

Solution-Phase Mechanistic Study and Solid-State Structure of a Tris(bipyridinium radical cation) Inclusion Complex

Albert C. Fahrenbach,^{†,⊥} Jonathan C. Barnes,^{†,⊥} Don Antoine Lanfranchi,[‡] Hao Li,[†] Ali Coskun,^{†,⊥} Jeremiah J. Gassensmith,[†] Zhichang Liu,[†] Diego Benítez,[§] Ali Trabolsi,^{†,||} William A. Goddard III,^{§,⊥} Mourad Elhabiri,^{*,‡} and J. Fraser Stoddart^{*,†,⊥}

[†]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

[‡]Laboratoire de Chimie Bioorganique et Médicinale, UMR 7509 CNRS-UdS, ECPM, Université de Strasbourg, 25 rue Becquerel, 67200 Strasbourg, France

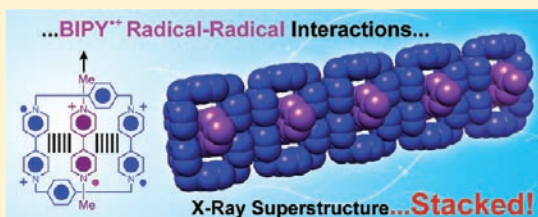
[§]Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, United States

^{||}Center for Science and Engineering, New York University Abu Dhabi, Abu Dhabi, United Arab Emirates

[⊥]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

Supporting Information

ABSTRACT: The ability of the diradical dicationic cyclobis(paraquat-*p*-phenylene) (CBPQT^{2(•+)}) ring to form inclusion complexes with 1,1'-dialkyl-4,4'-bipyridinium radical cationic (BIPY^{•+}) guests has been investigated mechanistically and quantitatively. Two BIPY^{•+} radical cations, methyl viologen (MV^{•+}) and a dibutynyl derivative (V^{•+}), were investigated as guests for the CBPQT^{2(•+)} ring. Both guests form trisradical complexes, namely, CBPQT^{2(•+)}CMV^{•+} and CBPQT^{2(•+)}CV^{•+}, respectively. The structural details of the CBPQT^{2(•+)}CMV^{•+} complex, which were ascertained by single-crystal X-ray crystallography, reveal that MV^{•+} is located inside the cavity of the ring in a centrosymmetric fashion: the 1:1 complexes pack in continuous radical cation stacks. A similar solid-state packing was observed in the case of CBPQT^{2(•+)} by itself. Quantum mechanical calculations agree well with the superstructure revealed by X-ray crystallography for CBPQT^{2(•+)}CMV^{•+} and further suggest an electronic asymmetry in the SOMO caused by radical-pairing interactions. The electronic asymmetry is maintained in solution. The thermodynamic stability of the CBPQT^{2(•+)}CMV^{•+} complex was probed by both isothermal titration calorimetry (ITC) and UV/vis spectroscopy, leading to binding constants of $(5.0 \pm 0.6) \times 10^4 \text{ M}^{-1}$ and $(7.9 \pm 5.5) \times 10^4 \text{ M}^{-1}$, respectively. The kinetics of association and dissociation were determined by stopped-flow spectroscopy, yielding a k_f and k_b of $(2.1 \pm 0.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $250 \pm 50 \text{ s}^{-1}$, respectively. The electrochemical mechanistic details were studied by variable scan rate cyclic voltammetry (CV), and the experimental data were compared digitally with simulated data, modeled on the proposed mechanism using the thermodynamic and kinetic parameters obtained from ITC, UV/vis, and stopped-flow spectroscopy. In particular, the electrochemical mechanism of association/dissociation involves a bisradical tetracationic intermediate CBPQT^{(2+)(•+)}CV^{•+} inclusion complex; in the case of the V^{•+} guest, the rate of disassociation ($k_b = 10 \pm 2 \text{ s}^{-1}$) was slow enough that it could be detected and quantified by variable scan rate CV. All the experimental observations lead to the speculation that the CBPQT^{(2+)(•+)} ring of the bisradical tetracation complex might possess the unique property of being able to recognize both BIPY^{•+} radical cation and π -electron-rich guests simultaneously. The findings reported herein lay the foundation for future studies where this radical–radical recognition motif is harnessed particularly in the context of mechanically interlocked molecules and increases our fundamental understanding of BIPY^{•+} radical–radical interactions in solution as well as in the solid-state.



INTRODUCTION

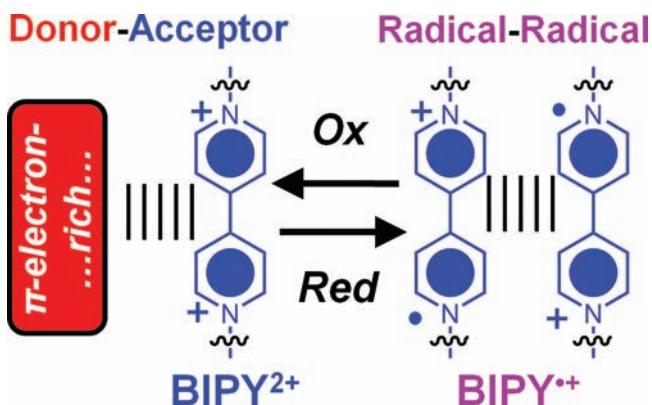
Noncovalent donor–acceptor charge-transfer (CT) interactions, which occur¹ between π -electron-poor 1,1'-dialkyl-4,4'-bipyridinium (BIPY²⁺) dications and a range of neutral π -electron-rich compounds have been known² since at least the 1960s. Since these times, the blossoming of the systematic investigation of noncovalent bonding interactions in general that followed hard on the heels of the discovery³ of the crown ethers⁴ by Pedersen⁵ led directly to the development of host–guest chemistry⁶ by Cram⁷ and the ushering in of chemistry

beyond the molecule, later to become known as supramolecular chemistry⁸ at the suggestion of Lehn.⁹ Both host–guest and supramolecular chemistry have evolved to embrace inclusion complexes of many different types, including those of a donor–acceptor nature where BIPY²⁺ units fulfill the role of guests¹⁰ in some cases and of components of hosts¹¹ in others. The large collection¹² of stable donor–acceptor complexes involving

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Scheme 1. Conceptual Portrayals of the Donor–Acceptor Interactions That Ensurue between π -Electron-Poor BIPY²⁺ (Acceptor) Units in Their Fully Oxidized States and π -Electron-Rich (Donor) Units and, upon Reduction to Their BIPY^{•+} Radical Cations, the Self-Loving, Radical–Radical Interactions That Exist between the Radical Cations^a



^aAlthough many examples of donor–acceptor recognition motifs have been described in the literature, relatively few radical–radical inclusion complexes have been reported in communications and papers.

BIPY²⁺ units as π -electron-poor acceptors alongside a suite of π -electron-rich donors has resulted in the use of donor–acceptor interactions to template the formation of the mechanical bond,¹³ paving the way for the development¹⁴ of mechanically interlocked molecules (MIMs) such as catenanes¹⁵ and rotaxanes.¹⁶ The introduction of bistability into these MIMs has transformed them from being intellectual curiosities into functioning molecular switches, which have been incorporated into integrated systems as disparate as molecular electronic devices¹⁷ (MEDs) in addressable memories¹⁸ based on crossbar architectures, artificial molecular muscles¹⁹ as examples of nanoelectromechanical systems (NEMS), and mechanized mesoporous silica nanoparticles (MSNPs) for drug delivery.²⁰

The radical chemistry of compounds containing BIPY²⁺ units has been well documented²¹ in the scientific literature since the 1930s. They have been referred to commonly^{21b} as viologen salts having acquired this name because, upon their reduction to BIPY^{•+} radical cations in aqueous solutions, they acquire a vibrant purple color, which was ascribed in 1964 by Kosower²² to the coming together of two radical cations to produce a [(BIPY^{•+})₂] dimer. On dilution, the purple color recedes and the aqueous solution becomes blue on account of the dissociation of the of the [(BIPY^{•+})₂] dimer into the BIPY^{•+} radical cation monomer.

Despite the fact that BIPY^{•+} radical cations have been known^{22,23} for over 40 years to undergo dimerization, sometimes referred to as pimerization,²⁴ under appropriate conditions, it is not so long ago that researchers began to synthesize host–guest systems that take advantage of the tendency for BIPY^{•+} radical cations to dimerize. In many ways, their self-recognizing radical–radical interactions serve (Scheme 1) to supplement the classical donor–acceptor interactions that occur in the fully oxidized form, that is, the BIPY²⁺ dication, with π -electron-rich donors. Kimoon Kim,²⁵ for example, has demonstrated that BIPY^{•+} radical cation dimers can be included inside the cavity of cucurbit[8]uril. On

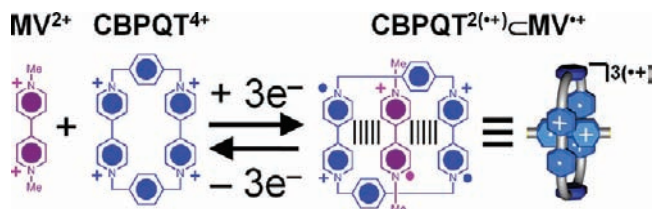
the other hand, we have discovered²⁶ very recently the ability of the cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) ring, which is composed of two BIPY²⁺ units held rigidly in place approximately 7 Å apart, when reduced to the diradical dication CBPQT^{2(•+)}, to form stable triradical tricationic inclusion complexes with appropriate guests containing BIPY^{•+} radical cationic centers on account of favorable radical–radical interactions. Moreover, we have demonstrated^{26b} that these radically stabilized inclusion complexes can act as an efficient means of templating the formation of mechanical bonds in the synthesis of a [2]rotaxane, employing^{13,27} a threading-followed-by-stopping approach.

In this paper, we describe the various methods that we have employed to probe the mechanism of formation of a triradical tricationic inclusion complex involving the CBPQT^{2(•+)} diradical dication, which encircles spontaneously BIPY^{•+}-containing guests, namely, methyl viologen (MV^{•+}) and also a butynyl derivative (V^{•+}), provided they are in their radical cationic redox states. We reveal that a bisradical tetracationic inclusion complex plays an important role as an intermediate in the redox-induced switching processes. Structural, thermodynamic, and kinetic parameters have all been elucidated using (i) single-crystal X-ray crystallography, (ii) quantum mechanical calculations, (iii) isothermal titration calorimetry (ITC) supported by UV/vis spectroscopy, and (iv) stopped-flow UV/vis spectroscopy, complemented by (v) variable scan rate cyclic voltammetry (CV) in conjunction with (vi) digital simulations based on the proposed mechanism for the complexation.

RESULTS AND DISCUSSION

Following a three-electron reduction, one going into each of the BIPY²⁺ units of the CBPQT⁴⁺ ring and one electron entering the BIPY²⁺ unit of the MV²⁺ guest, a stable thermodynamic state arises whereby the CBPQT^{2(•+)} ring encircles the MV^{•+} radical cation. The structural formulas and graphical representations of the [2]pseudorotaxane CBPQT^{2(•+)}CMV^{•+}, along with the simplified schematic of the redox-induced complexation processes, are illustrated in Scheme 2. Previously, we have shown^{26a} both experimentally and theoretically in solution that, because only two of the BIPY^{•+} radical cations of the complex are spin-paired at any

Scheme 2. Simplified Schematic Representation Using Structural Formulas of the Redox-Induced Formation of the Triradical Cationic Inclusion Complex CBPQT^{2(•+)}CMV^{•+} and Its Graphical Representation^a



^aUpon a three-electron reduction of an equimolar mixture of CBPQT⁴⁺ and MV²⁺, the MV^{•+} radical cation is included spontaneously inside the cavity of the CBPQT^{2(•+)} diradical dication ring as a result of favorable radical–radical interactions occurring between the three BIPY^{•+} radical cations. Reoxidation of the tricationic complex results in the regeneration of the initial uncomplexed CBPQT⁴⁺ host and MV²⁺ guest. For a more complete mechanistic description, see Figure 7 and the Supporting Information.

given time, the third unpaired BIPY^{•+} radical cation of the complex is not as strongly engaged in radical–radical interactions. This fact has important repercussions for the redox-induced mechanism of switching, which will be discussed in detail later on in this paper. Reoxidation of the complex results in its dissociation into its constituent components. Overall, the complexation and decomplexation processes are reversible.

X-ray Crystallography. Single crystals of the CBPQT^{2(•+)}CMV^{•+} complex were grown from MeCN using slow vapor diffusion of *i*Pr₂O inside a glovebox at room temperature. Zinc dust was used to bring about²⁸ the reduction of CBPQT⁴⁺ and MV²⁺ to their respective radical cationic forms. (For a general procedure on the use of zinc dust as a reducing agent, see the Experimental Section). The solid-state structure,²⁹ as determined by X-ray crystallography,³⁰ demonstrates (Figure 1) the formation of the trisradical tricationic complex. The inclusion complex was observed to be associated with three PF₆⁻ counterions in the solid state, supporting the hypothesis that each of the BIPY²⁺ units indeed has been reduced to their radical cationic form, BIPY^{•+}. The MV^{•+} radical cation is situated inside the cavity of the CBPQT^{2(•+)} ring in a centrosymmetric fashion, with 3.22 Å centroid-to-centroid separation from each of the BIPY^{•+} radical cation subunits of the cyclophane. The axis defined by the central aryl–aryl C–C bond in the MV^{•+} radical cation subtends an angle of 14° (Figure 1b) with the axis orthogonal to the plane defined by the four N atoms of the ring. We surmise that this deviation from orthogonality maximizes³¹ the amount of π -overlap between MV^{•+} and CBPQT^{2(•+)}. This deviation from orthogonality observed in the solid state for the CBPQT^{2(•+)}CMV^{•+} complex is in good agreement (*vide infra*) with that predicted from theoretical calculations. Virtually no torsional twisting of any of the three BIPY^{•+} units of the complex about their 4,4'-C–C bond is apparent, a phenomenon that is not observed for the CBPQT⁴⁺ ring in its fully oxidized form. This almost complete lack of torsional twists is consistent, however, with the solid-state structure of the MV^{•+} radical cation reported³² previously. The extended superstructure reveals (Figure 1c) a continuous BIPY^{•+} radical cation π -stack, with adjacent complexes aligned in register. A centroid-to-centroid separation of 3.28 Å characterizes the distance between the BIPY^{•+} radical cation subunits of the CBPQT^{2(•+)} of adjacent complexes. The PF₆⁻ counterions are observed to occupy (Figure 1d) the space between adjacent stacks. In particular, close contact (~2.6 Å) of the fluorines with the hydrogen atoms of the methylene groups and those of the α and β carbons of the CBPQT^{2(•+)} ring are observed. In all, this type of continuous radical cation stack is similar to that reported by Kochi³² in 1990 for the MV^{•+} radical cation in the solid state.

We have also investigated the crystal growth of the CBPQT^{2(•+)} diradical dication alone in solution. Crystals were obtained from slow vapor diffusion of *i*Pr₂O into a solution of the diradical dication in MeCN all inside of a glovebox. Remarkably, long, dark, opaque needle-like crystals up to three centimeters in length were observed after less than a week of crystal growth. Single-crystal X-ray analyses³⁰ revealed²⁹ (Figure 2) that CBPQT^{2(•+)} crystallizes with two PF₆⁻ counterions, confirming its diradical dicationic nature. Once again, virtually no torsional twisting was observed in the BIPY^{•+} units of the CBPQT^{2(•+)} ring, an observation that is consistent with that already observed for the trisradical

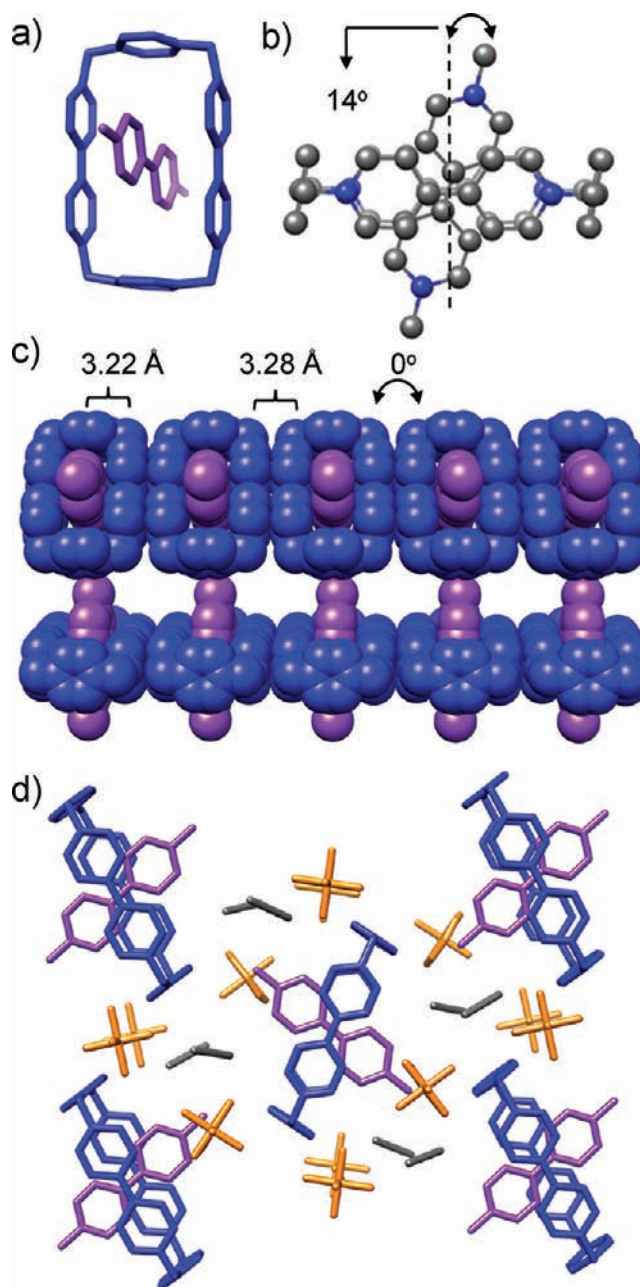


Figure 1. Solid-state superstructures of the trisradical cation CBPQT^{2(•+)}CMV^{•+} inclusion complex obtained by single-crystal X-ray crystallography. (a) Wireframe representation of the CBPQT^{2(•+)}CMV^{•+} inclusion complex. (b) Ball-and-stick representation of the CBPQT^{2(•+)}CMV^{•+} inclusion complex from a side-on perspective, illustrating the angle of offset from orthogonality of the MV^{•+} occupying the cavity of CBPQT^{2(•+)}. (c) Space-filling representation along the *a*-axis of the long-range packing order of the trisradical tricationic CBPQT^{2(•+)}CMV^{•+} inclusion complex, which forms a continuous radical–radical π -stack. The PF₆⁻ counterions have been omitted for clarity. (d) Side-on view of the unit cell of the CBPQT^{2(•+)}CMV^{•+} inclusion complex determined by X-ray crystallography revealing the superstructure and relative positioning of the PF₆⁻ counterions and MeCN solvent molecules.

complex. The centroid-to-centroid transannular distance spanning the gap between the planes of the two BIPY^{•+} units of the ring is 6.92 Å, a remarkably longer distance compared with that (6.43 Å) present in the trisradical complex.

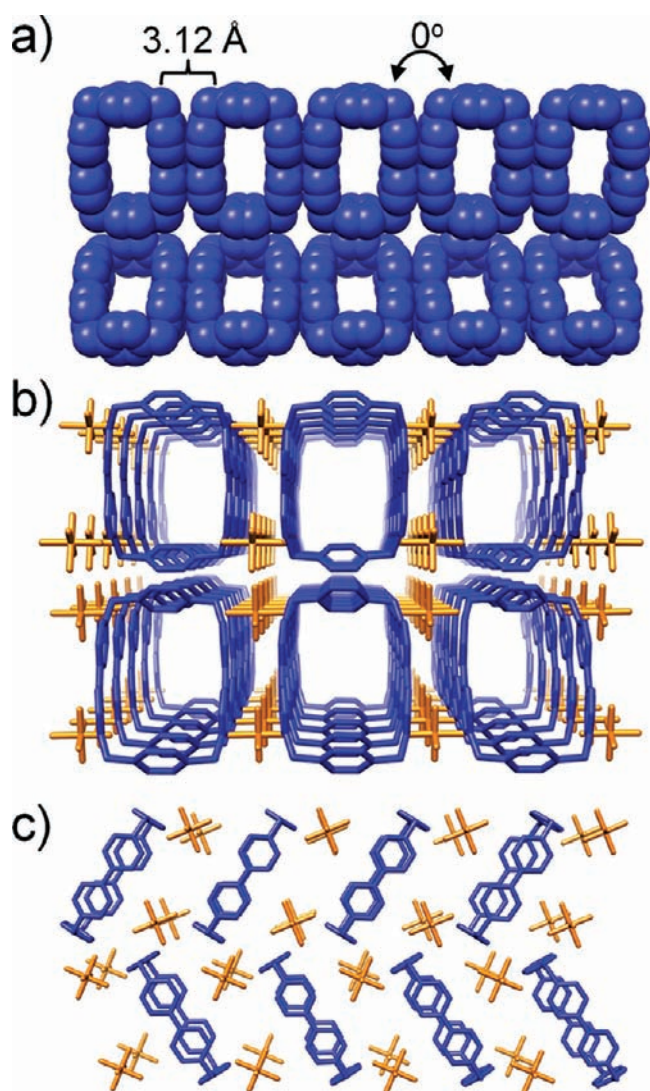


Figure 2. Solid-state superstructure of the diradical dication $\text{CBPQT}^{2(\bullet+)}$ ring obtained by single-crystal X-ray crystallography. (a) In common with the triradical $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$ inclusion complex, the $\text{CBPQT}^{2(\bullet+)}$ solid-state superstructure reveals a stack of $\text{CBPQT}^{2(\bullet+)}$ rings along the a crystallographic axis maintained by interactions between its $\text{BIPY}^{\bullet+}$ constituent subunits. The counterions, PF_6^- , have been omitted for clarity. (b) A wireframe representation of the solid-state superstructure of $\text{CBPQT}^{2(\bullet+)}$, depicting the porous channels formed by the diradical dicationic ring's unoccupied interiors. (c) Side-on view of the X-ray structure of the $\text{CBPQT}^{2(\bullet+)}$ revealing the superstructure and relative positioning of the PF_6^- counterions.

The centroid-to-centroid transannular separation between the phenylene units, which was observed in the solid-state structure of the $\text{CBPQT}^{2(\bullet+)}$ ring, is 10.2 Å and may be contrasted with the analogous distance of 10.3 Å for the triradical complex. These observations indicate that the $\text{CBPQT}^{2(\bullet+)}$ ring is able to expand in size in one direction while contracting in the other in order to accommodate the $\text{MV}^{\bullet+}$ guest in such a way that the bowing of the $\text{BIPY}^{\bullet+}$ units of the ring is reduced. The decreased degree of bowing of the $\text{BIPY}^{\bullet+}$ units brought about by the inclusion of $\text{MV}^{\bullet+}$ in the $\text{CBPQT}^{2(\bullet+)}$ ring serves to increase the distance between the phenylene units of the ring in the complex. Reminiscent of the way the triradical complex packs in the solid state, the superstructure reveals a continuous

stack of $\text{CBPQT}^{2(\bullet+)}$ rings. A centroid-to-centroid separation between the $\text{BIPY}^{\bullet+}$ units of adjacent $\text{CBPQT}^{2(\bullet+)}$ rings of 3.12 Å is observed along with a packing structure that is aligned in register, that is, no angle of offset between adjacently stacked rings is observed. The cavities of the rings arrange themselves in such a way as to form (Figure 2b) continuous porous channels that run the whole length of the crystal, with the PF_6^- counterions occupying the spaces between the rings. In a fashion similar to that of the triradical complex, close contact (~ 2.6 Å) of the fluorine atoms with the α , β , and methylene protons of the $\text{CBPQT}^{2(\bullet+)}$ ring is observed (Figure 2c). Overall, the superstructure is consistent with our understanding of the nature of $\text{BIPY}^{\bullet+}$ radical–radical interactions, which serve to “stitch” the $\text{CBPQT}^{2(\bullet+)}$ rings together into stacks.

Quantum Mechanical Calculations. In order to gain a better understanding of the nature of the binding in $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$, we have previously used^{26a} density functional theory³³ of the M06 flavor³⁴ to provide a quantum mechanical description of the binding in the superstructure. The superstructure for $[\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}][3\text{PF}_6^-]$ was minimized at the M06/6-31G** level, as depicted in Figure 3a. The calculated superstructure (Figure 3a) agrees well with that determined experimentally from X-ray crystallography, namely, that $\text{MV}^{\bullet+}$ resides inside the cavity of the $\text{CBPQT}^{2(\bullet+)}$ ring at an angle offset to the axis perpendicular to the plane defined by the four nitrogen atoms of the ring. Natural population analysis³⁵ of the inclusion complex shows that the charges on the $\text{CBPQT}^{2(\bullet+)}$ and $\text{MV}^{\bullet+}$ fragments are +1.71 and +1.18, respectively, which suggests some degree of charge transfer from the guest to the host. The asymmetry of the complex is also corroborated by the singly occupied molecular orbital (SOMO) being preferentially distributed (Figure 3b) over one of the two $\text{BIPY}^{\bullet+}$ units of the $\text{CBPQT}^{2(\bullet+)}$ ring. This electronic asymmetry in the SOMO supports our hypothesis (*vide infra*) that, as a consequence of radical pairing, one $\text{BIPY}^{\bullet+}$ unit of the $\text{CBPQT}^{2(\bullet+)}$ ring is not interacting as strongly with the $\text{MV}^{\bullet+}$ guest. As a result, this weaker interaction of one $\text{BIPY}^{\bullet+}$ unit of the $\text{CBPQT}^{2(\bullet+)}$ ring leads to a bisradical tetracationic $\text{CBPQT}^{2(\bullet+)(\bullet+)}\text{CMV}^{\bullet+}$ intermediate in the electrochemical mechanism of formation. In addition, the $\text{MV}^{\bullet+}$ guest in the

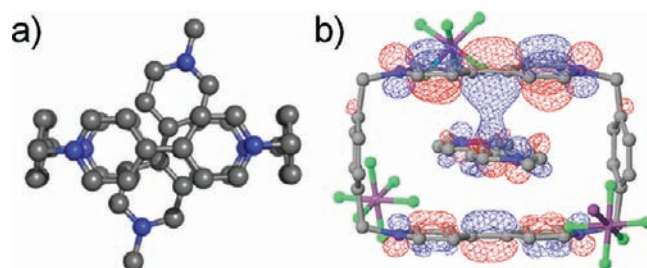


Figure 3. Results from quantum mechanical calculations of the triradical $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$ complex minimized at the M06/6-31G** level of DFT. (a) Calculated structure (side view) of the triradical $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$ complex with the PF_6^- counterions omitted for clarity. (b) Character of the singly occupied molecular orbital (SOMO), where positive and negative phases are shaded blue and red. The SOMO is asymmetrically distributed toward the top $\text{BIPY}^{\bullet+}$ radical cation subunit of the $\text{CBPQT}^{2(\bullet+)}$ ring component, a distribution of which is likely exaggerated by the asymmetry in the locations of the PF_6^- counterions. In the ball-and-stick representation of the framework, C is black, N is blue, F is green, and P is purple.

calculated structure is located ~ 0.14 Å closer to one of the BIPY $^{\bullet+}$ units in the CBPQT $^{2(\bullet+)}$ ring. Additional polarization affects brought about by the asymmetric positioning of the three PF $_6^-$ counterions may act to further exaggerate this distribution of electron density in the SOMO as well as influence the location of the guest within the host. The fact that the crystal structure reveals that the MV $^{\bullet+}$ guest resides equidistant from either side of the BIPY $^{\bullet+}$ units of the CBPQT $^{2(\bullet+)}$ ring is most likely a consequence of the continuous radical–radical packing superstructure, with the PF $_6^-$ counterions symmetrically placed on either side of each complex, which probably serves to “wash-out” this asymmetry in the solid state. We hypothesize that the electronic asymmetry predicted by theory continues to live-on in the solution phase, where no such stacking of complexes is occurring.

Isothermal Titration Calorimetry. Thermodynamic parameters governing the stability of the triradical complex in solution have been obtained by performing ITC experiments at room temperature in MeCN under the inert conditions provided by a glovebox. Solutions of CBPQT $^{2(\bullet+)}$ and MV $^{\bullet+}$ were prepared individually using zinc dust as the reducing agent. The results (Figure 4) confirm the 1:1 stoichiometry of the complex and reveal an association constant (K_a) of $(5.0 \pm 0.6) \times 10^4$ M $^{-1}$. As expected, the binding is enthalpically driven by a ΔH value of -15.2 ± 0.5 kcal mol $^{-1}$ for an entropic cost of

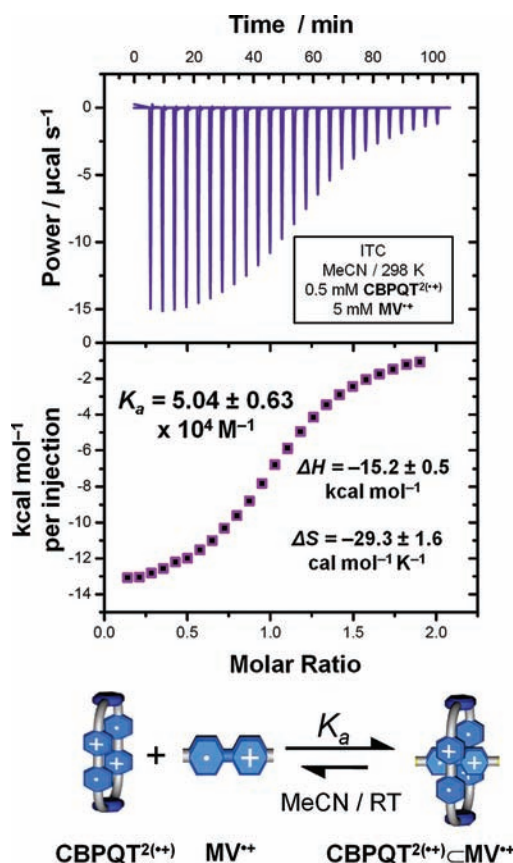


Figure 4. The isothermal titration calorimetry (ITC) traces obtained when measuring the thermodynamic parameters (K_a , ΔH , ΔS) governing the formation of the triradical CBPQT $^{2(\bullet+)}$ CMV $^{\bullet+}$ inclusion complex. All the ITC experiments were performed in MeCN at 298 K. The values for K_a , ΔH and ΔS reported above are averages over four runs, and the errors are the associated standard deviations from these four runs.

-29.3 ± 1.6 cal mol $^{-1}$ K $^{-1}$ in ΔS . The free energy of formation ΔG at 298 K is -6.41 ± 0.07 kcal mol $^{-1}$. By comparison with the free energies of formation determined³⁶ under identical conditions for classical donor–acceptor complexes involving the fully oxidized tetracationic CBPQT $^{4+}$ ring and the π -electron-rich guests, 1,5-bis[2-(2-hydroxyethoxy)ethoxy]-naphthalene (BHEEN) ($\Delta G = -6.26 \pm 0.04$ kcal mol $^{-1}$) and 2-[2-[[2-[4-[[2-(2-hydroxyethoxy)ethoxy]methyl]-1,3-dithiol-2-ylidene]-1,3-dithiol-4-yl]methoxy]ethoxy]ethanol (a bis(di(ethylene glycol))tetrathiafulvalene derivative) ($\Delta G = -7.66 \pm 0.07$ kcal mol $^{-1}$), one finds that the binding energy is on a par with these complexes. In these donor–acceptor complexes, a significant amount of the binding energy comes³⁷ from [C–H \cdots O] interactions involving particularly the terminal oxygen atoms of the oligo(ethylene glycol) chains to the hydrogen atoms of the α carbons in the ring. The additional affinity gained from these [C–H \cdots O] interactions is lost when the glycol chains are not present. It is worth noting that, in the case of the triradical complex in MeCN, [C–H \cdots O] interactions are not necessary in order to achieve binding constants of similar orders of magnitude. The binding affinities for the CBPQT $^{4+}$ ring, as measured previously³⁶ by ITC in MeCN at 298 K, for tetrathiafulvalene and 1,5-dihydroxynaphthalene, both of which lack oligo(ethylene glycol) chains, were determined to be $(6.9 \pm 0.18) \times 10^3$ M $^{-1}$ and 440 ± 130 M $^{-1}$, respectively.

UV/Vis and Stopped-Flow Spectroscopy. The absorption spectra of the radical cation MV $^{\bullet+}$ and of the diradical dication CBPQT $^{2(\bullet+)}$ were first of all recorded alone in MeCN at concentrations in the range of $\sim 5 \times 10^{-5}$ to 10^{-4} M in order to verify the absence of intermolecular radical–radical interactions³⁸ between like species under the experimental conditions employed. The absorption spectra of MV $^{\bullet+}$ and of CBPQT $^{2(\bullet+)}$ are both characterized (Figure 5a) by two sets of finely structured absorptions (vibronic coupling) centered on 390 and 600 nm, respectively. No absorption was observed in the near-IR region, an observation that confirms the absence³⁹ of intermolecular radical–radical interactions, namely, BIPY $^{\bullet+}$ dimerization, in MeCN.

The electronic spectrum of CBPQT $^{2(\bullet+)}$ was compared (Supporting Information) to the sum of the electronic spectra of 2 equiv. of MV $^{\bullet+}$ in order to further investigate the ability of the two BIPY $^{\bullet+}$ units in CBPQT $^{2(\bullet+)}$ to interact with each other in a noncovalent bonding fashion. The larger extinction coefficients (Supporting Information) of the CBPQT $^{2(\bullet+)}$ diradical dication, compared to the sum of two MV $^{\bullet+}$ radical cations, suggest an intramolecular dipole–dipole interaction in the ground state between the CBPQT $^{2(\bullet+)}$ ring’s two BIPY $^{\bullet+}$ radical cationic units. This observation is in good agreement⁴⁰ with EPR results obtained previously, data from which support the hypothesis of intramolecular dipole–dipole interactions.

The strength of the association between CBPQT $^{2(\bullet+)}$ and the MV $^{\bullet+}$ was then probed (Supporting Information) in MeCN using UV/vis absorption spectrophotometry, allowing us to assess the spectroscopic and thermodynamic parameters associated with the formation of the CBPQT $^{2(\bullet+)}$ CMV $^{\bullet+}$ triradical trication inclusion complex. The recognition of MV $^{\bullet+}$ by CBPQT $^{2(\bullet+)}$ occurs (Figure 5a) with a significant broadening of the absorption band centered around 604 nm, resulting effectively in the concomitant observation of a new band appearing at 550 nm, as well as the emergence⁴¹ of an intense absorption band straddling^{26a} the near-IR region.

Table 1. Thermodynamic Parameters Associated with the Formation of the Trisradical Inclusion Complex between the Diradical Dication CBPQT^{2(•+)} Ring and the Radical Cation MV^{•+}^a

	$K_a, 10^4 \text{ M}^{-1}$	$\Delta G, \text{ kcal mol}^{-1}$	$\Delta H, \text{ kcal mol}^{-1}$	$\Delta S, \text{ cal mol}^{-1} \text{ K}^{-1}$
CBPQT ^{2(•+)} CMV ^{•+}	5.04 ± 0.63^b	-6.41 ± 0.07^b	-15.2 ± 0.5^b	-29.3 ± 1.6^b
	7.9 ± 5.5^c	-6.7 ± 0.4^c		

^aSolvent, MeCN; $T = 298 \text{ K}$. ^bDetermined by ITC. ^cDetermined by UV/vis spectroscopy.

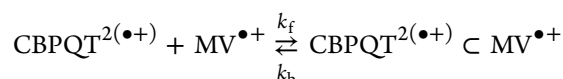
The processing^{42–44} of these spectrophotometric data made it possible to carry out an independent determination of the stability constant (K_a) for the trisradical trication inclusion complex, in addition to affording (Figure 5a) the corresponding electronic spectrum of the 1:1 trisradical tricationic CBPQT^{2(•+)}CMV^{•+} complex. It displays the characteristic spectroscopic features of BIPY^{•+} radical–radical interactions (pimerization), namely a broad near-IR band, as well as an increase in the intensities of the absorption bands in the

500–600 nm region compared with the free components dissolved on their own in solution. The results from this titration reveal⁴⁵ a K_a value of $(7.9 \pm 5.5) \times 10^4 \text{ M}^{-1}$, an association constant that is consistent within experimental error of that $((5.0 \pm 0.6) \times 10^4 \text{ M}^{-1})$ determined from the ITC experiments. The thermodynamic parameters obtained from both the ITC and UV/vis spectroscopic data are summarized in Table 1.

Stopped-flow UV/vis spectroscopy was performed to evaluate the kinetic parameters controlling the association and dissociation of the trisradical tricationic CBPQT^{2(•+)}CMV^{•+} inclusion complex. The absorption at 505 nm was used as a measure of the concentration of the inclusion complex as a function of time, employing pseudo-first-order experimental protocols. A monoexponential increase of the absorbance at 505 nm in the millisecond time range was recorded for the formation of the trisradical trication. From these experiments, a single rate-limiting step (Figure 5b), governing the formation of the inclusion complex, was deduced. The experimental data indicate that the formation of the 1:1 complex proceeds in a single, very fast rate-limiting step. The concentration of MV^{•+} was varied and the corresponding pseudo-first-order rate constant (k_{obs}) was shown to depend linearly on $[\text{MV}^{\bullet+}]_{\text{tot}}$ according to the following equation:

$$k_{\text{obs}} = a[\text{MV}^{\bullet+}]_{\text{tot}} + b$$

The experimental data led us to suggest the following concerted mechanism:



where

$$k_{\text{obs}} = k_f[\text{MV}^{\bullet+}]_{\text{tot}} + k_b$$

and $k_f = a \text{ (M}^{-1} \text{ s}^{-1}\text{)}$, the bimolecular association rate constant, and $k_b = b \text{ (s}^{-1}\text{)}$, the monomolecular dissociation rate constant.

The fact that the formation of the CBPQT^{2(•+)}CMV^{•+} complex proceeds very rapidly ($k_f = (2.1 \pm 0.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) in a single rate-limiting step indicates⁴⁶ the absence of either strong electrostatic repulsions or steric hindrance at play during this process. A plot of k_{obs} versus the concentration of MV^{•+} yielded (Figure 5c) a rate of association k_f of $(2.1 \pm 0.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, and a rate of dissociation k_b of $250 \pm 50 \text{ s}^{-1}$. The ratio of k_f/k_b ($0.84 \times 10^4 \text{ M}^{-1}$) is reasonably consistent with the thermodynamic equilibrium constants determined by ITC [$(5.04 \pm 0.63) \times 10^4 \text{ M}^{-1}$] and UV/vis [$(7.9 \pm 5.5) \times 10^4 \text{ M}^{-1}$] spectroscopy. The k_f value obtained for the formation of the trisradical CBPQT^{2(•+)}CMV^{•+} complex is an order of magnitude smaller compared⁴⁷ with the threading rate constant ($k_f = 3.0 \pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, MeCN, 293 K) for the BHEEN guest entering the cavity of the CBPQT⁴⁺ ring. The monomolecular dissociation rate constant ($k_b = 250 \pm 50 \text{ s}^{-1}$) for the CBPQT^{2(•+)}CMV^{•+} complex is comparable to that ($k_b = 530 \pm 50 \text{ s}^{-1}$, MeCN, 293 K) of the CPBQT⁴⁺CBHEEN

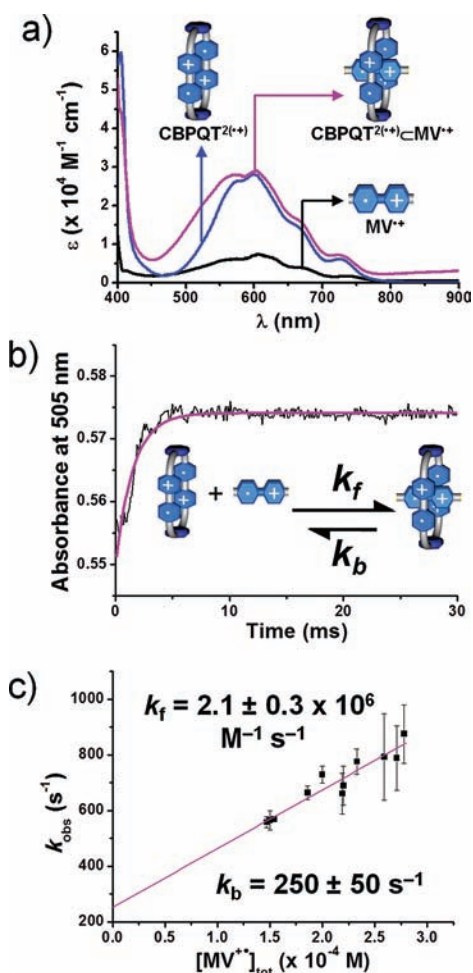


Figure 5. (a) UV/vis electronic spectra of CBPQT^{2(•+)}, MV^{•+}, and CBPQT^{2(•+)}CMV^{•+} recorded in MeCN at 298.0(2) K. Formation of the CBPQT^{2(•+)}CMV^{•+} inclusion complex is characterized by a broadening of the absorption band centered around 600 nm and formation of a broad band in the NIR. (b) Kinetic trace for the formation of the CBPQT^{2(•+)}CMV^{•+} inclusion complex obtained using stopped-flow spectroscopy in MeCN at 298.0(2) K. A single rate-limiting-step is observed. $[\text{CBPQT}^{2(\bullet+)}]_0 = 1.13 \times 10^{-5} \text{ M}$; $[\text{MV}^{\bullet+}]_0 = 2.18 \times 10^{-4} \text{ M}$. (c) A plot of the apparent pseudo-first-order rate constant, k_{obs} , versus the concentration of MV^{•+}, with concentration of CBPQT^{2(•+)} held constant. Solvent, MeCN; $T = 298.0(2) \text{ K}$; $[\text{CBPQT}^{2(\bullet+)}]_0 = 1.13 \times 10^{-5} \text{ M}$.

complex dissociation rate constant. Although the rate constant for formation of the triradical $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$ complex is an order of magnitude less than that for the formation of $\text{CPBQT}^{4+}\text{CBHEEN}$, we have shown previously for the formation⁴⁶ of [2]pseudorotaxanes with threads containing 1,5-dioxynaphthalene units together with terminal BIPY^{2+} units flanking either side that the threading of the CBPQT^{4+} ring is slowed ($k_f = (7.0 \pm 0.7) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, 0.1 M NaCl in H_2O , 298 K) by many orders of magnitude as a consequence of the BIPY^{2+} units serving the role of electrostatic barriers.

Cyclic Voltammetry and Digital Simulations. In a 1:1 mixture of CBPQT^{4+} and MV^{2+} , both in their fully oxidized forms, no binding between the two charged species is observed, presumably as a consequence of their similar π -electron-poor electronic characteristics, not to mention electrostatic repulsion. Upon a three-electron reduction, wherein two electrons contribute to the formation of the $\text{CBPQT}^{2(\bullet+)}$ ring and one to the formation of the $\text{MV}^{\bullet+}$ guest, production of the triradical $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$ inclusion complex ensues as a result of favorable radical–radical interactions, all of which can be stimulated electrochemically. The nature of these radical–radical interactions is largely a consequence of radical pairing, a phenomenon that has been studied^{21c} in considerable detail in the case of the classical viologen radical cation dimers and violenes in general.⁴⁸ When viologen radical cations dimerize, at distances defined by van der Waals contacts, the dimers become radically paired and hence EPR silent (inactive), while the viologen radical cation monomer results in a characteristic signal. This mechanism involving radical pairing has important implications when considering the electrochemical behavior of the triradical $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$ complex. Consider the hypothesis where only two of the $\text{BIPY}^{\bullet+}$ radical cation subunits of the complex are paired at any one time, leaving one $\text{BIPY}^{\bullet+}$ radical cation subunit of the $\text{CBPQT}^{2(\bullet+)}$ ring unpaired. One might anticipate that this unpaired $\text{BIPY}^{\bullet+}$ unit would not be as strongly engaged in radical–radical interactions as the other two paired $\text{BIPY}^{\bullet+}$ units. Theoretical investigations, based on DFT to calculate the SOMO of the triradical $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$ complex, support^{26a} this hypothesis (*vide supra*), by revealing that orbital overlap of the $\text{MV}^{\bullet+}$ guest occurs predominantly with only one of the $\text{BIPY}^{\bullet+}$ units in the $\text{CBPQT}^{2(\bullet+)}$ ring. The fact that one of the two $\text{BIPY}^{\bullet+}$ radical cations in the ring is not as strongly interactive with the $\text{MV}^{\bullet+}$ guest mandates, from a thermodynamic perspective, that this unpaired $\text{BIPY}^{\bullet+}$ unit undergoes reduction to its neutral BIPY^0 form at a less negative potential, that is, it should be easier to reduce in comparison with the two radically paired $\text{BIPY}^{\bullet+}$ units. The corollary to this argument is that the reoxidation of the unpaired $\text{BIPY}^{\bullet+}$ radical cation unit should also occur at less positive potentials, that is, it should be easier to oxidize, compared with the two paired $\text{BIPY}^{\bullet+}$ radical cation units. It follows therefore that the formation of a tetracationic $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$ bisradical inclusion complex must appear in any discussion of the electrochemical switching mechanism.

The CV of an equimolar mixture of the CBPQT^{4+} ring and MV^{2+} is presented in Figure 6a. The first reduction peak (-0.32 V , peak potential) is a three-electron process with two electrons going to CBPQT^{4+} , forming the diradical dication $\text{CBPQT}^{2(\bullet+)}$, and one electron going to MV^{2+} , forming the radical cation $\text{MV}^{\bullet+}$. As a consequence of this three-electron process, formation of the triradical tricationic $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$ inclusion complex ensues spontaneously. The result of this inclusion is that only one of the $\text{BIPY}^{\bullet+}$ radical cations of the

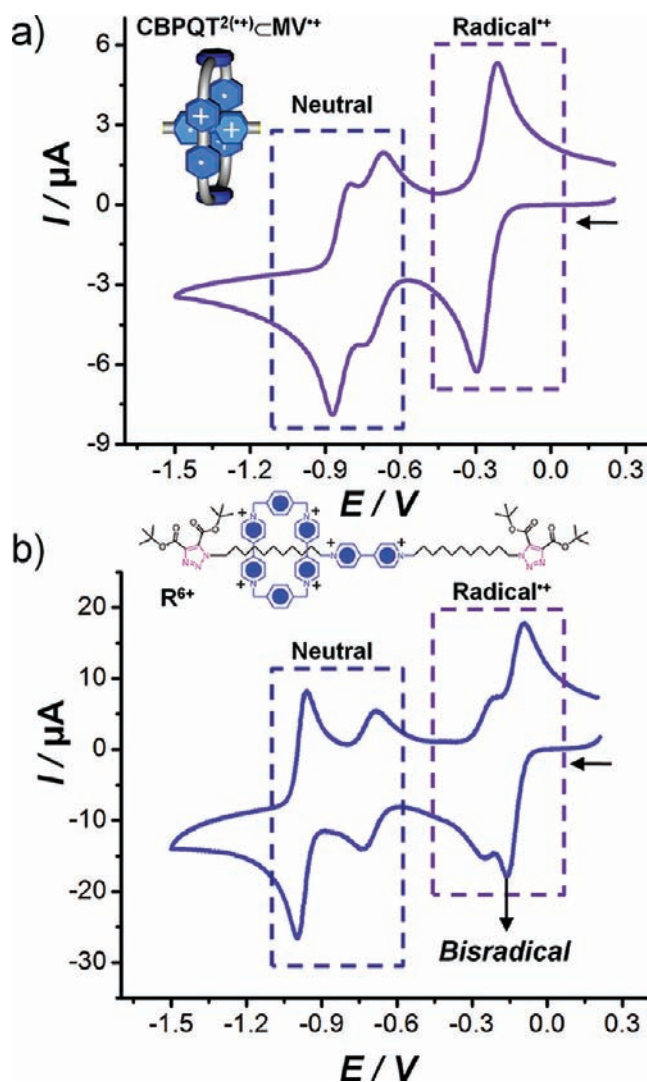


Figure 6. (a) Cyclic voltammogram of an equimolar mixture of CBPQT^{4+} and MV^{2+} in MeCN at 1.0 mM. The first reduction process is a three-electron one leading to the formation of the triradical $\text{CBPQT}^{2(\bullet+)}\text{CMV}^{\bullet+}$ inclusion complex. As a consequence of radical pairing between one $\text{BIPY}^{\bullet+}$ of the ring and that from $\text{MV}^{\bullet+}$, the reduction of the complex to its neutral form is observed to occur over, first by a one-electron process, followed by a two-electron one, the former (and less negative) one is assigned to the reduction of the unpaired $\text{BIPY}^{\bullet+}$ unit in the ring. (b) Cyclic voltammogram of the [2]rotaxane R^{6+} containing only a BIPY^{2+} recognition unit in its dumbbell component. As a consequence of both radical pairing and the mechanical bond, the first reduction process leading to the triradical species $\text{R}^{3(\bullet+)}$ is observed to occur over, first by a two-electron followed by a one-electron process. The first two-electron process is assigned to the simultaneous reduction of one BIPY^{2+} unit of the ring and the BIPY^{2+} unit of the dumbbell component, leading to the formation of a stable bisradical intermediate. Both voltammograms were recorded at a scan rate of 200 mV s^{-1} with an Ag/AgCl reference electrode.

complexed $\text{CBPQT}^{2(\bullet+)}$ interacts strongly with the $\text{MV}^{\bullet+}$ radical cation, leading to the fact that the second reduction of this weakly interacting, unpaired $\text{BIPY}^{\bullet+}$ occurs at a less negative potential (-0.76 V , peak potential), roughly at the same potential as the second reduction of CBPQT^{4+} alone in solution. The reduction of the paired $\text{BIPY}^{\bullet+}$ units of the complexed $\text{CBPQT}^{2(\bullet+)}$ and the $\text{MV}^{\bullet+}$ radical cation, occur

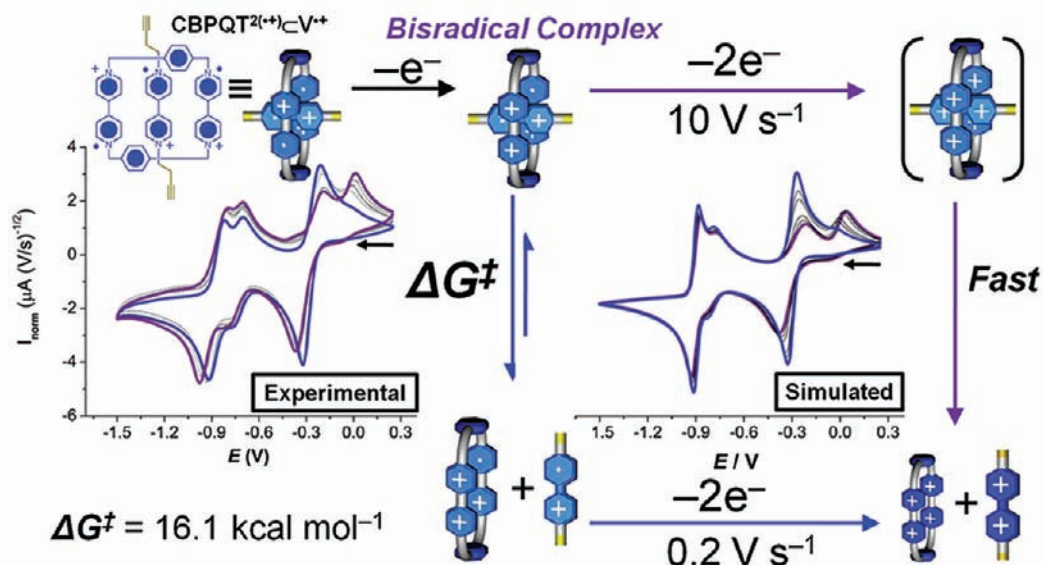


Figure 7. Experimental and simulated variable scan rate cyclic voltammograms of a 1:1 mixture of CBPQT^{4+} and V^{2+} in MeCN at 298 K. As a consequence of radical pairing, one of the $\text{BIPY}^{\bullet+}$ radical cation units is oxidized first (at a less positive potential) during the scan, leading to the formation of the bisradical $\text{CBPQT}^{(2+)(\bullet+)}\text{CV}^{\bullet+}$ intermediate. The presence of the BIPY^{2+} unit in the ring $\text{CBPQT}^{(2+)(\bullet+)}$ ring leads to dissociation of the complex observable on the time scale of the CV experiments. When the experimental data were fitted to the digital simulations, the free energy barrier, ΔG^\ddagger , to dissociation of the bisradical $\text{CBPQT}^{(2+)(\bullet+)}\text{CV}^{\bullet+}$ complex was determined to be $16.1 \text{ kcal mol}^{-1}$. Blue trace = 200 mV s^{-1} ; purple trace = 10 V s^{-1} . IR compensation was applied and an Ag/AgCl reference electrode was used.

simultaneously at a more negative potential (-0.87 V , peak potential) as a two-electron process.

The [2]rotaxane R^{6+} (Figure 6b, top), composed of a CBPQT^{4+} ring mechanically interlocked around a dumbbell containing a BIPY^{2+} unit, was obtained using a threading-followed-by-stoppering template-directed protocol^{26b} relying upon radical–radical interactions and employing a copper-free 1,3-dipolar cycloaddition in the final reaction step, thus forming the mechanical bond. The mechanical bond dictates that the CBPQT^{4+} ring cannot escape the influence of the BIPY^{2+} unit in the dumbbell component entirely. In this situation, both the trisradical and bisradical forms of the rotaxane are stable species! Electrochemical experiments reveal that reduction of R^{6+} to the trisradical tricationic form $\text{R}^{3(\bullet+)}$ occurs over two different electron-transfer processes. The first is a two-electron reduction process, which is assigned to the formation of the paired $\text{BIPY}^{\bullet+}$ radical cations of the dumbbell with one from the ring forming the bisradical tetracationic $\text{R}^{(2+)(\bullet+)}$. The subsequent one-electron transfer is assigned to the reduction of the remaining unpaired BIPY^{2+} in the $\text{CBPQT}^{(2+)(\bullet+)}$ ring, a process that generates the trisradical tricationic $\text{R}^{3(\bullet+)}$ form of the [2]rotaxane. Both of these redox processes are independent of the scan rate ($50\text{--}1000 \text{ mV s}^{-1}$, Supporting Information), that is, they are totally reversible because the mechanical bond excludes the possibility of dissociation and so serves to stabilize the bisradical form of the rotaxane in comparison with that of its bisradical tetracationic $\text{CBPQT}^{(2+)(\bullet+)}\text{CMV}^{\bullet+}$ supramolecular analogue.

In an effort to detect the bisradical tetracationic $\text{CBPQT}^{(2+)(\bullet+)}\text{CMV}^{\bullet+}$ inclusion complex, variable scan rate CV experiments were carried out initially on a 1:1 mixture of CBPQT^{4+} and MV^{2+} . They reveal (Supporting Information), however, that the reoxidation of the trisradical tricationic complex $\text{CBPQT}^{(2+)(\bullet+)}\text{CMV}^{\bullet+}$ is independent of scan rate⁴⁹ (up to 30 V s^{-1}). This observation suggests that dissociation of $\text{CBPQT}^{(2+)(\bullet+)}\text{CMV}^{\bullet+}$ is too fast to detect on the time scale of

the CV experiments. In order to probe the nature of the bisradical tetracationic intermediate, we performed variable scan rate CV experiments on a 1:1 mixture of CBPQT^{4+} and V^{2+} , where the butynyl functional groups of V^{2+} act to slow the rate of dissociation such that the intermediate can be more readily observed under the experimental conditions employed. We hypothesize that the extra steric bulk or favorable noncovalent bonding interactions resulting from the presence of the butynyl substituents of V^{2+} act to stabilize the bisradical tetracationic intermediate, $\text{CBPQT}^{(2+)(\bullet+)}\text{CV}^{\bullet+}$, kinetically by comparison with the methyl groups of MV^{2+} .

Evidence for the existence of the $\text{CBPQT}^{(2+)(\bullet+)}\text{CV}^{\bullet+}$ inclusion complex in solution can be obtained (Figure 7) from variable scan rate CV in MeCN. As a consequence of the presence of the dicationic BIPY^{2+} unit, the bisradical $\text{CBPQT}^{(2+)(\bullet+)}\text{CV}^{\bullet+}$ complex forfeits a substantial amount of stability compared with that of the trisradical $\text{CBPQT}^{(2+)(\bullet+)}\text{CV}^{\bullet+}$ complex. The bisradical complex begins to dissociate into its individual components, making reoxidation of the two remaining $\text{BIPY}^{\bullet+}$ radical cations of the separate host and guest components occur at a less positive redox potential (approximately -0.35 V), that is, easier to reoxidize. When the scan is performed at a rate slower than the time scale of the dissociation of the $\text{CBPQT}^{(2+)(\bullet+)}\text{CV}^{\bullet+}$ complex, reoxidation of the trisradical tricationic complex is observed to occur as a single, broad oxidation wave. When the reoxidation is performed at progressively faster scan rates, eventually reaching a point where dissociation of the $\text{CBPQT}^{(2+)(\bullet+)}\text{CV}^{\bullet+}$ is slow on the CV time scale, reoxidation of the trisradical tricationic complex is observed to occur by means of (i) a one-electron transfer, followed (ii) by another two-electron transfer, the latter of which occurs at a potential shifted to almost 0 V ! The first one-electron oxidation, leading to the formation of $\text{CBPQT}^{(2+)(\bullet+)}\text{CV}^{\bullet+}$, is assignable to the unpaired $\text{BIPY}^{\bullet+}$ subunit of the trisradical trication complex, which is more weakly engaged in radical–radical interactions. The second,

Table 2. Kinetic Parameters Associated with the Formation of the Trisradical Inclusion Complex between the Diradical Dication CBPQT^{2(•+)} Ring and the Radical Cation MV^{•+} and the Bisradical Complex of CBPQT^{2(•+)(•+)} with V^{•+}^a

	$k_p, 10^4 \text{ M}^{-1} \text{ s}^{-1}$	$k_r, \text{ s}^{-1}$	$\Delta G_i^\ddagger, \text{ kcal mol}^{-1}$	$\Delta G_b^\ddagger, \text{ kcal mol}^{-1}$
CBPQT ^{2(•+)} ⊂MV ^{•+}	210 ± 30 ^b	250 ± 50 ^b	8.8 ± 0.1 ^b	14.2 ± 0.1 ^b
CBPQT ^{2(•+)(•+)} ⊂V ^{•+}	6.6 ± 1 ^c	10 ± 2 ^c	11.0 ± 0.7 ^c	16.1 ± 0.5 ^c
		5.0 ± 1.0 ^d		16.5 ± 1.0 ^d

^aSolvent, MeCN; $T = 298 \text{ K}$. ^bDetermined by stopped-flow spectroscopy. ^cDetermined by cyclic voltammetry fitted to digitally simulated data.

^dDetermined by cyclic voltammetry using a relative integration analysis.

dramatically shifted two-electron process can be assigned to the simultaneous two-electron oxidation of the radically paired BIPY^{•+} units of CBPQT^{2(•+)(•+)}⊂V^{•+}, leading to the fully oxidized and highly unstable hexacationic CBPQT⁴⁺⊂V²⁺ complex, which quickly dissociates on the time scale of the CV experiment.

Because of the dissociation of the CBPQT^{2(•+)(•+)}⊂V^{•+} inclusion complex, we hypothesize that the reoxidation potentials for both separated components become shifted toward less positive potentials, resembling those of the free components alone in solution, than the first one-electron oxidation of the unpaired BIPY^{•+} radical cation in the scan, resulting in a single broad reoxidation peak. Mechanistically, we propose a first-order rate law for the dissociation of the CBPQT^{2(•+)(•+)}⊂V^{•+} inclusion complex into its individual components that is proportional to a rate constant and the concentration of the bisradical species.

Digital CV simulations of the proposed mechanism were performed (Figure 7) based on the results obtained from ITC and stopped-flow spectroscopy and are in good agreement with the experimental data. Comparisons between digital simulations and the experimental data using a X^2 fitting algorithm or by employing a relative integration analysis (see Supporting Information) of the reoxidation waves as a function of time (scan rate) establish the barrier ΔG_b^\ddagger governing the first-order dissociation of the bisradical tetracationic complex to be 16.1 or 16.5 kcal mol⁻¹, respectively, at room temperature. Table 2 summarizes the kinetic parameters obtained from stopped-flow UV/vis spectroscopic and CV data. It is worth noting that, since the kinetic reoxidation pathway of the trisradical tricationic complex is scan-rate dependent, it represents an example of a *bilabile* system.⁵⁰

CONCLUSIONS

As might be inferred by the fact that radically-based switching motifs are being integrated into host–guest and mechanically interlocked systems in only recent times, perhaps a prejudice against organic radicals as being useful building blocks in these contexts exists. Under appropriate conditions, we have shown^{26b} that it is possible to take advantage of favorable radical–radical interactions in order to template the synthesis of MIMs, as well as to induce them to switch^{26a,c} from one recognition unit to another in a reversible fashion. In the research reported in this paper, we investigated the thermodynamics and kinetics, as well as the overall electrochemical mechanism, of the formation of the trisradical inclusion complex whereby CBPQT⁴⁺ encircles MV²⁺ after reduction of each BIPY²⁺ species to their respective radical cations. Solid-state superstructural analysis confirms predictions that the MV^{•+} radical cation resides in a centrosymmetric fashion inside the cavity of the CBPQT^{2(•+)} ring. Further inspection of solid-state superstructure beyond the 1:1 complex reveals an infinite BIPY^{•+} radical cation stack of

adjacent CBPQT^{2(•+)}⊂MV^{•+} inclusion complexes. The electrochemical mechanism for formation and dissociation of the inclusion complex has been elucidated using CV, ITC, UV/vis, and stopped-flow spectroscopy. Variable scan rate CV reveals that the reoxidation pathway of the trisradical tricationic complex occurs through a bisradical tetracationic intermediate, which can be detected when the dibutynyl viologen, V^{•+}, is employed as the guest. We speculate that such a bisradical tetracationic complex, having both a BIPY^{•+} radical cation and a dicationic π -electron-poor BIPY²⁺ unit in the ring component, might possess “amphiphilic” behavior, that is, it can be both donor-loving and radical-loving. Such a property could clearly be harnessed in the context of MIMs in order to achieve more sophisticated control of their relative intramolecular motions. Greater control of the relative motions of MIMs will provide chemists with an enhanced ability to design and synthesize complex integrated systems.⁵¹

EXPERIMENTAL SECTION

General Methods. The tetracationic cyclophane, cyclobis (paraquat-*p*-phenylene) tetrakis(hexafluorophosphate)¹¹ (CBPQT·4PF₆), the dimethyl viologen^{21c} (MV·2PF₆), and the dibutynyl viologen⁵² (V·2PF₆), as well as the single-station [2]rotaxane^{26b} (R·6PF₆) were all prepared according to literature procedures. Zinc dust was activated by stirring it with dilute HCl during 10–15 min and then washing it several times with distilled H₂O, EtOH, and absolute Et₂O before drying rigorously. This procedure removes oxides, which form slowly upon standing in air from the surface of zinc.⁵³ All the physicochemical investigations were carried out with spectroscopic grade MeCN (Acros Organics ≥99.9% for spectroscopy). The stock solutions of CBPQT·4PF₆ and MV·2PF₆ were prepared by weighing using an AG 245 Mettler Toledo analytical balance (precision 0.01 mg). Complete dissolution of CBPQT·4PF₆ and MV·2PF₆ in MeCN was achieved using an ultrasonic bath (Bandelin Sonorex RK102 Transistor). The concentrations were thus obtained by weighing the appropriate amounts. Reduction of CBPQT⁴⁺ and MV²⁺ into the corresponding diradical dication CBPQT^{2(•+)} and radical cation MV^{•+} was achieved under argon (CO₂- and O₂-free argon using a Sigma Oxiclear cartridge) in less than 1 h by vigorous stirring with activated zinc dust. The formation of the radicals were monitored (see Supporting Information) by absorption spectrophotometry. Isothermal titration calorimetry (ITC) experiments were performed on a MicroCal system, VP-ITC model. Cyclic voltammetry (CV) was carried out at room temperature in argon-purged MeCN solutions with a Gamry Multipurpose instrument (reference 600) interfaced to a PC. The CV experiments were performed using a glassy carbon working electrode (0.071 cm², BASi). The electrode surface was polished routinely with 0.05 μm alumina–water slurry on a felt surface immediately before use. The counter electrode was a Pt coil, and the reference electrode was a Ag/AgCl electrode, unless otherwise noted. The concentrations of the sample and supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBA·PF₆), were 1.0 × 10⁻³ M⁻¹ and 0.1 M⁻¹, respectively. Experimental error of potential values was ±10 mV. All simulations of electrochemical data were performed using DigiSim.

UV/Vis Absorption Spectrophotometric Titration. A solution (50 mL) of CBPQT·4PF₆ (4.36 × 10⁻⁵ M) was introduced into a

jacketed cell (Metrohm) maintained at 25.0(2) °C (Lauda E200/O11 thermostat) while being deoxygenated continuously by CO₂- and O₂-free argon. In the first instance, an absorption spectrum was recorded using a Varian Cary 50 spectrophotometer, fitted with Hellma optical fibers (Hellma, 041.002-UV), and an immersion probe made of quartz suprazil (Hellma, 661.500-QX). Activated zinc dust was then added, and the formation of the diradical dication CBPQT^{2(•+)} was monitored by recording the absorption spectra as a function of time until complete reduction was achieved (~1 h). Concomitantly, a stock MeCN solution of MV^{•+} (3.35 × 10⁻³ M, 10 mL) was prepared from MV₂PF₆ under the same conditions, that is, continuous deoxygenation with CO₂- and O₂-free argon and vigorous stirring in the presence of activated zinc dust. Microvolumes of concentrated MeCN solutions of the radical cation MV^{•+} were added to a MeCN solution of CBPQT^{2(•+)}, and the reaction was allowed to stand for 15 min with vigorous stirring in the presence of activated zinc dust and under anaerobic conditions to ensure that both the complete reduction of the BIPY²⁺ derivatives and the host–guest association equilibration were attained. After each addition, a UV/vis spectrum was recorded from 230 to 900 nm on the Cary 50 (Varian) spectrophotometer maintained at 25(2) °C. The ratio [MV^{•+}]_{tot}/[CBPQT^{2(•+)}]_{tot} was varied (see the Supporting Information) from 0 to 4.38. The spectrophotometric data were analyzed with the Specfit program, which adjusts the absorptivities and the stability constants of the species formed at equilibrium. Specfit uses factor analysis to reduce the absorbance matrix and extract the eigenvalues prior to the multi-wavelength fit of the reduced data set according to the Marquardt algorithm.

Formation Kinetics. The formation kinetics of the triradical inclusion complex CBPQT^{2(•+)}CMV^{•+} were measured on a SX-18MV stopped-flow spectrophotometer from Applied Photophysics. The temperature was maintained at 25.0(2) °C with the help of a Lauda E200/RE220 cryothermostat, and the formation kinetics of the triradical species was monitored at λ = 505 nm (l = 1 cm), a wavelength that corresponds to the maximum of absorbance difference between the reactants (MV^{•+} and CBPQT^{2(•+)}) and the product (CBPQT^{2(•+)}CMV^{•+}) within the spectroscopic window employed under the experimental conditions. The CBPQT⁴⁺ concentration was fixed at 1.13 × 10⁻⁵ M, and the range of MV²⁺ concentrations was varied from 1.47 × 10⁻⁴ to 2.78 × 10⁻⁴ M by dilution of a concentrated stock solution. At least 10 times more concentrated solutions of MV²⁺ with respect to CBPQT⁴⁺ were used in order to impose pseudo-first-order conditions. Each solution, namely, the CBPQT⁴⁺ and the MV²⁺ samples, was reacted with activated zinc dust during more than 1 h to ensure complete reduction into CBPQT^{2(•+)} and MV^{•+} species. The data sets, averaged out of at least three replicates, were recorded and analyzed with the commercial software Biokine.⁵⁴ This program fits up to three exponential functions to the experimental curves with the Simplex algorithm⁵⁵ after initialization with a Padé–Laplace method.⁵⁶

■ ASSOCIATED CONTENT

● Supporting Information

Further details and characterization by ¹H DOSY NMR, CV, digital CV simulations, X-ray crystallography, ITC, and UV/vis spectroscopy. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

elhabiri@chimie.u-strasbg.fr; stoddart@northwestern.edu

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(30) Data were collected at 100 K using a Bruker d8-APEX II CCD diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$). Intensity data were collected using ω and φ scans spanning at least a hemisphere of reciprocal space for all structures (data were integrated using SAINT). Absorption effects were corrected on the basis of multiple equivalent reflections (SADABS). Structures were solved by direct methods (SHELXS) and refined by full-matrix least-squares against F^2 (SHELXL). Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. The crystal data for $[\text{CBPQT}^{2(\bullet+)}\cdot 2\text{PF}_6^-]$ contained diffuse, disordered solvent molecules that suggested penetration through the macrocycle consistent with acetonitrile but could not be adequately modeled. The bypass procedure in Platon was used to remove the electronic contribution from these solvents. The total potential solvent accessible void volume was 319 \AA^3 , and the electron count per cell is 73. As the exact solvent content is not known, the reported formula reflects only the atoms used in the refinement.

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(39) By contrast with aqueous solutions, the monomer–dimer equilibrium is indeed usually not observed in polar organic solvents such as MeOH, MeCN, or DMF except at relatively high concentrations or low temperatures.

(40) EPR investigations, which were performed in MeCN on the $\text{CBPQT}^{2(\bullet+)}$ diradical dication, reveal a lack of hyperfine splitting in the spectrum, while the 1,1'-dibutynyl-4,4'-bipyridinium $\text{V}^{\bullet+}$ radical cation displays the hyperfine splitting typically observed for these types of viologen derivatives. The lack of hyperfine splitting observed in the case of the $\text{CBPQT}^{2(\bullet+)}$ diradical dication is most likely a result of intramolecular dipole–dipole interactions between its two $\text{BIPY}^{\bullet+}$ radical cation units. For more details, see ref 26a.

(41) Although only the tail of this near-IR band has been observed because of the instrumental limitations ($200\text{--}900 \text{ nm}$) of the absorption spectrophotometer employed during this investigation, we have reported previously using another spectrometer the spectrum of the $\text{CBPQT}^{2(\bullet+)}\text{CV}^{\bullet+}$ complex, which shows that this near-IR band has a maximum at 1075 nm . For more details, see ref 26a. In addition, there are conflicting rationalizations in the literature as to the nature of this near-IR absorption band typical of $\text{BIPY}^{\bullet+}$ radical dimers. We are of the belief that this near-IR band is a result of through-space intermolecular charge transfer similar to that observed for mixed-valent radical cation dimers. For further discussion, see: (a) Lü, J.-M.; Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2003**, *125*, 12161. (b) Sun, D.-L.; Rosokha, S. V.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2003**, *125*, 15950.

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