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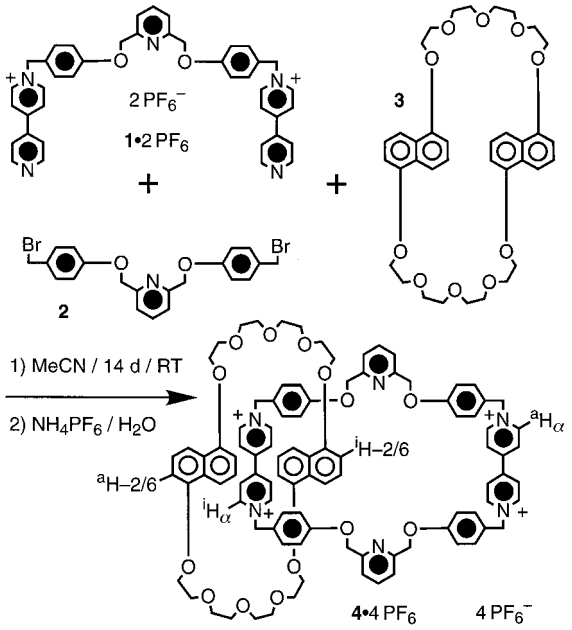
## A Self-Complexing [2]Catenane


Beatriz Cabezon, Jianguo Cao, Françisco M. Raymo, J. Fraser Stoddart,* Andrew J. P. White, and David J. Williams*


Molecules capable of recognizing one or more identical copies of themselves can be employed for the noncovalent synthesis[1] of supermolecules and/or supramolecular arrays. Indeed, self-replicating systems,[2] self-assembling capsules,[3] and supramolecular polymers[4, 5] have all been developed successfully by employing appropriate self-complementary molecules as precursors. Consequently, we contemplated the possibility of synthesizing receptor molecules incorporating mechanically interlocked[6] components by modifying the design of some [2]catenanes[7] such that they acquire receptor characteristics. These [2]catenanes incorporate a 1,5-dioxynaphthalene-based macrocyclic polyether component interlocked with cyclobis(paraquat-4,4′-biphenylene)[8] and are able to bind[7] π-electron-deficient and π-electron-rich substrates. These recognition phenomena have already been exploited in the synthesis of a "rotacatenane"[7b] composed of a 1,5-dioxynaphtho[38]crown-10 moiety interlocked with cyclobis(paraquat-4,4′-biphenylene)[8] and with a third acyclic polyether component containing a 1,5-dioxynaphthalene ring system threaded through the cavity of the bipyridinium-based cyclophane and stoppered by bulky groups.

To generate self-complementary [2]catenanes, we have lengthened and introduced some flexibility into the spacers separating the bipyridinium units in the tetracationic cyclophane component. By inserting a 2,6-bis(oxymethyl)pyridine unit between the two phenylene rings of the 4,4′-bitolyl spacers, the size of the cavity associated with cyclobis(paraquat-4,4′-biphenylene) can be enlarged and enriched with hydrogen bonding acceptors—namely, the nitrogen and oxygen atoms of the 2,6-bis(oxymethyl)pyridine unit. Here, we report the template-directed synthesis of a self-complementary [2]catenane and the formation of a supramolecular homodimer composed of two mutually interpenetrating [2]catenanes both in solution and in the solid state.

Reaction of $\mathbf{1}\cdot 2PF_6$ and **2**[9] in the presence of the 1,5-dioxynaphthalene-based macrocyclic polyether **3** gives the [2]catenane $\mathbf{4}\cdot 4PF_6$ in 18% yield after counterion exchange (Scheme 1), together with small amounts of a [3]catenane incorporating one tetracationic cyclophane and two macrocyclic polyether components.




Scheme 1. The template-directed synthesis of the [2]catenane $\mathbf{4}\cdot 4PF_6$.


[*] Prof. J. F. Stoddart, Dr. B. Cabezon, J. Cao, Dr. F. M. Raymo
Department of Chemistry and Biochemistry
University of California, Los Angeles
405 Hilgard Avenue, Los Angeles, CA 90095-1569 (USA)
Fax: (+1) 310-206-1843
E-mail: stoddart@chem.ucla.edu

Prof. D. J. Williams, Dr. A. J. P. White
Department of Chemistry, Imperial College
South Kensington, London, SW7 2AY (UK)
Fax: (+44) 171-594-5835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The X-ray structural analysis[10] of $\mathbf{4}\cdot 4PF_6$ reveals that the macrocyclic polyether encircles one of the bipyridinium units of the tetracationic cyclophane (Figure 1). The structure is

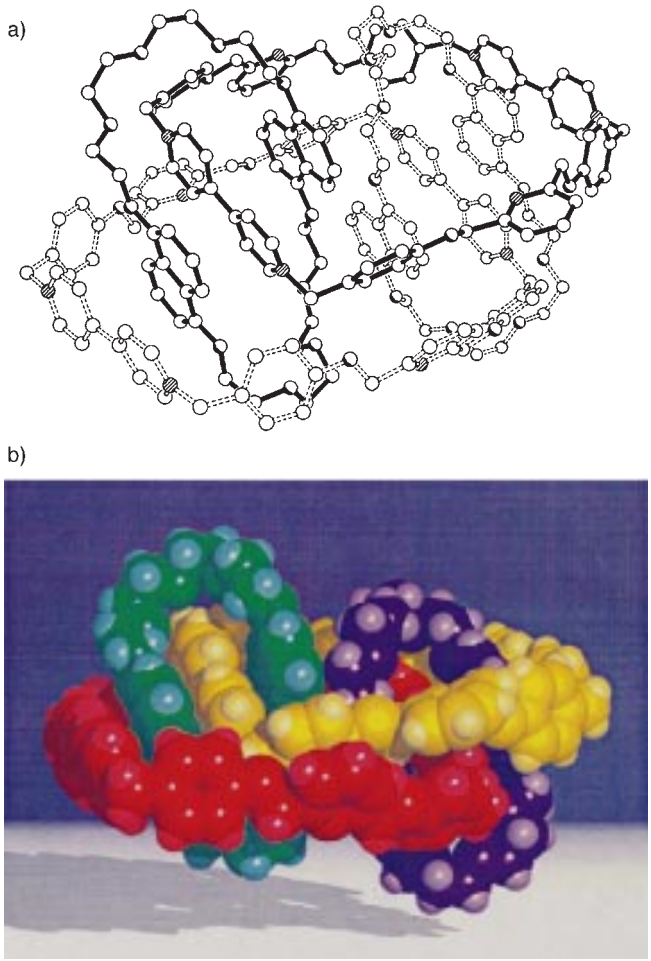


Figure 1. a) Ball-and-stick and b) space-filling representations of one of the supramolecular dimers formed by the [2]catenane $\mathbf{4}^{4+}$ in the solid state. One of the [2]catenanes is made up of the components colored green and yellow, and the other of the components colored red and mauve.

stabilized by $\pi\cdots\pi$ stacking interactions between the bipyridinium unit and the 1,5-dioxynaphthalene ring systems.[11] The only other interactions of note are a pair of C–H$\cdots$O hydrogen bonds between one of the methylene hydrogen atoms adjacent to the "inside" bipyridinium unit and the polyether oxygen atoms.[12] The most interesting feature of this [2]catenane is the open conformation adopted by the cyclophane component. As a consequence, there is a large central void between the inside 1,5-dioxynaphthalene ring system and the "alongside" bipyridinium unit, which are separated by about 14 Å. This void becomes occupied as a result of the mutual interpenetration of centrosymmetrically related pairs of [2]catenanes to form a supramolecular homodimer. The resulting superstructure is stabilized by $\pi\cdots\pi$ stacking interactions between 1) the alongside 1,5-dioxynaphthalene ring system of one [2]catenane and the alongside bipyridinium unit of the other, and between 2) one of the phenoxy rings adjacent to the inside bipyridinium unit in one [2]catenane and one of the pyridyl spacers in the other, and vice versa.[13] These noncovalent bonds are supplemented by a C–H$\cdots\pi$ interaction between one of the *peri* hydrogen atoms of the alongside 1,5-dioxynaphthalene ring system in one [2]catenane and one of the phenoxy rings adjacent to the alongside bipyridinium unit of the other.[14] The inside pair of 1,5-dioxynaphthalene ring systems are aligned parallel, but offset, such that there is no $\pi\cdots\pi$ overlap. However, there are a pair of C–H$\cdots\pi$ interactions between one of the $\beta$-methylene hydrogen atoms associated with the inside 1,5-dioxynaphthalene ring system of one [2]catenane and the inside 1,5-dioxynaphthalene ring system of the other, and vice versa.[15] Pairs of dimers form stepped stacks with the alongside bipyridinium unit of one dimer positioned parallel, but offset, to its counterpart in the next. The area of overlap is small but the interplanar separation short (ca. 3.4 Å).

The $^1$H NMR spectrum of $\mathbf{4}\cdot 4PF_6$ (Figure 2a; $T=$ 185 K, $(CD_3)_2CO$) shows only one signal for the $\alpha$-protons $^aH_\alpha$ of the alongside bipyridinium unit, indicating that the rotation of this unit around its N$\cdots$N axis is fast on the $^1$H NMR time scale. By contrast, the rotation of the inside bipyridinium unit around its N$\cdots$N axis and that of the inside 1,5-dioxynaphthalene ring system around its O$\cdots$O axis are slow. As a result, the $\alpha$-protons $^iH_\alpha$ of the inside bipyridinium unit give rise to two sets of signals in the $^1$H NMR spectrum (Figure 2a). Upon warming of the solution, one or both processes become fast on the $^1$H NMR time scale, and the two sets of signals for $^iH_\alpha$ coalesce into one (Figure 2b, c). With the coalescence treatment[16] a free energy of activation $\Delta G_c^{\neq}$ of 9.3 kcal mol$^{-1}$ was calculated at a coalescence temperature $T_c$ of 195 K. Upon a further increase in temperature, the circumrotation of the tetracationic cyclophane through the cavity of the macrocyclic polyether becomes fast. As a result, the two sets of signals for $^aH_\alpha$ and $^iH_\alpha$ coalesce into one (Figure 2d–g). A $\Delta G_c^{\neq}$ value of 13.5 kcal mol$^{-1}$ was determined at a $T_c$ of 288 K. At 185 K the circumrotation of the macrocyclic polyether through the cavity of the tetracationic cyclophane becomes slow and two distinct signals are observed (Figure 3a) for the

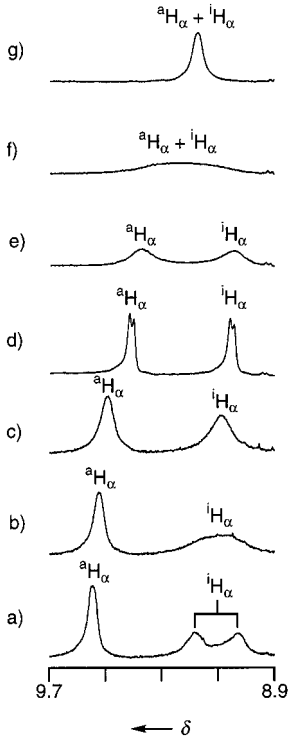


Figure 2. Portion of the $^1$H NMR spectra of the [2]catenane $\mathbf{4}\cdot 4PF_6$ recorded in $(CD_3)_2CO$ at a) 185, b) 195, c) 208, d) 252, e) 274, f) 288, and g) 309 K. The limiting frequency separation $\Delta\nu$ for the two signals associated with the protons $^iH_\alpha$ in a) is 62 Hz, and the derived rate constant $k_c$ at the coalescence temperature is 82 s$^{-1}$. For the two signals associated with the protons $^aH_\alpha$ and $^iH_\alpha$ in c), $\Delta\nu = 143$ Hz and $k_c =$ 317 s$^{-1}$.

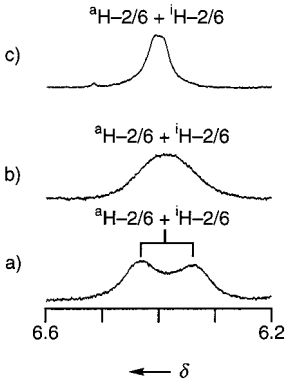


Figure 3. Portion of the $^1$H NMR spectra of the [2]catenane $\mathbf{4}\cdot 4PF_6$ recorded in $(CD_3)_2CO$ at a) 185, b) 190, and c) 208 K. The limiting frequency separation $\Delta\nu$ for the two signals associated with the protons $^aH_{2/6}$ and $^iH_{2/6}$ in a) is 37 Hz, and the derived rate constant $k_c$ at the coalescence temperature is 82 $s^{-1}$.

2,6-protons $^a$H-2/6 and $^i$H-2/6 of the alongside and inside 1,5-dioxynaphthalene ring systems, respectively. Upon warming of the solution, this process becomes fast and the two signals coalesce into one (Figure 3b, c). A $\Delta G_c^{\neq}$ value of 9.2 kcal $mol^{-1}$ was determined at a $T_c$ of 188 K.

As a result of the formation of a supramolecular homodimer, the $^1$H NMR spectra of $\mathbf{4}\cdot 4PF_6$ ($T = 185$ K, $(CD_3)_2CO$) showed concentration dependence. The observed change in chemical shift $\Delta\delta_0$ of the signal associated with the protons $^aH_\alpha$ (Figure 2a) was followed by varying the concentration $c$ from $3\times10^{-2}$ to $3\times10^{-3}$ M. An association constant $K_a$ of 20 $M^{-1}$ ($-\Delta G^\circ = 1.1$ kcal $mol^{-1}$) for the dimerization process was determined[17] by nonlinear curve fitting of the plot of $\Delta\delta_o$ against $c$.

Thus, we have established that the [2]catenane $\mathbf{4}\cdot 4PF_6$ forms a homodimeric superstructure both in solution and in the solid state as a result of a combination of intercatenane $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions. This homodimer is composed of a total of four macrocyclic components held together by two mechanical bonds and a range of cooperative noncovalent bonds. The intriguing recognition properties of this novel class of [2]catenane receptors offers the potential for the design and synthesis of even more intricate molecular and supramolecular systems incorporating interlocked components. This remarkable and unique example of self-recognition is reminiscent of the dimerization of certain glycopeptides whose antibiotic activity is promoted upon self-recognition.[18]

*Experimental Section*

$\mathbf{4}\cdot 4PF_6$: A solution of $\mathbf{1}\cdot 2PF_6$[9] (0.28 g, 0.3 mmol), **2** (0.15 g, 0.3 mmol), and **3** (0.59 g, 0.9 mmol) in dry MeCN (25 mL) was stirred for 14 d at ambient temperature. The solvent was evaporated off under reduced pressure and the residue was purified by column chromatography ($SiO_2$, 2 M $NH_4Cl$/MeOH/$MeNO_2$ (7/2/1, v/v/v)). The resulting purple solid was dissolved in $H_2O$ and a large excess of $NH_4PF_6$ was added. The resulting precipitate was isolated by filtration, washed with $H_2O$, and dried to afford $\mathbf{4}\cdot 4PF_6$ as a purple powder (12 mg, 18%). M.p. > 200 °C; FAB-MS: *m/z*: 2018 $[M-PF_6]^+$, 1872 $[M-2PF_6]^+$, 1728 $[M-3PF_6]^+$; $^1$H NMR (400 MHz, $CD_3CN$, 25 °C): $\delta = 8.76$ (8H, br s), 7.71–7.52 (16H, m), 7.49 (2H, t), 7.24 (4H, d), 7.10 (8H, br s), 6.57 (4H, t), 6.37 (8H, d), 5.72 (8H, s), 5.09 (8H, s), 3.92–3.71 (32H, m); $^{13}$C NMR (125.7 MHz, $CD_3CN$, 25 °C): $\delta = 160.6$, 157.1, 154.0, 145.5, 132.9, 132.2, 130.1, 126.7, 126.2, 121.8, 116.7, 113.8, 106.1, 72.0, 71.7, 71.6, 70.9, 68.9, 65.3.

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[9] The bis(hexafluorophosphate) salt $\mathbf{1}\cdot 2PF_6$ was prepared by treating the dibromide **2** with 4,4′-bipyridine. The dibromide **2** was synthesized in three steps by 1) allowing methyl 4-hydroxybenzoate to react with 2,6-bis(hydroxymethyl)pyridine ditosylate (tosylate = toluene-4-sulfonate), 2) reducing the ester groups, and 3) brominating the resulting hydroxymethyl groups.


  0044-8249/00/11201-0154 $ 17.50+.50/0 

[10] Crystal data for $\mathbf{4}\cdot 4PF_6$: $[C_{98}H_{98}N_6O_{14}][PF_6]_4\cdot 4MeCN\cdot 2.5H_2O$, $M_r=2373.0$, triclinic, space group $P\bar{1}$ (no. 2), $a=13.567(1)$, $b=17.762(2)$, $c=24.924(3)$ Å, $\alpha=74.41(1)$, $\beta=87.72(1)$, $\gamma=73.23(1)^\circ$, $V=5534.5(9)$ Å$^3$, $Z=2$, $\rho_{calcd}=1.424$ g cm$^{-3}$, $\mu(Cu_{K\alpha})=15.8$ cm$^{-1}$, $F(000)=2458$, $T=193$ K; red rhombs, $0.56\times 0.35\times 0.32$ mm, Siemens P4 rotating anode diffractometer, graphite-monochromated $Cu_{K\alpha}$ radiation, $\omega$ scans, 16246 independent reflections. The structure was solved by direct methods. The major-occupancy non-hydrogen atoms of the [2]catenane and of the hexafluorophosphate counterions, as well as the full-occupancy non-hydrogen atoms of the included solvent molecules, were refined anisotropically (the others isotropically) using full-matrix least squares based on $F^2$ to give $R_1=0.096$, $wR_2=0.243$ for 9537 independent observed reflections ($|F_o|>4\sigma(|F_o|)$, $2\theta\leq 120^\circ$) and 1507 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132674. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] The mean interplanar separations between the inside and alongside 1,5-dioxynaphthalene ring systems and the inside bipyridinium unit are 3.37 and 3.32 Å, respectively.

[12] The C···O and H···O distances and the C–H···O angles are 3.29 Å, 2.38 Å, 158° and 3.30 Å, 2.44 Å, 148°, respectively.

[13] The mean interplanar separations between the interacting 1,5-dioxynaphthalene and bipyridinium units and between the phenoxy and pyridyl rings are 3.42 and 3.67 Å, respectively.

[14] The H···π distance and the C–H···π angle are 2.95 Å and 139°.

[15] The H···π distance and the C–H···π angle are 2.77 Å and 132°. C–H···π interactions of this type have been observed previously; see, for example, a) M. Asakawa, P. R. Ashton, W. Hayes, H. M. Janssen, E. W. Meijer, S. Menzer, D. Pasini, J. F. Stoddart, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, 120, 920–931; b) P. R. Ashton, S. E. Boyd, A. Brindle, S. J. Langford, S. Menzer, L. Pérez-García, J. A. Preece, F. M. Raymo, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, *New J. Chem.* **1999**, 23, 587–602.

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