Templated Synthesis of Desymmetrized [2]Catenanes with Excellent Translational Selectivity[†]
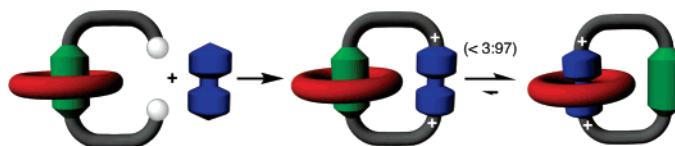
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ABSTRACT

Desymmetrized [2]catenanes were synthesized and shown to exhibit excellent translational selectivity. The templated synthesis takes effect from the formation of pseudorotaxanes between π-rich crown ethers and a π-deficient pyromellitic (PmI) unit, followed by macrocyclization around the crown ethers with the creation of a bipyridinium (BPy) unit. The crown ethers preferably encircle the BPy unit in the resulting [2]catenanes in both solution and the solid state, as indicated by various spectroscopic analyses.

Since the first templated synthesis[1] of [2]catenanes, interlocked molecular systems[2] can now be obtained efficiently relying on supramolecular assistance to covalent synthesis. Molecular recognition forces, such as donor−acceptor interactions,[3] metal−ligand coordination,[4] and amide hydrogen-

bonding interactions,[5] have been well adapted in the templated synthesis of interlocked molecules. Synthesis of the donor−acceptor [2]catenane **1**·4PF$_6$ (Scheme 1) that was pioneered by Stoddart et al. represents[6] an important milestone in this field. The two macrocyclic components of **1**·4PF$_6$ are held together at large by living donor−acceptor interactions between a π-electron deficient bipyridinium (BPy) cyclophane and a π-electron-rich crown ether macrocycle. Mechanical motions generated from intercomponent movements render these nanoscale objects ideal candidates for molecular level switches. Indeed, molecular machines[7]

[†] Dedicated to Prof. J. Fraser Stoddart on the occasion of his 65th birthday.

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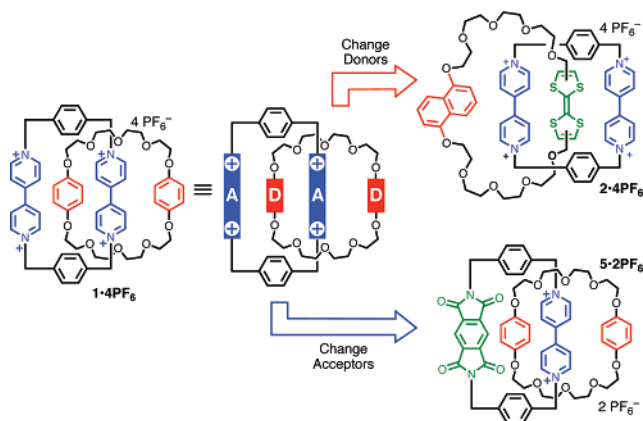
and molecular switches[8] of such kinds have found many applications, including molecular memories,[9] nanovalves,[10] and molecular muscles.[11]

Desymmetrized [2]catenanes[12] serve as a role model of controllable molecular motors.[7d] Efficient rotary movements can be implemented only if precise control of translational isomerism is achieved. The synthesis of such compounds remains challenging as it requires the selection of the right recognition pairs with different strength and their proper

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assembly. A nice example is[8a] the switchable [2]catenane **2**·4PF$_6$ (Scheme 1). By differentiating the two π-donors on the crown ether macrocycle, precise translational selectivity was achieved to give a nearly "all-or-nothing" situation.

Another way to implement control over the translational isomerism is to include two different π-accepting units. Neutral π-deficient units, such as pyromellitic diimide (PmI) and naphtho-diimide (NpI), have been used[13] as π-acceptors in [2]catenane synthesis. The considerably different π-accepting ability between PmI and BPy units[13d,14] prompts us to designate desymmetrized [2]catenanes incorporating these components. Here we report (1) the templated syntheses of two such [2]catenanes that (2) exist as a single translational isomer as expressed in the form of a preference for crown ether component to encircle the BPy unit in both solution and solid states.
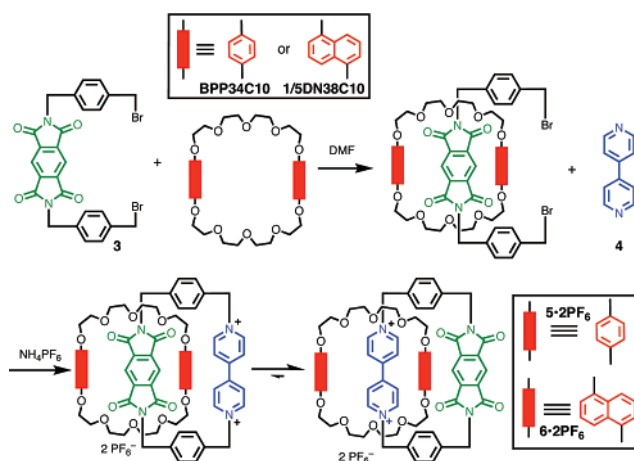
The synthesis (Scheme 2) was first attempted by reacting a PmI containing dibromide **3**, 4,4′-bipyridine (**4**), and a hydroquinone (HQ) containing crown ether, bis-*p*-phenylene-[34]crown-10 (BPP34C10), in DMF for 3 days. Although no noticeable color change occurred upon mixing the dibromide **3** and BPP34C10 owing to weak donor−acceptor interactions, a red color gradually developed overnight, suggesting the formation of bipyridium and its inclusion in the BPP34C10 cavity. After counterion exchange with an acetone/NH$_4$PF$_6$ mixture, the [2]catenane **5**·2PF$_6$ was isolated as a red solid in 30% yield. Similarly, when the more

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electron-rich crown ether 1,5-dinaphtho[38]crown-10 (1/5DN38C10) was used, the [2]catenane $6\cdot2PF_6$ was isolated as a purple solid in 52% yield.

The electrospray ionization (ESI) mass spectra of $5\cdot2PF_6$ and $6\cdot2PF_6$ reveal singly charged peaks at m/z 1260.2 and 1359.5, and doubly charged peaks at m/z 557.6 and 607.2, corresponding to the loss of one and two PF_6^- ions, respectively. The UV−vis spectrum of $5\cdot2PF_6$ in Me_2CO shows a broad charge-transfer (CT) band at $\lambda = 448$ nm ($\epsilon = 230$ M^{-1} dm^{-1}), characteristic for a BPy unit situated in the cavity of BPP34C10.[6] Similarly, the purple solution of $6\cdot2PF_6$ has a CT absorption at $\lambda = 508$ nm ($\epsilon = 230$ M^{-1} dm^{-1}), consistent with the BPy unit being included in the 1/5DN38C10 cavity.[14]
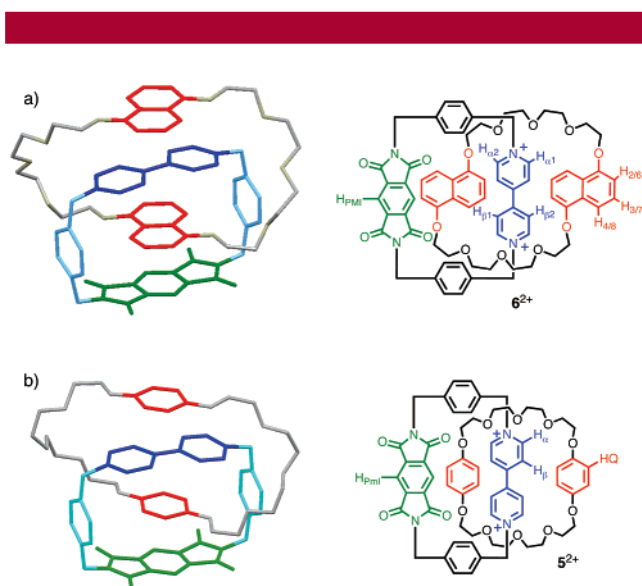

Figure 1. Stick representation of X-ray structures and structural formula of (a) [2]catenane 6^{2+} and (b) [2]catenane 5^{2+}. Hydrogen atoms and counterions are omitted for clarity.

The preference of a BPy unit being included in the crown's cavity is also indicated by X-ray structural analysis.[15] The crystal structure of $6\cdot2PF_6$ (Figure 1a) indicates that the dicationic cyclophane is interlocked with the crown ether such that (1) the 1,5-dioxynaphthalene (DNP) ring system is sandwiched between the nearly parallelly aligned BPy unit and the PmI unit with (2) the BPy unit sandwiched between the parallelly aligned DNP ring systems. The mean inter-planar separations are 3.3 Å, in keeping with stabilizing $[\pi-\pi]$ stacking interactions. The two pyridinium ring systems are twisted with an angle of 10.1° and the distance between the two quatery N^+ centers is 7.02 Å. The PmI unit is not strictly coplanar, with a dihedral angle between the mean planes of the diimide rings of 5.2°. The distance between the two N atoms of the PmI unit is 6.75 Å. The

conformation is also stabilized[16] by various [C−H···O] and [C−H···π] interactions. Similarly, the stacked array of complementary donor−acceptors is also observed in the crystal structure of $5\cdot2PF_6$[15] (Figure 1b). Intermolecular packings along the axes of the donor−acceptor stacks are present in both cases.

^{1}H NMR spectroscopy also provided insightful information for the relative location of the two ring components. The resonances of spectra of $5\cdot2PF_6$ or $6\cdot2PF_6$ are assignable to one single translational isomer. The "inside" and "outside" HQ or DNP ring systems in $5\cdot2PF_6$ or $6\cdot2PF_6$ are (Figure 2) clearly discernible, suggesting that the site exchange between HQ or DNP ring systems is slow at the ^{1}H NMR time scale. The "inside" and "outside" HQ protons of $5\cdot2PF_6$ resonate as two singlets at δ 6.26 and 3.80, respectively. In the case of $6\cdot2PF_6$, the resonances of the two DNP ring systems are expressed in the usual doublet−triplet−doublet coupling pattern. Characteristically, the $H_{4/8}$ of the inside DNP ring system appears as a doublet at δ 2.95 ppm (inset in Figure 2b) as a result of the shielding effect from the nearby dicationic cyclophane. In contrast to $5\cdot2PF_6$, all except the PmI protons of the dicationic cyclophane in $6\cdot2PF_6$ become diastereotopic. The chemical unequivalence occurs[13a] as a result of the local C_2 symmetry imposed from the DNP ring system on the dicationic cyclophane.
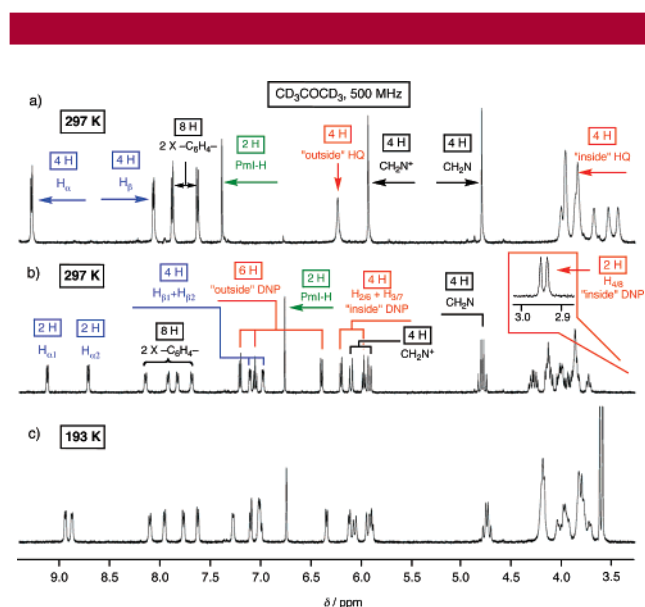

Figure 2. Partial ^{1}H NMR spectra of (a) $5\cdot2PF_6$ at 297 K, (b) $6\cdot2PF_6$ at 297 K, and (c) $6\cdot2PF_6$ at 193 K.

The observation of only one single set of resonances in both $5\cdot2PF_6$ and $6\cdot2PF_6$ implies that one translational isomer

(15) Red crystals suitable for X-ray single crystal analysis were obtained after diffusion of ether into a Me_2CO solution of $5\cdot2PF_6$. Purple crystals of $6\cdot2PF_6$ were obtained from a MeCN solution after diffusion of diisopropyl ether. For more crystallographic information, please see the crystallographic information files in the Supporting Information.

(16) Multiple [C−H···O] interactions are observed between several oxygen atoms in the polyether loops of the crown ether and one α-BPy proton, one p-phenylene proton, and one methylene proton of the dicationic cyclophane. The associated [H···O] distances are 2.61, 2.50, and 2.47 Å, respectively. The corresponding [C−H···O] angles are 165°, 127°, and 134°. In addition, there is [C−H···π] interaction between one of the H-4/8 protons of the "inside" DNP ring system and its proximal p-phenylene ring. The distances between the H atom and the centroid π-electron plane is 2.54 Å, and the corresponding [C−H···π] angle is 149°.
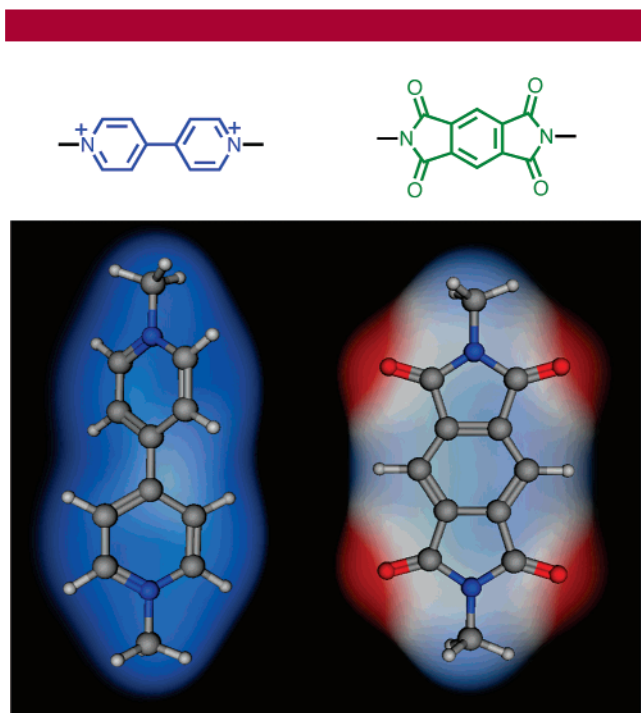
Figure 3. Electrostatic potential surfaces of two model compounds, paraquat (left) and *N,N′*-dimethylpyromellitic diimide (right). Blue represents positive electrostatic potential and red stands for negative electrostatic potential. The surfaces were optimized with the MMFF94x force field.

is dominant at this temperature, while the possibility cannot be excluded where the two isomers undergo fast exchange such that only an averaged spectrum is observed. To verify that, the temperature is further lowered to −80 °C, at which point the site exchange should be slow enough[17] to capture possible translational isomers in equilibrium. As shown in Figure 2c, all the peaks of **6**·2PF$_6$ remain sharp in CD$_3$COCD$_3$ and no new peaks are observed, suggesting that the observed single resonance is not a result of site exchange and indeed the excellent translational selectivity is maintained throughout. On the basis of the detection limit of ^{1}H NMR spectroscopy, a selectivity greater than 97:3 can be estimated for both [2]catenanes.

(17) Two mechanisms are possible for the exchange between the two translational isomers. Either the dicationic cyclophane rotates through the center of the crown ether component, or the outer DNP ring system can sweep round the dicationic cyclophane by pirouetting about the included DNP ring system. According to studies by the Stoddart group on structually similar [2]catenanes, the latter one is the lower energy process as it requires least energy for the breakdown of donor−acceptor interactions. The typical associated activation barrier for Stoddart's systems is around 12 to 14 kcal mol^{-1}. Correspondingly, those site exchange processes can be efficiently "frozen out" below −30 °C. For compounds **5**·2PF$_6$ and **6**·2PF$_6$, such activation barrier is difficult to measure on account of the absence of other isomers. However, they should be very similar to those reported systems, both of which involve the breaking of donor−acceptor interactions between BPy and the outer aromatic ring system.

The demonstrated selectivity can be well understood in terms of the significantly different electronic properties between PmI and BPy units. An electrostatic potential surface analysis[18] (Figure 3) of two model compounds, Paraquat and *N,N′*-dimethylpyromellitic diimide, clearly indicates that a BPy unit is more electron deficient than a PmI unit. Correspondingly, the BPy unit is more prone to stack with the π-donor units from the crown ether component than the PmI unit. Significantly different binding constants of these units toward crown ethers are reported previously. For example, the binding constant for a PmI derivative and 1/5DN38C10 is only 21 M^{-1} and is increased to 210 M^{-1} in the presence of LiI,[13d] while the binding constant for a PF$_6^-$ salt of dibenzylviologen and 1/5DN38C10 is 20 000 M^{-1}.[14] Such noncovalent bonding strength difference matches well with the acceptors' electron deficiency and possibly accounts for the excellent translational selectivity expressed in these desymmetrized [2]catenanes.

We have developed an efficient synthesis of desymmetrized [2]catenanes with precise control of translational isomerization. The engaged recognition units compose a fine set of modules where a balance is realized between templating and achieving translational selectivity—the donor−acceptor interaction between PmI and crown ether is strong enough to template the catenation while it is weak enough to be outperformed by the generated BPy unit. The demonstrated excellent translational selectivity could lead to high fidelity molecular switches for usage in the growing field of molecular electronics. Electrochemical- and photochemical-switching behavior of these catenanes are currently being investigated.

Supporting Information Available: Experimental details for the preparation of **3**, **5**·2PF$_6$, and **6**·2PF$_6$, and UV−vis spectra and X-ray crystallographic data of **5**·2PF$_6$ and **6**·2PF$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The electrostatic potential surfaces were generated with MOE2006, using the MMFF94x force field. MOE2006 is a product of the Chemical Computing Group, Montreal, Canada.