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Mechanical Bond-Protected Air-Stable Radicals

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MAIN TEXT
ABSTRACT: Radical templation centered around a heterotrisradical tricationic inclusion complex DB⁺⁺⁺⊂DAPQT³⁺⁺⁺, assembled from an equimolar mixture of a disubstituted 4,4'-bipyridinium radical cation (DB⁺⁺) and an asymmetric cyclophane bisradical dication (DAPQT³⁺⁺⁺), affords a symmetric [2]catenane (SC•7PF₆) and an asymmetric [2]catenane (AC•7PF₆) on reaction of the 1:1 complex with diazapyrene and bipyridine, respectively. Both these highly charged [2]catenanes have been isolated as air-stable mono-radicals and characterized by EPR spectroscopy. X-Ray crystallography reveals that the unpaired electrons are delocalized in each case across two inner 4,4'-bipyridinium (BIPY²⁺) units forming a mixed-valence (BIPY₂)³⁺ state inside both [2]catenanes, an observation which is in good agreement with spin-density calculations using density functional theory. Electrochemical studies indicate that by replacing the BIPY²⁺ units in homo[2]catenane HC⁷⁺—composed of two mechanically interlocked cyclobis(paraquat-p-phenylene) rings—with 0, 1, and 2 more highly conjugated diazapyrenium dication (DAP²⁺) units, respectively, a consecutive series of 5, 6, and 7 redox states can be accessed in the resulting SC•7PF₆ (0, 4+, 6+, 7+, and 8+), HC•7PF₆ (0, 2+, 4+, 6+, 7+, and 8+), and AC•7PF₆ (0, 1+, 2+, 4+, 6+, 7+, and 8+), respectively. These unique [2]catenanes present a promising prototype for the fabrication of high-density data memories.

INTRODUCTION

Ever since the landmark discovery of the triphenylmethyl radical¹ by Moses Gomberg, research on stable organic radicals² has attracted attention, not only on account of their exotic electronic properties, but also because of their potential applications as spin-labels³ and in organic lithium batteries⁴ as well as in conductive and magnetic materials.⁵ To date, however, most organic radicals experience a fleeting existence and readily undergo dimerization and/or
oxidation. The synthesis and isolation of persistent radicals in crystalline forms remains a challenge. In addition, molecular systems with adjustable number of accessible redox states are quite difficult to achieve.

$4,4'$-Bipyridinium radical cations ($\text{BIPY}^{+}$) tend to form ($\text{BIPY}^{+}$)$_2$ dimers in a ‘face-to-face’ manner in the solid state as a result of favorable radical-pairing interactions. Conversely, in a dilute solution, ($\text{BIPY}^{+}$)$_2$ dimers are prone to dissociate because of their low association constants. Recently, however, we found that a cyclobis(paraquat-$p$-phenylene) bisradical dication ($\text{CBPQT}^{2(+)}$) and a BIPY$^{+}$ radical cation are capable of assembling to afford a stable trisradical tricationic inclusion complex $\text{BIPY}^{+} \subset \text{CBPQT}^{2(+)}$ in MeCN, assisted by radical-pairing interactions. This 1:1 inclusion complex has been investigated extensively and employed in recognition motifs, either to template the formation of, otherwise difficult to synthesize highly energetic mechanically interlocked molecules (MIMs), or to enhance the switching performance of bistable MIMs. In particular, we have been able to synthesize (Figure 1) an air- and water-stable paramagnetic homo[2]catenane $\text{HC}^{7+}$ from the trisradical complex $\text{DB}^{+} \subset \text{CBPQT}^{2(+)}$. Up to six redox states of this [2]catenane can be accessed electrochemically.

Herein we demonstrate a molecular system—namely, a novel class of octacationic [2]catenanes—which exhibits adjustable multiple accessible redox states. We report the radical template-directed syntheses of two analogues (Figure 1) of $\text{HC}^{7+}$—namely, the asymmetric [2]catenane $\text{AC}^{7+}$ and the symmetric [2]catenane $\text{SC}^{7+}$—by incorporating simultaneously both the less conjugated BIPY$^{2+}$ and the more highly conjugated 2,7-diazapyrenium (DAP$^{2+}$) units into the [2]catenane structures in order to modulate the number of the accessible redox states of the resulting molecules. We show that these [2]catenanes, which exist as persistent air-stable radicals, can exist in a consecutive series of 5 ($\text{SC}^{7+}$: 0, 4+, 6+, 7+, and 8+), 6 ($\text{HC}^{7+}$: 0, 2+, 4+, 6+, 7+, and 8+),...
6+, 7+, and 8+), and 7 (AC7+: 0, 1+, 2+, 4+, 6+, 7+, and 8+) redox states. We have characterized these mixed-valence and other redox states by (i) electron paramagnetic resonance (EPR) and UV-Vis-NIR spectroscopies, (ii) high-resolution mass spectrometry (HR-MS), (iii) single crystal X-ray diffraction (XRD) analysis, and (iv) electrochemical means as well as (v) density functional theory (DFT) calculations.

■ RESULTS AND DISCUSSION

Since the N–N distances in both DAP2+ and BIPY2+ dications are11 essentially identical, and DAP2+ dications are known to undergo12 the one-electron reduction to form the corresponding DAP+ radical cations, DAP2+ dications were selected as substitutes for the BIPY2+ units in HC7+. The redox properties of the N,N'-dimethyl-2,7-diazapyrenium dication (MDAP2+) were explored by variable scan-rate cyclic voltammetry (CV) and compared with those of 1,1'-dimethyl-4,4'-bipyridinium (MV2+). CV of MDAP2+ at 10 mV s⁻¹ reveals (Figure 2a, black trace) that the reduction of MDAP2+ to MDAP+ occurs at a potential of –450 mV, which is similar to that of –480 mV for MV2+. As the scan rate is increased, the reduction wave remains the same, but the intensity of the original oxidation wave at –370 mV gradually decreases, and meanwhile a new oxidation wave appears at +40 mV. Eventually, at the scan rate of 1 V s⁻¹ (Figure 2a, purple trace), two oxidation waves reach the same intensity. These observations indicate13 that, in solution, the MDAP+ radical cations exist primarily as cationic radical dimers (MDAP+)_2, wherein oxidation leads firstly to the formation of a single unpaired spin mixed-valence dimer (MDAP2)3+ before it completely dissociates into two MDAP2+ dications. When the scan rate is slower than the time scale of the dissociation of (MDAP2)3+, oxidation of (MDAP+)2 is observed to occur as a single oxidation wave. Once the scan rate becomes faster than the dissociation rate, however, two separate oxidation waves corresponding to
(MDAP\textsuperscript{+})\textsubscript{2}→(MDAP\textsubscript{2})\textsuperscript{3+} and (MDAP\textsubscript{2})\textsuperscript{3+}→2 MDAP\textsuperscript{2+} can be observed. In contrast to MDAP\textsuperscript{+}, the MV\textsuperscript{+} radical cations exist mainly as monomers. It can be concluded that, in addition to radical pairing interactions, the (MDAP\textsuperscript{+})\textsubscript{2} dimers are most likely further stabilized\textsuperscript{14} by additional [\pi···\pi] interactions between the large aromatic \pi-surfaces of MDAP\textsuperscript{+}.

In the knowledge that both MDAP\textsuperscript{2+} and MV\textsuperscript{2+} can be reduced to their corresponding radical cationic states at similar potentials, we explored the possibility of forming trisradical tricationic complexes between DAP\textsuperscript{+} and BIPY\textsuperscript{+} units. Upon reducing\textsuperscript{15} an equimolar mixture of a 1,1'-disubstituted 4,4'-bipyridinium salt (DB\textbullet2PF\textsubscript{6}) and DAPQT\textbullet4PF\textsubscript{6} in MeCN, a purple solution was obtained. Its UV-Vis-NIR spectrum exhibits (Figure 2b) an absorption band centered on 920 nm, which is characteristic of radical cationic (BIPY\textsuperscript{+})\textsubscript{2} dimers.\textsuperscript{16} This observation implies that the DAP\textsuperscript{+} unit in DAPQT\textsuperscript{2(++)} interacts with the DB\textsuperscript{+} radical cation very weakly if at all and the radical-pairing interaction is mainly associated with the interaction between the two BIPY\textsuperscript{+} units and the DB\textsuperscript{+} radical cation. The association constant \( (K_a) \) of DB\textsuperscript{+}⊂DAPQT\textsuperscript{2(++)} was determined (Figure S7) to be \( (8.9 \pm 5.5) \times 10^3 \text{ M}^{-1} \) in MeCN by UV-Vis-NIR titration. It is\textsuperscript{8} smaller than the one \( (K_a = 5.0 \times 10^4 \text{ M}^{-1}) \) observed for DB\textsuperscript{+}⊂CBPQT\textsuperscript{2(++)}, suggesting that the DAP\textsuperscript{+} unit does not interact strongly with DB\textsuperscript{+}. An attempt to form the hetero trisradical tricationic complex MDAP\textsuperscript{+}⊂CBPQT\textsuperscript{2(++)} was not successful as indicated (Figure S6) by the absence of a NIR absorption band in its UV-Vis-NIR spectrum. This failure to form a 1:1 inclusion complex reflects the fact that the cavity of CBPQT\textsuperscript{2(++)} is not large enough to accommodate MDAP\textsuperscript{+}.

Single crystals of a 1:1 inclusion complex which does form were obtained by slow vapor diffusion of \textsuperscript{6}Pr\textsubscript{2}O into an MeCN solution of an equimolar mixture of DB\textsuperscript{+} and DAPQT\textsuperscript{2(++)} in an Ar-filled glovebox. The solid-state superstructure (Figures 2c and S9) reveals that each inclusion complex is surrounded by four PF\textsubscript{6}\textsuperscript{−} counterions, an observation which indicates\textsuperscript{17} that the
complex is indeed the bisradical tetracation ($\text{DB}\subset\text{DAPQT}^{2+4+}$) rather than a trisradical trication in the solid state. Since the torsional angles of both units A and B are less than $3^\circ$ and the plane-to-plane separation between them is only 3.1 Å, the implication is that both units A and B are in the radical cationic BIPY$^{2+}$ state and the remaining unit C is in the dicationic DAP$^{2+}$ state. The plane-to-plane separation between units B and C is 3.4 Å, a distance which is a typical one for $[\pi\cdots\pi]$ interactions. In addition, the complex is further stabilized by multiple $[\text{C–H}\cdots\pi]$ interactions between the $p$-phenylene rings on the unit B and C–H groups on the DAP$^{2+}$ unit. Overall, the superstructure is arranged (Figure 2d) in an infinite stack, driven by intermolecular $[\text{Br}\cdots\pi]$ interactions between adjacent inclusion complexes.

Since the hetero trisradical tricationic complex is stable in MeCN, we grasped$^{18}$ the opportunity to synthesize (Schemes S1 and S2) AC•7PF$_6$ and SC•7PF$_6$. The in situ formed complex DB$^{2+}\subset\text{DAPQT}^{4+}$ was allowed to react with 4,4'-bipyridine and 2,7-diazapyrene, respectively, for two weeks at room temperature to afford both AC•7PF$_6$ and SC•7PF$_6$ as purple solids. The $^1$H NMR spectra of both catenanes were obtained for their fully oxidized states AC•8PF$_6$ and SC•8PF$_6$ which were prepared by oxidizing the as-synthesized catenanes with an excess of NO•PF$_6$. AC$^{8+}$ possesses a time-averaged $C_{2v}$ symmetry and hence displays (Figure 3b) a relatively complicated $^1$H NMR spectrum on account of the interlock-induced desymmetrization. It is worth highlighting that the proton resonances for H$_{\beta2}$ and H$_{\beta3}$, belonging to the two innermost BIPY$^{2+}$ units are shifted dramatically upfield by 3.9 and 4.6 ppm because of the strong shielding effect imposed by their accompanying cyclophanes. The slightly larger upfield shift observed for H$_{\beta3}$ is ascribed to the stronger shielding effect on H$_{\beta3}$ exerted by the DAP$^{2+}$ unit on DAPQT$^{4+}$. SC$^{8+}$, which has a higher time-averaged $D_{2d}$ symmetry, exhibits
(Figure S3) a comparatively simple $^1$H NMR spectrum and is also characterized by the upfield shifted $H_\beta$.

In order to confirm beyond any doubt that the as-synthesized catenanes exist as persistent stable radicals, we performed EPR measurements. The results reveal (Figure 4a) that both catenanes are EPR active, an observation which is in good agreement with their containing an unpaired electron. Moreover, the spectra display indiscernible hyperfine splitting, an observation which suggests that rapid spin exchange exists within both catenanes. This conclusion is also supported$^{19}$ (Figure 4b) by the NIR absorption bands centered on ca. 1415 nm in their UV-Vis-NIR spectra.

In order to gain more insight into the location of the delocalized radical electron, single crystal XRD analyses were performed on single crystals of $\text{AC} \cdot 7\text{PF}_6$ and $\text{SC} \cdot 7\text{PF}_6$. The solid-state structures demonstrate (Figures 4c and d, S10 and S11) that each catenane crystallizes with 7 PF$_6^-$ counterions, an observation which is consistent with their mono-radical states. In the case of $\text{AC}^7^+$, the torsional angle of 34° for the unit D, is typical for the dicationic BIPY$^{2^+}$ unit and tells us that the unpaired electron is not located on the unit D. By contrast, units B and C have smaller torsional angles—namely, 8° and 10°, respectively—and thus the heterocyclic rings can be deemed as being almost coplanar. The flattening effect suggests that the unpaired electron is shared by units B and C. This conclusion is further supported by their short plane-to-plane separation, which is only 3.1 Å being$^9$ typical for single unpaired spin interactions. The large plane-to-plane separation (3.5 Å) between units A and B suggests that the unit A is unlikely to be involved in the electron sharing. In the same manner, it can be argued that the unpaired electron in $\text{SC}^7^+$ is shared by units B (8°) and C (10°) as well. Along with the observations for $\text{HC}^7^+$, it
can be concluded that the change from BIPY$^{2+}$ to DAP$^{2+}$ does not affect the location of the unpaired electrons.

DFT Calculations were performed on AC$^{7+}$ and SC$^{7+}$ in order to probe their electronic properties. The results illustrate (Figure S12) that the spin densities in both catenanes are located on their two inner BIPY$^{2+/+}$ units in line with the experimental results. The efficient electron delocalization across the two inner BIPY$^{2+/+}$ units could be one of the primary reasons for the stabilization of these radicals. The theoretical binding energies (Table S1) for the formation of catenanes from the corresponding cyclophanes were calculated$^{20}$ in MeCN at the M06/6-311++G** level. For both catenanes, the formation of the 8+ state has a significant larger unfavorable energy than that of the corresponding 7+ state and provides an explanation for the high resistance of the 7+ state towards oxidation.

The redox properties of AC$^{7+}$ and SC$^{7+}$ were investigated employing electrochemistry and compared with that of HC$^{7+}$. Differential pulse voltammetry (DPV) reveals that AC$^{7+}$ exhibits (Figure 5c) up to six redox processes and as many as seven discrete accessible redox states on account of its low symmetry, whereas SC$^{7+}$ has (Figure 5a) only four redox processes and five redox states. In contrast, there are five redox processes and six redox states in the differential pulse voltammogram (Figure 5b) of HC·7PF$_6$. These observations indicate the fact that the introduction of the DAP$^{2+}$ units to replace the BIPY$^{2+}$ units can precisely modulate the stereoelectronic effect in this octacationic [2]catenane system. As a consequence, a consecutive series of five, six, and seven redox states are achieved in the resulting SC·7PF$_6$ (0, 4+, 6+, 7+, and 8+), HC·7PF$_6$ (0, 2+, 4+, 6+, 7+, and 8+), and AC·7PF$_6$ (0, 1+, 2+, 4+, 6+, 7+, and 8+), respectively, which render these catenanes ideal for applications as memory devices. In particular, all these redox states can be accessed at low potentials, ranging from −1.1 to +0.5 V,
which guarantee very low write and erase voltages. As such, these three catenanes hold considerable promise in relation to creating high-density memory devices with low energy consumption.21

■ CONCLUSIONS

In summary, we have demonstrated that the DB•+ radical cation and the asymmetric cyclophane bisradical dication DAPQT2(•+) enable the formation of a stable heterotrisradical tricationic inclusion complex DB•+⊂DAPQT2(•+) with an association constant of (8.9 ± 5.5) × 10³ M⁻¹ in MeCN. This complex is stabilized by (i) radical-pairing reactions between DB•+ and the BIPY•+ unit of DAPQT2(•+), (ii) [π···π] stacking between DB•+ and the DAP•+ unit of DAPQT2(•+), and (iii) [C–H···π] interactions. Taking advantage of the radical templation of DB•+⊂DAPQT2(•+), we have prepared two catenanes, AC•7+ and SC•7+, both of which are air-stable persistent radicals. In particular, electrochemical studies indicate that, by replacing the BIPY2+ units with zero, one, and two the more conjugated DAP2+ units, a consecutive series of five, six, and seven redox states can be accessed electrochemically in the resulting SC•7PF₆ (0, 4+, 6+, 7+, and 8+), HC•7+ (0, 2+, 4+, 6+, 7+, and 8+), and AC•7PF₆ (0, 1+, 2+, 4+, 6+, 7+, and 8+), respectively, rendering this unique series of catenanes promising prototypes in the development of high-density data memories.

■ ASSOCIATED CONTENT

Supporting Information

Detailed information regarding the experimental methods and procedures, X-ray crystallographic data, and supportive figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org. CIF files for (DB⊂DAPQT)•4PF₆, AC•7PF₆ and SC•7PF₆ (CCDC 1559720–1559722).
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Notes

The authors declare no competing financial interest.

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(13) It is also possible that the MDAP$^{2+}$ radical cation forms oligomers in addition to dimer.
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(15) The reduction was carried out by the addition of an excess of Zn dust to the mixture of DB$^•$2PF$_6$ and DAPQT$^•$4PF$_6$ in MeCN. After stirring the suspension for 30 min, the unreacted Zn dust was filtered off.


(17) The bisradical tetracationic state could be the result of partial oxidation during crystallization, especially since the DAP$^+$ radical cation does not interact efficiently with DB$^•$. Such a situation has also been observed in several other systems. See example: Cheng, C.; McGonigal, P. R.; Liu, W.-G.; Li, H.; Vermeulen, N. A.; Ke, C.; Frasconi, M.; Stern, C. L.; Goddard, W. A., III; Stoddart, J. F. J. Am. Chem. Soc. 2014, 136, 14702.

(18) See SI for the details.


(21) Recently, considerable efforts have been devoted to developing multilevel memories in order to increase data density. One effective way is ((a) Busche, C.; Vila-Nadal, L.; Yan, J.; Miras, H. N.; Long, D.-L.; Georgiev, V. P.; Asenov, A.; Pedersen, R. H.; Gadegaard, N.; Mirza, M. M.; Paul, D. J.; Poblet, J. M.; Cronin, L. Nature 2014, 515, 545. (b) Liu, Z.; Shi, E.; Wan, Y.; Li, N.; Chen, D.; Xu, Q.; Li, H.; Lu, J.; Zhang, K.; Wang, L. J. Mater. Chem. C 2015, 3, 2033.) to utilize a collection of redox-active molecules wherein information can be stored in discrete redox states. As a result, increasing the number of redox states within a single molecule can potentially help to realize the high density data storage.
Captions to Figures

Figure 1. Structural formulas of the three radical catenanes HC•7PF₆, SC•7PF₆ and AC•7PF₆ (top), and the 1:1 trisradical tricationic complexes (DB⊂CBPQT)•3PF₆, (DB⊂DAPQT)•3PF₆, MDAP•2PF₆ and MV•2PF₆ (bottom).

Figure 2. (a) Variable scan-rate CV of MDAP²⁺ (1 mM in MeCN, 0.1 M TBAPF₆, 298 K) exhibiting an additional oxidation wave at +40 mV upon increasing the scan rate. (b) UV-Vis-NIR adsorption spectra (50 µM in MeCN, 298 K) of DB⁺, DAPQT⁻²⁺ and DB⁻⊂DAPQT⁻²⁺ indicating the formation of the heterogeneous 1:1 trisradical complex characterized by the appearance of an NIR band centered on 920 nm. (c) Perspective view of the crystal structure of (DB⊂DAPQT)⁻²⁺ showing the torsional angles and plane-to-plane separations. (d) Side-on view of the solid-state superstructure of (DB⊂DAPQT)⁻²⁺ demonstrating the intermolecular interactions.

Figure 3. Comparison of ¹H NMR spectra (500 MHz, CD₃CN, 298 K) of (a) CBPQT⁴⁺, (b) AC⁸⁺ and (c) DAPQT⁴⁺.

Figure 4. (a) EPR spectra of AC⁷⁺ and SC⁷⁺ (0.2 mM in MeCN, 298 K) displaying indiscernible hyperfine splitting patterns. (b) UV-Vis-NIR absorption spectra (50 µM in MeCN, 298 K) of AC⁷⁺ and SC⁷⁺, both showing a broad NIR absorption band centered on 1415 nm. Perspective views of X-ray crystal structures of (c) AC⁷⁺ and (d) SC⁷⁺ highlighting their torsional angles and plane-to-plane separations.

Figure 5. DPV of (a) SC⁷⁺, (b) HC⁷⁺, and (c) AC⁷⁺ (1 mM in MeCN, 0.1 M TBAPF₆, 200 mV s⁻¹, 298 K) showing five, six, and seven discrete redox states, respectively.
Figure 1

HC•7PF₆

SC•7PF₆

AC•7PF₆

(DB⊂CBPQT)•3PF₆

(DB⊂DAPQT)•3PF₆

MDAP•2PF₆

MV•2PF₆
Figure 2
Figure 3
Figure 4
Figure 5

a) $I / \mu A$ vs $E / V$ vs Ag/AgCl

b) $I / \mu A$ vs $E / V$ vs Ag/AgCl

c) $I / \mu A$ vs $E / V$ vs Ag/AgCl