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Assembly of Positively Charged Porphyrins Driven by Metal Ions: A Novel Polymeric Arrangement of Cationic Metalloporphyrin

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Crystallization and crystal structure analysis of chlorohydrates of either tri- or tetracationic copper porphyrins, namely copper(5,10,15-tris(*N*-methyl-pyridinium-4-yl)-20-pyridine-porphyrinato) (**1**) and copper(5,10,15,20-tetrakis(*N*-methyl-pyridinium-4-yl)-porphyrinato), respectively, have been performed. Two crystalline forms, **2** and **3**, of the latter have been obtained under different preparation conditions. A novel kind of slipped stack chains of these cationic porphyrins has been detected. The pronounced saddle conformation of the porphyrin reveals π-like interactions between the peripheral pyrrole C_b–C_b "double bond" and the metal center. DFT calculations on the isolated porphyrins clearly show the HOMO orbitals with the correct topology to yield a bonding interaction among the stacked porphyrin units. To our knowledge, a slipped stack chain of positively charged porphyrins has never been previously reported, if the arrangement of faced units of monocationic metalloporphyrins or phthalocyanins is excluded.

We have recently shown[1] that noncovalent conjugates between the tetracationic *meso*-tetrakis(*N*-methyl-pyridinium-4-yl)porphyrin (H_2T4, Chart 1a) and the anionic 5,11,17,23-tetrasulfonated-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (C_4TsTc, Chart 1b) are formed. Supramolecular species with H_2T4/C_4TsTc ratios of 3:4 and 5:4 have been detected in solution and structurally characterized in the solid state. Both complexes share a 1:4 core structure (Figure 1), where each of the four *N*-methyl pyridinium groups of H_2T4 is hosted by the sulfonate rim of a calixarene anion. The 3:4 and 5:4 complexes are formed by piling two and four H_2T4 units, respectively, to the 1:4 core. More recently, evidence has been obtained[2] for the formation in aqueous solution of mixed assemblies, by stoichiometric addition of various metalloporphyrins to the 1:4 species. Consequently, we were interested to see if the introduction of a central metal like copper(II) might affect the architecture of the supramolecular species. The CuT4 porphyrin was prepared according to the literature.[3] By adding CuT4 to calixarene in an 1:1 molar ratio (buffered, pH 9), single crystals isomorphous with those of the 5:4 species were obtained.[4]

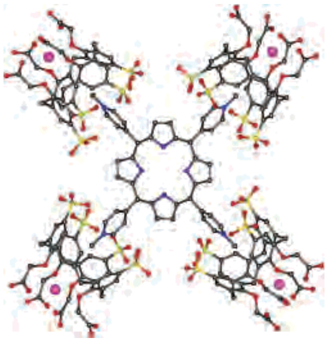
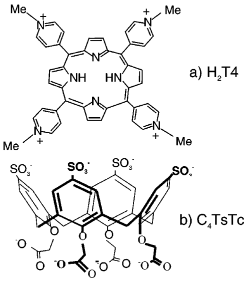


Figure 1. Host−guest interaction in the unit formed by the central porphyrin cation with the sulfonate rim of the calixarenes. Each calixarene hosts one sodium ion (magenta circles) on the carboxylate rim.

Chart 1



Surprisingly, when the crystallization was carried out in unbuffered solution (molar ratio $CuT4/C_4TsTc$ of 1:1), single crystals of a new species **1** were obtained.

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(1) Di Costanzo, L.; Geremia, S.; Randaccio, L.; Purrello, R.; Lauceri, R.; Sciotto, D.; Gulino, F. G.; Pavone, V. *Angew. Chem., Int. Ed.* **2001**, *40*, 4245−4247.

(2) Moschetto, G.; Lauceri, R.; Gulino, F. G.; Sciotto, D.; Purrello, R. *J. Am. Chem. Soc.* **2002**, *124*, 14536−14537.

(3) Herrmann, O.; Medhi, H.; Corsini, A. *Can. J. Chem.* **1978**, *56*, 1084−1087.

10.1021/ic049336q CCC: $27.50

The crystallographic analysis showed [5] that **1** contained neither calixarene nor CuT4, but that it was actually a novel polymeric arrangement of the porphyrin of the tri-chloride of Cu(T3py) (T3py = 5,10,15-tris-(*N*-methylpyridinium-4-yl)-20-pyridine-porphyrinato) (vide infra). It is known[6] indeed that H_2T3py is present in traces in H_2T4 samples, and consequently, it is also metalated together with the tetra-*N*-methylpyridyl compound.[7] In order to understand if this arrangement is peculiar to H_2T3py or of general relevance, we thought it would be interesting to also study the copper derivative of H_2T4. Crystallization of CuT4 in the absence of C_4TsTc gave two crystalline species (**2** and **3**), which are composed of chloride anions and polymeric cations, $(CuT4)_n^{4n+}$,[6] with an arrangement very similar to that of **1**.

The crystals of **1** are built up by Cu(T3py) trications, and those of **2** and **3**, by CuT4 tetracations, arranged in such a way to form polymeric chains, by Cl^- anions and crystallization water molecules. The cations form one-dimensional slipped-stack chains, shown on the top side of Figure 2, where a view of the polymer chains projected in a plane perpendicular to the copper plane is also shown on the bottom side. The chains are very similar in both compounds. The chloride anions are located close (3.4−3.7 Å) to N atoms of the positively charged pyridinium groups. The stacking, arranged approximately on a 2-fold screw axis, is characterized by porphyrin mean plane separations of 3.7 Å in all structures and mean lateral shifts of 4.0 Å.[8] In the chains, the copper ions, coordinated in the equatorial positions by the porphyrin four N donors (mean Cu−N distance of 1.935(5) Å in **1**, 1.970(6) Å in **2**, and 1.972(6) Å in **3**), are held at the axial positions by π-like interactions with the peripheral pyrrole C_b-C_b "double bond" [9] of two porphyrin units, one above and one below. These axial interactions are indicated by broken lines in Figure 2.

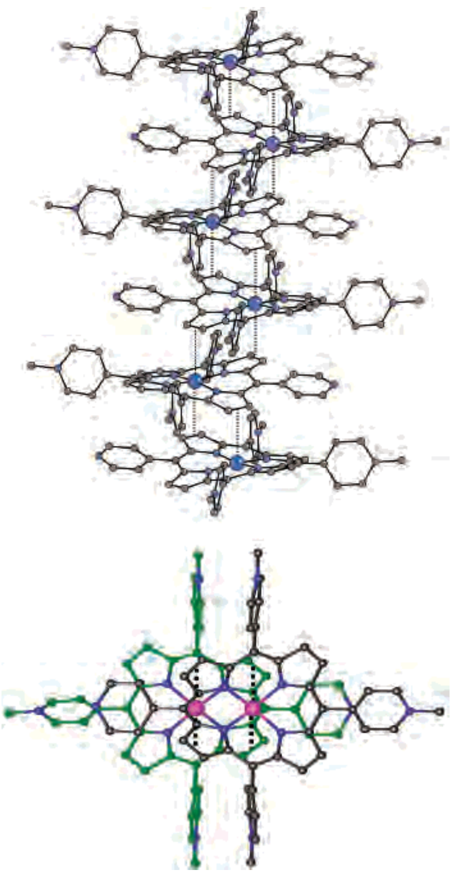

Figure 2. Top: side view of the porphyrin chains in **1** (metal ions in blue). The chains in **2,** where all the porphyrins are however related by crystallographic symmetry centers, and **3** are identical, making allowance for the different cationic porphyrin. Bottom: a view of the chain projected in a plane perpendicular to that of the metal ion (magenta).

The axial Cu−C_m mean distance is 3.14 Å, where C_m is the C_b-C_b middle point. The arrangement of the positively charged porphyrins is such that two adjacent pyrrole rings are involved in the interaction with one Cu above and one below the porphyrin plane. The pronounced saddle conformation [10] of the porphyrin "facilitates" the axial Cu−pyrrole interaction. In fact, the pyrrole ring bends up toward the copper ion above, whereas the adjacent pyrrole bends down toward the copper ion below the porphyrin (Figure 2).

Relevant geometrical features of the pyrrole−copper interaction in **1** and **2** are given in Figure 3, where the two C_b-C_b bonds rotated with respect to each other by about 90° are also evidenced. A metal−pyrrole π-bonding interaction was suggested[11] to be present in the polymeric structure of the monoclinic crystalline form of the neutral (5,10,15,-20-tetramethylporhyrinato)nickel(II), NiTMP, where the essentially planar NiTMP units are stacked with a mean interplanar distance of 3.35 Å, as shown in Figure 4a.

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(4) Lauceri, R.; Di Costanzo, L.; Geremia, S.; Gulino, F: G.; Nardin, G.; Randaccio, L.; Sciotto, D.; Sortino, S.; Purrello, R. Manuscript in preparation.

(5) Crystals of **1** and **3** were obtained by the hanging drops method adapted for supramolecular complexes (see ref 1). Drops were formed by mixing water solutions. For **1**: 2 mL of 7 mM C_4TsTc, 1 mL of 14 mM CuT_4, and 2 mL poly(ethylene glycol) (PEG 300) in the range 20−50% (v/v). For **3**: 2.5 mL of 14 mM CuT_4 and 2.5 mL of NaCl (in the range 1.07−0.74 M) plus PEG 300 (in the range 30−32% (v/v)). Drops were set to equilibrate at 20 °C against 1 mL of the PEG solutions. Crystals of **2** were obtained by cooling to 5 °C a satured solution of CuT_4 in 2 M NaCl. Data collection was performed at the XRD1 beamline of Elettra Synchrotron, Trieste (Italy). Crystal data for **1**: orthorhombic, space group $Pna2_1$, $a = 30.3627(8)$ Å, $b = 9.2951(4)$ Å, c = 33.0295(15) Å; $V = 9321.7(6)$ Å^3, $(CuC_{43}H_{33}N_8)_2$-$Cl_6 \cdot 16H_2O$, $M_w = 1951.58$, $Z = 4$, $\rho_{calc} = 1.391$ g/cm^3; 10761 intensities, 1162 parameters, 24653 restraints $R_1[I > 2\sigma(I)] = 0.091$, $wR_2 = 0.238$. Crystal data for **2**: monoclinic, space group $C2/c$, $a = 42.248(4)$ Å, $b = 9.4568(9)$ Å, $c = 30.229(3)$ Å, $\beta = 129.82(4)$°; $V = 9276(2)$ Å^3, $CuC_{44}H_{36}N_8Cl_4 \cdot 6H_2O$, $M_w = 990.24$, $Z = 8$, $\rho_{calc} = 1.418$ g/cm^3; 5055 intensities, 609 parameters, 774 restraints $R_1[I > 2\sigma(I)] = 0.124$, $wR_2 = 0.325$. Crystal data for **3**: triclinic, space group $P\bar{1}$, $a = 9.5360(8)$ Å, $b = 22.726(3)$ Å, $c = 23.347(3)$ Å, $\alpha = 82.240(6)$°, $\beta = 81.820(7)$°, $\gamma = 81.132(7)$°; $V = 4915(1)$ Å^3, $(CuC_{44}H_{36}N_8)_2Cl_8 \cdot 15H_2O$, $M_w = 2034.54$, $Z = 2$, $\rho_{calc} = 1.375$ g/cm^3; 10625 intensities, 1218 parameters, 768 restraints $R_1[I > 2\sigma(I)] = 0.128$, $wR_2 = 0.366$. Crystallographic information in CIF format can be obtained from the Cambridge Crystallographic Data Centre (CCDC No. 236877-236879), 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; or e-mail deposit@ccdc.cam.ac.uk.

(6) Hambright, P.; Fleischer, E. B. *Inorg. Chem.* **1970**, *9*, 1757−1761.

(7) Buchler, J. W.; Künzel, F. M.; Mayer, U.; Nawro, M. *Fresenius' J. Anal. Chem.* **1994**, *348*, 371−376.

(8) Scheidt, W. R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: New York, 2000; Vol. 3, Chapter 16.

(9) Stevens, E. D. *J. Am. Chem. Soc.* **1981**, *103*, 5087−5095.

(10) The C_b-C_b bonds are alternatively above and below the porphyrin mean plane by about 0.5 Å.

(11) Kutzler, F. W.; Swepston, P. N.; Berkovitch-Telli, Z.; Ellis, D. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 2996−3004.

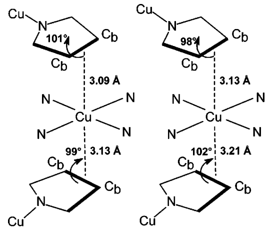

Figure 3. Relevant geometric parameters for the Cu−pyrrole interaction in **1** (left) and **2** and **3** (right). The mean C_m−Cu−C_m angle is 177° (**1**) and 176° (**2**, **3**); the other coordination bond angles range from 82° to 96°.

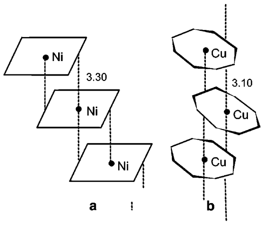

Figure 4. Schematic illustration of the slipped-stack arrangements: (a) Ni(TMP); (b) **1** and **2**. The essentially parallel mean planes of the porphyrins are inclined by about 50° in both **1** and **2,** with respect to the plane containing the Cu ions. The mean metal−C_m distances are indicated. The porphyrin interplanar distance is 3.35 Å in part a and 3.70(3) Å in part b.

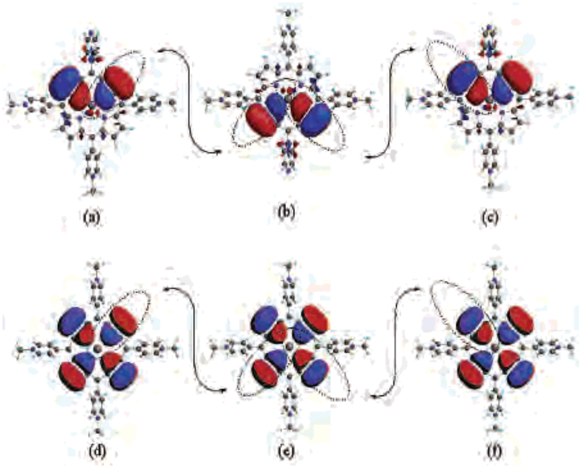

Figure 5. Orbital interactions among the (a−c) HOMO−6 of isolated Cu(T3py) and (d−f) HOMO−5 of isolated CuT4. Porphyrins a, c and d, f are arranged above and below porphyrins b and e, respectively.

In this case, the two opposite pyrrole C_b−C_b bonds of each planar porphyrin are involved in the interaction with the metal. The axial Ni−C_m distance is 3.30 Å, and the two C_b-C_b bonds above and below Ni are parallel. The schematic arrangements of the porphyrin chains in **1** and **2** and in NiTMP are compared in Figure 4.

In order to shed light on the orbital interactions that are operative among stacked Cu−porphyrins, density functional theory (DFT) calculations[12] were performed on the isolated Cu(T3py) and CuT4 molecules. As shown in Figure 5a−c, it appears that HOMO−6 (α orbital) of Cu(T3py) has the correct symmetry and topology to yield a bonding interaction throughout the polymer chain. If we consider porphyrin b of the figure, it is clear that the left-side lobes of its HOMO−6 match with those (not visible) on the right side of the upper porphyrin, while those on the right side (not visible) match with those on the left side of the lower porphyrin. Note that the first and third porphyrin in the figure are rotated in the plane by about 180° with respect to the second one at the center, as observed in the experimental structure shown in Figure 2. This arrangement is likely to arise from the antiparallel orientation of their dipole moments (23 D). On the other hand, the magnitude of the computed dipole moment of CuT_4 is practically zero.

The interstacking orbital interaction operative in this case is analogous to the one described above, as shown in Figure 5d−f. Here, the HOMO−5 (α orbital) has the correct topology to yield a bonding interaction among the stacked CuT_4 monomers. Owing to the quasisymmetric distribution of positive charge, however, four rather than two pyrrole units contribute with their p_π orbitals to HOMO−5. The optimized Cu−N distances in both cases are about 0.1 Å longer than those found in **1** and **2**. Both optimized structures do not display significant distortion of the porphyrin plane from planarity, as experimentally found in several isolated MT4 species.[16] We interpret the observed distortion in the crystal as an effect arising from the interorbital interactions within the porphyrin stack. DFT calculations suggest that orbital interactions [17] among stacked porphyrins do contribute to stabilizing the observed supramolecular architecture.

To our knowledge, a slipped stack chain of positively charged porphyrins has never been previously reported, if the arrangement of faced units of monocationic metalloporphyrins or phthalocyanins is excluded.[18]

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(12) DFT calculations were performed with a parallel version of the Gaussian98 software package[13] on the Fujitsu-Siemens Prime-Power (ITBL) supercomputer of JAERI, Kyoto (Japan). The UB3LYP method of Becke[14] in conjunction with the LANL2DZ basis set[15] of Hay and Wadt was employed in the geometry optimizations.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A11.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(15) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310.

(16) See for example: Körber, F. C. F.; Lindsay Smith, J. R.; Prince, S.; Rizkallah, P.; Reynolds, S. D.; Showcross, D. R. *J. Chem. Soc., Dalton Trans.* **1991**, 3291−3294 and references therein.

(17) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley & Sons: New York, 1985.

(18) Lion, K.; Newcomb, T. P.; Heagy, M. D.; Thompson, J. A.; Hesser, W. B.: Musselman, R. L.; Jacobsen, C. S.; Hoffman, B. M.; Ibers, J. A. *Inorg. Chem.* **1992**, *31*, 4517−4523.