

Influence of Constitution and Charge on Radical Pairing Interactions in Triradical Tricationic Complexes

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Abstract The results of a systematic investigation of triradical tricationic complexes formed between cyclobis(paraquat-*p*-phenylene) bisradical dicationic (CBPQT²⁽⁺⁺⁾) rings and a series of 18 dumbbells containing centrally located 4,4'-bipyridinium radical cationic (BIPY^{•+}) units within oligomethylene chains terminated for the most part by charged 3,5-dimethylpyridinium (PY⁺) and neutral 3,5-dimethylphenyl (PH) groups are reported. The complexes were obtained by treating equimolar amounts of the CBPQT⁴⁺ ring and the dumbbells containing BIPY²⁺ units with zinc dust in acetonitrile (MeCN) solutions. Whereas UV-VIS-NIR spectra revealed absorption bands centered on ca. 1100 nm with quite different intensities for the 1:1 complexes depending on the constitutions and charges on the dumbbells, titration experiments show that the association constants (K_a) for complex formation vary over a wide range from K_a values of 800 M⁻¹ for the weakest to 180000 M⁻¹ for the strongest complexes. While Coulombic repulsions emanating from PY⁺ groups located at the ends of some of the dumbbells undoubtedly contribute to the destabilization of the triradical tricationic complexes, solid-state superstructures support the contention that those dumbbells with neutral PH groups at the ends of flexible and

appropriately constituted links to the BIPY^{•+} units stand to gain some additional stabilization from C–H··· π interactions between the CBPQT^{2(•+)} rings and the PH termini on the dumbbells. A fundamental understanding of molecular recognition in radical complexes has relevance when it comes to the design and synthesis of non-equilibrium systems.

■ INTRODUCTION

Noncovalent bonding interactions have become an important consideration, along with molecular recognition when designing materials during the past couple of decades.¹ The bottom-up approach of supramolecular chemistry² has contributed to many areas with potential for applications such as chemical sensors³, responsive materials⁴, drug delivery vehicles⁵, catalysis⁶ etc. Weak interactions such as hydrogen bonding⁷, metal coordination⁸, hydrophobic forces⁹, van der Waals forces¹⁰, π - π stacking¹¹ and electrostatic effects¹² have all been investigated widely in the context of supramolecular systems. Radical-radical interactions, however, have found only limited attention¹³ in such systems.

1,1'-Dialkyl-4,4'-bipyridinium (BIPY²⁺) dications are commonly used units¹⁴ in supramolecular chemistry, mostly as π -electron poor acceptors in π - π stacking and in host-guest complexes. By contrast, the radical-radical dimerization of the reduced form – namely BIPY^{•+} – of BIPY²⁺ was discovered¹⁵ much earlier than the charge transfer complexation¹⁶ of BIPY²⁺ dications with electron donors. The radical-radical dimerization¹⁷ of BIPY^{•+} radical cations, also known as pimerization¹⁸, however, was not widely employed¹⁹ in the design of supramolecular systems because of the low binding ability^{17a,17b,17d} of radical pairs, resulting in pimerization only being observable at significantly high concentrations. Cyclobis(paraquat-*p*-phenylene)²⁰ (CBPQT⁴⁺) as a higher homologue of BIPY²⁺, containing two BIPY²⁺ units connected in a rigid fashion by two para-xylylene linkers, has been exploited as an electron deficient host^{20c,21} during the past quarter century. Recently, we discovered (Figure 1) that BIPY²⁺ forms a triradical tricationic complex²² – namely BIPY^{•+}CBPQT^{2(•+)} – with the CBPQT⁴⁺ ring under reducing conditions. The binding constant²³ ($K_a \sim 10^4 \text{ M}^{-1}$ in MeCN) associated with this 1:1 complex is comparable or even stronger than donor-acceptor complexes²⁴ ($K_a = 10^3\text{--}10^5 \text{ M}^{-1}$ in MeCN) involving CBPQT⁴⁺. The strength of the triradical tricationic complex outstrips that ($K_a < 10^3 \text{ M}^{-1}$ in MeCN) involving dimerization^{15e} of BIPY^{•+} units on account of the macrocyclic effect.²⁵ Subsequently, we have introduced radical-radical interactions into templating the synthesis of rotaxanes²⁶ and}

catanenes²⁷ as well as into foldmers²⁸, daisy chains²⁹, molecular switches³⁰, molecular motors³¹, molecular pumps³², and semiconducting materials³³.

In this full paper, we assess the binding aptitudes of the CBPQT²⁽⁺⁺⁾ ring towards a series of dumbbells in which oligomethylene chains incorporate BIPY⁺⁺ units in their midribs and carry variously (i) two positively charged 3,5-dimethylpyridinium (PY⁺) termini, (ii) two neutral 3,5-dimethylphenyl (PH) termini, and (iii) a PY⁺ terminus at one end and a PH terminus at the other, in addition to controls with (iv) only one PY⁺ terminus and with (v) no PY⁺ or PH termini. We demonstrate that these PY⁺ and PH termini, together with lengths from 0 to 12 methylene units separating them from the centrally located BIPY⁺⁺ units influence significantly the strength of their triradical tricationic complexes with the CBPQT²⁽⁺⁺⁾ ring. Both the number of PY⁺ termini and the number of methylene groups between the positively charged PY⁺ termini and the BIPY⁺⁺ units influence the stability of the triradical tricationic complexes formed between these BIPY⁺⁺ units and the CBPQT²⁽⁺⁺⁾ ring. Doubling the number of PY⁺ termini, as well as curtailing the number of methylene decreases the strength of the complexes. By contrast, introducing electron rich PH units in the vicinity of the triradical tricationic midribs leads to much stronger radical pairing interactions. Experimental results and quantum mechanical (QM) calculations reveal that additional C–H··· π interactions exist in some of the triradical tricationic complexes, i.e., the binding between the CBPQT²⁽⁺⁺⁾ rings and the BIPY⁺⁺ units in the dumbbells can be enhanced by introducing π -electron rich functions at appropriate positions. Data have been collected for the interactions of 18 different BIPY⁺⁺ dumbbells with the CBPQT²⁽⁺⁺⁾ rings using (i) UV-VIS-NIR spectroscopies, (ii) single crystal X-ray diffraction (XRD), supported by (iii) density function theory (DFT) calculations, as well as (iv) cyclic voltammetry (CV).

■ RESULTS AND DISCUSSION

Design Strategies and Syntheses. Recently, we have shown³⁴ that Coulombic forces can change significantly the kinetic barriers associated with the threading of CBPQT⁴⁺/CBPQT²⁽⁺⁺⁾ rings onto both charged and neutral dumbbells. In this investigation, we explore the influence of Coulombic forces on the thermodynamics of pseudorotaxane formation. The 1,1'-didodecyl-4,4'-bipyridinium dication (DB1²⁺) was chosen as the standard viologen recognition counterpart for the CBPQT⁴⁺/CBPQT²⁽⁺⁺⁾ rings. Positively charged 3,5-dimethylpyridinium (PY⁺) units were then attached to both ends of oligomethylene chains emanating from the central BIPY²⁺ unit. The

length of the linkers between the PY^+ termini and the central BIPY^{2+} units cover the range from 11 to 8 to 6 to 5 to 4 to 3 to 2 ($\text{DB}2^{4+}$ – $\text{DB}8^{4+}$) methylene groups. In order to probe the influence of the positive charge on the terminal PY^+ units, $\text{DB}9^{3+}$ and $\text{DB}10^{3+}$ with 2 and 3 methylene groups separating one PY^+ terminus from the central BIPY^{2+} unit, while the other substituent is a neutral propyl group, were synthesized. The dumbbell $\text{DB}11^{3+}$ can be viewed as being derived from $\text{DB}9^{3+}$ by replacement of terminal methyl group on the neutral end by a 3,5-dimethylphenyl (PH) unit, i.e., the neutral analogue of a PY^+ unit. This PH unit terminates both ends of $\text{DB}12^{2+}$ – $\text{DB}18^{2+}$ with 0, 1, 2, 3, 4, 5 and 6 methylene units between the PH termini and the central BIPY^{2+} units. The structural formulas and the corresponding graphical representations of the 18 compounds $\text{DB}1^{2+}$ – $\text{DB}18^{2+}$ are shown in Table 1.

The syntheses of 18 compounds were tackled employing three different approaches (Scheme 1) depending on their constitutions. The symmetric dumbbells ($\text{DB}1^{2+}$ – $\text{DB}7^{4+}$ and $\text{DB}13^{2+}$ – $\text{DB}18^{2+}$) were prepared in one step by performing $\text{S}_{\text{N}}2$ reactions between 4,4'-bipyridine and 2.0 equiv of the corresponding chloride/bromide/tosylate, followed by counterion exchange to give their PF_6^- salts. The dumbbell $\text{DB}8^{4+}$ had to be synthesized in two steps on account of the poor solubility of the intermediate bromide salt following the first $\text{S}_{\text{N}}2$ reaction and the low reactivity of the second pyridyl unit, deactivated by the electron withdrawing pyridinium unit. Constitutionally unsymmetrical dumbbells ($\text{DB}9^{3+}$ – $\text{DB}11^{3+}$) were also prepared in two steps by nucleophilic substitutions, followed by counterion exchange to give their PF_6^- salts. The dumbbell $\text{DB}12^{2+}$ was obtained using the Zincke reaction, followed by substitution of the 2,4-dinitrophenyl groups with 3,5-dimethylaniline. All the details describing the synthetic procedures can be found in the Supporting Information.

UV-VIS-NIR Spectroscopic Investigations. To begin with we recorded the UV-VIS-NIR spectra of the triradical tricationic complexes formed between the BIPY^{*+} -containing dumbbells under reductive conditions and the $\text{CBPQT}^{2(+)}$ ring. Activated Zn dust was added to MeCN solutions containing equimolar amounts of $\text{CBPQT}\cdot 4\text{PF}_6$ and each of the dumbbells at concentrations of 0.5 mM. After stirring in an Ar glovebox for 5 min, the excess of Zn dust was filtered off: the purple filtrates were sealed in a 1 mm quartz cuvette and the UV-VIS-NIR spectra were recorded. Although all the dumbbells display characteristic²²⁻²³ triradical tricationic bands around 1100 nm, the intensities of their absorption bands differ.

First of all, let us compare the UV-VIS-NIR spectra of an equimolar mixture of $\text{DB}1^{*+}$ and

CBPQT²⁽⁺⁺⁾ with those mixtures derived from dumbbells containing two PY⁺ units (Figure 2a). As expected, the equimolar mixture containing DB1⁺⁺ exhibits a stronger NIR absorption band around 1100 nm, while the triradical tricationic bands for equimolar mixtures of dumbbells DB3²⁺⁽⁺⁺⁾, DB4²⁺⁽⁺⁺⁾, DB6²⁺⁽⁺⁺⁾ and DB8²⁺⁽⁺⁺⁾ decrease in their intensities as the oligomethylene linkers between the PY⁺ and BIPY⁺⁺ units become shorter. This observation can be explained by the fact that the positively charged PY⁺ units destabilize the triradical tricationic complex the closer they are to it. The corresponding increase in the absorption band of the BIPY⁺⁺ radical cation at ca. 600 nm confirms the presence of more and more free BIPY⁺⁺ radical cations in solution. The influence of the positively charged PY⁺ units also becomes evident with comparing spectra (Figure 2b) of equimolar mixtures of CBPQT²⁽⁺⁺⁾ with DB10⁺⁽⁺⁺⁾ and DB9⁺⁽⁺⁺⁾ and those of CBPQT²⁽⁺⁺⁾ with DB7²⁺⁽⁺⁺⁾ and DB8²⁺⁽⁺⁺⁾: in these cases, the band for the triradical trications at ca. 1100 nm is stronger for the former than for the latter. The Coulombic effect is also evident when making comparisons between equimolar mixtures involving CBPQT²⁽⁺⁺⁾ with DB9⁺⁽⁺⁺⁾ and DB10⁺⁽⁺⁺⁾ and also with DB7²⁺⁽⁺⁺⁾ and DB8²⁺⁽⁺⁺⁾: irrespective of whether the dumbbells are mono- or bis-PY⁺ functionalized, the shorter linkers between the PY⁺ and BIPY⁺⁺ units result in weaker triradical tricationic absorptions. The differences between equimolar mixtures of CBPQT²⁽⁺⁺⁾ and those dumbbells (DB14⁺⁺, DB11⁺⁽⁺⁺⁾, DB9⁺⁽⁺⁺⁾ and DB8²⁺⁽⁺⁺⁾) containing neutral PH units and positively charged PY⁺ units are then compared in Figure 2c. As in the case of the equimolar mixture of CBPQT²⁽⁺⁺⁾ with neutral didodecyl-functionalized DB1⁺⁺, the equimolar mixture of CBPQT²⁽⁺⁺⁾ and DB14⁺⁺ with two neutral PH termini exhibits a much stronger triradical tricationic NIR band compared with that of an equimolar mixture of CBPQT²⁽⁺⁺⁾ with its positively charged DB8²⁺⁽⁺⁺⁾ analogue carrying two PY⁺ termini. The intensity of the triradical tricationic band of the equimolar mixture of CBPQT²⁽⁺⁺⁾ with PY⁺/PH terminated DB11⁺⁽⁺⁺⁾ resides between those of the equimolar mixture of CBPQT²⁽⁺⁺⁾ with DB14⁺⁺ and DB8²⁺⁽⁺⁺⁾. Moreover, we also notice that the equimolar mixture of CBPQT²⁽⁺⁺⁾ and DB11⁺⁽⁺⁺⁾ has a stronger triradical tricationic absorption band than the equimolar mixture of CBPQT²⁽⁺⁺⁾ with DB9⁺⁽⁺⁺⁾, although both DB11⁺⁽⁺⁺⁾ and DB9⁺⁽⁺⁺⁾ contain the same positively charged PY⁺ terminus. Although neither DB1⁺⁺ nor DB14⁺⁺ contains any positively charged PY⁺ termini, the equimolar mixture of CBPQT²⁽⁺⁺⁾ with DB14⁺⁺ exhibits a stronger triradical tricationic absorption band compared with the case of the equimolar mixture of CBPQT²⁽⁺⁺⁾ with DB1⁺⁺ (Figure 2d). These observations might suggest that the neutral PH unit can provide some extra interactions to

stabilize the triradical tricationic complexes.

Binding Constant Measurements. The strengths of binding between the CBPQT²⁽⁺⁾ ring and the 18 dumbbells containing BIPY⁺ units were measured by carrying out titration experiments in an Ar-filled glovebox. The titration experiments were monitored after transfer of samples in the glovebox to cuvettes which were sealed to the air by UV-VIS-NIR spectroscopy at ca. 1100 nm. For the experimental details and results from these measurements, see the Supporting Information, in particular Table S1 and Figures S1–S20. The results, which are summarized in Figure 3, reveal that the association constants (K_a) for the formation of the triradical tricationic complexes between the CBPQT²⁽⁺⁾ ring and the 18 dumbbells containing BIPY⁺ units in MeCN vary (Table 2) over a wide range from 10^2 to 10^5 M⁻¹ with the weakest being DB8²⁽⁺⁾ with a K_a value of 800 M⁻¹ and the strongest being DB14⁺ with a K_a value of 180000 M⁻¹. In general, the association constants for the complexes involving dumbbells with positively charged PY⁺ termini (the pink, blue and black line/points in Figure 3) are significantly smaller than those for dumbbells with neutral PH termini (the red and green line/points in Figure 3). The K_a values for the dumbbells terminated by PY⁺ groups are influenced by the number of positive charges (one or two) and the number of methylene groups separating the PY⁺ termini from the centrally located BIPY⁺ units, i.e., the distance between positive charges in the complexes. For the series of PY⁺-terminated dumbbells, a decrease is observed (black line in Figure 3) in the K_a values for the complexes as the oligomethylene chains become shorter ($n = 11$ down to 2 in Table 1) in going from DB2²⁽⁺⁾ ($K_a = 7600$ M⁻¹) to DB8²⁽⁺⁾ ($K_a = 800$ M⁻¹). The two half-dumbbells with only one PY⁺ terminus exhibit (blue line in Figure 3) higher K_a values than the series of dual-terminated PY⁺ dumbbells with DB10⁺⁽⁺⁾ where $n = 3$ in Table 1 having a higher K_a value than DB9⁺⁽⁺⁾ where $n = 2$ in Table 1. The neutral PH-terminated dumbbells (green line in Figure 3) reveal higher K_a values and a more complicated behavior. Dumbbells DB15⁺ to DB18⁺ containing oligomethylene chains with three methylene units ($n = 3$ in Table 1) or longer ($n = 4,5,6$ in Table 1) show very similar binding strengths to each other and also to DB1⁺ carrying only dodecyl chains: in these cases, there is no Coulombic repulsion to destabilize the triradical tricationic complexes. Dumbbell DB12⁺ to DB14⁺ where $n = 0, 1$ and 2, respectively, in Table 1, however, exhibit a dramatic increase in K_a values from 34000 M⁻¹ for DB12⁺ to 180000 M⁻¹ for DB14⁺ reflecting the fact that additional C–H $\cdots\pi$ interactions are coming into play as sources (vide infra) of extra stabilization of their complexes. This interpretation is strengthened further

on comparing the K_a value of 2100 M^{-1} for the half-dumbbell $\text{DB9}^{+(++)}$ with that of 6600 M^{-1} for the full dumbbell $\text{DB11}^{+(++)}$ terminated by a PH unit which can enter into $\text{C-H}\cdots\pi$ interactions with the $\text{CBPQT}^{2(++)}$ ring.

Single-Crystal X-Ray Diffraction (XRD). In an attempt to gain a better understanding of the inconsistencies in binding strengths between the $\text{CBPQT}^{2(++)}$ rings and the different dumbbells containing BIPY^{++} units, we decided that solid-state superstructures might yield some valuable co-conformation information.³⁵ Single crystals were grown in an Ar-filled glovebox by slowly diffusing $i\text{Pr}_2\text{O}$ into MeCN solutions (0.5 mM) of the triradical tricationic complexes derived from the $\text{CBPQT}^{2(++)}$ ring and dumbbells $\text{DB7}^{2+(++)}$, $\text{DB8}^{2+(++)}$, $\text{DB9}^{+(++)}$, $\text{DB10}^{+(++)}$, DB12^{++} , DB13^{++} and DB14^{++} . The X-ray crystal data associated with these solid-state superstructures are summarized in the Experimental Section. The superstructures are illustrated in Figures 4 and 5 and also in the Supporting Information in Figure S21–S27. They all reveal 1:1 inclusion complexes in which the BIPY^{++} units in the dumbbells are encircled²³ by $\text{CBPQT}^{2(++)}$ rings. In the case of both the full-dumbbells terminated by two PY^+ units and half dumbbells with only one PY^+ terminus, the PY^+ units are directed (Figure 4) away from the charged centers of complexation in order to minimize Coulombic repulsion. It is worthy of note that both $\text{DB7}^{2+(++)}$ and $\text{DB10}^{+(++)}$ with trimethylene liners form stronger complexes in solution than do $\text{DB8}^{2+(++)}$ and $\text{DB9}^{+(++)}$ with bismethylene linkers. The solid-state superstructures (Figure 5) of the triradical tricationic complexes formed between the $\text{CBPQT}^{2(++)}$ ring and dumbbells DB12^{++} , DB13^{++} and DB14^{++} terminated with neutral PH groups are very different. In the $\text{DB12}^{++}\subset\text{CBPQT}^{2(++)}$ complex, the dumbbell is rigid and directed away from the $\text{CBPQT}^{2(++)}$ ring. When there are methylene groups, however, between the BIPY^{++} unit and the PH termini as in DB13^{++} , the latter fold back to create close contacts between the 3,5-dimethylphenyl phenyl rings and the phenylene linkers in the $\text{CBPQT}^{2(++)}$ rings. The distances from the phenylene protons to the PH planes are 2.84 and 2.90 Å. When the spacers between the BIPY^{++} units and the PH termini are bismethylenes as in DB14^{++} , even more promoted fold backs by the PH termini take place as indicated by close contacts of 2.71 Å between the β -protons on BIPY^{++} units of the $\text{CBPQT}^{2(++)}$ rings and the PH planes of the 3,5-dimethylphenyl rings. The fact that the PH termini fold back in the solid-state superstructures of $\text{DB13}^{++}\subset\text{CBPQT}^{2(++)}$ and $\text{DB14}^{++}\subset\text{CBPQT}^{2(++)}$ suggests that there are $\text{C-H}\cdots\pi$ interactions³⁶ between the electron-deficient $\text{CBPQT}^{2(++)}$ rings and the electron rich 3,5-dimethylphenyl rings. In the former complex

the PH termini form relatively weak C–H $\cdots\pi$ interactions with the phenylene linkers in the CBPQT²⁽⁺⁾ ring whereas in the latter complex the C–H $\cdots\pi$ interactions involving the more electron deficient β -protons in the BIPY⁺ units of the CBPQT²⁽⁺⁾ rings are stronger, commensurate with the complex having the highest association constant ($K_a = 180000 \text{ M}^{-1}$) of all the 18 dumbbells in MeCN solution. Although we did not obtain crystals of the DB11⁺⊂CBPQT²⁽⁺⁾ complex, we can infer that C–H $\cdots\pi$ interactions result in it forming a stronger complex than DB9⁺⊂CBPQT²⁽⁺⁾ complex devoid of C–H $\cdots\pi$ interactions. In the case the dumbbells DB15⁺, DB16⁺, DB17⁺ and DB18⁺ with linkers containing 3, 4, 5 and 6 methylene groups, respectively, presumably the conformations of the linkers exclude the folding back to form C–H $\cdots\pi$ interactions and so they exhibit very similar association constants to each other and to DB1⁺⊂CBPQT²⁽⁺⁾.

Quantum Mechanism (QM) Calculations. QM calculations were carried out in order to probe the binding free energies ($\Delta G_{\text{binding}}$) between the reduced CBPQT²⁽⁺⁾ rings and dumbbells involving reduced BIPY⁺ units. Only triradical tricationic complexes with bismethylene linkers and different termini (2PY⁺, 1PY⁺, 1PY⁺ plus 1PH and 2PH) corresponding to DB8²⁽⁺⁾, DB9⁺⁽⁺⁾, DB11⁺⁽⁺⁾ and DB14⁺, respectively, were subjected to calculations. A model dumbbell DB0⁺ – 1,1'-diethyl-4,4'-bipyridinium, an analogue without any termini – was also included in the calculations in order to gain a better understanding of the relationships between the different termini and $\Delta G_{\text{binding}}$. The superstructures of these calculated complexes are shown in Table S3 in the Supporting Information. With van der Waals (D3) and basis set superposition error (BSSE) corrections, the QM calculations have reproduced (Table 3) qualitatively the experimental $\Delta G_{\text{binding}}$ data. DB8²⁽⁺⁾ with two PY⁺ termini has the lowest calculated binding energy of -1.39 kcal/mol compared with the experimental value of -4.0 kcal/mol . DB14⁺ with two PH groups has the highest calculated binding free energy of -13.4 kcal/mol , compared with the experimental value of -7.2 kcal/mol . The calculated $\Delta G_{\text{binding}}$ values for the other complexes are in between those for DB8²⁽⁺⁾ and DB14⁺ in accordance with the sequence –

$$\Delta G_{\text{binding}}^{\text{DB8}} < \Delta G_{\text{binding}}^{\text{DB9}} < \Delta G_{\text{binding}}^{\text{DB0}} < \Delta G_{\text{binding}}^{\text{DB11}} < \Delta G_{\text{binding}}^{\text{DB14}}$$

– which agrees well with the experimental data.

Cyclic Voltammetry (CV). In order to gain a better understanding of the redox processes involved in the assembly and disassembly of radical complexes, CV experiments were performed. The redox processes exhibited by the dumbbells alone (e.g. Figure 6a for DB7•4PF₆)

are very similar to that (Figure 6b) for CBPQT•4PF₆. The BIPY²⁺ units experience two one-electron processes during reduction to their radical cation and neutral states sequentially and back reversibly to their fully oxidized states. Since the redox peaks for the PY⁺ units are outside the scan-range (< -1.20 V), they are considered to be inert under the experimental conditions. The redox peaks for the dumbbells are shifted to more positive potentials on account of increased electron inductive effects as the linkers between the BIPY²⁺ and PY⁺ units become shorter. See Supporting Information, Figure S28–S30 and Table S2. When the dumbbells are mixed in a 1:1 molar ratio with CBPQT•4PF₆, the peaks corresponding to the oxidation of triradical states back to the fully oxidized states become separated into one-electron processes. The CV spectrum (Figure 6c) of a 1:1 mixture of DB7•4PF₆ and CBPQT•4PF₆ in MeCN illustrates the separations into three peaks. When variable scan-rate CV experiments (Figure 6d and Figure S31) were performed, the three peaks are observed to merge to give one single broad peak at low scan rate (20 mV/s). A mechanism explaining the CV spectra is proposed in Figure 7. The triradical complex, first of all, loses one electron to form a bisradical complex, resulting in much weaker binding interactions. Under slow scan-rate conditions, we propose that the bisradical complex disassembles in solution, followed by both CBPQT^{+(•+)} and BIPY^{•+} being oxidized separately, giving rise to the same broad peak. Under fast scan-rate conditions, however, the loss of a second electron is faster than the bisradical complex disassembly process. The bisradical complex has less of a tendency to lose electron compared with the triradical complex on account of the increase in the positive charge which renders the second oxidation peak more positive than the first one. Once the complex has been oxidized back to the monoradical state, the kinetic barrier for the CBPQT⁴⁺ ring to dethread increases significantly on account of Coulombic repulsions between PY⁺ and the four positive charges on the CBPQT⁴⁺ ring. Consequently, the loss of the last electron is faster than the dethreading process. The cumulated positive charges causes the oxidation processes to take place at even more positive potentials, resulting in the third oxidation peak. The proposed mechanism has been tested by digital simulation^{23,30c,37} which reveals similar results (Figure 6e) similar to the experiment spectra. The three peaks are not observed in all the dumbbells. For those dumbbells (DB2•4PF₆, DB3•4PF₆ and DB4•4PF₆) containing long linkers between the PY⁺ and the BIPY²⁺ units, there is sufficient space for the CBPQT⁴⁺ ring to reside on the linkers instead of being forced to encircle the BIPY^{•+} units and so the final oxidation occurs at the same potential as the second one, resulting (Figure 6f and Figure S31) in only two

peaks^{22-23,30c}. Three oxidation peaks are only observed in the cases of DB6•4PF₆, DB7•4PF₆ and DB8•4PF₆ in which the third oxidation potential moves significantly as the number of carbon atoms in the linkers is decreased from four to two since the CBPQT⁴⁺ ring is more restricted in DB8^{2+(•+)} than it is in DB6^{2+(•+)}. In DB11^{+(•+)} with Coulombic repulsion operating only from one end of the dumbbell, a third oxidation peak is not observed (Figure 6f) since the CBPQT⁴⁺ ring can make a quick exit from the neutral end of the dumbbell.

■ CONCLUSION

An assortment of no less than 18 dumbbells containing within their oligomethylene chains centrally located 4,4'-bipyridinium radical cationic (BIPY^{•+}) unit and terminated in some instances by positively charged 3,5-dimethylpyridium (PY⁺) groups and in other cases by neutral 3,5-dimethylphenyl (PH) groups have been evaluated for their propensities to act as substrates for the cyclobis(paraquat-*p*-phenylene) bisradical dicationic (CBPQT^{2+(•+)}) receptor. The BIPY^{•+} units in these dumbbells serve as radical recognition sites for the CBPQT^{2+(•+)} ring. The dumbbells exhibit a wide range of binding abilities for the ring depending on whether their termini are charged (PY⁺) or neutral (PH). The strengths of the 1:1 complexes formed between the dumbbells and the ring are curtailed severely by the existence of charged termini and enhanced in the presence of neutral termini. Solid-state superstructures of some of the 1:1 radical complexes reveals that the neutral aromatic termini can serve as sources of additional stabilization involving C–H···π interactions between the ring and them in folded back conformations of the dumbbells. Cyclic voltammetry shows quite convincingly that the charged ring dissociates more rapidly from the neutral ends of the dumbbells than from their charged ends. The thermodynamic and kinetic data gleaned from this radical study in physical organic chemistry finds relevance in the design and synthesis of machines that operate away-from-equilibrium.³¹⁻³²

■ EXPERIMENTAL SECTION

Synthesis. The detailed synthetic procedures and characterizations are provided in the Supporting Information (SI). CBPQT•4PF₆³⁸, DB1•2PF₆³⁹, DB7•2PF₆³¹ were prepared according to literature procedures. New compound characterizations are summarized below briefly.

DB2•4PF₆: ¹H NMR (500 MHz, CD₃CN) δ 8.90 (d, *J* = 7.0 Hz, 4H), 8.38 (d, *J* = 6.8 Hz, 4H),

8.34 (s, 4H), 8.12 (s, 2H), 4.60 (t, $J = 7.5$ Hz, 4H), 4.37 (t, $J = 7.5$ Hz, 4H), 2.46 (s, 12H), 2.05 – 1.95 (m, 4H), 1.93 – 1.89 (m, 4H), 1.43 – 1.23 (m, 28H). ^{13}C NMR (126 MHz, CD_3CN) δ 149.5, 146.2, 145.2, 140.8, 138.6, 126.8, 61.7, 61.1, 30.7, 30.4, 28.8, 28.8, 28.7, 28.4, 28.3, 25.3, 25.3, 17.0. ESI-HRMS calcd for $m/z = 1113.4520$ [$M - \text{PF}_6$] $^+$, found $m/z = 1113.4532$.

DB3•4PF₆: ^1H NMR (500 MHz, CD_3CN) δ 8.89 (d, $J = 7.0$ Hz, 4H), 8.37 (d, $J = 6.3$ Hz, 4H), 8.33 (s, 4H), 8.13 (s, 2H), 4.59 (t, $J = 7.4$ Hz, 4H), 4.38 (t, $J = 7.6$ Hz, 4H), 2.46 (s, 12H), 2.04 – 1.97 (m, 4H), 1.93 – 1.89 (m, 4H), 1.41 – 1.31 (m, 16H). ^{13}C NMR (126 MHz, CD_3CN) δ 149.5, 146.2, 145.2, 140.8, 138.6, 126.8, 61.7, 61.1, 30.6, 30.3, 28.0, 28.0, 25.2(2C), 17.0. ESI-HRMS calcd for $m/z = 1029.3581$ [$M - \text{PF}_6$] $^+$, found $m/z = 1029.3607$.

DB4•4PF₆: ^1H NMR (500 MHz, CD_3CN) δ 8.89 (d, $J = 6.9$ Hz, 4H), 8.38 (d, $J = 6.4$ Hz, 4H), 8.34 (s, 4H), 8.14 (s, 2H), 4.60 (t, $J = 7.5$ Hz, 4H), 4.39 (t, $J = 7.6$ Hz, 4H), 2.04 – 1.98 (m, 4H), 1.98 – 1.92 (m, 4H), 1.47 – 1.36 (m, 8H). ^{13}C NMR (126 MHz, CD_3CN) δ 149.6, 146.2, 145.2, 140.9, 138.7, 126.8, 61.5, 60.9, 30.2, 30.0, 24.6, 24.6, 17.0. ESI-HRMS calcd for $m/z = 973.2955$ [$M - \text{PF}_6$] $^+$, found $m/z = 973.2975$.

DB5•4PF₆: ^1H NMR (500 MHz, CD_3CN) δ 8.90 (d, $J = 6.9$ Hz, 4H), 8.40 (d, $J = 6.3$ Hz, 4H), 8.35 (s, 4H), 8.15 (s, 2H), 4.61 (t, $J = 7.6$ Hz, 4H), 4.40 (t, $J = 7.5$ Hz, 4H), 2.48 (s, 12H), 2.10 – 1.97 (m, 8H), 1.49 – 1.40 (m, 4H). ^{13}C NMR (126 MHz, CD_3CN) δ 150.6, 147.3, 146.2, 141.8, 139.7, 127.8, 62.2, 61.5, 30.7, 30.5, 22.7, 17.9. ESI-HRMS calcd for $m/z = 945.2642$ [$M - \text{PF}_6$] $^+$, found $m/z = 945.2668$.

DB6•4PF₆: ^1H NMR (500 MHz, CD_3CN) δ 8.90 (d, $J = 6.9$ Hz, 4H), 8.42 (d, $J = 6.6$ Hz, 4H), 8.36 (s, 4H), 8.19 (s, 2H), 4.66 (t, $J = 7.5$ Hz, 4H), 4.48 (t, $J = 7.5$ Hz, 4H), 2.50 (s, 12H), 2.08 – 2.05 (m, 8H). ^{13}C NMR (126 MHz, CD_3CN) δ 149.7, 146.5, 145.3, 140.9, 138.8, 126.9, 60.7, 60.1, 27.0, 26.7, 17.0. ESI-HRMS calcd for $m/z = 917.2329$ [$M - \text{PF}_6$] $^+$, found $m/z = 917.2344$.

DB8•4PF₆: ^1H NMR (500 MHz, CD_3CN) δ 8.86 (d, $J = 6.9$ Hz, 4H), 8.45 (d, $J = 6.9$ Hz, 4H), 8.37 (s, 4H), 8.27 (s, 2H), 5.17 (t, $J = 6.6$ Hz, 4H), 5.01 (t, $J = 6.6$ Hz, 4H), 2.49 (s, 12H). ^{13}C NMR (126 MHz, CD_3CN) δ 150.6, 148.1, 145.9, 141.4, 139.6, 127.7, 59.6, 59.0, 17.1. ESI-HRMS calcd for $m/z = 861.1703$ [$M - \text{PF}_6$] $^+$, found $m/z = 861.1712$.

DB9•3PF₆: ^1H NMR (500 MHz, CD_3CN) δ 8.94 (d, $J = 6.4$ Hz, 2H), 8.82 (d, $J = 7.0$ Hz, 2H), 8.45 (d, $J = 6.9$ Hz, 2H), 8.41 (d, $J = 6.2$ Hz, 2H), 8.36 (s, 2H), 8.30 (s, 1H), 5.17 (t, $J = 6.5$ Hz, 2H), 5.02 (t, $J = 6.6$ Hz, 2H), 4.64 (t, $J = 7.4$ Hz, 2H), 2.51 (s, 6H), 2.13 – 2.04 (m, 2H), 1.04 (t, $J = 7.3$ Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.0, 150.1, 149.0, 146.7, 146.2, 142.3, 140.6,

128.5, 127.9, 64.1, 60.5, 59.9, 25.0, 18.0, 10.1. ESI-HRMS calcd for $m/z = 624.1566 [M - PF_6]^+$, found $m/z = 624.1572$.

DB10•3PF₆: ¹H NMR (500 MHz, CD₃CN) δ 8.95 – 8.89 (m, 4H), 8.45 (d, $J = 6.6$ Hz, 2H), 8.42 – 8.39 (m, 4H), 8.24 (s, 1H), 4.72 (t, $J = 7.8$ Hz, 2H), 4.63 (t, $J = 7.4$ Hz, 2H), 4.58 (t, $J = 7.5$ Hz, 2H), 2.73 – 2.63 (m, 2H), 2.53 (s, 6H), 2.13 – 2.04 (m, 2H), 1.03 (t, $J = 7.4$ Hz, 3H). ¹³C NMR (126 MHz, CD₃CN) δ 151.2, 150.4, 147.8, 146.3, 146.2, 142.0, 140.1, 128.1, 127.8, 64.0, 58.9, 58.2, 32.2, 25.0, 18.0, 10.1. ESI-HRMS calcd for $m/z = 638.1718 [M - PF_6]^+$, found $m/z = 638.1726$.

DB11•3PF₆: ¹H NMR (500 MHz, CD₃CN) δ 8.85 – 8.80 (m, 2H), 8.76 (d, $J = 6.9$ Hz, 2H), 8.43 (d, $J = 7.0$ Hz, 2H), 8.37 (s, 2H), 8.33 (d, $J = 6.3$ Hz, 2H), 8.30 (s, 1H), 6.98 (s, 1H), 6.81 (s, 2H), 5.17 (t, $J = 6.5$ Hz, 2H), 5.02 (t, $J = 6.5$ Hz, 2H), 4.88 (t, $J = 7.1$ Hz, 2H), 3.28 (t, $J = 7.1$ Hz, 2H), 2.51 (s, 6H), 2.27 (s, 6H). ¹³C NMR (126 MHz, CD₃CN) δ 150.9, 149.2, 148.1, 145.8, 145.3, 141.4, 139.7, 138.4, 134.8, 128.6, 127.6, 126.6, 126.2, 62.7, 59.6, 59.0, 36.3, 19.9, 17.1. ESI-HRMS calcd for $m/z = 714.2031 [M - PF_6]^+$, found $m/z = 714.2040$.

DB12•2PF₆: ¹H NMR (500 MHz, CD₃CN) δ 9.16 (d, $J = 7.1$ Hz, 4H), 8.62 (d, $J = 6.9$ Hz, 4H), 7.46 (s, 2H), 7.42 (s, 4H), 2.49 (s, 12H). ¹³C NMR (126 MHz, CD₃CN) δ 150.7, 146.0, 142.9, 141.8, 134.0, 127.8, 122.5, 20.8. ESI-HRMS calcd for $m/z = 511.1732 [M - PF_6]^+$, found $m/z = 511.1735$.

DB13•2PF₆: ¹H NMR (500 MHz, CD₃CN) δ 8.94 (d, $J = 6.9$ Hz, 4H), 8.34 (d, $J = 6.6$ Hz, 4H), 7.14 (s, 2H), 7.11 (s, 4H), 5.72 (s, 4H), 2.32 (s, 12H). ¹³C NMR (126 MHz, CD₃CN) δ 147.4, 146.1, 140.1, 133.0, 132.0, 128.0, 127.5, 65.4, 20.8. ESI-HRMS calcd for $m/z = 539.2045 [M - PF_6]^+$, found $m/z = 539.2043$.

DB14•2PF₆: ¹H NMR (500 MHz, CD₃CN) δ 8.72 (d, $J = 6.9$ Hz, 2H), 8.30 (d, $J = 6.3$ Hz, 2H), 6.97 (s, 1H), 6.79 (s, 2H), 4.85 (t, $J = 7.1$ Hz, 2H), 3.26 (t, $J = 7.1$ Hz, 2H), 2.26 (s, 6H). ¹³C NMR (126 MHz, CD₃CN) δ 149.5, 145.1, 138.4, 134.8, 128.6, 126.5, 126.2, 62.7, 36.3, 19.9. ESI-HRMS calcd for $m/z = 567.2358 [M - PF_6]^+$, found $m/z = 567.2360$.

DB15•2PF₆: ¹H NMR (500 MHz, CD₃CN) δ 8.84 (d, $J = 6.3$ Hz, 4H), 8.27 (d, $J = 6.3$ Hz, 4H), 6.84 (s, 2H), 6.81 (s, 4H), 4.65 (t, $J = 7.3$ Hz, 4H), 2.69 (t, $J = 7.6$ Hz, 4H), 2.35 (t, $J = 7.4$ Hz, 4H), 2.23 (s, 12H). ¹³C NMR (126 MHz, CD₃CN) δ 150.3, 146.2, 140.5, 138.8, 128.3, 127.4, 126.6, 62.5, 32.4, 32.2, 20.9. ESI-HRMS calcd for $m/z = 595.2671 [M - PF_6]^+$, found $m/z = 595.2668$.

DB16•2PF₆: ¹H NMR (500 MHz, CD₃CN) δ 8.86 (d, *J* = 6.7 Hz, 4H), 8.35 (d, *J* = 6.2 Hz, 4H), 6.85 (s, 2H), 6.81 (s, 4H), 4.62 (t, *J* = 7.4 Hz, 4H), 2.60 (t, *J* = 7.6 Hz, 4H), 2.25 (s, 12H), 2.06 – 1.98 (m, 4H), 1.73 – 1.57 (m, 4H). ¹³C NMR (126 MHz, CD₃CN) δ 150.5, 146.1, 142.1, 138.5, 128.0, 127.8, 126.7, 62.6, 35.1, 31.2, 28.0, 20.9. ESI-HRMS calcd for *m/z* = 623.2984 [*M* – PF₆]⁺, found *m/z* = 623.2983.

DB17•2PF₆: ¹H NMR (500 MHz, CD₃CN) δ 8.91 (d, *J* = 6.8 Hz, 4H), 8.39 (d, *J* = 6.3 Hz, 4H), 6.92 – 6.79 (m, 6H), 4.64 (t, *J* = 7.6 Hz, 4H), 2.58 (t, *J* = 7.7 Hz, 4H), 2.28 (s, 12H), 2.11 – 2.03 (m, 4H), 1.75 – 1.60 (m, 4H), 1.56 – 1.38 (m, 4H). ¹³C NMR (126 MHz, CD₃CN) δ 150.4, 146.1, 142.8, 138.3, 127.8, 127.7, 126.7, 62.5, 35.5, 31.3, 31.0, 25.7, 20.9. ESI-HRMS calcd for *m/z* = 651.3297 [*M* – PF₆]⁺, found *m/z* = 651.3293.

DB18•2PF₆: ¹H NMR (500 MHz, CD₃CN) δ 8.91 (d, *J* = 6.9 Hz, 4H), 8.39 (d, *J* = 6.2 Hz, 6H), 6.96 – 6.74 (m, 7H), 4.63 (t, *J* = 7.6 Hz, 5H), 2.56 (t, *J* = 7.7 Hz, 5H), 2.28 (s, 13H), 2.09 – 2.01 (m, 5H), 1.67 – 1.58 (m, 5H), 1.47 – 1.39 (m, 10H). ¹³C NMR (126 MHz, CD₃CN) δ 150.4, 146.1, 143.1, 138.3, 127.7, 127.7, 126.7, 62.7, 35.7, 31.6, 31.4, 28.8, 26.0, 20.9. ESI-HRMS calcd for *m/z* = 679.3610 [*M* – PF₆]⁺, found *m/z* = 679.3609.

Binding Constant Measurements. An excess of activated Zn dust was added to a MeCN solution (~2 mL, ~5.0 × 10⁻⁴ M) of CBPQT•4PF₆ and the reaction mixture was stirred under Ar in a glovebox for 5 min. An MeCN solution (~3.0 × 10⁻² M) of DB1•2PF₆, DB2–7•4PF₆, DB8–10•3PF₆, or DB11–18•2PF₆ was titrated into CBPQT•4PF₆ solution. After each titration, the mixture was stirred for 1 min, then 0.35 mL of the reaction mixture was filtered and sealed in a 1 mm UV cuvette. Vis/NIR spectra were recorded from 1500 to 450 nm and the cuvette was then returned to the glovebox. The combined reaction mixture was titrated repeatedly until the trisradical band (~1080 nm) reached saturation (4~8 equiv of the dumbbells). The detailed data processing can be found in the Supporting Information (SI).

Single-Crystal X-Ray diffraction (XRD). Excess of activated Zn dust was added to a mixture of CBPQT•4PF₆ (0.6 mg, 0.5 μmol) and the dumbbells (0.5 μmol, DB8•4PF₆, DB9•4PF₆, DB10•4PF₆, DB12•2PF₆, DB13•2PF₆, or DB14•2PF₆) in MeCN (1 mL) in a glovebox under an atmosphere of Ar and the mixtures were stirred for 30 min. After filtering, the purple solutions were subjected to slow vapor diffusion with ⁱPr₂O at 0 °C. The solid-state superstructure of DB7⊂CBPQT•6PF₆ has been published in a previous report.³¹ All the other crystal data are summarized briefly below. Detailed data can be found in the Supporting Information (SI).

DB8 \subset **CBPQT**•**5PF**₆ C₇₂H₇₈F₃₀N₁₂P₅, $M=1836.34$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.9238(14)$, $b = 18.0258(17)$, $c = 19.2008(18)$ Å, $\alpha = 87.542(5)$, $\beta = 74.700(6)$, $\gamma = 83.934(6)^\circ$, $V = 4621.8(8)$ Å³, $Z = 2$, $T = 99.99$, $\mu(\text{CuK}\alpha) = 1.858$, 31230 reflections measured, 14749 unique ($R_{\text{int}} = 0.0624$) which were used in all calculations. The final $wR(F_2)$ was 0.5072 (all data).

DB9 \subset **CBPQT**•**4PF**₆ C₅₉H₆₂F₂₄N₇P₄, $M=1449.03$, triclinic, space group $P\bar{1}$ (no. 2), $a = 16.640(4)$, $b = 16.710(3)$, $c = 17.160(4)$ Å, $\alpha = 75.037(13)$, $\beta = 70.814(13)$, $\gamma = 62.956(14)^\circ$, $V = 3979.9(16)$ Å³, $Z = 2$, $T = 100.02$ K, $\mu(\text{CuK}\alpha) = 1.710$ mm⁻¹, $D_{\text{calc}} = 1.209$ g/mm³, 12511 reflections measured ($5.498 \leq 2\Theta \leq 108.322$), 8609 unique ($R_{\text{int}} = 0.0596$, $R_{\text{sigma}} = 0.1371$) which were used in all calculations. The final R_1 was 0.1078 ($I > 2\sigma(I)$) and wR_2 was 0.3129 (all data).

DB10 \subset **CBPQT**•**4PF**₆ C₆₁H_{64.5}F₂₄N_{8.5}P₄, $M=1496.59$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.8924(9)$, $b = 19.3041(11)$, $c = 28.5592(17)$ Å, $\alpha = 87.962(4)$, $\beta = 83.733(4)$, $\gamma = 75.084(4)^\circ$, $V = 7356.5(8)$ Å³, $Z = 4$, $T = 100(2)$ K, $\mu(\text{CuK}\alpha) = 1.874$ mm⁻¹, $D_{\text{calc}} = 1.351$ g/mm³, 14372 reflections measured ($3.112 \leq 2\Theta \leq 101.114$), 14372 unique ($R_{\text{sigma}} = 0.1201$) which were used in all calculations. The final R_1 was 0.1187 ($I > 2\sigma(I)$) and wR_2 was 0.3391 (all data).

DB12 \subset **CBPQT**•**3PF**₆ C₆₄H₆₁F₁₈N₇P₃ ($M=1363.10$): monoclinic, space group $C2/m$ (no. 12), $a = 27.8633(18)$, $b = 19.6876(13)$, $c = 14.3635(9)$ Å, $\beta = 121.019(2)^\circ$, $V = 6752.5(8)$ Å³, $Z = 4$, $T = 99.99$ K, $\mu(\text{CuK}\alpha) = 1.635$ mm⁻¹, $D_{\text{calc}} = 1.341$ g/mm³, 23953 reflections measured ($7.182 \leq 2\Theta \leq 130.168$), 5897 unique ($R_{\text{int}} = 0.0279$, $R_{\text{sigma}} = 0.0237$) which were used in all calculations. The final R_1 was 0.1005 ($I > 2\sigma(I)$) and wR_2 was 0.3082 (all data).

DB13 \subset **CBPQT**•**3.5PF**₆ C₁₄₆H₁₅₁F₄₂N₂₁P₇ ($M=3214.66$): monoclinic, space group $P2_1/n$ (no. 14), $a = 16.6492(7)$, $b = 19.7296(9)$, $c = 22.6647(10)$ Å, $\beta = 95.147(3)^\circ$, $V = 7414.9(6)$ Å³, $Z = 2$, $T = 99.99$ K, $\mu(\text{CuK}\alpha) = 1.751$ mm⁻¹, $D_{\text{calc}} = 1.440$ g/mm³, 35068 reflections measured ($5.95 \leq 2\Theta \leq 130.378$), 12522 unique ($R_{\text{int}} = 0.0514$, $R_{\text{sigma}} = 0.0529$) which were used in all calculations. The final R_1 was 0.0582 ($I > 2\sigma(I)$) and wR_2 was 0.1747 (all data).

DB14 \subset **CBPQT**•**3PF**₆ C₇₀H₇₂F₁₈N₈P₃, $M=1460.26$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.938(2)$, $b = 13.616(3)$, $c = 14.482(3)$ Å, $\alpha = 113.563(6)$, $\beta = 99.933(7)$, $\gamma = 101.953(7)^\circ$, $V = 1684.5(6)$ Å³, $Z = 1$, $T = 99.99$, $\mu(\text{CuK}\alpha) = 1.682$, 31989 reflections measured, 6073 unique ($R_{\text{int}} = 0.0257$) which were used in all calculations. The final $wR(F_2)$ was 0.0824 (all data).

Crystallographic data (excluding structure factors) for all the structures reported in this full paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC-XXXXX**, **CCDC-XXXXX**, **CCDC-XXXXX**, **CCDC-XXXXX**, **CCDC-**

XXXXXX, and CCDC-XXXXXX.

Density Functional Theory (DFT) Calculations. DFT Calculations were performed at the level of M06⁴⁰/6-311G(d,p)⁴¹ with D3 van der Waals correction⁴² in the presence of the Poisson-Boltzmann solvation model⁴³ for MeCN ($\epsilon=37.5$ and $R_0=2.18$ Å) as implemented in with Jaguar 8.2.⁴⁴ Unrestricted calculations were applied to molecules and complexes with unpaired electrons. The detail information of charges and multiplicities used in the calculation is listed in the SI. Counterpoise calculations were used to correct for the problem of basis-set superposition error (BSSE)⁴⁵ to binding energies. Frequencies were derived from semi-empirical quantum chemistry method PM7⁴⁶ with consideration of solvation implemented in MOPAC 2012.⁴⁷

Gibbs free energies calculated by the following formula:

$$G_{298K} = E + G_{\text{solv}} + \text{ZPE} + H_{\text{vib}} + 6kT - TS_{\text{mod}},$$

where $S_{\text{mod}} = S_{\text{vid}} + 0.54(S_{\text{trans}} + S_{\text{rot}}) + 0.24$ is the Wertz's approximation⁴⁸ for the entropy fit to the experimental solvation of small molecules.

Cyclic Voltammetry (CV). Each dumbbell compound (1 mmol) was dissolved in a 1 mL MeCN solution (TBA•PF₆, 0.1 M). 0.5 mL of the dumbbell solution which was mixed with 0.5 mL MeCN solution (CBPQT•4PF₆ 1 mM, TBA•PF₆ 0.1 M) in order to prepare the 1:1 dumbbell/CBPQT⁴⁺ samples, while the other 0.5 mL of the dumbbell solution was diluted with 0.5 mL MeCN solution (TBA•PF₆ 0.1 M) in order to prepare the dumbbell only samples with an analyte concentration of 0.5 mM.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic procedures and further details and characterization by UV-Vis-NIR spectroscopy, X-Ray crystallography, EPR spectroscopy and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>

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