Sliding-Ring Catenanes

Isurika R. Fernando,† Marco Frasconi,†,§ Yilei Wu,†,‡ Wei-Guang Liu,†
Michael R. Wasielewski,†,‡ William A. Goddard III,†,# J. Fraser Stoddart*†

†Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA
‡Department of Chemical Sciences, University of Padova, Via Marzolo 1, Padova 35131, Italy
§Argonne-Northwestern Solar Energy Research (ANSER) Center, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA
┴Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, USA
#NanoCentury KAIST Institute and Graduate School of EEWS (WCU), Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong Dong, Yuseong Gu, Daejeon 305-701, Republic of Korea
*e-mail: stoddart@northwestern.edu

MAIN TEXT

*Correspondence Address

Professor J Fraser Stoddart
Department of Chemistry
Northwestern University
2145 Sheridan Road
Evanston, IL 60208-3113 (USA)
Tel: (+1)-847-491-3793
E-Mail: stoddart@northwestern.edu
ABSTRACT:
Template-directed protocols provide a routine approach to the synthesis of mechanically interlocked molecules (MIMs), in which the mechanical bonds are stabilized by a wide variety of weak interactions. In this paper, we describe a strategy for the preparation of neutral [2]catenanes with sliding interlocked electron-rich rings, starting from two degenerate donor-acceptor [2]catenanes, consisting of a tetracationic cyclobis(paraquat-p-phenylene) cyclophane (CBPQT\(^{4+}\)) and crown ethers containing either (i) hydroquinone (HQ) or (ii) 1,5-dioxynaphthalene (DNP) recognition units and carrying out four-electron reductions of the cyclophane components to their neutral forms. The donor-acceptor interactions between the CBPQT\(^{4+}\) ring and both HQ and DNP units present in the crown ethers that stabilize the [2]catenanes are weakened upon reduction of the cyclophane components to their radical cationic states and are all but absent in their fully reduced states. Characterization in solution performed by UV-Vis, EPR and NMR spectroscopic probes reveals that changes in the redox properties of the [2]catenanes result in a substantial decrease of the energy barriers for the circumrotation and pirouetting motions of the interlocked rings, which glide freely through one another in the neutral states. The solid-state structures of the fully reduced catenanes reveal profound changes in the relative dispositions of the interlocked rings, with the glycol chains of the crown ethers residing in the cavities of the neutral CBPQT\(^{0}\) rings. Quantum mechanical investigations of the energy levels associated with the four different oxidation states of the catenanes support this interpretation. Catenanes and rotaxanes with sliding rings are expected to display unique properties.

INTRODUCTION
Mechanically interlocked molecules\(^1\) (MIMs), such as catenanes\(^2\) and rotaxanes\(^3\), are an important class of compounds as a consequence of their unique physical, chemical and electrochemical properties\(^4\) which make them potential candidates for a wide range of applications,\(^5\) including—but not limited to—providing switches for molecular electronic devices\(^6\) (MEDs) and drug delivery systems.\(^7\) In order to construct MIMs, template-directed protocols\(^8\) that rely on, for example, (i) metal-ligand coordination,\(^9\) (ii)
aromatic donor-acceptor interactions,\textsuperscript{10} (iii) hydrogen bonding,\textsuperscript{11} (iv) anion coordination,\textsuperscript{12} (v) radical-radical interactions,\textsuperscript{13} (vi) halogen bonding,\textsuperscript{14} and (vii) hydrophobic interactions,\textsuperscript{15} have been utilized widely. In particular, template-directed methodologies which rely upon donor-acceptor interactions\textsuperscript{10} have emerged as some of the most extensively explored approaches for the synthesis of MIMs, following the introduction\textsuperscript{16} of the electron-deficient tetracationic cyclophane, cyclobis(paraquat-p-phenylene) (CBPQT\textsuperscript{4+}), more than quarter of a century ago. The molecular recognition that exists between the rigid, electron-deficient cavity of the CBPQT\textsuperscript{4+} ring and the electron-rich cavities of aromatic crown ethers containing hydroquinone\textsuperscript{17} (HQ) and 1,5-dioxynaphthalene\textsuperscript{18} (DNP) units was exploited in the design and construction of the first generation of degenerate donor-acceptor catenanes.\textsuperscript{19} Subsequently, the introduction\textsuperscript{20} of an even better source of electron-donation in the form of electrochemically addressable tetrathiafulvalene (TTF) units led to the development\textsuperscript{21,22} of a second generation of non-degenerate catenanes that exhibit externally governed, dual-mode, reversible switching of a CBPQT\textsuperscript{4+} ring between TTF units and either HQ\textsuperscript{21} or DNP\textsuperscript{22} units present in the crown ether components of the catenanes.

The chemistry of 1,1′-dialkyl-4,4′-bipyridinium (BIPY\textsuperscript{2+}) derivatives, especially the reduction and dimerization (pimerization) of the mono-reduced species BIPY\textsuperscript{•+}, was explored in considerable detail by Kosower\textsuperscript{23} and Hünig\textsuperscript{24} in the 1960s. The electrochemical behavior of CBPQT\textsuperscript{4+} is consistent\textsuperscript{25} with the two BIPY\textsuperscript{2+} units of the CBPQT\textsuperscript{4+} ring being chemically equivalent and undergoing two consecutive reversible redox processes passing through a partially reduced diradical dicaticon CBPQT\textsuperscript{2(+)} on the way to a fully reduced neutral CBPQT\textsuperscript{0} state. Thus, the diradical dicaticon form and the neutral form of the cyclophane are comprised of two BIPY\textsuperscript{••} and two BIPY\textsuperscript{0} units, respectively. In more recent times, we have witnessed\textsuperscript{26} the formation of a host-guest complex wherein the radical-cation of the smallest BIPY\textsuperscript{2+} derivative—namely, methyl viologen (MV\textsuperscript{•+})—becomes inserted into the cyclophane, forming a trisradical-tricationic inclusion complex denoted by CBPQT\textsuperscript{2(+)}⊂ MV\textsuperscript{•+}. Following the identification of this strong 1:1 complex in solution as well as in the solid-state, this inclusion
complex has infiltrated many different aspects of supramolecular chemistry and mechanostereochemistry, including (i) the radical templation\textsuperscript{13} of MIMs, (ii) the folding and unfolding of oligoviologens,\textsuperscript{27} (iii) the extension and contraction of oligorotaxane radicals,\textsuperscript{28} and (iv) the design and construction of artificial molecular pumps.\textsuperscript{29}

Recently, we investigated the properties of the neutral CBPQT\textsuperscript{0}, the so-called red box,\textsuperscript{25} by chemical reduction of the tetracationic CBPQT\textsuperscript{4+}, followed by extraction of the neutral species into an organic phase using an aqueous-organic biphasic procedure.\textsuperscript{30,31} Following four-electron reduction, a change in the electronic properties of the CBPQT\textsuperscript{4+} ring leads\textsuperscript{25} to the binding of electron-poor substrates, such as 1,4-dicyanobenzene, in the electron rich cavity of CBPQT\textsuperscript{0}. Additionally, a comparison of the solid-state structures of CBPQT\textsuperscript{4+}, CBPQT\textsuperscript{2(++)} and CBPQT\textsuperscript{0} reveals (Figure 1) a progressively wider cavity size with [N...N′] distances ranging from 6.36 to 6.58 to 6.88 Å, respectively, while the [C4...C4′] distances increase from 6.81 to 6.92 to 6.99 Å, respectively. Moreover, the C4...C4′ bond distances associated with the BIPY\textsuperscript{2(++)}, BIPY\textsuperscript{++} and BIPY\textsuperscript{0} units decrease from 1.49 to 1.41 to 1.37 Å, respectively, signifying a progressive loss of aromaticity. Dramatic changes in the stereoelectronic properties result from reversing electronically the role of the cyclophane from being a π-electron deficient host, in its tetracationic form, to having an electron rich cavity in the fully reduced CBPQT\textsuperscript{0} state. This observation raises the question as to whether it might be possible to perturb the compact structures originating from the donor-acceptor interactions within the molecular frameworks of the first generation of degenerate donor-acceptor [2]catenanes in which bisparaphenylene-[34]crown-10,\textsuperscript{17,19,20} (BPP34C10) and 1,5-dinaphtho[38]crown-10\textsuperscript{18,19,22} (DNP38C10) are both interlocked mechanically with CBPQT\textsuperscript{4+} rings. These tetracationic [2]catenanes undergo not two but three consecutive redox processes, leading to the identification (Figure 2), upon electrochemical reduction in solution, of tricationic monoradical and diradical dicationic catenanes, as well as the fully neutral ones.

Here we present our detailed investigations of the structure-property relationships characteristic of the [2]catenanes DNP38C10 / CBPQT (1) and BPP34C10 / CBPQT (2) in their different redox states. Both experimental (in solution and in the solid-state)
and computational investigations were carried out. In an attempt to shed light on the nature of the molecular recognition between the mechanically interlocked rings in all four of their redox states, quantum mechanical calculations were performed. The partially charged (3+ and 2+) and the fully reduced neutral (0) states of [2]catenanes 1 and 2 in solution were accessed by chemical reduction of their oxidized 4+ states and characterized by UV-Vis and continuous-wave electron paramagnetic resonance (EPR) spectroscopies. $^1$H NMR Spectra recorded for $^{10}$ and $^{20}$ in CD$_3$C$_6$D$_5$ at room temperature reveal line broadening of the resonances for the CBPQT$^0$ rings but not for the signals associated with the mechanically interlocked crown ethers, pointing to the existence of dynamic processes within the neutral catenanes. Finally, in order to elucidate the nature of the residual noncovalent bonding interactions between their mechanically interlocked electron rich rings, single crystal X-ray diffraction analyses were performed on the neutral catenanes $^{10}$ and $^{20}$.

**EXPERIMENTAL SECTION**

**Materials and General Methods**

All reagents were used as received from chemical suppliers (Aldrich and VWR) and reactions were carried out in anhydrous solvents under an inert N$_2$ atmosphere, unless otherwise stated. The compounds CBPQT•4PF$_6$,$^{16a,32}$ DNP38C10,$^{33}$ BPP34C10$^{19,34}$ and the [2]catenanes$^{19}$ 1•4PF$_6$ and 2•4PF$_6$ were all prepared according to previously reported literature procedures with minor modifications. Thin layer chromatography (TLC) was performed on silica gel 60 F254 TLC plates (Merck) and chromatograms were viewed under UV light at either 256 or 354 nm. All samples employed in UV-Vis, NMR and EPR experiments were prepared inside an Ar-filled glovebox and the measurements were carried out immediately following sample preparation. Solvents were degassed by purging with Ar gas for 2 h prior to transferring them to the glovebox. The different oxidation states, namely 3+, 2+, 1+ and 0 of 1•4PF$_6$ and 2•4PF$_6$ were obtained by adding 1.0, 2.0, 3.0 and 4.0 equiv, respectively, of cobaltocene to the solutions. Cobaltocene was assayed in dried and degassed MeCN using a colorimetric method$^{35}$ prior to the additions. In the cases of the UV-Vis and EPR experiments, MeCN was used$^{36}$ as the solvent while NMR spectroscopic analyses were performed$^{37}$ in CD$_3$CN or C$_6$D$_5$CD$_3$. UV-Vis Spectra were obtained on a
UV-3600 Shimadzu spectrophotometer. $^1$H, $^{13}$C, ROESY, DOSY and Variable Temperature (VT) NMR spectra were recorded on a Bruker Avance III instrument operating at 600 MHz for protons. The temperature ($T$) was calibrated using neat MeOH for $T < 295$ K and ethylene glycol for $T > 295$ K. Chemical shifts are referenced to the residual non-deuterated solvents—C$_6$D$_5$CD$_3$ at δ 2.09 ppm and CD$_3$CN at δ 1.94 ppm. EPR Spectroscopic measurements were performed at room temperature using a Bruker Elexsys E580 X-Band (9.5 GHz) spectrometer outfitted with a variable Q splitting ring resonator (ER-4118X-MS5-W1). High resolution mass spectra (HRMS) were recorded on an Agilent 6210 Time-of-Flight (TOF) LC-MS employing an electrospray ionization (ESI) source coupled with an Agilent 1100 HPLC stack using direct infusion (0.6 mL min$^{-1}$). Single crystal X-ray diffraction analyses of the [2]catenanes in their 0 and 3+ oxidation states, i.e., $^1$0, $^2$0, $^1$•/3+ and $^2$•/3+ were performed on a Bruker Kappa Apex II CCD diffractometer using Cu-K$_\alpha$ ($\lambda = 0.15418$ nm) radiation at 100 K. Structure solutions and refinements were carried out using the Olex 21.2 Suite$^{38}$ of programs. Data collection and structure refinement details are available in CIF files. CCDC Depositions 1479750, 1479752, 1479755 and 1479751. The supplementary crystallographic data for this manuscript can be obtained free of charge from the www.ccdc.cam.ac.uk/data_request/cif website.

**Redox Titration**

Cobaltocene was employed$^{39}$ as a reducing agent because (i) the redox potential of the CoCp$_2^+/CoCp_2$ couple is −0.89 V vs SCE along with our recent investigations$^{25}$ which show that CBPQT$^{4+}$ can be reduced by cobaltocene to its neutral oxidation state (CBPQT$^0$) without harm to the cyclophane and (ii) since it is a single-electron reducing agent, oxidation states 3+, 2+, 1+ and 0 can be addressed precisely and achieved starting from the fully oxidized (4+) catenanes by adding 1.0, 2.0, 3.0 and 4.0 molar equiv of cobaltocene, respectively, while (iii) cobaltocene is readily soluble in a range of polar and apolar solvents including pentane, PhMe, THF, CH$_2$Cl$_2$, Me$_2$CO and MeCN, and (iv) the reduction potential of the oxidized product—namely, the cobaltocenium ion—does not become involved in any side reactions. Reductions with
cobaltocene were used in crystal growth experiments in addition to preparing samples for UV-Vis and EPR spectroscopy.

**UV-Vis Spectroscopy**

A series of MeCN solutions with the catenanes in their 4+, 3+, 2+, 1+ and 0 redox states were prepared by reduction of the fully oxidized catenanes using 0.0, 1.0, 2.0, 3.0 and 4.0 molar equiv of cobaltocene, respectively. The entire range of spectra for the redox states of the catenanes with 1:0, 1:1, 1:2, 1:3 and 1:4 molar ratios of catenane:cobaltocene were recorded in a final volume of 1.0 mL using stock solutions of catenane (100 μM) and cobaltocene (1.7 mM). The concentration of catenanes, $1\cdot4PF_6$ and $2\cdot4PF_6$ in MeCN were maintained at 100 μM in order to hold their optical densities below 1.5 using a standard 2 mm quartz cuvette.

**EPR Spectroscopy**

Samples were prepared as described for the UV-Vis spectroscopic measurements with the exception that the concentration of the catenane stock solutions was maintained at 250 μM. All EPR spectra were recorded in MeCN at 298 K following reduction with cobaltocene.

**NMR Spectroscopy**

Samples of catenanes $1^0$ and $2^0$ were prepared as follows. The tetrachloride salts $1\cdot4Cl$ (12.0 mg, 7.3 μmol) and $2\cdot4Cl$ (10.0 mg, 8.3 μmol) were dissolved in an aqueous CO$_3^{2-}$/HCO$_3^-$ buffer (pH 8–9, 1.0 mL) and CD$_3$C$_6$D$_5$ (1 mL) was added to the buffered solution. After adding activated Zn dust to the biphasic mixture, it was stirred at room temperature for 30 min. The initial color intensities of the aqueous layers—violet for $1\cdot4Cl$ and red for $2\cdot4Cl$, respectively—decreased gradually while the colors of the CD$_3$C$_6$D$_5$ layers changed from colorless to light yellow, followed by the emergence of a dark yellowish-orange color, indicating that the neutral catenanes had been extracted into the CD$_3$C$_6$D$_5$ layers. The organic layers were washed with D$_2$O (3 x 1.0 mL), transferred to Wilmad NMR tubes and capped. The caps on the NMR tubes
were wrapped with parafilm to avoid oxidation of the neutral catenanes by air and the NMR spectra were measured immediately thereafter.

^1^H NMR Data (600 MHz, CD\textsubscript{3}C\textsubscript{6}D\textsubscript{5}, 298 K) for \textbf{1}\textsuperscript{0}: δ 8.02 (br, 4H, H\textsubscript{4/8}), 7.20 (br, 4H, H\textsubscript{3/7}), 7.10 (s, 8H, H\textsubscript{Xy}), 6.47 (br, 4H, H\textsubscript{2/6}), 5.28 (br, 8H, H\textsubscript{α/β}), 3.96 (br, OCH\textsubscript{2a}), 3.60-3.55 (m, OCH\textsubscript{2b-d}, N\textsubscript{5}CH\textsubscript{2}).

^1^H NMR Data (600 MHz, CD\textsubscript{3}C\textsubscript{6}D\textsubscript{5}, 298 K) for \textbf{2}\textsuperscript{0}: δ 7.22 (br, 8H, H\textsubscript{Xy}), 6.57 (s, 8H, H\textsubscript{HQ}), 5.43 (br, 8H, H\textsubscript{α}), 5.31 (br, 8H, H\textsubscript{β}), 3.85 (t, J = 5.4 Hz, 8H, OCH\textsubscript{2a}), 3.65 (br, 8H, N\textsubscript{5}CH\textsubscript{2}), 3.57 (t, J = 5.4 Hz, 8H, OCH\textsubscript{2b}), 3.53 (s, 16H, OCH\textsubscript{2c-d}).

**X-Ray Crystallography**

Unless otherwise stated, crystals of the [2]catenanes in their different redox states were grown under an atmosphere of Ar in a glovebox at 273 K.

\textbf{1}\textsuperscript{0}: A solution of \textbf{1}•4PF\textsubscript{6} (4.75 mg, 2.7 mmol) in MeCN (1.00 mL) was treated with 5.0 equiv of a saturated cobaltocene solution (110 µL) in MeCN. The solution was filtered and, after standing for 1 h at room temperature, dark orange elongated single crystals of \textbf{1}\textsuperscript{0} were obtained.

Crystal data for \textbf{1}\textsuperscript{0}•2MeCN. (C\textsubscript{76} H\textsubscript{82} N\textsubscript{6} O\textsubscript{10}), M = 1239.47, monoclinic, space group \textit{P12}_1/\textit{c}, a = 13.9493(8), b = 48.567(3), c = 10.9451(5) Å, α = 90.00, β = 112.934(3), γ = 90.00°, V = 6829.0(6) Å\textsuperscript{3}, T = 100.01 K, Z = 4, \( D_{\text{calc}} = 1.206 \) g cm\textsuperscript{-3}, \( \mu(\text{CuKα}) = 0.642 \) mm\textsuperscript{-1}, Reflections collected/unique = 20417 / 9824, Observed reflections \([I > 2σ(I)] = 6648, \text{GOF (on } F^2) = 1.067, R(F), R_w(F) [I > 2σ(I)] = 0.1095, 0.2433, \text{CCDC Number: 1479750.}\)

\textbf{2}\textsuperscript{0}: A solution of \textbf{2}\textsuperscript{0} in PhMe was obtained using the biphasic extraction method\textsuperscript{40} starting from \textbf{2}•4PF\textsubscript{6} (5.0 mg, 3.0 mmol) as described for the NMR sample preparation. Diffusion of n-hexane vapor into a solution of \textbf{2}\textsuperscript{0} in PhMe yielded bright orange-colored elongated crystals of \textbf{2}\textsuperscript{0}.

Crystal data for 4(\textbf{2}\textsuperscript{0}•1.5PhMe•0.25H\textsubscript{2}O). (C\textsubscript{298} H\textsubscript{338} N\textsubscript{16} O\textsubscript{41}), M = 4799.82, triclinic, space group \textit{P\text{ı}}, a = 20.1201(9), b = 26.1627(12), c = 26.4880(12) Å, α = 87.674(3), β = 78.983(3)°, V = 12793.9(10) Å\textsuperscript{3}, T = 100.01 K, Z = 2, \( D_{\text{calc}} = 1.246 \) g cm\textsuperscript{-3}, \( \mu(\text{CuKα}) = 0.642 \) mm\textsuperscript{-1}, Reflections collected/unique = 20417 / 9824, Observed reflections \([I > 2σ(I)] = 6648, \text{GOF (on } F^2) = 1.067, R(F), R_w(F) [I > 2σ(I)] = 0.1095, 0.2433, \text{CCDC Number: 1479750.}\)
cm⁻³, μ(CuKα) = 0.660 mm⁻¹, Reflections collected/unique 83250 / 43042, Observed reflections [I > 2σ(I)] = 27965, GOF (on F²) 1.034, R(F), Rw(F) [I > 2σ(I)] = 0.0849, 0.2244, CCDC Number: 1479752.

1•3PF₆: A solution of 1•4PF₆ (3.30 mg, 1.9 mmol) in MeCN (660 µL) was treated with activated Zn dust. After 30 min of stirring at room temperature, the suspension was filtered and the filtrate was subjected to vapor diffusion with iPr₂O. Within 2 weeks, dark violet-purple colored needles of 1•3PF₆ were obtained.

Crystal data for 1•3PF₆•2MeCN. (C₇₆H₈₂F₁₈N₆O₁₀P₃), M = 1674.38, monoclinic, space group C12/c 1, a = 21.9335(5), b = 13.4484(3), c = 27.6224(6) Å, α = 90.00, β = 113.1366(7), γ = 90.00°, V = 113.1366(7) Å³, T = 100.01 K, Z = 4, D(calc) = 1.484 g cm⁻³, μ(CuKα) = 1.685 mm⁻¹, Reflections collected/unique 56084 / 6377, Observed reflections [I > 2σ(I)] = 6276, GOF (on F²) 1.047, R(F), Rw(F) [I > 2σ(I)] = 0.0408, 0.1037, CCDC Number: 1479755.

2•3PF₆: Dark violet-purple colored needles of 2•3PF₆ were obtained after following a procedure similar to that described for 1•3PF₆ except that 2•4PF₆ (3.50 mg, 2.1 mmol) was used at the outset.

Crystal data for 2(2•3PF₆•5.5MeCN). (C₁₅₀H₁₇₇F₃₆N₁₉O₂₀P₆), M = 3435.92, monoclinic, space group P12₁/n1, a = 19.1189(5), b = 19.7795(6), c = 45.0588(12) Å, α = 90.00, β = 93.421(2), γ = 90.00°, V = 17009.2(8) Å³, T = 100.01 K, Z = 4, D(calc) = 1.342 g cm⁻³, μ(CuKα) = 1.509/mm⁻¹, Reflections collected/unique 128195 / 28831, Observed reflections [I > 2σ(I)] = 22524, GOF (on F²) 1.041, R(F), Rw(F) [I > 2σ(I)] = 0.0749, 0.2042, CCDC Number: 1479751.

RESULTS AND DISCUSSION

In order to explore the properties of neutral BIPY units in confined environments and shed more understanding on the structure-property relationships in MIMs at different oxidation states, we have investigated two degenerate donor-acceptor [2]catenanes, 1•4PF₆ and 2•4PF₆, in which macrocyclic polyethers DNP38C10 and BPP34C10,
respectively, are interlocked mechanically with CBPQT$^{4+}$ rings. Their syntheses rely on a template-directed protocol driven by $\pi \cdots \pi$ donor-acceptor and [C–H···O] interactions as reported previously.$^{10a,18}$ As a consequence of intramolecular donor-acceptor charge transfer interactions transitions between the electron rich DNP unit in 1•4PF$_6$ and the HQ unit in 2•4PF$_6$ and the electron deficient CBPQT$^{4+}$, 1•4PF$_6$ is purple, while 2•4PF$_6$ is red, in the solid-state.

**Electrochemistry and UV-Vis Spectroscopy**

The redox behavior of 1•4PF$_6$ and 2•4PF$_6$, as demonstrated$^{18}$ by cyclic voltammetry experiments in MeCN solution, indicates that the reduction of the interlocked CBPQT$^{4+}$ ring from the fully oxidized state (4+) involves two well-resolved-single-electron reductions to reach, consecutively, the 3+ and 2+ oxidation states, followed by a two-electron reduction that leads to the fully reduced neutral form. The first one-electron process can be attributed to the reduction of the BIPY$^{2+}$ unit alongside the macrocyclic polyether, affording the tricationic monoradical catenane. The diradical dicationic state is formed upon reduction of the encircled BIPY$^{2+}$ unit, which is involved in strong donor-acceptor interactions. The two simultaneous one-electron reductions of the two spin-paired BIPY$^{+}$ units result in the production of the fully reduced (neutral) catenane. These processes occur for 1•4PF$_6$ and 2•4PF$_6$ at redox potentials of $-911$ and $-895$ mV, respectively, as measured$^{18}$ in MeCN solution versus a SCE reference. These reduction potentials are shifted to substantially more negative values, compared to the reduction potential of the diradical dicationic CBPQT$^{2(\pi^+)}$ going to the neutral CBPQT$^{0}$ ring, indicating some potential stabilization provided by the macrocyclic polyether towards the radical cationic BIPY$^{+}$ units of the CBPQT$^{2(\pi^+)}$ ring within the [2]catenanes.

In an effort to explore the noncovalent bonding interactions occurring within the catenanes in their fully- and partially-charged forms, as well as in their neutral oxidation states, we isolated 1•4PF$_6$ and 2•4PF$_6$ in their different oxidation states and probed their physicochemical properties both in solution and in the solid-state. The reduced forms of the catenane were generated by titrating solutions of 1•4PF$_6$ and 2•4PF$_6$ in MeCN with the chemical reductant cobaltocene (CoCp$_2$) under an atmosphere of Ar. The radical character of catenanes in their different oxidation states
in solution was probed by UV–Vis and EPR spectrosopies. The UV–Vis spectra of
1•4PF₆ (Figure 3a) and 2•4PF₆ (Figure 3b) exhibit absorbance maxima at 530 and 470
nm, respectively. These absorption bands can be attributed to intramolecular charge
transfer transitions between the electron-rich DNP or HQ units of the crown ether and
the electron deficient BIPY²⁺ units of the CBPQT⁴⁺ ring in solution, as supported by
DFT calculations (see the Supporting Information). Upon addition of 1.0 equiv of
CoCp₂, the color of both catenane solutions changes to a dark blue which is
characteristic of the radical cation, BIPY⁺. This color change is accompanied by the
emergence of two absorption bands in the UV–Vis spectra at 418 and 620 nm.
Following the stepwise addition of 2.0 equiv of CoCp₂ to the catenane solutions, the
dark blue color intensifies and the absorbance of the radical-cation bands nearly
doubles. These two observations provide evidence for conversion of the remaining
BIPY²⁺ units into the radical cationic BIPY⁺⁺ ones in both 1•4PF₆ and 2•4PF₆. In the
presence of more than 2 equiv of the reductant, the color of both catenane solutions
changes to bluish-green and their UV–Vis spectra show a decrease of the absorption
band at 620 nm, while a new band emerges at 375 nm, indicating the formation of
neutral BIPY⁰ units. The fully reduced catenanes 1⁰ and 2⁰ are generated upon
addition of 4.0 equiv of CoCp₂, as confirmed by the disappearance of the broad band
at 620 nm and the concomitant increase of the band at 375 nm.

Solutions of the neutral catenanes 1⁰ and 2⁰ are stable under ambient condition for
more than one day prior to the slow reappearance of radical cationic bands in their
UV–Vis spectra. The intermediate radical cationic states, namely the tricationic
monoradical and the diradical dicationic catenanes, are stable for several days under
an Ar atmosphere while, upon exposure to air, they undergo oxidation much more
readily when compared with to their neutral counterparts.

**EPR Spectroscopy**

Continuous wave (CW) EPR spectroscopy was performed in an effort to shed even
more understanding on the radical state of the catenanes at different oxidation states.
Upon stepwise addition of the reducing agent to 250 µM solutions of catenanes 1•4PF₆
and 2•4PF₆, significant changes were observed in the EPR spectra in comparison with those of the fully-oxidized catenanes, which are both EPR silent in their 4+ oxidation states. A gradual increase in the radical signal intensities, along with well-resolved hyperfine splitting patterns, was observed for the spectra of the tricationic monoradicals 1⁺³⁺ and 2⁺³⁺ as well as for the diradical dicationic 1²⁺⁺ and 2²⁺⁺, revealing the existence of a low-spin exchange regime for these oxidation states. The hyperfine splittings associated with 1⁺³⁺ and 2⁺³⁺ are similar to those commonly observed⁴¹ for the radical cationic state of methyl viologen. The hyperfine structure disappears almost completely in the spectrum of 2²⁺⁺ as a result of spin-exchange interactions between unpaired electrons in the two BIPY⁺⁺ units. In contrast, the reduction of 1⁺³⁺ to the diradical dicationic state 1²⁺⁺ is accompanied by only a slight broadening of the hyperfine line compared with that observed in the EPR spectra of 2²⁺⁺, a characteristic which is most likely the result of a reduced spin-exchange interaction on account of the ‘isolation’ of the BIPY⁺⁺ units in 1²⁺⁺. These subtly different observations suggest that a co-conformation with a π-electron-rich DNP unit located inside the CBPQT²⁺⁺ ring is favored. Addition of CoCp₂ up to 4.0 equiv results in the formation of the fully reduced catenanes, both of which are EPR silent.

NMR Spectroscopy

The diamagnetic character of the neutral catenanes 1⁰ and 2⁰ in solution means that they can be characterized by ¹H NMR spectroscopy, providing additional information about the nature of the noncovalent bonding interactions in these π-electron-rich neutral catenanes. It is evident that—as a consequence of the lack of donor-acceptor interactions upon chemical reduction—the molecular recognition between the fully neutral macrocycles—namely, the crown ether and CBPQT⁰ ring—is presumably weakened to the extent that the relative circumrotation movements between the two interlocked rings are very much faster compared to other previously studied donor-acceptor catenanes. We have employed ¹H, ¹³C, ROESY and DOSY NMR spectroscopies to investigate the co-conformational behavior of both 1⁰ and 2⁰. Solutions of these neutral catenanes for NMR characterization were prepared using an organic-aqueous biphasic extraction procedure⁴² which was previously established by using different reducing agents to isolate the fully reduced methyl viologen. The
procedure was developed further by us during the isolation of the red box CBPQT\textsuperscript{0}. By employing this procedure, which takes advantage of the different solubilities of the fully oxidized (4+) and neutral (0) catenanes, 1\textsuperscript{0} and 2\textsuperscript{0} were extracted from aqueous solutions into C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3} layers after being reduced to their neutral states using Zn dust in the alkaline aqueous phase under an atmosphere of Ar. Catenanes 1\textsuperscript{0} and 2\textsuperscript{0} display slightly different solubilities with 2\textsuperscript{0} being more soluble in C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3} than 1\textsuperscript{0}, most likely as a consequence presumably of the compatibility of this solvent with the 1,4-dioxynapthalene units of the crown ether. Analysis by diffusion-ordered \textsuperscript{1}H NMR spectroscopy (see Supporting Information, Figures S4 and S5), performed on solutions of 1\textsuperscript{0} and 2\textsuperscript{0} following extraction into the C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3} phase, confirmed the presence in solution of one species in each case. The \textsuperscript{1}H NMR spectra of 1\textsuperscript{0} and 2\textsuperscript{0} reveal shifts in the resonances of the protons in positions α and β to the nitrogens of the BIPY units corresponding to chemical shifts of around 5.43 and 5.36 ppm which are characteristic of the neutral cyclophane CBPQT\textsuperscript{0}. These upfield shifts confirm the conversion of the BIPY units to nonaromatic planar constitutions as a result of their reduction to their neutral states. It is important to note that the resonances associated with the α and β protons, along with those for N-methylene (NCH\textsubscript{2}) and phenylene (H\textsubscript{xy}) groups of the CBPQT ring in 1\textsuperscript{0} and 2\textsuperscript{0} are broadened (Figure 5) compared with those observed for the neutral cyclophane. This observation indicates the occurrence of dynamic bond rotation, presumably around the axis defined by the phenylene unit within the CBPQT\textsuperscript{0} ring in solution at 298 K. In order to gain a better understanding of the dynamic nature of the neutral catenanes, variable-temperature \textsuperscript{1}H NMR spectroscopy was carried out in C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3} (Figure S2 and S3) over a range of temperature from 203 to 373 K. Only one set of peaks were observed for the protons in 2\textsuperscript{0} over the entire temperature range, commensurate with fast circumrotation of the BPP34C10 and CBPQT\textsuperscript{0} rings occurring within the [2]catenane. By contrast, the \textsuperscript{1}H NMR spectra on the fully oxidized 2\textsuperscript{4+} in CD\textsubscript{3}CN, measured for comparison over a 233 to 343 K temperature range, exhibit (Figure S3b) two sets of peaks for the inside and alongside protons of the HQ units, indicating that the crown ether undergoes slow exchange dynamics on NMR time scale within the temperature window of liquid CD\textsubscript{3}CN. The observed coalescence temperature of 343 K at 600 MHz, along with the
limiting chemical shift (Δν) difference of 1320 Hz between the two peaks for the slowly exchanging protons, allows a determination of the free energy of activation (ΔG‡) of 61.6 kJ mol⁻¹. Although the DNP38C10 macrocyclic polyether places considerable geometric constraints on the 1⁰ catenane with respect to 2⁰, the presence of a single set of signals in the ¹H NMR spectrum of 1⁰ in C₆D₅CD₃ (Figure S2) indicates that the dynamic processes between the interlocked electron rich rings of these neutral catenanes remain fast on the ¹H NMR time-scale. Although the DNP38C10 macrocyclic polyether contains much larger aromatic units with respect to BPP34C10, the presence, once again, of only one single set of signals in the ¹H NMR spectrum of 1⁰ in C₆D₅CD₃ (Figure S2) at room temperature indicates that the dynamic processes between the interlocked electron rich rings of these neutral catenanes are still fast on the ¹H NMR time-scale. The proton resonances on the DNP38C10 ring of 1⁰, however, separate out into two equal intensity resonances on cooling the solution below 263 K. By following the temperature dependence of the signals from the H₂/₆ protons (Δν = 150 Hz), a ΔG‡ value of 12.3 kJ mol⁻¹ was obtained, indicating an energy barrier which can be associated with the “flipping” of the DNP units. The resonances associated with the α and β protons of the neutral BIPY in 1⁰ undergo broadening and coalescence at the temperature of 323 K, which is slightly higher than that observed for 2⁰ as a result of a greater geometrical constraint imposed by the DNP38C10 as compared with the BPP34C10 ring.

**X-Ray Crystallography**

The redox controlled organization of the mechanically interlocked rings was revealed in the solid-states by X-ray crystallographic analysis on single crystals of the catenanes in their different oxidation states. Reduction of the catenane 1•4PF₆ in MeCN with slightly more than 4 equiv of CoCp₂ yielded dark orange elongated single crystals in less than 1 h upon standing in an atmosphere of Ar at room temperature. This observation is consistent with our recent results²⁵ obtained for CBPQT⁰ where crystallization of the neutral box from a concentrated solution of the reduced form in MeCN resulted in dark reddish-orange cubes under the same conditions as those employed for growing crystals of 1⁰. This case of crystallization is a result of the low solubility of the neutral species in polar solvents, such as MeCN. Orange crystals with
the same unit cell were also obtained by slow vapor diffusion of iPr₂O into a dilute MeCN solution of the fully reduced catenane 1⁰. The neutral state of the catenane is confirmed by the absence of counterions in the unit cell of the crystal, which is monoclinic and belongs to the P2₁/c space group. The increased double bond character in the BIPY units as a consequence of the conversion of the aromatic pyridinium into dihydropyridine rings confirms that the conversion of the cyclophane to its neutral state was successful. After disrupting, by full reduction, the donor-acceptor interactions between the DNP units in DNP38C10 and the BIPY²⁺ recognition sites in CBPQT⁴⁺ ring, the CBPQT⁰ ring encircles (Figure 6a) the glycol chain of DNP38C10 in the solid-state structure of 1⁰. Relocation of the CBPQT⁰ ring within the catenane is governed by weak interactions (Figure 6b), that can be ascribed to two sets of factors. The first set includes edge-to-face aromatic [C–H···π] interactions between the alongside phenylene ring of the CBPQT⁰ and the two DNP units in DNP38C10, which lie within a 2.62–2.48 Å distance range. The second set includes weak aliphatic [C–H···π] interactions emanating from the glycol chain of the crown ether and directed at a distance of 3.20 Å towards the phenylene group in the CBPQT⁰ encircled by DNP38C10. Reduction of the cyclophane component to its uncharged state induces rotation of the phenylene group by almost 52° around the axis defined by the two methylene carbon atoms of CBPQT⁰. As a result of this rotation, the phenylene group can become engaged (Figure 6c) in edge-to-face intermolecular [C–H···π] interactions (approximately 3.13–3.39 Å) with DNP units of the neighboring catenane. Intermolecular [C–H···O] interactions with a mean distance of 3.24–3.45 Å exist between the β protons of the BIPY units and the oxygen atoms of the crown ether of the neighboring catenane. In the crystal structure of fully oxidized 1⁴⁺, intramolecular [C–H···O] interactions were observed¹⁸ between the CBPQT⁴⁺ ring and the ethylene glycol chain of the DNP38C10 ring.

In the case of the neutral catenane 2⁰, bright-orange elongated single crystals were obtained by diffusion of n-hexane into a PhMe solution of 2⁰, which was obtained by extraction from a heterogeneous two-phase system composed of PhMe and an alkaline aqueous layer. X-ray structural analysis of crystalline 2⁰ revealed a triclinic unit cell with a P₁ space group displaying (Figure S8) four different co-conformations of the
catenane $2^0$ catenane. In all four co-conformations, the BPP34C10 ring’s glycol chain is located in the cavity of the CBPQT$^0$ ring in an almost centrosymmetric fashion. In two of the co-conformations, the CBPQT$^0$ ring sits (Figure S9) on the first CH$_2$–O–CH$_2$ linker of the glycol chain, while, in the other two co-conformations, the ring is located around the second CH$_2$–O–CH$_2$ linker of the glycol chain. The strikingly different geometrical arrangement of the mechanically interlocked rings in the [2]catenane in its different oxidation states is highlighted in Figure 7 which depicts the solid-state structures of fully oxidized $2^{4+}$ previously reported$^{18}$ (and we reproduce here for the sake of comparison) along with one of the co-conformations of the fully reduced $2^0$ catenane. The loss of aromaticity by the BIPY units in their fully reduced states results in a co-conformational change in the catenane. One of the hydroquinone (HQ) units in the BPP34C10 ring is situated alongside on the phenylene unit of the CBPQT$^0$ ring, separated by a plane-to-plane distance of 3.5 Å. Noncovalent bonding interactions help to sustain the other HQ unit located outside the cavity of the CBPQT$^0$ ring, resulting in edge-to-face [C–H···π] interactions between the HQ and the phenylene units. The co-conformations of these degenerate [2]catenanes—which are governed by donor–acceptor π-orbital overlap when the cyclophane component is in the fully oxidized state—change dramatically upon reduction of the CBPQT$^{4+}$ ring to its neutral CBPQT$^0$ form, resulting in a completely new set of noncovalent bonding interactions accompanied by very different molecular geometries contained within the same topology.

Geometrical changes within the cyclophane were also observed as a function of the oxidation state of the catenanes in the solid-state. The geometrical parameters of the CBPQT$^0$ ring in $1^0$ and $2^0$ include (i) the dimension of the cavity, measured as a centroid-to-centroid distance between the planes of the two BIPY$^0$ units, and (ii) the torsion angle between the two rings in the BIPY$^0$ units. The geometries undergo significant changes when compared$^{25}$ with those observed for the ‘free’ CBPQT$^0$. The encirclement of the CBPQT$^0$ ring around the glycol chain in the fully reduced [2]catenanes results in the ‘breathing’ of the neutral cyclophane cavity. The breathing movements were confirmed by measuring the centroid-to-centroid distances between
two parallel BIPY\textsuperscript{0} units of CBPQT\textsuperscript{0} that spans from 6.99 Å in empty CBPQT\textsuperscript{0} to 7.37 and 7.70 Å in the case of the neutral catenanes \textsuperscript{10} and \textsuperscript{20}, respectively.

The intermediate radical cationic states of each of the [2]catenanes—namely \textsuperscript{1i3+} and \textsuperscript{2i3+}, were also investigated in the solid-state. Upon addition of an excess of Zn dust to \textsuperscript{1•4PF\textsubscript{6}} and \textsuperscript{2•4PF\textsubscript{6}}, the colors of the solutions change from the purple and red, characteristic of donor–acceptor charge transfer complexes, to dark blue, an indication that reduction of the CBPQT\textsuperscript{4+} ring to the diradical dicationic form has taken place in solution. Slow vapor diffusion of \textsubscript{iPr\textsubscript{2}}O into solutions of the reduced catenanes, following removal of the Zn dust under an atmosphere of Ar, afforded violet, elongated single cube-shape crystals suitable for X-ray diffraction analysis.\textsuperscript{43} The analysis revealed the presence of three PF\textsubscript{6}– counterions per catenane, indicating the adoption of tricationic monoradical states for these catenanes in the solid-state even although UV-Vis spectroscopic analysis of the initial catenane solutions revealed that the compounds had been reduced to their diradical dicationic states. This behavior, which was observed\textsuperscript{44} previously during the crystallization of [2]catenanes containing radical cationic BIPY\textsuperscript{+} units, could be the result of redox-mediated disproportionation during the crystallization of radical cationic species in nanoconfined environments. The solid-state structural analyses of \textsuperscript{1i3+} and \textsuperscript{2i3+} reveal (Figure 8) ordered molecular arrangements in which one of the DNP (or HQ) units is sandwiched between the BIPY components (mean interplanar distance of 3.4 Å), whilst the other π-electron donor unit lies immediately adjacent to one of the BIPY units. The alongside BIPY unit of the CBPQT\textsuperscript{i3+} exists in its radical cationic BIPY\textsuperscript{+} form, as deduced from analyses of bond lengths and torsional angles, which is typical of radical cationic species. On the other hand, the dicationic BIPY\textsuperscript{2+} units are located between the π-electron donor units of the macrocyclic polyethers, stabilized by donor-acceptor interactions with the two DNP (Figure 8b) and HQ (Figure 8d) units. The torsion angles for the radical cationic BIPY\textsuperscript{++} and dicationic BIPY\textsuperscript{2+} units are 7° and 10°, respectively, for \textsuperscript{1i3+}. In the case of \textsuperscript{2i3+}, the alongside BIPY\textsuperscript{+} unit reveals a smaller torsional angle (2°) compared to that (20°) of the BIPY\textsuperscript{2+} unit inside the DNP38C10 ring. An important influence of BIPY\textsuperscript{+} on the
structural properties of the catenanes is observed (Figure 9) in the extended solid-state superstructure of the $2^{2/3+}$ catenane. The packing in the crystal reveals an arrangement in which two BIPY$^{2+}$ units of adjacent $2^{2/3+}$ catenanes undergo dimerization, with a centroid-to-centroid separation of 3.21 Å between the two BIPY$^{2+}$ units of the CBPQT$^{7/3+}$ rings. Weak [C–H···O] interactions are observed between the alongside HQ unit of one catenane and the second oxygen atoms in the polyether loop of a neighboring catenane. The superstructure of the catenane $2^{2/3+}$ in its tricationic monoradical form shows a packing with discrete domains of alternating radical-radical and donor-acceptor interactions. This superstructure confirms, along with previously reported$^{44a,45}$ bistable [2]rotaxanes, that the manipulation of the redox chemistry allows us to control these interactions beyond the molecule.

**Quantum Mechanical Calculations**

In order to examine the energies that govern the intramolecular noncovalent bonding interactions in the catenanes in their different oxidation states, density functional theory (DFT) was brought to bear on the problem. The initial geometries were taken from the crystal structures of the catenanes in their neutral (0) and fully oxidized (4+) states, wherein the CBPQT ring encircles the glycol chain and the π-electron donor groups, respectively. From these states the structures were relaxed$^{46}$ to the local minimum at the level of M06-HF / 6-31G* with the Poisson-Boltzmann solvation model$^{47}$ ($r_{\text{probe}}=2.19\text{Å}$, $\varepsilon=37.5$) to mimic the polarization in the condensed phase. The single-point energy was refined at the M06-HF/6-311++G** level. The high percentage of HF exchange helps the description of charge localization, which is important because of the drastic change in the oxidation state. The geometries predicted from the quantum mechanical calculations (Figure S10) carried out on catenanes $1^{n+}$ and $2^{n+}$ ($n = 0, 3$ and $4$) are in agreement with the experimental observations. Comparison of the calculated structures with the solid-state crystal structures reveals similar positioning of CBPQT$^{n+}$ ($n = 0–4$) ring on the macrocyclic polyethers for both catenanes. Quantum mechanical calculations (Table 1) show that the two BIPY$^{2+}$ units of CBPQT$^{4+}$ in the catenane $1^{4+}$ enter into a strong stabilizing interaction with the DNP units of the crown ether with 46.1 kcal mol$^{-1}$ energy. Similarly,
the BIPY$^{2+}$ units of the CBPQT$^{4+}$ ring reside on the HQ units of $2^{4+}$ with 36.7 kcal mol$^{-1}$ energy. This energy difference for the fully-charged catenanes, $1^{4+}$ and $2^{4+}$, can be attributed to the strength of the donor-acceptor interactions between the DNP–BIPY$^{2+}$ couples compared with the HQ–BIPY$^{2+}$ recognition units. The DFT calculations show that, after reduction of CBPQT$^{4+}$ ring by one electron, the CBPQT$^{3/3+}$ ring still prefers (although less so) to locate itself on the HQ or DNP units of the crown ether with the dicatonic BIPY$^{2+}$ units residing inside the macrocyclic polyethers, stabilized by donor-acceptor interactions, as observed in the solid-state crystal structures of the catenanes $1^{3/3+}$ and $2^{3/3+}$. The co-conformation of $1^{3/3+}$ (Figure S11) with the dicatonic BIPY$^{2+}$ unit positioned alongside the macrocyclic polyether and the radical cationic BIPY$^{•+}$ unit residing inside the DNP38C10 ring results in a higher energy (5.0 kcal mol$^{-1}$) in comparison to the co-conformation that has the BIPY$^{2+}$ unit residing outside the macrocyclic polyether. Such a change in co-conformation in the case of the catenane $2^{3/3+}$ (Figure S12) does not occur because of the strong tendency of the dicatonic unit to remain inside the macrocyclic polyether on account of stronger donor-acceptor and [CH···O] interactions. The energy optimized geometries (Figure S13) for the calculated structures of $1^{2(•+)}$ and $2^{2(•+)}$ show that, even after formation of the diradical dicationic CBPQT$^{2(•+)}$, the BIPY$^{•+}$ units encircle the aromatic units of the crown ethers. Interestingly, in the case of the calculated structure (Figure S14) of the catenane $1^{•+}$, the CBPQT$^{•+}$ ring prefers (by 22.8 kcal mol$^{-1}$) to reside on the DNP unit rather than on the glycol chain, in stark contrast with the computed structure (Figure S15) for the catenane $2^{•+}$, in which the CBPQT$^{•+}$ ring prefers (by 5.7 kcal mol$^{-1}$) to reside on the glycol chain. The distinctively different co-conformations adopted by these two catenanes result from the higher polarizability of DNP over HQ units, resulting in larger stabilization energies for the CBPQT$^{•+}$ ring located on the DNP unit. The energy for the co-conformation obtained by switching the position of the radical cationic BIPY$^{•+}$ unit of $1^{•+}$ from inside to alongside the DNP38C10 ring (Figure S14b) is 9.3 kcal mol$^{-1}$ higher because of the lower polarization arising from the DNP units. The calculated structures for the neutral catenanes $1^0$ and $2^0$ demonstrate that fully neutral CBPQT rings prefer to relocate along the glycol chain. In order to investigate the stability of the neutral catenanes in different co-conformations, we have calculated
the potential energy surface for the sliding of the CBPQT ring through the crown ether and compared it with the energy for the movement of the CBPQT$^{4+}$ ring in the fully oxidized catenanes. The neutral CBPQT ring encircling the DNP38C10 (or BPP34C10) crown ether was initially pushed away from the equilibrium position by 0.5 and 1.0 Å in the direction perpendicular to the plane defined by the carbons in four bismethylene units and then optimized with all the other coordinates relaxed. The potential energy surface is higher for both tetracationic catenanes $1^{4+}$ and $2^{4+}$ in comparison with the neutral catenanes (Figure S16). The higher energy cost calculated to move the CBPQT ring away from the equilibrium position for the catenanes in the 4+ charge state indicates a stronger interaction between CBPQT$^{4+}$ ring and DNP (or HQ), an observation which is also reflected by the much greater stability (Table 1) of the co-conformations when the CBPQT$^{4+}$ ring encircles the aromatic units.

In order to elucidate the individual contributions of the interactions in the calculated catenane structures, we carried out the energy decomposition analysis (EDA) on different geometries and oxidation states of the $1^{4+}$ catenane. This analysis was performed with absolutely localized molecular orbitals$^{48}$ at M06-HF/6-311G**, which allows the decomposition of the interaction energy into three terms: (i) Coulomb and exchange-correlation (CEC, also known as frozen density component), (ii) polarization (PO), and (iii) charge-transfer (CT). The results of the energy decomposition analysis, which are recorded in Table 2, highlight the individual contributions to the calculated differences in energy for the $1^{4+}$ catenane at different oxidation states and in different co-conformations—namely, when the CBPQT ring encircles the DNP unit or the glycol (GLY) chain. The comparison between this analysis, performed in vacuum, and the energies calculated in MeCN solution, shows (Table 1) that, while the relative calculated energies are different, the overall trend of the stabilization energies from the positively charged catenane to the neutral catenane is similar. The results indicate that CEC and polarization interactions are the dominant contributors to the stabilization of the CBPQT$^{4+}$ ring and DNP38C10 in the fully oxidized catenanes. In the 4+ oxidation state, the CEC and polarization afford stabilization energies of 17.4 and 9.9 kcal mol$^{-1}$, respectively, for the CBPQT$^{4+}$ ring encircling the DNP unit. As the positive charge on
the ring decreases, the driving force from CEC becomes less positive and it assumes negative values for the oxidation state corresponding to the trisradical cationic catenane (1+). This trend can be explained by the increase in the electron-rich character of the system on reducing the oxidation state of the catenane and, therefore, causing an increase in the repulsion from Pauli exclusion. It is important to note that such an effect becomes significant in the case of the neutral CBPQT ring residing around the electron-rich DNP unit. Indeed, a driving force of 23.5 kcal mol\(^{-1}\) is calculated on moving the CBPQT ring from the DNP unit to the glycol chain and explains the tendency for the CBPQT ring in its lower oxidation states to encircle the glycol chain. The magnitude of polarization is also reduced as charge becomes neutralized, but it always favors the binding between the DNP unit and the CBPQT ring. From this analysis, we conclude that the changes in co-conformations within these catenanes by varying their oxidation states are determined the interplay between polarization interactions and Pauli exclusion.

**CONCLUSIONS**

The redox-controlled structure-property relationships involving two degenerate donor-acceptor [2]catenanes have been characterized both in the solution and solid-states by altering the redox state of the electron-poor cyclophane CBPQT\(^{4+}\) component from its fully oxidized state (4+) to its fully reduced neutral (0) form, including the two intermediate states, namely 3+ and 2+. Single-crystal X-ray diffraction analyses, along with solution state investigations by UV-Vis, EPR and NMR spectroscopies, have revealed the noncovalent bonding interactions between the components of the [2]catenanes in their different oxidation states. Donor-acceptor interactions direct the assembly of the [2]catenanes, 1\(^{4+}\) and 2\(^{4+}\), and ensure the existence of ordered, compact structures which contain an alternating pattern of electron-rich units (DNP or HQ) and electron-deficient BIPY\(^{2+}\) components. On reduction of the CBPQT\(^{4+}\) ring to its neutral state, a drastically different situation pertains. The formation of the electron-rich CBPQT\(^{0}\) ring within the molecular frameworks of these [2]catenanes results in the complete disruption of donor-acceptor interactions. Indeed, the isolation of neutral [2]catenanes comprising two electron-rich interlocked rings leads to the investigation
of these MIMs from a different perspective. Our investigations demonstrate a complete change in the intramolecular interactions between the two interlocked rings such that, upon formation of the neutral species, the rings can glide freely through one another in solution, as confirmed by variable-temperature $^1$H NMR spectroscopy. Single-crystal X-ray diffraction analyses of the neutral catenanes $1^0$ and $2^0$ demonstrate that the glycol chains of the DNP38C10 and the BPP34C10 rings reside inside the cavity of the CBPQT$^0$ ring, while the electron-rich DNP and HQ units are located outside the cavity. This loss of molecular recognition results in completely different molecular geometries for the neutral catenanes in comparison with those of their fully oxidized states, despite their having the same topologies.

We have uncovered a strategy which allows access to catenanes—in good yields by template-directed protocols, relying either on donor-acceptor or radical-pairing interactions—that afford, upon reduction of the cyclaphane component to its neutral form, catenanes in which the molecular recognition between the two rings is exceedingly low. Access to catenanes with very low energy barriers to the gliding of their interlocked rings is important for the design and synthesis of artificial molecular machines.$^{29, 49}$ Moreover, the extension of this concept into the realm of polyrotaxanes could lead$^{50}$ to novel sliding-ring materials under redox control with mechanical properties that could find applications as adhesive, coatings and soft-actuators.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Full details of instrumentation and materials and general methods; detailed NMR spectroscopic investigations of $1^0$, $2^0$, $1^{4+}$ and $2^{4+}$; solid-state characterization using X-ray diffraction analysis and quantum mechanical calculations.

X-ray crystallographic analysis data for $1^0$ (CIF)

X-ray crystallographic analysis data for $2^0$ (CIF)
X-ray crystallographic analysis data for $1^{3+}$ (CIF)

X-ray crystallographic analysis data for $2^{3+}$ (CIF)

AUTHOR INFORMATION

Corresponding Author

stoddart@northwestern.edu

Notes

Authors declare no competing financial interest

AKNOWLEDGEMENTS

We thank Dr. Amy Sarjeant and Charlotte C. Stern for solving the single-crystal X-ray structures. This research is part of the Joint Center of Excellence in Integrated Nano-Systems (JCIN) at King Abdulaziz City for Science and Technology (KACST) and Northwestern University (NU). The authors would like to thank both KACST and NU for their continued support of this research. This work was also supported by the US National Science Foundation (NSF) under grant no. CHE-1565925 (M.R.W.). W.A.G. gratefully acknowledges support (EFRI-1332411) from the NSF. Y.W. thanks the Fulbright Scholar Program for a Research Fellowship and gratefully acknowledges support from a Ryan Fellowship awarded by the NU International Institute of Nanotechnology (IIN).

REFERENCES


(36) Characterization by UV-Vis and EPR spectroscopy of the entire range of redox states occupied by the [2]catenanes from 4+ to 0 was carried out in MeCN because (i) the reducing agent, cobaltocene, (ii) the 4PF$_6^-$ salts of the fully oxidized catenanes 1$^{4+}$ and 2$^{4+}$, and (iii) their partially reduced charged species, i.e., 1$^{3+}$, 1$^{2(+)2}$, 2$^{3+}$, 2$^{2(+)2}$, and 2$^{+}$ are readily soluble in MeCN while (iv) the neutral catenanes 1$^0$ and 2$^0$ are also soluble in MeCN, albeit at low concentrations (0.25 mM).

(37) In an attempt to overcome the solubility issues and at the same time be able to use the same solvent for charged and neutral catenanes, the 4PF$_6^-$ counterions of the fully oxidized
Catenanes were exchanged with apolar non-coordinating bulky counterions such as tetrakis[3,5-bis(trifluoromethyl)phenyl]borate and tetrakis(pentafluorophenyl)borate.


(40) Upon changing the pH of the aqueous medium from pH 7 to 8–9, the reduction potential of Zn of –0.76 V decreases to –1.34 to –1.92 V. Since 1•4Cl and 2•4Cl are readily soluble in H2O and stable in aqueous CO32−/HCO3− buffer at pH 8–9, the reduction potential of 14+ and 24+ going to the neutral state can be reached in this buffer using activated Zn as the reducing agent. Also, since 10 and 20 are completely insoluble in H2O (D2O), they can be extracted into C6D5CD3 prior to recording their NMR spectra.


(43) Freshly generated crystals of 1•3PF6 and 2•3PF6 are stable for almost 12 h under ambient conditions. After this time, a decrease in intensity of the color of the crystals is observed and the solids become colorless in one day. In comparison to other crystals containing bipyridinium radical cations, that have shorter lifetimes, the stability of the radical species of the tetracationic monoradical catenanes is achieved by the close packing of the BIPY units within the catenane framework.


(47) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.;

    **2007**, *111*, 8753‒8765.

(49) (a) Li, H.; Cheng, C. Y.; McGonigal, P. R.; Fahrenbach, A. C.; Frasconi, M.; Liu, W. G.; Zhu, Z.;
    Zhao, Y. L.; Ke, C. F.; Lei, J. Y.; Young, R. M.; Dyar, S. M.; Co, D. T.; Yang, Y. W.; Botros, Y. Y.;
    **2013**, *135*, 18609‒18620. (b) McGonigal, P. R.; Li, H.; Cheng, C.; Schneebeli, S. T.;

(50) (a) Kato, K.; Yasuda, T.; Ito, K. *Macromolecules* **2013**, *46*, 310‒316. (b) Imran, A. B.; Esaki,
CAPTIONS TO FIGURES

Figure 1. Structural formulas (top) and solid-state structures (bottom) of the cyclophane in its tetracationic CBPQT$^{4+}$ (blue), the diradical dicationic CBPQT$^{2+}$ (purple) and the fully neutral CBPQT$^0$ (red) forms. Plan view of the rings as tubular representations with distances, angles and bond lengths summarizing the rings’ geometry in their three different oxidation states.

Figure 2. Schematic representation of the redox processes associated with the donor-acceptor [2]catenanes 1$^{4+}$ and 2$^{4+}$ comprising the redox-active CBPQT$^{4+}$ cyclophane and the DNP38C10 or BPP34C10 crown ether, respectively. Upon reduction, the fully charged species undergoes two consecutive reversible one-electron processes, affording the tricationic monoradical and the diradical dicationic states, followed by a third reduction involving two electrons, yielding the fully neutral catenane. The redox potentials were measured (see ref. 18) in MeCN solution versus a SCE reference.

Figure 3. UV–Vis Absorption spectra of 1•4PF$_6$ (a) and 2•4PF$_6$ (b) recorded in Ar-purged MeCN solutions (100 $\mu$M) at 298 K along with their reduced states upon addition of 1.0, 2.0, 3.0 and 4.0 equiv of CoCp$_2$.

Figure 4. Continuous-wave EPR spectra of (a) 1•4PF$_6$ and (b) 2•4PF$_6$ (250 $\mu$M in MeCN at 298K) and their reduced species obtained after addition of 1.0, 2.0, 3.0 and 4.0 equiv of CoCp$_2$ to Ar-purged MeCN solutions.

Figure 5. $^1$H NMR spectra (600 MHz, C$_6$D$_5$CD$_3$, 298 K) of the neutral CBPQT$^0$ (a) and 2$^0$ (b). Assignments of the resonances of the neutral catenane have been confirmed with the assistance of data from 2D $^1$H–$^1$H COSY experiments. See the Supporting Information.
Figure 6. Solid-state (super)structure of the neutral $1^0$ obtained from single-crystal X-ray crystallography. (a) Space-filling representation of the catenane from a perspective view, highlighting the encirclement of the neutral CBPQT$^0$ (pink) ring around the ethylene glycol chain of the DNP38C10 component (red) with both 1,5-dinaphtho units lying outside the ring. (b) Side-on view of catenane $1^0$ in a tubular representation, showing the [CH····π] distances between the hydrogen atoms (yellow) of the polyether loop and the phenylene units of the ring. (c) Top-view of the long-range packing of neutral catenanes represented in a tubular format showing the intermolecular [CH····π] interactions between the hydrogens of the phenylene rings in CBPQT$^0$ and the 1,5-dinaphtho units in the neighboring catenanes.

Figure 7. Solid-state structures of the fully oxidized $2^{4+}$ and the neutral $2^0$ in tubular representations displaying different interactions present in the catenanes, from an ordered donor-acceptor stack to a structure with a BPP34C10 ring that is capable of free movement with respect to the CBPQT$^0$ ring. The counterions, PF$_6^-$, have been omitted for the sake of clarity. Only one co-conformation of $2^0$, which is present as four co-conformations in the solid-state, is shown. See the Supporting Information.

Figure 8. Perspective (a,c) and top (b,d) views employing tubular representations of the solid-state structure of $1'^3+$ (a,b) and $2'^3+$ (c,d). The bond lengths and the torsional angles associated with the alongside bipyridinium unit reflect its radical cationic nature, while the one encircled by two DNP or HQ units is in the dicationic state. The counterions, PF$_6^-$, have been omitted for the sake of clarity.

Figure 9. Solid-state superstructure of the $2'^3+$ catenane in a space-filling representation showing the radical-radical π····π stacking interaction between the alongside BIPY$^{++}$ units of the catenanes. The face-to-face distance between the radical cations is 3.22 Å. The PF$_6^-$ counterions and solvent molecules have been omitted for the sake of clarity.
Figure 1

[Diagram showing X-Ray Crystal Structures of CBPQT$^{4+}$, CBPQT$^{2(+)}$, and CBPQT$^{0}$]
Figure 2

1$^{4+}$ $\rightarrow$ e$^-$ $\rightarrow$ 1$^{1+/3+}$ $\rightarrow$ e$^-$ $\rightarrow$ 1$^{2(++)}$ $\rightarrow$ 2e$^-$ $\rightarrow$ 1$^0$

$E_1 = -404$ mV

1$^{1+/3+}$ $\leftrightarrow$ e$^-$ $\leftrightarrow$ 1$^{2(++)}$ $\leftrightarrow$ 2e$^-$ $\leftrightarrow$ 1$^0$

$E_1' = -622$ mV

2$^{4+}$ $\rightarrow$ e$^-$ $\rightarrow$ 2$^{1+/3+}$ $\rightarrow$ e$^-$ $\rightarrow$ 2$^{2(++)}$ $\rightarrow$ 2e$^-$ $\rightarrow$ 2$^0$

$E_1 = -360$ mV

$E_1' = -487$ mV

$E_2 = -895$ mV

$E_2 = -911$ mV

Tetracationic Catenane

Tricationic Monoradical Catenane

Dicationic Diradical Catenane

Neutral Catenane
Figure 3

(a) Absorbance vs. wavelength for various concentrations of Eq CoCp₂. The peaks at 625 nm are highlighted for each concentration level.

(b) Similar absorbance vs. wavelength plot for another compound, with peaks at 625 nm also marked for different concentration levels.
Figure 4

a) Eq CoCp$_2$

b) Eq CoCp$_2$
Figure 8
Table 1. Calculated Energy Differences (A–B) Between the Co-Conformation of CBPQT Residing on the BPP/ DNP Groups (A) or on the Glycol Chain (B) at Different Charge States.\textsuperscript{a}

<table>
<thead>
<tr>
<th>[2]Catenane</th>
<th>Charges on CBPQT\textsuperscript{n+}</th>
<th>4+</th>
<th>3+</th>
<th>2+</th>
<th>1+</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{n+}</td>
<td></td>
<td>−46.1</td>
<td>−40.6</td>
<td>−28.8</td>
<td>−22.8</td>
<td>0.5</td>
</tr>
<tr>
<td>2\textsuperscript{n+}</td>
<td></td>
<td>−36.7</td>
<td>−29.4</td>
<td>−12.8</td>
<td>7.3</td>
<td>14.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Energy in kcal mol\textsuperscript{−1}.
Table 2. Energy Decomposition Analysis of the Calculated Interaction Energies between the CBPQT Residing on the DNP Unit or the Glycol (GLY) Chain of the DNP38C10 Macrocycle at Different Charge States in Vacuum. a

<table>
<thead>
<tr>
<th>Catenane 1\textsuperscript{n+}</th>
<th>Charges on CBPQT\textsuperscript{n+}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4+</td>
</tr>
<tr>
<td>Location of CBPQT\textsuperscript{b}</td>
<td>DNP</td>
</tr>
<tr>
<td>CEC\textsuperscript{c}</td>
<td>-38.2</td>
</tr>
<tr>
<td>PO\textsuperscript{d}</td>
<td>-39.9</td>
</tr>
<tr>
<td>CT\textsuperscript{e}</td>
<td>-4.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Calculated at M06-HF/6-311G** level. Energy in kcal mol\textsuperscript{-1}. \textsuperscript{b}DNP: CBPQT ring encircles the DNP unit. GLY: CBPQT ring encircles the glycol chain. \textsuperscript{c}Coulomb and exchange-correlation (CEC): frozen density component as in reference 48. \textsuperscript{d}Polarization (PO): defined as the energy lowering due to the intramolecular relaxation of each molecule’s absolutely localized MOs in the field of all other molecules in the system. \textsuperscript{e}Charge-transfer (CT): defined as the energy lowering when the constraint of wave function localization is removed. The contribution from basis set superposition error is subtracted from this term.
X-Ray Crystal Structures

CBPQT$^{4+}$  
- $E_1 / \text{mV}$  
- $-328$

CBPQT$^{2(+)}$  
- $E_2 / \text{mV}$  
- $-753$

CBPQT$^{0}$  
-  
- $6.36 \text{ Å}$
- $6.81 \text{ Å}$
- $1.48 \text{ Å}$
- $21^\circ$

-  
- $6.58 \text{ Å}$
- $6.92 \text{ Å}$
- $1.43 \text{ Å}$
- $7^\circ$

-  
- $6.88 \text{ Å}$
- $6.99 \text{ Å}$
- $1.37 \text{ Å}$
- $8^\circ$
Tetracationic Catenane

1$^{4+}$

$E_1 = -404$ mV

Tricationic Monoradical

1$^{•/3+}$

$E_1' = -622$ mV

Dicationic Diradical Catenane

1$^{2(++)}$

$E_2 = -911$ mV

$2e^-$

Neutral Catenane

$2^0$

$E_2 = -895$ mV

$2e^-$

$E_1 = -360$ mV

$e^-$

$E_1' = -487$ mV

$e^-$

$E_1 = -404$ mV

$E_1' = -622$ mV

$e^-$
**a)**

The absorbance spectra for different concentrations of Eq CoCp$_2$ showing transitions between $1^0$, $1^{2(+)}$, $1^{2(+)}/1^0$, and $1^{4+}$.

<table>
<thead>
<tr>
<th>Number of Eq CoCp$_2$</th>
<th>Abs at 625 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

**b)**

The absorbance spectra for different concentrations of Eq CoCp$_2$ showing transitions between $2^0$, $2^{4+}$, $2^{2(+)}$, $2^{2(+)}/2^0$, and $2^{*3+}$.

<table>
<thead>
<tr>
<th>Number of Eq CoCp$_2$</th>
<th>Abs at 625 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>
(a) Eq CoCp₂

0
1
2
3
4

Magnetic Field / Gauss

(b) Eq CoCp₂

0
1
2
3
4

Magnetic Field / Gauss
2.67 Å
2.62 Å
2.68 Å
2.48 Å
2.67 Å
2.62 Å

C–H⋯π interactions