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Self-assembly of a [2]catenane incorporating a fluorenonophane-containing azobenzene moiety

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The first [2]catenane, in which the 4,4′-azobiphenoxy unit of the fluorenonophane resides inside the cavity of the tetracationic cyclophane has been synthesised and characterised.

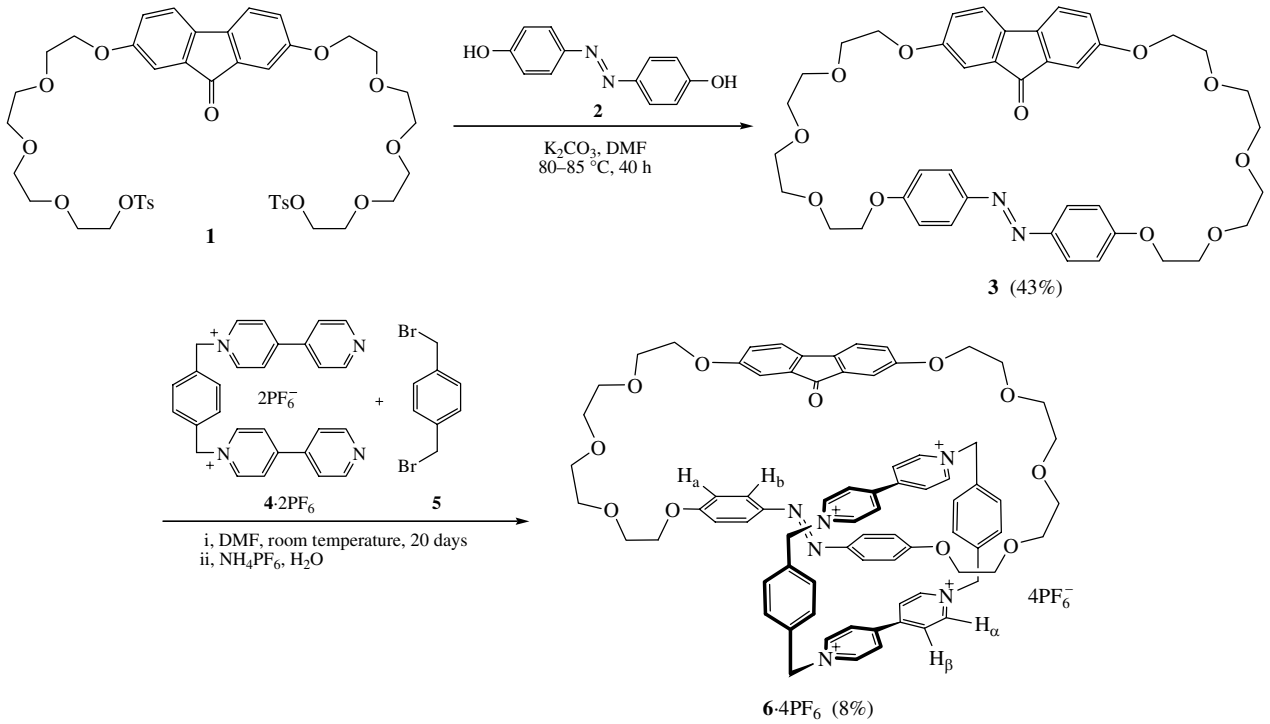
The potential opportunity of using interlocked molecular structures, such as catenanes and rotaxanes, in nanotechnology, molecular cybernetics and molecular informatics is based on the relative movements of interlocked components that can be controlled chemically, electrochemically and/or photochemically by introducing appropriate fragments into the structure of these supramolecules.[1] In this sense, azobenzene units, which can be photochemically isomerised from *trans* to *cis* isomers and *vice versa*, are attractive.[2] Molecular and supramolecular systems incorporating one or more azobenzene units have been designed.[3] However, only a few examples of catenanes containing an azobenzene moiety have been prepared.[4] These catenanes exist as translational isomers in which the azobenzene units reside preferably outside the cavity of the tetracationic components of catenanes. It essentially restricts possibilities to manage photochemically the translational isomerism of catenanes.

Within a study of [2]catenanes incorporating fluorenonocrownophanes mechanically interlocked with the cyclobis(paraquat-*p*-phenylene) tetracation ($CBPQT^{4+}$), we report here for the first time the template-directed synthesis, characterisation and solid-state structure of the [2]catenane containing azobenzene unit in its π-electron-rich component. The synthetic pathways leading to cyclophane **3** and [2]catenane **6**·$4PF_6$ are shown in Scheme 1. Macrocyclization of bistosylate **1**[5] with bisphenol **2**, under high dilution conditions, gave crownophane **3** in 43% yield after work-up and chromatographic purification over silica gel.† The template-directed catenation of **3** was carried out with a two-fold excess of the bis(bipyridinium) derivative **4**·$2PF_6$ and 1,4-bis(bromomethyl)benzene **5** under atmospheric pressure to afford [2]catenane **6**·$4PF_6$ in 8% yield after counterion exchange.‡ The synthesis of **6**·$4PF_6$ can be presumably enhanced by performing the reaction under ultrahigh pressure (8–12 kbar) conditions, which accelerate the Menshutkin reaction[6] and, as a rule, increase the yields of catenanes.[7(c)–(g)] However, we did not investigate the catenation process under these conditions.

[2]Catenane **6**·$4PF_6$ was characterised by positive-ion FAB MS. The spectra revealed peaks for the successive loss of one, two and three PF_6^- ions from the molecular ion. Besides this fragmentation at the periphery of the catenane leaving intact the interlocked structure, cleavage of a bond within one of the macrocycles leads to dethreading and loss of 'half' the catenane. It results in peaks, which correspond to the loss of one, two and three counterions, respectively, from the tetracationic cyclophane

† *Selected data for* **3**: yellow solid (yield 43%); mp 145–147 °C. ^{1}H NMR (CD_3CN, 293 K, 300 MHz) δ: 3.55–3.69 (m, 16H), 3.72–3.78 (m, 4H), 3.79–3.85 (m, 4H), 3.93–3.99 (m, 4H), 4.10–4.17 (m, 4H), 6.76 (dd, 2H, *J* 8.40 and 2.49 Hz), 6.92 (d, 2H, *J* 2.49 Hz), 6.94 (d, 4H, H_a, *J* 9.03 Hz), 7.11 (d, 2H, *J* 8.40 Hz), 7.64 (d, 4H, H_b, *J* 9.03 Hz). ^{13}C NMR ($CDCl_3$, 293 K, 75.5 MHz) δ: 67.9, 69.6, 70.7, 70.8, 70.9, 110.2, 114.7, 120.4, 120.5, 124.2, 135.7, 137.4, 146.9, 159.0, 160.7, 193.4. FAB MS, *m/z*: 765 $[M + Na]^+$, 743 $[M + H]^+$.

‡ **6**·$4PF_6$: a solution of **3** (149 mg, 0.2 mmol), **4**·$2PF_6$ (282 mg, 0.4 mmol), and **5** (132 mg, 0.5 mmol) in dry DMF (25 ml) was stirred at room temperature for 20 days. The solvent was removed *in vacuo*, and the resulting red/orange solid was washed with $CHCl_3$ (30 ml), dissolved in a 2 M aqueous solution of NH_4Cl (75 ml), and filtered to remove insoluble materials. The water was removed *in vacuo*, and the residue was purified by column chromatography (SiO_2, MeOH–2 M NH_4Cl–$MeNO_2$, 7:2:1). The catenane-containing fractions were combined and evaporated *in vacuo* to give a residue, which was dissolved in a minimal amount of warm H_2O, and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation occurred. The precipitate was filtered off, washed with H_2O (20 ml) and dried *in vacuo*. Recrystallization from MeCN–Pr^iOH (4:3, v/v) gave **6**·$4PF_6$ as orange crystals (29 mg, 8%); mp > 300 °C (decomp.). ^{1}H NMR (CD_3CN, 293 K, 400 MHz) δ: 3.61–4.09 (m, 32H), 5.59 (br. s, 4H, H_a), 5.68 (s, 8H), 6.12 (br. s, 4H, H_b), 6.45–6.62 (m, 2H), 6.65–6.82 (m, 2H), 6.86–7.09 (m, 2H), 7.61 (d, 8H, H_β, *J* 6.23 Hz), 7.82 (s, 8H), 8.77 (d, 8H, H_α, *J* 6.23 Hz). ^{13}C NMR (CD_3CN, 293 K, 75.5 MHz) δ: 65.7, 69.1, 70.3, 71.1, 71.3, 71.5, 71.7, 110.7, 115.1, 121.5, 122.1, 124.6, 127.0, 131.8, 136.2, 137.7, 137.9, 145.7, 146.6, 147.2, 160.1, 161.2, 193.3. FAB MS, *m/z*: 1697 $[M - PF_6]^+$, 1552 $[M - 2PF_6]^+$, 1407 $[M - 3PF_6]^+$, 955 $[M - \mathbf{3} - PF_6]^+$, 810 $[M - \mathbf{3} - 2PF_6]^+$, 665 $[M - \mathbf{3} - 3PF_6]^+$, 765 $[\mathbf{3} + Na]^+$, 743 $[3 + H]^+$, 742 $[\mathbf{3}]^+$.



Scheme 1 Synthesis of crownophane **3** and [2]catenane **6**·4PF$_6$.

CBPQT^{4+}, and peaks of neutral and protonated fluorenonophane **3** (Figure 1). Such a fragmentation followed by ring cleavage and dethreading does not occur in macrocyclic or open chain compounds and indicates the presence of [2]catenane **6**·4PF$_6$.[8] This characteristic process of catenane fragmentation has been predicted and offered to use as a 'finger-print' of the catenane structure by R. G. Kostyanovsky.[9] This idea has been confirmed experimentally and soon put into widespread usage.[7]

A comparison of the ^{1}H NMR spectrum (CD_3CN, 293 K) of crownophane **3** with that of [2]catenane **6**·4PF$_6$ shows spectrum-line broadening and upfield shifts of the signals of all protons attached to the aromatic units, suggesting that the circumrotation of the neutral macrocycle through the cavity of the tetracationic cyclophane is slow or non-existent on the ^{1}H NMR timescale. The resonances corresponding to the protons of the fluorenone moiety are slightly shifted upfield within the range $\Delta\delta \approx [(-0.14) - (-0.22)]$ ppm. It implies weak interactions between the fluorenone fragment and the 'inside' bipyridinium unit of the CBPQT^{4+}. The most significant chemical shift is undergone by the 4,4′-azobiphenoxy protons ($\Delta\delta = -1.35$ and -1.52 ppm for the protons H_a and H_b, respectively), which, coupled with the downfield shift of the *p*-phenylene protons of the tetracationic component ($\Delta\delta = +0.28$ ppm), indicates the edge-to-face [C–H···π] interaction between 4,4′-azobiphenoxy CH hydrogen atoms and *p*-phenylene rings. This suggests that the 4,4′-azobiphenoxy unit resides preferentially within the tetracationic cyclophane cavity in solution, like observed in a solid state (vide infra). The H_a and H_b protons of both phenyl rings of the azobenzene unit give rise only to two broad singlets suggesting that the CBPQT^{4+} is in slow reciprocation between these phenyls on the ^{1}H NMR timescale. The resonances of protons in the α and β positions, with respect to the nitrogen atoms, on the bipyridinium units of the CBPQT^{4+} are shifted upfield with respect to those of the CBPQT·4PF$_6$ in its 'free' form ($\Delta\delta = -0.10$ and -0.57 ppm for H_α and H_β protons, respectively). These protons give rise to relatively sharp and resolved only one set of signals in the ^{1}H NMR spectrum of **6**·4PF$_6$, indicating that the inside and alongside bipyridinium units of the CBPQT^{4+} are in fast exchange on the ^{1}H NMR timescale.

Single crystals suitable for X-ray crystallography were obtained by layering hexane onto a solution of **6**·4PF$_6$ in acetone. The X-ray diffraction study§ of [2]catenane **6**·4PF$_6$ shows that the 4,4′-azobiphenoxy unit of **3** is located inside the cavity of the tetracationic cyclophane, while the fluorenone unit is posi-

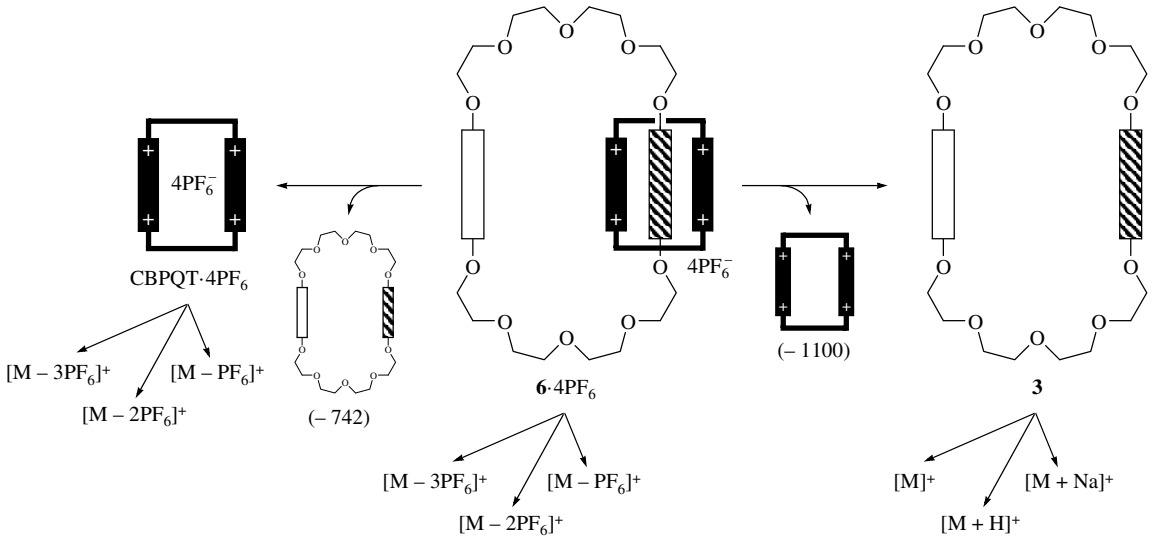


Figure 1 Cartoon representation of [2]catenane **6**·4PF$_6$ FAB MS fragmentation pathways.

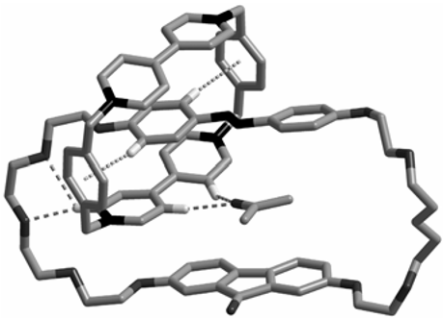


Figure 2 Polytube representation of the solid-state structure of [2]catenane **6**·4PF_6. Colour code: carbon, gray; oxygen, dark grey; nitrogen, black; the selected hydrogens, light gray. The water molecules and counterions are not shown for clarity. Dots and dashed lines indicate [C–H···π] and [C–H···O] interactions, respectively.

tioned outside (Figure 2). The tetracationic macrocycle interacts with only one phenyl ring of the azobenzene unit. The mean interplanar separation distances between this phenyl ring and the internal and external bipyridinium units of the $CBPQT^{4+}$ are 2.98–3.20 and 3.41–3.63 Å, respectively; angles between the planes do not exceed 15°. Such distances in the donor-acceptor array, coupled with the near parallel alignments and considerable overlap degree of these aromatic moieties, indicate their involvement in strong face-to-face π–π stacking interactions.

In addition, the catenane structure is stabilised by the bifurcated [C–H···O] hydrogen bond between the H_α atom of the internal pyridine ring and the nearest oxygen atoms in the polyether chain of crownophane **3** (H···O, 2.28–2.59 Å; C–H···O, 120–165°), and by the [C–H···π] interactions between the diametrically opposite H_a and H_b atoms of the azobenzene phenyl ring and π-systems of the *para*-xylyl rings of $CBPQT^{4+}$ (C–H···π distances are 2.57–2.88 Å, and the C–H···π angles are 167–174°). The acetone molecule, which resides within the cavity of crownophane **3**, is bound with the bipyridyl fragment of $CBPQT^{4+}$ by two C–H···O hydrogen bonds (H···O, 2.26–2.36 Å; C–H···O, 142–177°).

In the asymmetric part of a unit cell, two molecules of the catenane are connected into dimers by the stacking interactions between almost parallel fluorenone fragments with a distance of 3.5 Å between their planes. These dimers contain enantiomers of different planar chirality associated with the local C_{2h} symmetry of the 4,4′-azobiphenoxy unit. The formation of similar π-stacked dimers involving the partial overlap of fluorenone units was observed in the solid structure of the catenane incorporating fluorenonophane containing 2,5-dioxynaphthalene fragment and the $CBPQT^{4+}$ as a second macrocyclic component.[10] It is significant that the formations of π-stacked dimers are not a trivial case for the solid-state structure of the catenanes containing π-donor and π-acceptor cyclic components. Usually, such catenanes crystallise to form continuous polar stacks of the π-donor and the π-acceptor units.[7(c)–(e),11]

In summary, we reported a [2]catenane, which is the first example of azobenzene-containing catenanes with the 4,4′-azobiphenoxy unit residing inside the cavity of the tetracationic cyclophane in the solid-state and, very likely, in a solution.

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§ *Crystal data for* **6**·4PF_6: $[C_{77}H_{78}O_{11}N_6](PF_6)_4 \cdot 5Me_2CO \cdot 0.5H_2O$, $M = 2142.7$, triclinic, $P\bar{1}$, $a = 21.161(3)$, $b = 23.014(3)$, $c = 23.659(3)$ Å, $\alpha = 95.75(1)°$, $\beta = 111.54(1)°$, $\gamma = 107.33(1)°$, $V = 9942(2)$ Å^3, $F(000) = 4444$, $d_{calc} = 1.432$ g cm^{-1}, $Z = 2$, $\mu = 0.19$ mm^{-1}. Data were obtained on an Xcalibur-3 diffractometer ($T = 100$ K, graphite-monochromated MoKα radiation, ω-scan, CCD detector, $2\theta_{max} = 55°$). It was collected 1743487 reflections (45158 unique reflections, $R_{int} = 0.060$). The structure was solved by a direct method using the SHELX97 program package. The hydrogen atoms were placed in calculated positions and refined using riding model. Some bond lengths in disordered fragments were restrained to following values: C_{sp^3}–C_{sp^3} 1.49(1) Å, C_{sp^3}–O 1.42(1) Å, C_{sp^2}–C_{sp^3} 1.48(1) Å, C=O 1.21(1) Å, P–F 1.59(1) Å. Refinement against F^2 in an anisotropic approximation for non-hydrogen atoms by a full-matrix least-squares method for 45158 reflections was carried out to $wR_2 = 0.173$ [2688 parameters, $R_1 = 0.069$ for 29423 reflections with $F_0 > 4\sigma(F_0)$, $S = 1.12$].

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 298935. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.