Palladium(II)-Directed Self-Assembly of Dynamic Donor–Acceptor [2]Catenanes
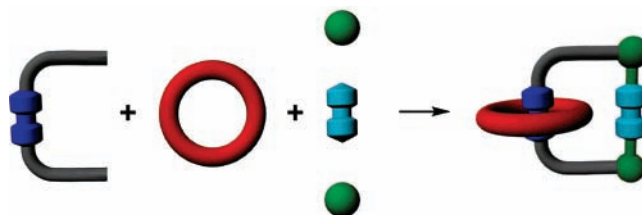
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ABSTRACT

Highly efficient syntheses of donor–acceptor [2]catenanes were developed using a combination of templation and reversible metal–ligand coordination. The desired [2]catenanes were obtained within minutes through a five-component assembly, involving a donor-containing crown ether, an acceptor-containing ligand, two Pd(II) metal centers, and a dipyridyl ligand. The [2]catenane formation was characterized by ^{1}H NMR and UV–vis spectroscopies and cold-spray ionization mass spectrometry. In particular, great translational selectivity was observed when a crown ether with two different donor units was employed.

[2]Catenanes[1] have attracted great attention owing to the nontrivial interlocking topology[2] and nanoscale motions[3] associated with their movable macrocyclic components. The advancement on templated synthesis[4] has led to multistable catenanes that function as reconfigurable molecular switches[5] and artificial molecular motors.[6] Indeed, bistable donor–

acceptor [2]catenanes[7] have become one of the representative species in the molecular based electronic devices.[8] A majority of donor–acceptor [2]catenanes was assembled through a *kinetically* controlled process to contain two interlocked macrocyclic components, one being a π-electron-donating crown ether and the other being a tetracationic cyclophane. Meanwhile, assembly of donor–acceptor [2]catenanes through *thermodynamic* processes was exercised to a lesser extent. An elegant example was reported[9] recently where the donor–

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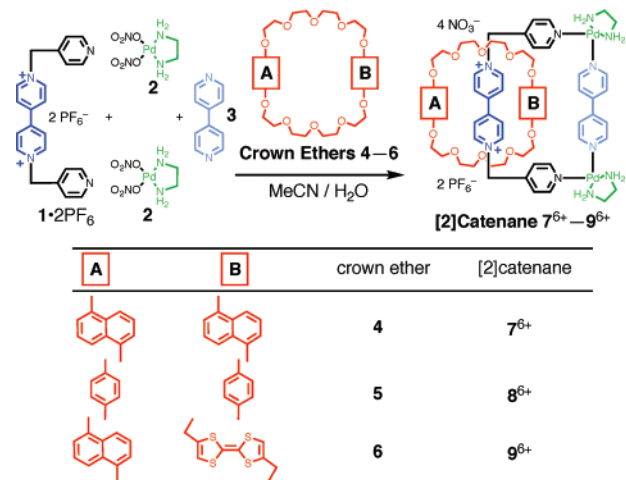
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of two [Pd(en)(II)]$^{2+}$ (en = ethylenediamine) 2^{2+} and one neutral bipyridine **3** would close the macrocycle to give a rectangular cavity that is optimal for alternative arrangement of the π-systems.
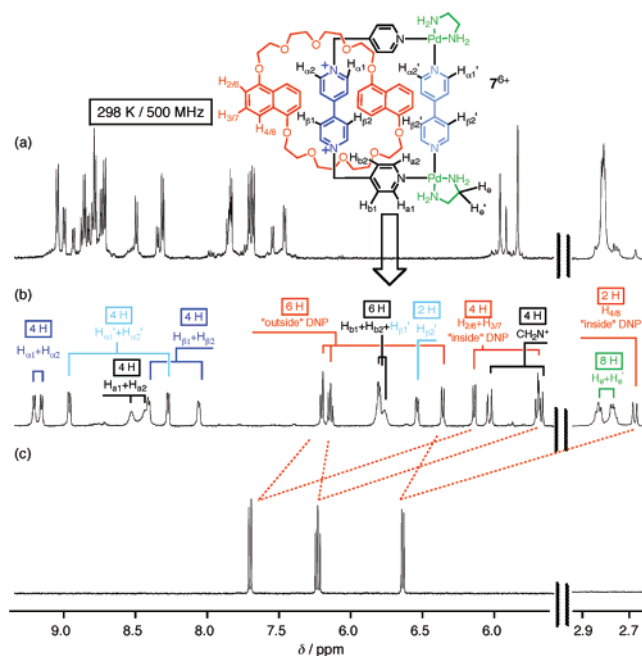

Figure 1. Partial ^{1}H NMR (500 MHz, 298 K) spectra of (a) a mixture of **1·2PF$_6$**, **2**, and **3** (1:2:1) in CD$_3$CN/D$_2$O (9:1), (b) the [2]catenane **7·6PF$_6$** in CD$_3$CN, and (c) the DNP-containing crown ether **4** in CD$_3$CN.

acceptor [2]catenanes were obtained from two isolated ring components through iodide-catalyzed dynamic covalent chemistry (DCC).[10] Besides the DCC approach, metal–ligand coordination also proves[11] to be an efficient synthetic means for thermodynamically controlled self-assembly of catenanes.[12] Examples are rare, however, where metal–ligand coordination operates cooperatively with donor–acceptor templation to give donor–acceptor [2]catenanes.[13,14] Here we report (Scheme 1) the highly efficient syntheses of donor–acceptor [2]catenanes through a reversible self-assembly approach by utilizing the versatile Pd(II)–pyridine coordination.[15] Ideally, donor–acceptor interactions between the crown ether and the bipyridinium 1^{2+} would lead to the formation of an inclusion complex, while the involvement

A mixture of **1·2PF$_6$**, Pd(en)(NO$_3$)$_2$ (**2**), **3**, and dioxynaphthalene (DNP) containing crown ether **4** in the ratio of 1:2:1:1 was dissolved in CD$_3$CN/D$_2$O (9:1) after sonication. ^{1}H NMR spectroscopy of the resulting purple solution revealed that (Figure 1b) the [2]catenane **7^{6+}** was formed quantitatively as the sole product, which could be isolated in 90% yield after exchanging the anions to PF$_6^-$. The pyridyl protons of the coordination macrocyclic component resonated as 12 well-resolved peaks in the aromatic region. The breakdown of symmetry resulted from the local C_2 symmetry imposed by the nearby DNP ring systems. In contrast to the free crown ether **4** (Figure 1c), the two DNP ring systems in **7^{6+}** were now resonating at higher field as two sets of doublet–triplet–doublets, indicating a slow site exchange for the "inside" and "outside" aromatic rings on the ^{1}H NMR time scale. Characteristically, the H$_{4/8}$ of the inside DNP ring system appeared as a doublet at δ = 2.67 ppm as a result of a shielding effect from the nearby pyridine ring. For comparison, the assembly was also tested in the absence of the crown ether **4** under otherwise identical conditions. The ^{1}H NMR spectrum (Figure 1a) indicated only a complex mixture of oligomeric species. In addition, it appeared that neither CD$_3$CN nor D$_2$O was a suitable solvent by itself; rather a combination of both worked effectively. The efficient catenation appeared to be a result of an interplay of donor–

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Scheme 2. Chemical Structures and Labeling of [2]Catenanes 8^{6+} and 9^{6+}
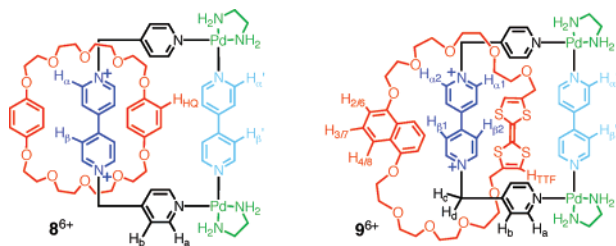
acceptor interactions and the reversible Pd(II)−pyridine coordination, as well as proper solvation.

When the hydroquinone (HQ)-containing crown ether **5** was used for the [2]catenane formation, 3 equiv of **5** were required to reequilibrate the oligomeric Pd(II)−pyridine complexes toward the assembly of [2]catenane 8^{6+} (Scheme 2). The ^{1}H NMR spectra (Figure 2b) of an equilibrated mixture of **1·2PF$_6$**, **2**, **3**, and **5** in the ratio of 1:2:1:3 revealed the presence of [2]catenane 8^{6+} as the only product. Pure [2]catenane 8^{6+} could be isolated as a PF$_6^-$ salt in 90% after anion exchange and removal of excess **5** by rinsing with CH$_2$-Cl$_2$. Partial dissociation of **8·6PF$_6$** was observed when redissolved in CD$_3$CN (2.4 mM). The ^{1}H NMR spectrum (Figure 2c) indicated not only the presence of **8·6PF$_6$** as the
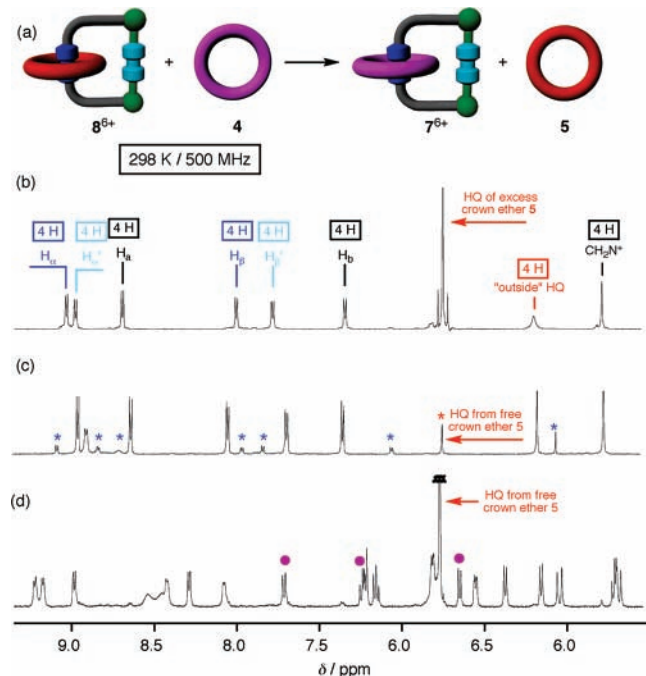
Figure 2. (a) Illustration of the ring-exchange process. ^{1}H NMR spectrum of 8^{6+} (b) before anion exchange in CD$_3$CN/D$_2$O (9:1), together with excess **5**, (c) after anion exchange (CD$_3$CN, 2.4 mM), and (d) after addition of crown ether **4** (1.4 equiv). The blue asterisks in (c) indicate the resonances from the free coordination macrocycle, and the purple dots in (d) indicate the DNP protons from excess crown ether **4**.

major specie but also an equal amount of free crown ether **5** and the free coordination metallocyclophane. An association constant was calculated to be 1.8×10^4 M^{-1} using a single-point method.[16] In contrast, no dissociation was observed for the DNP-based [2]catenane 9^{6+} at 1.0 mM, attesting that the DNP ring system is a better donor than the HQ ring system in holding the π-accepting coordination macrocycle around itself. Such differences in the donor−acceptor interactions prompted us to test a ring-exchange experiment reminiscent of a magician's magic ring trick (Figure 2a). When DNP-containing crown ether **4** (1.4 equiv) was added to the above solution of 8^{6+}, the color of the solution changed immediately from red to purple. The resulting ^{1}H NMR spectrum revealed (Figure 2d) the disappearance of 8^{6+}, together with the emergence of 7^{6+} and the released crown ether **5**. The ring-exchange experiment clearly demonstrated the dynamic yet selective nature of the five-component self-assembly process.
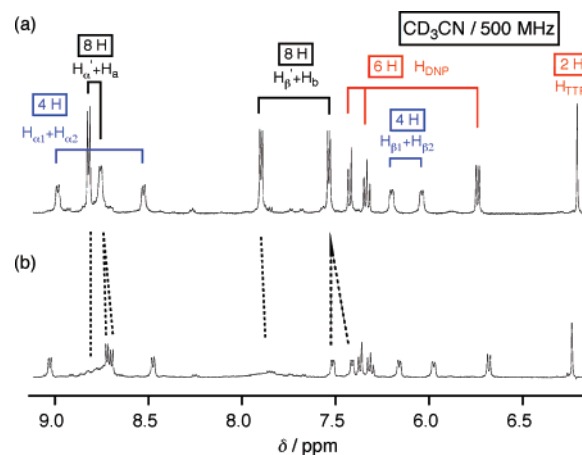
Figure 3. Partial ^{1}H NMR spectrum of 9^{6+} at (a) 298 K and (b) 228 K.

Furthermore, crown ether **6**[7b] bearing both DNP and tetrathiafulvalene (TTF) π-donating ring systems was tested in the self-assembly process. A green product **9·6PF$_6$** (Scheme 2) could be isolated in 92% yield after counterion exchange. Noticeably, translational selectivity[7b,17] was well maintained where the TTF unit sits inside the cavity of the coordination macrocycle. ^{1}H NMR spectroscopy (Figure 3a) at 298 K indicated one single specie in the solution. The absence of DNP protons between 2−3 ppm clearly indicated the "alongside" location of the DNP ring system with respect to the coordination macrocycle. When temperature was lowered to 228 K, both TTF and DNP resonances remained sharp (Figure 3b), while splitting and broadening of the resonances of the pyridyl protons in **1·2PF$_6$** and the 4,4′-dipyridyl protons were observed as a result of restrained

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rotation at low temperature. No resonances corresponding to two translational isomers were observed, suggesting the absence of site exchange, and indeed the translational selectivity was maintained throughout. It is worth noting that out of the usual *cis/trans* TTF positional isomers, only one was observed, which was probably the *trans* one.[7b−c,18]
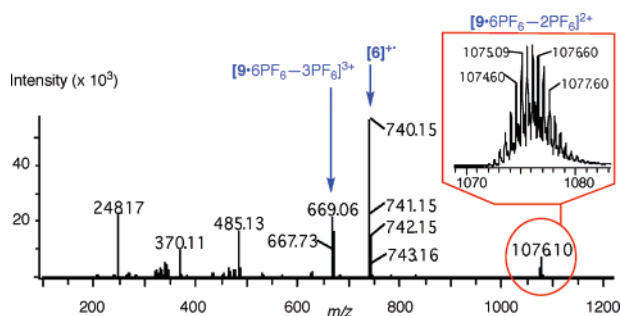

Figure 4. CSI-TOFMS spectrum of **9**·6PF$_6$. (Inset) Isotopic distribution of the [**9**·6PF$_6$−2PF$_6$]$^{2+}$ ion.

The formation of the [2]catenanes was further verified[19] by elemental analysis, cold-spray ionization mass spectrometry (CSI-MS),[20] and UV−vis spectra. The significant results agreed well with their empirical structures. For example, the CSI-TOFMS spectrum of **9**·6PF$_6$ indicated (Figure 4) ions at m/z 1076 and 669, corresponding to the doubly and triply charged [M − 2PF$_6$]$^{2+}$ and [M − 3PF$_6$]$^{3+}$ ions, respectively.[19] The inset in Figure 4 revealed the isotopic distribution for the fragment [M − 2PF$_6$]$^{2+}$, which was consistent with the theoretical distribution. The UV−vis spectra of the [2]-catenanes **7**−**9**·6PF$_6$ indicated (Figure 5) charge-transfer absorption bands centered at 535, 463, and 821 nm, corresponding respectively to the purple, red, and green color of the individual donor−acceptor [2]catenanes.

In summary, highly efficient synthesis of [2]catenanes was developed using a combination of donor−acceptor templation

(18) However, the sample stored in the dry solid form for more than three months was found to partially isomerize to give a mixture of *cis* and *trans* isomers. See Supporting Information for a comparison of the ^{1}H NMR spectra before and after storage. For a similar observation of TTF *cis/trans* isomerization in the solid state, see: Liu, Y.; Flood, A. H.; Moskowitz, R. M.; Stoddart, J. F. *Chem. Eur. J.* **2005**, *11*, 369−385.

(19) See Supporting Information for details of characterization data.

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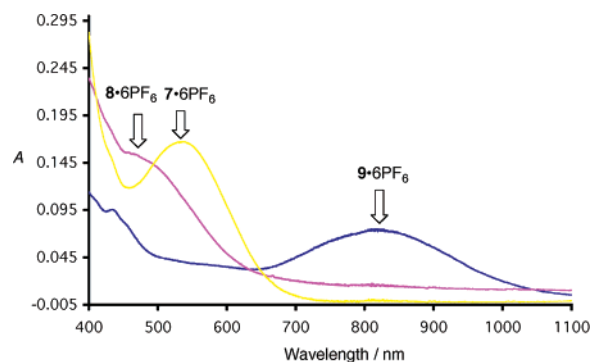
Figure 5. UV−vis spectra of **7**·6PF$_6$ (2.0 × 10^{-4} M), **8**·6PF$_6$ (2.8 × 10^{-4} M), and **9**·6PF$_6$ (4.4 × 10^{-5} M) in MeCN, showing the charge-transfer absorption maximum at $\lambda = 535$ nm ($\epsilon = 840$ M^{-1} dm^{-1}), 463 nm ($\epsilon = 560$ M^{-1} dm^{-1}), and 821 nm ($\epsilon = 1700$ M^{-1} dm^{-1}), respectively.

and metal−ligand coordination. The [2]catenanes were easily obtained within minutes through a five-component assembly process from three crown ethers. The [2]catenane formation was fully characterized by ^{1}H NMR and UV−vis spectroscopies and cold-spray ionization mass spectrometry. The dynamic nature of the [2]catenanes was further demonstrated in a ring-exchange experiment. In particular, translational selectivity was maintained when a crown ether with two different donor units was employed. The current approach is remarkable in the perspective of bistable molecular devices as it could potentially provide a fast, mild, convenient, and high-yielding means to install bistability in molecular species. Such an assembly process could be utilized in high-throughput screenings of matching donor−acceptor pairs for the design of sophisticated multistable molecular switches.

Supporting Information Available: Experimental details for the preparation of **1**·2PF$_6$, **7**−**9**·6PF$_6$ and spectroscopic data thereof. This material is available free of charge via the Internet at http://pubs.acs.org.

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