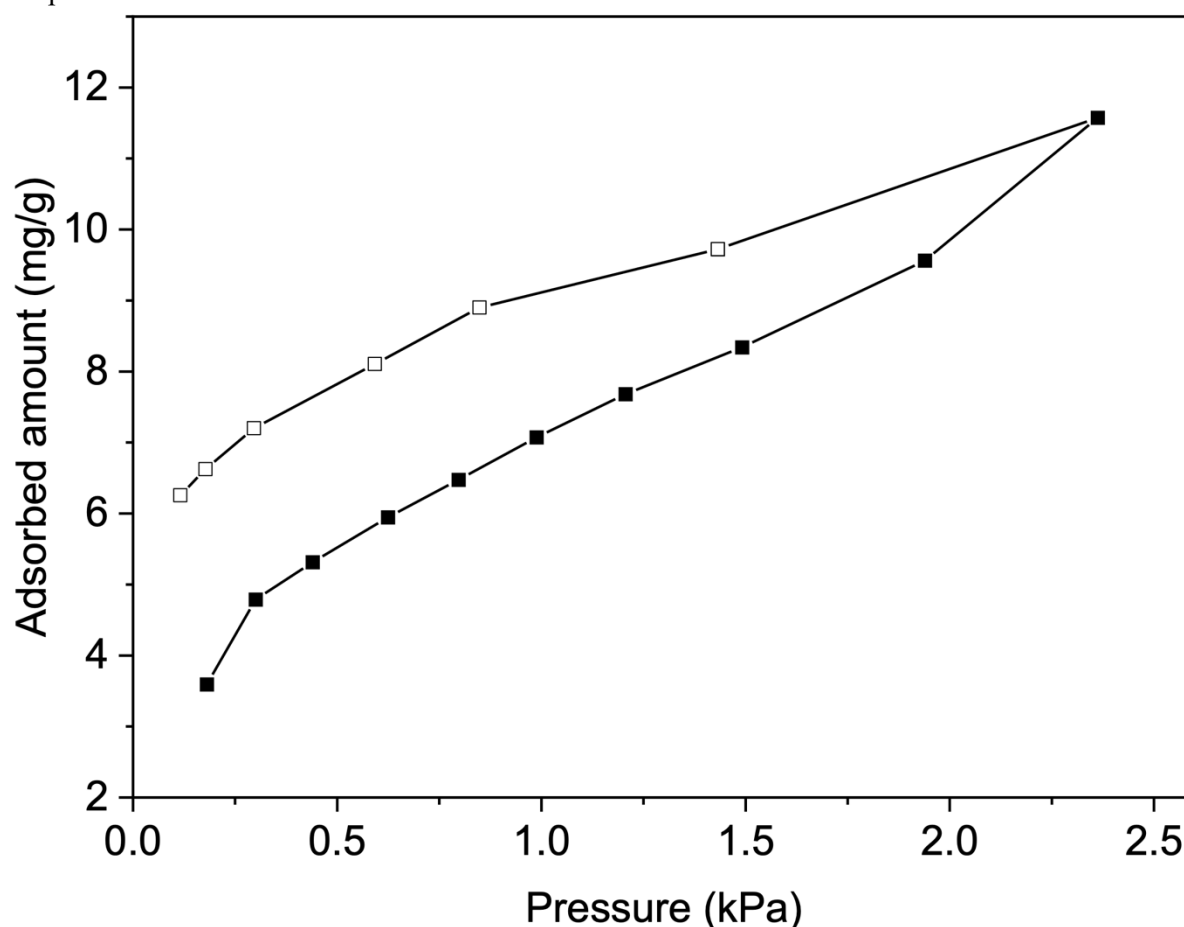


Figure S11. Water sorption isotherm in mg/g at 293 K (filled adsorption, empty desorption).

Water sorption isotherm at 293 K (**Figure S11**) was measured with clearly detectable adsorption and a hysteresis over the whole measurement range. The adsorption isotherm most closely resembles Type II of the IUPAC classification which indicates relatively strong water-surface interactions of a hydrophilic material. [6] The high slope in the intermediate pressure range and the pronounced hysteresis point to additional adsorption in very narrow, water accessible domains that are not detected in nitrogen sorption but become available after removal of water of crystallization. This interpretation is also in line with the crystal structure.

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3.4 Co-Author contributions

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

Abstract:

The reaction of the diprotonated linker precursor in the form of the salt $[\text{H}_4\text{bpe}^{2+}](\text{TFA}^-)_2$ (H_2bpe = 1,2-bis(1*H*-pyrazol-4-yl)ethyne; HTFA = trifluoroacetic acid) with $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in DMF at 75 °C for 9 days led to single crystals of the metal–organic framework (MOF) $[\text{Zn}(\text{bpe})] \cdot 1.8\text{DMF}$ (ortho-**1** · 1.8DMF) (HHUD-5). The compounds crystallize in the orthorhombic space group *Fddd* with rhombic channels, and is a polymorph of the previously reported structure of $[\text{Zn}(\text{bpe})] \cdot 1.2\text{DMF}$ (tetra-**1** · 1.2DMF) that crystallizes in the tetragonal space group *P4₂/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 m²/g (0.77 cm³/g at $p/p_0 = 0.95$) and 1904 m²/g (0.73 cm³/g at $p/p_0 = 0.95$) when an optimized activation is employed (1380 m²/g was reported previously for tetra-**1**). Reaction of the boc-protected linker precursor Boc₂bpe with $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in DMF/water under reflux yielded the MOF $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2(\text{bpe})_6] \cdot n\text{Solv}$ (**2** · *n*Solv, 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 $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2\text{L}_6]$ (L = bis-pyrazolate or carboxylate-pyrazolate) and exhibits a surface area of 1415 m²/g and a pore volume of 0.78 cm³/g at $p/p_0 = 0.80$. The CO₂ uptake at 273 K and 1 bar was 3.99 mmol/g for ortho-**1** and 5.84 mmol/g for **2**; the CH₄ 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 CO₂, and above 6 bar for CH₄, the uptake in ortho-**1** surpasses that in **2** due to the higher surface area of ortho-**1**. Both MOFs show high H₂ 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 CO₂, CH₄, and H₂ 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 $-\text{C}\equiv\text{C}-$ 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 bpe²⁻ linker.

Contributions to the publication:

- Conducted vapor sorption isotherm measurements for various volatile organic compounds (VOCs).
- Review and correction of the final manuscript as co-author

4. Summary

The goal of this work was to establish stable metal phosphonates and phosphonate-based coordination networks as electrode materials for aqueous electrolytes. The materials should operate reliably while still offering tunable redox chemistry. A key objective was to identify framework motifs that remain intact across a broad pH range and in concentrated salt solutions. The work also examined how ion accessibility and redox site density control the pseudocapacitive response. Another aim was to translate chemical robustness into practical electrodes. Where needed, phosphonate phases were embedded in a conductive carbon scaffold to ensure electronic percolation. The contribution of conductive additives was kept as low as possible. To attribute charge storage to the framework, additive blank values were measured and subtracted. Electrochemical testing was combined with phase sensitive post-mortem characterisation whenever feasible.

In the first project, lanthanide-based phosphonate coordination networks were explored using Eu^{3+} , Er^{3+} and Gd^{3+} together with diamantane-4,9-bis(hydrogenphosphonate) as a linker. The work shows that crystalline and structurally well-defined metal phosphonates can be obtained from this linker class under hydrothermal conditions, and it highlights key challenges that are characteristic for phosphonate chemistry, in particular controlled deprotonation and structure directing effects during framework formation. At the same time, the study revealed a practical limitation. Reproducibility, phase purity and scalability were not sufficiently robust to enable systematic functional measurements in the targeted directions of sensing and proton conduction. Nevertheless, the project provided an important methodological outcome. It identified critical synthetic parameters and bottlenecks that govern the transition from structural chemistry to reliable application testing. Based on these insights, the thesis then shifted to redox active Cu, Ni and V phosphonate frameworks, where robustness and function could be evaluated directly as electrode materials for aqueous supercapacitors.

The Cu/V compound, $[\text{Cu}(2,2'\text{-bpy})\text{VO}(\text{O}_3\text{PC}_6\text{H}_5)_2]$, demonstrates that phosphonate frameworks can be both robust and electrochemically active over a broad, practically relevant pH range. The material does not require highly concentrated acid or base to operate. Notably, the solvothermally obtained crystals exhibit unusual mechanical compliance and can exfoliate into thin crystalline sheets while retaining structural integrity upon bending. In mild aqueous electrolytes, the material reaches about 140 F g^{-1} at 1 mV s^{-1} under mildly acidic and mildly alkaline conditions, while charge storage in near neutral electrolyte is kinetically slower, consistent with increased diffusion contributions, as also reflected by impedance analysis. Here, chemical stability refers to phase retention in stirring tests, whereas electrochemical stability is assessed by phase-sensitive post-mortem analyses after cycling under the respective electrolyte conditions. Importantly, this work shows that meaningful stability claims require verification beyond morphology. After extended cycling up to 10000 cycles, Raman spectroscopy, PXRD and SEM-EDX confirm no evidence for major loss of phase identity and elemental distribution, with characteristic diffraction features preserved after cycling at pH 7 and pH 10, supporting genuine phase integrity under these conditions. Complementary stirring tests further support chemical robustness over a wide pH window, with phase purity maintained from pH 2 to pH 12.

In the final work, a new hybrid MOF, $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}[(\text{VO}(\text{H}_2\text{O}))_2(\text{VO})_4(\mu\text{-O})^2(\text{C}^6\text{H}_5\text{PO}_3)^6]^{2-} \cdot 2\text{H}_2\text{O}$, was obtained via a reproducible one pot hydrothermal synthesis. The redox active $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}$ complex forms in situ and is incorporated between anionic vanadium phosphonate layers. This was confirmed by comprehensive analyses using SCXRD, PXRD, XPS,

ICP-OES and measurement of magnetic properties. Temperature dependent PXRD indicates high thermal robustness, with the main reflections retained up to about 300 °C. In aqueous supercapacitor tests, the material delivers competitive capacitance in neutral Na₂SO₄ (pH 7) and acidic H₃PO₄ (pH 4). It maintains stable performance beyond 10000 cycles. The crystals also remain chemically stable for at least one week between pH 2 and pH 10, confirmed by PXRD. Kinetic analysis and impedance spectroscopy reveal a pronounced electrolyte dependence. Charge transfer is most facile in neutral electrolyte. The response is also more surface controlled under these conditions. In acidic and alkaline media, diffusion contributions become more dominant. Interfacial kinetics are more hindered. Overall, these results demonstrate that phosphonate backbones can expand the operational window of MOF like electrodes in water. They also show that electrolyte dependent interfacial kinetics must be addressed through electrode architecture and conductive composites to fully exploit the advantages of the high density of redox active metal centres. Preliminary Li-ion battery tests indicate additional potential of this material, but these results are outside the scope of the present thesis and will be reported separately.

In summary, these results support three conclusions. First, phosphonate coordination networks in aqueous media can combine chemical robustness with tunable redox behaviour. This also applies to nearly neutral salt electrolytes as well as moderately acidic and basic electrolytes, in which many coordination networks and MOFs rapidly decompose or achieve only limited capacity. Second, electrode architecture is crucial for performance. Many phosphonate networks have low intrinsic conductivity, so a conductive carbon framework is often needed to improve charge transport. Future work should therefore focus on developing intrinsically conductive phosphonate MOFs to reduce or completely eliminate the need for conductive additives. Third, reliable statements on stability and mechanism require phase-sensitive testing after measuring a sufficient number of charge/discharge cycles. Whenever possible, Raman spectroscopy, PXRD and/or related methods should be used after measurement, as morphology alone can easily lead to misinterpretation of the active phase.

Overall, this work supports the thesis that phosphonate coordination polymers and phosphonate MOFs are a promising, yet under-explored family of electrodes for supercapacitors with aqueous electrolytes. In particular, it demonstrates their potential in salt solutions and in mildly acidic or basic media. At the same time, it supports more sustainable device concepts because it reduces dependence on highly corrosive acids, bases or organic electrolytes, thereby also increasing safety in applications. Finally, it formulates practical design rules for converting robust crystals into reproducible, device-relevant composite electrodes.

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