Structural-Change-Induced Two-Stage Redox Behavior of Pentacenebisquinodimethane with Tricolor Chromism

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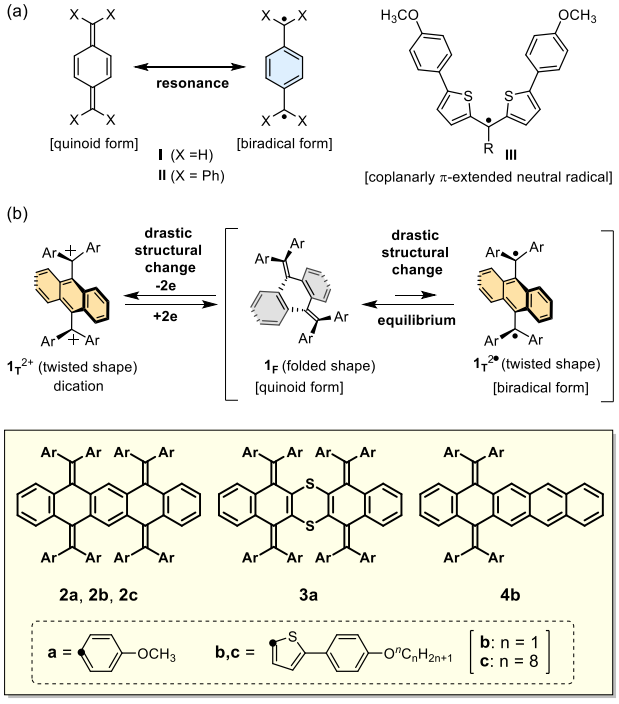
Abstract: Tricolor electrochromism was realized through the interconversion among the neutral (yellow), dicationic (green), and tetracationic (blue) states, even though only one kind of chromophore is generated upon oxidation. Both dicationic and tetracationic states were isolated as stable salts, and their different colors come from the effective interchromophore interaction only in the tetracationic state but not in the dicationic state. Despite the negligible Coulombic repulsion in the tetracationic state with four cyanine-type chromophores, pentacenebisquinodimethane undergoes stepwise two-stage two-electron oxidation when radical-stabilizing 5-(4-octyloxyphenyl)-2-thienyl groups are attached on the exomethylene bonds. A contribution from the biradical form only in the neutral state but not in the dicationic state is the reason for the observed negative cooperativity during the electrochemical oxidation.

Introduction

para-Quinodimethane (*p*QD, **I**)[1] is a representative cross-conjugated π-system,[2] the high reactivity of which can be accounted for by a resonance contribution from the biradical form with an aromatized hexagon (Scheme 1a). Tetraarylanthraquinodimethane (AQD) **1**[3,4] is the π-extended analogues of *p*QD or Thiele's hydrocarbon[5] (tetraphenyl-*p*QD, **II**). Different from the latter two, the biradical contribution to AQD **1** is generally very small, due to a smaller aromatic stabilization upon the formation of an anthracene unit than that of an unfused benzene unit.

A drastic change in structures between the quinoid form AQD $\mathbf{1}_F$ (folded shape) and the biradical form AQD $\mathbf{1}_T^{2\bullet}$ (twisted shape) is another characteristic,[6] and similar geometry to the latter has been often observed in the dicationic state $\mathbf{1}_T^{2+}$ (Scheme 1b), as in the case of tetrakis(4-methoxyphenyl) derivative $\mathbf{1a}_T^{2+}$.[4] Such a class of stable dications has been attracting recent attentions due to their near-infrared (NIR) absorptions,[7] which could be used to develop new materials that are applicable to security marking,[8] lithography,[9] optical filter,[10] and photovoltaic cells.[11] Dication $\mathbf{1a}^{2+}$ was generated by two-electron (2e) oxidation of **1a** nearly at the same potential [anodic peak potential: E^{pa} (2e) = +1.03 V vs SCE in CH_2Cl_2],[4] due to the dynamic structural change from $\mathbf{1}_F$ of the folded shape into $\mathbf{1}_T^{2+}$ of the twisted shape during the redox process ("dyrex" behavior),[2] with showing the corresponding return peak at far cathodic region [cathodic peak potential: E^{pc} (2e) = +0.39 V].

By attaching four 5-(4-methoxyphenyl)-2-thienyl groups, whose radical stabilizing nature was demonstrated very recently in the neutral radicals shown as a general formula **III**,[12] AQD **1b** can exist as an equilibrium mixture of the most stable folded form $\mathbf{1b}_F$ and the metastable biradical form $\mathbf{1b}_T^{2\bullet}$, which exhibits unprecedented thermally controlled spin state.[13] To attain such a situation, a small energy difference between the two states as well as a small energy barrier for the interconversion are the key factors.[14]



Scheme 1. (a) *p*-Quinodimethane and (b) its extended analogues. Molecules **2b**, **2c**, and **4b** were newly designed in this study.

On the other hand, when the two units of tetraaryl quinodimethane (QD)-type electrophores are connected to construct four-electron (4e) donors, as in octaarylbisquinodimethane (BQD) **2** with a 5,7,12,14-tetrahydropentacene skeleton, both electrophores act almost independently. Thus, 4e-oxidation of $\mathbf{2a}_{FF}$[15] (Ar = 4-

methoxyphenyl) of doubly folded shape occurs nearly at the same potential [E^{pa} (4e) = +1.12 V] to that of $\mathbf{1a}_F$, which can be accounted for by only marginal interaction between the two QD units in the neutral state as well as negligible Coulombic repulsion in tetracationic state $\mathbf{2a}_{TT}^{4+}$ (Scheme 2a). On the other hand, due to strong interaction between two QD units in **3a** with a non-planar 1,4-dithiin spacer, a domino-type electron transfer occurs to realize 4e-oxidation at a much lower potential [E^{pa} (4e) = +0.44 V].[16] At any event, there has been no effective molecular design concept to realize the stepwise oxidation of two QD-type electrophores when incorporated in one molecule, unless two kinds of electron-donating groups (e.g., methoxy- and aminophenyl were properly attached on each of QD units.[17]

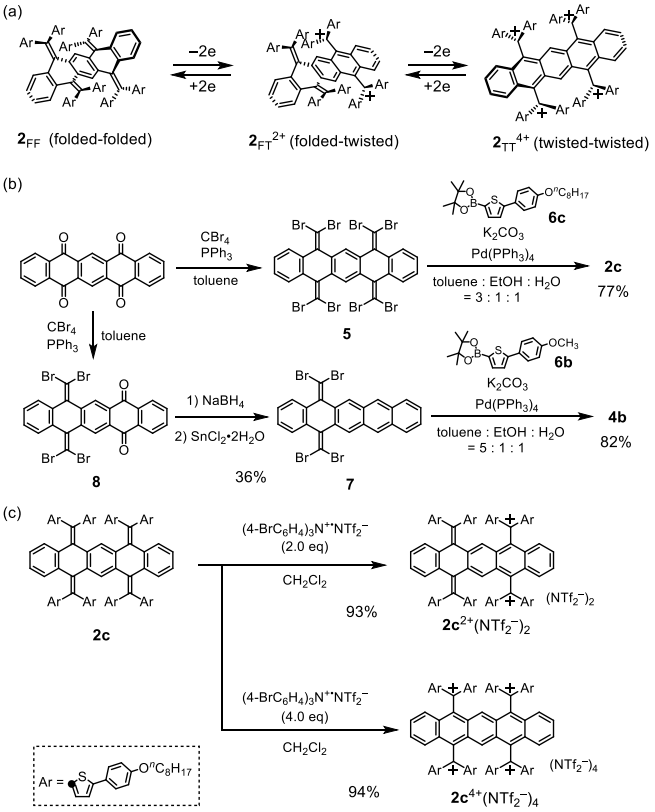
Here we studied the title BQD derivative **2c** attached with eight 5-(4-octyloxyphenyl)-2-thienyl groups. We found that the two oxidation peaks corresponding to each of QD units in **2c** differ significantly, namely, by more than 0.7 V. Such a negative cooperativity for the sequential two-stage 2e-oxidation could not be explained by a simple Coulombic consideration, which prompted us to conduct detailed studies of **2c** with isolating the corresponding dicationic and tetracationic salts. The reason for the intriguing phenomenon was unveiled by consideration of the biradical contribution only in the neutral state **2c** but not in the dicationic state $\mathbf{2c}^{2+}$. Furthermore, even though the dicationic and tetracationic states have only one kind of chromophore units, tricolor electrochromism was realized upon the sequential 2e-oxidation of **2c**. Quite different colors of dicationic and tetracationic states are accounted for by the effective inter-chromophore interaction only in tetracation $\mathbf{2c}^{4+}$ but not in the dication $\mathbf{2c}^{2+}$. The detailed are shown herein.

Results and Discussion

When 5,7,12,14-tetrakis(dibromomethylene)-5,7,12,14-tetrahydropentacene (**5**)[18] was derived from the corresponding tetraone and subjected to eight-fold Suzuki-Miyaura coupling reaction using 5-(4-methoxyphenyl)-2-thienylboronic acid pinacol ester (**6b**),[12] BQD **2b** was generated as confirmed by MS spectrum. However, it was much less soluble in common solvents than the corresponding AQD **1b**, which prevented the further experimental studies on **2b**. Such a low solubility is in sharp contrast to the case of **4b** with only one quinodimethane unit on the pentacene core, which was obtained in 82% yield from 5,14-bis(dibromomethylene)dihydropentacene (**7**) prepared by reduction of the corresponding dione **8**[15] (Scheme 2b). Figure 1a shows the molecular geometry of **4b** determined by X-ray analysis at 150 K. Such a folded structure is typical for AQDs and their π-extended analogues.[14-17]

Thus, a BQD derivative with longer alkyl chains was pursued and prepared using 5-(4-octyloxyphenyl)-2-thienylboronic acid pinacol ester (**6c**) to generate **2c** in 77% yield. To confirm only marginal effects of the alkyl chain length other than solubility, a reference AQD **1c** with four 5-(4-octyloxyphenyl)-2-thienyl groups was prepared from 9,10-bis(dibromomethylene)dihydroanthracene[19] in 51% yield, which has a folded form similar to that of **1b**[13] (Figure 1b). Redox behavior and physical properties for **1c** with octyloxy groups are also quite similar to those for **1b** with methoxy groups.

Upon treatment of **2c** with two or four equivalents of one-electron oxidant $[(4\text{-}BrC_6H_4)_3N^{+\bullet}NTf_2^-$ (Tf = CF_3SO_2)] in CH_2Cl_2, dication salt $\mathbf{2c}^{2+}(NTf_2^-)_2$ and tetracation salt $\mathbf{2c}^{4+}(NTf_2^-)_4$ were obtained in 93% and 94% yields, respectively (Scheme 2c). Presence of bis[5-(4-octyloxyphenyl)-2-thienyl]methylium chromophore in those cations was confirmed by ^{1}H NMR spectroscopy. Isolation of these stable cationic salts demonstrates the electron-donating properties of **2c**, which undergoes up to 4e-oxidation.



Scheme 2. (a) Two-stage two-electron redox behavior of pentacenebisquinodimethane. (b) Synthetic schemes for **2c** and **4b**. (c) Two-electron and four-electron oxidation schemes of **2c** giving stable dicationic and tetracationic salts.

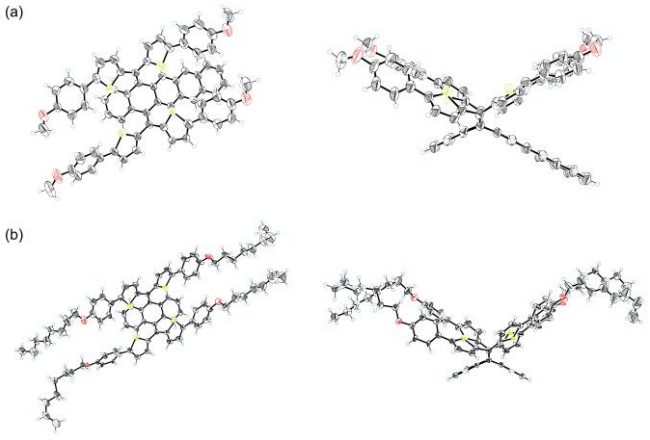


Figure 1. (a) ORTEP drawings of **4b** determined by X-ray analysis at 150 K. (b) ORTEP drawings of **1c** determined by X-ray analysis at 100 K: (left) front view; (right) top view.

In the cyclic voltammogram of **2c** measured in CH_2Cl_2, two 2e-oxidation peaks were observed [E_1^{pa} (2e) = +0.28 V; E_2^{pa} (2e) = +0.99 V vs SCE in CH_2Cl_2], which can be assigned to the oxidation process of each of the QD electrophores. In the return cycle, two waves were also observed [E_1^{pc} (2e) = +0.30 V; E_2^{pc} (2e) = +0.13 V] (Figure 2). By the independent voltammetric analyses on dication salt $\mathbf{2c}^{2+}(NTf_2^-)_2$ and tetracation salt $\mathbf{2c}^{4+}(NTf_2^-)_4$ (Figure S7), it was shown that the pair of E_1^{pa} and E_2^{pc} (ΔE_1 = 0.15 V) corresponds to the interconversion between **2c** and $\mathbf{2c}^{2+}$ whereas that of E_2^{pa} and E_1^{pc} (ΔE_2 = 0.69 V) is assigned to the conversion between $\mathbf{2c}^{2+}$ and $\mathbf{2c}^{4+}$ (Figure 2a).

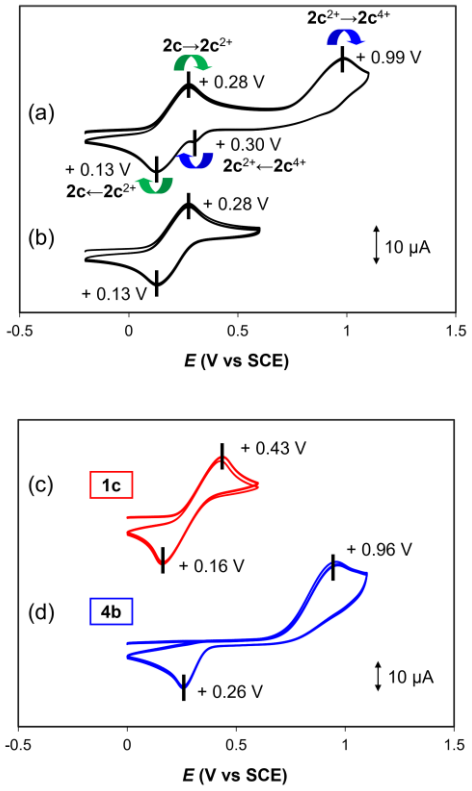
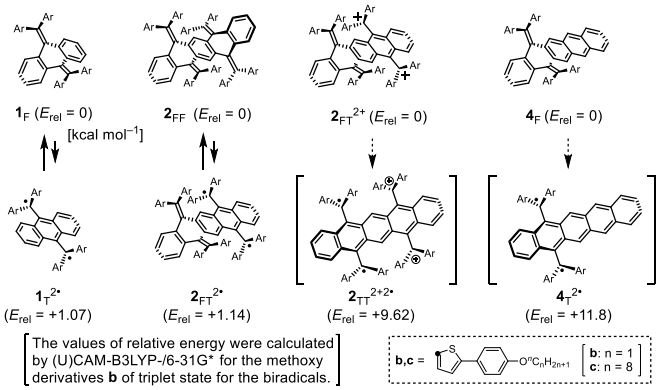


Figure 2. Cyclicvoltammograms of (a) **2c** (from −0.2 to +1.1 V), (b) **2c** (from −0.2 to +0.6 V), (c) **1c**, and (d) **4b** measured at 297 K in CH_2Cl_2 containing 0.1 M Bu_4NBF_4 as a supporting electrolyte. *E*/V vs SCE, scan speed 100 mV s^{-1}, glassy carbon electrode.

The large ΔE value for the conversion between **2c** and $\mathbf{2c}^{2+}$ indicates that the drastic change in structures occurs upon redox interconversion (dyrex behavior), showing that the QD unit in the dication state adopts a folded geometry as in $\mathbf{2c}_{FT}^{2+}$ which is converted into the twisted geometry in the tetracation as in $\mathbf{2c}_{TT}^{4+}$ (Scheme 2a). The large ΔE value is quite similar to the voltammogram of $\mathbf{4b}_F$ with only one QD unit on the pentacene (Figure 4b), which was oxidized to $\mathbf{4b}_T^{2+}$ accompanied by a drastic structural change. From the observed similarity, it was concluded that dication $\mathbf{2c}^{2+}$ has the pentacene-5,14-quinodimethane skeleton with two diarylmethylium units which are perpendicularly attached at 7,12-positions, i.e., $\mathbf{2c}_{FT}^{2+}$.

The small ΔE value for the conversion between **2c** and $\mathbf{2c}^{2+}$ is akin to that of conventional reversible redox pairs, which maintain the similar geometry upon electron transfer. Since only the twisted geometry is possible in the dicationic state, as shown by the studies of AQD dications such as $\mathbf{1b}_T^{2+}$,[13] the redox-active form of **2c** has a QD unit which adopts the twisted biradical form, i.e., $\mathbf{2c}_{FT}^{2\bullet}$, similar to AQD biradical $\mathbf{1b}_T^{2\bullet}$. Thus, it is highly likely that the $\mathbf{2c}_{FF}$ is in rapid equilibrium with the biradical form $\mathbf{2c}_{FT}^{2\bullet}$ (Scheme 3), which has a much higher HOMO/SOMO level to induce easier oxidation than the doubly folded form $\mathbf{2c}_{FF}$. The above idea is supported by close similarity of the first-stage redox wave of **2c** in voltammogram to that of **1b** or **1c** (Figure 5c), in which twisted biradical $\mathbf{1b}_T^{2\bullet}$ or $\mathbf{1c}_T^{2\bullet}$ is oxidized.



Scheme 3. Contribution from the biradical state of the twisted geometry with showing the relative energy. Note that the QD unit with 9,10-dihydroanthracene can be interconvertible with the biradical whereas the QD unit with 5,14-dihydropentacene cannot, due to a very large energy loss upon the formation of the corresponding biradical.

As shown above, AQD **1b** with four 5-(4-methoxyphenyl)-2-thienyl groups can undergo facile 2e-oxidation because of the presence of a certain amount of metastable biradical form $\mathbf{1b}_T^{2\bullet}$ which can exist as an equilibrium mixture with the most stable folded form $\mathbf{1b}_F$.[13] Actually, those two forms are different in energy only by 1.07 kcal mol^{-1}, as estimated by DFT calculations at (U)CAM-B3LYP/6-31G* level. A quite similar value (1.14 kcal mol^{-1}) was estimated for the BQD (singlet $\mathbf{2b}_{FF}$ and triplet $\mathbf{2b}_{FT}^{2\bullet}$) with eight 5-(4-methoxyphenyl)-2-thienyl groups. By considering the only marginal effects of alkyl groups, **2c** can exist as an equilibrium mixture of the most stable doubly folded form $\mathbf{2c}_{FF}$ and the metastable biradical form $\mathbf{2c}_{FT}^{2\bullet}$, which can explain low oxidation potential of **2c**. A certain contribution from the biradical form $\mathbf{2c}_{FT}^{2\bullet}$ is also the reason for very broad ^{1}H NMR spectrum of **2c** over a wide range of temperature (213–293 K) (Figure S8).

On the other hand, pentacenemonoquinodimethane **4b** shows a set of sharp ^{1}H NMR signals, suggesting that its solution contains the folded form $\mathbf{4b}_F$, as in crystal, without any contribution from biradical form $\mathbf{4b}_T^{2\bullet}$, which can be accounted for by the much smaller aromatic stabilization energy upon generating a pentacene skeleton ($\mathbf{4b}_F$ to $\mathbf{4b}_T^{2\bullet}$) than an anthracene skeleton ($\mathbf{2c}_{FF}$ to $\mathbf{2c}_{FT}^{2\bullet}$). The similar scenario is seen for the hypothetical generation of the biradical form for dication $\mathbf{2c}_{TT}^{2+2\bullet}$. Again, due to the smaller energy gain upon aromatization of the pentacyclic core, the triplet biradical form of the methoxy analogue $\mathbf{2b}_{TT}^{2+2\bullet}$ has a much larger energy (9.62 kcal mol^{-1}) than $\mathbf{2b}_{FT}^{2+}$ containing a folded-shaped QD unit, thus resulting in negligible contribution from the biradical form in the dicationic state of octyloxy derivative $\mathbf{2c}_{FT}^{2+}$. By considering that twisted biradical form has a higher HOMO/SOMO level than the folded form, biradical contribution for the neutral state but not for the

dicationic state is the reason why **2c** undergoes sequential two-stage 2e-oxidation with the very large separation of E_1^{pa} and E_2^{pa}.

The UV/Vis/NIR absorption spectra of BQD dication salt **2c**$^{2+}$(NTf_2^-)$_2$ (λ_{max} 727 nm, log ε 5.21 in CH_2Cl_2) is quite similar to that of AQD dication salt **1b**$^{2+}$($SbCl_6^-$)$_2$ (λ_{max} 727 nm, log ε 5.02) or **1c**$^{2+}$(BF_4^-)$_2$ (λ_{max} 730 nm, log ε 5.41), the latter of which was generated in 99% yield upon treatment of **1c** with two equivalents of (4-BrC_6H_4)$_3$N$^{+\bullet}BF_4^-$. On the other hand, a considerable blue shift of ca. 50 nm was observed in BQD tetracation salt **2c**$^{4+}$(NTf_2^-)$_4$ (λ_{max} 682 nm, log ε 5.70), which can be accounted for by assuming the H-aggregate-like π -π stacking of cationic chromophores attached on the same side of pentacene periphery (e.g., 5,7-positions) in **2c**$^{4+}$. TD-DFT calculations [CAM-B3LYP-D3/6-31G*] on the methoxy derivative support the above explanation on the spectral differences, with giving the estimated absorption maxima for **1b**$^{2+}$ (λ_{max} 578 nm), **2b**$^{2+}$ (λ_{max} 572 nm), and **2b**$^{4+}$ (λ_{max} 543 nm), respectively (Figure S10). A similar spectral difference between **2c**$^{2+}$ and **2c**$^{4+}$ was also observed when measured in toluene (Figure 3) with negligible change in wavelength for the absorption maximum.

The inter-chromophore interaction skipping over the *peri*-hydrogen[19] on the pentacene periphery would be also possible in other BQD tetracations such as **2a**$^{4+}$,[15,17] however, higher planarity as well as π–extended structure of the cyanine-type chromophore in **2c**$^{4+}$ would be more favorable to attain effective interaction. The attractive but not repulsive nature of noncovalent interaction (NCI) between the two chromophores can be clearly shown by the NCI plot for the optimized structure of methoxy analogue **2b**$^{4+}$ (Figure 4).

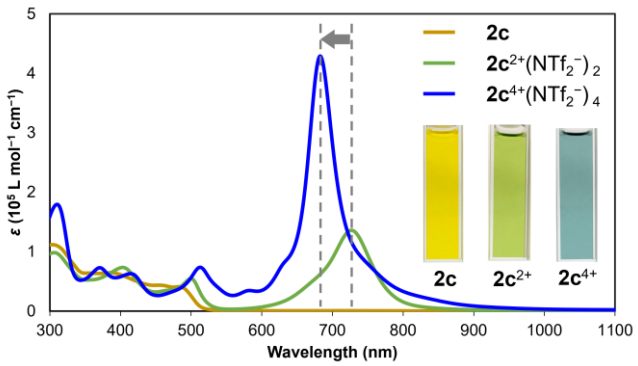


Figure 3. UV-Vis-NIR spectra of **2c**, **2c**$^{2+}$(NTf_2^-)$_2$, and **2c**$^{4+}$(NTf_2^-)$_4$ in toluene. The first absorption bands are 483 nm (log ε 4.61), 727 (5.13), and 683 (5.63), respectively.

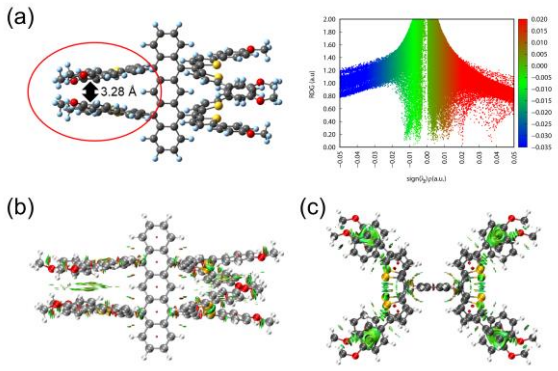


Figure 4. (a) The optimized structure of **2b**$^{2+}$ by DFT calculations at the CAM-B3LYP-D3/6-31G* level. The shortest C···C contact between two facing chromophore is 3.28 Å, which is much smaller than the sum of the van der Waals radii of carbon atoms (3.40 Å). (b,c) NCI plot (color: blue: strong attractive interaction; green: van der Waals interaction; red: strongly repulsive interaction).

Finally, tricolor electrochromic behavior was investigated by constant-current electrochemical oxidation of **2c** in CH_2Cl_2 (Figure 5). Upon electrolysis, a yellow solution of **2c** turned into green with showing continuous growth of a new band at 727 nm, which is assigned to **2c**$^{2+}$ (stage 1). When the oxidation was continued, a new band at 682 nm assigned to **2c**$^{4+}$ appeared with a decrease of the absorption at 727 nm (stage 2), exhibiting color change from green to blue. The clean conversion was also demonstrated by the reversal process upon the electrochemical reduction of as-generated **2c**$^{4+}$ (Figure S9).

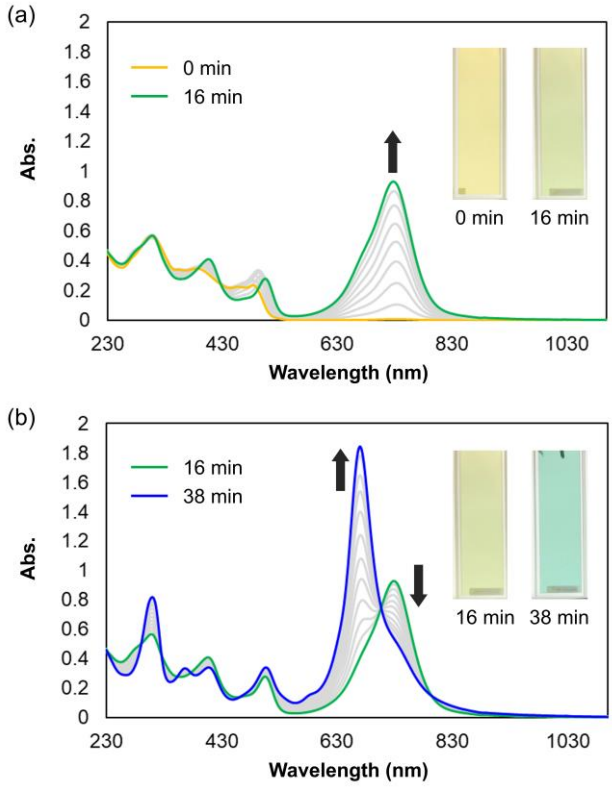


Figure 5. Changes in UV/Vis/NIR spectrum upon constant-current electrochemical oxidation of **2c** (4.38 μM, 20 μA, every 2 min) in CH_2Cl_2 containing 0.05 M Bu_4NBF_4 as a supporting electrolyte: (a) the first stage (0-16 min) converting from **2c** to **2c**$^{2+}$; (b) the second stage (16-38 min) converting from as-generated **2c**$^{2+}$ to **2c**$^{4+}$.

Conclusion

Hitherto, there have been only a limited number of tricolor electrochromic molecules,[17,21,22] in which the sequential electron transfer is warranted by the Coulombic repulsion or by involving two electrochemically different electrophores. As shown above, the present work demonstrated a system which works under a different mechanism by involving only one kind of electrophore without the aid of Coulombic effects.

5-(4-Alkoxyphenyl)-2-thienyl groups can stabilize both neutral radical and carbocation due to a coplanarly extended π-skeleton.[12] This substituent allows the QD electrophore to behave as the easily oxidizable species due to thermally accessible biradical state with forming an anthracene skeleton (as in $\mathbf{1b}_F$ to $\mathbf{1b}_T^{2\bullet}$, or $\mathbf{2c}_{FF}$ to $\mathbf{2b}_{FT}^{2\bullet}$) but not with forming a pentacene skeleton (as in $\mathbf{4b}_F$ to $\mathbf{4b}_T^{2\bullet}$, or $\mathbf{2c}_{FT}^{2+}$ to $\mathbf{2b}_{TT}^{2+2\bullet}$), thus providing a different degree of open-shell nature for **2c** and $\mathbf{2c}^{2+}$. In addition, planar geometry of the cationic dye unit allows inter-chromophore electronic interaction to result in a considerable blue shift for the absorption spectrum in $\mathbf{2c}^{4+}$ but not in $\mathbf{2c}^{2+}$. By a proper molecular design controlling the biradical character and inter-chromophore interaction, it was shown that a simple accumulation of two QD units enables tricolor electrochromic material, the design concept of which can be used for future development of advanced material.

Supporting Information

The authors have cited additional references within the Supporting Information.[23-28]

Acknowledgements

This work was supported by Grant-in-Aid from MEXT and JSPS (Nos. JP23K20275 to T.S. and JP21H01912 and JP23H04011 to Y.I.). Y.I. acknowledges JST PRESTO (No. JPMJPR23Q1). This work was also supported by the "Five-star Alliance" in "NJRC Mater. & Dev." MEXT.

Keywords: Cations • Radicals • Thermal equilibrium • Chromism• Electrochemistry

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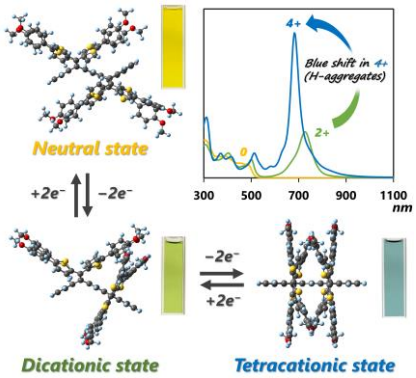
[28] CCDC Deposition numbers of **1c** and **4b**: 2340993 and 2340994.

Entry for the Table of Contents



Despite the presence of only one kind of chromophore on the title twin-type electron donor, two-stage two-electron oxidation is realized by redox-state-dependent conformational preference. Both dicationic and tetracationic states were isolated as stable salts, and their different colors come from the effective inter-chromophore interaction only in the tetracation but not in the dication.

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