Supporting Information

Expanding the Horizons of Porphyrin Metal-Organic Frameworks via catecholate coordination: exploring structural diversity, materials stability and redox properties

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1. Materials and Methods

Single crystal XRD: crystal data of CatPMOF-2(Al) were collected at room temperature on the Cristal beamline at Synchroton Soleil (L'Orme les Merisiers, France), using a set up adapted for small crystals on an Xcalibur, Atlas four-circle diffractometer and equipped with a CCD plate detector. As discussed in the article, initial indexing of numerous crystals led systematically to a tetragonal unit-cell, for which it was impossible to identify a proper space group. Peaks splitting on the PXRD pattern of the Ga analogue suggested a lower, orthorhombic, symmetry. Data reduction was then performed imposing an orthorhombic unitcell using the software CrysAlis. An empirical absorption correction was applied using spherical harmonics on the basis of multiple scans of equivalent reflections, implemented in SCALE3 ABSPACK scaling algorithm. The structure was solved using SHELXT and refined with the full matrix least squares routine SHELXL.¹ Due to the poor quality of the dataset, only the Al atoms were refined anistropically, and restrains on bond distances and angles were applied to both the phenyl and pyrrole rings on the porphyrinic ligands (command AFIX 66 and 59 in SHELXL, respectively). H atoms were added as rigid bodies, and the pores content was not considered. The same strategy was applied for 3(In). Structure solution lead to the identification of the In trimer surrounded by oxygen atoms, as well as the core of the porphyrin, including the In-Cl motif. Refinements were carried out using restrains on bond distances and angles on both the phenyl and pyrrole rings on the porphyrinic ligands (command AFIX 66 and 59 in SHELXL, respectively). H atoms were added as rigid bodies, and the pores content was not considered. The poor quality of the refinement for both structures led obviously to poor reliability factors and low precision on bond distances, generating both alerts A and B in checkcif. The nets were analyzed with the help of the software TOPOS Pro.

For $[In(H_7TcatP)]_{1.5}(H_2O)_{0.5} \cdot H_2O$, a suitable crystal was selected and mounted on a Geminini Oxford Diffractometer equipped with an Atlas CCD detector and using Mo radiation ($\lambda = 0.71069$ Å). Intensities were collected at room temperature by means of the CrysalisPro software. Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysalisPro software. An analytical absorption correction was applied using the modeled faces of the crystals. The structure was solved using SHELXS and refined with the full matrix least squares routine SHELXL. All non-hydrogen atoms were refined anisotropically, and H atoms were added as rigid bodies. 4 out of the the 6 catechols motifs were found to be disordered over two positions,

whose occupancies were refined with constraints of C-O distances and anisotropic displacement parameter. One of the In atoms was also found to be disordered over two positions around a center of inversion. Protons belonging to water molecules, as well as those occupying positions shared with the disordered OH group on the aromatic rings were not added.

Routine PXRD patterns were collected either on flat samples using a high-throughput Bruker D8 Advance diffractometer working on transmission mode, equipped with a focusing Göbel mirror and a LynxEye detector, or in a Debye-Scherrer mode with an INEL XRG3500 diffractometer, both equipped with a Cu anode Temperature-dependent PXRD patterns were measured using a Bruker D8 Advance diffractometer producing Cu K α radiation and equipped with a LynxEye detector and an Anton-Parr HTK1200 furnace. Patterns were collected every 10°C.

High resolution X-ray powder diffraction data were collected on the CRISTAL beamline at Soleil Synchrotron (Gif-sur-Yvette, France). A monochromatic beam was extracted from the U20 undulator beam by means of a Si(111) double monochromator. Its wavelength (0.72610 Å) was refined from a LaB₆ (NIST Standard Reference Material 660a) powder diagram recorded prior to the experiment. High angular resolution was obtained with, in the diffracted beam, a 21 perfect crystal Si(111) multi-analyzer. The solid was loaded in a 0.7 mm capillary (Borokapillaren, GLAS, Schönwalde, Germany) mounted on a spinner rotating at about 5 Hz to improve the particles' statistics. Diffraction data were collected for less than 4 hrs in continuous scanning mode and the diffractogram was obtained from the precise superposition and addition of the 21 channels data. Extractions from the peak positions, pattern indexing, whole powder pattern decomposition, the direct space strategy used for structural determination as well as difference Fourier calculations and Rietveld refinements were carried out with the TOPAS program.² Direct methods calculations were undertaken by using the EXPO software³

Checkcif leads to A and B alerts which could not be eliminated:

For the structures solved by SCXRD (CatPMOF-2(Al) and CatPMOF-3(In)), main alerts (low $\sin(\theta \max)/\lambda$ value and low C-C bond precision) are related to the poor diffracting ability of the crystals, even when using synchrotron radiation. For In(3), an additional alert B relates to the space group, but the use of the proposed space group (P-3c1 instead of P3c1) lead to a worse refinement, and thus P3c1 was kept. For 2(Al), the remaining alerts B deal with short O-O interatomic distances, but are related to oxygen atoms belonging to the same AlO6 octahedron and are thus imposed by coordination features of Al(III).

For the structures solved by PXRD (Ni-CatPMOF-2(Al) and Ni-CatPMOF-3(In), remaining alerts A and B are related to the treatment of the pore content. Guests could not be unambiguously located, but must be taken into account in the refinement process (no SQUEEZE procedure available contrary to SCXRD), and give rise to several alerts: presence of voids (expected for MOFs), short intermolecular distances associated with the ambiguous location of the guests, discrepancy between the experimental formula and the structural model because of incomplete localization of the guests. This does not obiter the structural analysis given in the manuscript, which, as explicitly stated, focuses on the nature of the SBUs and the network topology rather than precise analysis of interatomic distances and guest location.

Regarding the structure of 1(Fe)-pz, geometry optimization calculations were performed to determine the plausible structure. For that purpose, using Forcite implemented in Materials Studio,⁴ qEq partial charges were calculated following the electronegativity equalization formalism and UFF⁵ for Lennard-Jones parameters were combined to estimate the electrostatic and van der Waals parts respectively. The Ewald summation was considered for calculating electrostatic interactions while short-range interactions were evaluated using a cut-off distance of 12 Å. The convergence criteria were set at: 1.0×10^{-4} kcal mol⁻¹ (energy), 0.005 kcal mol⁻¹ Å⁻¹ (forces), and 5.0×10^{-5} Å (displacement). Calculations were performed starting from the structural model obtained from XRD experiments.

Thermogravimetric analysis (TGA) was performed with a TGA/DSC 1 STARe System from Mettler Toledo. Around 5 mg of sample was heated at a rate of 10 K \cdot min-1 from 25 to 800 °C, in a 70 µl alumina crucible, under air atmosphere (20 mL.min-1).

Surface areas were measured by N₂ adsorption and desorption at 77.3 K using a BEL Japan Belsorp Mini apparatus volumetric adsorption analyzer. The sample was pre-activated under vacuum at 150°C prior to sorption measurement. The BET surface calculations were performed using points at the pressure range 0 < P/P0 < 0.10.

For the ICP-AES experiments, solids were first dissolved in a 20% w/w aqueous solution of HNO₃, and further analysed thanks to an iCAP 6300 radial analyser (Thermo Scientific).

Scanning electron microscopy (SEM) was carried out FEI Quanta 250 FEG and Zeiss Merlin Compact microscopes in the microscopy center of Lyon1 University. Samples were mounted on stainless pads covered with carbon tape and sputtered with \sim 2 nm of carbon to prevent charging during observation.

Solid state UV-vis spectroscopy was performed with Perkin Elmer Lambda 365 Spectrophotometer at room temperature using an integrating sphere. MOF samples were diluted in KBr so the absorption maximum signal remained lower than 0.6. . The Kubelka–Munk

$$\frac{(1-R)^2}{2}$$

equation was applied [F(R) = 2R] and the Tauc plots were normalized with respect to $[F(R)hv]^2$ at 3 eV. The optical band gaps were estimated by a least-squares linear fit.

¹H and ¹³C NMR spectroscopy was performed on Bruker AVL 300 spectrometer and on Bruker AV 500 spectrometer respectively at the Centre Commun de RMN at the University of Claude Bernard Lyon 1.

The ²⁷Al solid-state MAS and MQ-MAS NMR spectra were recorded on a Bruker 500 WB NMR spectrometer (11.7 T) equipped with a NEO console. The sample was packed in a 2.5 mm outer diameter zirconia rotor and spun at 25 kHz. The ²⁷Al chemical shifts were externally referenced to a 0.1 M solution of aluminum nitrate. The three-pulse z-filter version of the multiple-quantum MAS (MQMAS) experiment was used.⁶ The pulse durations were set to 3.1, 1.2 and 6.7 µs, respectively. The recycle delay was set to 0.5 s. 40 t1 slices with 2400 transients each were accumulated. A two-dimensional Fourier Transformation followed by a shearing transformation yielded a pure absorption 2D spectrum. The spectra were analyzed using the dmfit software.⁷

EPR assays were all carried out at 120K and 290K using a Bruker E500 spectrometer operating at X-band (9.4 GHz), rectangular cavity (ST520), with 100 KHz modulation frequency. The instrument settings were as follows: microwave power; 7mW; modulation amplitude; 1 G.

The ⁵⁷Fe Mossbauer spectra were recorded at 300 K and 77K in a transmission geometry using a ⁵⁷Co/Rh source mounted on an electromagnetic driving unit with a triangular velocity form (rate 2 mm s⁻¹) and an Oxford bath cryostat. The transducer was calibrated using an α -Fe foil. The sample consists of a thin layer of powder containing about 5 mg Fe/cm². Data were fitted with homemade software MOSFIT;⁸ the values of isomer shifts are quoted to that of α -Fe at 300 K.

For the electrical measurements, powders of CatPMOF-1(Fe)-pz, CatPMOF-2(Al) and CatPMOF-3(In) were loaded into glass tubes and pressed between stainless steel rods under approximately 6 Ton and contacted with 4 copper wires and carbon paste (Graphite conductive Adhesive 112 12693-30). Four-contact probe measurements were carried out at 300 K in

ambient atmosphere on pressed pellets using a home-built four-probe in situ press set-up⁹.^x Linear I-V curves were obtained by sweeping the voltage between -0.5 to +0.5 V or -1 to +1 V and measuring the current using a sourcemeter (Keithley 2450, KickStart software) connected to the press via test leads. Pellet thicknesses were measured after the measurement using a micrometer (Mitutoyo) (the area was determined from the top view). The batch conductivity values were averaged to give the average conductivity value for the phase. The standard error of the batch conductivity values was used for the error estimation on the average conductivity value for each compound.

Solid-state electrochemical experiments were carried out by using a two-electrode Swagelok®type cell with a Li metal disc as the negative electrode and a glass fiber separator soaked with either a 1 M LiClO₄ in propylene carbonate (PC) or 1 M LiPF₆ in 1:1 ethylene carbonate (EC) dimethylcarbonate (DMC) electrolyte. The composite positive electrodes were prepared in an argon filled glovebox by grinding the solid and Ketjenblack® EC-600JD (Akzo Nobel) carbon conducting additive to insure proper electronic conduction (MOF:carbon ratio = 66:33 wt%, ca. 3 mg of active material per electrode). The electrochemical cells were then cycled in galvanostatic mode at the current rate summarized in Table S1 by using a MPG-2 multi-channel system (Bio-Logic SAS, Seyssinet-Pariset, France).

Solid	electrolyte	pot. window	current	C-
		(V vs. Li ⁺ /Li)	(mA g ⁻¹)	rate
CatPMOF-1(Fe)-pz	1 M LiPF ₆ in 1:1 EC:DMC	3.0 < E < 3.6	21.88	~ 5
CatPMOF-1(Fe)-pz	1 M LiTFSI in PC	2.0 < E < 3.9	5.47	~ 20
CatPMOF-2(Al)	1 M LiPF ₆ in 1:1 EC:DMC	2.2 < E < 4.0	5.07	~ 20
CatPMOF-3(In)	1 M LiPF ₆ in 1:1 EC:DMC	2.2 < E < 3.8	3.92	~20
CatPMOF-3(In)	1 M LiPF ₆ in 1:1 EC:DMC	3.0 < E < 3.6	15.63	~ 5

Table S1. Conditions of galvanostatic cycling of MOFs in Li-half-cells.

2. Synthesis

2.1 Ligands

5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin was isolated in its dicationic (bromide salt) form, by following a synthesis inspired from a previously reported procedure.¹⁰ The dicationic form of the porphyrin allowed to achieve better reproducibility and crystallinity in all MOFs synthesis and was obtained as follows. Dry 5,10,15,20-tetrakis(3,4-dimethoxyphenyl)porphyrin (1.07 g, 1.25 mmol) was dissolved in anhydrous dichloromethane (120 mL) in around bottom flask in inert atmosphere. Then pure BBr₃ (4.0 ml, 41.2 mmol) was carefully added in a dropwise manner at -70 °C and the reaction mixture was left to return to room temperature slowly. After 24 hours, the reaction was quenched by adding cold methanol (90 mL) dropwise in an ice bath. Then most of the solvent was removed and deionised water was added (100 mL). The green precipitate was filtered and washed with water and dried at 100 °C overnight to yield the green product (0.920 g, ~85% yield).

¹H NMR (DMSO- d_6 , 300 MHz)

 δ /ppm: 0.39 (s, 4H, NH), 7.49 (d, 4H, phenyl H, *J* = 8.1 Hz), 7.90 (d, 4H, phenyl H, *J* = 7.2 Hz), 8.11 (s, 4H, phenyl H), 8.49 (s, 8H, porphyrin β–H), 9.78 (s, 4H, OH H), 10.21 (s, 4H, OH H) H)

Nickel(II)5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin or NiH₈TcatPP was prepared from 5,10,15,20-tetrakis(3,4-dimethoxyphenyl)porphyrin in two steps. A mixture of 5,10,15,20-tetrakis(3,4-dimethoxyphenyl)porphyrin (1.00 g, 1.11 mmol, 1 eq.), anhydrous NiCl₂ (2.01 g, 15.5 mmol, 14 eq.) and 2,6-dimethylpyridine (2 mL) in dichloromethane/ethanol (1:1) was refluxed with stirring for ca. 64 hours. All the solvent was evaporated under vacuum and the solid product was the extracted in chloroform (4 x 100 mL). The organic phase was washed with water and dried over MgSO₄. The solvent was evaporated in vacuum and the solid crystallized in the refrigerator in a minimum of dichloromethane and methanol. The suspension was filtered on a sintered glass crucible and the solid was washed with cold methanol to afford nickel(II) 5,10.15,20-tetrakis(3,4-dimethoxyphenyl)porphyrin, as a reddish-purple powder, 0.94 g, 0.98 mmol, 88 %. Nickel(II) 5,10.15,20-tetrakis(3,4-dimethoxyphenyl)porphyrin (0.897 g, 0.93 mmol, 1 eq.) and pyridine hydrochloride (20.09 g, 383 mmol, 51 eq.) were heated with stirring until all pyridine hydrochloride had melted and then the mixture was left to reflux for ca. 3 hours. After cooling to room temperature, 150 mL water was added to the flask and the mixture was left to stir for ca. 90 minutes. The solid was washed with water via centrifugation (3 x 30 minutes) and left to dry in air overnight. The dry solid was dissolved in tetrahydrofuran (ca. 100 mL) and filtered with a silica pre-column on a sintered glass crucible. The resulting solution was evaporated in vacuum to give 5,10.15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin nickel(II) or NiH₈TcatPP, as a shiny purple, glass-like solid (0.59 g, 0.70 mmol, 70 %). ¹H NMR (200 MHz)

Nickel(II)5,10.15,20-tetrakis(3,4-dimethoxyphenyl)porphyrin (in CD₂Cl₂)

δ/ppm: 8.83 (s, 8H), 7.60-7.54 (m, 8H), 7.22 (d, 4H, J = 8 Hz), 4.07 (s, 12H), 3.89 (s, 12H).

Nickel(II)5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin (in DMSO-d₆)

 δ /ppm: 9.35 (s, 8H), 8.80 (s, 8H), 7.40 (d, 4H, J_{HH} = 2 Hz, 4H), 7.30 (dd, 4H, J₁ = 8 Hz, J₂ = 2 Hz), 7.11 (d, 4H, J = 8 Hz).

NMR spectra of the ligands



Fig. S1 ¹H NMR spectrum of 5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin dication



Fig. S2 ¹³C NMR spectrum of 5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin dication (isolated as the bromide salt, in DMSO-d₆, 400 MHz)



Fig. S3 ¹H NMR spectrum of Nickel(II)5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin (in DMSO-d₆)



Fig. S4 ¹³C NMR spectrum of Nickel(II)5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin (in DMSO-d₆)

2.2 MOFs

Exploratory and small-scale syntheses were carried out in the 24x2.5 mL high-throughput (HT) solvothermal setup developed by Stock *et al.*,¹¹ while "large-scale" syntheses were done either in 20 mL teflon capped high-pressure glass vessels or 24 mL Parr autoclaves.

Ni-CatPMOF-1(Al)

AlCl₃·xH₂O (5.1 mg, <0.04 mmol) and NiH₈TcatPP (5.0 mg, 0.006 mmol) of were placed in a 2.5 mL HT Teflon liner, together with 0.125 mL of DMF and 0.375 mL of water. 0.01 mL of a 2 M KOH aqueous solution was added. The reactor was sealed in the autoclave, and heated (heating rate 11° C hr⁻¹) at 150°C for 48 hours. The resulting dark solid was recovered by filtration, washed with DMF, and dried in air.

Ni-CatPMOF-2(Al)

 $AlCl_3 \cdot xH_2O$ (59.3 mg, <0.44 mmol), NiH₈TcatPP (60.4 mg, 0.076 mmol) and H₂cat (418.2 mg, 3.8 mmol) were placed in a 24 mL Teflon liner, together with 6 mL of DEF. The reactor was sealed in the autoclave, and heated (heating rate 11°C hr⁻¹) at 150°C for 48 hours. The resulting dark solid was recovered by filtration, washed extensively with DEF, and ethanol, and dried in air.

Ni-CatPMOF-2(Ga)

 $Ga(NO_3)_3 \cdot xH_2O$ (230.4 mg, <0.9 mmol), NiH₈TcatPP (119.7 mg, 0.15 mmol) and H₂cat (499.2 mg, 4.5 mmol) were placed in a 24 mL Teflon liner, together with 12 mL of DEF. 0.24 mL of a 2 M KOH aqueous solution was added. The reactor was sealed in the autoclave, and heated (heating rate 11°C hr⁻¹) at 150°C for 48 hours. The resulting dark solid was recovered by filtration, washed extensively with DEF, and dried in air.

Ni-CatPMOF-1(Fe)

 $FeCl_3 \cdot xH_2O$ (6.2 mg, <0.038 mmol), NiH₈TcatPP (5.2 mg, 0.007 mmol) and H₂cat (20.9 mg, 0.19 mmol) were placed in a 2.5 mL HT teflon liner, together with 0.5 mL of DMF. The reactor

was sealed in the autoclave, and heated (heating rate 11°C hr⁻¹) at 150°C for 48 hours. The resulting dark solid was recovered by filtration, washed extensively with DMF, and dried in air.

Ni-CatPMOF-2(Fe)

FeCl₃·xH₂O (6.0 mg, <0.037 mmol), NiH₈TcatPP (5.2 mg, 0.007 mmol) and H₂cat (20.9 mg, 0.19 mmol) were placed in a 2.5 mL HT teflon liner, together with 0.5 mL of DEF. The reactor was sealed in the autoclave, and heated (heating rate 11° C hr⁻¹) at 150°C for 48 hours. The resulting dark solid was recovered by filtration, washed extensively with DEF, and dried in air.

Ni-CatPMOF-1(In)

InCl₃·xH₂O (8.3 mg, <0.038 mmol), NiH₈TcatPP (5.0 mg, 0.006 mmol) and H₂cat (20.9 mg, 0.19 mmol) were placed in a 2.5 mL HT teflon liner, together with 0.5 mL of DMF. 0.01 mL of a 2 M KOH aqueous solution was added. The reactor was sealed in the autoclave, and heated (heating rate 11° C hr⁻¹) at 150°C for 48 hours. The resulting dark solid was recovered by filtration, washed extensively with DMF, and dried in air.

Ni-CatPMOF-3(In)

InCl₃·xH₂O (8.4 mg, <0.038 mmol), NiH₈TcatPP (5.0 mg, 0.006 mmol) and H₂cat (20.7 mg, 0.19 mmol) were placed in a 2.5 mL HT teflon liner, together with 0.5 mL of DEF. 0.01 mL of a 2 M KOH aqueous solution was added. The reactor was sealed in the autoclave, and heated (heating rate 11°C hr⁻¹) at 150°C for 48 hours. The resulting dark solid was recovered by filtration and washed extensively with DEF.

CatPMOF-1(Fe)-pz

In a 20 ml teflon capped high-pressure vessel, FeCl₃.6H₂O (54 mg, 0.19 mmol) was combined with H₂cat (120 mg, 1.09 mmol) and pyrazine (15 mg, 0.18 mmol) in 8 mL mixture of DMF and water (with a ratio of v/v = 1/4). Then H₁₀TcatPP (54 mg, 0.073 mmol) was added to it and the dark solution was mixed well at room temperature. The reactor was placed in an oven and heated at 160 °C for 48 hours. Dark crystals were isolated by filtration and purified via vigorous washing with DMF. The MOF crystals were dried under vacuum at 140 °C for overnight (58 mg, after drying).

CatPMOF-2(Al)

In a 20 ml teflon capped glass vial, AlCl₃.6H₂O (36 mg, 0.150 mmol) was combined with H₂cat (240 mg, 2.18 mmol) in 12 mL mixture of DEF and water (with a ratio of v/v = 1/1). Then H₁₀TcatPP (60 mg, 0.076 mmol) was added to it and the dark red solution was mixed well at room temperature. The reactor was placed in an oven and heated at 150 °C for 48 hours. Cubic dark red crystals were isolated by filtration and purified via vigorous washing with DMF. The MOF crystals were dried under vacuum at 140 °C for overnight (56 mg, after drying).

CatPMOF-3(In)

In a 20 ml Teflon capped glass vial, $InCl_3.4H_2O$ (44.4 mg, 0.152 mmol) was combined with H_2cat (251 mg, 2.28 mmol) in 9 mL mixture of DEF and 2M aqueous HCl (with a ratio of v/v = 8/1). Then $H_{10}TcatPP$ (60 mg, 0.076 mmol) was added to it and the green solution was mixed well at room temperature. The reactor was placed in an oven and heated at 150 °C for 48 hours. Then the mixture was allowed to cool down slowly at room temperature. Rod-shaped dark green crystals were isolated by filtration and purified via vigorous washing with DMF. The MOF crystals were dried under vacuum at 140 °C for overnight (58 mg, after drying).

3. Isolation of the different phases with free base and Ni porphyrin



Fig. S5 experimental PXRD patterns of the as prepared solids ($\lambda = 1.5418$ Å), the calculated patterns for each phase are included in black.

4. Structural data for the In-based compounds isolated in DMF/H₂O mixtures



Fig. S6 PXRD patterns of the samples obtained after the reaction of H₂TCatP with InCl₃.4H₂O in variable solvent compositions. Supramolecular Assemblies (SA) are formed for V_{water}/V_{DMF} = 4 (in combination with CatPMOF-1 phase when pyrocatechol is used), whereas CatPMOF-1 phase is obtained as the only product for V_{water}/V_{DMF} = 1.5. * corresponds to the Bragg peaks of In(OH)₃ (λ = 1.5418 Å).



Fig. S7. Crystal structure of the supramolecular assembly obtained upon reaction of H_{10} TcatP with In(III) in DMF/H₂O 1/4 at 160°C, and formulated [In(H₇TcatP)]_{1.5}(H₂O)_{0.5}·H₂O. a) Atomic representation showing the connection of the metallated porphyrins through the axial coordination of the In ions by phenolate groups; b) representation of the derived 2-D net (porphyrins are pictured in pink and green, and axial connection in dash yellow).

5. Structure analysis of the proposed models for phase CatPMOF-1 compound



Fig. S8. Structural models of Co-CatPMOF-1(Fe) and Co-CatPMOF-1(In) taken from reference ¹².

The quantitative evaluation of the coordination environment of the cations in phase 1 and related structures was carried using the software SHAPE (version 2.1), which allows evaluating/quantifying the deviation of the coordination sphere of a cation from the ideal geometries and comparing quantitatively different structures. For a given coordination number (CN), a value between 0 and 100 is calculated based on bond distances and angles for each ideal geometry (e.g. octahedron, trigonal prism, hexagon, for CN = 6), and the value closest to zero indicates the closer regular geometry. Details on the theory behind and the methodology can be found in the related articles by Alvarez *et al.*¹³ For the proposed structure M_2 (CoTCatPP) (M = Fe, In) by Cheng et al., the closest ideal geometry of the cation is pentagonal pyramid. This structure of was compared to data from the literature. To do so, a systematic search was carried out with the CCDC (last update June 2022) for structures containing M = In or Fe bound to at least 4 oxygen atoms and at least 2 catechol(ate) (not necessarily chelating). This leads to 12 and 107 structures for In and Fe, respectively presenting various coordination numbers (CN): 5, 6 or 8 for In, and 5 or 6 for Fe, the 6-fold coordination being by far the most common. For each CN, all the standard geometries were tested (see details at the bottom of the table). For example, for M = In and CN = 8, a single structure was found (CCDC reference code QOFNIL), in which the InO₈ polyhedron adopts a square antiprism (SAPR) geometry. As expected, most of the structures have CN = 6, with the cations having either an octahedral (90 and 58% for Fe

and In, respectively) or a trigonal prismatic environment (10 and 42% for Fe and In, respectively).

Μ	CCDC		results												
	ref														
	code														
	coue														
In							CN :	= 8							
		OP	HPY	HBPY	CU	SAPR	TDD	JGBF	JE	TBPY	JBTPR	BTP	JS	TT	ETBPY
												R	D		
	QOFNIL												5.7		
		29.36	24.57	13.86	5.97	0.83	2.06	15.84	29	.39	3.64	3.06	1	6.87	24.11
							CN	= 6							
		HP		PPY		OC				TPR				JPPY	
	ILIKOE	35.078		15.739		16.557				0.474				19.783	
	ILIKUK	32.064		23.206		2.184				10.479)			27.458	
	BIXWIQ	32.022		17.131		5.369				7.585				21.54	
	BIXWIQ	31.649 19.255			4.082 10			10.06				22.786			
	KURTAS	34.219 19.868			3.352			8.87				23.453			
	OHEDOX	31.712 23.418			2.326 9			9.223				27.357			
	FOCMUH	35.951		16.654		16.799 0			0.474				20.816		
	ILIKIY	35.029		15.039					0.724				19.011		
	ILILAR	31.451		22.566		1.985			11.564				26.932		
		30.486		23.868		1.704			10.894				27.794		
	ZEFBAP	34.61/		15.822		12.717			0.753				19.783		
	InTCP-Co	23.031		7 173		13.265			12 235				8 732		
	InTCP-Co	23.031		7 171		25.012			12.235				8.732		
		201020				23.021 12.230 8.					0.701				
								- 3							
		PP			vOC		TBP	Υ		SI	PY		JJ	ГВРҮ	
	GIJJUG	32.243			7.202		7.17	2		2.	265		11	1.516	
	GIJJUG	34.127			9.358		7.69	8		3.	264		12	2.652	
	GIJJUG	33.225			6.649		6.49	9		1.	869		10).636	
Fe							CN	= 6							
		HP			PPY		OC			TI	PR		JPI	PY	
	AGUVIJ	32.286			24.505		1.2	65		10	.715		28.	221	
	AVUPEP	30.256			25.458		0.8	83		13	.749		28.	928	
	BICSEL	32.71			24.504		1.0.	39		11	.185		28.	251	
	BIHKUY	BIHKUY 33.555 22.674					1.7	74		9.0)88		26.	359	

Table S2. Quantitative analysis of the geometry of MO_n polyhedra (M = In, Fe, n = 5-8) in structure containing M-catecholate complexes.

CEZYIR	31.645	25.906	0.77	12.239	29.695
COBCIH	32.955	20.169	2.543	7.972	23.938
COBCIH	32.901	21.123	2.137	8.87	24.873
COBCIH	32.992	20.807	2.191	8.997	24.706
CUTQIU	32.25	23.269	1.476	10.489	27.21
CUTSOC	32.17	23.356	1.408	10.672	27.29
DOPQOQ	32.771	24.12	1.284	10.474	27.87
DORFUM	34.941	15.135	11.915	0.866	19.282
DUCZOQ	29.198	16.85	4.277	8.029	20.729
DUCZOQ	29.198	16.85	4.277	8.029	20.729
FEPHSQ	32.898	22.184	1.658	10.302	26.034
FUDRUR	34.757	16.74	16.67	0.122	20.85
FUHNII	32.926	23.716	1.353	10.385	27.716
GARWUR	33.506	22.964	1.648	9.435	27.088
GARWUR	33.506	22.964	1.648	9.435	27.088
GARWUR	33.506	22.964	1.648	9.435	27.088
GARWUR	33.558	25.055	1.022	10.743	28.932
GEFKAG	34.334	23.558	1.716	8.832	27.458
GIRJUO	35.25	19.519	6.607	3.64	23.408
GIRKAV	35.293	19.532	6.596	3.675	23.419
GOPJAY	32.386	23.013	1.48	10.636	26.874
GOPJEC	34.321	22.064	1.97	8.669	26.001
GOPJIG	33.235	20.977	2.22	8.849	24.942
GOPJIG	32.88	21.022	2.181	8.801	24.855
GOPJIG	33.089	20.423	2.49	8.07	24.244
GUVFAF	35.205	20.035	5.55	4.526	24.001
IGIROI	33.02	24.269	1.486	9.885	28.156
JEDCAX	30.282	26.381	0.762	13.029	30.241
JETGIY	28.438	27.814	0.773	15.737	30.625
JOVSOC	33.362	26.806	0.486	13.574	30.605
JUTVOJ	34.704	16.522	11.71	0.612	20.6
JUTWAW	34.173	21.739	2.173	8.098	25.574
JUTWEA	34.689	23.044	2.052	8.415	27.017
KAFTIX	30.796	26.039	0.915	12.215	29.914
KCATFE	33.126	23.793	1.231	10.205	27.717
LUDNUW	30.209	24.263	1.139	13.089	27.967
LUMCEC	32.06	15.838	6.245	5.684	19.631
LUMCEC	32.426	17.259	5.071	6.906	20.971
LUMCOM	32.834	21.762	3.54	11.706	25.017
LUMCOM	29.453	21.159	2.087	9.77	24.232
LUMCUS	31.763	18.407	3.564	7.615	22.216
LUMCUS	31.331	24.473	1.459	13.245	27.839
LUMDAZ	33.561	19.086	2.786	9.932	22.511
LUMDED	31.412	21.532	2.096	9.036	25.387
LUPDOP	29.412	28.47	0.45	16.024	31.574
LUPDUV	27.694	27.851	0.714	15.971	30.869
LUZVOU	33.068	24.432	1.233	12.87	28.306
MIVXAS	31.395	24.765	1.134	11.446	28.647

MIVXOG	30.982	24.588	1.12	12.137	28.262
MOMLOR	35.232	19.662	5.989	3.86	23.534
MOTYOM	33.376	20.697	2.33	8.211	24.435
MOTYUS	34.452	22.117	2.047	8.685	25.964
NIHJEW	31.131	25.722	0.985	11.999	29.73
OWITUK	29.772	26.052	1.108	12.336	29.888
PABDFE1					
0	32.337	23.379	1.788	12.879	27.361
PABDFE1					
0	31.432	23.083	1.941	12.415	26.496
PABDFE1					
0	32.815	21.021	2.271	11.46	24.222
PABDFE1					
0	31.852	22.223	2.082	10.577	25.96
PALXUY	29.815	24.666	1.111	12.298	28.545
PALXUY	29.55	24.97	1.015	12.735	28.84
PALYAF	29.599	24.988	1.04	12.501	28.779
PALYAF	29.912	24.832	1.026	12.623	28.662
PALYEJ	29.489	24.609	1.12	12.204	28.417
QAMDOB	30.226	28.14	0.422	14.782	32
QEFPID	23.883	26.374	1.388	15.69	29.169
QEFPOJ	25.011	26.815	1.142	15.577	29.719
QEGPAT	29.073	26.891	0.519	14.372	30.149
QEGPEX	32.357	24.111	1.005	12.627	27.969
QOCHEV	32.546	24.793	0.833	12.107	28.722
QUJJOW	31.8	23.038	1.692	10.393	26.877
QUJKOX	31.222	24.329	1.06	11.884	28
QURPOL	30.056	24.549	1.109	13.262	28.227
QURQAY	31.497	24.127	1.253	11.797	27.846
QURQAY	31.962	23.68	1.478	10.942	27.496
QURQEC	29.992	24.424	1.159	13.077	28.12
QURQIG	31.949	23.721	1.462	10.981	27.571
QURQIG	31.598	24.052	1.254	11.748	27.751
QURQOM	31.74	23.739	1.507	11.04	27.591
QURQOM	31.436	24.181	1.249	11.826	27.899
QURQUS	32.197	23.524	1.504	10.767	27.338
QURQUS	31.466	24.067	1.258	11.798	27.802
QURRED	32.274	23.496	1.505	10.685	27.3
QURRED	31.598	24.011	1.275	11.679	27.76
QURRIH	32.296	23.476	1.486	10.702	27.273
QURRIH	31.563	24.052	1.262	11.718	27.79
QURRON	32.184	23.517	1.48	10.774	27.296
QURRON	31.48	24.068	1.243	11.811	27.806
QURRUT	30.541	24.095	1.145	12.79	27.809
QURSAA	32.234	23.517	1.449	10.785	27.311
QURSAA	31.687	24.038	1.26	11.633	27.788
QURSOO	30.645	24.122	1.138	12.675	27.856
QURTAB	32.314	23.519	1.45	10.741	27.316
QURTAB	31.617	24.112	1.254	11.689	27.876

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	QURTEF	32.343	23.538	1.425	10.726	27.351
	QURTEF	31.671	24.164	1.256	11.571	27.97
	RACZUT	31.973	25.424	1.083	11.447	29.298
	RADBAC	31.349	24.718	0.936	12.108	28.553
	REJSEF	31.787	25.468	0.982	11.752	29.364
	RUYXIU	29.252	25.749	0.912	13.163	29.383
	RUZBOF	33.247	25.209	1.115	10.889	28.934
	SEPRAJ	33.666	21.309	2.807	6.847	24.981
	SESGED	31.761	24.502	1.761	11.414	27.93
	SIQPIU	32.172	23.549	1.494	10.777	27.344
	SIQPIU	31.491	24.067	1.268	11.761	27.798
	SUCCUO	34.538	22.106	2.608	7.219	26.144
	SUCDAV	34.49	23.536	1.736	8.933	27.473
	TAXXIZ	32.087	22.449	1.524	10.881	26.492
	TEMKUR	33.725	20.873	2.912	10.519	24.559
	TEMKUR	33.725	20.873	2.912	10.519	24.559
	TEQGUT	31.929	22.95	1.759	10.141	26.791
	TEQGUT	32.856	23.412	1.719	10.284	27.149
	THMOFE	33.314	21.399	3.831	6.227	25.146
	TORGUF	30.858	25.19	0.978	12.172	28.986
	TORHAM	34.614	21.208	3.358	5.895	25.199
	TUTQAC	35.333	19.502	6.621	3.656	23.397
	VAKCOZ	33.944	21.364	2.541	7.737	25.102
	VAKCUF	32.695	21.957	2.633	10.462	25.517
	VAKCUF	30.726	14.152	7.168	5.494	16.892
	WEDDUF	33.357	22.727	1.546	10.012	26.567
	WIDLUS	32.808	20.355	2.662	9.861	24.005
	WIDMAZ	32.861	20.296	2.741	9.845	23.927
	XARDIG	31.235	25.5	1.099	11.497	29.349
	XECTUX	29.563	24.816	1.166	12.877	28.824
	XECTUX	28.937	26.606	1.035	13.132	30.44
	XESPIU	28.38	28.056	0.501	16.042	31.125
	YEGWUF	30.742	24.433	1.168	12.209	28.23
	YUQCAR	30.548	23.749	1.229	11.583	27.602
	ZACDAL	32.846	24.216	1.541	9.858	28.108
	ZOVRIL	32.58	22.638	1.856	10.288	26.134
	ZOVROR	31.375	20.071	3.146	7.287	23.585
	JAWGOH	32.189	23.913	1.332	10.722	27.888
	JAWGOH	32.811	22.991	1.512	10.364	26.897
	QARVUE	33.513	23.227	1.405	10.245	27.202
	QARVUE	33.513	23.227	1.405	10.245	27.202
	QARVUE	33.98	24.74	1.149	10.263	28.563
	QARVUE	33.513	23.227	1.405	10.245	27.202
	FeTCP-Co	23.461	7.891	25.16	13.036	9.434
	FeTCP-Co	23.461	7.891	25.16	13.036	9.434
	1(Fe)	28.147	23.272	4.297	13.311	24.863
	1(Fe)	32.284	13.686	7.860	6.294	17.399
	1(Fe)	31.974	24.715	1.617	12.216	28.054

CN = 5							
	PP	vOC	ТВРУ	SPY	JTBPY		
PARCUI	24.977	5.463	4.511	4.348	6.571		
POXJAN	24.261	4.758	4.776	2.993	7.207		
1(Fe)	9.877	0.517	7.079	1.567	8.537		

For CN = 8

OP = Octagon, HPY = Heptagonal pyramid, HBPY = Hexagonal bipyramid, CU = Cube, SAPR = Square antiprism, TDD = Triangular dodecahedron, JGBF = Johnson gyrobifastigium J26, JETBPY = Johnson elongated triangular bipyramid J14, JBTPR = Biaugmented trigonal prism J50, BTPR = Biaugmented trigonal prism, JSD = Snub diphenoid J84, TT = Triakis tetrahedron, ETBPY = Elongated trigonal bipyramid.

For CN = 6

HP = Hexagon, PPY = Pentagonal pyramid, OC = Octahedron, TPR = Trigonal prism, JPPY-6 = Johnson pentagonal pyramid J2

For CN = 5

PP = Pentagon, vOC-5 = Vacant octahedron, TBPY = Trigonal bipyramid, SPY = Spherical square pyramid, JTBPY = Johnson trigonal bipyramid J12

6. Structural data for CatPMOF-2 phase.



Fig. S9 PXRD analysis of phase 2. a) Zoom on the 5.0-6.6° 20 region for Ni-CatPMOF-2(Ga) showing the peaks splitting allowing the accurate indexation of the pattern in an orthorhombic unit-cell rather than in a tetragonal one; b) Final Rietveld refinement for Ni-CatPMOF-2(Ga); c) Comparison of the experimental PXRD pattern of Ni-CatPMOF-2(Al) with that calculated from the model for Ni-CatPMOF-2(Ga), evidencing that both compounds are isostructural ($\lambda = 0.72610$ Å).

The least square indexing (LSI) method converged unambiguously to an orthorhombic unit cell with very close *a* and *b* parameters (a = 21.7828(2), b = 21.7555(2), c = 39.3019(2) Å) with satisfactory Fig. of Merit ($M_{20} = 60$). Systematic extinctions were consistent among other things with the $P_{21}2_{12}$ pace group, which was used to initialize the structural determination by direct methods and simulated annealing. Although an idea of the structural model could be highlighted; powder diffraction alone did not allow solving this structure. Atomic coordinates of the structural model determined from SCXRD data were then used to initialize the Rietveld refinement, for which organic ligands were treated as rigid bodies. DEA, DEF and water molecules were localized by simulated annealing and successive difference Fourier calculations. The final Rietveld plot (Fig. S6b), corresponds to satisfactory model indicator and profile factors ($R_{\rm B} = 0.043$, $R_{\rm p} = 0.042$ and $R_{\rm wp} = 0.062$) and involves 24 structural parameters: 1 scale factor, 12 atomic coordinates for Ga atoms, 8 rotation angles for the catecholate moieties as well as 2 torsion angles in the porphyrin and 1 overall temperature factor.

7. Structural data for CatPMOF-3 phase.



Fig. S10 PXRD patterns obtained when CatPMOF-3(In) is synthesized in presence of acidic (pink), neutral (teal) and basic (purple) aqueous solution ($V_{water}/V_{DEF} = 1/8$), the reactions were tested with (solid line) and without (dotted line) 30 eq. of pyrocatechol per porphyrin ($\lambda = 1.5418$ Å).



Fig. S11 Comparison of the nets in CatPMOF-3(In) (left) and PCN-600 (right), shown along (top) and perpendicular to (bottom) the hexagonal pore axis. The 6-fold and 4-fold nodes associated to the inorganic secondary building unit (iSBU) and porphyrin ligand, respectively, are shown in violet and green. As illustrated with the red arrows, a rotation along the 3-fold axis of the octahedral iSBU and a flattening of the 4-fold node in the net derived from **3(In)** gives rise to that of PCN-600.



Fig. S12 PXRD analysis of phase **3**: Final Rietveld refinement for Ni-CatPMOF-3(In) ($\lambda = 0.72610$ Å).

The LSI-indexing method converged unambiguously to a trigonal unit cell (a = 28.5321(3), c = 29.1054(2) Å) with satisfactory Fig. of Merit ($M_{20} = 318$). Systematic extinctions were consistent among other things with the P3c1 space group, which was used to initialize the structural determination by direct methods and simulated annealing. Indium trimers could be localized, but satisfactory Rietveld refinement could not be obtained without the help of SCXRD data. At the final stage, organic ligands were treated as rigid bodies as well as DEA. Guest molecules were localized by simulated annealing and successive difference Fourier calculations. The final Rietveld plot (Fig. SX), corresponds to satisfactory model indicator and profile factors ($R_{\rm B} = 0.032$, $R_{\rm p} = 0.043$ and $R_{\rm wp} = 0.065$) and involves 12 structural parameters: 1 scale factor, 6 atomic coordinates for In atoms, 4 rotation angles for the catecholate and 1 overall temperature factor.

8. CatPMOF-1(Fe)-pz with variable ligand to metal ratio



Fig. S13 a) TGA analysis and b) PXRD diagrams for the materials obtained at variable ligand to metal ratio

Table S3. TGA data analysis for the materials obtained with variable ligand to metal ratio, showing the defective Fe content of CatPMOF-1(Fe)-pz

Ligand/Metal (L/M)	observed dry MOF mass %	observed oxide mass %	expected oxide mass % for L/M = 1/3	Calculated oxide mass % for L/M = 1/2.6
1/2	97.9	17.1	21.9	18.4
1/2.75	97.8	18.2	21.9	18.4
1/3.2	98	18.5	21.7	18.4

9. Inductively Coupled Plasma Optical Emission Spectroscopy analysis



Fig. S14 ICP-AES calibration curves used to quantify the elemental composition of CatPMOF-1(Fe)-pz (left). The composition was quantified by averaging the results obtained from 4 replicates at 4 different wavelengths (right)

9. NMR and EPR analysis of CatPMOF-2(Al) and CatPMOF-3(In)



Fig. S15 ²⁷Al MAS-NMR spectrum of CatPMOF-2(Al) with the spectrum deconvolution (a). The quadrupolar coupling constant is 5.6 MHz (asymmetry parameter 0.3) for the Al^[6] at 25 ppm (green line). The second Al^[6] (purple line) is deconvoluted with a Gaussian line, indicating local disorder around the Al atoms, the 2D MQMAS-NMR spectrum (b).



Fig. S16 ¹H spectrum of dissolved CatPMOF-2(Al) in DMSO-d₆ containing a small amount of concentrated HCl solution. Note that 1 molecule of DEF solvent per porphyrin is visible in solution NMR of the activated sample together with the formic acid and diethylammonium.



Fig. S17 ¹³C NMR spectra of dissolved CatPMOF-2(Al). in DMSO-d₆ containing a small amount of concentrated HCl solution., the peaks at 164.3 ppm and (42.3 + 11.7 ppm) are attributed to the formic acid and diethylammonium respectively



Fig. S18 EPR spectra at 290K for fresh (blue) and activated (green) CatPMOF-2(Al) the signals were fitted to g = 2.004 and g = 2.005 respectively, the quantification of radicular species per molecular unit gives 0.05 % and 1.2 mol % per porphyrin respectively.



Fig. S19 a) ¹H and NMR spectra of CatPMOF-3(In) dissolved in DMSO-d₆ containing a small amount of concentrated HCl solution.



Fig. S20 13 C NMR spectra of CatPMOF-3(In) DMSO-d₆ containing a small amount of concentrated HCl solution., the peaks at 42.11 and 11.53 ppm are attributed to diethylammonium cations.

•



Fig. S21 EPR spectra, at 290K of the CatPMOF-3(In), after synthesis (blue dash-dotted line) and after activation and BET analysis (blue plain line), the same sample was recorded after 9 weeks (green lines) showing no evolution for both materials. The quantification of the radical species accounts for 0.2 and 1.6 mol % per porphyrin in the fresh and activated samples respectively.

11.Porosity

• CatPMOF-1(Fe)



Start point	1	
End point	18	
Slope	0.0061279	
Intercept	1.39E-07	
Correlation coefficient	1	
BET range limit $(p/p_0=2.5878E-02)$	18th	point
$V_a(p_0-p)$ Max value	16290	
Vm	163.18	[cm ³ (STP) g ⁻¹]
$a_{s,BET}$	710.24	$[m^2 g^{-1}]$
С	43957	
Total pore volume $(p/p_0=0.3300)$	0.2752	[cm ³ g ⁻¹]

Fig. S22 BET plot for the sample CatPMOF-1(Fe) and the corresponding calculation parameters.





HK-Plot

• CatPMOF-2(Al)



Start point	1	
Start point	1	
End point	33	
Slope	0.0050597	
Intercept	6.27E-07	
Correlation coefficient	1	
BET range limit $(p/p_0=5.1049E-02)$	33th	point
$V_a(p_0-p)$ Max value	19640	
V_m	197.61	$[cm^{3}(STP) g^{-1}]$
a _{s.BET}	860.09	$[m^2 g^{-1}]$
С	8069.3	
Total pore volume ($p/p_0=0.3300$)	0.3469	[cm ³ g ⁻¹]

Fig. S24 BET plot for the sample CatPMOF-2(Al) and the corresponding calculation parameters.



Fig. S25 Horvath-Kawazoe (HK)-Plot of pore width distribution for the sample CatPMOF-2(Al) and the corresponding average and median pore width values.

• CatPMOF-3(In)



Fig. S26 BET plot for the sample CatPMOF-2(Al) and the corresponding calculation parameters.

HK-Plot



Fig. S27 Horvath-Kawazoe (HK)-Plot of pore width distribution for the sample CatPMOF-2(Al) and the corresponding average and median pore width values.

12.Stability



Fig. S28 TGA for the compounds CatPMOF-1(Fe)-pz, CatPMOF-2(A1) and CatPMOF-3(In) performed under air at a heating rate of 10°C·min⁻¹.



Fig. S29 Temperature-dependent powder XRD analyses of CatPMOF-1(Fe)-pz, CatPMOF-2(Al) and CatPMOF-3(In) carried out from 30 (bottom) to 250°C (top) with a 10°C step (diagrams collected at 50, 100, 150, 200 and 250°C in red). Analyses were performed both a) under air and b) under nitrogen ($\lambda = 1.5418$ Å).



Fig. S30 Evaluation of the stability of the MOFs CatPMOF-1(Fe)-pz, NiCatPMOF-1(In), Ni-CatPMOF-2(Al), Ni-CatPMOF-3(In), in air. PXRD pattern, of the solids stored in air at room temperature for various time ($\lambda = 1.5418$ Å).



Fig. S31 PXRD patterns of CatPMOF-1(Fe)-pz from top to bottom: fresh sample, after activation and BET measurement and after immersion in water (2.5 mg·mL⁻¹ for 24 hours) ($\lambda = 1.5418$ Å).



Fig. S32 PXRD patterns of CatPMOF-2(Al) from top to bottom: fresh sample, after activation and BET measurement and after immersion in water (2.5 mg·mL⁻¹ for 24 hours) ($\lambda = 1.5418$ Å).



Fig. S33 PXRD patterns of CatPMOF-3(In) from top to bottom: fresh sample, after activation and BET measurement and after immersion in water (2.5 mg·mL⁻¹ for 24 hours) ($\lambda = 1.5418$ Å).

13. Electrical conductivity

Table	S4 .	Geometrical	factors (an	rea, A, a	nd thickness	s, L), con	ductance (G)	and	conductivity
(S·cm⁻	1) at	300 K for C	atPMOF-1	(Fe)-pz,	CatPMOF-2	2(Al) and	CatPMOF-3(In).	

MOF	Essay	Area (A, cm ²)	Thickness (L, cm)	Conductance (G)	Conductivity (S·cm ⁻¹)*
CatPMOF-	1	0.0221	0.233	3.135E-08	3.31E-07
1(Fe)-nz	2	0.0178	0.215	3.134E-08	3.78E-07
I(I ¢) p2	3	0.0216	0.197	3.110E-08	2.84E-07
CatPMOF-	1	0.0115	0.185	1.704 E-8	2.73 E-07
2(Al)	2	0.0132	0.132	1.621 E-8	1.62 E-07
2(111)	3	0.0128	0.145	1.901E-8	2.15E-07
CatPMOF-	1	0.0102	0.198	5.386E-10	1.05E-08
3(In)	2	0.0100	0.201	5.171E-10	1.04E-08
U(III)	3	0.0124	0.156	7.870E-10	9.90E-09



Fig. S34 Device and electrical response of CatPMOF-1(Fe)-pz. a) Representative *I-V* curve at 300 K with the corresponding linear fit of the ohmic regime for four-contact probe pressed pellets devices of CatPMOF-1(Fe)-pz and b) top view of the four-contact pressed pellet device.



Fig. S35 Device and electrical response of CatPMOF-2(Al). a) Representative *I-V* curve at 300 K with the corresponding linear fit of the ohmic regime for four-contact probe pressed pellets devices of CatPMOF-2(Al) and b) top view of the four-contact pressed pellet device.



Fig. S36 Device and electrical response of CatPMOF-3(In). a) Representative *I-V* curve at 300 K with the corresponding linear fit of the ohmic regime for four-contact probe pressed pellets devices of CatPMOF-3(In) and b) top view of the four-contact pressed pellet device.

14. Electrochemistry



Fig. S37 Electrochemical behavior upon galvanostatic cycling of CatPMOF-1(Fe)-pz electrode material measured in a Li half-cell. Electrolyte: 1 M LiClO₄ in PC, $(2.0 < E < 3.9 \text{ V vs. Li}^+/\text{Li})$, rate C/20. Potential vs. specific capacity curve, with the plain and dashed lines corresponding to the first cycle and second cycles, respectively. Less than 0.1 electron per catecholate can be exchanged, and no clear plateau is detected suggesting that the redox activity is hindered by poor Li⁺ transport properties.



Fig. S38 Electrochemical behavior upon galvanostatic cycling of CatPMOF-3(In) electrode material measured in a Li half-cell (electrolyte: 1 M LiPF₆ in EC/DMC), rate C/5. Potential vs. specific capacity curves for the 2^{nd} , 10^{th} , 50^{th} , 100^{th} , 150^{th} and 200^{th} cycles.

• Sample characterization after electrochemical testing



Fig. S39 PXRD patterns of CatPMOF-3(In) (black) and the corresponding composite positive electrodes before (red) and after (green) electrochemical cycling (11 cycles).

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