Self-Assembling of Nanoscopic Molecular Rectangles, Extended Helicates and Porous-like Materials Based on Macrocyclic Dicopper Building Blocks Under Fine Supramolecular Control

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Materials. Solvents were purchased from SDS as reagent grade. Unless noted otherwise, all reagents were purchased from commercial sources and used as received.

3,6,9,16,19,22-hexamethyl-3,6,9,16,19,22-hexaazatriclo[22.2.2.211,14]triaconta-(26),11(12),13,24,27,29-hexaene, Me2p, and 3,6,9,17,20,23-hexamethyl-3,6,9,17,20,23-hexaazatriclo[23.3.1.111,15]triaconta-1(29),11(30),12,14,25,27-hexaene, Me2m, and NaBArF, BArF = [B{3,5-(CF3)2-C6H3}4] were prepared according to or through slight modifications of the published procedures. 1-4

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. While we have not encountered any problems, it is advisable to use only small amounts and handle the compounds with care.

Physical Measurements. FT-IR spectra were taken in a Mattson-Galaxy Satellite FT-IR spectrophotometer containing a MKII Golden Gate Single Reflection ATR System. Elemental analyses were conducted in a Carlo Erba Instrument, Mod. CHNS 1108. UV-Vis spectroscopy was performed on a Cary 50 Scan (Varian) UV-vis spectrophotometer.
with 1 cm quartz cells. ESI-MS spectra were performed on a Bruker Daltonics Esquire 3000 spectrometer.

**Syntheses**

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[Cu_4(O_2CC_{12}H_8CO_2)_2(Me2p)_2](CF_3SO_3)_4, \quad 3CF_3SO_3 \quad \text{and}
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\[
[Cu_4(O_2CC_{12}H_8CO_2)_2(Me2m)_2](CF_3SO_3)_4, \quad 4CF_3SO_3 \quad \text{were prepared in analogous manners as exemplified for} \quad 3CF_3SO_3.
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\[
[Cu_4(O_2CC_{12}H_8CO_2)_2(Me2p)_2](CF_3SO_3)_4 \cdot 1.75CH_3CN \cdot 3H_2O,
\]

\[
3CF_3SO_3 \cdot 1.75CH_3CN \cdot 3H_2O. \quad \text{Me2p} \ (50.0 \ mg, \ 0.10 \ mmol) \ \text{and} \ \text{Cu(CF_3SO_3)_2} \ (74.6 \ mg, \ 0.20 \ mmol) \ \text{were charged in a 10 mL flask and dissolved in CH_3CN} \ (2 \ mL) \ \text{to form a reddish-blue solution. The mixture was stirred for 30 min and then, a suspension of biphenyl-4,4'-dicarboxylic acid} \ (25.2 \ mg, \ 0.10 \ mmol) \ \text{and triethylamine} \ (28.3 \ \mu L, \ 0.20 \ \text{mmol}) \ \text{in CH_3CN} \ (1 \ mL) \ \text{was added dropwise to the stirred solution. The resulting dark blue solution was stirred for 10 h and then filtered through Celite. Ether diffusion after 5 days afforded blue needles. The solvent was decanted and the crystalline solids dried under vacuum.} \ (88.99 \ mg, \ 0.038 \ mmol, \ 76.7\%). \ \text{FT-IR; } v_{\text{max/cm}^{-1}} \ 3525, \ 1614, \ 1340, \ 1255, \ 1223, \ 1150, \ 1028 \ \text{and} \ 635 \ \text{cm}^{-1}. \ \text{Elemental analysis calcd for C}_{92}H_{116}Cu_{4}F_{12}N_{12}O_{20}S_4 \cdot 1.75CH_3CN \cdot 3H_2O \ (2446.15): \ C \ 46.90, \ N \ 7.87, \ H \ 5.24, \ S \ 5.24 \ %; \ \text{found:} \ C \ 47.10, \ N \ 7.69, \ H \ 5.44, \ S \ 4.97 \ %. \ \text{UV-vis; } \lambda_{\text{max (DMF)/nm}} \ 287 (\varepsilon/\text{dm}^3 \ \text{mol}^{-1} \ \text{cm}^{-1} \ 61 \ 500), \ 502 (578), \ 632 (774). \ \text{Single crystals suitable for X-ray diffraction analysis were obtained by slow diethyl-ether diffusion over a CH_3CN:DMF 1:1 v:v solution of the complex.}
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\[
[Cu_4(O_2CC_{12}H_8CO_2)_2(Me2m)_2](CF_3SO_3)_4 \cdot 0.75CH_3CN \cdot 2.5H_2O,
\]

\[
4CF_3SO_3 \cdot 0.75CH_3CN \cdot 2.5H_2O. \ \text{Blue needles.} \ (92.4 \ mg, \ 0.04 \ mmol, \ 79.6\%). \ \text{FT-IR; } v_{\text{max/cm}^{-1}} \ 3463, \ 1585, \ 1370, \ 1248, \ 1224, \ 1156, \ 1028 \ \text{and} \ 636. \ \text{Elemental analysis calcd} \]
(%) for C₉₂H₁₁₆Cu₄F₁₂N₁₂O₃₀S₄·0.75CH₃CN·2.5H₂O (2396.09): C 46.87, N 7.45, H 5.18, S 5.35 %; found: C 47.00, N 7.17, H 5.48, S 4.98 %. UV-vis; λₘₐₓ (CH₃CN)/nm 644 (ε/dm³ mol⁻¹ cm⁻¹ 1 190), 292 (80 000). Single crystals of 4ClO₄ suitable for X-ray diffraction analysis were obtained by slow diethyl ether diffusion into acetonitrile solutions of 4CF₃SO₃ containing NaClO₄.

\[ \text{[Cu}_4\text{(O}_2\text{C}_{10}\text{H}_6\text{CO}_2)_2(\text{Me}_2\text{p})_2](\text{CF}_3\text{SO}_3)_4}, \quad 5\text{CF}_3\text{SO}_3 \quad \text{and} \]

\[ \text{[Cu}_4\text{(O}_2\text{C}_{10}\text{H}_6\text{CO}_2)_2(\text{Me}_2\text{m})_2](\text{CF}_3\text{SO}_3)_4}, \quad 6\text{CF}_3\text{SO}_3 \quad \text{were prepared in analogous manners as exemplified for } 5\text{CF}_3\text{SO}_3. \]

\[ \text{[Cu}_4\text{(O}_2\text{C}_{10}\text{H}_6\text{CO}_2)_2(\text{Me}_2\text{p})_2](\text{CF}_3\text{SO}_3)_4}\cdot\text{CH}_3\text{CN·6H}_2\text{O}, \quad 5\text{(CF}_3\text{SO}_3)_4}\cdot\text{CH}_3\text{CN·6H}_2\text{O.} \]

Me2p (60.0 mg, 0.125 mmol) and Cu(CF₃SO₃)₂ (90.6 mg, 0.250 mmol) were charged in a 25 mL flask and dissolved in CH₃CN:H₂O 20:1 (10 mL) to form a reddish-blue solution. The mixture was stirred during 30 minutes and then, 27 mg of 2,6-naphthalenedicarboxylic acid (0.125 mmol) were added directly as a solid to the stirred solution. 25.4 mg (0.250 mmol) of triethylamine were added via syringe over this suspension, causing the progressive dissolution of the solid diacid, while the solution turned dark blue. Water (1 mL) was added and the resulting dark blue-violet mixture was stirred for 48 hours and then filtered through Celite. Ether diffusion after a week affords large blue-violet rectangles. The solvent was decanted and the crystalline solids dried under vacuum (116 mg, 0.048 mmol, 76.8%). FT-IR; νₘₐₓ/cm⁻¹ 3522, 1623, 1335, 1253, 1223, 1154, 1028, 769 and 635. Elemental analysis calcd (%) for C₈₈H₁₁₂Cu₄F₁₂N₁₂O₃₀S₄·CH₃CN·6H₂O (2417.47): C 44.71, N 7.53, H 5.30, S 5.31; found: C 44.45, N 7.46, H 5.22, S 5.41. UV-vis; λₘₐₓ (DMF)/nm 295 (ε/dm³ mol⁻¹ cm⁻¹ 19 500), 509 (225), 630 (330).
Single crystals suitable for X-ray diffraction analysis were obtained by slow diethyl-ether diffusion over a CH₃CN:DMF 1:1 v:v solution of the complex.

\[ \text{[Cu}_4(\text{O}_2\text{CC}_{10}\text{H}_6\text{CO}_2)_2(\text{Me}_2\text{p})_2](\text{CF}_3\text{SO}_3)_4\cdot\text{CH}_3\text{CN} \cdot 12\text{H}_2\text{O}, \]

6CF₃SO₃·CH₃CN·12H₂O. Blue needles (144 mg, 0.057 mmol, 82.8%). FT-IR; \( \nu_{\text{max}}/\text{cm}^{-1} \) 3476, 1606, 1569, 1463, 1390, 1360, 1248, 1224, 1155, 1028, 780 and 636 Elementtal analysis calcd (%) for C₈₈H₁₁₂Cu₄F₁₂N₁₂O₂₀S₄·CH₃CN·12H₂O (2525.56): C 42.80, N 7.21, H 5.55, S 5.08; found: C 42.74, N 7.24, H 5.68, S 5.52. UV-vis; \( \lambda_{\text{max}} \) (CH₃CN)/nm 291 (ε/dm³ mol⁻¹ cm⁻¹ 15 750), 295 (15 500), 620 (395).

Single crystals of 6CF₃SO₃ suitable for X-ray diffraction analysis were obtained by slow diethyl ether diffusion into acetonitrile solutions of the complex.

\[ \text{[Cu}_4(\text{O}_2\text{CC}_{10}\text{H}_6\text{CO}_2)_2(\text{Me}_2\text{p})_2](\text{BArF})_4, \]

5BArF. 5CF₃SO₃ (10.0 mg, 4.14 µmol) was charged in a 25 mL flask and suspended in CH₂Cl₂ (5 mL). The mixture was stirred while a CH₂Cl₂ (5 mL) solution of NaBArF (15.6 mg, 17.6 µmol) was added. The resulting mixture was stirred overnight, causing progressive dissolution of the copper complex and precipitation of a fine colorless solid. The resulting solution was filtered through Celite, and layered with pentane. Large blue-violet crystals suitable for X-ray analysis appeared over a week. The solvent was decanted and the solid dried under vacuum. (11.0 mg, 2.05 µmol, 49.5%). FT-IR; \( \nu_{\text{max}}/\text{cm}^{-1} \) 3522, 1611, 1353, 1307, 1272, 1231, 1112, 982, 886, 838, 712, 681 and 670. Elementtal analysis calcd (%) for C₈₈H₁₁₂Cu₄F₁₂N₁₂O₂₀S₄·2CH₂Cl₂·3H₂O (5348.80): C 48.05, N 3.14, H 3.20; found: C 47.75, N 3.40, H 3.33.
Crystal data collection, structure solution and refinement details:

Crystals of $\text{3CF}_3\text{SO}_3$, $\text{4ClO}_4$, $\text{5CF}_3\text{SO}_3$, $\text{5BArF}$ and $\text{6CF}_3\text{SO}_3$ (CCDC 648098, 648099, 648100, 648101 and 648102, respectively) were mounted on a nylon loop and used for 300K ($\text{3CF}_3\text{SO}_3$) or low temperature (100(2) K) ($\text{4ClO}_4$, $\text{5CF}_3\text{SO}_3$, $\text{5BArF}$ and $\text{6CF}_3\text{SO}_3$) X-ray structure determination. The measurements were carried out on a BRUKER SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The measurements were made in the range 2.10 to 29.62 ($\text{3CF}_3\text{SO}_3$), 1.92 to 28.52° ($\text{4ClO}_4$), 1.93 to 28.39° ($\text{5CF}_3\text{SO}_3$) 2.18 to 27.85° ($\text{5BArF}$), 1.94 to 28.55 ($\text{6CF}_3\text{SO}_3$) for 0. Full-sphere data collection was carried out with $\omega$ and $\phi$ scans. A total of 46175 ($\text{3CF}_3\text{SO}_3$), 87725 ($\text{4ClO}_4$), 94392 ($\text{5CF}_3\text{SO}_3$), 97776 ($\text{5BArF}$) 170433 ($\text{6CF}_3\text{SO}_3$) reflections were collected of which 14726 [R(int) = 0.1348] ($\text{3CF}_3\text{SO}_3$), 27652 [R(int) = 0.0845] ($\text{4ClO}_4$), 15381 [R(int) = 0.1294] ($\text{5CF}_3\text{SO}_3$), 29315 [R(int) = 0.0616] ($\text{5BArF}$), 27839 [R(int) = 0.1515] ($\text{6CF}_3\text{SO}_3$) were unique.

Programs used: data collection, Smart version 5.631 (Bruker AXS 1997-02); data reduction, Saint + version 6.36A (Bruker AXS 2001); absorption correction, SADABS version 2.10 (Bruker AXS 2001). Structure solution and refinement was done using SHELXTL Version 6.14 (Bruker AXS 2000-2003). The structures were solved by direct methods and refined by full-matrix least-squares methods on $F^2$. The non-hydrogen atoms were refined anisotropically. The H-atoms were placed in geometrically optimized positions and forced to ride on the atom to which they are attached. In the structures $\text{3CF}_3\text{SO}_3$, $\text{4ClO}_4$, $\text{5CF}_3\text{SO}_3$ and $\text{5BArF}$, the SQUEEZE option of the PLATON Program (Spek, A. L. (2005). PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands) was used to eliminate electron density from disordered solvent molecules. Those solvent molecules are, however,
included in the reported chemical formula and derived values (reported crystal-data formula, formula weight, Dx, Mu and F(000)).

For the $4\text{ClO}_4$ structure, the phenyl ring geometry was fixed to a regular hexagon for the rings C10-C15, C25-C30, C40-C45, C55-C60, C63-C68, C77-C82, C83-C88

The cationic macrocyclic complex moieties of $3\text{CF}_3\text{SO}_3$, $5\text{CF}_3\text{SO}_3$ and $5\text{BARF}$ lie about inversion centres.

The crystals used for structure determination contain in most of the cases solvent molecules what makes their manipulation extremely difficult. The structures also include disordered anions. Due to these difficulties some of the data sets are complicated to collect and not of best quality for refinement.

References

**Figure S1.** ESI-MS spectra of complexes a) 3CF$_3$SO$_3$ (4CF$_3$SO$_3$ gave identical peaks and isotopic distribution ensuring the same composition), b) 5CF$_3$SO$_3$ (6CF$_3$SO$_3$ gave identical peaks and isotopic distribution ensuring the same composition). Simulated spectra of each selected peak are included.
Simulated [S CF$_3$SO$_3$ - 4OTf]$^+$

Simulated [S CF$_3$SO$_3$ - 3OTf]$^+$

Simulated [S CF$_3$SO$_3$ - 2OTf]$^+$
**Figure S2.** a) Crystal packing view perpendicular to $b$ axis of compound $[(\text{Cu}_2(\text{Me}_2\text{p}))_2(\text{O}_2\text{CC}_{12}\text{H}_8\text{CO}_2)_2](\text{CF}_3\text{SO}_3)_4$ ($3\text{CF}_3\text{SO}_3$) with one of the $\text{CF}_3\text{SO}_3$ anions depicted in space-filling mode to highlight its encapsulation inside the pocket depicted by walls of two rectangular molecules; b) Detailed view of the encapsulated triflate anion with some C-H···F_{triflate} and C-H···O_{triflate} contact distances.