Electronic Supplementary Information (ESI) for: A bifunctionalized porous material containing discrete assemblies of copper-porphyrins and calixarenes metallated by ion diffusion

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Structure determination of 1:

The structure of **1** was solved in $I 4_{1/2}$ space group by the heavy atom method, using the software SHELXS¹ and Fourier analyses, and refined by the full-matrix least-squares based on F², using SHELXL-97². The analysis of the Patterson map revealed the presence of two copper sites: one in a general position and one in a special position (centre of symmetry). The first Fourier map allowed the determination of one and a half crystallographycally independent porphyrins coordinated to these metal ions. Moreover, the shape of two independent calixarenes was recognized. Each calixarene hosts a sodium ion between the substituents on the lower rim. At the interface between the calixarenes a bridging sodium ion was detected. In the asymmetric unit, 7 further sodium ions were identified. A polyethylenglicol HO(CH₂CH₂O)₅H molecule at partial occupancy (50%), a water molecule at full occupancy and 3 at partial occupancy (50%) complete the determined asymmetric unit. During the refinement, restraints for a disordered sulfonic group of a calixarene molecule and for the PEG molecule have been introduced in the model. In the final refinement, hydrogen atoms were included at calculated positions with exclusion of methyl groups that can rotate about their local three-fold axes. All non-hydrogen non-disordered atoms were treated anisotropically. The SQUEEZE function of the program PLATON³ reveals a residual electron density of 7342 electrons/cell (corresponding to 25 water molecules in the asymmetric unit) in cell-remaining voids (52.7% of cell volume). A refinement using reflections modified by the SQUEEZE procedure behaved well, and the R-factors were significantly reduced from 0.15 to 0.10. Details of the refinement are reported in Table S1.

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	Calixarene – copper porphynn (pH 9.5)
Formula	$C_{276}H_{204}N_{24}O_{96}S_{16}Na_6Cu_3 \cdot C_{12}O_7H_{26} \cdot 14Na \cdot 56H_2O$
Formula weight	7851.6
Ζ	8
Calculated density (g cm ⁻³)	0.854
F(000)	32603
μ (mm ⁻¹)	0.554
Reflections (all / independent)	75771 / 27353
Observed reflections [Fo>4o(Fo)]	16988
Data / restraints / parameters	27353 / 2963 / 2116
R[I>2.0σ(I)]	0.1023
R(all data)	0.1242
wR2 [I>2.0σ (I)]	0.2637
Goodness of fit	1.053

Table S1: Refinement statistics of the calixarene-copper porphyrin complex at pH 9.5.

Structure determination of 2:

The structure of **2** was solved in *I* $4_1/a$ space group by direct methods, using the software SHELXS¹ and Fourier analyses, and refined by the full-matrix least-squares based on F², using SHELXL-97². The asymmetric unit is isomorphic to the previous, containing: 2 calixarene molecules, each hosting a sodium ion among the substituents of the lower rim; a whole copper-porphyrin molecule and a half porphyrin molecule, with a copper ion at half occupancy located on a crystallographic inversion centre; a bridging sodium ion at the interface between calixarene molecules. Moreover, in the same region, two zinc ions were found to interact with two carboxylate groups of the lower rims of calixarenes, externally with respect to the central sodium ion. The tetrahedral coordination sphere of both ions is completed by a chloride ion and a water molecule. 2 further water molecules at full occupancy and 6 at partial occupancy, 3 partially molecules of PEG (HO(CH₂CH₂O)₂H) at 0.5 occupancy and 5 further sodium ions complete the determined asymmetric unit.

During the refinement, restraints for bond distances and angles of PEG molecules have been introduced in the model. In the final refinement, hydrogen atoms were included at calculated positions with exclusion of methyl groups that can rotate about their local three-fold axes. All non-hydrogen non-disordered atoms were treated anisotropically. The SQUEEZE function of the program PLATON³ reveals a residual electron density of 6973 electrons/cell (corresponding to 24 water molecules in the asymmetric unit) in cell-remaining voids (50.6% of cell volume). A refinement using reflections modified by the SQUEEZE procedure behaved well, and the R-factors were significantly reduced from 0.11 to 0.08. Details of the refinement are reported in Table S2.

	Calixarene – copper porphyrin (pH 9.5) soaked with Zn ²⁺
Formula	$C_{276}H_{212}N_{24}O_{100}S_{16}Na_6Cu_3Zn_4Cl_4\cdot 3C_4H_{10}O_3\cdot 10Na\cdot 12H_2O$
Formula weight	8241.9
Ζ	8
Calculated density (g cm ⁻³)	0.898
F(000)	33768
μ (mm ⁻¹)	0.977
Reflections (all / independent)	44701 / 23966
Observed reflections [Fo>4o(Fo)]	15709
Data / restraints / parameters	23966 / 2713 / 2121
R[I>2.0σ(I)]	0.0867
R(all data)	0.1137
wR2 [l>2.0σ (l)]	0.2337
Goodness of fit	0.985

Table S2: Refinement statistics of the calixarene-copper porphyrin complex at pH 9.5, soaked with a zinc solution.

Structure determination of 3:

The structure of **3** was solved in $I 4_1$ space group by molecular replacement using the software AMORE⁴. The spatial coordinates of the 4:3 calixarene-porphyrin unit of **1** was used as searching model. The coordinates of the atoms in the non-centrosymmetric system were reduced to the centrosymmetric $I 4_1/a$ space group, locating the additional centre of inversion in the position of the copper ion in the middle of the central porphyrin. The structure was refined by the full-matrix least-squares based on F², using SHELXL-97². In the $I 4_1/a$ space group, the asymmetric unit contains 2 calixarene molecules, a porphyrin molecule, a half porphyrin molecule, 2 sodium atoms hosted in the calixarene lower rims and 1.5 copper ions hosted by the

porphyrins. Moreover, a bridging sodium ion and three nickel ions at partial occupancy, close to the carboxylate substituents on the lower rim of calixarene molecules, were identified. The coordination sphere of these Ni²⁺ ions is completed by 9 water molecules, at partial occupancy (50%) and only partially recognizable due to the low resolution of the structure. Two further water molecules, 5 sodium ions and a partially visible PEG molecule (HO(CH₂CH₂O)₂H), all with partial occupancy, complete the asymmetric unit.

During refinement, geometric restraints for carboxylic groups and solfonic groups of calixarene molecules, for N-methylpyridinium groups of porphyrin molecules and for the PEG molecule have been introduced in the model. In the final refinement, hydrogen atoms were included at calculated positions with exclusion of methyl groups that can rotate about their local three-fold axes. Because of the low resolution of the structure and to the low number of data, nickel, copper, sulphur, oxygen and sodium atoms at full occupancy were treated anisotropically, while all other atoms were refined isotropically. During refinement, thermal parameters of neighbouring atoms were restrained to be approximately equal, using the SIMU card of SHELXL-97². An extinction parameter has been refined using the card EXTI of the program SHELXL-97².

The SQUEEZE function of the program PLATON³ reveals a residual electron density of 13060 electrons/cell (corresponding to 45.5 water molecules in the asymmetric unit) in cell-remaining voids (55.3% of cell volume). A refinement using reflections modified by the SQUEEZE procedure behaved well, and the R-factors were significantly reduced from 0.33 to 0.13. Essential crystal data and refinement details are reported in Table S3.

	Calixarene – copper porphyrin (pH 9.5) soaked
	with Ni ²⁺
Formula	$C_{276}H_{222}N_{24}O_{105}S_{16}Na_6Cu_3Ni_3C_4H_{10}O_3Na^{-95}H_2O$
Formula weight	8547.8
Ζ	8
Calculated density (g cm ⁻³)	0.912
F(000)	35679
μ (mm ⁻¹)	0.813
Reflections (all / independent)	27009 / 9419
Observed reflections [Fo>4o(Fo)]	5894
Data / restraints / parameters	9419 / 963 / 1056
R[I>2.0σ(I)]	0.1287
R(all data)	0.1523
wR2 [I>2.0σ (I)]	0.3237
Goodness of fit	1.296

 Table S3: Refinement statistics of the calixarene-copper porphyrin complex at pH 9.5, soaked with nickel ions.

Figure S1: Electron density map (contour level: 2σ) in the calixarene bridging region of crystal structure of calixarene-copper porphyrin complex **1** at pH 9.5. The interaction found in this structure is closely related to that observed in the analogous complex obtained using a free base porphyrin.



Figure S2: The two-dimensional network formed by copper-porphyrin : calixarene 3:4 units, in the structure obtained from co-crystallization experiments at pH 9.5. The square grid network is very similar to that observed in the structure of the calixarene-free base porphyrin complex obtained at the same pH values⁵.



Figure S3: Projections of the structure along (a) the *z* axis and (b) the *x* axis. The view along the *y* axis is referred to that in (b) by a translation of the origin of $\frac{1}{4}$ along the two axes.



Figure S4: Mean planes passing through the methylenic atoms bridging the aromatic units of calixarene molecules, defining the α angles in (a) **1**, (b) **2** and (c) **3**.



Figure S5: Electron density map (contour level: 2σ) in the calixarene bridging region of **2**. Three sodium ions (purple spheres) are coordinated to the carboxylate groups of the calixarene lower rims. Furthermore, two zinc ions (blue spheres) were found to bridge two carboxylate groups of different calixarenes. Their tetrahedral coordination is completed by a chloride ion (green spheres) and a water molecule (red spheres), as shown in the inset.



Figure S6: Electron density map (contour level: 1.5σ) in the calixarene bridging region of **3**. Three sodium ions (purple spheres) are coordinated to the carboxylate groups at the calixarene lower rims, although the central one with an occupancy factor of 50%. Furthermore, three nickel ions (green spheres) were found to bridge two carboxylate groups of different calixarenes. Further ligands, tentatively assigned as water molecules (red), were detected as part of the coordination sphere of nickel ions.



Figure S7: Coordination geometries of the three nickel ions located at the interface between the calixarene molecules (electron density maps, contour level: 1.5σ) in the crystal structure of **3**. In (a) and (c), the metal ion is coordinated to two oxygen atoms of carboxylate groups belonging to different cavitands and to four water molecules, showing a octahedral geometry. Instead, in (b), a carboxylate group shows a chelate coordination to the nickel, while another carboxylate binds it with a single O-Ni coordination bond. In the latter case, the distorted coordination sphere is completed by two water molecules and it is not octahedral. As shown in (b)-(c), one of the water molecules bridges between two nickel ions.



References:

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