

A bifunctionalized porous material containing discrete assemblies of copper-porphyrins and calixarenes metallated by ion diffusion†

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Nanoporous crystals of discrete stacks of metallo-porphyrins together with exogenous metal centers have been obtained by synergistic non-covalent interactions of tetra-cationic copper(II)-meso-tetrakis(4-*N*-methylpyridyl)porphyrin and polyanionic tetra-sulfonato-tetrakis(hydroxylcarbonylmethoxy)calix[4]arene building blocks successively functionalized by diffusion and coordination of Zn^{2+} or Ni^{2+} ions.

The efficient conversion of solar energy into chemical energy by artificial systems is certainly one of the most challenging goals in chemistry.¹ Natural systems have been extensively investigated to understand the principles that rule the high efficiency of photosynthesis. Large differences are observed in the photosynthetic organisms, but all of them use a common basic strategy: a light harvesting system containing many chromophores for the photon absorption and a specialized reaction centre at which the captured energy is converted into chemical energy by means of electron-transfer reactions.¹ In the quest for building blocks for the construction of antenna systems able to harvest the light, porphyrins are very attractive candidates.^{2,3} Structural,⁴ optical^{5,6} and redox⁷ properties of porphyrins can be easily tuned through metallation and functionalization. However, the aromatic planar porphyrin molecules exhibit a strong tendency to stack among themselves in solution into ill-defined or infinite aggregates and chemists have long endeavored to engineer discrete stacks of specific lengths and orientation.⁸ The synthesis of discrete porphyrin systems has been mainly obtained using strong directional covalent or coordination bonds. Supramolecular approaches to the synthesis of non-covalent porphyrin aggregates have exploited electrostatic interactions,^{9–12} hydrogen bonding,^{13,14} coordinative bonding^{15,16} or π – π aromatic stacking.^{17–19} The fine control of the stoichiometry and geometry of these assemblies is very important in order to design porphyrin systems with specific photochemical properties.

In our previous studies, various supramolecular complexes of calixarenes and porphyrins were synthesized and characterized through spectroscopy, electrochemistry and single crystal X-ray diffraction.^{9–11} By the templating action of the positively charged meso-tetrakis(4-*N*-methylpyridyl)porphyrin (H_2TMPyP) onto the poly-anionic calixarene 5,11,17,23-tetra-sulfonato-25,26,27,28-tetrakis(hydroxylcarbonylmethoxy)calix[4]arene (C4TsTc), crystals of

porphyrin/calixarene complexes with stoichiometry tuned by pH were obtained.^{9,11} In a recent work,¹² we have reported the synthesis of a new highly porous crystalline material consisting of a three-dimensional multicomponent porphyrin/calixarene supramolecular framework. This tetragonal crystal form is assembled by interpenetrated 2D meshes in which the nodes are supramolecular units of three π -stacked porphyrins surrounded by four host/guest complexed calixarenes (3 : 4 units) (Fig. 1). The approximately two-dimensional square network is formed by sodium ions bridging the calixarene carboxylate rims of adjacent 3 : 4 units (Fig. 1). This material has an exceptionally large void volume (more than 60%) accessible to solvent molecules. In order to change the properties of porphyrins through metallation, we diffused various metal ions in the pores of this structure, using a soaking technique. The X-ray structures showed that the metallation reaction involves only the porphyrins in solution, while in the crystal the reaction is prevented by the stacking among the porphyrins and the protection of the calixarene molecules, which were metallated on the lower rim.¹²

Obtaining a discrete stacking of metallo-porphyrins represents a notable achievement¹⁸ and further efforts were made to produce bifunctionalized porous crystals containing copper-porphyrins. The formation of host–guest complexes between cavitands and metallo-porphyrins has been already demonstrated both in solution and in the solid state.¹¹ In particular, triclinic crystals of a copper-porphyrin/calixarene complex obtained at pH 9 showed a compact polymeric arrangement of stacked 3 : 4 units.¹¹ Thus, in order to obtain the highly porous tetragonal crystal form with a discrete stacking of metallo-porphyrins, new co-crystallization experiments were performed at pH 9.5 using the copper-porphyrin instead of free base

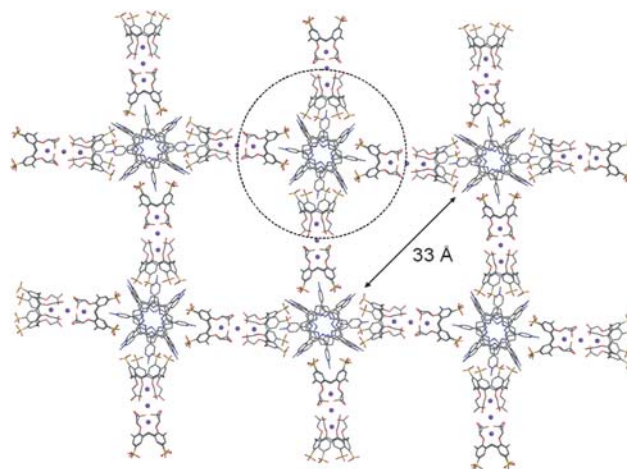


Fig. 1 Two-dimensional network of 3 : 4 $\text{H}_2\text{TMPyP}/\text{C4TsTc}$ units (dashed circle).¹²

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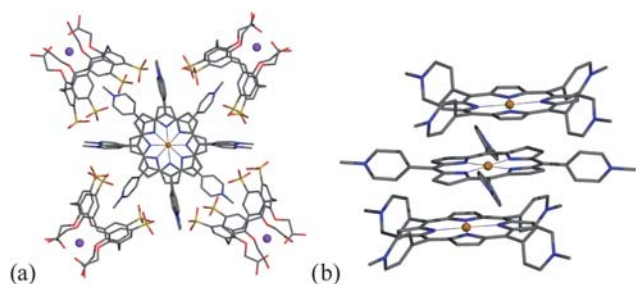


Fig. 2 (a) The 3 : 4 copper-porphyrin/calixarene supramolecular unit and (b) stacking of a discrete unit of three copper-porphyrins.

porphyrin. The crystallographic analysis of the obtained crystals (**1**), isomorphic to the tetragonal form,¹² shows that each calixarene molecule behaves like a host for the *N*-methylpyridinium moiety of the central copper-porphyrin (Fig. 2a), as in the analogous non-metallated complex.[‡] Two additional copper-porphyrin molecules stack above and below the host/guest complexed porphyrin through π - π interactions (Fig. 2b). The macro-rims, laying on almost parallel planes, are mutually rotated by 45°. The copper ions are coplanar with the porphyrin rings and the distance between the ions is 4.158(1) Å. Each calixarene hosts a sodium ion, coordinated to the lower rim substituents, with a coordination number 8. As in the free base porphyrin/calixarene complex (Fig. 1),¹² the anionic 3 : 4 units are held together by the interaction of carboxylate groups on the lower rims of calixarenes with a bridging sodium ion (Fig. S1†), forming an approximately two-dimensional squared network (Fig. S2†). Moreover, these 2D networks, parallel to the crystallographic *x,z* and *y,z* planes, are interpenetrated, thereby forming large void channels (Fig. S3†). The mutual orientation of the calixarenes involved in the interaction between different 3 : 4 units can be evaluated considering the α angle formed by the mean planes of the methylenic carbon atoms bridging the aromatic units of each calixarene molecule (Fig. S4a†). In **1** (Fig. S3a†), the α angle is 2.5(2)°, very close to the value of 2.8(2)° obtained for the free base porphyrin/calixarene complex.¹² Such a low value indicates that adjacent cavitands are concentric, *i.e.* the four-fold non-crystallographic symmetry axis of calixarenes is coincident. Hence, the 2D grid assumes a regular square mesh. The distance between sodium ions hosted on the calixarene lower rims is 6.703(3) Å and they are at 3.346(3) Å and 3.358(3) Å from the central bridging sodium ion. Comparison with the analogous free base porphyrin complex indicates that the presence of a copper ion in the centre of porphyrin rings does not affect significantly the overall three-dimensional structure.

Considering the results obtained in previous experiments,¹² a soaking technique was used on crystals of **1** to introduce a second transition metal ion in the framework. 1 μ L of a zinc chloride, nickel chloride or cadmium acetate solution (20 mM) was added to 4 μ L crystallization drop containing crystals of **1**. While addition of a zinc ion solution results in relatively small crystal damage, addition of either nickel ion or cadmium ion solutions causes remarkable changes in the appearance of crystals. Moreover, a significant reduction of their diffraction power was evident, allowing the collection of only low resolution datasets for Ni²⁺ soaked crystals, while it was not possible to obtain suitable diffraction data for Cd²⁺ soaked crystals. In both structures of **2** and **3**, obtained by soaking crystals of **1** for 20 hours in zinc chloride and in nickel chloride solutions, respectively,

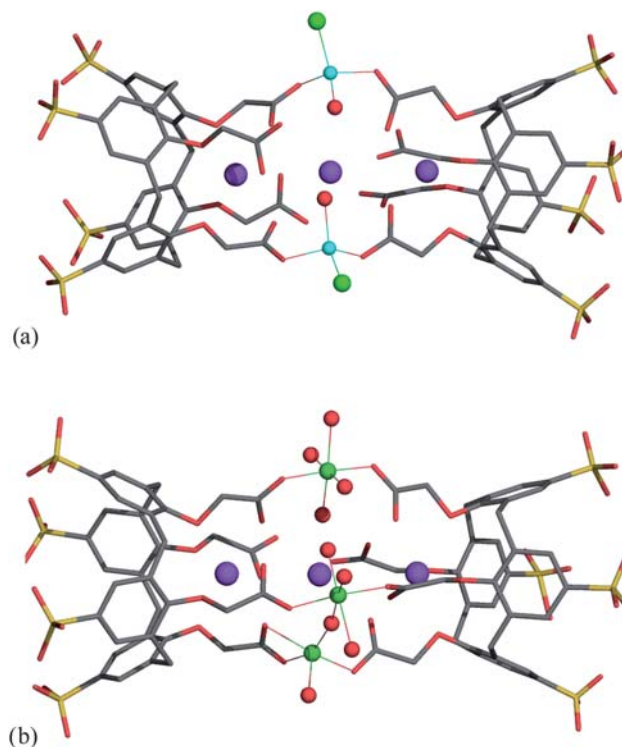


Fig. 3 (a) Two exogenous zinc ions (blue spheres) bridge two carboxylate groups of adjacent calixarenes in **2**. Their tetrahedral coordination is completed by a chloride ion (green spheres) and a water molecule (red spheres). (b) Three exogenous nickel ions (green spheres) bridge two carboxylate groups of adjacent calixarenes in **3**. Further ligands, tentatively assigned as water molecules (red), were detected as part of the coordination spheres of nickel ions.

several exogenous metal ions were localized between the calixarene lower rims, joining two neighbouring 3 : 4 units (Fig. 3). In **2**, two zinc ions are found to bridge the neighbouring calixarene molecules, being coordinated to two oxygen atoms of carboxylate groups of the two lower rims, at 1.934(8) Å mean distance. The tetrahedral coordination spheres of these ions are completed with a water molecule (mean coordination distance Zn–O: 1.97(1) Å) and a chloride ion (mean coordination distance Zn–Cl: 2.229(6) Å) (Fig. 3a and S5†). The analysis of the structure of **2** reveals that the distances between the central sodium ion and those embedded among the substituents of the lower rims of calixarenes increases to 3.665(5) Å and 3.729(5) Å. Then, the two hosted sodium ions are elongated about 0.7 Å with respect to **1**. The relative orientation of calixarene molecules in the structure of **2** corresponds to a value of 13.2(5)° for the α angle (Fig. S4b†), higher than in the structure of **1**, confirming that the coordination of zinc ions to carboxylate groups causes a distortion in the calixarene bridging region, *i.e.*, a small tilt of the cavitands as well as an opening of the bridging interactions between calixarene molecules.

Due to the damage of the crystals of **1** after soaking with nickel solution, the resolution limit of X-ray diffraction data for the nickel derivative, **3**, is quite low. Thus, the interpretation of the electron density is less unambiguous than for **2**. In the crystal structure of **3**, the central sodium ion is found at a mean distance of 3.64(5) Å from the sodium ions hosted among the calixarene lower rims (which are 7.27(1) Å apart). The relative orientation of calixarene molecules is

very similar to that found in **2** (α angle: $13.2(5)^\circ$) (Fig. S4c†). The sodium ion bridging the two adjacent calixarene molecules in **3** has higher thermal parameters than in **1** and **2**, indicating a weakening of coordination bonds or a partial displacement of this ion. Between the lower rims of the crystallographically independent calixarene molecules, three nickel ions were found (Fig. 3b) to bridge the carboxylate groups of the cavitands. These three Ni^{2+} sites are only half-occupied. Due to the low resolution and the partial occupancy of these sites, the ligands in the coordination spheres of these ions are difficult to identify. The electron density peaks around Ni^{2+} ions are tentatively interpreted as water molecules (Fig. S6†). In the final model, an octahedral geometry was recognized for two Ni^{2+} ions, with two *trans* positions occupied by oxygen atoms of the cavitands and four equatorial positions occupied by water molecules (Fig. S7a and 7c†). A square pyramid coordination was identified for the third nickel ion, bridging a chelating carboxylate group of a cavitand and an oxygen atom of the other cavitand (Fig. S7b†). The two remaining sites were assigned to water molecules. The coordination sphere of this ion is not regular and, probably, not complete. It should be noted that the flexibility in coordination geometry of the nickel ion is an essential feature of the Ni-Fe hydrogenase enzyme.²⁰ Finally, a striking difference was noticed comparing the structure of **3** with the analogous structure containing the free base porphyrin.¹² In the latter case, the diffusion of nickel ions in the channels of the crystal caused a complete displacement of the central sodium ion and an increase of the overall symmetry of the crystal (from $I4_1/a$ space group to $I4_1/amd$ space group). Actually, a partial displacement of the bridging sodium ion is probably present also in the structure of **3**. However, the reaction is not complete in this case.

In conclusion, through co-crystallization, we were able to obtain crystals of a copper-porphyrin/calixarene complex with discrete stacks of three metallo-porphyrins. Exploiting the large channels in the crystals, additional metal centres were introduced in the negatively charged framework by soaking techniques.

Notes and references

† Crystal data for **1**: $\text{C}_{144}\text{H}_{171.2}\text{Cu}_{1.5}\text{Ni}_{12}\text{Na}_{10}\text{O}_{79.6}\text{S}_8$, $M = 3925.81$, $a = 50.411(1) \text{ \AA}$, $c = 48.082(1) \text{ \AA}$, $V = 122\,189(3) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $I4_1/a$, $Z = 16$, 75 771 reflections measured, 27 353 independent reflections ($R_{\text{int}} = 0.068$). The final R_1 value was 0.1023 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.2637 ($I > 2\sigma(I)$). The final R_1 value was 0.1242

(all data). The final $wR(F^2)$ value was 0.2839 (all data). Crystal data for **2**: $\text{C}_{144}\text{H}_{133}\text{Cl}_2\text{Cu}_{1.5}\text{Ni}_{12}\text{Na}_8\text{O}_{84.5}\text{S}_8\text{Zn}_2$, $M = 4120.97$, $a = 49.630(1) \text{ \AA}$, $c = 49.490(1) \text{ \AA}$, $V = 121\,901(3) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $I4_1/a$, $Z = 16$, 44 701 reflections measured, 23 966 independent reflections ($R_{\text{int}} = 0.089$). The final R_1 value was 0.0867 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.2337 ($I > 2\sigma(I)$). The final R_1 value was 0.1137 (all data). The final $wR(F^2)$ value was 0.2625 (all data). Crystal data for **3**: $\text{C}_{140}\text{H}_{209.1}\text{Cu}_{1.50}\text{Ni}_{12}\text{Na}_{6.4}\text{Ni}_{1.8}\text{O}_{100.6}\text{S}_8$, $M = 4273.92$, $a = 50.170(4) \text{ \AA}$, $c = 49.460(2) \text{ \AA}$, $V = 124\,492(14) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $I4_1/a$, $Z = 16$, 27 009 reflections measured, 9419 independent reflections ($R_{\text{int}} = 0.073$). The final R_1 value was 0.1287 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.3237 ($I > 2\sigma(I)$). The final R_1 value was 0.1523 (all data). The final $wR(F^2)$ value was 0.3530 (all data).

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