5428 *Inorg. Chem.* **2000,** *39,* 5428−5429

Facile Synthesis of Stacked, Heteronuclear Porphyrin Arrays with Varied Architectures

Michael Harmjanz and Michael J. Scott*

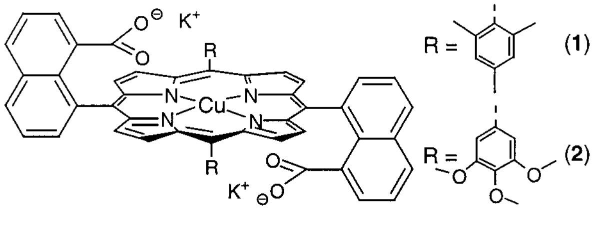
Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611-7200

Received September 21, 2000

Considerable effort has been devoted to the preparation of extended, linear porphyrin arrays, principally to model the biological multi-porphyrinic electron transport chains and photosynthetic reaction centers, and this challenge has led to the development of a wide variety of primarily covalently bound multi-porphyrin constructs.[1] Along with mimicking biological arrays, 1-dimensional assemblies of porphyrins may offer many exciting opportunities in material science including compounds with interesting photochemistry, magnetic behavior, and electronic conductivity. In general, preparation of oligomeric cofacial porphyrin arrays entails tremendous preparative efforts, and changes in the distance, orientation, or shape of the porphyrin units require entirely new synthetic pathways. Due to these limitations, we have developed a new, general method, based on supramolecular aggregation, for the predictable self-assembly of a rigid porphyrin subunit into 1-dimensional heterogeneous coordination polymers.

Noncovalent supramolecular syntheses have been successfully applied to the design of 1-, 2-, and 3-dimensional porphyrin networks;[2] however, due to the lack of suitable building blocks, none of these examples contain porphyrins with recognition sites positioned directly above and below the plane of the macrocycle. Utilizing a naphthalene spacer at the *meso* position to maintain the rigidity of the subunits,[3] a two-step protocol for the synthesis of *trans*-porphyrins bearing two carboxylate groups was developed, and owing to the simplicity of this methodology, the steric and electronic properties of the porphyrin can easily be tuned (Chart 1).[4] With two recognition sites, we reasoned that these macrocycles would be adept at associating with other subunits or interacting with a suitable metal ion. Both the metalated and unmetalated α,*β*-atropisomer free acid of the porphyrin macrocycle were exceedingly insoluble in common organic solvents, independent of the substitution pattern at the porphyrin core, and the insolubility may be attributed to strong intermolecular hydrogen-bonding interactions between carboxylic acid groups in the solid. Deprotonation of the acid groups with potassium hydroxide yielded a remarkably soluble and crystalline material. Initial work has focused on the Cu-porphryins **1** and **2**, and in the solid state of **1**, each carboxylate group binds to and shares two potassium atoms with an adjacent porphyrin (Figure 1), producing a 1-dimensional stacked polymer with a significant slipped arrangement of the two porphyrin ligands. The perpendicular distance between neighboring porphyrins[5] is 10.3 Å, while the Cu···Cu separation is 11.3 Å.[6]

Chart 1



Since metal ions with well-defined coordination spheres can serve as precise templates, and their inherent properties may influence the chemical and physical behavior of the prepared material, the substitution of the potassium ions by suitable divalent transition metal ions was undertaken. As a starting point, we reacted both **1** and **2** with a variety of first row transition metal salts {[M(OAc)$_2$]; M = Mn, Co, Ni, Zn}. Addition of a methanolic solution of the respective metal salts directly to solutions of **1** and **2** induces the spontaneous formation of microcrystalline products, exemplifying the considerable driving force toward the association of the rigid building blocks. Careful diffusion of the two solutions produced single crystals suitable for structural analysis with M = Mn (**3**),[7] Co (**4**), Ni (**5**), R = mesityl and M = Mn (**6**),[8] Zn (**7**), R = 3,4,5-trimethoxybenzene. Inasmuch as complexes **3**, **4**, and **5** are isostructural as are **6** and **7**,[8] discussion of the structural aspects is restricted to the Mn derivatives **3** and **6**.

Figure 2 depicts the heteronuclear single-stranded porphyrin array for **3** in the solid state. The octahedral Mn(II) cations are

---

(1) For example: (a) Anderson, H. L. *Chem. Commun.* **1999**, 2323. (b) Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 11166. (c) Sessler, J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618. (d) Nagata, T.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1990**, *112*, 3054. (e) Beavington, R.; Burn, P. L. *J. Chem. Soc., Perkin Trans. 1*, **1999**, 583. (f) Mak, C. C.; Pomeranc, D.; Montalti, M.; Prodi, L.; Sanders, J. K. M. *Chem. Commun.* **1999**, 1083. (g) Vicente, M. G. H.; Jaquinod, L.; Smith, K. M. *Chem. Commun.* **1999**, 1771. (h) Kumble, R.; Palese, S.; Lin, V. S.-Y.; Therien, M. J.; Hochstrasser, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11489. (i) Burrell, A. K.; Officer, D. L.; Reid, D. C. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 900. (j) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435 and references therein.

(2) For example: (a) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727. (b) Kobayashi, K.; Koyanagi, M.; Endo, K.; Masuda, H.; Aoyama, Y. *Chem. Eur. J.* **1998**, *4*, 417. (c) Bhyrappa, P.; Wilson, S. R.; Suslick, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 8492. (d) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704. (e) Diskin-Posner, Y.; Goldberg, I. *Chem. Commun.* **1999**, 1961. (f) Renner, M. W.; Barkigia, K. M.; Melamed, D.; Smith, K. M.; Fajer, J. *Inorg. Chem.* **1996**, *35*, 5120. (g) Harriman, A.; Sauvage, J.-P. *Chem. Soc. Rev.* **1996**, *25*, 41. (h) Chichak, K.; Branda, N. R. *Chem. Commun.* **1999**, 523. (i) Drain, C. M.; Nifiatis, F.; Vasenko, A.; Batteas, J. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2344. (h) Kim, H.-J.; Bampos, N.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1999**, *121*, 8120.

(3) Fillers, J. P.; Ravichandran, K. G.; Abdalmuhdi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 417.

(4) (a) Harmjanz, M.; Scott, M. J. *Chem. Commun.* **2000**, 397. (b) Harmjanz, M.; Gill, H. S.; Scott, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 10476.

(5) Planes are defined by the four nitrogen atoms of the porphyrin.

(6) Details are contained in the Supporting Information.

(7) **3**: UV/vis (CHCl$_3$/MeOH) $\lambda_{\text{max:}}$ 544, 422 nm. Anal. Calcd for **3**·(−)-2MeOH ($C_{64}H_{58}N_4O_8MnCu$): C, 68.05; H, 5.18; N, 4.96; Cu, 5.63; Mn, 4.86. Found: C, 68.15; H, 5.06; N, 4.99; Cu, 5.51; Mn, 4.92. **6**: UV/vis (CHCl$_3$/MeOH): λ_{max}: 546, 424 nm. Anal. Calcd for **6**·(−)3MeOH ($C_{63}H_{54}N_4O_{13}MnCu$): C, 63.39; H, 4.56; N, 4.69; Cu, 5.32; Mn, 4.60. Found: C, 62.68; H, 4.40; N, 4.65, Cu, 5.24; Mn, 4.41. X-ray crystallographic data. **3**·10.25MeOH: space group $P\bar{1}$, $a = 13.298(4)$ Å, $b = 14.363(4)$ Å, $c = 22.526(4)$ Å, $\alpha = 81.372(6)°$, $\beta = 76.735(5)°$, $\delta = 75.879(5)°$, $V = 4041(2)$ Å^3, $T = 173$ K, $Z = 2$, $D_c = 1.251$ g cm^{-3}, R1 = 0.0923 [$I > 2\sigma(I)$], wR2 = 0.2043. **6**·6.5MeOH: space group $P\bar{1}$, $a = 10.9439(9)$ Å, $b = 14.144(1)$ Å, $c = 14.337(1)$ Å, $\alpha = 95.221(2)°$, $\beta = 94.625(2)°$, $\delta = 108.933(1)°$, $V = 2076.0(3)$ Å^3, $T = 173$ K, $Z = 1$, $D_c = 1.193$ g cm^{-3}, R1 = 0.0735 [$I > 2\sigma(I)$], wR2 = 0.1940.

(8) Minor differences in the coordination sphere of the linking metals were apparent, but the orientation of the building blocks was identical.

10.1021/ic0010656 CCC: $19.00

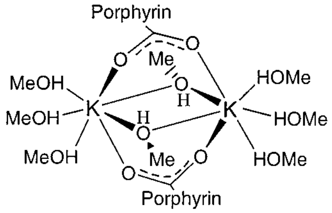


Figure 1. Illustration of the bridging dipotassium unit.

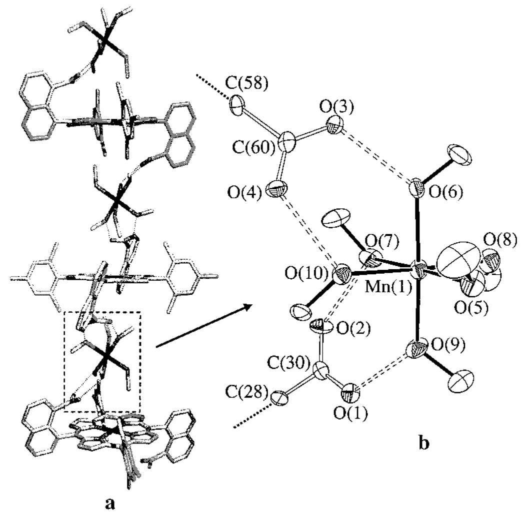


Figure 2. (a) Diagram of the twisted, columnar arrangement of the porphyrin units in **3** generated from crystallographic coordinates. (b) ORTEP diagram of the [Mn(HOMe)$_6$]$^{2+}$ units in **3**. All hydrogen atoms have been omitted for clarity. The dashed lines indicate hydrogen-bonding interactions between the carboxylic groups and the coordinated methanol molecules. Selected bond lengths (Å): Mn(1)−O(5) 2.185(8), Mn(1)−O(6) 2.132(7), Mn(1)−O(7) 2.213(8), Mn(1)−O(8) 2.176(7), Mn(1)−O(9) 2.139(7), Mn(1)−O(10) 2.173(6).

surrounded by six methanols [Mn−O(mean), 2.17(3) Å], and these metals are situated between the bifunctional nonchelating porphyrin units to take advantage of the close contact to the carboxylate counterions. In addition to these electrostatic interactions, hydrogen bonds between the coordinated methanols and the naphthalene carboxylate groups are evident with average O⋯O separations of 2.60(3) Å. Since the two carboxylate groups are bound to the metal in a cis fashion, the neighboring cofacial porphyrin planes are slightly inclined (6.1°) and twisted (111°) against each other. In contrast to the potassium salt, no significant slip of the porphyrin rings is observed and the Cu⋯Cu distance (11.7 Å) has only slightly increased. In the magnetization data for **3**, there were no detectable interactions between the metal ions, consistent with the large Cu(1/2)⋯Mn separations (5.90, 5.92 Å) and the absence of bridging ligands.

The cis orientation of the carboxylates may be attributed to the steric congestion of the *meso*-mesityl substituents, whereby the ortho methyl groups point directly toward the octahedral metal center. Since the interactions of the transition metal motif with the adjoining naphthalene donor functions govern the orientation, the perpendicular distance, and the overlap of two adjacent porphyrin units, they control the hetero- and homonuclear metal−metal distances. Thus, we examined the solid-state structure of the 3,4,5-trimethoxyphenyl derivative (**6**).

Figure 3 displays the polymeric columnar structure of **6** with the periodic composition $\{[\mathrm{CuPorphyrin(COO)_2}]^{2-}[\mathrm{Mn(HOMe)_6}]^{2+}\}_n$. Due to the absence of ortho groups at the two *meso*-aryl substituents, the Mn(II) complex now has the capability to interact in a more symmetric, trans fashion with the carboxylate groups (calculated O⋯H distances: 1.77, 1.80 Å). This orientation allows for an in-plane alignment of the porphyrin rings and significantly decreases the intermetal (Cu⋯Cu) separations within the array [10.9 (**6**) vs 11.7 Å (**3**)]. The Cu−Mn distance in each centrosymmetric porphyrin "sandwich" is 5.47 Å, and no winding of the porphyrin planes is observed (Figure 3). In comparison to **3**, this highly symmetric aggregation affords a controlled packing of the porphyrin columns wherein the single porphyrin straps are held together by van der Waals forces. As a consequence, organized channels with well-defined void spaces[9] form, highlighting the profound influence of small variations in the building blocks on the aggregation in the solid state.

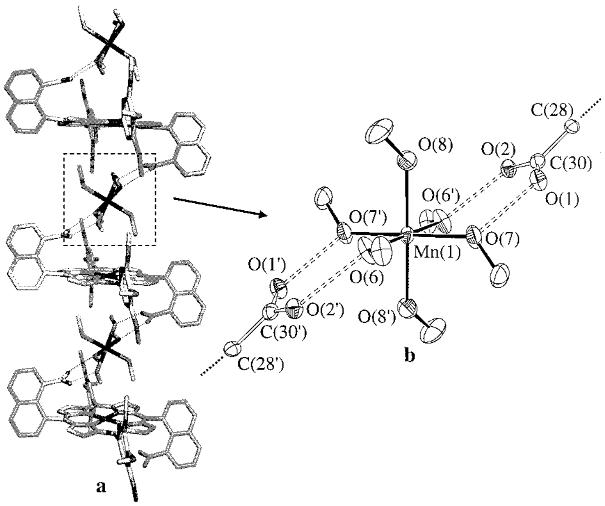


Figure 3. (a) Illustration of the columnar, axially symmetric architecture in **6** derived from crystallographic coordinates. (b) ORTEP diagram of the [Mn(HOMe)$_6$]$^{2+}$ units in **6**. All hydrogen atoms have been omitted for clarity. Primed and unprimed atoms are related by a center of inversion. The dashed lines indicate hydrogen-bonding interactions between the carboxylic groups and the coordinated methanol molecules. Selected bond lengths for **6** (Å): Mn(1)−O(6) 2.137(4), Mn(1)−O(7) 2.136(4), Mn(1)−O(8) 2.176(5).

In summary, a new approach for the preparation of heteronuclear, cofacial porphyrin arrays has been developed, and on the basis of the examples presented herein, the properties of the macrocycles appear to have a significant influence on the aggregation of the units. Single-stranded porphyrin arrays with a slipped, a twisted, and a columnar axial symmetric arrangement of the porphyrins and the respective metal ions have been synthesized. Through the judicious choice of building blocks, a range of porphyrinic solids can be isolated, some of which may have value for the preparation of new materials or solids with tunable photochemical properties. In addition, insertion of metal ions capable of maintaining axial ligation into the porphyrin macrocycle offers the potential for ligand-driven metal−metal interactions and the possibility of electronic communication between the metal centers in the homo- or heterometallic strap.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (fellowship for M.H.) and the Research Corporation for financial support of this work. The NSF (CAREER Award, 9874966) is also gratefully acknowledged.

Supporting Information Available: Reaction conditions and analytical data for **1**, **2**, **3**, and **6** and X-ray structural details for **1**, **3**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0010656

---

[9] 49.6% calculated free space without considering lattice solvent molecules. PLATON for MS-Windows, Version 02-11-00, by A. L. Spek.