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ABSTRACT. Porphyrin based Metal Organic Frameworks (MOFs) have generated high interest for their unique combination of light absorption, electron transfer and guest adsorption/desorption properties. In this study, we expand the range of available MOF materials by focusing on the seldom studied porphyrin ligand H_{10}TcatPP, functionalized with tetracatecholate coordinating groups. A systematic evaluation of its reactivity with M(III) cations (Al, Fe, In) led to the synthesis and isolation of three novel MOF phases. Through a comprehensive characterization approach involving single crystal and powder synchrotron X-Ray diffraction (XRD) in combination with the local information gained from spectroscopic techniques, we elucidated the structural features of the solids which are all based on different

inorganic secondary building units (SBUs). All the synthesized MOFs demonstrate an accessible porosity, with one of them presenting mesopores and the highest reported surface area to date for a porphyrin catecholate MOF (> 2000 m^2 g^{-1}). Eventually, the redox activity of these solids was investigated in half-cell vs Li with the aim at evaluating their interest as electrode positive materials for electrochemical energy storage. One of the solids displayed reversibility during cycling at a rather high potential (~3.4 V *vs.* Li^+/Li), confirming the interest of redox active phenolate ligands for applications involving electron transfer. Our findings expand the library of porphyrin-based MOFs and highlight the potential of phenolate ligands for advancing the field of MOFs for energy storage materials.

Introduction

The ubiquity of carboxylates is prominent in the field of Metal-Organic Frameworks (MOFs), however, alternative complexing groups are also being investigated with increasing interest. Whereas azolates have shown promise when coupled with soft cations of low (typically +2) charge, oxygenated ligands are also appealing for building up new frameworks, especially those based on harder and highly charged (≥ +3) cations. Thus, phenolate derivatives, in particular catecholates (cat^{2-}, 1,2-dioxobenzene) and gallates (gal^{3-}, 1,2,3-trioxobenzene) are of particular interest. This is because of their rather high basicity ($pK_a \geq 9$) and high charge density when fully deprotonated (≤ -2) which could drive the formation of MOFs with higher chemical stability,[1,2] while their non-innocent character is responsible for their unique electronic conductivity, redox activity and magnetic properties,[3–24] leading to potential applications in gas sensing,[25–30] electrochemical charge storage[31–43] and electrocatalysis.[44–47] While molecular and

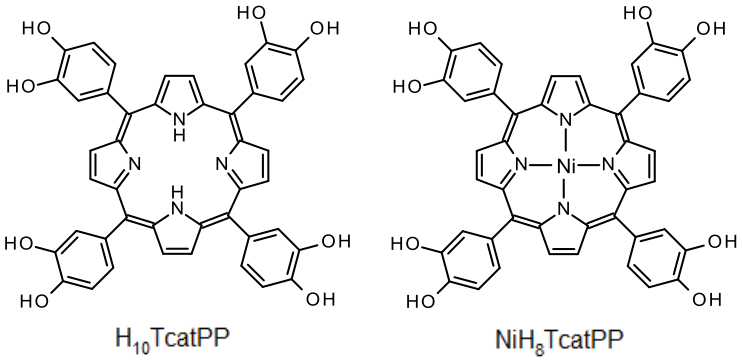
infinite (rod-like) carboxylate-based Secondary Building Units (SBUs) are well documented,[48,49] less diversity is found for MOFs built up with pure catecholate and gallate ligands.

To our knowledge, considering gallate, all but most of the porous structures rely on a single inorganic 1-D motif formulated as $[Zr_2(gal)]_n$,[1,2,50–52] with the exception of a recently reported MOF made of tetrahydroxybenzoquinone (which might be considered as the smallest bis-gallate) and an octameric SBU formulated as $Fe^{III/II}_8(gal)_8$.[53,54]

In contrast, the vast majority of MOFs with catecholate linkers are built up from isolated metal (II, III, IV) ions surrounded by two ($M(cat)_2$ or $M(sq)_2$) or three ($M(cat)_3$ or $M(sq)_3$) ligands[55–68] (with $sq^{-\cdot}$ = semiquinolate, the hemi-oxidized form of catecholate). Only very recently (≥2019), examples of 3-D nets based on of polymetallic phenolate SBUs have appeared in the literature. Regarding molecular SBUs, one can mention the dimeric unit $Zr^{IV}_2(OH)_2(sq)_6$,[69] the trimeric units $Fe^{III}_3(H_2O)_2(cat)_6$[47] and $M^{III}_3O(cat)_3(sq)_3$ (M = Al, Ga, Fe)[70,71] and the hexameric unit $Ln^{III}_6(NO_3)(cat)_6$ (Ln = Y, La, Eu).[22,72] Two MOFs based on rod-like SBUs, $[Bi^{III}_2O(H_2O)_2(cat)_2]_n$[73] and disordered $[Ln^{III}(OH)_{1+x}(cat,sq)_3]_n$[74,75] were also reported. All these SBUs have been yet observed in very few structures, hence their use in designed reticular chemistry is still in its infancy.

For the specific case of functional porphyrin-based MOFs, carboxylate ligands again dominate the field although alternative complexing groups have also attracted interest.[76] As part of our general interest in porphyrin-based MOFs, we focused our attention on tetracatechol porphyrins (H_{10}TcatPP and NiH_8TcatPP), depicted in Scheme 1. Metal catecholates are indeed well suited for redox-active materials and enhanced charge transfer compared to carboxylate-based hybrid compounds.[11,15,22,77] The free-base H_{10}TcatPP was already reported in the literature to produce few poorly crystallized, moderately porous coordination polymers based on different transition

metals (Fe, Co, Ni, Cu, Ti). Nevertheless, none of these solids was structurally characterized.[78–81] We also reported low dimensional supramolecular assemblies (SA) composed of $M^{III}H_7$TcatPP (M = Fe, Mn, In), in which few phenolic oxygen atoms act as terminal ligands to define polymetallic (dimer, tetramer, chain) entities.[82] Eventually, in the course of the present work, a 3-D porous network based on this ligand and Fe^{III} and In^{III} has been reported,[83,84] the proposed structure will be discussed later in this article.



Scheme 1. Chemical structures of the polyphenolic porphyrins H_{10}TcatPP (left) and NiH_8TcatPP (right) used in this work.

We describe here the systematic investigation of the reactivity of both H_{10}TcatPP and NiH_8TcatPP with different M(III) (Fe, Al, In) cations. Optimization of synthesis parameters enables the successful isolation and growth of three porous phases as large single crystals. These MOF are built up from three distinct inorganic SBUs (1D chain, 4-connected dimeric unit and 6-connected trimeric unit) whose formation is closely related to specific experimental parameters. The impact of the key parameters driving the SBU formation is discussed. The crystal structures of the resulting materials have been experimentally determined by both powder and single crystal X-ray diffraction techniques and further corroborated by classical geometry optimization calculations for one of them. Spectroscopic studies (UV-vis, NMR, EPR, Mössbauer) provided valuable insights into the composition and the redox state of each material. Thermal and

chemical stabilities, porosity, electrical conductivity and solid-state redox-activity of the MOFs were also assessed. This significant work not only advances the understanding of reactivity and MOF crystal growth but also broadens the scope of porous coordination network structures accessible for porphyrin-based solids.

Results and discussion

1. Synthesis

Three trivalent cations, namely Al(III), Fe(III) and In(III), presenting markedly different ionic radii (0.535, 0.645 and 0.80 Å, respectively)[85] but known to commonly adopt an octahedral coordination environment when bound to catecholate ligands, were selected. Their reactivity with both free base (H_{10}TcatPP) and Ni(II) metallated (NiH_8TcatPP) porphyrins was investigated. It is important to note the diverse possible outcomes depending on the metal and linker used. In particular, when the free base H_{10}TcatPP is combined with Fe(III) and In(III), metal chelation takes place leading to the formation of metalloporphyrin-based compounds that can be either MOFs or supramolecular assemblies (SAs). The latter ones arise from the axial coordination of a metal atom lying in the porphyrinic core by a catechol(ate) from another porphyrinic ligand. The SA formation is precluded in case of Al(III) as its insertion into the porphyrinic core is incompatible with the synthesis conditions employed here. When combining the nickel porphyrin NiH_8TcatPP with any of the investigated metals, SA formation is hindered due to the inherent square planar geometry of nickel.

The syntheses were explored in both *N,N*-dimethylformamide (DMF) or *N,N*-diethylformamide (DEF), using metal chloride salts, with or without water, initially using the high-throughput solvothermal setup developed by Stock *et al.*[86] The effect of organic (pyrazine

(pz), pyrocatechol (H_2cat)) and inorganic (hydrochloric acid, potassium hydroxide) additives, as well as the reactants concentration, was also investigated. Regarding the formation conditions, it was found that rather high temperatures were favorable for the crystallization of MOFs (140°C and above), that for all metals at least two phases could be isolated, and that the solvent composition was the main parameter controlling this pseudo-polymorphism. Although the associated phase diagram is rather complex, it is possible to qualitatively draw a scheme represented in Fig. 1. Overall, three new MOF phases were identified, initially with NiH_8TcatPP and later obtained with a higher crystallinity starting from H_{10}TcatPP, allowing their structure determination (Ga(III) was also used to solve the structure of one phase, see below). These solids are denoted CatPMOF-1(M) to CatPMOF-3(M) and Ni-CatPMOF-1(M) to Ni-CatPMOF-3(M) depending on the nature of the porphyrin reactant. In addition to the MOF phases, four types of supramolecular assemblies (SA) were isolated in the case of Fe and In, which will not be discussed here in detail.

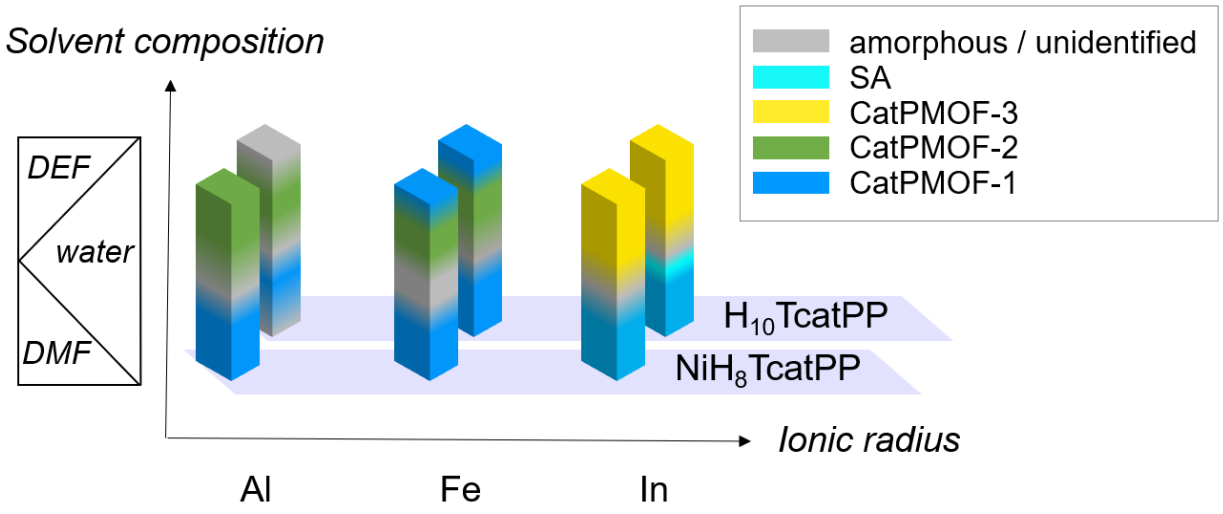


Fig. 1 Qualitative phase diagram in the systems NiH_8TcatPP-M(III) and H_{10}TcatPP-M(III): influence of the nature of the cation and the solvent mixture (for synthesis at 150-160°C).

Solvent as the main phase directing parameter

Although pure formamides could lead to the formation of crystalline phases, addition of water was always found to be favorable. In fact, for all metals, the solvent composition is observed to play a pivotal role in driving the formation of a specific compound. This remarkable solvent-dependent pseudo-polymorphism is particularly well illustrated in the case of In. At a V_{water}/V_{DMF} ratio of 4 and without any additive, a 2D supramolecular assembly (see Fig. S3) is obtained along with indium hydroxide. When pyrocatechol is introduced, a mixture of phase 1: CatPMOF-1and a previously reported 1D supramolecular assembly[82] is isolated under the same solvent composition. Decreasing the V_{water}/V_{DMF} ratio to 1.5 or less results in the formation of pure CatPMOF-1, irrespective to the modulator presence. Pyrocatechol addition turns out beneficial to avoid the co-crystallization of indium hydroxide and to slightly increase the crystallinity of the MOF (Fig. S2). When DMF is replaced by DEF, phase 3 MOF (CatPMOF-3) is isolated in presence of water (V_{water}/V_{DEF} = 1/8), and this holds true with or without pyrocatechol (Fig. S6). These observations highlight the dominant role of the solvent in driving the formation of MOFs. In contrast, the modulator influence is less decisive in terms of MOF phase selection, unlike what is observed for the Zr carboxylate porphyrin-based MOFs series.[87–91]

A similar trend is observed for the harder cations Al and Fe: CatPMOF-1 phase is formed in DMF/H_2O mixtures, but a high proportion of either water or formamide results in the formation of amorphous or unidentified solids. More importantly, the choice of the formamide again has a profound effect on the crystallized phase. While DMF leads exclusively to the formation of phase 1 (in agreement with recent reports[83,84]), its replacement by DEF promotes the formation of phase 2 (CatPMOF-2) based on a very different inorganic SBU and with larger

pores (see below). Overall, this difference in reactivity observed for all the metals in DEF is tentatively attributed to a templating effect of the solvent and/or the presence of a small amount of dimethylamine, which can form helicoidal supramolecular assemblies[92] promoting the formation of MOFs with larger pores.

Optimization of the crystal growth.

The optimized synthesis conditions for each phase are summarized in Supporting Information, together with the corresponding powder X-ray diffraction (PXRD) patterns and the calculated patterns of each phase (Fig. S1). The subsequent discussion focuses on the optimization of crystallinity for each phase. Notably, the addition of pyrocatechol (H_2cat), acting as a modulator (see below), was generally favorable to enhance crystal growth. The discussion is structured in a way to highlight the key synthesis parameters to achieve high crystallinity for each material.

CatPMOF-1(Fe) phase: Effect of temperature and pyrazine additive.

In the case of Fe and H_{10}TcatPP, at the solvent composition V_{water}/V_{DMF} = 4, the synthesis at 120°C leads to the isolation of discrete SA species: either iron porphyrin dimers or tetramers depending on whether pyrocatechol is added to the reactants solution.[82] When, the temperature is raised to 150°C the MOF phase CatPMOF-1(Fe) is formed in presence of pyrocatechol. Thus, lower temperatures (typically 120°C) favor the formation of the low dimensional coordination compounds[82] indicating that while the metalation of the porphyrin core by Fe(III) occurs easily, harsher conditions are required to build the inorganic SBUs. The MOF crystallinity is dramatically increased when pyrazine (pz) is added to the reaction. As shown in Fig. 2, the solid indeed evolves from sub-micrometric aggregates to isolated single crystals of CatPMOF-1(Fe)-

pz upon addition of 3 eq. of pyrazine. This result is in line with our previous findings on carboxylate and tetrazolate porphyrin MOFs,[93,94] where we found that pyrazine (or DABCO, 1,4-diazabicyclo(2.2.2)octane) can act as a bridging axial ligand in phases containing stacked metallated porphyrins, leading to a large increase in crystallinity when the pillar matches the metrics of the inorganic building unit (~6.7-6.9 Å, see structure below).

For CatPMOF-1(Fe)-pz phase, single crystals growth could be optimized by further adjusting the reaction temperature and modulator content. Note that as pyrazine easily coordinates to the iron located inside the porphyrin core, it precludes the formation of SA even at lower temperatures, and CatPMOF-1(Fe)-pz with good crystallinity is obtained from 140°C to 160°C, however a decrease in the crystal quality is observed at 180°C (Fig. 2a and d). The reaction conditions were optimized at 150°C and large crystals (> 100 μm) are obtained by adjusting the modulator content (Fig. 2e).

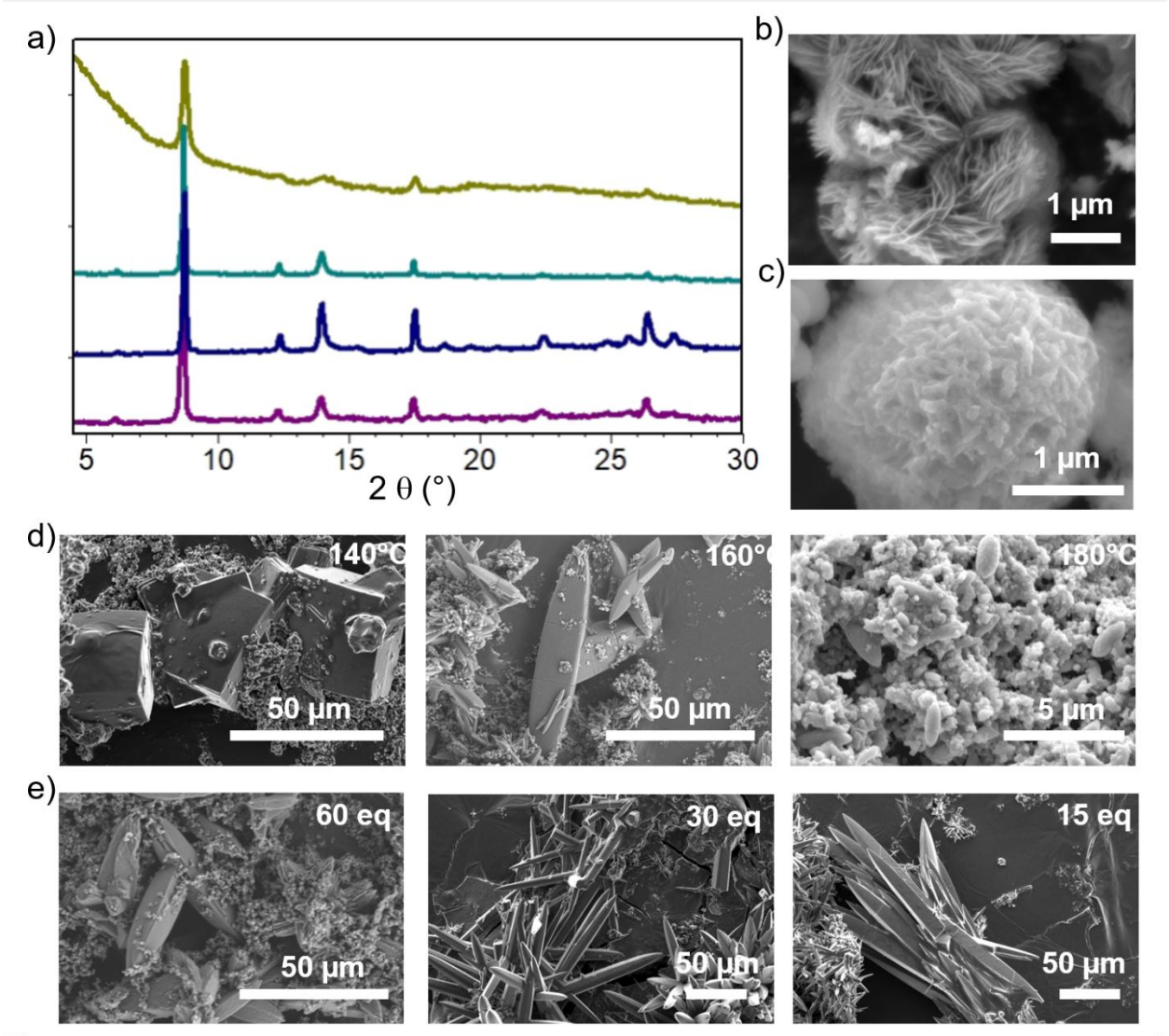


Fig. 2 a) PXRD patterns from top to down: CatPMOF-1(Fe) (synthesis at 160°C), CatPMOF-1(Fe)-pz synthesized at 140°C, 160°C and 180°C. SEM images of b) Ni-CatPMOF-1(Fe); c) CatPMOF-1(Fe); d) the crystal size and morphology evolution of CatPMOF-1(Fe)-pz as a function of temperature with synthesis parameters H_{10}TcatPP/$FeCl_3$/pz/H_2cat = 1/3/3/60, DMF/H_2O 1/4; e) as a function of the H_2cat modulator content at 150°C.

CatPMOF-2(Al) phase: the effect of concentration

In case of Al, two distinct MOF phases can be isolated: namely, CatPMOF-1 and CatPMOF-2, depending on the solvent composition. When using DMF/H_2O mixtures, CatPMOF-1(Al) is formed but with a low degree of crystallinity. In contrast, CatPMOF-2(Al) with good crystallinity can be obtained in a series of DEF/H_2O mixtures (Fig. 3a). The later material growth was meticulously optimized for both the Ni and free base porphyrin precursors and high-quality crystals were successfully obtained.

Regarding the formation of Ni-CatPMOF-2(Al), the addition of pyrocatechol (H_2cat) was found to significantly enhance the quality of crystals. In the absence of H_2cat, thin platelets of submicronic size are recovered, while the addition of 100 eq. of H_2cat leads to the formation of 2-5 micrometer sized thicker platelets. We hypothesize that H_2cat competes with the tetratopic ligand NiH_8TcatPP to bind to the Al and thus acts as a modulator, decreasing the number of nuclei and slowing down the reaction, similar to what is found with monocarboxylic acids in the field of Zr-carboxylate (and to a lesser extent Ti-carboxylate) MOFs.[95] This is supported by the fact that increasing the reaction time from 2 to 8 days in the presence of 100 eq. of H_2cat produces crystals approximately ten times larger (Fig.s 3c). This observation confirms that the H_2cat significantly slows down the crystal growth rate. Steinert *et al.* recently showed that the addition of various monocarboxcylic acids has no significant positive effect on the growth of Al-carboxylate MOFs (at least MIL-160), and attributed this to the relative inertness of such a cation.[96] Given that catecholate presents a stronger affinity for Al(III) than carboxylate,[97] this suggests that in addition to using modulators and ligands with similar binding strength as generally accepted,[50] this binding strength must be high enough to achieve a proper control of the crystal growth.

Even larger single crystals can be grown from the free base porphyrin linker. The growth was optimized in presence of 30 eq. of H_2cat and among the parameters tested, the solution concentration has the most significant impact. As shown in Fig. 3b, lowering twice the concentration allows the crystal size to be increased over twenty times, yielding large (>100 μm) crystals of CatPMOF-2(Al). The reactant concentration affects both nucleation and crystal growth, but its impact on the former is a few orders of magnitude stronger. Therefore, our results indicate that slowing down the nucleation by reducing the concentration is the most effective pathway to increase crystals size and quality in this case. This is different from what is observed for the third isolated phase CatPMOF-3(In) (see below) and is consistent with the higher Lewis acidity of Al compared to In, which makes Al centers more reactive.

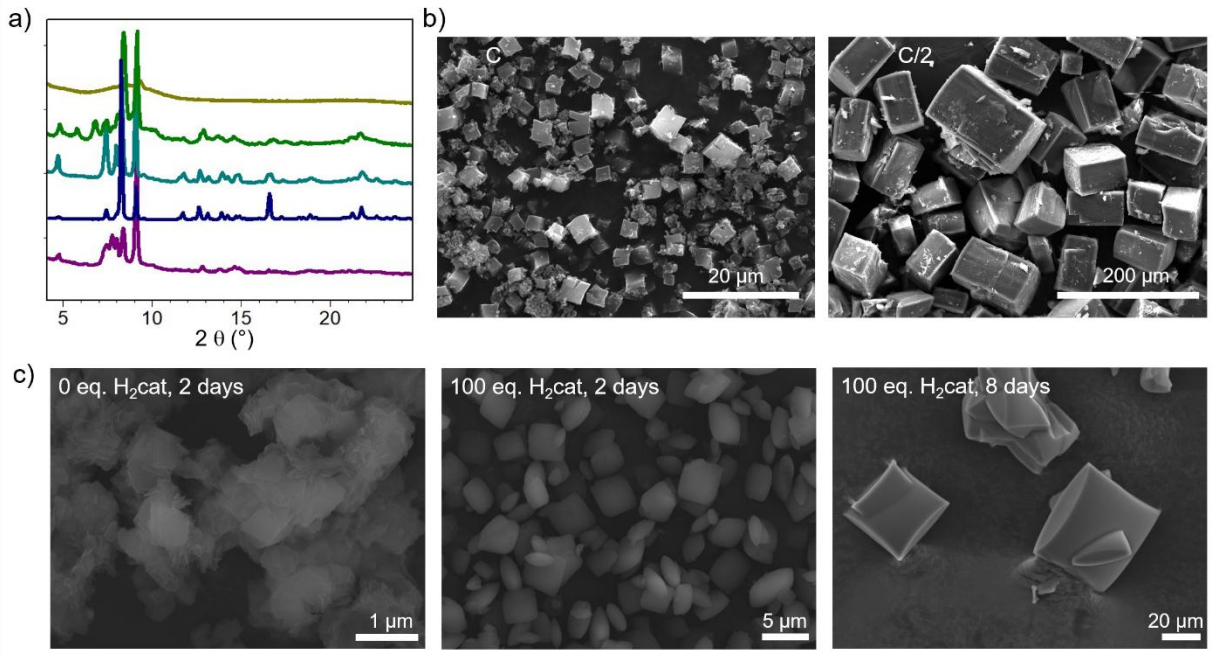


Fig. 3 a) PXRD patterns of the samples synthesized in various solvents; from top to down: pure DEF, DEF/H_2O = 3, DEF/H_2O = 1, DEF/H_2O = 1 and concentration lowered twice, DEF/H_2O = 1/3; b) SEM images of CatPMOF-2(Al): effect of the concentration of reactants; c) SEM images

of Ni-CatPMOF-2(Al): effect of the amount of H_2cat and reaction time (H_{10}TcatPP/$AlCl_3$ = 1/2, DEF, 160°C).

CatPMOF-3(In) phase: the effect of pH

In the case of In, two MOF phases can be formed, as described above: phases 1 and 3 depending on the formamide employed. Among them, CatPMOF-3(In) with a higher crystallinity is isolated in DEF/water mixtures. The pH effect of the aqueous phase was investigated using pure water, 2 M HCl and 2 M KOH solutions. In all cases, CatPMOF-3(In) is isolated as evidenced by PXRD analysis (Fig. S6), however the pH has a strong influence on the crystal growth as it is observed from the SEM images (Fig. 4). Under basic conditions sub-micronic hexagonal platelets or needles are obtained whereas neutral or acidic conditions result in the growth of hexagonal rods. This demonstrates that the pH strongly influences the morphology and particularly the aspect ratio of the crystals. By acidifying the reaction, the deprotonation of the catechol is hindered which likely results in a slower metal coordination and MOF nucleation and growth. This change in reaction kinetics influences the growth process. Without modulator, a rapid coordination reaction at basic pH leads to lateral crystal growth in form of platelets when a slower coordination reaction results in elongated morphologies of hexagonal rods. The addition of H_2cat, particularly for a high pH aqueous solution, has a significant influence on the crystal shape as the introduction of 30 eq. results in the formation of needles instead of platelets. This can be attributed to the coordination of pyrocatechol to In which retards its release in solution and consequently promotes crystal growth with higher aspect ratio crystals. This observation is in line with the growth behavior observed for layered metal hydroxides, where a controlled release of metal ions through complexation equilibrium facilitates the growth in the stacking direction resulting in high aspect ratio crystals.[98] Overall, optimizing the crystal growth by

maintaining a low pH and introducing the modulator allows to isolate CatPMOF-3(In) single crystals with lengths of up to 100 μm. This example highlights the significance of pH and coordination modulation role to tune both the shape and size of crystals without altering the phase formation.

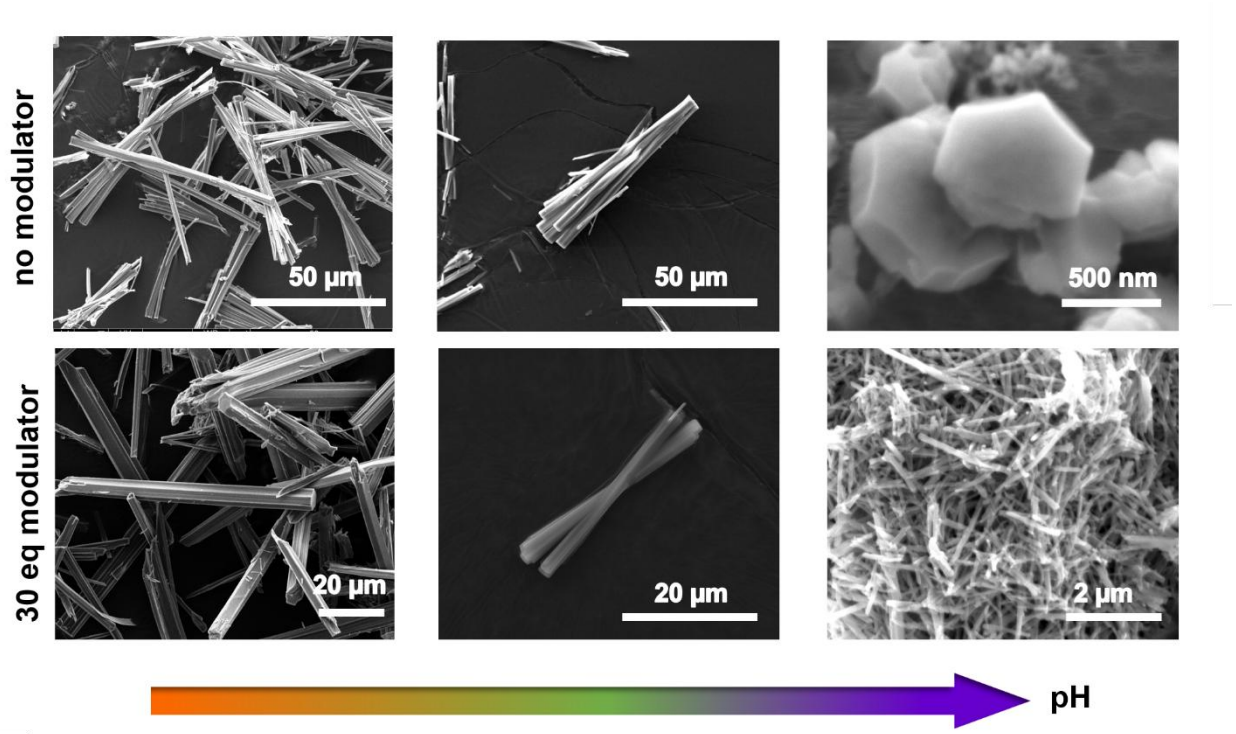


Fig. 4 Morphology evolution of CatPMOF-3(In) crystals due to the pH variation of water solution (left 2 M HCl solution, middle pure water, right 2 M KOH solution), synthesis conditions: H_{10}TcatPP/$InCl_3$/H_2cat = 1/2/0 (top) and 1/2/30 (bottom), DEF/aqueous solution = 4/0.5, 150°C, 2 days.

To conclude, three different crystalline phases are formed and isolated under closely related synthetic conditions. The size of the cation seems to be important: when using DEF-water mixtures as a solvent, CatPMOF-2 phase is found with the smallest cations (Al, Fe and in case of Ga, see below), whereas the largest cation (In) gave rise only to CatPMOF-3 phase under similar

experimental conditions. With DMF-water mixture, CatPMOF-1 phase is observed for all cations. The pseudo-polymorphism observed here is reminiscent of that described for the Zr(IV) / tetrakis(4-carboxyphenyl)porphyrin (TCPP) system, for which several phases (MOF-525, MOF-545/PCN-222, PCN-225, NU-902, PCN-224) also exist in a narrow range of experimental conditions.[87–91] Nevertheless, they are all based on the same Zr_6 unit, although presenting different connectivities (from 12 to 6). In the present study, as described below, the three phases are based on very different SBUs. Although it might be challenging to use the knowledge acquired here to *a priori* fully design new MOFs from other polycatechol linkers, the formation of one SBU vs. the other seems to be mainly driven by the nature of the solvent mixture. Hence, there is certainly great potential for discovering new compounds based on one of the SBUs identified in this study by using related synthesis conditions. Moreover, all the polyphenolate phases obtained in this work present a remarkably high degree of tunability in terms of crystallites morphology and size. Functional materials properties are often related to their morphology and crystallite size and our study contributes to the advancement of crystal growth control strategies, which are highly relevant in materials chemistry.

2. Structure and materials chemical composition determination

As shown above, crystal of hundreds of microns of phase CatPMOF-1(Fe)-pz, CatPMOF-2(Al) and CatPMOF-3(In) were successfully obtained. Their structures were accessed by using synchrotron radiation (beamline Cristal at Soleil, France) combining high resolution powder and single crystal XRD (PXRD and SCXRD, respectively), with the help of local information gained from solid-state UV-visible absorption spectroscopy, EPR, liquid and solid-state NMR spectroscopy (phases 2 and 3) and Mössbauer spectrometry (phase 1) as detailed below. It should

be noted that although the crystals were rather large (for synchrotron radiation), structure determination was not straightforward, and final refinement required several restraints on interatomic distances even during the last stages. For this reason, the following discussion focuses on the nature of the building units and topologies, while accurate analysis of the local geometry (bond distances and angles…) would be irrelevant.

CatPMOF-1(Fe)-pz

SCXRD and PXRD analyses revealed the same *I* centered tetragonal unit-cell ($a \sim 20.35$, $c \sim 6.70$ Å). In the *I*4 space group, the Fe metallated porphyrin core, as well as one pyrazine molecule, were easily located. The porphyrin cores are stacked in an eclipsed manner, and bound to each other through pyrazine molecules bridging the Fe(II) ions, which then present an octahedral coordination environment (Fig. 5a). This structural feature was already observed in other porphyrin carboxylate and azolate MOFs,[93,94] and explains the strong beneficial impact of the addition of pyrazine on the crystallinity of phase 1 as described above. The full metalation of the ligand was also confirmed by solid-state UV-vis absorption spectroscopy (see Fig. 6).

More surprisingly, although residual electronic density was detected near the phenyl arms of the ligand, the heavy Fe cations building the SBU could not be located even using synchrotron datasets and lowering the symmetry. This suggests the occurrence of a complex crystal structure with odd cation environment, as confirmed by Mössbauer and EPR studies (see below). Solids presenting a PXRD pattern similar to that of CatPMOF-1(Fe)-pz were reported in two recent articles. However, in these cases synthesis was carried out without pyrazine, hence the local environment of the cation embedded in the porphyrin is different. Daliran *et al.* first suggested a structure isotopic to MOF-1992, a MOF made from the related phthalocyanine (Pc)

tetracatecholate ligand.[84] This seems very implausible considering that the symmetry of Pc and the related porphyrin are markedly different. Another structural model in a similar tetragonal unit cell, but in the *P*4*mm* space group was recently proposed by Cheng *et al.* for materials built up from CoTcatPP and M(III) = In, Fe.[83] The proposed structure formulated M_2(CoTCatPP) was generated by removing 1/3 of the O atom of the porphyrin tetragallate MOF MIL-173[2,51] and further refining. This leads to a 3-D structure with channels of ~6 Å free diameter running parallel to the porphyrin stacks. The position of the porphyrin is consistent with our findings and seems to agree with Fe EXAFS data, while the asymmetry observed on the provided Mössbauer spectrum suggests the occurrence of at least two distinct Fe sites, which is inconsistent with the proposed model. Eventually, the coordination sphere of Fe (or In) is astonishing: although quoted octahedral, the 6 coordination environment of the cation is extremely distorted (see Fig. S4). A systematic analysis of the structure using the software SHAPE, which allows a quantitative analysis of the coordination environment,[99–101] indicates that the environment of Fe or In proposed in the above model does not match with any of the crystal structures of In and Fe catecholates reported to date, suggesting that the coordination sphere of the cation is not properly described (see Supporting Information, Table S2 for details).

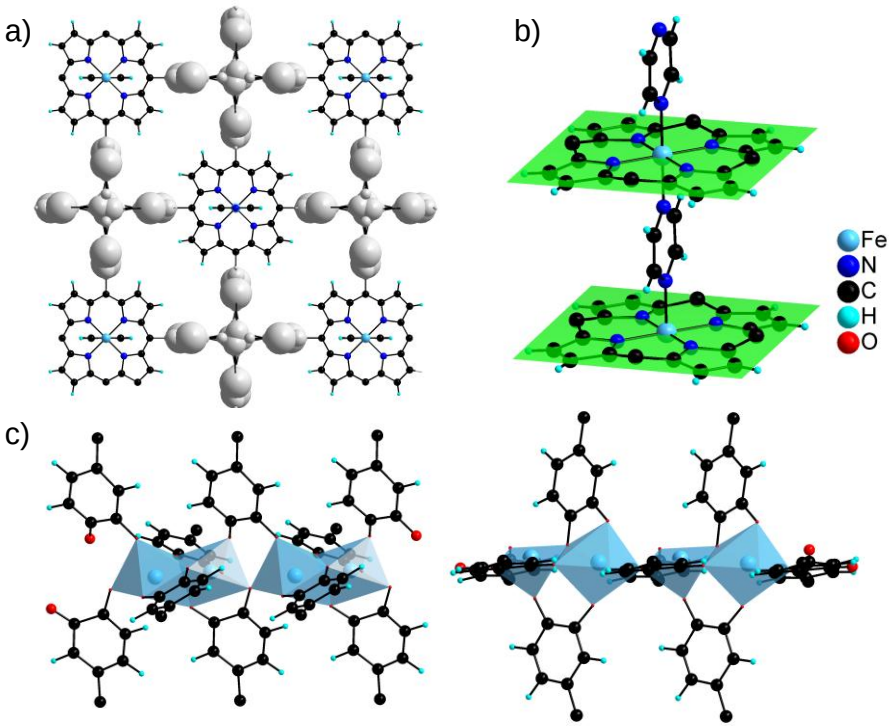


Fig. 5 Structural model of CatPMOF-1(Fe)-pz. a) Result of the SCXRD analysis, with the residual electronic density shown in grey; b) Fe(II) porphyrin cores connected through pyrazine molecules; c) model of the defective SBU obtained from classical geometry optimization calculations, with the presence of both FeO_6 and FeO_5 motifs.

The fact the SBUs are not detected by XRD suggests that the positions of the Fe atoms poorly correlate with those of the porphyrin core. This could arise from the free rotation of the catechol ring, which gives rise to a number of conformers for the ligand, and thus numerous possible positions for the cation, independently of that of the porphyrin macrocycle. Additional analyses were thus carried out to try to get a better description of the SBU in CatPMOF-1(Fe)-pz. First, exact amount of Fe was evaluated by TGA analysis and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) after dissolving the solid in an acidic aqueous medium. From the TGA data the amount of Fe per porphyrin was evaluated to give a value of 2.6 +/- 0.1. Given that 1 Fe is located inside the porphyrin core, this analysis indicates that the SBU is composed of

1.6 +/- 0.1 Fe per porphyrin (instead of 2 if the SBU was built up of continuous chains). The amount of defect was found to be independent on the metal-to-porphyrin ratio used in the synthesis, suggesting that it is truly intrinsic to the structure (see Fig. S9 and Table S3). Furthermore, ICP analysis of the activated solid shows that it contains 13.4(4) wt% of Fe (see Fig. S10), which is in good agreement with the TGA data as it corresponds to 2.65 Fe per porphyrin. Combining these results, it is possible to propose the formula $Fe^{III}_{x}(DMA)_{(8-3x)}[Fe^{II}(Pz)(TcatPP)]$ (DMA = dimethylammonium), with x ~1.6). Hence, when compared to the aforementioned structure model, the SBU holds ~ 20% of defects.

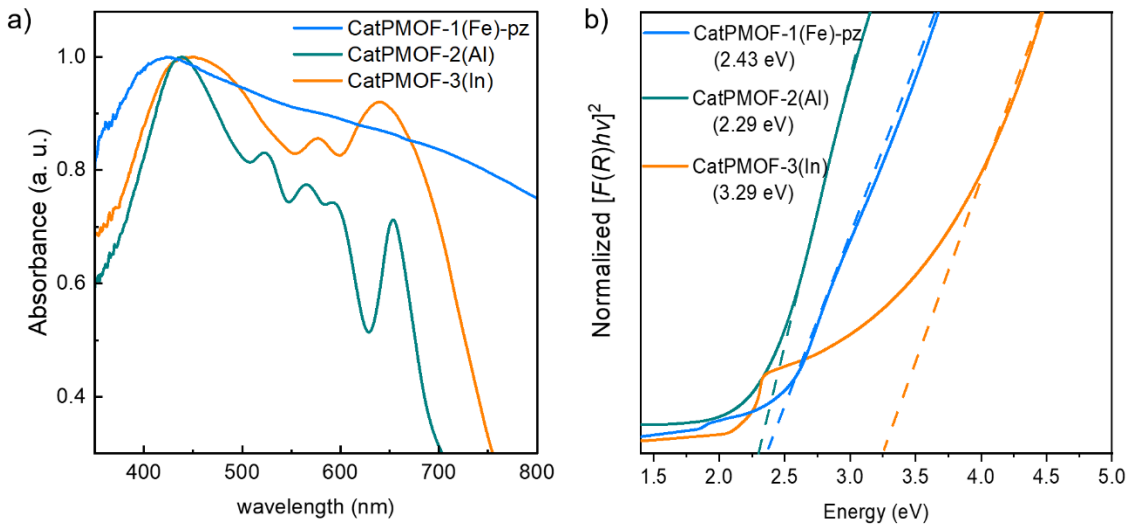
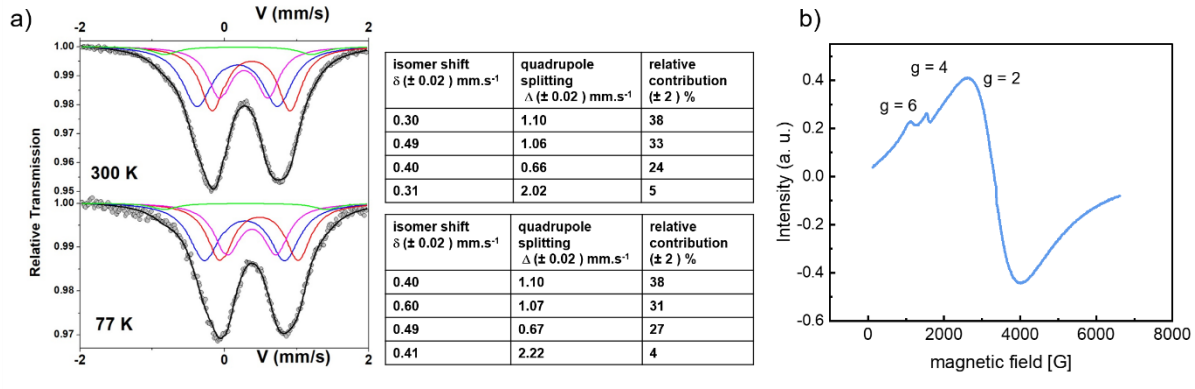


Fig. 6 Solid-state UV-visible absorption spectra (a) and normalized Tauc plot of the Kubelka–Munk-transformed data (b) for CatPMOF-1(Fe)-pz, CatPMOF-2(Al) and CatPMOF-3(In). Dashed lines indicate linear fits to the absorption onsets (b).

Considering that the position of the porphyrin core found by XRD is accurate, classical geometry optimization was used to build up a reasonable model of the inorganic SBU for M = Fe. Whatever the starting point, no chain based on reasonably distorted Fe octahedra could be

obtained. Relaxation of various models rather suggests that some defects along the inorganic "chains" are mandatory to achieve a reasonable environment (in terms of geometry) for all Fe cations, and that both 6-fold and 5-fold connected Fe cations are present (Fig. 5c). This model is supported by a deeper analysis of the Mössbauer and EPR data. Mössbauer spectra of activated CatPMOF-1(Fe)-pz at 77 and 300 K are shown Fig. 7a. The lack of resolution of Mössbauer spectra, which show complex hyperfine structures with broadened and asymmetric lines, leads to a large number of solutions, and fitting requires certain assumptions. Assuming that the porphyrinic core is coordinated to low spin (LS) Fe(II) ions as observed in other MOFs containing the same porphyrin-pyrazine-Fe motif,[93,94] the spectrum can be fitted with four main contributions, one LS Fe(II), and three contributions accounting for high spin (HS) Fe(III) species. The LS Fe(II) content represents about 38% of Fe species, which is consistent with the quantitative results from the TGA and ICP-AES analysis (1 LS Fe(II) in the porphyrin core for a total of 2.6 +/- 0.1 Fe). The HS Fe(III) species need three different components to be fitted correctly (Fig. 7), clearly indicating the presence of several Fe sites in the SBU. The main Fe(III) species is deconvoluted with an isomer shift (δ) of 0.60 mm s^{-1} at 77 K, compatible with octahedral geometry and at the upper limit δ value for HS Fe(III), suggesting some extent of electron delocalization from the catecholate to the Fe(III) sites. The second Fe(III) site is fitted with a δ of 0.49 mm s^{-1}, consistent with HS Fe(III), and a minor contribution representing 5% of Fe(III) is obtained at δ = 0.41 mm s^{-1} with a large quadrupole splitting of 2.22 mm s^{-1} indicating a highly asymmetrical site. The deconvolution of the Mössbauer spectra to these 4 components leads to a good fit at both 77 and 300 K indicating that the proposed analysis is physically representative of the sample. The complexity of the Fe(III) signals reflects the difficulty to properly disclose the SBU from diffraction data and is attributed to the presence of both terminal

Fe (next to the vacant sites), isolated Fe (minor signal) and Fe surrounded by other Fe atoms. Eventually, EPR analysis (Fig. 7b) confirmed the presence of a majority of inorganic unpaired electrons, in agreement with the presence of HS Fe(III) and a negligible amount of organic radicals. Again, the deconvolution of the spectrum suggests the presence of 3 different types of Fe (III) at g = 2, 4 and 6.



isomer shift δ (± 0.02) mm.s^{-1}	quadrupole splitting Δ (± 0.02) mm.s^{-1}	relative contribution (± 2) %
0.30	1.10	38
0.49	1.06	33
0.40	0.66	24
0.31	2.02	5

isomer shift δ (± 0.02) mm.s^{-1}	quadrupole splitting Δ (± 0.02) mm.s^{-1}	relative contribution (± 2) %
0.40	1.10	38
0.60	1.07	31
0.49	0.67	27
0.41	2.22	4

Fig. 7 a) Mössbauer spectra of CatPMOF-1(Fe)-pz at 330 and 77K and the respective deconvolutions; b) EPR spectra of CatPMOF-1(Fe)-pz at 120 K.

To conclude, this structural model made of ordered porphyrin cores and disordered 5- and 6-fold coordinated Fe(III) defining fragments of chains is in better agreement with the experimental spectroscopic data that the fully ordered model mentioned above, and thus seems to better describe CatPMOF-1(Fe)-pz. Nevertheless, on the Fourier difference map obtained by comparing the synchrotron PXRD pattern with this model, residual electronic density located along the chain axis is still detected, suggesting that the real inorganic motif is even more complex. Eventually, the presence of a poorly defined inorganic SBU might arise from the fact that the whole molecule has a low symmetry, whereas its core is highly symmetrical. Indeed, when switching to the more symmetrical tetragallate porphyrin ligand and the closely related crystal structure of MIL-173, this issue does not occur.[2,51]

CatPMOF-2(Al)

First single SCXRD and PXRD synchrotron analyses of CatPMOF-2(Al) suggested a tetragonal unit-cell ($a \sim 21.59$, $c \sim 39.23$ Å), but it was impossible to identify a proper space group and further a structural model. Nevertheless, for the Ga analogue, a splitting of specific Bragg peaks was identified by PXRD, which agreed with an orthorhombic unit-cell, with almost equal *a* and *b* parameters in the unit-cell (see Fig. S5). This lower symmetry was then used to re-index the data for CatPMOF-2(Al), and led to the $P2_12_12_1$ space group. The structure was eventually solved in this space group for CatPMOF-2(Al), and also refined for Ni-CatPMOF-2(Ga). Both compounds present similar structures and hence only CatPMOF-2(Al) is described.

The asymmetric unit contains four independent Al cations and two porphyrin molecules. All the Al cations adopt an oxygenated distorted octahedral environment (SHAPE indexes are < 2 for an octahedron, and >12 for other geometries), with Al-O distance ranging from 1.77(2) to 1.99(2) Å. Specifically, no significantly elongated Al-O distance was detected, suggesting that the catechol moieties are fully deprotonated. Each Al cation is surrounded by two chelating catecholates, and they assemble into edge-sharing dimers through two bridging-chelating catecholates and one bridging formate coming from the degradation of DEF (Fig. 8a). The ^{27}Al solid-state magic-angle spinning (MAS) and 2D multiple quantum MAS (MQMAS) NMR spectra are shown Fig. S11: two distinct signals of similar intensities with chemical shifts indicative of AlO_6 are detected, supporting an SBU composed of two distinct Al octahedra. The quadrupolar coupling constant is 5.6 MHz (asymmetry parameter 0.3) for the $Al^{[6]}$ at 25 ppm. The second $Al^{[6]}$ is deconvoluted with a Gaussian line, indicating local disorder around the second type of Al atoms. Note that an additional minor signal (~10%) characteristic of

pentavalent AlO_5 unit is detected, which could arise from the partial departure of the formate ion. The SBUs are surrounded by four catecholates, and act as distorted square planar motifs (Fig. 8a right). To the best of our knowledge, a single related compound was reported to date, namely a molecular complex based on Fe(III) and pyrocatecholate formulated $(pip)_3Fe_2(cat)_2(Ac)$ (pip = piperidinium, ac = acetate), which was formed in very different synthetic conditions.[102,103] Regarding the organic part, the porphyrin is found to be non-metallated, in agreement with the solid-state UV-vis absorption spectrum which presents typical Q bands of free-base porphyrin, indicating that the porphyrin core is neither fully protonated (Fig. 6).

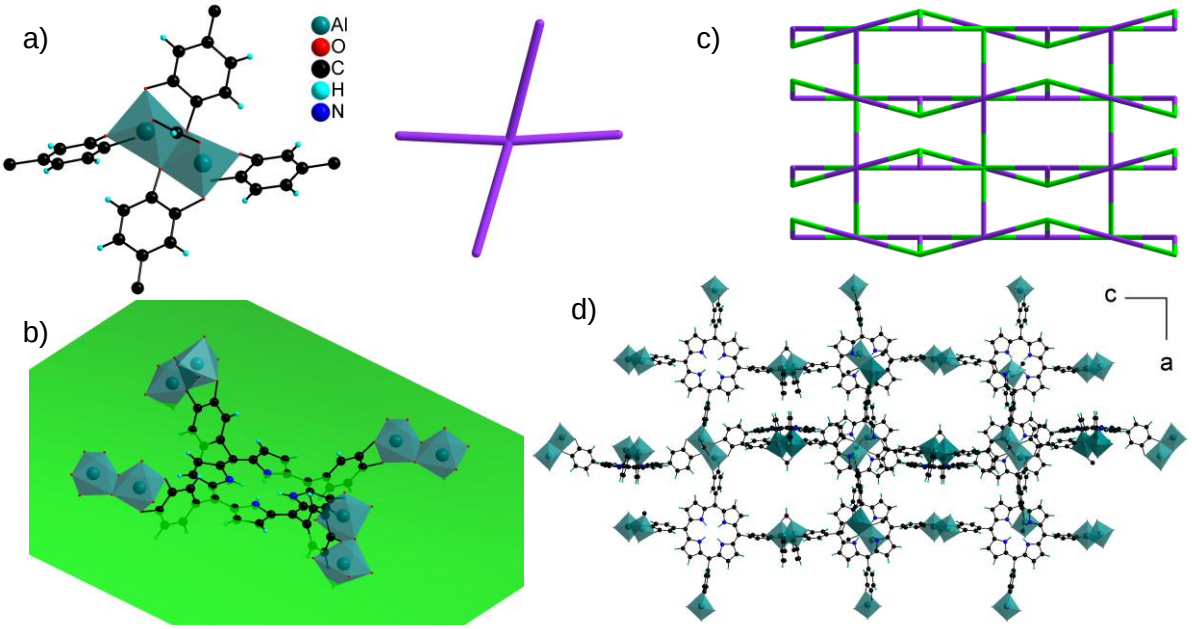


Fig. 8 Crystal structure of CatPMOF-2(Al). a) Inorganic SBU (left) acting as a distorted square planar node (right); b) H_2TcatPP ligand, with the mean plane of the macrocycle shown in green; c) **cds** net (the ligand and the inorganic SBU are shown in green and violet, respectively); d) full structure shown along the b axis.

The macrocycle is rather flat (mean plane shown in Fig. 8b), with all the catecholate units pointing towards the same face of the plane. The ligand then acts as a second distorted square

planar motif, giving rise when combined to the inorganic SBU to a 3-D net presenting the **cds** topology with the point symbol $\{6^5.8\}$ (Fig. 8c). This gives rise to a tortuous 3-D pore network with large apertures (~6x14 $Å^2$) along the a and b directions (Fig. 8d).

In order to evaluate the potential oxidation of the catecholate groups, EPR analysis was carried out on fresh and activated samples. A signal characteristic of an organic radical was detected (Fig. S14), but accounts for less than 0.1 and 2% of the porphyrin unit for fresh and activated solids respectively, indicating that the catecholate units are almost exclusively in the reduced, dianionic state. The framework is thus negatively charged, with the general formula $[Al_2(formate)(H_2TcatPP)]^{3-}$. In attempt to identify the counterions accounting for the charge balance, solution NMR study was performed by dissolving a dry activated solid in *d6*-DMSO containing a small amount of concentrated HCl solution. The ^1H NMR spectrum in Fig. S12 clearly displays a quartet and triplet signals at 2.86 and 1.13 ppm respectively that are assigned to the ethyl groups of diethylammonium (DEAH) cations originating from the decomposition of DEF solvent during the synthesis course. The integration of these signals gives an approximate number of 3 DEA cations per porphyrin, agreeing well with the MOF molecular formula and charge balance. Moreover, a singlet at 8.1 ppm is assigned to the formate anion originating from the DEF decomposition with its integration giving approximately one formate per porphyrin, here again agreeing well with the molecular formula proposed from single crystal structure resolution. Both the presence of DEAH and formate was further confirmed by ^{13}C NMR (signals at 11.67 (CH_3), 42.35 (CH_2) and 164 ppm (C=O), see Fig. S13). Phase 2(Al) can then be positively formulated $[Al_2(formate)(H_2TcatPP)](DEAH)_3$.

CatPMOF-3(In)

Crystals were found to poorly diffract even using SCXRD synchrotron radiation. It was nevertheless possible to determine a trigonal cell (a ~ 27.63, c ~ 29.84 Å) and the space group ($P3c1$), which were also further confirmed by PXRD analysis. Heavy atoms (In, Cl) were localized, as well as few oxygen atoms and the central part of the porphyrinic ligands, while catecholate arms were added applying severe constraints to reach convergence of the refinement. The structure was also refined against PXRD for Ni-CatPMOF-3(In), giving rise to similar results.

The structure of CatPMOF-3(In) consists of two independent In cations building the inorganic SBU, and one metallated porphyrin. Both In ions defining the inorganic motifs adopt a distorted octahedral coordination sphere (SHAPE indexes are < 6 for an octahedron, and >10 for other geometries) with In-O distances ranging from 1.95 to 2.39 Å, with five O atoms arising from catecholate moieties (one chelating, one bridging-chelating, one bridging), and one from a μ_3-oxo unit. The octahedra share two edges to define a trimeric SBU surrounded by six catecholate groups (Fig. 9a, left) and adopting an octahedral geometry (Fig. 9a, right). This trimer has already been identified in the molecular complex $H_2Ti_3O(cat)_6$,[104] and more recently in the Al and Ga MOFs CAU-42 and the Fe analogue.[70,71] It obviously differs from the well-known M(III/II)-carboxylate trimer found in numerous MOFs (MIL-100, -101...), which consists of corner-sharing MO_6 octahedra forming a trigonal prismatic SBU. An additional In ion is found in the porphyrin core, lying slightly above the macrocyclic ring. It adopts a square pyramidal coordination environment, with the last position occupied by a chloride ion; as a result, the porphyrin core has a zero net charge. This metalation was again confirmed by solid-state UV-vis absorption spectroscopy (Fig. 6). As found in CatPMOF-2(Al), all catecholate moieties point towards the same face of the mean plan of the porphyrinic core (Fig. 9b). The combination of the

organic and inorganic moieties leads to a 3-D network with large channels (up to ~ 20 Å) running along the *c*-axis direction, with the porphyrin ring aligned with the pore axis (Fig. 9d). From a topological point of view, the structure presents a **stp** net with point symbol $\{4^4.6^2\}3\{4^9.6^6\}2$ (Fig. 9c). This net, has been reported in the MOF PCN-600 based on porphyrin tetracarboxylate and M(III/II) timers,[105,106] and is usually built up from square planar 4-fold nodes and trigonal prismatic, rather than octahedral, 6-fold nodes. Nevertheless, the distortion of the square planar motif coming from the loss of the planar symmetry of the porphyrin unit mentioned above, accommodates the change of symmetry of the inorganic node to ultimately build up the same network (see Fig. S10). EPR analysis was again carried out on the fresh and activated samples to quantify the amount of oxidized catecholate (Fig. S17). Organic radicals were found to account for less than 1 and 2% of the catecholate respectively, indicating that these later are very predominantly in a reduced state. To check the bulk sample composition solution NMR analysis was performed by dissolving CatPMOF-3(In) in d_6-DMSO containing a small amount of concentrated HCl solution. Similar to the case of CAtPMOF-2(Al), DEA signals are clearly visible on the ^{1}H and ^{13}C NMR spectra (Fig. S15) that integrate for about 3.5 DEA ions per metalloporphyrin. In this case, no other molecular components such as formic acid are detected by solution NMR in conformity to the proposed structure. Eventually, the absence of carbonyl signals on the ^{13}C NMR spectrum rules out ligand oxidation (Fig. S16), and the compound can be safely formulated $[In_3O(InClTcatPP)_{1.5}](DEA)_5$. This suggests that the catecholate moieties are fully deprotonated, in contrast to the study by Boyle *et al.* on the molecular compound $Ti_3(O)(cat)_4(Hcat)_2$,[104] and fully reduced contrary to the case of CAU-42 where the trimers are formulated $M_3O(cat)_3(sq)_3$ (M = Al, Ga).[70]

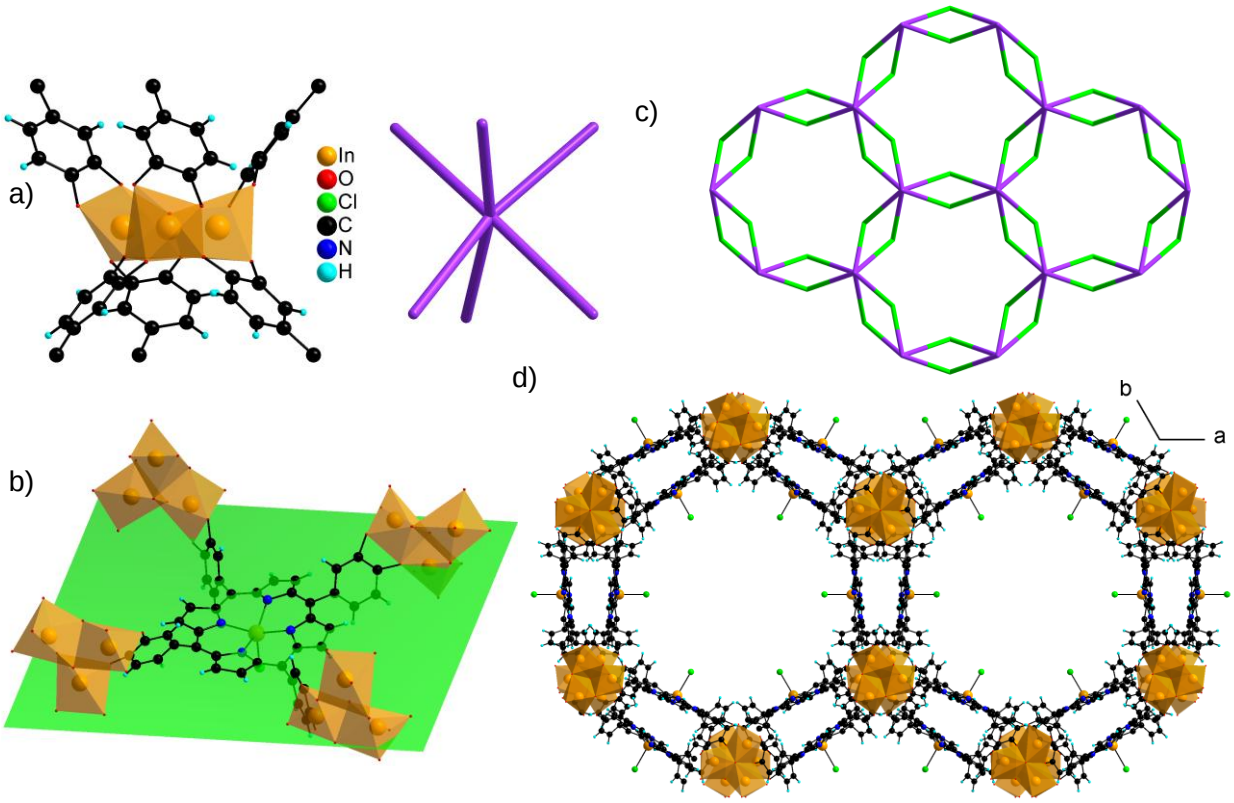


Fig. 9 Crystal structure of **3(In)**. a) Inorganic secondary building unit (left) acting as a distorted octahedron (right); b) InClTcatPP ligand surrounded by four inorganic SBUs, with the mean plane of the macrocycle shown in green; c) distorted **stp** net (the ligand and the inorganic SBU are shown in green and violet, respectively); d) full structure showing the channels running along the *c*-axis.

Overall, the structural characterization of the new porphyrinic MOF phases presented significant challenges, demonstrating the necessity of employing comprehensive approach that integrates both single crystal and powder diffraction techniques complemented by spectroscopic analysis. Specifically, the structure determination of CatPMOF-2(Al) critically relied on PXRD to accurately determine the unit cell parameters and detect the orthorhombic symmetry, without which the single crystal data could never have led to the structural model. Moreover, the major impact of the pore content on PXRD data hindered the achievement of a complete structural

model through this technique alone, requiring information gained from single crystal diffraction and spectroscopic analysis (in case of Ni-CatPMOF-2(Al), Ni-CatPMOF-2(Ga) and Ni-CatPMOF-3(In)). In summary, three MOF structures based on different SBUs were obtained. While molecular SBUs, analogous to those found in molecular compounds were obtained for MOFs in DEF, the solids prepared in DMF exhibited highly disordered, defective chain-like motifs. Furthermore, the larger DEF solvent and DEA derivative, which is known to form supramolecular assemblies, seems to favor the formation of larger pores, with non-stacked porphyrin units, possibly through a templating effect.

3. Porosity, thermal and chemical stability

The thermal stability of the three phases was evaluated by temperature dependent powder XRD, both under air and nitrogen (Fig.s S19 a and b, respectively). For CatPMOF-3(In), when the experiment is carried out in air, a first peak broadening is observed between 30 and 40°C. From 40 to 130°C, the patterns are almost unchanged, while above this temperature a rapid loss of crystallinity is observed. Both CatPMOF-1(Fe)-pz and CatPMOF-2(Al) do not present any transformation at low temperature, but show a similar thermal stability, whith a loss of crystallinity starting at ~130°C in air. Hence, the three compounds present a moderate thermal stability in air, significantly lower than that of standard porphyrin carboxylate MOFs. This behavior, which was already observed in other phenolate-based MOFs,[107,50,70,108,83] likely relates to the easier oxidation of the ligand. This is supported by the fact that the three solids present a significantly higher thermal stability under nitrogen: as shown Fig. S19b, all solids remain crystalline up to 170-190°C, and the transformation observed for CatPMOF-3(In) at 40°C in air is not present anymore.

The chemical stability of the three phases was also evaluated after activation, upon storage in air and suspended in water. As shown Fig.s S20-S23, all the compounds preserve their crystallinity upon activation. Although EPR analysis reveal an increase of radical species (at least for CatPMOF-2(Al) and CatPMOF-3(In)) after activation, the relative amount of these radicals remains very low (less than 2% of porphyrinic linkers). When EPR measurement was repeated on fresh and activated compound CatPMOF-3(In) after 9 weeks, no evolution of the signal was observed, evidencing that the solid is not further oxidized when left in air at room temperature (Fig. S17), unlike the previously reported behavior for few M^{3+}-catecholate MOFs,[22,70] suggesting that the sensitivity of these solids towards air oxidation is ligand dependent. Indeed, when compared to fully conjugated polycatecholate ligands such as hexahydroxytriphenylene (HTTP), the redox potential of the $H_{10-n}TcatPP^{-n}$ is expected to be higher, leading to a lower sensitivity to O_2 oxidation.

When the solids were exposed to air for several days, no drastic changes of the PXRD patterns was detected for both CatPMOF-1(Fe)-pz and CatPMOF-2(Al) (Fig. S20). On the opposite, the crystallinity of the mesoporous PMOF-3(In) decreased, with a complete amorphization detected after 8 days. The main parameter driving this difference of stability is likely the pore size, as already observed in the field of M(III,IV) carboxylates MOFs.

When suspended in water for 24 hours (2.5 mg mL^{-1}), none on the solids retains its crystallinity (Fig. S21-S23). This result differs from previous findings from Chen *et al*., showing Co-CatPMOF-1(Fe) to be stable in water from pH =4 to 11.[83] Hence, at least in our hands, and contrary to the initial expectations, porphyrin based M^{3+}-catecholate MOFs present a moderate stability. The benefit associated with phenolic ligands eventually is far more pronounced when

moving to M(IV) and gallate ligands,[2,51] likely because of the increased charge of both components leading to stronger metal-ligand connections.

Based on the variable temperature diffraction data, the samples were activated at 150°C under vacuum after being washed in DMF. Nitrogen adsorption measurements revealed that the three materials are permanently porous compounds (Fig. 10). In agreement to their structures, CatPMOF-3(In) displays the larger accessible BET surface area (2130 m^2 g^{-1}) and a type IV isotherm that agrees with the microporous/mesoporous structure of the network. For the compounds CatPMOF-1(Fe)-pz and CatPMOF-2(Al), as expected a type I isotherm is observed, and the corresponding BET surface areas are of 710 m^2 g^{-1} and 860 m^2g^{-1} respectively. This indicates that although being moderately stable, all these solids withstand activation (solvent removal) and present an accessible porosity that could be further exploited.

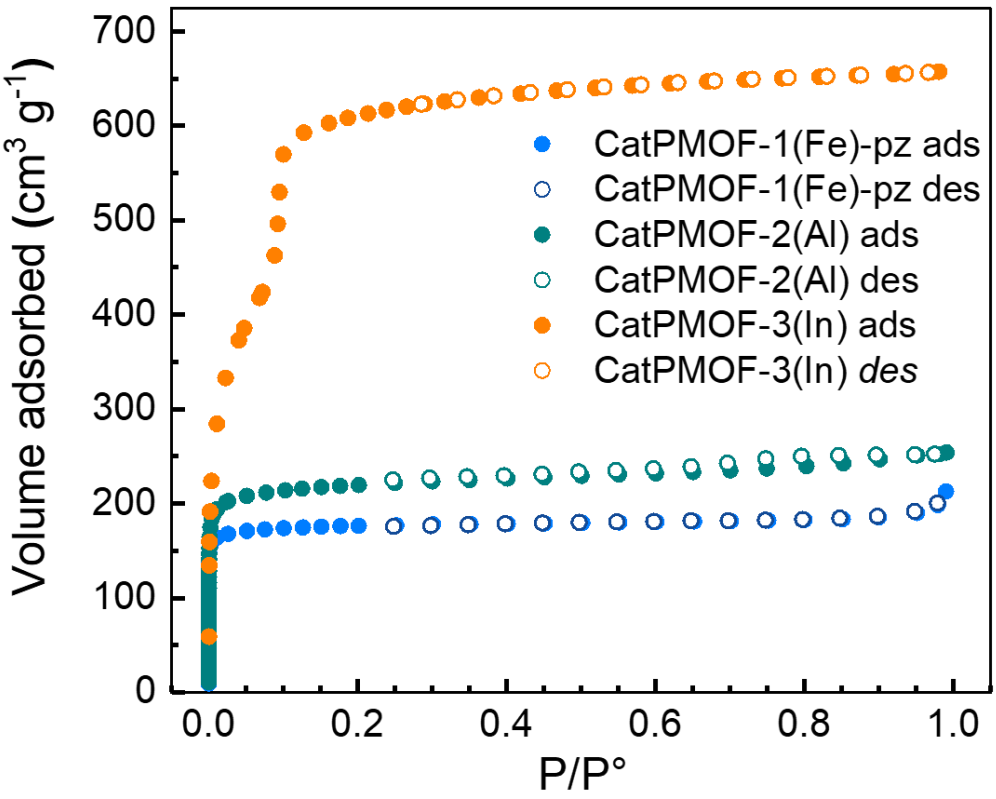


Fig. 10 Nitrogen sorption isotherms measured at 77 K, evidencing that all phases are porous.

4. Electrical conductivity and redox activity

To evaluate the electrical properties of the MOFs, conductivity measurements of the different samples (CatPMOF-1(Fe)-pz, CatPMOF-2(Al) and CatPMOF-3(In)) were performed using four-contact probe pressed pellet devices with three independent samples for each compound (see SI for experimental details). The average room-temperature conductivities were 3.3(±0.5) × 10^{-7}, 2.2(±0.6) × 10^{-7} and 1.03(±0.03) × 10^{-8} S cm^{-1} for CatPMOF-1(Fe)-pz, CatPMOF-2(Al) and CatPMOF-3(In), respectively (Table S4 and Fig.s S24 to S26). Note that grain boundaries and anisotropic effects present in bulk pressed pellets may result in larger resistances compared to

single-crystal measurements.[109] Nevertheless, all MOFs present semiconducting behavior and similar conductivities as other porphyrin-based MOFs.[110–113] However, the conductivities are lower than those of other catecholate-based MOFs[31,14,114] which could be related to the almost negligible amount of organic radical species acting as charge carriers (see EPR section) or to a weaker delocalization between the linker and the metal at least for the 3p cations (Al, In) .[115] Notably, the conductivity of CatPMOF-3(In) is one order of magnitude lower than that of CatPMOF-1(Fe)-pz and CatPMOF-2(Al) which is consistent with its higher porosity and larger distances between the porphyrin units, as the charge transport mechanism is expected to be redox hopping as observed in other porphyrin-based MOFs.[110] Although some mixed-valence $Fe^{II/III}$-based 3D MOFs with high conductivities (1 S cm^{-1}) have been reported,[116] this is not the case for CatPMOF-1(Fe)-pz probably due to the predominant presence of Fe(III) species (only the porphyrins contains LS Fe(II) ions). The optical band gaps (E_g) of CatPMOF-1(Fe)-pz, CatPMOF-2(Al) and CatPMOF-3(In) were calculated by linearly fitting the absorption onsets in Tauc plots of the Kubelka-Munk-transformed data, obtaining values of 2.58, 2.29 and 2.95 eV, respectively (Fig. 6b). The larger optical band gap of CatPMOF-3(In) is consistent with the lower conductivities in comparison to CatPMOF-1(Fe)-pz and CatPMOF-2(Al).

Considering the redox activity of the quinone/phenolate couple, the electrochemical properties of the three solids were investigated in the solid state, with the aim to evaluate their interest as positive electrodes for Li-ion batteries. The MOFs were activated prior to assess their electrochemical behavior in Li half-cell by using 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) as the electrolyte (see Supporting Information for details). As discussed earlier, all solids contain almost exclusively the reduced catecholate form,

hence tests were carried out starting in oxidation, on a potential range matching with the redox activity of the quinone/phenolate redox couple (~2 ≤ *E* ≤ ~4 V *vs.* Li^+/Li), in galvanostatic conditions. Note that a narrower potential window (3.0 ≤ *E* ≤ 3.6 V *vs.* Li^+/Li) was first used for CatPMOF-1(Fe)-pz to prevent any interference with the redox activity of the cation. The corresponding potential *vs.* capacity curves for the first and second cycles are shown in Fig. 11a, where the capacity refers to the number of electrons exchanged per catecholate unit. The redox activity strongly depends on the structure type. For CatPMOF-1(Fe)-pz, almost no redox activity is detected, neither in oxidation nor in reduction. Analysis carried out with another electrolyte (1 M $LiClO_4$ in propylene carbonate (PC)) and a broader potential range (2.0 ≤ *E* ≤ 4 V *vs.* Li^+/Li) leads to a similar result (Fig. S27), suggesting that the diffusion of cations is hindered in this solid. For CatPMOF-2(Al), a plateau centered at 3.5 V *vs.* Li^+/Li is detected during the first oxidation, followed by a second event spanning from ~3.8 to 4.0 V, with a total of ~0.7 electron per catecholate unit. These events are likely associated to the stepwise oxidation of catecholate to semiquinone and further to quinone, associated with the release of cations (DEA/Li^+) from the pores. It should be mentioned that the first oxidation potential is higher than the reduction potential of O_2 (~3.0 V *vs.* Li^+/Li), explaining why this solid is isolated in its fully reduced form, as deduced from the EPR analysis (see above). Indeed, the redox potential observed for other phenolate-based MOFs, which are typically isolated in a mixed phenolate/semiquinone form in ambient air, are significantly lower (~2.5-3V *vs.* Li^+/Li).[33–35,37,41,42] The peculiar behavior of CatPMOF-2(Al) (and CatPMOF-3(In), see below) likely arises from the fact that TcatPP presents a lower level of conjugation, and hence a higher redox potential than the ligands used in these examples (such as HHTP). Coordination to a highly charged cation such as Al(III) also further increases the redox potential by inductive effects.[117,118] Nevertheless, this redox activity is

found to be almost irreversible upon further reduction and cycling, indicating that this solid is not suited for reversible electrochemical energy storage. CatPMOF-3(In) presents a similar behavior during the first oxidation, with two marked plateaus at 3.45 and 3.7 V *vs.* Li^+/Li, accounting each for ~0.6 electron per catecholate unit. Interestingly, and contrary to what is observed for CatPMOF-2(Al), a clear plateau centered at 3.4V *vs.* Li^+/Li is also detected in reduction. During the second cycle, this plateau remains both in oxidation and reduction, while the one at higher potential tends to disappear. This indicates that the event centered at ~3.4 V *vs.* Li^+/Li and attributed to the transformation catecholate ↔ semiquinone is reversible, while the one at 3.7 V *vs.* Li^+/Li associated to the reaction semiquinone ↔ quinone is not. This can be clearly seen on the dQ/dE *vs.* E curve shown Fig. 11b, where the anodic and cathodic peaks at ~3.4 V *vs.* Li^+/Li are visible, while only the anodic one is present at 3.7 V *vs.* Li^+/Li. The irreversibility of the second oxidation step towards quinone could be related to the decrease of the cation-ligand bonds strength and its dissociation upon formation of the neutral quinone, ultimately leading to the degradation of the coordination network. Further experiments were then carried out focusing on the reversible redox event only ($3.0 \leq E \leq 3.6$ V *vs.* Li^+/Li) at a ~x5 faster cycling rate (current = 15.63 vs. 3.92 mA g^{-1}) with the aim to evaluate the capacity retention upon cycling. As shown Fig.s 11c and S28, the capacity slowly decreases upon cycling, but remains around 0.2 electrons per catecholate even after 200 cycles, suggesting that CatPMOF-3(In) can sustain long term cycling, with an average potential close to 3.4 V *vs.* Li^+/Li. In the field of batteries, there is a continuous interest for the development for new materials achieving high energy storage. This energy is the product of the capacity (number of electron exchanged per mass or volume) by the voltage; for this reason, high potential material are of particular interest. While potential above 4.0 V *vs.* Li^+/Li are reached by transition metal based inorganic materials, 3.4 V *vs.* Li^+/Li is at

the upper limit of what is found in organic materials,[119] and appealing for the development of new, more sustainable, positive materials for Li-ion batteries. Although CatPMOF-3(In) is not competitive because of its large molar weight leading to a modest specific gravimetric capacity (~15 mAh g^{-1}), these results suggest that low molecular weight, non-conjugated polycatecholate ligands are of interest for this purpose.

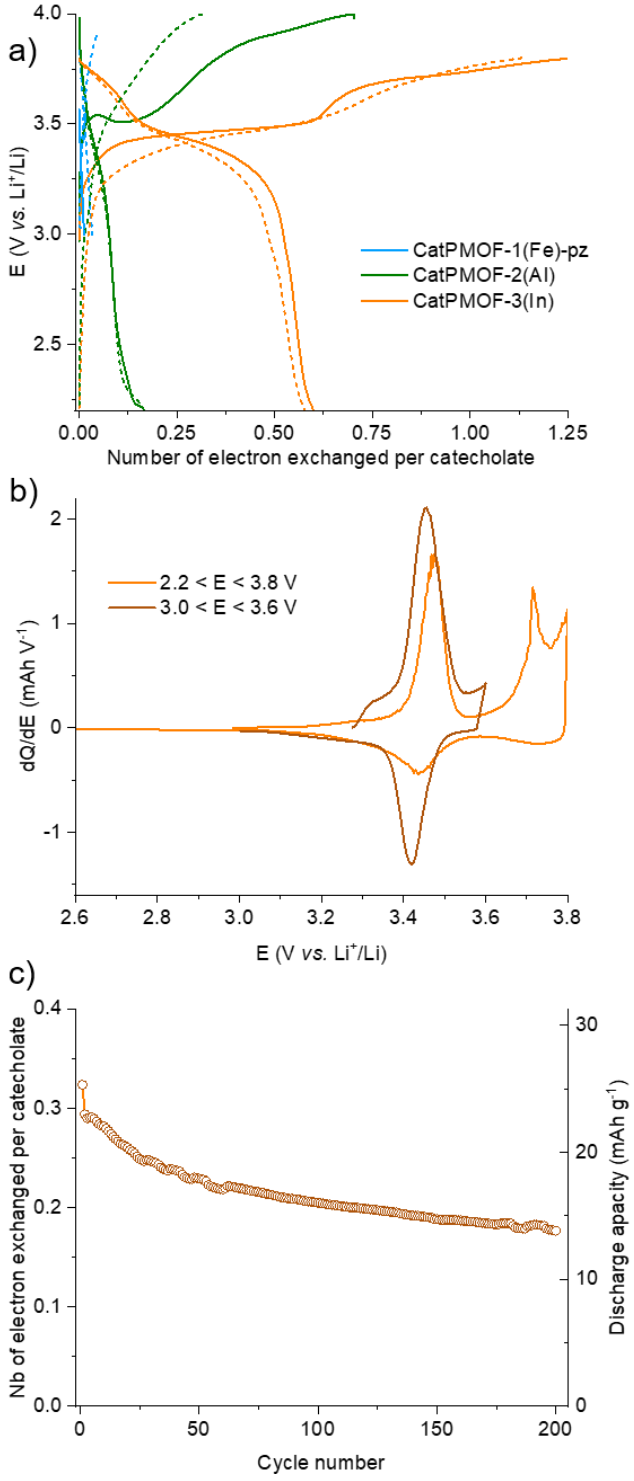


Fig. 11 Electrochemical behavior upon galvanostatic cycling of CatPMOF-1(Fe)-pz, CatPMOF-2(Al) and CatPMOF-3(In) electrode materials measured in a Li half-cell (electrolyte: 1 M $LiPF_6$ in EC/DMC). a) Potential *vs.* specific capacity curve, with the plain and dashed lines

corresponding to the first cycle and second cycles, respectively (current 21.88, 5.07 and 3.92 mA g^{-1} for CatPMOF-1(Fe)-pz, CatPMOF-2(Al) and CatPMOF-3(In), respectively); b) comparison of the dQ/dE *vs.* E curves for CatPMOF-3(In) during the first cycle with respect to the potential window; c) capacity retention curve for CatPMOF-3(In) (current 15.63 mA g^{-1}).

Conclusion

Three novel porphyrinic MOFs of very different topology have been successfully synthesized both with the free base and the nickel(II) porphyrin ligand. These materials are based on the coordination of trivalent metals (Al, Fe, In) by the catecholate moieties, thus extending the landscape of porphyrin-based coordination networks. Meticulous crystal growth optimization allowed to isolate single crystals of different sizes and morphologies, reaching sizes exceeding 100 µm. Combining in-depth diffraction studies including single crystal and powder diffraction data along with classical geometry optimization calculations allowed to propose reliable structural models for all three phases. Spectroscopic investigations revealed the anionic nature of the three networks. While of strongly different topology and based on markedly different inorganic SBUs, these MOFs are formed in closely related synthetic conditions, with the solvent playing a pivotal role in driving the phase formation. Noteworthy, the use of DEF leads to the formation of molecular SBUs, previously identified in the field of molecular or extended coordination chemistry. This finding suggests that a certain level of design might be achieved in these systems, encouraging further exploration with the use of different metals. All the solids exhibit accessible porosity towards nitrogen. Notably, and to the best of our knowledge, among all the catechol porphyrin based porous frameworks, CatPMOF-3(In) displays the highest

accessible BET surface area and larger pores. Contrary to the initial expectations, the chemical stability of all three solids is modest. However, the redox properties of the ligand can be exploited in the solid state, confirming the potential of phenolate ligands when compared to redox inert carboxylates or azolate, especially for applications involving electron transfer. In summary, this study introduces three new porphyrinic MOFs with distinct topologies, expanding the scope of porphyrin-based coordination networks. These MOFs exhibit noticeable porosity and original redox properties which opens up opportunities for further materials investigations. It is anticipated that tetravalent cations incorporation could improve chemical stability and advance the potential in the energy-related fields combining photo and redox activity offered by these solids.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Supporting information with all the experimental data and additional characterizations (PDF)

CCDC-2284767 to 2284771 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. S.D., G. M., F. L., M. A., B. A. : investigation, data curation, methodology, N. G. : investigation, methodology, visualization, validation, E. J., J. M. G., L.K., C. M. C, L. B., F.S.: investigation, methodology, visualization, P. S. A., G. V. : investigation, M. S. : visualization, writing-original draft, A. F. and T. D. : conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, supervision, validation, visualization and writing original draft and review and editing.

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Conflicts of interest

There are no conflicts of interest to declare.

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