

Mechanical Bond-Assisted Full-Spectrum Investigation of Radical Interactions

Yang Jiao, Haochuan Mao, Yunyan Qiu, Guangcheng Wu, Hongliang Chen, Long Zhang, Han Han, Xuesong Li, Xingang Zhao, Chun Tang, Xiao-Yang Chen, Yuanning Feng, Charlotte L. Stern, Michael R. Wasielewski,* and J. Fraser Stoddart*



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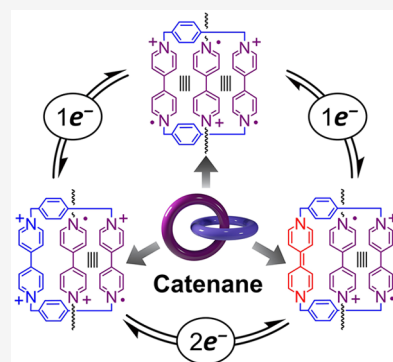


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ABSTRACT: Molecular recognition, based on noncovalent bonding interactions, plays a central role in directing supramolecular phenomena in both chemical and biological environments. The identification and investigation of weakly associated recognition motifs, however, remains a major challenge, especially when the motifs are interlinked with and obscured by other robust binding modes in complicated systems. For example, although the host–guest recognition between the radical cations of both cyclobis(paraquat-*p*-phenylene) (CBPQT) and 4,4'-bipyridinium (BIPY) salts has been thoroughly investigated, the question of whether other binding modes exist between these two positively charged entities is the subject of some debate because of the complexity and dynamic nature of this supramolecular system. In order to address this conundrum, we have synthesized a [2]catenane—formed by mechanical interlocking between CBPQT and another BIPY-containing ring—which enhances the weak interactions between components and reduces significantly the complexity of the system for easier characterization. By employing this [2]catenane as a model compound, we have performed a full-spectrum investigation of radical interactions and revealed unambiguously a total of three possible binding modes between CBPQT and BIPY—to be specific, a bisradical tetracationic, a trisradical tricationic, and a bisradical dicationic association—as demonstrated by various methods of characterization including UV/vis/NIR, EPR, and NMR spectroscopies, electrochemical measurements and X-ray crystallography. The two newly discovered bisradical binding modes have potential applications in the construction of self-assembled materials and in mediating supramolecular catalysis. The mechanical bond-assisted approach used in this research is broadly applicable to investigating noncovalent bonding interactions.



INTRODUCTION

Noncovalent bonding interactions^{1–4} lay the foundation for almost all the communications between molecules in chemical and biological systems, such as molecular recognition,^{5–8} self-assembly,^{9–13} signal transduction,^{14,15} and catalysis.^{16–20} Understanding these interactions not only can offer keys to mimicking^{21,22} the structural and functional aspects of living systems, but also can enrich the toolkit for advanced noncovalent syntheses.^{23–26} Whereas the dynamic nature of noncovalent bonding interactions is beneficial^{27–30} for the construction of smart materials with responsiveness and adaptivity, a large proportion of these interactions are weak, labile, and sometimes transient, making it difficult to characterize and investigate them in depth. Particularly when it comes to complicated supramolecular systems involving multiple interactions, the contribution of weak interactions tends to be obscured by stronger ones. As a result, the existence of weak interactions—as well as their indispensable roles in directing or regulating self-assembly processes—is likely to be overlooked. It follows that efficient strategies^{31–35}

are required for revealing the noncovalent bonding interactions with low binding strengths.

In 2010, we reported³⁶ the strong, selective host–guest recognition between the bisradical dication of cyclobis(paraquat-*p*-phenylene), namely CBPQT^{2(•+)}, and the radical cation of methyl viologen (MV^{•+}) that leads to the formation of a [MV^{•+}CBPQT]^{3(•+)} trisradical tricationic complex. Although the host and guest molecules—bearing one and two 4,4'-bipyridinium radical cations (BIPY^{•+}), respectively—are both positively charged, radical interactions^{37–39} between adjacent BIPY^{•+} units, driven by the pairing of single electrons, overwhelm Coulombic repulsion and thus render the noncovalent association overall to be thermodynamically favorable. Since its discovery⁴⁰ over a decade ago, this radically enhanced

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molecular recognition has been subjected to extensive applications, including (i) the templated synthesis^{41,42} of mechanically interlocked molecules, (ii) the fabrication^{43–45} of air-stable radicals, and (iii) the construction^{46–49} of artificial molecular machines. Considering that the host–guest system comprises three BIPY units with each of them having three redox states⁵⁰—i.e., dicationic, radical cationic and neutral states—we are left wondering if there could be any other binding modes between CBPQT and a BIPY derivative under different experimental conditions.

In an attempt to answer this question, we introduced (Figure 1) 1, 2, 3, 4, and 5 equiv, respectively, of cobaltocene (CoCp₂),

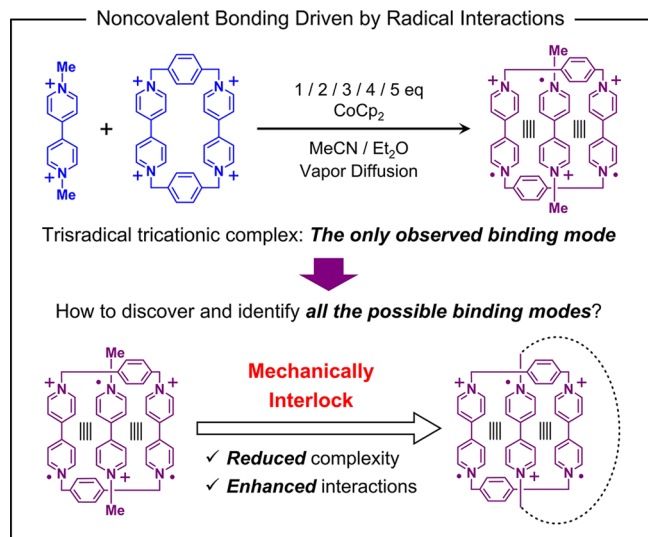


Figure 1. Design concept behind this research. In a host–guest system composed of CBPQT⁴⁺ and MV²⁺, the [MV₃CBPQT]^{3(•+)} trisradical tricationic complex is the only observable binding mode, as indicated by the results of X-ray crystallography performed on different redox states. In order to discover all other possible binding modes, we have constructed a mechanically interlocked [2]catenane for a full-spectrum investigation of the radical interactions.

a chemical reductant, into acetonitrile (MeCN) solutions containing equimolar amounts of CBPQT⁴⁺ and MV²⁺ as their hexafluorophosphate salts. The resulting solutions were subjected to vapor diffusion with diethyl ether (Et₂O), producing single crystals. Despite the differences in their redox states, all the samples afforded the same single crystal—namely the [MV₃CBPQT]^{3(•+)} trisradical tricationic complex. In other words, we failed to discover other binding modes in this supramolecular system. It is worth noting, however, that this system is a complicated network³⁹ composed of multiple sources of electron transfer and host–guest complexation that can result in the existence and interconversion of up to 13 species.⁵¹ Consequently, if the trisradical tricationic complex has the strongest binding affinity and crystallinity, this species will most likely stand out during crystallizations and behave as the dominant binding mode, while obscuring the presence of all the other recognition motifs.

Mechanically interlocked molecules^{52–54} (MIMs) can serve as a powerful platform (Figure 1) to study^{55,56} weak interactions because of their advantages over supramolecular systems in at least two aspects. On the one hand, the single-molecule nature of MIMs can reduce significantly the complexity of systems, providing increased convenience

when it comes to characterization. On the other hand, the nanoconfined environment,⁵⁷ created by mechanical bonds, is favorable for enhancing the weak interactions between components. Herein, by synthesizing⁴² a [2]catenane (Cat⁶⁺) model compound—in which a CBPQT⁴⁺ ring containing two BIPY²⁺ units and another ring (MC²⁺) bearing only one BIPY²⁺ unit are mechanically interlocked—we have performed a full-spectrum investigation of all the radical interactions⁵¹ in the context of tris-BIPY noncovalent systems. A total of three possible binding modes—to be specific, a bisradical tetracationic, a trisradical tricationic, and a bisradical dicationic association—have all been revealed and identified by running the gamut of characterization techniques including electrochemistry, UV/vis/near-infrared (NIR) spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and X-ray crystallography.

RESULTS AND DISCUSSION

Synthesis and Structural Identification. The [2]-catenane Cat-6PF₆ was synthesized (Figure 2a) using a modified radical-templation^{41,42} approach. CBPQT-4PF₆ and dibutynyl viologen (BV-2PF₆) were dissolved in MeCN and reduced by excess Cu dust in a N₂-filled glovebox for 4 h, leading to the formation of [BV₂CBPQT]^{3(•+)} trisradical tricationic complex. The mixture was treated with 1,12-diazidododecane and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), and copper(I)-catalyzed alkyne–azide cycloaddition was conducted at room temperature for 6 days before being oxidized by nitrosonium hexafluorophosphate (NOPF₆). Purification using reversed-phase column chromatography, followed by a counterion exchange from CF₃COO[−] to PF₆[−], afforded Cat-6PF₆ in 46% overall yield. Notably, the use of an aliphatic diazide is intended to avoid the introduction of additional aromatic interactions, so that only intrinsic binding modes between the three BIPY units can be detected in the [2]catenane. A macrocyclic control compound (MC-2PF₆) was also synthesized (Figure 2a) in 30% yield by performing copper(I)-catalyzed alkyne–azide cycloaddition between BV-2PF₆ and 1,12-diazidododecane in the absence of CBPQT-4PF₆. This macrocyclization, which occurs in acetone (Me₂CO), involves the use of tris(benzyl-triazolylmethyl)amine (TBTA) and Cu(MeCN)₄PF₆ as a catalyst.

The structural formula, purity, and co-conformation of Cat⁶⁺ were investigated by a variety of NMR spectroscopic techniques (Figure 2b and Figures S1–S4). Compared with MC²⁺, the signals for protons 8–11 in Cat⁶⁺ show dramatic upfield shifts, indicating that the oligomethylene chain in the MC²⁺ ring is encircled by the CBPQT⁴⁺ ring. This co-conformation, which is a result of the Coulombic repulsion between three BIPY²⁺ units, was further confirmed by a ¹H NOESY spectrum (Figure S4) wherein the spatial proximity between the CBPQT⁴⁺ ring and the oligomethylene chain is evident. In the DOSY NMR spectra (Figure S8), Cat⁶⁺ exhibits only one diffusion coefficient in CD₃CN, verifying the mechanically interlocked nature of the [2]catenane. Moreover, we have obtained high-quality single crystals (Figure 2c) of Cat-6PF₆ under ambient conditions for X-ray crystallographic analysis. In the solid-state structure, six PF₆[−] anions surround the cationic [2]catenane, and the CBPQT⁴⁺ ring is indeed located in the middle of the chain in the MC²⁺ ring so as to minimize Coulombic repulsions.

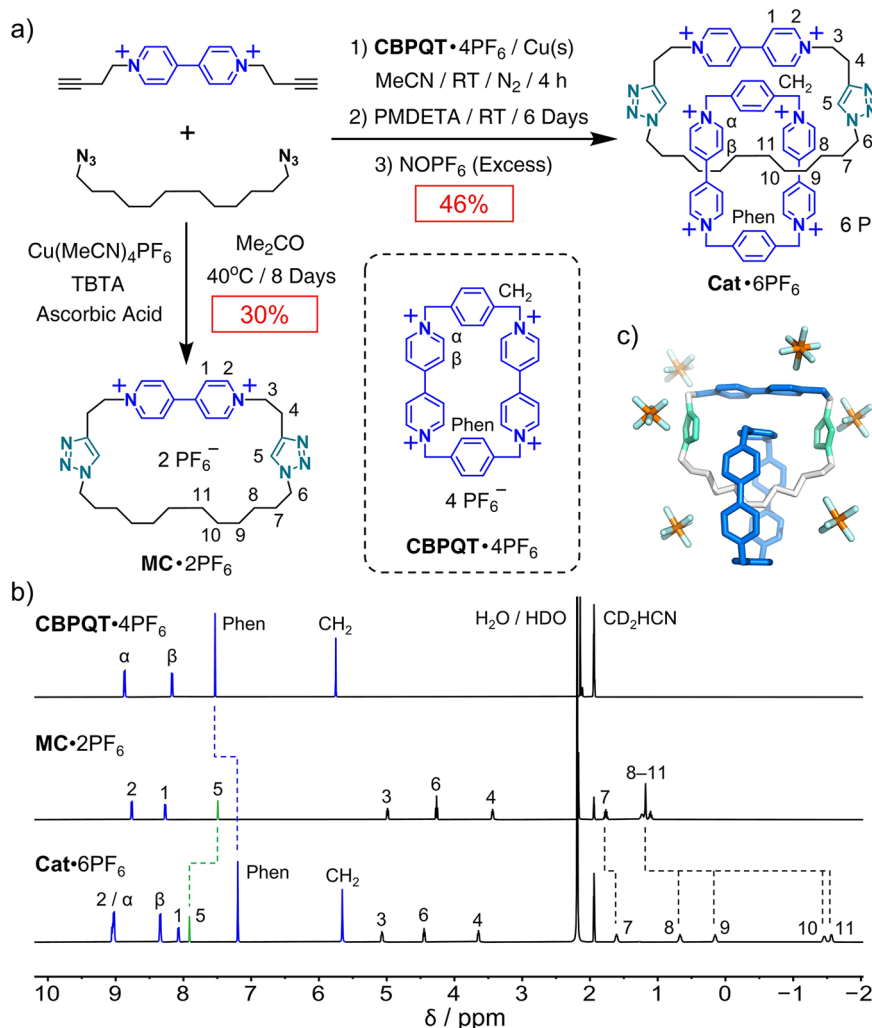


Figure 2. (a) Syntheses of the [2]catenane **Cat-6PF₆** and a macrocyclic control compound **MC-2PF₆** using copper(I)-catalyzed alkyne–azide cycloaddition. (b) Stacked ¹H NMR spectra (500 MHz, CD₃CN, 298 K) of **CBPQT-4PF₆**, **MC-2PF₆** and **Cat-6PF₆**. (c) The single-crystal structure of **Cat-6PF₆** confirming its co-conformation in the solid state. Hydrogen atoms are omitted for the sake of clarity.

Electrochemistry and UV/vis/NIR Spectroscopy. The redox properties of **Cat**⁶⁺, which were investigated (Figure 3) by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), can be compared with the redox properties of its component rings **CBPQT**⁴⁺ and **MC**²⁺. The CV traces for both **CBPQT**⁴⁺ and **MC**²⁺ are relatively simple, comprising two well-defined peaks corresponding to the stepwise reduction from BIPY²⁺ to BIPY^{•+} and then to BIPY⁽⁰⁾. In contrast, both the CV and DPV data for **Cat**⁶⁺ display four reversible reduction peaks with an intensity ratio of approximately 2:1:1:2, indicating the acceptance of six electrons by **Cat**⁶⁺ in a 2e[−]/1e[−]/1e[−]/2e[−] sequence to generate a total of five accessible redox states. Moreover, the mechanical bonding between **CBPQT**⁴⁺ and **MC**²⁺ rings has a clear influence on the redox potentials of BIPY²⁺ units. On the one hand, the first two reduction peaks in the case of **Cat**⁶⁺ at −0.09 and −0.25 V versus Ag/AgCl are positively shifted, compared with the first reduction peak from BIPY²⁺ to BIPY^{•+} for either **CBPQT**⁴⁺ (−0.30 V) or **MC**²⁺ (−0.37 V). On the other hand, the fourth reduction peak in the case of **Cat**⁶⁺ at −1.01 V is more negative than the second reduction peak from BIPY^{•+} to BIPY⁽⁰⁾ for either **CBPQT**⁴⁺ (−0.73 V) or **MC**²⁺ (−0.81 V). These changes in redox potentials suggest the presence of more than

one binding mode within the [2]catenane as well as their stabilizing effects^{39,58} on BIPY^{•+} radical cations toward both oxidation and reduction.

In order to access all the possible binding modes under different redox states, we performed (Figures 4 and 5) a titration on **Cat**⁶⁺ using CoCp₂ and monitored the process by UV/vis/NIR spectroscopy. The overall titration can be divided into four stages: the first two stages involve the reduction (Figure 4a) of three BIPY²⁺ units to BIPY^{•+} radical cations. Prior to Stage 1 (Figure 4b), the MeCN solution of **Cat-6PF₆** is colorless and has no absorption in the visible or NIR region. With the addition of 2 equiv of CoCp₂, the color of the solution changes to magenta, accompanied by a gradual increase in an absorption peaked at 520 nm. These changes indicate the transformation from **Cat**⁶⁺ to **Cat**^{2+2(•+)}, during which two of the three BIPY²⁺ units are reduced to BIPY^{•+} radical cations. Whereas the absorption at 865 nm signifies^{59,60} the formation of (BIPY^{•+})₂ radical dimers, a more pronounced and red-shifted NIR absorption band appears at around 1900 nm, confirming the presence of noncovalent interactions within **Cat**^{2+2(•+)} not only between the two BIPY^{•+} radical cations but also between the radical dimer and the remaining BIPY²⁺ unit. In other words, the bisradical tetracationic state of

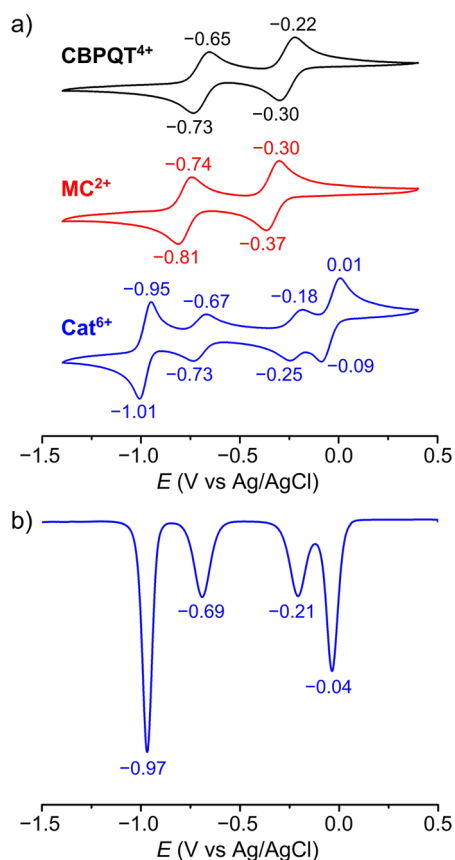


Figure 3. (a) Cyclic voltammograms of CBPQT⁴⁺, MC²⁺, and Cat⁶⁺. (b) Differential pulse voltammogram of Cat⁶⁺. All the electrochemical measurements were performed in MeCN (1.0 mM) with 0.1 M TBAPF₆ as the supporting electrolyte and Ag/AgCl as the reference electrode.

this [2]catenane could be a mixed-valence^{61–63} compound wherein two electrons and four positive charges are shared by

three BIPY units, leading to the emergence of an extremely narrow HOMO/LUMO band gap. Moreover, based on the linear relationship between the NIR absorbance of the solution and the amount of added CoCp₂, we can claim the absence of intermediates between Cat⁶⁺ and Cat^{2+2(•+)}.

In Stage 2 (Figure 4c) of the titration, 1 equiv of CoCp₂ was added to the MeCN solution, resulting in its color changing from magenta to purple. Correspondingly, the absorption band ($\lambda_{\text{max}} = 1900$ nm) of the bisradical tetracationic state was found to decrease gradually, accompanied by the appearance and increase of the characteristic absorption⁵⁸ ($\lambda_{\text{max}} = 1080$ nm) for the trisradical tricationic state with an isosbestic point at 1276 nm. This spectral evolution supports the transformation from Cat^{2+2(•+)} to Cat^{3(•+)}, in which the only remaining BIPY²⁺ unit is also reduced to a BIPY^{•+} radical cation so that the system reaches a full radical state rather than a mixed-valence state.

Stages 3 and 4 of the titration involve the reduction (Figure 5a) of three BIPY^{•+} radical cations to BIPY⁽⁰⁾ neutral states. In Stage 3 (Figure 5b), one more equivalent of CoCp₂ was introduced, leading to the solution changing color from purple to brown. The NIR absorption of Cat^{3(•+)} at 1080 nm decreases, along with the appearance of a new, red-shifted NIR absorption band at 1630 nm as well as the observation of an isosbestic point at 1220 nm. Concurrently, the visible absorption by Cat^{3(•+)} at 535 nm undergoes a blue shift to 462 nm with an isosbestic point at 508 nm, suggesting⁵⁰ that one-third of the BIPY^{•+} radical cations in Cat^{3(•+)} are reduced to BIPY⁽⁰⁾ in order to allow for the formation of a bisradical dicationic state—namely Cat^{2(•+)}. In common with another bisradical state Cat^{2+2(•+)}, Cat^{2(•+)} is also a mixed-valence compound in which two electrons and two positive charges are shared by three BIPY units. As a result, the HOMO/LUMO band gap for Cat^{2(•+)} is narrower than that associated with the Cat^{3(•+)} trisradical tricationic state.

In Stage 4 (Figure 5c) of the titration, much more than two (even above 20) equivalents of CoCp₂ are required to reduce

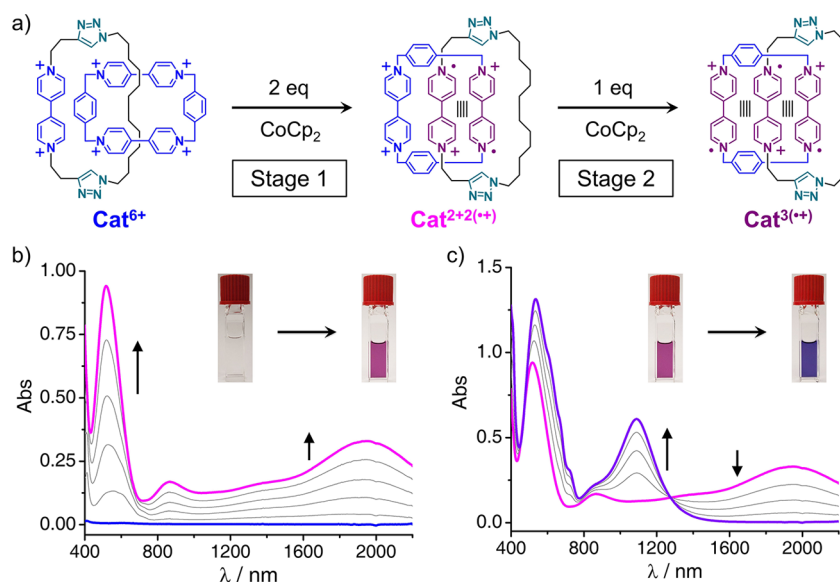


Figure 4. First two stages of the titration of Cat⁶⁺ with CoCp₂ monitored by UV/vis/NIR spectroscopy. (a) The transformation from Cat⁶⁺ to Cat^{2+2(•+)} and then to Cat^{3(•+)} during Stages 1 and 2 of the titration with CoCp₂. (b) The evolution of UV/vis/NIR spectra during Stage 1. (c) The evolution of UV/vis/NIR spectra during Stage 2. Photographs of the MeCN solutions before and after Stages 1 and 2 in the titration are portrayed above the corresponding UV/vis/NIR spectra, showing the color changes caused by chemical reduction.

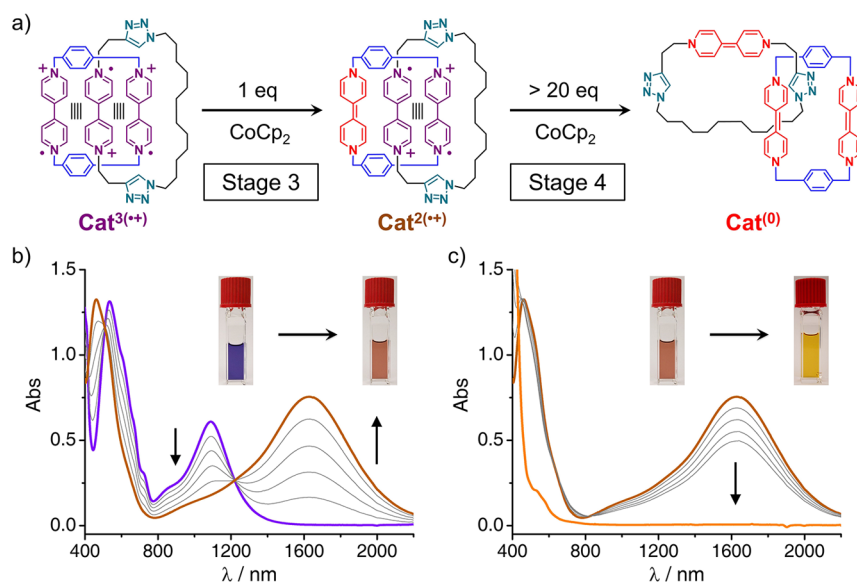


Figure 5. Last two stages of the titration of Cat^{6+} with CoCp_2 monitored by UV/vis/NIR spectroscopy. (a) The transformation from $\text{Cat}^{3(\bullet+)}$ to $\text{Cat}^{2(\bullet+)}$ and finally to $\text{Cat}^{(0)}$ during Stages 3 and 4 of the titration with CoCp_2 . (b) The evolution of UV/vis/NIR spectra during Stage 3. (c) The evolution of UV/vis/NIR spectra during Stage 4, in which complete disappearance of the NIR absorption was observed after introducing a large excess of CoCp_2 or two equivalents of $\text{Co}(\text{Cp}^*)_2$ (decamethylcobaltocene). Photographs of the MeCN solutions before and after Stages 3 and 4 in the titration are portrayed above the corresponding UV/vis/NIR spectra, showing the color changes caused by chemical reduction.

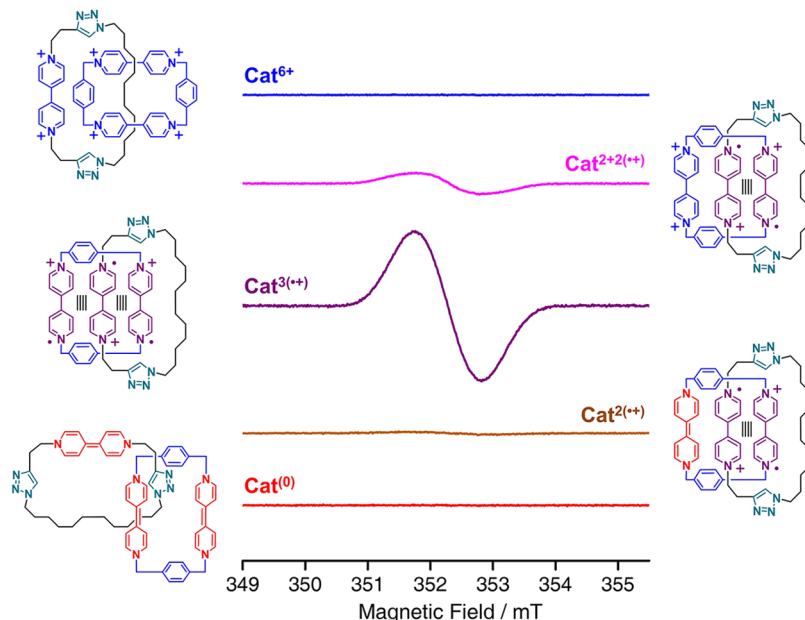


Figure 6. Stacked EPR spectra of Cat^{6+} , $\text{Cat}^{2+2(\bullet+)}$, $\text{Cat}^{3(\bullet+)}$, $\text{Cat}^{2(\bullet+)}$, and $\text{Cat}^{(0)}$ recorded in MeCN solutions (1.0 mM) at room temperature, illustrating their different magnetic properties.

all the remaining $\text{BIPY}^{\bullet+}$ radical cations to $\text{BIPY}^{(0)}$ neutral states. This observation is reasonable, given the fact that the redox potential⁶⁴ of CoCp_2 (-0.91 V versus Ag/AgCl) is slightly more positive than the last reduction peak of Cat^{6+} , i.e., -0.97 V versus Ag/AgCl according to the DPV data in Figure 3b. With the addition of CoCp_2 , the absorption of $\text{Cat}^{2(\bullet+)}$ at 1630 nm declines gradually, and no new NIR absorption bands appear, ruling out the possibility of other mixed-valence states formed between $\text{Cat}^{2(\bullet+)}$ and $\text{Cat}^{(0)}$. In order to achieve quantitative reduction, CoCp_2 was replaced by decamethylcobaltocene— $\text{Co}(\text{Cp}^*)_2$, a more powerful reductant with a redox potential⁶⁴ of -1.51 V versus Ag/AgCl . Accordingly, 2

equiv of $\text{Co}(\text{Cp}^*)_2$ are sufficient (Figure S19) for the transformation from $\text{Cat}^{2(\bullet+)}$ to $\text{Cat}^{(0)}$ as evidenced by the complete disappearance of NIR absorption bands as well as a color change of the solution from brown to yellow. The co-conformation of $\text{Cat}^{(0)}$ was investigated by comparing its ^1H NMR spectrum (Figure S9) with the spectra obtained for $\text{CBPQT}^{(0)}$ and $\text{MC}^{(0)}$. From an analysis of the changes in chemical shifts, the $\text{CBPQT}^{(0)}$ ring in $\text{Cat}^{(0)}$ resides most likely on one of the triazole units rather than remaining on the $\text{BIPY}^{(0)}$ site. This result indicates the complete loss of attractive noncovalent interactions between CBPQT and BIPY moieties when both of them reach their neutral states.

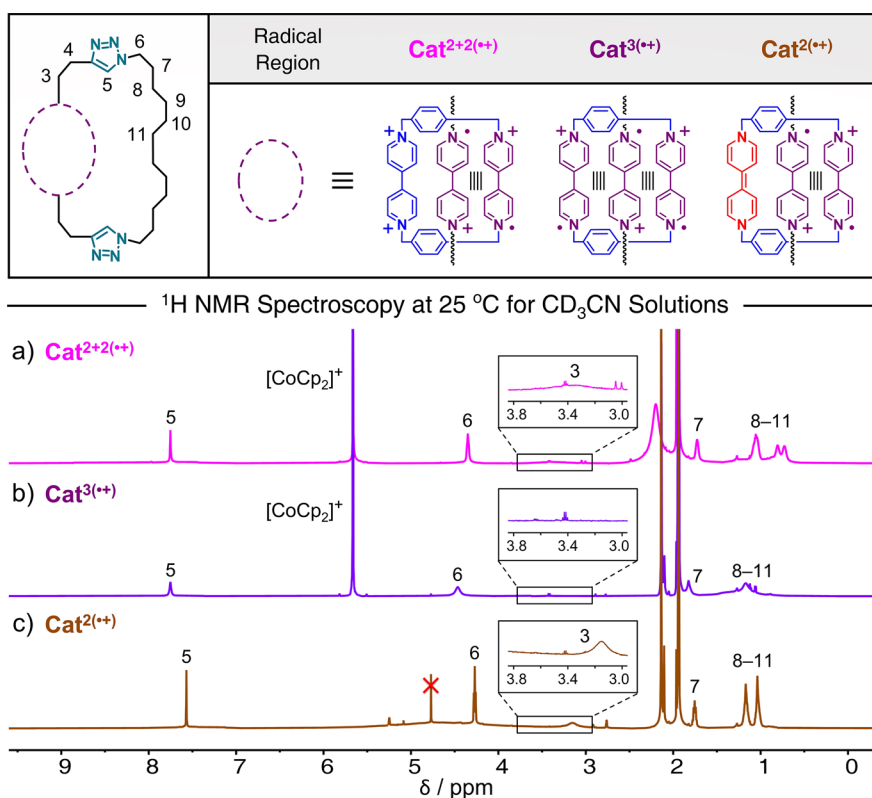


Figure 7. ^1H NMR Spectra (600 MHz, CD_3CN , 298 K) of (a) $\text{Cat}^{2+2(\bullet+)}$, (b) $\text{Cat}^{3(\bullet+)}$, and (c) $\text{Cat}^{2(\bullet+)}$, the three radical states of the [2]catenane. Signals for the protons in the “radical region”—which is defined as a combination of the CBPQT ring and the BIPY unit in the MC ring—are not observable in these spectra at room temperature. The partial spectra from 3.0 to 3.8 ppm are magnified as insets in order to show the presence or absence of the signal for proton 3.

Instead, the electron-rich CBPQT⁽⁰⁾ ring prefers to bind with the slightly electron-deficient triazole unit on account of weak charge transfer interactions.

In summary, five electrochemically accessible redox states of the [2]catenane—i.e., Cat^{6+} , $\text{Cat}^{2+2(\bullet+)}$, $\text{Cat}^{3(\bullet+)}$, $\text{Cat}^{2(\bullet+)}$, and $\text{Cat}^{(0)}$ —have been generated by chemical means and identified by UV/vis/NIR spectroscopy. Three of these states exhibit remarkable and divergent NIR absorptions, as a result of different binding modes between the CBPQT ring and the BIPY unit in the MC ring. In contrast with the previously reported³⁶ triradical binding mode which is present in $\text{Cat}^{3(\bullet+)}$ and involves only radical interactions, the bisradical binding modes present in $\text{Cat}^{2+2(\bullet+)}$ and $\text{Cat}^{2(\bullet+)}$ incorporate two types of noncovalent interactions: (i) a radical-pairing interaction between two BIPY^{•+} radical cations and (ii) a charge transfer interaction between the (BIPY^{•+})₂ radical dimer and a BIPY²⁺ unit (in the case of $\text{Cat}^{2+2(\bullet+)}$) or a BIPY⁽⁰⁾ unit (in the case of $\text{Cat}^{2(\bullet+)}$). From this perspective, radical species are potentially ambident when involved in charge transfer interactions: they can serve either as a donor or as an acceptor, depending on the electronic properties of the aromatic units with which they interact. In terms of the redox reversibility of this [2]catenane, the transformations between any two states among Cat^{6+} , $\text{Cat}^{2+2(\bullet+)}$, $\text{Cat}^{3(\bullet+)}$, and $\text{Cat}^{2(\bullet+)}$ are completely reversible. A fly in the ointment, however, is the poor chemical stability (Figure S9) of $\text{Cat}^{(0)}$, especially the long-term stability. As a result, after being reduced to $\text{Cat}^{(0)}$, not all the [2]catenane molecules can be recovered as Cat^{6+} even if treated with sufficient amounts of oxidants.

EPR and NMR Spectroscopy. EPR Spectra of the [2]catenane in different redox states were recorded (Figure 6) in order to compare their magnetic properties. Both Cat^{6+} and $\text{Cat}^{(0)}$ are completely EPR silent, in line with their diamagnetic nature and absence of radical species. By contrast, the three radical states—i.e., $\text{Cat}^{2+2(\bullet+)}$, $\text{Cat}^{3(\bullet+)}$, and $\text{Cat}^{2(\bullet+)}$ —exhibit EPR signals with very different intensities. The signal for $\text{Cat}^{3(\bullet+)}$ is broad with considerable intensity as a result of the odd number of unpaired electrons. The lack of hyperfine splitting is indicative of the spin exchange among three BIPY^{•+} radical cations, consistent with the previous observation of the [MVCBPQT]^{3(•+)} triradical tricationic complex in the literature.³⁶ The intensity of the EPR signal for $\text{Cat}^{2+2(\bullet+)}$ was found to be much lower than two-thirds of that for $\text{Cat}^{3(\bullet+)}$, an observation which can be attributed to the formation of a singlet radical dimer through antiferromagnetic coupling between two adjacent BIPY^{•+} radical cations. The residual EPR signal for this bisradical tetracation may result⁶⁵ from a slight disproportionation (Figure S15) of $\text{Cat}^{2+2(\bullet+)}$ leading to the formation of $\text{Cat}^{3(\bullet+)}$ and Cat^{6+} . Further attenuation of the EPR signal was observed in the spectrum of $\text{Cat}^{2(\bullet+)}$. It means that, compared with $\text{Cat}^{2+2(\bullet+)}$, the radical interaction in $\text{Cat}^{2(\bullet+)}$ is much stronger and so this bisradical dication behaves more diamagnetically.

^1H NMR spectroscopy was employed to investigate the structural information on the [2]catenane under different redox states. To produce $\text{Cat}^{2+2(\bullet+)}$, $\text{Cat}^{3(\bullet+)}$, and $\text{Cat}^{2(\bullet+)}$, respectively, 2, 3, and 4 equiv of CoCp_2 were added to a CD_3CN solution of Cat^{6+} . In all the ^1H NMR spectra (Figure 7) collected at 25 °C, we did not observe any signals for the

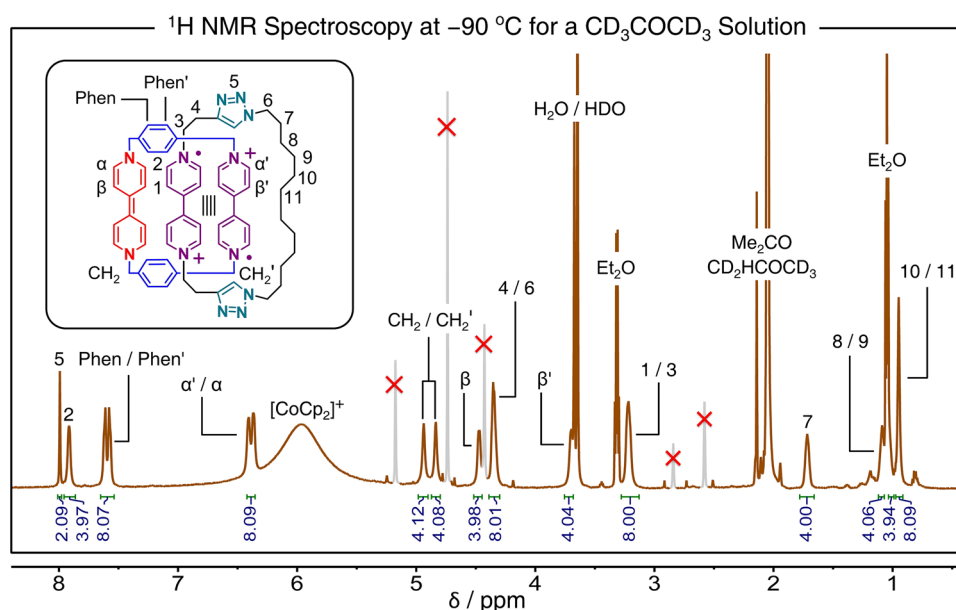


Figure 8. An annotated low-temperature ^1H NMR spectrum (600 MHz, CD_3COCD_3 , 183 K) of $\text{Cat}^{2(\bullet+)}$ containing well-resolved signals for all the protons in this [2]catenane.

protons from either the CBPQT ring or the BIPY unit in the MC ring. Protons 5–11 distant from aromatic moieties, however, give rise to observable resonances. These observations indicate that noncovalent association occurs between the CBPQT ring and the BIPY unit in the MC ring under all three of these redox states, constituting a confined “radical region” that is NMR silent at room temperature. By comparison, the NMR signals for protons 5–11 in $\text{Cat}^{3(\bullet+)}$ are broadest and of lowest intensity among the three redox states, followed by those in $\text{Cat}^{2+2(\bullet+)}$, while these protons in $\text{Cat}^{2(\bullet+)}$ display the sharpest signals with multiplicity. Moreover, proton 3 which is closer to the radical region turns out to be invisible in the ^1H NMR spectrum of $\text{Cat}^{3(\bullet+)}$, hardly visible in the spectrum of $\text{Cat}^{2+2(\bullet+)}$, but relatively pronounced in the spectrum of $\text{Cat}^{2(\bullet+)}$. These comparisons of ^1H NMR spectra are consistent with the EPR results (Figure 6), revealing jointly the order of paramagnetism for different redox states of the [2]catenane as follows: $\text{Cat}^{3(\bullet+)} > \text{Cat}^{2+2(\bullet+)} > \text{Cat}^{2(\bullet+)}$.

Furthermore, variable temperature ^1H NMR spectra obtained for $\text{Cat}^{2+2(\bullet+)}$, $\text{Cat}^{3(\bullet+)}$, and $\text{Cat}^{2(\bullet+)}$ were also collected (Figures S12–S14) in CD_3CN by lowering the temperature stepwise from +40 to -40 °C. On account of the remarkable paramagnetism of $\text{Cat}^{3(\bullet+)}$, its ^1H NMR spectrum remains unchanged regardless of temperature. By contrast, the ^1H NMR signals for $\text{Cat}^{2+2(\bullet+)}$, particularly the resonance arising from proton 3, become increasingly sharp and observable along with the decrease in temperature. Notably, at -40 °C, a broad signal appears in the range 7.0–8.5 ppm: presumably it results from some aromatic protons in the radical region of $\text{Cat}^{2+2(\bullet+)}$. Similar but more significant changes were noted in the ^1H NMR spectrum of $\text{Cat}^{2(\bullet+)}$ recorded at low temperatures, where a number of broad signals—corresponding to the protons in the radical region—emerge gradually over a wide range from 3.0 to 8.0 ppm.

In attempts to resolve all the resonances associated with the protons in $\text{Cat}^{2+2(\bullet+)}$ and $\text{Cat}^{2(\bullet+)}$, we have performed ^1H NMR spectroscopic analysis on these bisradical states at -90 °C—a much lower temperature that we have accessed by changing the solvent from CD_3CN to CD_3COCD_3 . The

experiment we carried out on $\text{Cat}^{2+2(\bullet+)}$ afforded a complicated ^1H NMR spectrum: it may be that the disproportionation of $\text{Cat}^{2+2(\bullet+)}$ is enhanced at low temperatures, producing NMR-observable amounts of $\text{Cat}^{3(\bullet+)}$ and Cat^{6+} . See Figure S15 and related discussions in the Supporting Information for details. In contrast, $\text{Cat}^{2(\bullet+)}$ exhibits (Figure 8) a well-defined ^1H NMR spectrum at -90 °C. The resonances in this spectrum have been assigned through a global analysis of (i) the chemical shift of each type of protons, (ii) the integral of each resonance, and (iii) correlation signals shown in the ^1H – ^1H COSY spectrum (Figure S18). The signal for proton 1 displays a remarkable upfield shift to 3.2 ppm, an observation supporting the proposed co-conformation of $\text{Cat}^{2(\bullet+)}$ where the BIPY unit in the MC ring is encapsulated by the CBPQT ring on account of radical interactions. Proton 2 that is next to proton 1, however, gives rise to a signal with the usual chemical shift (7.9 ppm) for pyridinium protons, suggesting that proton 2 is not located in a highly shielded chemical environment. This finding is indicative of a nearly perpendicular alignment between the CBPQT ring and the BIPY unit, an energetically favorable geometry according to theoretical predictions⁶⁰ involving radical interactions.

All the protons belonging to the CBPQT ring are separated into two sets of signals, suggesting the asymmetric structure of $\text{Cat}^{2(\bullet+)}$ —to be specific, one BIPY unit of the CBPQT ring is located inside the cavity of the MC ring, while the other one is outside—as well as the slow circumrotation and/or pirouetting motions of component rings with respect to each other at -90 °C. Meanwhile, the through-space hopping of electrons in $\text{Cat}^{2(\bullet+)}$ is still very fast at this temperature. It follows that the redox states of three BIPY units are indistinguishable on the ^1H NMR time scale, although they are drawn in the form as one $\text{BIPY}^{(0)}$ and two $\text{BIPY}^{\bullet+}$ units in Figure 8. This assumption is validated by the minor differences between the chemical shifts of protons α and α' ($\Delta\delta = 0.04$ ppm), protons Phen and Phen' ($\Delta\delta = 0.03$ ppm) and protons CH_2 and CH_2' ($\Delta\delta = 0.10$ ppm). Exceptionally, the signal for proton β' shows a large upfield shift ($\Delta\delta = 0.78$ ppm) compared with that for proton β . This observation can be rationalized by the fact that proton

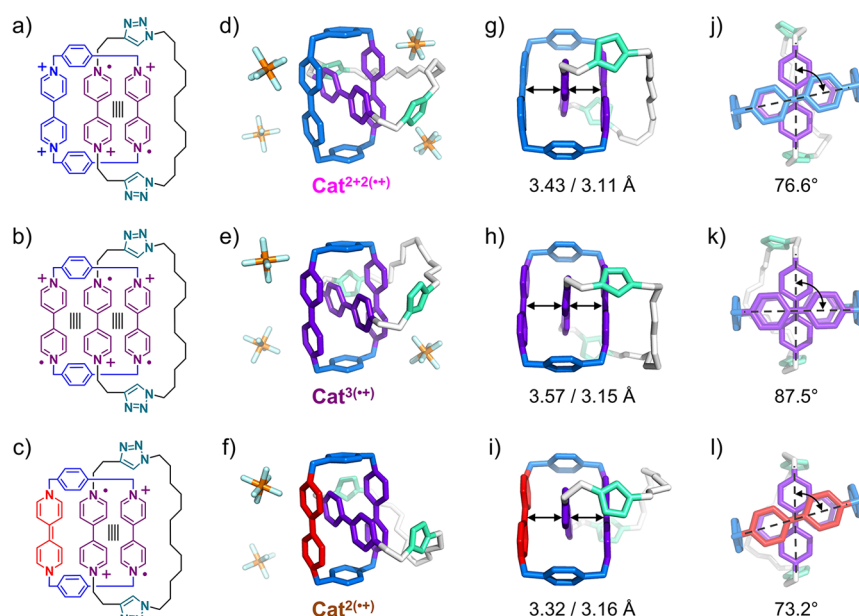


Figure 9. X-ray crystallography carried out on different redox states of the [2]catenane. Structural formulas for (a) $\text{Cat}^{2+2(\bullet+)}$, (b) $\text{Cat}^{3(\bullet+)}$, and (c) $\text{Cat}^{2(\bullet+)}$. Perspective views of the solid-state structures of (d) $\text{Cat}^{2+2(\bullet+)}$, (e) $\text{Cat}^{3(\bullet+)}$, and (f) $\text{Cat}^{2(\bullet+)}$ with two, three, and four PF_6^- counterions surrounding each [2]catenane, respectively. Top-down views of the solid-state structures of (g) $\text{Cat}^{2+2(\bullet+)}$, (h) $\text{Cat}^{3(\bullet+)}$, and (i) $\text{Cat}^{2(\bullet+)}$, illustrating the centroid-to-centroid distances between adjacent BIPY units. Side-on views of the solid-state structures of (j) $\text{Cat}^{2+2(\bullet+)}$, (k) $\text{Cat}^{3(\bullet+)}$, and (l) $\text{Cat}^{2(\bullet+)}$ with annotated dihedral angles between the CBPQT ring and the BIPY unit in the MC ring.

β' is deeply embedded inside the MC ring while proton β is on the periphery. Resolving the ^1H NMR spectrum of $\text{Cat}^{2(\bullet+)}$ has, not only confirmed the presence of radical interactions and antiferromagnetic spin coupling in this bisradical dicationic species, but also provided evidence for its mixed-valence nature that involves the through-space delocalization of two electrons over three BIPY units.

X-ray Crystallography. The co-conformations of $\text{Cat}^{2+2(\bullet+)}$, $\text{Cat}^{3(\bullet+)}$, and $\text{Cat}^{2(\bullet+)}$ as well as the radical interactions under these redox states were verified (Figure 9 and Figures S20–S24) by obtaining solid-state structures following X-ray crystallography on their single crystals. The MeCN solution of $\text{Cat} \cdot 6\text{PF}_6$ was treated with certain equivalents of CoCp_2 (homogeneous reduction) or appropriate metals (heterogeneous reduction) so as to generate (Figure 9a–c) different redox states of the [2]catenane. Vapor diffusion of Et_2O into the resulting solutions under a N_2 atmosphere over 1 week afforded three different kinds of single crystals (Figure 9d–f) suitable for X-ray crystallographic analysis. In the solid-state structure, each $\text{Cat}^{2+2(\bullet+)}$ was found to crystallize (Figure 9d) with four PF_6^- counterions, confirming its bisradical tetracationic state. Similarly, the triradical tricationic state of $\text{Cat}^{3(\bullet+)}$ and the bisradical dicationic state of $\text{Cat}^{2(\bullet+)}$ were validated by the presence (Figure 9e and 9f) of three and two surrounding PF_6^- counterions, respectively. For all three different redox states, the BIPY unit in the MC ring was encapsulated inside the cavity of CBPQT ring, providing solid evidence for the existence of noncovalent bonding interactions.

Unlike the torsional angles that are readily affected⁴⁵ by nanoconfinement, the bond lengths in BIPY units prove to be a reliable indicator for deducing their redox states. In particular, the length of the central bond in a BIPY unit—i.e., the bond between two pyridinium groups—has been reported^{50,63} to undergo a redox-induced variation from ~ 1.49 Å in BIPY^{2+} to ~ 1.43 Å in $\text{BIPY}^{\bullet+}$ and ~ 1.37 Å in $\text{BIPY}^{(0)}$, in line with the

character of this covalent bond changing from a single bond to a radical-delocalized bond and finally to a double bond. Based on the bond-length analysis (Table S1), we have detected different binding modes that are incorporated in the three redox states of the [2]catenane. In the case of $\text{Cat}^{2+2(\bullet+)}$, the BIPY unit in the MC ring is in a radical cationic state ($\text{BIPY}^{\bullet+}$), while both BIPY units in the CBPQT ring adopt an intermediate state between $\text{BIPY}^{\bullet+}$ and BIPY^{2+} , sharing three positive charges through electron hopping. In the case of $\text{Cat}^{3(\bullet+)}$, however, all three BIPY units were determined to be $\text{BIPY}^{\bullet+}$ radical cations regardless in which component ring they reside. In the case of $\text{Cat}^{2(\bullet+)}$, its similarity with $\text{Cat}^{2+2(\bullet+)}$ lies in the fact that the BIPY unit in the MC ring is also fixed in the $\text{BIPY}^{\bullet+}$ radical cationic state, but in contrast, the other two BIPY units in $\text{Cat}^{2(\bullet+)}$ adopt an intermediate state between $\text{BIPY}^{\bullet+}$ and $\text{BIPY}^{(0)}$ and thus share only one positive charge. These results reflect the mixed-valence nature of the bisradical binding modes present in $\text{Cat}^{2+2(\bullet+)}$ and $\text{Cat}^{2(\bullet+)}$, in stark contrast with the complete radical character of the triradical binding mode present in $\text{Cat}^{3(\bullet+)}$.

The asymmetric structure of the [2]catenane, resulting from two different component rings, has led to an uneven stacking of BIPY units in all three redox states. Specifically, the centroid-to-centroid distances between adjacent BIPY units were measured (Figure 9g–i) to be 3.43 and 3.11 Å for $\text{Cat}^{2+2(\bullet+)}$, 3.57 and 3.15 Å for $\text{Cat}^{3(\bullet+)}$, and 3.32 and 3.16 Å for $\text{Cat}^{2(\bullet+)}$. For each redox state, the longer one of the two distances is more than 3.30 Å, a typical value⁶⁶ associated with $[\pi \cdots \pi]$ or charge transfer interactions, while the shorter distance of less than 3.20 Å confirms the existence of radical interactions—i.e., spin-pairing interactions between two π -radicals through the overlap of their singly occupied molecular orbitals. Radical interactions involved in $\text{Cat}^{2+2(\bullet+)}$, $\text{Cat}^{3(\bullet+)}$, and $\text{Cat}^{2(\bullet+)}$, which are enabled by the presence of at least two radical units, serve as the major driving force for the noncovalent associations between CBPQT and BIPY. In

addition, the dihedral angles between the CBPQT ring and the BIPY unit in the MC ring were measured (Figure 9j–l) to be 76.6° for Cat^{2+2(•+)}, 87.5° for Cat^{3(•+)}, and 73.2° for Cat^{2(•+)}. In the case of the angle (87.5°) being closest to a perpendicular geometry, the radical interactions involved in Cat^{3(•+)} are maximized as predicted⁶⁰ by theoretical calculations. Therefore, among different redox states of the [2]catenane, the binding affinity between CBPQT and BIPY in the triradical state is probably higher than those in the bisradical states.

CONCLUSIONS

The program of research that we followed from the very beginning has answered comprehensively the fundamental scientific question: “How many kinds of complexes can be formed noncovalently between cyclobis(paraquat-*p*-phenylene) (CBPQT) and a 4,4'-bipyridinium (BIPY) derivative?” By employing a mechanically interlocked [2]catenane as the probe compound, we have circumvented the difficulties of dealing with complicated supramolecular systems and managed to realize a full-spectrum investigation of radical interactions at a molecular level. By running the gamut of characterization, including UV/vis/NIR, EPR, and NMR spectroscopies, electrochemical measurements, and X-ray crystallographic analysis, we have revealed unambiguously three kinds of noncovalent associations between CBPQT and BIPY in different redox states: they include the bisradical tetracationic and bisradical dicationic binding modes, in addition to the triradical tricationic binding mode reported³⁶ previously. In common with the conventional triradical tricationic complex, the newly discovered binding modes are also driven by radical interactions, albeit with somewhat lower strengths. Both bisradicals exhibit remarkable mixed-valence states, giving rise to the NIR absorptions at wavelengths beyond 1600 nm. We anticipate that the discovery of these two recognition motifs will open up new opportunities for the construction of self-assembled materials and the development of highly efficient supramolecular catalysts. In a broader sense, the unique advantages of mechanically interlocked molecules deserve more attention when it comes to the investigation of weak, noncovalent bonding interactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c10882>.

Detailed synthetic procedures and supplemental characterization data (NMR and UV/vis/NIR absorption spectroscopies as well as X-ray crystallographic analysis). (PDF)

Accession Codes

CCDC 2211841–2211844 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

J. Fraser Stoddart – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; Stoddart

Institute of Molecular Science, Department of Chemistry, Zhejiang University, Hangzhou 310027, China; ZJU-Hangzhou Global Scientific and Technological Innovation Center, Hangzhou 311215, China; School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia; orcid.org/0000-0003-3161-3697; Phone: (+1)-847-491-3793; Email: stoddart@northwestern.edu

Michael R. Wasielewski – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; Institute for Sustainability and Energy at Northwestern, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0003-2920-5440; Phone: (+1)-847-491-3002; Email: m-wasielewski@northwestern.edu

Authors

Yang Jiao – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-8437-0038

Haochuan Mao – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; Institute for Sustainability and Energy at Northwestern, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0001-8742-089X

Yunyan Qiu – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0001-9279-4714

Guangcheng Wu – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

Hongliang Chen – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; Stoddart Institute of Molecular Science, Department of Chemistry, Zhejiang University, Hangzhou 310027, China; ZJU-Hangzhou Global Scientific and Technological Innovation Center, Hangzhou 311215, China; orcid.org/0000-0002-4442-7984

Long Zhang – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-4631-158X

Han Han – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

Xuesong Li – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-2794-8390

Xingang Zhao – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0001-5852-9757

Chun Tang – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

Xiao-Yang Chen – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0003-3449-4136

Yuanning Feng – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-8832-0767

Charlotte L. Stern – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-9491-289X

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/jacs.2c10882>

Notes

The authors declare no competing financial interest.

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