Self-assembling of nanoscopic molecular rectangles, extended helicates and porous-like materials based on macrocyclic dicopper building blocks under fine supramolecular control†

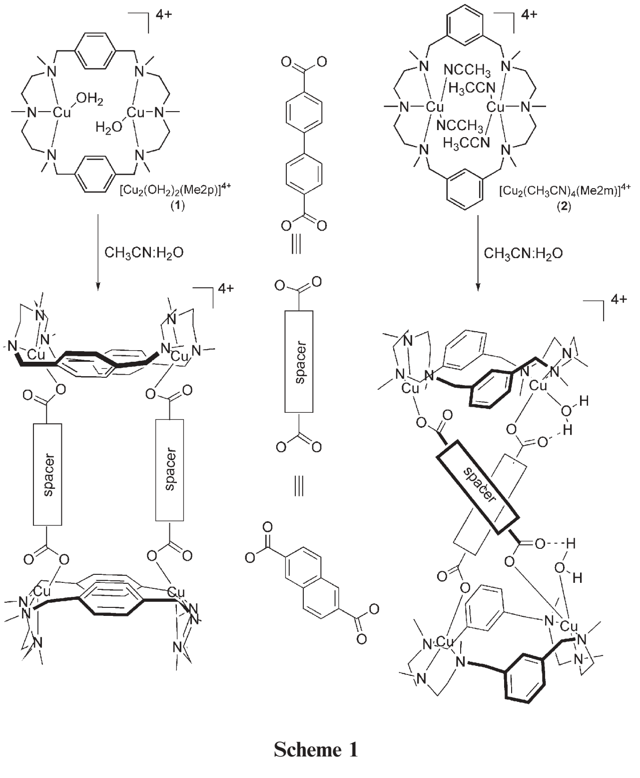
Laura Gómez,[a] Anna Company,[a] Xavier Fontrodona,[b] Xavi Ribas*[a] and Miquel Costas*[a]

Received (in Cambridge, UK) 18th May 2007, Accepted 26th July 2007
First published as an Advance Article on the web 14th August 2007
DOI: 10.1039/b707508a

Upon reaction with a dicarboxylate linker, macrocyclic dicopper complexes encode for a selective supramolecular 2 + 2 self-assembly of nanoscopic rectangles, a new class of molecular helicates, and porous-like materials *via* fine structural control at three supramolecular levels.

Coordination-driven self-assembly is emerging as a very powerful tool to rationally construct large and chemically complex suprastructures, barely reachable by traditional covalent chemistry.[1] Particular outcomes of these phenomena have been the preparation of discrete metal containing cyclic nanostructures and molecular helicates which hold potential use in molecular recognition, photophysics and catalysis.[2,3] On the other hand, macrocyclic molecules based on crown ethers or polyamines are among the first ligand backbones reported to create controlled cavities where the selective recognition of cation, anion or neutral molecules can take place.[4] However, their use as building blocks in the assembly of larger supramolecular structures has so far only been explored in rather limited examples.[5] Inspired by recent work on the self-assembly of calixarene-type of hosts into highly complex superstructures,[6] we envisioned that the preorganized structure of polyazamacrocyclic complexes would make them very attractive as sophisticated supramolecular building blocks, provided rational directed self-assembly could be applied. Indeed, molecular rectangles with a rather simple structure were recently described by us as a proof of concept of this approach.[7] Further exploration of this idea led us to discover unexpected subtleties in this chemistry that further expand the potential of this approach. Herein we report that isomerically related macrocyclic dicopper complexes selectively encode the supramolecular self-assembly of nanoscopic molecular rectangles and a new class of extended helicates upon reaction with an aromatic dicarboxylate linker. Control over the rectangle dimensions can also be tuned *via* anion–π–aromatic interactions between a molecular rectangle and BArF anions (BArF = $[B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]^-$). Finally, control over 3D organization of the structures leading to selective crystal engineering is attained *via* the judicious choice of ligands and counterions.

Reaction between dicopper(II) precursor complexes $[Cu_2(OH_2)_2(Me2p)](CF_3SO_3)_4$, **1**$CF_3SO_3$ or $[Cu_2(CH_3CN)_4(Me2m)](CF_3SO_3)_4$, **2**$CF_3SO_3$ (Scheme 1)[7] with a diacid aromatic linker ($HO_2CC_{12}H_8CO_2H$ or $HO_2CC_{10}H_6CO_2H$) and triethylamine in acetonitrile : water 10 : 1 (v/v) mixtures gives rise to tetranuclear copper complexes of general formula $[(Cu_2L)_2(O_2CArCO_2)_2](CF_3SO_3)_4$ (**3**CF_3SO_3, L = Me2*p* and Ar = $C_{12}H_8$; **4**CF_3SO_3, L = Me2*m*, Ar = $C_{12}H_8$; **5**CF_3SO_3, L = Me2*p* and Ar = $C_{10}H_6$; **6**CF_3SO_3, L = Me2*m*, Ar = $C_{10}H_6$). These compounds were obtained as crystalline materials in good yields (77 to 83%) after diethyl ether diffusion over the reaction mixtures. Complexes of general formula $[(Cu_2L)_2(O_2CArCO_2)_2]X_4$, **4**$ClO_4$ (L = Me2*m*, Ar = $C_{10}H_6$) and **5**BArF (L = Me2*p*, Ar = $C_{10}H_6$) were respectively prepared by crystallization of **4**CF_3SO_3 from acetonitrile : diethyl ether solutions containing $NaClO_4$, and *via* anion metathesis of **5**CF_3SO_3 with NaBArF in CH_2Cl_2, followed by slow pentane diffusion. The molecular structures of **3**CF_3SO_3, **4**ClO_4, **5**CF_3SO_3, **5**BArF and **6**CF_3SO_3 were established by X-Ray diffraction analysis (XRD).[8] The integrity of these compounds in CH_3CN solutions was confirmed by ESI-MS (see ESI†). The crystal



Scheme 1

---

[a] *Departament de Química, Universitat de Girona, Campus de Montilivi, 17071, Girona, Spain. E-mail: xavi.ribas@udg.edu; miquel.costas@udg.edu; Fax: +34 972-418150; Tel: +34 972-418333*
[b] *Serveis Científico-Tècnics, Universitat de Girona, Campus de Montilivi, 17071, Girona, Spain*

† Electronic supplementary information (ESI) available: Full experimental details and crystallographic information. See DOI: 10.1039/b707508a

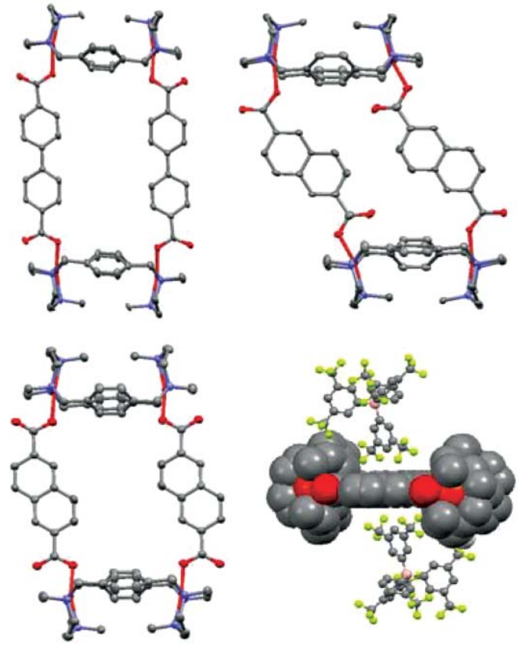


Fig. 1 ORTEP diagrams (ellipsoids, 50%) of the cationic part of **3**CF_3SO_3 (top left), **5**CF_3SO_3 (top right), **5**BArF (bottom left), and space filling diagram of **5**BArF showing interaction with two BArF anions (bottom right). Color code; blue (N), red (O), yellow (F), pink (B), gray (C).

structures of the cationic units of these complexes are displayed in Fig. 1 and Fig. 2. This analysis evidences that fine tuning of the molecular structure is attained at three different levels.

Both **3**CF_3SO_3 and **5**X (X = CF_3SO_3 and BArF) adopt rectangle topologies resulting from a 2 + 2 self-assembly process. The copper ions adopt a square planar coordination geometry, and they are bound to three N atoms of the macrocycle and an O atom of the carboxylate group which coordinates in a monodentate mode. Nevertheless, **5**CF_3SO_3 and **5**BArF contain cavities with different geometric parameters which originate from the relative orientation of the two binding oxygen atoms of a carboxylate linker, being *anti* in **5**CF_3SO_3 and *syn* in **5**BArF. The molecular cavity generated within **5**CF_3SO_3 evidences a rhombohedral distortion that can be estimated by considering Cu ions as the hypothetical corners of a polyhedron. The polyhedral angles are 85.5(1)°/94.5(1)° (**3**CF_3SO_3), 68.6(1)°/111.4(1)° (**5**CF_3SO_3) and 86.4(1)°/93.6(1)° (**5**BArF). In addition, as a first approach to estimate the dimensions of the cavities, Cu$\cdots$Cu distances in **3**CF_3SO_3, **5**CF_3SO_3 and **5**BArF are 0.65 × 1.47 nm, 0.69 × 1.28 nm, and 0.69 × 1.29 nm, respectively. Interestingly, two BArF anions reside above and below the hydrophobic pocket of the cavity generated in **5**BArF, and each of them contains five fluorine atoms at distances $\leqslant$ 3.5 Å from the centroid of aromatic rings of the hexaaza macrocyclic ligand and/or the naphthalene linkers, evidencing C–F$\cdots\pi$ and C–H$\cdots\pi$ aromatic interactions.[9] Despite the weak nature of this type of interactions, it is likely that they are at the origin of the more expanded rectangular structure of the cavity in **5**BArF, when compared with **5**CF_3SO_3. Indeed, in the latter all CF_3SO_3 anions reside outside of the cavity, suggesting negligible interactions. Overall, structural differences between **5**CF_3SO_3 and **5**BArF suggest that the walls of the cavity are flexible and may respond to the anionic guest's shape. The chemical nature of the anion allows suprastructural control on a primary level.

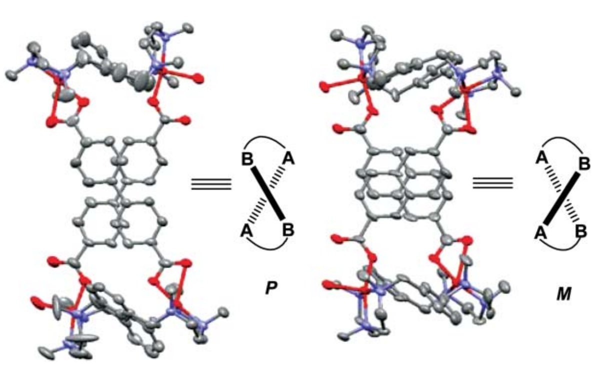


Fig. 2 ORTEP diagrams (ellipsoids, 50%) of the cationic part of **4**ClO_4 (left), **6**CF_3SO_3 (right). Color code; blue (N), red (O), yellow (F), pink (B), gray (C).

Much to our surprise, the use of extended aromatic dicarboxylate spacers and Me2*m*-containing dicopper complexes does not simply enlarge the dimensions of the rectangle,[7] but also gives double-stranded molecular helicates **4**ClO_4 and **6**CF_3SO_3 as revealed by XRD analysis.[8] However, unlike the vast majority of such structures,[3] the chirality does not originate from the chiral topological orientation of the ligands in a tetrahedral or octahedral metal coordination geometry but from a helical twist of the two macrocyclic dicopper complexes. Because of this somewhat more complex architecture, **4**ClO_4 and **6**CF_3SO_3 constitute a new example of the recently described expanded molecular helicates.[10] The coordination environment of the Cu ions in **4**ClO_4 and **6**CF_3SO_3 is also different from **3**CF_3SO_3 and **5**CF_3SO_3. In the former cases, the Cu ions are five-coordinate; in one of the copper ions three coordination sites are occupied by N atoms of the macrocyclic ligand, and one oxygen atom from a water molecule and a monodentated carboxylate moiety fulfil the coordination environment. The water molecule is H-bonded to an O atom of the carboxylate group. However, there is no water molecule in the second copper ion, in which the carboxylate binds in a bidentated asymmetric O,O: η^1:η^1 binding mode. Careful analysis shows that the cationic units of **4**ClO_4 and **6**CF_3SO_3 are chiral. The chirality of the molecules is arbitrarily depicted in Fig. 2, showing that **4**ClO_4 and **6**CF_3SO_3 adopt *P* and *M* handedness, respectively. However, **4**ClO_4 and **6**CF_3SO_3 crystallize in non-chiral space groups $P\bar{1}$ and $Pna2_1$, respectively, thus both *P* and *M* isomers are present in the crystal. A closer inspection of the structures also reveals a network of short interaromatic distances ($\leqslant$ 3.5 Å) between the two aromatic linkers, which indicates strong π-stacking interactions (see overlapping linkers in Fig. 2). Interestingly, these interactions are found neither in **3**CF_3SO_3, **5**CF_3SO_3 and **5**BArF, nor in the previously described rectangle $[(Cu_2(Me2m))_2(O_2CC_6H_4CO_2)_2](ClO_4)_4$.[7] Thus we conclude that these interactions play a major role in directing the assembly of the helicate structure. In conclusion, linker structure but most remarkably, the nature of the hexaazamacrocyclic ligand allows a second level of control over the supramolecular structure by encoding for the selective formation of rectangles or helicates.

Besides the two structural levels already described, analysis of crystal packing evidences also dramatic differences in the three-

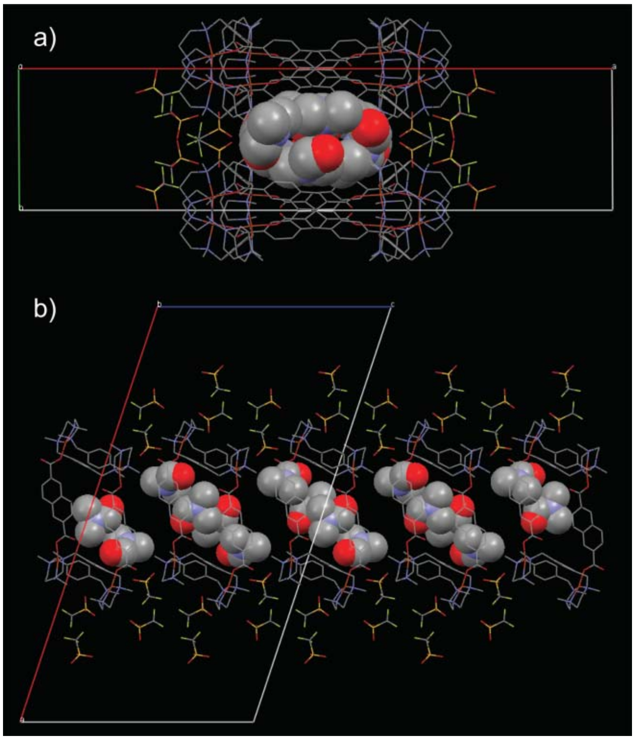


Fig. 3 Crystal packing of **5**CF_3SO_3 showing (a) channels along the *c* axis containing DMF solvent molecules and (b) a perpendicular view of the channels (DMF molecules depicted in space-filling mode for clarity).

dimensional packing network. The crystal packing of helicates **4**ClO_4 and **6**CF_3SO_3 does not reveal any unique extended supramolecular chirality, and shows typical perchlorate and trifluoromethanesulfonate mediated hydrogen bonds. On the other hand, compound **3**CF_3SO_3 shows hydrogen bonded interactions between the anions and also DMF solvent molecules from crystallization. It is interesting to observe one $CF_3SO_3^-$ anion nicely placed inside a pocket depicted by the walls of adjacent macrocyclic moieties (Fig. S2†). Finally, it is remarkable how the different 3D packings in **5**X depend on the counteranion used. The BArF counteranion favors multiple C–F···π and C–H···π interactions that result in the isolation of the rectangle molecules surrounded by BArF anions in **5**BArF, thus excluding the possibility of guest encapsulation. The crystal packing of **5**CF_3SO_3 does allow the formation of infinite monodimensional channels (approx. 1 nm in diameter) delimited by the aromatic moieties of spacer and macrocyclic ligands along the *c* axis, that host 6 DMF molecules per unit cell (Fig. 3). The latter is a direct consequence of the selection of $CF_3SO_3^-$ as counteranion and constitutes the third supramolecular level control observed within this family of self-assembled metal–organic entities.

In conclusion, the supramolecular outcome of the present family of compounds can be controlled by the initial design of the macrocyclic ligand, the length and nature of the dicarboxylate spacer and also the selected counteranion, giving the possibility of obtaining structures ranging from differently sized rectangles to double-stranded helicates. Further subtle control on the 3D packing of these compounds allows, for instance, the creation of nanosized monodimensional channels shown to host a large number of DMF molecules in the crystal structure of **5**CF_3SO_3. Noteworthy, the non-restricted rotation of the –COO^- groups along with the possibility of mono or bidentation, allows the richness of the supramolecular structures described and it should be taken into account in the design of future self-assembled carboxylate-based metal–organic compounds. The structural versatility of our approach and its synthetic simplicity offers a powerful method to prepare complex suprastructures *via* the use of different polycarboxylate linkers, metal ions and counterions.

Notes and references

1 (*a*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853–907; (*b*) M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 369–378; (*c*) B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022–2043; (*d*) D. Fiedler, D. H. Leung, R. G. Bergman and K. N. Raymond, *Acc. Chem. Res.*, 2005, **38**, 349–358; (*e*) J. M. Lehn, *Supramolecular Chemistry*, VCH, New York, 1995; (*f*) D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975–982.

2 (*a*) P. Thanasekaran, R.-T. Liao, Y.-H. Liu, T. Rajendran, S. Rajagopal and K.-L. Lu, *Coord. Chem. Rev.*, 2005, **249**, 1085–1110; (*b*) S.-S. Sun, C. L. Stern, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2004, **126**, 6314–6326; (*c*) P. H. Dinolfo, M. E. Williams, C. L. Stern and J. T. Hupp, *J. Am. Chem. Soc.*, 2004, **126**, 12989–13001; (*d*) S. Bélanger, J. T. Hupp, C. L. Stern, R. V. Slone, D. F. Watson and T. G. Carrell, *J. Am. Chem. Soc.*, 1999, **121**, 557–563; (*e*) C. G. Oliveri, N. C. Gianneschi, S. T. Nguyen, C. A. Mirkin, C. L. Stern, Z. Wawrzak and M. Pink, *J. Am. Chem. Soc.*, 2006, **128**, 16286–16296; (*f*) N. C. Gianneschi, P. A. Bertin, S. T. Nguyen, C. A. Mirkin, L. N. Zakharov and A. L. Rheingold, *J. Am. Chem. Soc.*, 2003, **125**, 10508–10509; (*g*) G. S. Papaefstathiou, Z. Zhong, Lei Geng and L. R. MacGillivray, *J. Am. Chem. Soc.*, 2004, **126**, 9158–9159; (*h*) M. L. Merlau, M. d. P. Mejia, S. T. Nguyen and J. T. Hupp, *Angew. Chem., Int. Ed.*, 2001, **40**, 4239–4242.

3 (*a*) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005–2062; (*b*) M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457–3498.

4 (*a*) L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1992; (*b*) R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1995, **95**, 2529–2586.

5 (*a*) W. He, F. Liu, C. Duan, Z. Guo, S. Zhou, Y. Liu and L. Zhu, *Inorg. Chem.*, 2001, **40**, 7065–7071; (*b*) P. J. Stang, D. H. Cao, K. Chen, G. M. Gray, D. C. Muddiman and R. D. Smith, *J. Am. Chem. Soc.*, 1997, **119**, 5163–5168; (*c*) F. Huang, H.-B. Yang, N. Das, U. Maran, A. M. Arif, H. W. Gibson and P. J. Stang, *J. Org. Chem.*, 2006, **71**, 6623–6625; (*d*) W. Huang, H.-B. Zhu and S.-H. Gou, *Coord. Chem. Rev.*, 2006, **250**, 414–423.

6 E. Menozzi, M. Busi, R. Ramingo, M. Campagnolo, S. Geremia and E. Dalcanale, *Chem.–Eur. J.*, 2005, **11**, 3136–3148.

7 A. Company, L. Gomez, J. M. Lopez Valbuena, R. Mas-Balleste, J. Benet-Buchholz, A. Llobet and M. Costas, *Inorg. Chem.*, 2006, **45**, 2501–2508.

8 Crystallographic and refinement details can be found as ESI†.

9 (*a*) V. R. Vangala, A. Nangia and V. M. Lynch, *Chem. Commun.*, 2002, 1304–1305; (*b*) N. Hayashi, T. Mari and K. Matsumoto, *Chem. Commun.*, 1998, 1905–1906.

10 Z. Grote, S. Bonazzi, R. Scopelliti and K. Severin, *J. Am. Chem. Soc.*, 2006, **128**, 10382–10383.