

Synthesis and characterization of new tetra-substituted porphyrins with exo-donor carboxylic groups as building blocks for supramolecular architectures. Catalytic and structural studies of their metalated derivatives

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> **ABSTRACT:** We report herein the synthesis of the porphyrins 5,10,15,20-tetrakis(4-carboxybiphenyl)porphyrin (H₂TCBP) and 5,10,15,20-tetrakis(4-carboxy-2,6-dimethylbiphenyl)porphyrin (H₂TCDMBP) bearing diphenyl units on *meso*-positions, and of their cobalt and silver derivatives. The silver complexes of H₂TCDMBP and of H₂TCPP (H₂TCPP = 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin) were investigated by X-ray crystallography and their supramolecular organization elucidated. Co(TCBP) was reacted with copper formate, yielding a polymeric compound that showed a catalytic activity in the benzylic amination of hydrocarbons using arylazide as aminating agent.

KEYWORDS: coordination network, cobalt, silver, catalysis, amination.

INTRODUCTION

The crystal engineering of functional coordination networks [1] extensively exploited, in the past few years, the networking ability of tetra-*meso*-substituted porphyrins and metalloporphyrins [2]. Open-lattice zeolite-like species with large free-void volumes can be produced when porphyrin units act as tetradentate planar donor nodes. More in general, porphyrin supramolecular arrays show potential applications in many fields of materials chemistry, as photonic devices, conductive polymers, chemical sensors and receptors for selective catalysis.

Multi-porphyrin architectures include networks assembled through hydrogen bond bridges [2a,b],

coordinative bonds to the metals of identical neighboring metalloporphyrin units [3–11], or bonds to external metal centers [12–24]. The last strategy seems especially promising for the engineering of open networks. In principle, these can be programmed by carefully selecting both the different porphyrin *meso*-substituents and the different external metal ions with suitable coordination geometries. Many years ago, Robson and co-workers showed that metalloporphyrins bearing four peripheral pyridyl donors can produce coordination networks with the CdSO₄ topology (**cds**) using Cd(II) centers as linear spacers [12], or with the PtS topology (**pts**) using tetrahedral Cu(I) centers [13]. A variety of remarkable multiporphyrin architectures have been described by Goldberg and co-workers [2].

The two tetra-substituted porphyrins most widely investigated and characterized in the above context are surely 5,10,15,20-tetrakis(4-piridyl)porphyrin (H₂TPYP) and 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H₂TCPP), according, at least, to the number of hits present in the Cambridge Structural Database.

[◊]SPP full member in good standing

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Metalloporphyrins should be suitable building blocks for the synthesis of catalytic metal organic frameworks (MOFs), thanks to their thermal and chemical stability. However, few examples of catalytically active porphyrin-strut-based MOFs have been reported so far [25, 26]. This is mainly due to the difficulty to synthesize MOFs with appropriate pores for catalysis that do not collapse during the reaction solvent removal. It is quite difficult to build networks with free-base porphyrins because of the great aptitude of the porphyrin core to coordinate every metal present in the reaction mixture. Nevertheless, the development of new methodologies for the synthesis of porphyrin strut-based MOFs is encouraged by the facility of porphyrin skeleton modifications and by the high catalytic activity of metalloporphyrins.

The first report of porphyrin strut-based catalysis described a MOF constituted by [tetrakis(phenyl-carboxylate)porphyrin]Mn(III) complexes as building blocks and trinuclear manganese clusters as second-ary building blocks units (SBUs) [27]. The framework, dubbed PIZA-3 (Porphyrinic Illinois Zeolite Analogue-3), showed a non-interpenetrating structure and was an effective catalyst in hydroxylation and epoxidation reactions.

We are currently interested in obtaining new porphyrins building blocks for the formation of extended arrays in the form of open nanoporous framework or immobilized on different supporting matrices for catalytic purposes. Some of us have previously reported investigations on the ability of free-base H₂TPYP and of its Zn^{II}-metalated derivative to give networks with different silver(I) salts [23, 24]. We have now turned our attention towards tetra-carboxyporphyrins, analogous to H₂TCPP but bearing longer donor side arms (see Fig. 1) in order to



Fig. 1. 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP), 5,10,15,20-tetrakis(4-carboxybiphenyl)porphyrin (H_2TCBP) and 5,10,15,20-tetrakis(4-carboxy-2,6-dimethylbiphenyl)porphyrin ($H_2TCDMBP$)

possibly produce frames with greater openings suitable for catalytic applications.

We report here the synthesis and characterization of 5,10,15,20-tetrakis(4-carboxy-2,6-dimethylbiphenyl) porphyrin (H₂TCDMBP) and an improvement of the already published synthesis of 5,10,15,20-tetrakis(4-carboxybiphenyl)porphyrin (H₂TCBP) [28] (Fig. 1). Both porphyrins have been used for the preparation of metalated derivatives and as building blocks for networking. The Ag(II)-metalated derivatives [Ag(TCPP)] (H₂O)₂(solv)_x and [Ag(TCDMBP)](DMF)₄(solv)_x were obtained as single crystals and their structures are herewith reported.

The cobalt complex of H_2TCBP was prepared and reacted with $Cu(HCOO)_2(H_2O)_x$ to obtain a polymeric material that showed catalytic properties in the benzylic amination of toluene by p-NO₂C₆H₄N₃. The same reaction was also catalyzed by PIZA-1 that was prepared by reacting cobalt(III) tetra(*p*-carboxyphenyl)porphyrin (Co(TCPP)) with a linear trinuclear cobalt(II) cluster according to the protocol reported by Suslick and co-workers [29].

RESULTS AND DISCUSSION

Synthesis of 5,10,15,20-tetrakis(4-carboxybiphenyl)porphyrin (H₂TCBP) (3)

The reported synthesis of H_2TCBP [28], a modification of Alder's method [40], consists of a condensation in acetic acid of pyrrole with 4'-formyl-biphenyl-4-carboxylic acid. The latter was obtained by Suzuki coupling between the corresponding arylbromide and arylboronic acid using Pd(PPh₃)₄ as catalyst.

To improve the synthesis of H_2TCBP we used a different strategy to achieve 4'-formyl-biphenyl-4-carboxylic acid employing 10% of Pd(OAc)₂ as catalyst. The sodium salt of the commercially available 4-iodobenzoic acid was coupled with 4-formyl-phenylboronic acid in water to form 4'-formyl-biphenyl-4-carboxylic acid (2) in quantitative yield. It should be noted that up to now 2 was obtained starting from ester derivatives of 4-iodobenzoic acid and using palladium posphine complexes as catalysts [41] or supporting the acid on PEG [42]. Conversely, we here report an almost quantitative synthesis of 2 starting from commercially available compounds using a cheap catalyst and a safe, economic and environmentally benign solvent.

Then, the corresponding porphyrin ligand was synthesized in a good yield by using the usual methodology (Scheme 1).

Synthesis of 5,10,15,20-tetrakis(4-carboxy-2,6-dimethylbiphenyl)porphyrin (H₂TCDMBP) (8)

The novel 5,10,15,20-tetrakis(4-carboxy-2,6-dimethylbiphenyl)porphyrin ($H_2TCDMBP$) was synthesized using



Scheme 1. Synthesis of 5,10,15,20-tetrakis(4-carboxybiphenyl)porphyrin (H₂TCBP) (3)

the Adler's method by reacting 4'-formyl-2,6-dimethylbiphenyl-4-carboxylic acid with freshly distilled pyrrole in refluxing propionic acid. The starting aldehyde 4'-formyl-2,6-dimethyl-biphenyl-4-carboxylic acid was first synthesized from the commercial 4-bromo-2,6dimethylaniline through the four different steps shown in Scheme 2 with an overall yield of 46%.

The first step involved a Sandemeyer reaction to transform 4-bromo-2,6-dimethylaniline into 2,5-dibromo-mxylene (4). In the second step, n-BuLi was used in an exchange reaction of the less hindered bromine of 2,5dibromo-m-xylene to form the corresponding organolithium derivative, which was promptly reacted with CO₂.



Scheme 2. Synthesis of 5,10,15,20-tetrakis(4-carboxy-2,6-dimethylbiphenyl)porphyrin (H₂TCDMBP) (**8**)

The two methyl groups of the 2,5-dibromo-*m*-xylene control the regioselectivity of the process, leading to the formation of a single compound.

The described synthesis of **5** was preferred to the direct oxidation of 2-bromo-1,3,5-trimethylbenzene with chromic acid ($K_2Cr_2O_7/H_2SO_4$) which was characterized by a lower yield (<10%) and required a more difficult purification process.

The coupling reaction between **6** and 4-formylphenylboronic acid was performed using 1 mol% of bis(triphenylphosphine)palladium(II)succinimide as precatalyst, following the procedure developed by Fairlamb *et al.* [30]. Efficient cross-coupling catalysts for the synthesis of biaryls starting from *ortho*-hindered aryl bromides are not ordinary.

The catalytic system $Pd_2(dba)_3/P(t-Bu)_3/KF$, developed by Fu and co-workers [43], was tested in THF at room and reflux temperature and even though it was very successful with other sterically hindered aryl bromides, in this case it gave only traces of the desired coupled product.

Attempts to effect the coupling using the catalytic systems $Pd(PPh_3)_4/Na_2CO_3(aq.)$ or NaOH (aq.) or *t*-BuOK/ *t*-BuOH in refluxing DME were unsuccessful (in the case of Na₂CO₃) or led to traces of 4'-formyl-2,6-dimethylbiphenyl-4-carboxylic acid (7) (in the other two cases). Increasing the strength of the base was observed to improve the performance of the reaction, in accordance with what was expected.

The methodology employed for the synthesis of **2**, $Pd(OAc)_2$ as catalyst in water at 150 °C afforded 11% of the desired product, but this was associated to extensive catalyst decomposition.

The H₂TCDMBP porphyrin was obtained in 15% yield as a pure product at the end of the reaction and did not require further purification. Its ¹H NMR spectrum, acquired in DMSO, shows a broad signal at -2.83 ppm for the pyrrolic NH groups and a singlet at 2.30 ppm for the two methyl groups; the aromatic CH groups give doublets at 7.38 ppm (${}^{3}J_{\text{H-H}} = 7.15$ Hz) and 8.10 ppm (${}^{3}J_{\text{H-H}} = 7.15$ Hz) and a singlet at 7.86 ppm. The broad singlet at 12.89 ppm was assigned to COOH groups.

Synthesis of silver complexes of H_2TCPP and $H_2TCDMBP$

Despite the commercially available H_2TCPP have been widely employed both in the preparation of novel metalated complexes and in the crystal engineering of coordination networks, their silver derivatives have never been reported. We have been able to obtain the silvermetalated derivative of H_2TCPP and characterized it by X-ray analysis. The metalation was performed by reacting H_2TCPP with $Ag(O_2CCH_3)$ in pyridine/ H_2O/NH_3 at 150 °C for four days. The resulting solution was left to evaporate slowly at room temperature to obtain small single crystals of the pyridine chlatrate complex $[Ag(TCPP)](H_2O)_2(solv)_x$ (9). Similarly, single crystals of the silver-metalated $H_2TCDMBP$ porphyrin (10) were obtained by slow diffusion of a methanolic solution of $Ag(O_2CCH_3)$ into a solution of $H_2TCDMBP$ in DMF. This is the first example of a crystal structure reported for a tetra-carboxylic biphenyl porphyrin. Note that a very limited number of Ag(II)-metalated porphyrin structures have been reported [44].

Single crystal structure of [Ag(TCPP)](H₂O)₂(solv)_x (9)

The crystallographic analysis of **9**, in spite of the poor quality of the isolated single crystals, was carried out considering the limited number of reported silver-metalated porphyrins.

The Ag(II)-porphyrinate complex shows a saddle-type distortion of the tetrapyrrolic core with large deviations from the mean plane of the pyrrolic rings that are in the range 0.355–0.472 Å. The four Ag–N distances are in the range 2.067(5)–2.078(5) Å, similar to previously reported Ag–N bonds in metalated porphyrins [44]. The four carboxylic groups are protonated and the molecules form an extended hydrogen bond pattern (O–H…O 2.613(6)–3.036(7) Å, O–HO 123–168°) (Fig. 2). A rationalization neglecting the chlatrate water molecules results in a hydrogen-bonded unusual 2D layer illustrated in Fig. 3. The porphyrinate units employ three of the four exocarboxylic groups to form hydrogen-bond bridges with

adjacent units. These bridges consist of chains of three –COOH groups generating a T shaped node (see Fig. 2).

To describe the layer topology we observe that it is comprised of two types of 3-conn nodes (the C atom of the central -COOH group of the chains bridges in Fig. 2 and the Ag ions, Ag. C edge lengths 9.20, 13.44, 13.53 Å). It is an unprecedented uninodal 3-connected 2D net with point symbol (Schläfli) 10^3 (Vertex Symbol: $10_2.10_4.10_4$). A special feature is the presence of self-catenation (illustrated in Fig. 4). The fourth side arms of the porphyrins not involved in the hydrogen-bonding bridges protrude on both sides of the layers, showing deep interdigitation with the two adjacent layers (see Fig. 5). These thick layers superimpose in an ABAB sequence. A chlatrate water molecule gives hydrogen-bonding bridges between the carboxylic group of the dangling arm and the three-connected node of an adjacent layer. If these hydrogen bonds are also considered, the resulting framework is a complex 3D architecture. The other chlatrate water molecules are involved in an intricate hydrogen-bonding pattern.

Crystal structure of [Ag(TCDMBP)](DMF)₄(solv)_x (10)

The $[Ag(TCDMBP)](DMF)_4(solv)_x$ crystallizes in the triclinic P-1 space group, giving centrosymmetric silver(II)-porphyrinate monomeric units. All the four carboxylic groups are protonated and their involvement in strong hydrogen bonds (O–H…O in the range 2.55–2.56 Å,



Fig. 2. A view of the hydrogen bonds involving the carboxylic groups in $[Ag(TCPP)](H_2O)_2(solv)_x$ (9)



Fig. 3. A top view of the 2D layer in $[Ag(TCPP)](H_2O)_2(solv)_x$ (9)



Fig. 4. A schematic view of the 2D layer showing self-catenation in $[Ag(TCPP)](H_2O)_2(solv)_x$ (9)

O–H…O 179.5°) with a molecule of dimethylformamide (DMF) prevents a possible extension of the hydrogenbonding pattern, giving discrete 1:4 porphyrinate:DMF assembly (Fig. 6). The metalated tetrapyrrolic macrocycle core is very flat and the deviation from the mean plane is up to 0.015 Å. The Ag-N distances are 2.077(6) Å and 2.085(6) Å and are in the typical range of the Ag-porphyrinate systems [44]. The four side arms are slightly oriented up or down with respect to the flat core plane. As expected for steric reasons the presence of two methyl groups in the 2,6-positions of the external phenyl rings makes these groups almost orthogonal to the other one (dihedral angles: 70.7° and 81.4°). The distances between the silver atom and the H-bonded oxygen atom of the carboxylic groups are respectively 13.85 Å and 13.92 Å. A side view of the molecule is also shown in Fig. 6.

The porphyrinate units are stacked down the crystallographic a axes with an AAA sequence to generate a square-like rod packing (Fig. 7). The void left is only 12.3% of the cell volume and is mainly distributed in channels along the *a* axis with an average cross-section diameter of 3.3 Å.

Synthesis of cobalt complexes of H_2TCPP and $H_2TCDMBP$

The porphyrin H_2TCPP was employed to synthesize the network PIZA-1 following Suslick's procedure [29]. The compound PIZA-1, which molecular structure was elucidated by X-ray analysis [29], is a neutral network of cobalt(III) porphyrin cores linked to each other by cobalt(II)-carboxylate clusters. The presence of large internal cavities in the non-interpenetrating PIZA-1 framework allowed us to suppose a catalytic activity of this compound in the benzylic amination of toluene, a reaction efficiently catalyzed by monomeric cobalt porphyrin complexes [45].

The reaction, shown in Scheme 3, was performed at reflux temperature. The consumption of the azide was followed by IR spectroscopy and the formation of the corresponding benzylic amine by TLC.

Although PIZA-1 was insoluble in toluene, 70% of azide conversion was observed after 48 h. Its catalytic activity partially decreased when additional amounts of the reagents were added; in 53 h only 35% of azide conversion was achieved. The presence of the corresponding benzylic imine was confirmed by GC-MS analysis of the reaction mixture.

In order to build MOF with larger pores, H_2TCBP instead of H_2TCPP was used as porphyrin ligand for the synthesis of Co(TCBP) (11) (80% yield). Complex 11



Fig. 5. A schematic view of the packing in $[Ag(TCPP)]-(H_2O)_2(solv)_x$ (9) showing the interdigitation and the inter-layer hydrogen bonds

was employed as catalyst in the amination of toluene (R = H), ethylbenzene ($R = CH_3$) and isopropylbenzene ($R = CH(CH_3)_2$) by 4-nitrophenylazide and a complete azide conversion was observed in 12, 8 and 9 h, respectively. The GC-MS analyses of the reaction mixtures revealed the presence of benzylic imine as the only aminated compound (Scheme 4).

In view of the catalytic activity of complex **11** and of the coordinative environment of the porphyrin periphery, we employed **11** as a building block to synthesize a tridimensional complex using $Cu(HCOO)_2(H_2O)_x$ as *secondary building units* (SBUs) [46]. Copper carboxylates are often employed as SBUs in the assembling of MOFs because they form dicopper units with a paddlewheel structure that is well-suited for regular propagation of the structural motif. The solvotermic reaction between $Cu(HCOO)_2(H_2O)_x$ and **11** yielded a brown powder whose elemental analysis is in accord with the formula $\{Cu_2[Co(TCBP)]\}_n$ (**12**) and its polymeric nature is proposed on the base of extreme insolubility in any organic solvent. On this bulk material we performed XRPD analysis that revealed an amorphous powder. SEM images and EDS analyses on the same sample showed a heterogeneous distribution of copper and cobalt elements. Thermal gravimetric analysis (TGA), performed in the range 50–650 °C, showed a first weight loss of about 5% in the range 50–230 °C, followed by an almost continual weight loss to 68% at 650 °C.

Unfortunately, attempts to obtain single crystals of **12** for a structure determination failed. However, this material was tested as a catalyst in the reaction in Scheme 3 and within 48 h 63% of the azide was converted to form the corresponding imine. A comparison of this catalytic result with those illustrated above using complex **11** as catalyst evidences a lower catalytic activity for polymer **12**. This is not unexpected as it is quite the rule that heterogenized catalysts show lower activity than their homogeneous counterpart. On the other hand, UV spectroscopy of the solution at the end of the catalytic reaction showed the absence of any porphyrin complex, indicating that the catalyst is indeed heterogeneous and easily recovered.

In order to exclude a catalytic role of the copper atom, we repeated the reaction between toluene and 4-nitrophenylazide in the presence of Cu(TPP). We did not observe any arylazide conversion after 20 h in refluxing toluene. Then, to better investigate this catalytic aspect, the porphyrin H₂TCBP (**3**) was reacted with Cu(HCOO)₂(H₂O)_x in a 1:2 molar ratio using the same experimental procedure employed for the synthesis of **12**. The obtained compound was tested as catalyst in the model reaction described above (Scheme 3). Again, no arylazide conversion was observed, strongly supporting the catalytic inactivity of copper atoms.

EXPERIMENTAL

General

The reaction solvents were of analytical grade and were freshly distilled under a dry nitrogen atmosphere prior to use. Tetrahydrofuran and toluene were purified by distillation over sodium. Dichloromethane and pyrrole were purified by distillation over calcium hydride. 5,10,15,20tetrakis(4-carboxyphenyl)porphyrin (H₂TCPP) and the other reagents were purchased from Sigma-Aldrich and used without further purification. Bis(triphenylphosphine) palladium(II)succinimide [30] and PIZA-1 [29] were prepared according to the reported procedures.

All the reactions were monitored by thin-layer chromatography carried out on 0.2-mm Fluka silica gel plates



Fig. 6. Front and side views of $[Ag(TCDMBP)](DMF)_4(solv)_x$ (10)



Fig. 7. A view of the packing down the crystallographic a axis in [Ag(TCDMBP)](DMF)₄(solv)_x (10)



Scheme 3. PIZA-catalyzed amination of toluene by 4-nitrophenylazide

| $Ph-CH_2R + 2 ArN_3 -$ | complex 11 | ₽h−C=NAr | + ArNH ₂ |
|------------------------|------------|----------|---------------------|
|------------------------|------------|----------|---------------------|

 $R = H, CH_3, CH(CH_3)_2; Ar = 4-NO_2C_6H_4$

Scheme 4. Complex **11**-catalyzed amination of hydrocarbons by 4-nitrophenylazide

using UV light as a detector. Column chromatographic separations were performed using silica gel (Merck 60, 0.040-0.060 mm) and solvents of analytical grade as eluents. ¹H NMR spectra were recorded on a Bruker DRX-300 instrument; δ values are given in ppm relative to tetramethylsilane. IR spectra were recorded on PerkinElmer Paragon 1000 PC FTIR or Varian Scimitar FTS 1000 spectrophotometers. Thermogravimetric analysis (TGA) were performed on a PerkinElmer TGA 7 instrument under dynamic nitrogen (total flow rate 20 cm³/min). Powder patterns were recorded on a Philips PW1820 diffractometer (Cu K α radiation, $\lambda = 1.5405$ Å), in the 5–35° 2θ range (0.02° and 2.5 s per step). Semiquantitative Scanning Electron Microcospy (SEM) analyses were performed with a Jeol JSM-5500LV instrument equipped with EDS spectrometer IXRF EDS 2000.

Synthesis of 5,10,15,20-tetrakis(4-carboxybiphenyl)porphyrin (H₂TCBP) (3)

Preparation of sodium 4-iodo-benzoate (1). 4-iodobenzoic acid (5.08 g, 20.5 mmol) was added to a water solution of NaOH 0.1 M (205 mL, 20.5 mmol). The mixture was stirred at 70 °C until a solution was formed. The solvent was evaporated to dryness and the residue was dried by azeotropic distillation with *n*-hexanes using a Dean-Stark apparatus. Sodium 4-iodo-benzoate was quantitatively recovered as a white solid.

Preparation of 4'-formyl-biphenyl-4-carboxylic acid (2). 4-formyl-phenylboronic acid (1.39 g, 9.25 mmol), Pd(OAc)₂ (0.17 g, 0.77 mmol) and K₂CO₃ (2.69 g, 19.5 mmol) were added to a degassed solution of sodium 4-iodo-benzoate (2.09 g, 7.75 mmol) in H₂O (125 mL). The mixture was stirred at 70 °C for 2 h. The green suspension was filtered through celite to remove palladium and washed with H₂O. The filtrate was treated with conc. HCl to reach pH ~ 2. The resulting suspension was stirred for 30 min and then filtered. The recovered solid was washed with H_2O and dried by azeotropic distillation with *n*-hexanes. The desired product was recovered as a white solid (1.75 g, 99.0%). ¹H NMR (300 MHz, DMSO): δ , ppm 8.08–7.89 (m, 8H, Ar), 10.08 (s, 1H, CHO), 13.07 (brs, 1H, COOH). Anal. calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46%. Found: C, 74.34; H, 4.44.

Preparation of 5,10,15,20-tetrakis(4-carboxybiphenyl)porphyrin (H₂TCBP) (3). A solution of pyrrole (1.30 mL, 18.7 mmol) in propionic acid (2.00 mL) was added dropwise to a solution of 4'-formyl-biphenyl-4-carboxylic acid (3.92 g, 17.3 mmol) in propionic acid (25.0 mL). The resulting mixture was refluxed for 1 h and then allowed to cool to room temperature. The resulting green solid was collected, washed with H₂O, EtOH, *n*-hexanes, and dried by azeotropic distillation with *n*-hexanes (2.16 g, 46.0%). ¹H NMR (300 MHz, DMSO): δ, ppm 7.67–8.16 (m, 32H, Ar), 10.60 (brs, 8H, pyrrole), 12.80 (s, 4H, COOH). IR (nujol): v_{max}, cm⁻¹ 3428 (br), 1732 (m), 1716 (m), 1699 (m), 1651 (w), 1557 (w), 1260 (w). UV-vis (DMF): λ_{max} , nm (log ϵ_{M}) 423 (5.60), 514 (4.27). Anal. calcd. for C₇₂H₄₆N₄O₈: C, 78.96; H, 4.23; N, 5.12%. Found: C, 78.55; H, 4.60; N, 5.30.

Synthesis of 5,10,15,20-tetrakis(4-carboxy-2,6-dimethylbiphenyl)porphyrin (H,TCDMBP) (8)

Preparation of 1,4-dibromo-*m***-xylene (4).** A solution of NaNO₂ (1.08 g, 15.6 mmol) in conc. H_2SO_4 (12.0 mL) was prepared and maintained below 10 °C. A solution of 4-bromo-2,6-dimethylaniline (3.00 g, 15.0 mmol) in acetic acid (12.0 mL) was added portionwise. The mixture was stirred for 1 h below 10 °C and then added in portions to a vigorously stirred solution of CuBr (2.27 g, 15.6 mmol) in 48.0% HBr (15.0 mL) and H₂O (12.0 mL) at 50 °C. The addition was made over 30 min. After the addition was completed, the reaction mixture was heated for 30 min at 70 °C. The mixture was left to cool to room temperature, then H₂O (120 mL) and *n*-hexane (180 mL) were added. The organic phase was isolated, washed with H₂O (120 mL), and dried over MgSO₄. The salt was filtered off and the solvent was evaporated to dryness. The residue was purified by chromatography column (silica gel, elution with *n*-hexanes). The desired product was obtained as a light yellow liquid which crystallized on standing (2.06 g, 52.0%). Analytical data is in accord with the literature [31].

Preparation of 4-bromo-3,5-dimethylbenzoic acid (5). Under a nitrogen atmosphere, *n*-BuLi 2.5 M in *n*-hexanes (19.5 mL, 48.7 mmol) at -78 °C was added to a solution of 1,4-dibromo-*m*-xylene (10.7 g, 40.6 mmol) in anhydrous THF (100 mL). The mixture was stirred at -78 °C for 1 h, and then was added dropwise to an excess of dry ice. The reaction mixture was then stirred for 3 h and allowed to warm to room temperature. A solution of HCl 1 M was added to reach pH = 1–2. The mixture was extracted with ethyl acetate (500 mL)

and the organic phase was washed with H_2O (100 mL) and dried over MgSO₄. The salt was filtered off and the solvent was evaporated to dryness to obtain 4-bromo-3,5-dimethylbenzoic acid as a white solid (8.80 g, 95%). Analytical data is in accord with the literature [32].

Preparation of sodium 4-bromo-3,5-methylbenzoate (6). A water solution (2.00 mL) of NaOH (17.6 mg, 0.44 mmol) was added to 4-bromo-3,5-dimethylbenzoic acid (0.10 g, 0.44 mmol). The mixture was heated to 50 °C and stirred until the solid was fully dissolved. The water was evaporated to dryness to quantitatively obtain the product as a white solid.

Preparation of 4'-formyl-2,6-dimethyl-biphenyl-4-carboxylic acid (7). Sodium 4-bromo-3,5-methylbenzoate (0.44 mmol), 4-formyl benzoic acid (0.07 g, 0.47 mmol), Na₂CO₃ (0.11 g, 1.00 mmol), H₂O (1.00 mL), THF (1.50 mL) and $[(PPh_3)_2Pd(N-succ)_2]$ $(3.30 \text{ mg}, 4.10 \times 10^{-3})$ mmol) were degassed by freeze-pump-thaw method. The reaction mixture was heated at 60 °C for 23 h. The solvent was evaporated to dryness and H₂O (60.0 mL) was added. The water solution was washed with diethyl ether $(3 \times 20.0 \text{ mL})$ and then treated with conc. HCl to reach pH = 1. The product was extracted with ethyl acetate $(3 \times 60.0 \text{ mL})$. The organic phases were combined and dried over MgSO4. The salt was filtered off and the solvent was evaporated to dryness to obtain the desired product as a white solid (104 mg, 93.0%). ¹H NMR (300 MHz, CDCl₃): δ , ppm 2.11 (s, 6H, CH₃), 7.36 (d, 2H, ${}^{3}J_{H-H} =$ 8.04 Hz, ArH), 7.91 (s, 2H, ArH), 8.02 (d, 2H, ${}^{3}J_{H-H} = 8.04$ Hz, ArH), 10.12 (s, 1H, CHO). Anal. calcd. for C₁₆H₁₄O₃: C, 75.57; H, 5.55%. Found: C, 75.71; H, 5.69.

Preparation of 5,10,15,20-tetrakis(4-carboxy-2,6-dimethylbiphenyl)porphyrin (H2TCDMBP) (8). 4'-formyl-2,6-dimethyl-biphenyl-4-carboxylic acid (500 mg, 1.97 mmol) and pyrrole (0.140 mL, 2.02 mmol) were added dropwise to refluxing propionic acid (12.0 mL). After the addition the reflux was maintained for 45 min. The mixture was allowed to cool to room temperature, after which the precipitated purple solid was collected in a filter, washed with hot H₂O and MeOH, and dried under reduced pressure (87.1 mg, 15%). ¹H NMR (300 MHz, DMSO): δ, ppm -2.83 (s, 1H, NH), 2.30 (s, 24H, CH₃), 7.38 (d, 8H, ${}^{3}J_{H-H} = 7.15$ Hz, ArH), 7.86 (s, 8H, ArH), 8.10 (d, 8H, ${}^{3}J_{H-H}$ = 7.15 Hz, ArH), 12.89 (s, 4H, COOH). IR (nujol): v_{max}, cm⁻¹ 3434 (br), 3317 (w), 2697 (w), 2597 (w), 2525 (w), 1682 (s), 1606 (m), 1571 (w), 1508 (w), 1417 (w), 1392 (w), 1347 (w), 1306 (m), 1266 (w), 1236 (m), 1218 (m), 1182 (w), 1157 (w), 1104 (w). UV-vis (DMF): λ_{max} , nm (log ε_{M}) 420 (5.50), 515 (4.23). Anal. calcd. for C₈₀H₆₂N₄O₈: C, 79.58; H, 5.18; N, 4.64%. Found: C, 79.95; H, 5.29; N, 4.31.

Synthesis of [Ag(TCPP)](H₂O)₂(solv)_x (9)

 H_2TCPP (6.90 mg, 87.0 × 10⁻³ mmol), Ag(O₂CCH₃) (4.50 mg, 27 × 10⁻³ mmol), 28% NH₃ solution (0.50 mL), and pyridine (0.80 mL) were added to a steel reactor. The mixture was stirred at room temperature for 20 min, then heated at 150 °C for four days and slowly cooled (0.1 °C/min) to room temperature. The obtained solution was slowly evaporated at atmospheric pressure and room temperature. After two months, purple-green needles formed. UV-vis (DMF): λ_{max} , nm 420, 515, 549.

Synthesis of [Ag(TCDMBP)](DMF)₄(solv)_x (10)

Crystals suitable for X-ray analysis were obtained by slow diffusion of a solution of Ag(O₂CCH₃) (1.80 mg, 11.0 × 10³ mmol) in MeOH (4.00 mL) into a solution of *meso*-tetrakis(4-carboxy-2,6-dimethylbiphenyl)porphyrin (H₂TCDMBP) (2.00 mg, 1.70 × 10⁻³ mmol) in DMF (4.00 mL), after a period of five months. UV-vis (DMF): λ_{max} , nm 425, 517, 446.

Synthesis of [Co(TCBP)] (11)

CoCl₂(H₂O)₆ (109 mg, 4.60×10^{-1} mmol) was added to a DMF (18.0 mL) solution of H₂TCBP (502 mg, 4.60×10^{-1} mmol) and the resulting suspension was refluxed for 1.5 h and cooled to room temperature. Then CoCl₂(H₂O)₆ (109 mg, 4.60×10^{-1} mmol) was re-added to the reaction mixture that was refluxed for another 1.5 h. The mixture was cooled and water (40.0 mL) was added. The resulting solid was collected in a filter and refluxed in *n*-hexane to eliminate the residual water by azeotropic distillation. The brown solid was collected in a filter and dried *in vacuo* (417 mg, 80%). IR (nujol): v_{max}, cm⁻¹ 3447 (br), 1733 (m), 1717 (m), 1700 (m), 1653 (w), 1558 (w), 1377 (w). Anal. calcd. (%) for C₇₂H₄₄CoN₄O₈: C, 75.06; H, 3.85; N, 4.86%. Found: C, 74.85; H, 4.12; N, 4.39. UV-vis (DMF): λ_{max}, nm (log ε_M) 430 (4.90), 540 (4.32).

Synthesis of {Cu₂[Co(TCBP)]}_n (12)

A mixture of HCOOH (0.20 mL, 5.30 mmol) and $Cu(HCOO)_2(H_2O)_x$ (31.0 mg) was added to a suspension of Co(TCBP) (102 mg, 8.85×10^{-2} mmol) in CH₃OH (20.0 mL). The resulting brown suspension was placed in a glass liner inside an autoclave. The autoclave was frozen at dry ice temperature, evacuated and filled with dinitrogen three times. N_2 (10 bar) was then added at room temperature and the autoclave was heated at 160 °C for 12 h. The reaction was cooled to room temperature and the brown solid was collected in a filter, washed with CH₃OH, and dried under vacuum (85.0 mg). Anal. calcd. (%) for C₇₂H₄₄Cu₂CoN₄O₈: C, 67.60; H, 3.47; N, 4.38%. Found: C, 67.35; H, 3.60; N, 4.55. UV-vis (DMF): λ_{max} , nm (log ε_{M}) 421 (5.07), 533 (4.26). {Cu₂[Co(TCBP)]}_n was analyzed by Scanning Electron Microscopy (SEM), Thermal Gravimetric Analysis (TGA) and X-ray Powder Diffraction (XRD) (see Results and Discussion sections).

General procedure for catalytic reactions

In a typical run, the catalyst $(1.22 \times 10^{-2} \text{ mmol})$ was added to a hydrocarbon (30.0 mL) solution of *p*-nitrophenylazide (100 mg, 6.09×10^{-1} mmol). The resulting solution was refluxed using a preheated oil bath. The consumption of the arylazide was monitored by TLC up to the point that its spot was no longer observable, and then by IR spectroscopy measuring the N₃ characteristic absorbance at 2120 cm⁻¹. The solution was then analyzed by GC-MS.

Crystallography

Crystal data for all the compounds is listed in Table 1. Data were collected on a APEX II-CCD Bruker diffractometer with Mo-K α λ = 0.71073 Å. Empirical absorption corrections (SADABS) [33] were applied to all data. The structures were solved by direct methods (SIR97) [34] and refined by full-matrix least-squares on F^2 (SHELX-97) [35] with WINGX interface [36]. All hydrogen atoms were placed in geometrically calculated positions and thereafter refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. All the diagrams were produced using TOPOS program [37]. The accessible free voids were calculated by PLATON [38]. Details on the refinements can also be found in the cif file under _refine_special_ details. The crystals are unstable in air and were collected under mineral oil. Both contain disordered solvents and because it was difficult to refine a consistent model, their contribution was subtracted from the observed structure factors according to the BYPASS procedure [39], as implemented in PLATON with the command SQUEEZE. The R before the procedure was R1 = 0.1977 for 6884

Table 1. Crystallographic data for all compounds

| | $Ag(TCPP) \cdot 2H_2O$ | Ag(TCDMBP) · 4DMF |
|---------------------------------|---------------------------|--|
| Formula | $C_{48}H_{32}AgN_4O_{10}$ | C ₉₂ H ₈₈ AgN ₈ O ₁₂ |
| М | 932.65 | 1605.57 |
| System | monoclinic | triclinic |
| Space group | C2/c | P-1 |
| <i>a</i> , Å | 46.612(8) | 7.7821(10) |
| b, Å | 8.8465(15) | 12.2156(15) |
| <i>c</i> , Å | 33.738(6) | 24.305(3) |
| α, ° | 90 | 83.551(2) |
| β, ° | 131.705(2) | 87.161(2) |
| γ, ° | 90 | 74.649(2) |
| U, Å ³ | 10387(3) | 2213.5(5) |
| Z | 8 | 1 |
| Temperature, K | 150(2) | 150(2) |
| Reflections collected | 51962 | 27718 |
| Indep. refls, R (int) | 9251, 0.0687 | 7061, 0.0642 |
| Crystal decay, % | 0 | 0 |
| Observed [Fo > 4 σ (Fo)] | 6730 | 4759 |
| Data/restr./param. | 9251/0/258 | 7061/0/415 |
| R1 [Fo > 4 σ (Fo)] | 0.1068 | 0.1190 |
| wR2 (all data) | 0.3252 | 0.3798 |

Fo > $4\sigma(Fo)$ for $[Ag(TCPP)](H_2O)_2(solv)_x$ and R1 = 0.1551 for 4797 Fo > $4\sigma(Fo)$ for $[Ag(TCDMBP)](DMF)_4$. Due to difficulty in the refinement, arising from the very weak diffraction, anisotropic thermal parameters in $[Ag(TCPP)](H_2O)_2(solv)_x$ were used only for the central silver atom and in $[Ag(TCDMBP)](DMF)_4$ all the atoms were treated as anisotropic except for the 12 independent atoms of the porphyrin ring. Further details are reported in the .cif files (see Supporting Information section).

CONCLUSION

In conclusion, we report the synthesis of the novel 5,10,15,20-tetrakis(4-carboxy-2,6-dimethylbiphenyl)porphyrin ($H_2TCDMBP$) (8) and an improvement in the synthesis of 5,10,15,20-tetrakis(4-carboxybiphenyl)porphyrin (H_2TCBP) (3). Both porphyrins have long diphenyl units on *meso*-positions and are suitable building blocks to be used for the synthesis of porous MOFs. The porphyrins reactivity towards metal cations has been preliminarily explored obtaining cobalt and silver derivatives. X-ray analyses of the silver derivatives of 8 and of the commercial 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin(H₂TCPP) have been carried out considering that structurally characterized Ag(II)-metalated porphyrins are scarce. The cobalt derivative of **3** was reacted with $Cu(HCOO)_2(H_2O)_x$ to yield $[Cu_2Co(TCBP)]_n$ (12), a polymeric complex that showed a catalytic activity in the benzylic amination of hydrocarbons using arylazide as aminating agent.

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Supporting information

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition numbers CCDC 769846–769847. Copies can be obtained on request, free-of-charge, *via* www.ccdc. cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

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