

π -Stacking Enhanced Dynamic and Redox-Switchable Self-Assembly of Donor–Acceptor Metallo-[2]Catenanes from Diimide Derivatives and Crown Ethers

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Research interest in nanoscale molecular machines and devices has grown dramatically in the past a few decades.^[1] Interlocked molecules,^[2] for example, switchable catenanes^[3] and rotaxanes,^[4] have become the representative class of active components in molecular-based devices, such as molecular memories,^[5] nanovalves,^[6] and molecular muscles.^[7] Accompanying the quest for molecular machines with more sophisticated functions is the need for the convenient synthesis of such materials from readily available precursors. With the aid of preprogrammed interactions, such as hydrogen bonding,^[8] π stacking,^[9] anion templating,^[10] and metal–ligand coordination,^[11] many assembly strategies have been developed for the synthesis of functional interlocked molecules. In particular, donor–acceptor interactions have become a favorable driving force in the synthesis of electro-

and photoactive molecular machines because of the rich electrochemical and photophysical properties of π -electron donors and acceptors. Following the first template-directed synthesis^[12] of donor–acceptor [2]catenanes through a kinetic approach,^[9a] thermodynamic approaches that use dynamic covalent chemistry,^[13] such as olefin metathesis,^[14] imine bond formation,^[15] and iodide-catalyzed $N^+–C$ cleavage,^[16] have also been employed for the synthesis of such [2]catenanes. Recently, metal–ligand coordination has been utilized^[17] together with donor–acceptor interactions to give metallocatenanes. Scheme 1 illustrates an assembly strategy in which donor–acceptor [2]catenanes were obtained in high yields from an electron-rich crown ether (the donor), an electron-deficient ditopic ligand (the acceptor), two Pd^{II} centers (the connectors), and a linking ditopic ligand (the filler). Donor–acceptor interactions between a crown ether (**4–6**) and bipyridinium **1c** (BPy^{2+}) led to the formation of an inclusion complex, and the involvement of two $[Pd^{II}(en)]^{2+}$ (**2**; en = ethylenediamine) and one neutral bipyridine **3a** closed the macrocycle to give a rectangular cavity that was optimal for alternative arrangements of the π systems. Although it was obvious that both donor–acceptor interactions and metal–ligand coordination were responsible for the high self-assembly efficiency, the way in which the two types of interaction balance with each other to ensure that efficiency still remains to be investigated.

This issue was tested by comparing the self-assembly results while varying donor–acceptor pairs with different interaction strengths. Among the limited examples, BPy^{2+} -based π acceptors have been the major electron-deficient unit used to template the formation of donor–acceptor [2]catenanes. Neutral naphthalene diimide (NDI) and Pyromellitic diimide (PmI) units, on the other hand, are readily available electron-deficient π acceptors that have been incorporated in a variety of supramolecular systems.^[18] Similarly to BPy^{2+} derivatives, they were able to form inclusion complexes with π -electron-rich crown ethers. Their π -accepting ability, how-

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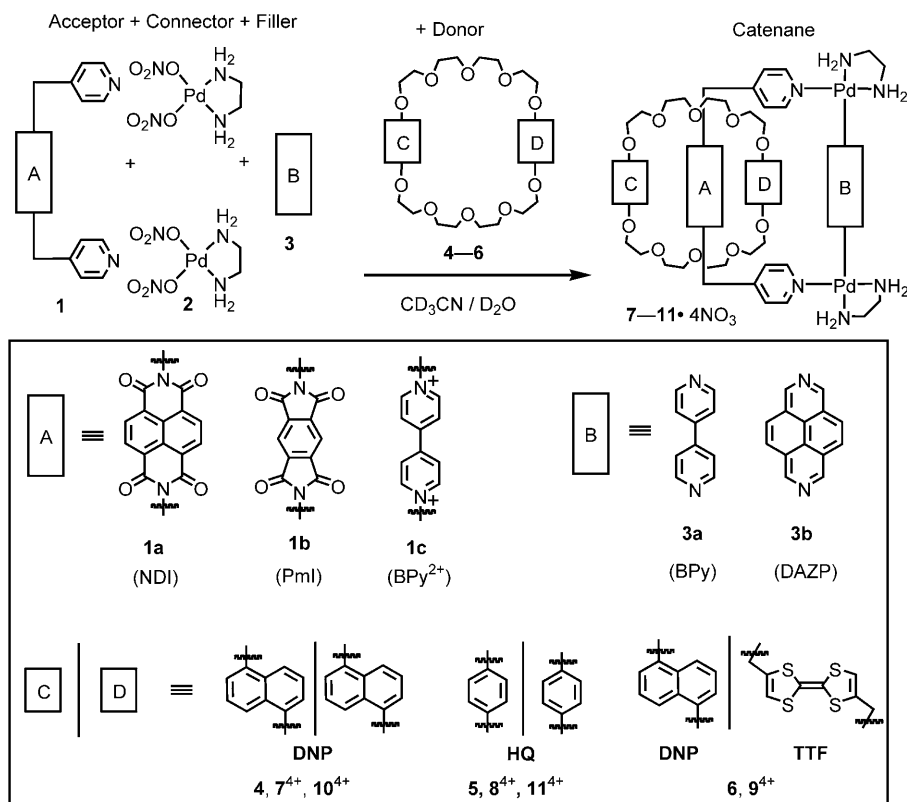
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Scheme 1. Self-assembly of donor-acceptor [2]catenanes from various building blocks. Abbreviations: NDI = naphthalene diimide, PmI = pyromellitic diimide, BPy^{2+} = bipyridinium, BPy = 4,4'-bipyridine, DAZP = 2,7-diazapyrene, DNP = 1,5-dioxynaphthalene, HQ = hydroquinone, TTF = tetrathiafulvalene.

ever, was much weaker. For example, the typical binding constants of PmI and NDI derivatives with [38]crown-10 (DNP38C10) were only around $20^{[18b]}$ and 100 M^{-1} ,^[18j] respectively, whereas the binding constant between dibenzyl 4,4'-bipyridinium and DNP38C10 was around 20000 M^{-1} .^[18j] The difference in the strength of donor-acceptor interactions from these neutral π units entails a question: will such interactions be strong enough to overcome the entropy costs in the ring closure process to give the desired interlocked [2]catenanes? Herein, we demonstrate that along with the donor-acceptor and metal-ligand coordinations, the π -stacking interaction from the neutral filler unit also contributes significantly to the self-assembly efficiency. With the proper choice of filler unit to provide extra stabilizing π -stacking interactions, NDI- and PmI-based derivatives can effectively hold the crown ethers to give donor-acceptor [2]catenanes, despite their weak electron-accepting ability. Moreover, by using a TTF donor^[3c,4g,k,m] in the crown as a redox switch, the metallo-catenane was reversibly disassembled and reassembled by using electrochemistry.

We have previously shown that if BPy^{2+} -based ligand **1c** was used as the acceptor, 4,4'-dipyridyl (**3a**) could effectively bridge the two Pd^{II} metal centers to give the [2]catenane.

Under similar reaction conditions, **3a** was tested as the filler unit for NDI-based ligand **1a**. If **1a**, DNP-containing crown ether **4**, **3a**, and **2** were mixed in a 1:1:1:2 ratio and dispersed in a mixture of $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (0.8:0.2 mL), an ill-defined spectrum with many unassignable peaks was obtained (Figure 1b), which suggests that the assembly is not a well-controlled process. The difference in efficiency of [2]catenane formation on changing from BPy^{2+} to NDI was ascribed to a weaker donor-acceptor interaction between the NDI and DNP ring systems that was not strong enough to hold the crown ether around the acceptor unit. To compensate for the weak strength of the donor-acceptor interaction, extra stabilization must be sought and thus, 2,7-diazapyrene (DAZP) was chosen as the filler unit for multiple reasons, DAZP is 1) complementary to the NDI unit in length ($\sim 6.7\text{ \AA}$),^[19] 2) more rigid than 4,4'-dipyridyl, and 3) more electron deficient because the π electrons are more delocalized. Such properties would benefit the stacking interaction with the donor units in the crown ether.

If a mixture of NDI-based ligand **1a**, **4**, **2**, and DAZP (**3b**) (1:1:2:1) was dissolved in $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (3:1), a well-resolved ^1H NMR spectrum was obtained (Figure 1c), which clearly indicated the formation of [2]catenane **7**⁴⁺ (Table 1).

The internal and external DNP ring protons underwent a slow site exchange process and could be identified as two sets of doublet-triplet-doublet. The $\text{H}_{4/8}$ of the internal DNP ring system appeared as a doublet at around $\delta = 3.0$ ppm, which was characteristic for the DNP ring system being positioned in a shielding cyclophane. As a result of the C_2 symmetry imposed by the surrounding DNP ring systems, the NDI protons underwent an upfield shift and became nonequivalent, resulting in two doublets at $\delta = 7.5$ and 7.1 ppm. The pyridyl and the diazapyrene units in the metallocyclophane were all similarly desymmetrized.

If HQ-containing crown ether **5** was used, three equivalents of it were needed for the complete formation of [2]catenane **8**⁴⁺. The ^1H NMR spectrum indicated (Figure 1d) the formation of a symmetrical species in the solution. The internal and external HQ units could be identified as two singlets at around $\delta = 2.7$ and 5.2 ppm, respectively. Although

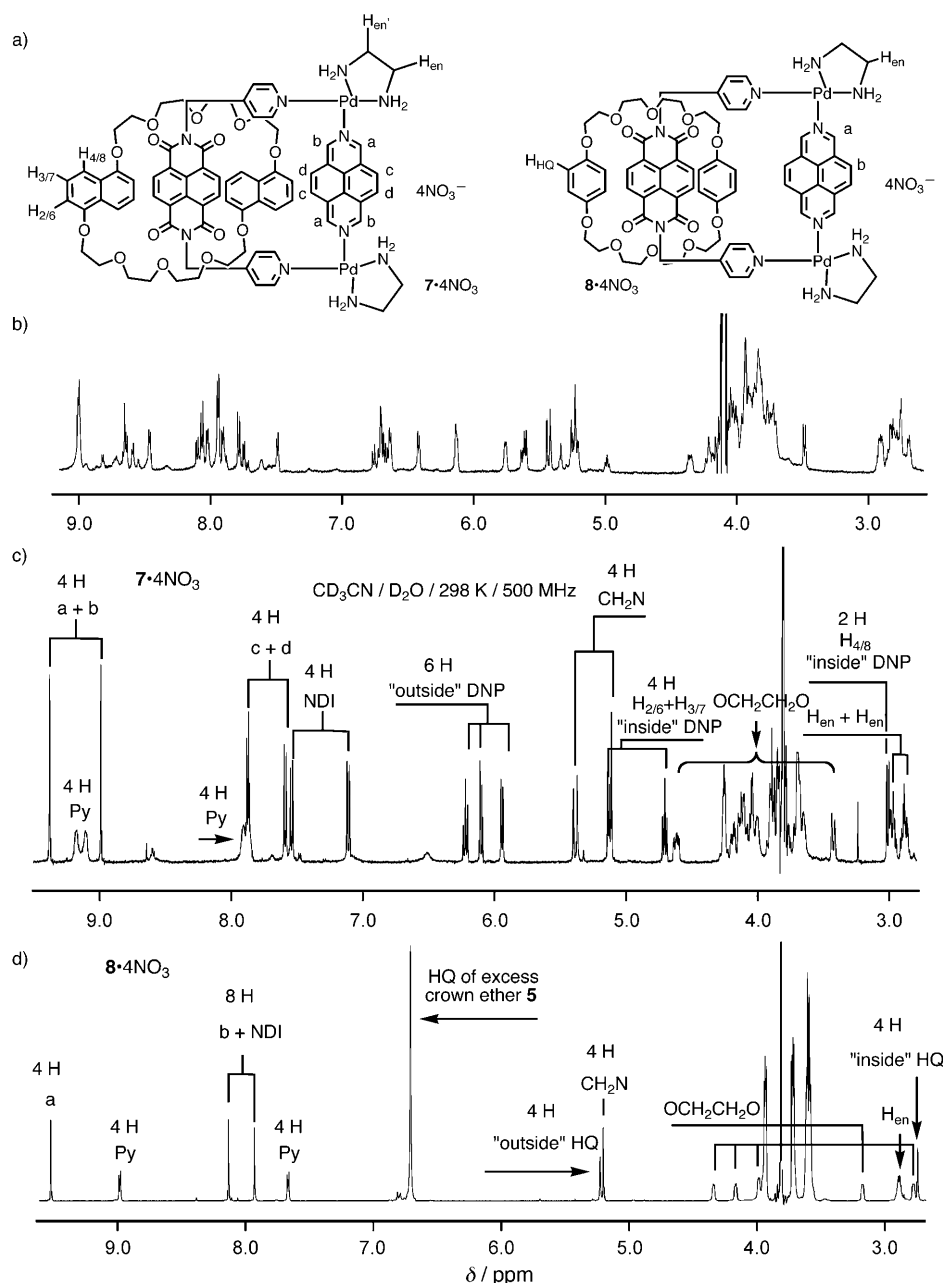


Figure 1. a) Chemical formulae of [2]catenanes 7^{4+} and 8^{4+} ; b) the ill-defined ^1H NMR spectrum of a mixture of $1a$, 2 , $3a$, and 4 in $\text{CD}_3\text{CN}/\text{D}_2\text{O}$; c) and d) the ^1H NMR spectra of [2]catenanes 7^{4+} and 8^{4+} , respectively.

Table 1. List of self-assembled donor–acceptor [2]catenanes based on DAZP.

Acceptor	Filler	Crown Ether	[2]Catenane
1a	3b	4	7⁴⁺
1a	3b	5	8⁴⁺
1a	3b	6	9⁴⁺
1b	3b	4	10⁴⁺
1b	3b	5	11⁴⁺

the binding between NDI and **5** was very weak, the successful formation of the [2]catenane clearly indicated that further stabilization could be provided from the alternative

stacking interaction between DAZP and the HQ ring system to give the entropically unfavorable [2]catenane.

For the purpose of generating bistable [2]catenanes, a crown ether that contained two different π donors, that is, TTF and DNP ring systems, was used under similar [2]catenane-forming conditions. A dark-purple-tinted solution was obtained upon dissolving all the components. The ^1H NMR spectroscopy indicated the coexistence of two isomers of 9^{4+} in a ratio of 1.2:1 (Figure 2), which could be ascribed to the presence of *trans* and *cis* TTF positional isomers. The usual translational selectivity was maintained,^[4k] that is, the TTF unit was located inside the cavity of the metallocyclophane whereas the DNP ring system was outside. Specifically, two TTF singlets that corresponded to both *cis* and *trans* isomers were resonating at around $\delta = 5.5$ ppm, whereas two sets of DNP protons in the usual doublet–triplet–doublet split pattern were observed between $\delta = 6.3$ and 7.1 ppm. The absence of a diagnostic doublet^[17f] at high field between $\delta = 2$ –3 ppm for internal $\text{H}_{4/8}$ DNP protons affirmed the location of the DNP ring system outside the metallocyclophane. It is interesting to note that unlike the BPy^{2+} -based systems in which *cis/trans* isomerization of the TTF unit is greatly favored towards the *trans* isomer in the

[2]catenane,^[17f,20] the NDI unit imposed no preference on the TTF *cis/trans* isomerization.

The cold-spray ionization mass spectroscopy (CSI-MS) provided conclusive evidence for the formation of metallocatenanes.^[21] The samples, in deuterated solvents, that had been used for NMR spectroscopy were also used for CSI-MS analysis after 5-fold dilution with MeCN. The CSI mass spectrum of 9^{4+} revealed (see the Supporting Information) ions at m/z 929.1, 598.7, and 577.7, which correspond to $[M-2\text{NO}_3]^{2+}$, $[M-3\text{NO}_3]^{3+}$, and $[M-3\text{NO}_3-\text{HNO}_3]^{3+}$, respectively. The isotopic distribution for the fragment $[M-$

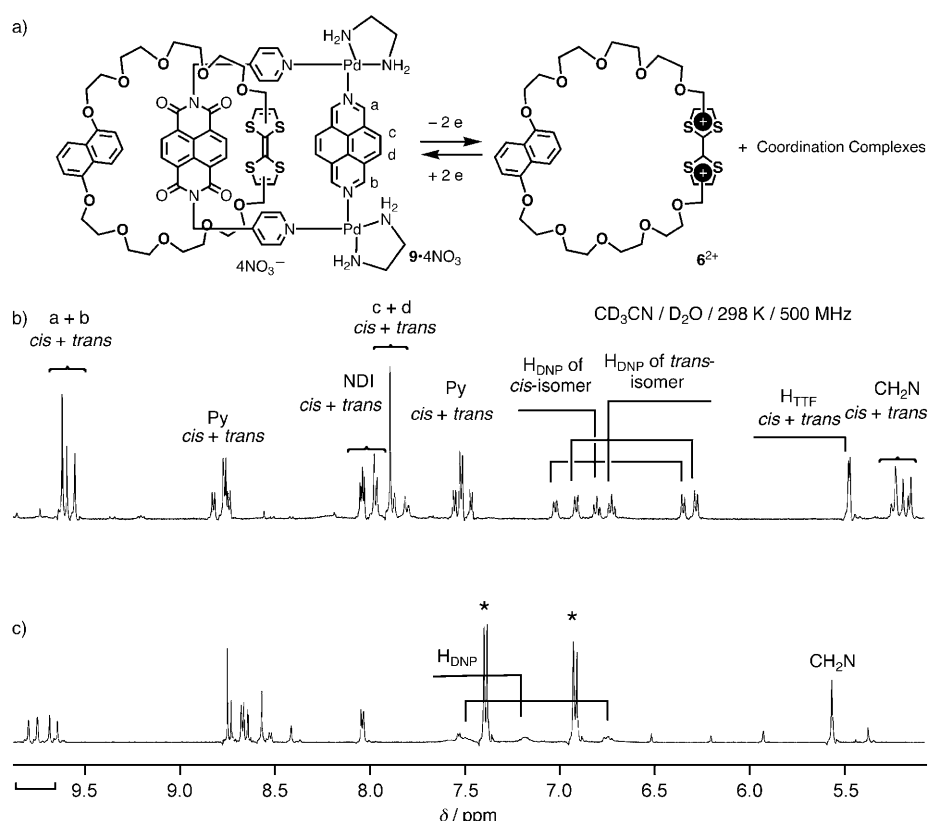


Figure 2. a) The redox-induced disassembly–assembly process of [2]catenane 9^{4+} . Partial ^1H NMR spectrum of 9^{4+} before oxidation (b) and after oxidation (c). The asterisked peaks in c) indicate the 4-bromophenyl protons of the oxidant.

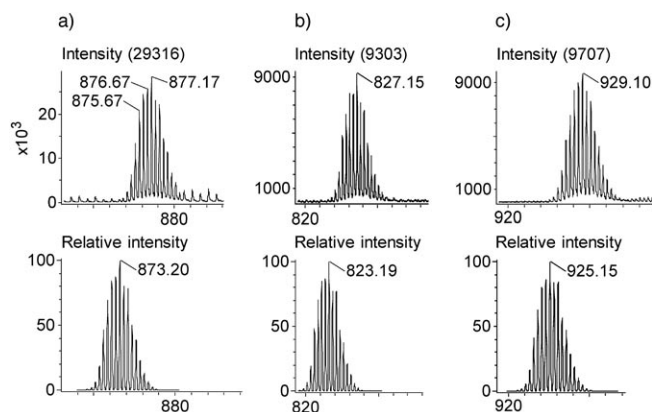


Figure 3. The isotopic distribution of $[M-2\text{NO}_3]^{2+}$ signals and the theoretical isotopic distribution of a) $7\cdot 4\text{NO}_3$, b) $8\cdot 4\text{NO}_3$, and c) $9\cdot 4\text{NO}_3$.

$2\text{NO}_3]^{2+}$ was consistent with the theoretical distribution (Figure 3c). It should be noted that the eight active hydrogen atoms of the ethylenediamine ligands were exchanged for deuterium atoms with D_2O , which led to an 8 Da increase in the observed m/z of the molecular ion. Similarly, for $8\cdot 4\text{NO}_3$, molecular ions that correspond to the consecutive loss of several nitrate anions were identified at m/z 827.2 and 530.9. For $7\cdot 4\text{NO}_3$, the $[M-2\text{NO}_3]^{2+}$ and $[M-$

$3\text{NO}_3]^{3+}$ fragments were revealed by molecular ions at m/z 877.2 and 564.1, respectively. In all cases, there were extra fragments that arose from the attachment of CD_3CN molecules to the molecular ions under the cold-spray conditions (see the Supporting Information).

The UV/Vis spectra of [2]catenanes $7\cdot 4\text{NO}_3$ and $8\cdot 4\text{NO}_3$ indicated charge-transfer (C-T) absorption bands centered at $\lambda = 535$ and 463 nm (Figure 4), which correspond to the purple and red colors of the individual donor–acceptor [2]catenanes, respectively. [2]Catenane $9\cdot 4\text{NO}_3$ displayed two bands at $\lambda = 821$ and 543 nm that were assigned to C-T transitions involving the TTF unit as a donor after comparison with the spectra of the other two [2]catenanes. The large shift in the NIR band to low energy was consistent with the stronger π -donor properties of TTF. The visible C-T band only appeared with stronger intensity in the presence of TTF. This excitation could involve the DAZP unit, however, we assigned it to the involvement of a higher molecular orbital on the NDI unit.

The bistability of $9\cdot 4\text{NO}_3$ was initiated by chemical redox agents and characterized by using ^1H NMR spectroscopy. After the addition of two equivalents of oxidant, tris(4-bromophenyl)iminium hexafluoroantimonate, substantial spectroscopic changes were observed. The TTF signals shift-

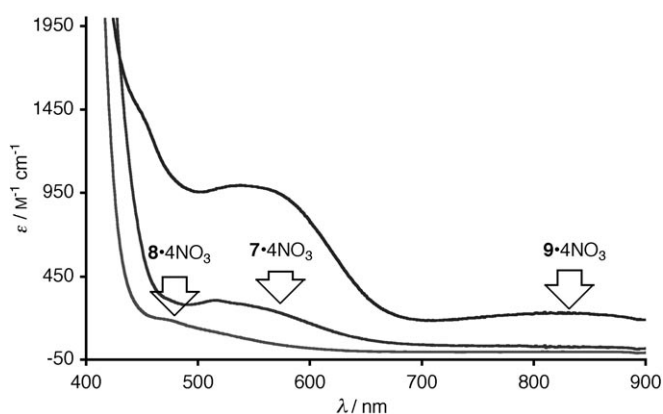


Figure 4. UV/Vis spectra showing the CT absorption bands of [2]catenanes $7\cdot 4\text{NO}_3$ ($\lambda = 535$ nm), $8\cdot 4\text{NO}_3$ ($\lambda = 463$ nm), and $9\cdot 4\text{NO}_3$ ($\lambda = 821$ nm).

ed from around $\delta = 5.5$ to 8.8 ppm (Figure 2c) on the formation of TTF^{2+} .^[4k] The absence of the characteristic peaks between $\delta = 2$ and 3 ppm for the DNP protons suggested that the DNP ring system was not encircled within any cyclophane. Instead, the DNP protons now resonated as broad peaks in the usual aromatic region. These observations were consistent (Figure 2a) with the oxidation-induced disassembly of [2]catenane **9**- 4NO_3 .

Attempts to monitor its reassembly by using ^1H NMR spectroscopy and reducing the TTF^{2+} unit back to neutral with Zn powder was unsuccessful because of precipitate formation. Instead, the redox-initiated cycle of disassembly and reassembly was investigated by using electrochemical methods. The free TTF-containing crown (1 mM) was examined in aqueous MeCN (3:1 MeCN/ H_2O , 0.1 M TBAPF₆; TBA = tetrabutylammonium), which was required for the solubility of the catenane. The cyclic voltammetry study showed two well-separated oxidation processes (Figure 5a). The first oxidation, $\text{TTF} \rightarrow \text{TTF}^+$, was observed at +150 mV (Ag/AgCl), whereas the second oxidation, $\text{TTF}^+ \rightarrow \text{TTF}^{2+}$, occurred at +540 mV. Compared with pure MeCN, these redox processes were shifted by 350 mV for the first oxidation and by 280 mV for second oxidation, however, they retain the typical redox pattern.^[3c,4k,m]

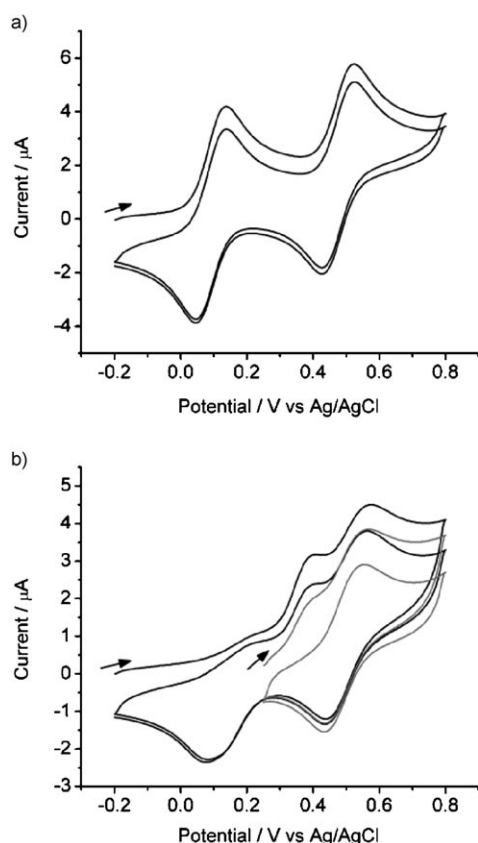


Figure 5. Cyclic voltammetry experiments of a) crown **6** and b) [2]catenane **9**- 4NO_3 recorded with full (—) and smaller (---) scan windows in MeCN/ H_2O (3:1) at a glassy carbon electrode (~ 1 mm, 0.1 M TBAPF₆, Ag/AgCl, 200 mV s^{-1}).

The cyclic voltammograms (CVs) of [2]catenane **9**- 4NO_3 (Figure 5b), recorded by cycling through different potential windows, showed behavior consistent with reversible and oxidation-driven disassembly and reassembly. In the forward scan of the CV, three oxidation peaks were observed. These peaks were each assigned to oxidations of the TTF unit in different environments by comparison to a related catenane,^[3c] in the following order: noninteracting $\text{TTF}^{0/+}$ (+100 mV), encircled $\text{TTF}^{0/+}$ (+400 mV), and unencircled $\text{TTF}^{+/2+}$ (+600 mV). The noninteracting $\text{TTF}^{0/+}$ peak was attributed to a small population of either the circumrotated isomer^[3c] of the catenane or the free crown. The peak assigned to the first oxidation of encircled TTF is anodically shifted 300 mV, which is consistent with previous studies.^[3c] The redox couple associated with $\text{TTF}^{+/2+}$ occurs in the same place as for the free crown. The anodic peak at +600 mV in the forward cycle is slightly broadened. These behaviors indicate that the disassembled state was preferred for the TTF^{2+} dication. Continuing through the reverse scan, the peak observed at +80 mV is assigned to the $\text{TTF}^{0/+}$ re-reduction. The shoulder on this peak was attributed to dimers of TTF^+ on the basis of spectroelectrochemistry (vide infra). The second-cycle CV reproduced the first one and is therefore consistent with the fact that the catenane can be re-assembled once neutrality is restored to the TTF unit.

We next confirmed that the monocationic TTF^+ state also favors disassembly. Consequently, we measured a CV (Figure 5b, —) that started at +250 mV, which is the potential after oxidation of the noninteracting $\text{TTF}^{0/+}$. The first cycle is ostensibly the same as the original CV. However, in the forward scan of the second cycle, there was no evidence of the +200 mV peak attributed to the encircled TTF^+ unit. These data indicated that the formation of the monocation, TTF^+ , did not lead to reassembly on the timescale of the CV.

The UV/Vis/NIR spectroelectrochemistry was investigated to confirm these interpretations (Figure 6). The associat-

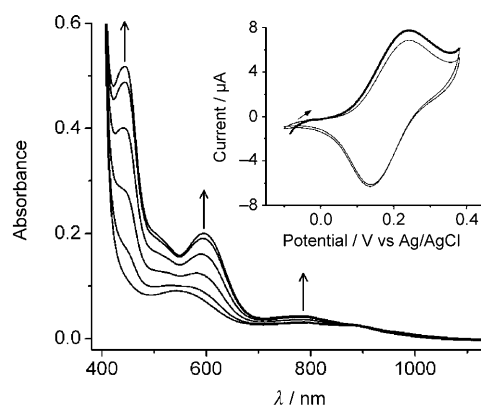


Figure 6. UV/Vis/NIR spectroelectrochemistry data of **9**- 4NO_3 . Arrows show the changes in absorption through the first oxidation (spectra recorded every 60 $\text{mV} = 4$ min). Inset: The slow-scan-rate CV (0.25 mV s^{-1}) recorded in MeCN/ H_2O (3:1) at a transparent Pt mesh electrode (~ 2.5 mm, 0.1 M TBAPF₆).

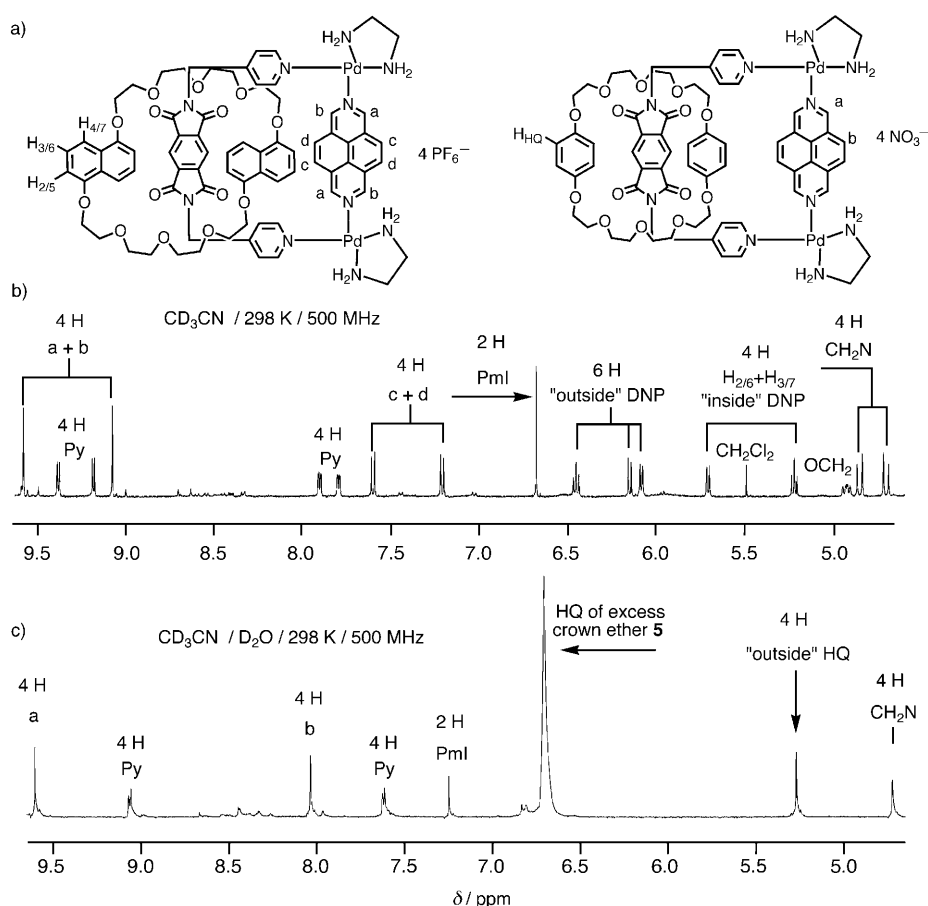


Figure 7. a) Structural formulae of [2]catenanes **10**⁴⁺ and **11**⁴⁺; b) and c) are the ¹H NMR spectra of the PF₆⁻ salt of **10**⁴⁺ and the NO₃⁻ salt of **11**⁴⁺, respectively.

ed slow-scan-rate CV (0.25 mVs⁻¹) was reversible through the first oxidation with a broad peak at +400 mV. A second peak at +640 mV (see the Supporting Information) is consistent with disassembly after the formation of TTF⁺. During the first oxidation process, the λ = 850 nm C-T band bleached, which is concomitant with growth in the known absorption region of the TTF⁺ chromophore (λ = 450 and 600 nm).^[7b] A low-intensity peak at λ = 777 nm is assigned to a small degree of π dimer formation by TTF⁺ in the aqueous solution.^[22] Formation of TTF²⁺ was confirmed by cyclic voltammetry and led to spectroscopic changes, however, the transformation was not reversible on the timescale of the experiment.

If the chemical and electrochemical redox switching experiments are taken together, it can be seen that disassembly is driven by mono- or dication formation and reassembly by the formation of neutral TTF. In both situations, the reversibility of the process depended upon the conditions, with time appearing to be a more important factor.

As an ultimate test, Pml-based ligand **1b** was subjected to the same assembly conditions. Formation of [2]catenane **10**·4NO₃ from DNP38C10 was immediately confirmed by ¹H NMR spectroscopy. The nitrate salt was further exchanged to its PF₆⁻ form and the ¹H NMR spectra were re-

taken in CD₃CN (Figure 7b). The well-resolved spectrum could be readily assigned to [2]catenane **10**·4PF₆⁻, in which two characteristic, shielded DNP ring systems were identified. Remarkably, [2]catenane **11**·4NO₃⁻ could also be formed effectively (Figure 7c) if three equivalents of HQ-based crown **5** were used, despite the fact that the binding between Pml unit and **5** is extremely weak.

It is worth noting that the solvent plays an important role in determining the assembly efficiency. Neither D₂O nor CD₃CN alone could drive the assembly to completion due to insufficient solvation of all components.^[23] If the D₂O content was increased to 25%, clear solutions were obtained, commensurate with the formation of [2]catenanes. Although water had to be used for the initial assembly, the hydrophobic effect appeared not to be a critical driving force on account of the fact that [2]catenane **10**·4PF₆⁻ remained intact in an all organic environment (CD₃CN).

In conclusion, a modular approach was demonstrated in which readily available diimide-based electron acceptors have effectively templated the formation of [2]catenanes in the presence of Pd^{II} and a π-stacking diazapyrene unit. The choice of the filler group proved to be vital for providing extra stabilization interactions and compensating the relatively weak donor–acceptor interactions. In addition, the redox-driven disassembly–reassembly process of a bistable [2]catenane was characterized by electrochemical methods. The rich electrochemical and photochemical properties associated with these acceptors and donors could allow for the design and synthesis of more functional molecular assemblies.

Experimental Section

General procedure for the assembly of donor–acceptor [2]catenanes: CD₃CN/D₂O (0.9:0.3 mL) was added to a mixture of diimide **1a** or **1b** (5 μmol), [Pd(en)(NO₃)₂] (**2**; 10 μmol), 2,7-diazapyrene (**3b**; 5 μmol), and crown ether **4**, **6** (5 μmol), or **5** (15.0 μmol). The mixture was stirred at 60 °C for 5 min to ensure the dissolution of all components, and filtered through a cotton plug to give the self assembled [2]catenanes **7–11**⁴⁺.

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Keywords: catenanes • coordination • donor–acceptor systems • stacking interactions • supramolecular chemistry

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