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Catenation through a Combination of Radical Templation and Ring-Closing Metathesis

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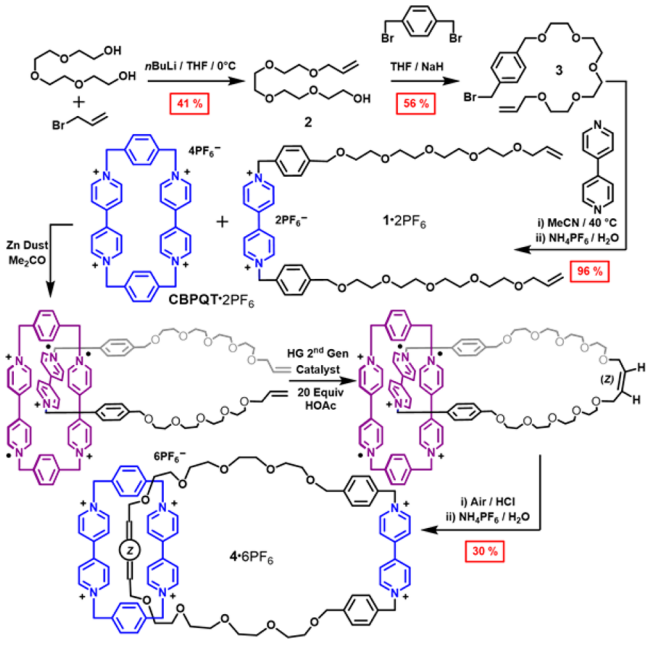
Supporting Information

ABSTRACT: Synthesis of an electrochemically addressable [2]catenane has been achieved following formation by templation of a [2]pseudorotaxane employing radically enhanced molecular recognition between the bisradical dication obtained on reduction of the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), and the radical cation generated on reduction of a viologen disubstituted with *p*-xylylene units, both carrying tetraethylene glycol chains terminated by allyl groups. This inclusion complex was subjected to olefin ring-closing metathesis, which was observed to proceed under reduced conditions, to mechanically interlock the two components. Upon oxidation, Coulombic repulsion between the positively charged and mechanically interlocked components results in the adoption of a co-conformation where the newly formed alkene resides inside the cavity of the tetracationic cyclophane. ^{1}H NMR spectroscopic analysis of this hexacationic [2]catenane shows a dramatic upfield shift of the resonances associated with the olefinic and allylic protons as a result of them residing inside the tetracationic component. Further analysis shows high diastereoselectivity during catenation, as only a single (*Z*)-isomer is formed.

Olefin ring-closing metathesis[1] (RCM) has been employed to construct a diverse array of mechanically interlocked molecules (MIMs), specifically catenanes.[2] This reversible reaction has proven to be effective in the synthesis of relatively small ring compounds—typically five- to eight-membered ones.[3] The additional robustness of Grubbs's ruthenium catalysts has allowed RCM to be applied to much larger ring systems and so feature in catenane synthesis, a situation in which macrocyclization proceeds in the presence of a wide range of templation procedures under both neutral and oxidative conditions. In these synthetic protocols, transition metal−ligand coordination,[4] donor−acceptor interactions,[5] and both neutral[6] and charged[7] hydrogen-bonding, as well as anion recognition,[8] have served as sources of template direction, providing access to catenated compounds.

Recently, we demonstrated[9] that radically enhanced molecular recognition offers a route toward positively charged MIMs in which the individual molecular components, in their ground states, naturally repel one another. Here, intermediate bipyridinium radical cations present in viologens and cyclobis(paraquat-*p*-phenylene)[10] (**CBPQT**$^{4+}$) when they are reduced exhibit radical−radical dimerization and have allowed for the expedient syntheses of otherwise inaccessible MIMs. The stable inclusion complex formed between a reduced viologen radical cation and diradical dicationic state of the cyclophane has allowed for the synthesis of (i) a series of rotaxane derivatives[11] devoid of stabilizing interactions in their oxidized states, (ii) a homo[2]catenane[12] harboring a stable organic radical, and (iii) an artificial molecular pump[13] capable of exhibiting an energy ratchet mechanism where components are shifted away from equilibrium toward higher local concentrations. While these MIMs and their properties are novel, a wider variety of methods for their synthesis would be welcome.

Scheme 1. Synthesis of the Hexacationic [2]Catenane 4·6PF$_6$



We report herein the synthesis and characterization of an electrochemically addressable [2]catenane, $\mathbf{4}^{6+}$ (Scheme 1), where Grubbs's RCM is employed to install the mechanical bond following the radically driven inclusion of $\mathbf{1}^{\bullet+}$ by $\mathbf{CBPQT}^{2(\bullet+)}$. The existence of the mechanical bond in $\mathbf{4}^{6+}$ was confirmed in the solution phase by ^{1}H NMR and UV-vis-NIR spectroscopies as

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well as cyclic voltammetry (CV). Degradation analysis led to the identification of high diastereoselectivity during the carbon−carbon double bond formation in $\mathbf{4}^{6+}$ when compared to a control involving the formation of the non-catenated macrocycle.

The [2]catenane $\mathbf{4}\cdot 6PF_6$ was obtained (Scheme 1) following a sequence of reactions that involved (i) the allylation of tetraethylene glycol to afford its mono-allyl ether **2**, which was then (ii) reacted (NaH/THF) with 1,4-bis(bromomethyl)-benzene to give the benzylic bromide **3** which, (iii) on reaction with 4,4′-bipyridine in MeCN (40 °C), followed by counterion exchange (NH_4PF_6/H_2O), yielded the bis-allyl ether $\mathbf{1}\cdot 2PF_6$. After $\mathbf{1}\cdot 2PF_6$ was dissolved in Me_2CO, it was treated with a large excess of Zn dust under N_2 in a glovebox in the presence of $\mathbf{CBPQT}\cdot 4PF_6$, producing a dark blue solution which indicates the initial formation of cationic bipyridinium radicals, giving way rapidly to a deep purple solution, indicative of the formation of a trisradical complex. Following the addition[14] of 20 equiv of HOAc, the second-generation Hoveyda−Grubbs catalyst was added to promote macrocyclization of $\mathbf{1}^{\bullet+}$ under radical templation conditions with $\mathbf{CBPQT}^{2(\bullet+)}$ to give the [2]catenane. Following treatment of the crude reaction product with an excess of HCl, it was subjected to reverse-phase HPLC with TFA in H_2O and MeCN as eluents. Treatment of the hexachloride with NH_4PF_6, after removal of the MeCN, produced $\mathbf{4}\cdot 6PF_6$ in 30% yield.

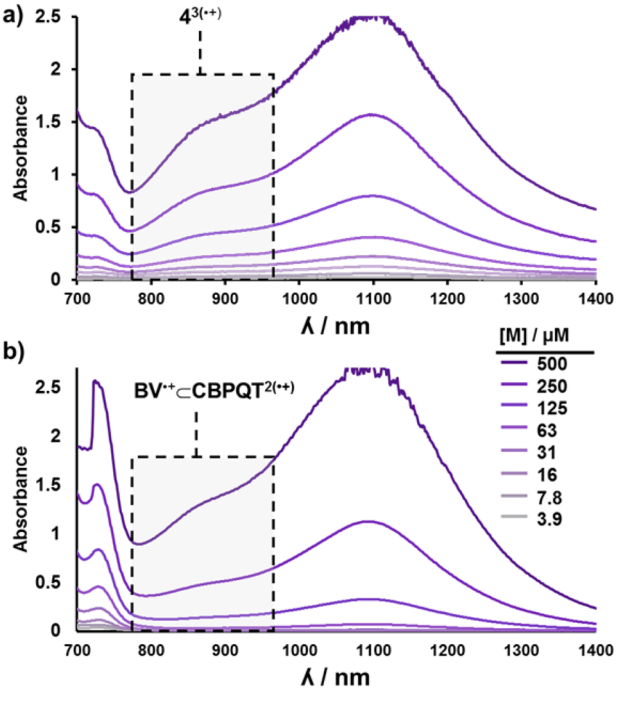

Figure 1. UV-vis spectra of $\mathbf{4}^{3(\bullet+)}$ (a) and $\mathbf{BV}^{\bullet+}\subset\mathbf{CBPQT}^{2(\bullet+)}$ (b) in Me_2CO at increasing concentrations.

UV-vis spectroscopy was employed (Figure 1) in a comparison of $\mathbf{4}\cdot 6PF_6$ to an equimolar mixture of $\mathbf{CBPQT}^{4+}$ and the guest, *N,N′*-dibenzyl-4,4′-bipyridinium ($\mathbf{BV}^{2+}$). Solutions of the reduced $\mathbf{4}^{3(\bullet+)}$ (Figure 1a) and $\mathbf{BV}^{\bullet+}\subset\mathbf{CBPQT}^{2(\bullet+)}$ (Figure 1b) were analyzed between 450 and 1400 nm. The emergence of a peak at 850 nm associated with viologen radical dimerization[15] was observed for both the [2]catenane and the corresponding mixture of components. Plots of the absorbance at 850 nm for $\mathbf{BV}^{\bullet+}\subset\mathbf{CBPQT}^{2(\bullet+)}$ versus concentration (see Figure S24) revealed an exponential trend, indicative of a two-component system, in keeping with the Beer−Lambert law. Conversely, plots of the absorbance at 850 nm against the concentrations of $\mathbf{4}^{3(\bullet+)}$ afford a linear fit, indicative of a single compound in solution (see Figure S26).

Data obtained by electrochemical analysis of a 0.5 mM solution of $\mathbf{4}\cdot 6PF_6$ in Me_2CO using CV at various scan rates (Figure 2) allowed us to qualitatively distinguish the [2]catenane

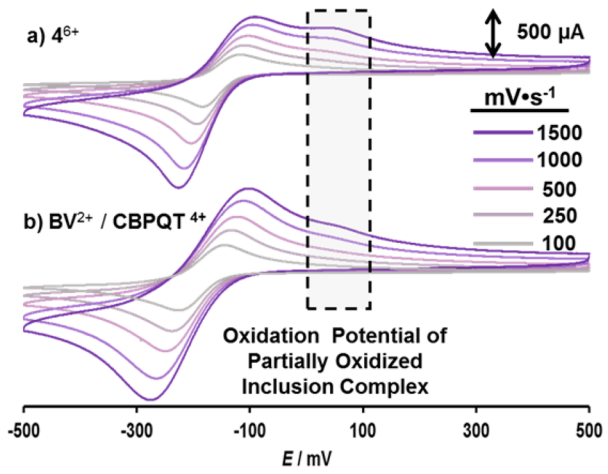

Figure 2. CV spectra of 0.5 mM (a) $\mathbf{4}^{6+}$ and 0.5 mM (b) $\mathbf{BV}^{2+}$/$\mathbf{CBPQT}^{4+}$ as PF_6^- salts in Me_2CO, 0.1 M $TBAPF_6$ supporting electrolyte, at increasing scan rates (mV/s). At low scan rates (100−250 mV/s), a single oxidation peak near −100 mV is indicative of rapid dissociation between the partially reduced benzyl viologen ($\mathbf{BV}^{\bullet+}$) and $\mathbf{CBPQT}^{2(\bullet+)}$ subunits of (a) $\mathbf{4}^{2(\bullet+)(2+)}$ and separate (b) $\mathbf{BV}^{\bullet+}$ and $\mathbf{CBPQT}^{2(\bullet+)}$ species before oxidation to their fully oxidized states. At higher scan rates (500−1500 mV/s), a new oxidation peak at +50 mV is observed, indicating the presence of the diradical inclusion complexes associated with (a) $\mathbf{4}^{2(\bullet+)(2+)}$ and (b) $\mathbf{BV}^{\bullet+}\subset\mathbf{CBPQT}^{(\bullet+)(2+)}$ during the CV measurements. Because of the interlocked nature of $\mathbf{4}^{2(\bullet+)(2+)}$, there is a higher population of the radical metastable state.

from a 0.5 mM solution containing a mixture of the separate components, $\mathbf{CBPQT}^{4+}$ and $\mathbf{BV}^{2+}$. Previous work[9] has demonstrated that $\mathbf{CBPQT}^{2(\bullet+)}$ inclusion complexes with partially reduced viologen guests such as $\mathbf{BV}^{\bullet+}$ are able to undergo two $1e^-$ oxidations at separate potentials from the proposed transient species $\mathbf{BV}^{2+}\subset\mathbf{CBPQT}^{4+}$. Following the first $1e^-$ reduction, the metastable intermediate complex $\mathbf{BV}^{\bullet+}\subset\mathbf{CBPQT}^{(\bullet+)(2+)}$ is destabilized from the dicationic component of the $\mathbf{CBPQT}^{(\bullet+)(2+)}$ host, and the complex dissociates rapidly to afford $\mathbf{CBPQT}^{4+}$ and $\mathbf{BV}^{2+}$ (see Figure S22a). The equilibration of the oxidized species from the $\mathbf{BV}^{\bullet+}\subset\mathbf{CBPQT}^{(\bullet+)(2+)}$ is rapid on the time scale of the experiment and can only be observed using scan rates exceeding 1000 mV/s. Figure 2b shows the emergence of a peak at +50 mV, of rising intensity with increasing scan rate, corresponding to the two $1e^-$ oxidations of the $\mathbf{BV}^{\bullet+}$ and $\mathbf{CBPQT}^{(\bullet+)(2+)}$ components in $\mathbf{BV}^{\bullet+}\subset\mathbf{CBPQT}^{(\bullet+)(2+)}$ to their respective $\mathbf{BV}^{2+}$ and $\mathbf{CBPQT}^{4+}$ states.[16] The analogous peak at +50 mV can be observed (Figure 2a) in the 0.5 mM $\mathbf{4}\cdot 6PF_6$ sample but with greater intensity on account of a shift in the equilibrium to the $\mathbf{BV}^{\bullet+}\subset\mathbf{CBPQT}^{(\bullet+)(2+)}$ co-conformation of the components of $\mathbf{4}^{2(\bullet+)(2+)}$ and away from the corresponding $\mathbf{BV}^{\bullet+}$ and $\mathbf{CBPQT}^{(\bullet+)(2+)}$ separated co-conformation (see Figure S22b, middle entry).

Figure 3 presents the ^1H NMR spectra recorded in CD_3CN for $\mathbf{CBPQT}^{4+}$, $\mathbf{4}^{6+}$, and $\mathbf{5}^{2+}$ in order that a comparison can be drawn between the resonances for the [2]catenane and those for its

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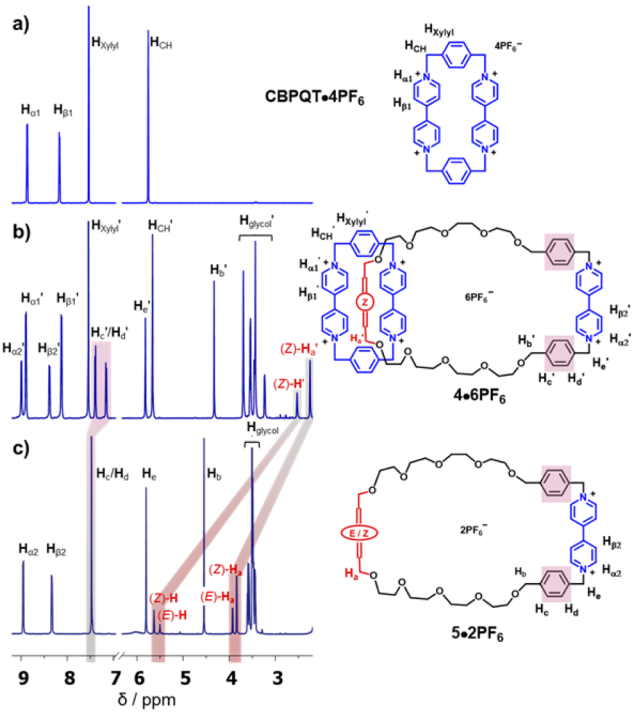

Figure 3. ^{1}H NMR spectra in CD_3CN at room temperature of (a) **CBPQT**·4PF_6, (b) the [2]catenane **4**·6PF_6, and (c) the non-catenated macrocycle **5**·2PF_6. The resonances associated with the alkene and allylic protons (c, (*Z*/*E*)-H and (*Z*/*E*)-H_a) of **5**·2PF_6 are shifted upfield significantly (b, (*Z*)-H′ and (*Z*)-H_a′) in **4**·6PF_6. The accidentally equivalent resonances for the constitutionally heterotopic protons (c, H_c and H_d) associated with the phenylene rings in the non-catenated macrocycle **5**·2PF_6 become anisochronous (b, H_c′ and H_d′) when the macrocycle is a component of the [2]catenane **4**·6PF_6.

component rings. With the exception of resonances for the *p*-xylylene ring, the chemical shift differences for the aromatic protons on going from $\mathbf{5}^{2+}$ (Figure 3b) to $\mathbf{4}^{6+}$ (Figure 3c) are not all that dissimilar. While the resonances for the *O*-methylene protons in the glycol loops in these two compounds experience some small changes in chemical shifts, by far the most pronounced differences are observed for the olefinic and neighboring allylic protons. Significant upfield shifts are registered in the case of the [2]catenane for the olefinic ((*Z*)-H′) and allylic ((*Z*)-H_a′) proton resonances at 2.75 and 2.53 ppm, compared with 5.63 ((*Z*)-H) and 3.83 ppm ((*Z*)-H_a), respectively, in the macrocycle. The (*E*)-isomer for the macrocycle also has resonances at 5.50 and 3.93 ppm for the respective olefinic and allylic protons. The dramatic upfield shifts for these resonances in the ^{1}H NMR spectrum of $\mathbf{4}^{6+}$ suggest the olefinic and allylic portions of the mechanically interlocked macrocycle are spending nearly all of their time in the cavity of the $\mathbf{CBPQT}^{4+}$ ring.

The ^{1}H–^{1}H NOESY NMR spectrum (see Figure S11) of the [2]catenane reveals through-space correlations between the olefinic and allylic protons in the macrocyclic component with all the protons ($H_{\alpha 1}$, $H_{\beta 1}$, and H_{xyl}) on the $\mathbf{CBPQT}^{4+}$ ring component. A noteworthy observation resides in the difference between the stereochemistry of the alkene fragment in the [2]catenane and that associated with the free macrocycle $\mathbf{5}^{2+}$ prepared by RCM using the second-generation Hoveyda–Grubbs catalyst. In the case of $\mathbf{5}^{2+}$, a mixture of the (*Z*)- and (*E*)-isomers associated with the alkene fragment was obtained in a 5:2 ratio, whereas, in the case of the [2]catenane, only a single isomer—the (*Z*)-isomer—is present in the mechanically interlocked macrocycle. See the ^{1}H NMR spectra in Figures 3b and S13.

The diastereoselectivities of the RCMs in the synthesis of $\mathbf{4}^{6+}$ and the free macrocycle $\mathbf{5}^{2+}$ were probed (Figure 4) by subjecting the two compounds to the same degradation conditions. Aqueous solutions of **4**·6PF_6 and **5**·2PF_6 were treated with an excess of base (NaOD) to afford the diols (*Z*)-**7** and (*E*/*Z*)-**7**, respectively, as shown in Figure 4a,b, after hydrolytic removal of the bipyridine units from their respective macrocycles. The ^{1}H NMR spectrum (Figure 4c) recorded in CD_3CN of the diol from **4**·6PF_6 reveals the presence of only the (*Z*)-isomer, whereas the ^{1}H NMR spectrum (Figure 4d) of the diol from **5**·2PF_6 reveals the presence of both the (*Z*)- and (*E*)-isomers in a ratio of 5:2.

In summary, we have described the synthesis of a hexacationic [2]catenane, constructed through olefin ring-closing metathesis following radical–radical templation under reducing conditions. Solution-phase analysis through UV-vis-NIR spectroscopy and cyclic voltammetry reveals that the radical–radical dimerization observed within the [2]catenane is indicative of a single molecular species. Coulombic repulsion between the tetra- and dicationic rings of the fully oxidized [2]catenane forms a single co-conformation, as observed by ^{1}H NMR spectroscopy. Further spectroscopic analyses show that the olefinic and allylic resonances are shifted significantly upfield as a result of residing within the tetracationic cavity of cyclobis(paraquat-*p*-phenylene) on account of Coulombic repulsion experienced within the molecule. High diastereoselectivity within the [2]catenane differs from that of a free macrocycle synthesized through RCM under

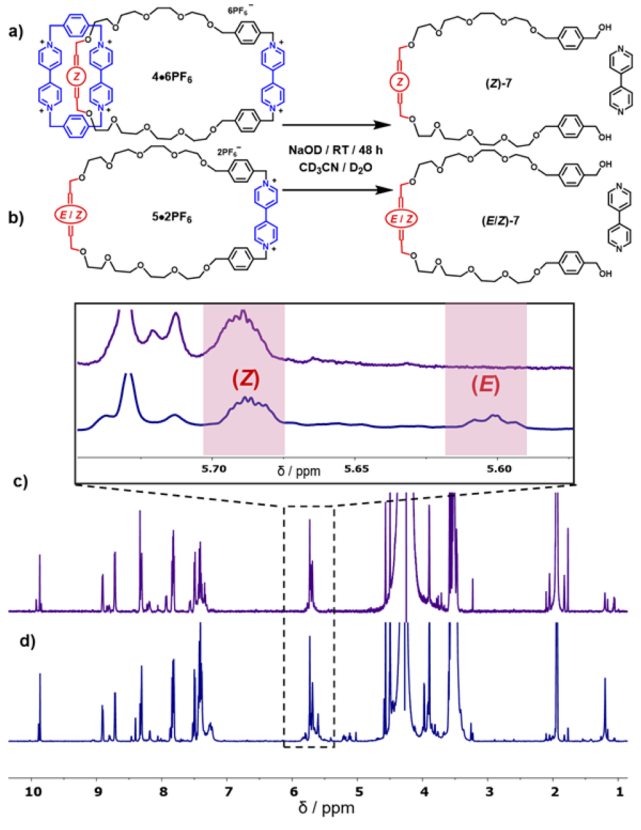

Figure 4. Degradation conditions of (a) **4**·6PF_6 and (b) **5**·2PF_6, and the resulting ^{1}H NMR spectra (c,d) in CD_3CN/D_2O at room temperature, of the respective [2]catenane- and bipyridinium-based macrocycle after exposure to an excess of NaOD.

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ambient conditions, as only the (*Z*)-isomer is present in the mechanically interlocked molecule. This synthetic protocol serves as a proof-of-concept demonstrating that olefin metathesis is able to proceed in the presence of persistent organic radical cations and can be utilized in the synthesis of increasingly elaborate mechanically interlocked compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b10623.

Experimental procedures and spectral data (^{1}H and ^{13}C NMR, HRMS, CV) for all new compounds, as well as NOESY and DOSY spectra of **4**·6PF$_6$ (PDF)

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Notes

The authors declare no competing financial interest.

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(16) At relatively slow scan rates (<100 mV/s), the reduced inclusion complex between the interacting species has ample time to dissociate and oxidize to the non-interlocked components (see Figure S22). At relatively rapid scan rates (>1500 mV/s), the trisradical inclusion complex can be observed for both samples. The difference in peak intensity between the two systems can be explained by the difference in the relative binding constants between the mixture of two components and the [2]catenane.

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