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# Double Dynamic Structural Change Enabling Tricolor Chromism by the Realization of Apparent Two-electron Transfer to Skip the Open-shell State

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**Abstract:** Most redox systems generally cannot avoid the involvement of open-shell species upon generating multiply charged species, which often reduces reversibility in multi-color electrochromic systems. In this study, we newly synthesized octakis(aminophenyl)-substituted pentacenebisquinodimethane (BQD) derivatives and their hybrids with alkoxyphenyl analogues. Thanks to apparent two-electron transfer accompanied by double dramatic changes in the structure of the arylated quinodimethane skeleton, the dicationic and tetracationic states were generated and isolated quantitatively because of the negligible steady-state concentration of intermediary open-shell species such as monocation or trication radicals. When two electrophores with different donating abilities are attached to the BQD skeleton, a dicationic state with a different color can be isolated in addition to the neutral and tetracationic states. For the latter of these, an interchromophore interaction induces a red-shift of the NIR absorptions, thus realizing tricolor UV/Vis/NIR electrochromic behavior involving only closed-shell states.

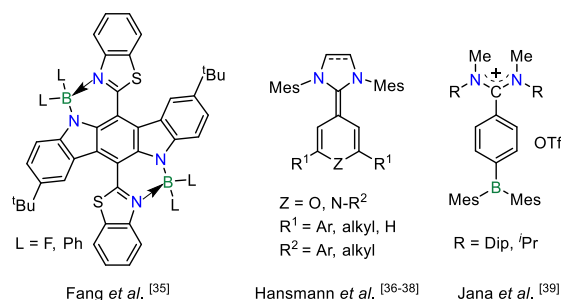
## Introduction

Electrochromic systems exhibit a drastic change in color based on interconversion among differently charged species upon electron transfer.<sup>[1–4]</sup> Representative examples include robust inorganic compounds, such as tungsten oxide (WO<sub>3</sub>), which have been used in auto-dimming mirrors, smart windows, and displays.<sup>[5–9]</sup> On the other hand, due to the advantages of organic molecules in terms of affordability, flexibility, modularity, and biocompatibility, organic and related materials with redox activity have also been actively studied in recent years.<sup>[10–15]</sup> From the viewpoint of achieving a multicolor response with the use of organic electrochromic systems, it is essential to stabilize several redox states. Some organic polymeric materials including covalent organic frameworks and/or metal organic frameworks have been reported as multicolor electrochromic materials.<sup>[16–25]</sup> In these systems, multiple electrophores have to be integrated and controlled by the corresponding operating potential to output multiple colors.

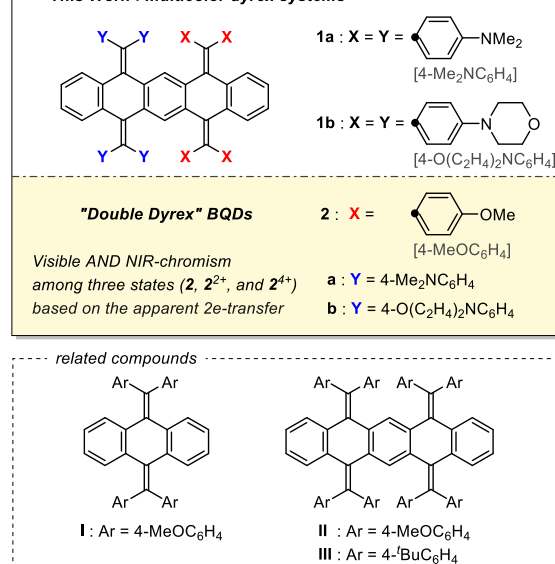
A well-designed single molecule, which can adopt multiple redox states with different colors, would be very useful, since it could work under a simple setup without the fabrication of multiple layers.<sup>[26–36]</sup> Despite this attractiveness, it remains challenging to stabilize and/or isolate all of the different-color states, especially when some of the states are open-shell species. These states have often been observed only under electrolytic conditions. Fang

*et al.*, Hansmann *et al.*, and Jana *et al.* successfully constructed multi-color electrochromic systems by well-considered molecular design (Figure 1a).<sup>[37–41]</sup> These are quite rare examples for which not only the neutral state but also other redox states were isolated, and their structures were determined by X-ray analyses.

(a) Previous Examples : multicolor electrochromic systems



(b) << This Work : multicolor dyrex systems >>



**Figure 1.** (a) Previous examples: multi-color electrochromic systems [Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, Dip = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]. (b) This work: newly designed BQDs **1** with the same aryl groups and multi-color dyrex systems **2** with two different aryl groups on each quinodimethane unit.

As one of these rare cases, we recently reported pentacenebisquinodimethanes (BQDs): **II** with eight 4-methoxyphenyl groups and **III** with eight 4-*tert*-butylphenyl groups,<sup>[42]</sup> which were designed as twin-type compounds of tetraarylanthraquinodimethane (AQD) **I**<sup>[43]</sup> undergoing a one-

wave two-electron (2e) oxidation process accompanied by a drastic change in structure, which is a characteristic of dynamic redox (*dyrex*) system<sup>[44]</sup> (Figure 1b).

Although  $I^{2+}$  is generated via the intermediary cation radical, its steady-state concentration is negligible, and thus it exhibits bicolor electrochromism consisting of **I** and  $I^{2+}$ . Accordingly, the BQD derivatives **II** and **III** were then found to be converted into dicationic and tetracationic states with negligible steady-state concentrations of intermediary open-shell species such as monocation radical or trication radical. Thus, the BQD skeleton would be the best platform for constructing tricolor electrochromic systems with high reversibility due to the apparent 2e-transfer for mutual interconversion among three-color states. However, based on a consideration of the similar absorption bands [ $\lambda_{\max}/nm$  (log  $\epsilon$ ) in  $CH_2Cl_2$ : 517(5.30) for  $II^{4+}(SbCl_6^-)_4$  and 498 (5.08) for  $III^{4+}(SbCl_6^-)_4$ ], a methoxyphenyl group and a *tert*-butylphenyl group would not make a good combination to construct a tricolor electrochromic system.

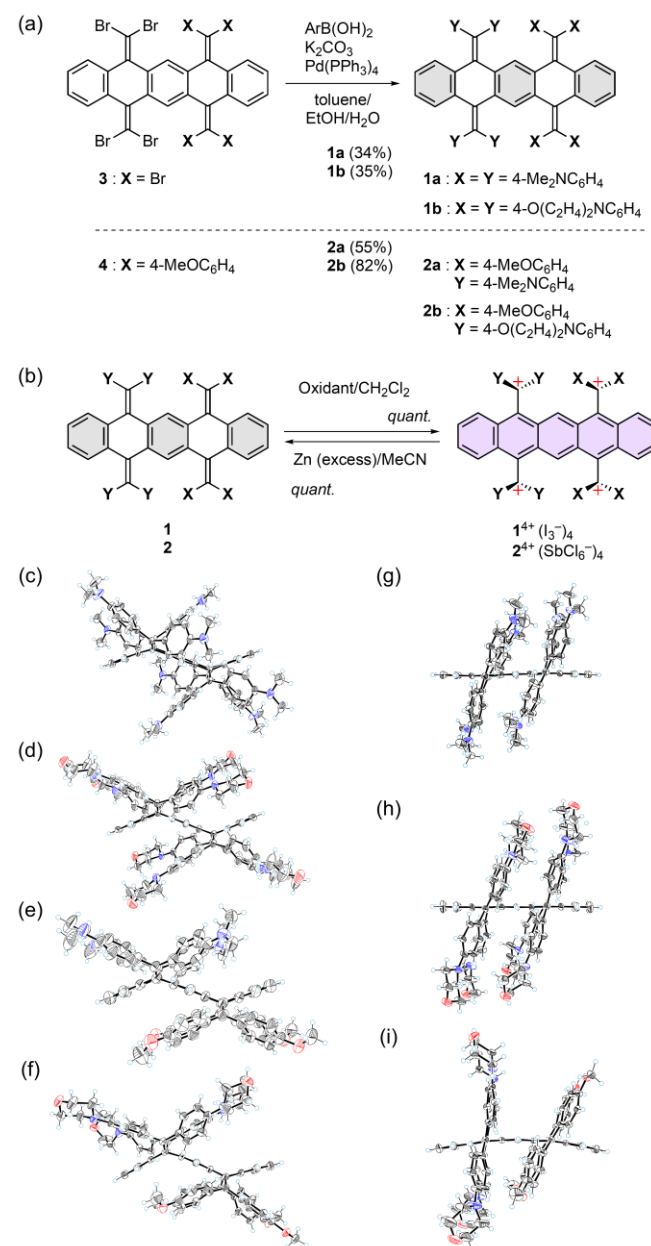
Here, we design BQD-based tricolor electrochromic molecules **2a** and **2b**, which have four 4-methoxyphenyl groups and four 4-aminophenyl groups, by considering that quite different colors are expected for the aryl groups when incorporated in the diarylmethylium unit. Before we examined such hybrid compounds, octakis(4-dimethylaminophenyl) and octakis(4-morpholinophenyl) derivatives **1a** and **1b** were also investigated. All of the redox states of the neutral donor, dication, and tetracation for **2a** and **2b** were successfully isolated, and their electronic and structural properties were clarified both experimentally and theoretically. Special attention was paid to the intramolecular interaction between diarylmethylium-type chromophores in  $2a^{4+}$  and  $2b^{4+}$ , which can account for the red-shift of the first band around 1000 nm, the second band around 650 nm, and the third band around 420 nm, when compared to the spectra of the corresponding BQD tetracations  $II^{4+}$ ,  $1a^{4+}$ , and  $1b^{4+}$  with the same eight aryl groups. Furthermore, electrochemical and spectroscopic measurements showed clean tricolor electrochromism with drastic color changes in the UV/Vis/NIR region.

## Results and Discussion

### Syntheses and X-ray Structures of BQDs and Their Tetracations

As the aminophenyl group, we selected 4-dimethylaminophenyl and 4-morpholinophenyl groups, since they appear at nearly the same wavelength when incorporated in the diarylmethylium skeleton despite their different electron-donating abilities.<sup>[45]</sup> By an eight-fold Suzuki-Miyaura cross-coupling reaction, the octakis(aminophenyl) BQDs **1a** and **1b** were synthesized in respective yields of 34% and 35% in a one-step manner from 5,7,12,14-tetrakis(dibromomethylene)-5,7,12,14-tetrahydropentacene **3**.<sup>[46]</sup> The hybrid compounds **2a** and **2b** were isolated in respective yields of 55% and 82% by the Suzuki-Miyaura cross-coupling reaction to introduce dimethylaminophenyl or morpholinophenyl groups, respectively, into the tetrahydropentacene derivative **4**<sup>[42]</sup> with four methoxyphenyl groups (Figure 2). Single-crystal X-ray structural analyses revealed that all of these newly synthesized BQDs adopt a zigzag conformation, as in **II**. The structural parameters of the quinodimethane units contained in the newly synthesized BQDs,

such as dihedral angles and bond lengths, are quite similar to those of AQDs **I** and BQD **II** (Tables S1-S3).<sup>[44]</sup>



**Figure 2.** (a) Preparation of newly designed BQDs **1** and **2**. (b) Redox interconversion between neutral donors and tetracations. Six equivalents of  $I_2$  and four equivalents of  $(4-BrC_6H_4)_3N^+SbCl_6^-$  were used for the oxidation of **1** and **2**, respectively. X-ray crystal structures (ORTEP drawings) of (c) **1a**, (d) **1b**, (e) **2a**, (f) **2b**, (g)  $1a^{4+}(I_3^-)_4$ , (h)  $1b^{4+}(I_3^-)_4$  and (i)  $2b^{4+}(SbCl_6^-)_4$  determined at 150 K. The counterions, solvent molecules, and disordered atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. \*One of the two crystallographically independent molecules.

The tetracationic salts  $2a^{4+}(SbCl_6^-)_4$  and  $2b^{4+}(SbCl_6^-)_4$  were isolated in respective yields of 96% and 97% upon treatment of each of the neutral donors **2a** and **2b** with 4 equivalents of  $(4-BrC_6H_4)_3N^+SbCl_6^-$  (Magic Blue). For octakis(aminophenyl) BQDs **1a** and **1b**, a weaker oxidant, such as iodine, was enough for four-electron (4e) oxidation. Upon treatment with 6 equivalents of iodine,  $1a^{4+}(I_3^-)_4$  and  $1b^{4+}(I_3^-)_4$  were isolated in respective yields of 99% and 99%. X-ray analyses were successfully conducted for the tetracationic salts of  $2b^{4+}(SbCl_6^-)_4$ ,  $1a^{4+}(I_3^-)_4$  and  $1b^{4+}(I_3^-)_4$ . These tetracations have a fully conjugated planar pentacene core,

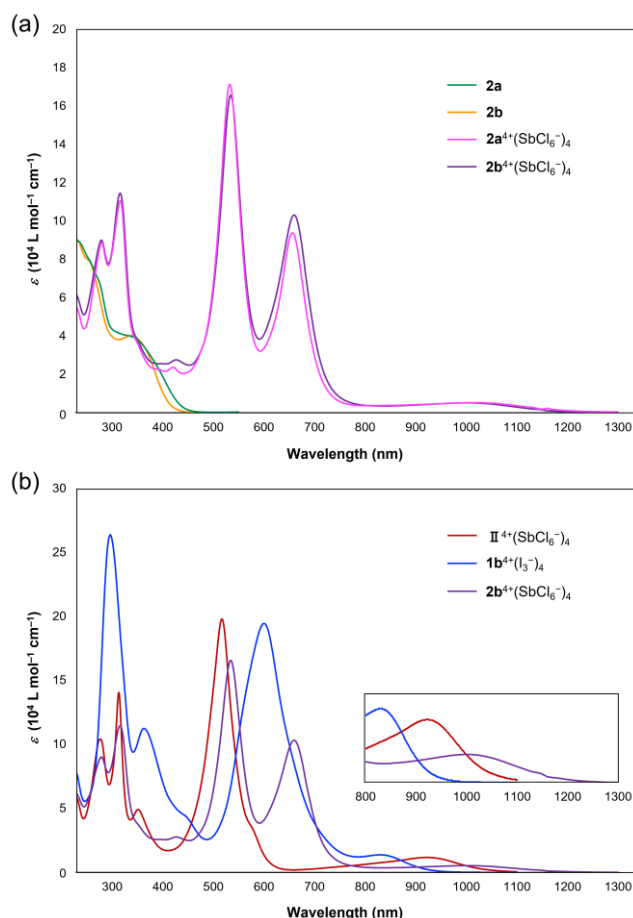
to which diarylmethyl cation moieties are attached in a nearly orthogonal manner (Figure 2). Treatment of all of the tetracationic salts with an excess amount of Zn powder resulted in quantitative regeneration of the original neutral BQDs **2a**, **2b**, **1a**, and **1b**. These results show that a reversible redox interconversion proceeds between the neutral state and the tetracationic state, accompanied by a dynamic change in structure upon 4e-transfer. The structures of both neutral BQDs and their tetracations determined by X-ray analyses are quite similar to those estimated as globally energy-minimized geometries by density functional theory (DFT) calculations at the CAM-B3LYP level (Figures S11-S12, Tables S1-S6).

### Absorption Spectra of Tetracations and Interchromophore Interaction

In contrast to the neutral state, which has absorptions only in the UV region, hybrid tetracations **2a**<sup>4+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>4</sub> and **2b**<sup>4+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>4</sub> exhibit two strong absorptions in the visible region [ $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ) in CH<sub>2</sub>Cl<sub>2</sub>: 656 (4.97) and 532 (5.23) for **2a**<sup>4+</sup> and 659 (5.01) and 534 (5.22) for **2b**<sup>4+</sup>] (Figure 3a). The absorption around 650 nm and that around 530 nm are characteristic to bis(aminophenyl)methyl cation- and bis(methoxyphenyl)methyl cation-based chromophores, respectively. When the bands of bis(aminophenyl)methyl cation in **2a**<sup>4+</sup> and **2b**<sup>4+</sup> were compared to those in BQD tetracations with eight aminophenyl groups [592 for **1a**<sup>4+</sup>(I<sub>3</sub><sup>-</sup>)<sub>4</sub> and 600 (5.29) for **1b**<sup>4+</sup>(I<sub>3</sub><sup>-</sup>)<sub>4</sub>], considerable red-shifts were observed in both hybrid tetracations **2**<sup>4+</sup>. This holds true for the absorption band of bis(methoxyphenyl)methyl cation since BQD tetracation **II**<sup>4+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>2</sub> shows absorption at 517 nm (log  $\epsilon$  5.30) (Figure 3b). These results clearly show that the intramolecular interaction between two different diarylmethyl cations in **2a**<sup>4+</sup> and **2b**<sup>4+</sup> induces a red-shift of the intrinsic absorptions of these chromophores. A hypochromic shift of the absorption band of bis(aminophenyl)methyl cation would also be related to such interchromophore interactions, and the differences in the oscillator strength  $f$  were reproduced by time-dependent (TD)-DFT calculations (Figures S14, S15, and S17).

In addition to the bands in the visible region, all of the BQD tetracations exhibit NIR absorptions, which are assigned to the intramolecular charge-transfer (CT)-type transition from the pentacene core (major contribution of HOMO) to the electron-deficient diarylmethyl cations (major contribution of nearly degenerated LUMOs), as assigned by TD-DFT calculations at the CAM-B3LYP/6-31G\* level. Notably, such NIR absorption bands are also red-shifted in **2a**<sup>4+</sup> [1025 (3.71)] and **2b**<sup>4+</sup> [1000 (3.71)] compared to those of tetracations with the same eight chromophores [922 (4.06) for **II**<sup>4+</sup>, 780 for **1a**<sup>4+</sup>, and 830 (4.13) for **1b**<sup>4+</sup>] (Figures 2b and S16, Tables 1 and S8). The red-shift of the NIR band in the hybrid tetracations can be qualitatively accounted for by considering that the strongly electron-deficient bis(methoxyphenyl)methyl cation can warrant a lower LUMO in **2a**<sup>4+</sup>, **2b**<sup>4+</sup>, and **II**<sup>4+</sup>. Although four-fold substitution of bis(methoxyphenyl)methyl cation in **II**<sup>4+</sup> causes lowering of the HOMO level by its electron-withdrawing effects, these red-shifts in hybrid tetracations **2a**<sup>4+</sup> and **2b**<sup>4+</sup> indicate that the HOMO level can be maintained to be higher due to the strong electron-donating ability of two bis(aminophenyl)methyl cations. In this way, we found that all of the first band around 1000 nm, the second band around 650 nm, and the third band around 420 nm in hybrid tetracations **2**<sup>4+</sup> can be red-shifted relative to the corresponding bands in the simple BQD tetracations by attaching two different

diarylmethyl cation chromophores on the pentacene core. This finding can provide useful guidelines, especially in terms of the red-shift of the NIR band, which is the cause of the recent attention regarding potential application as functional dyes.



**Figure 3.** (a) UV/Vis/NIR spectra of **2a** (green), **2b** (orange), **2a**<sup>4+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>4</sub> (magenta), and **2b**<sup>4+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>4</sub> (violet) in CH<sub>2</sub>Cl<sub>2</sub>. (b) UV/Vis/NIR spectra of **II**<sup>4+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>4</sub> (red), **1b**<sup>4+</sup>(I<sub>3</sub><sup>-</sup>)<sub>4</sub> (blue), and **2b**<sup>4+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>4</sub> (violet) in CH<sub>2</sub>Cl<sub>2</sub>. **II**: Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>; **1b**: X = Y = 4-O(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; **2a**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; **2b**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-O(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>]

**Table 1.** UV/Vis/NIR spectral data of the tetracationic salts in CH<sub>2</sub>Cl<sub>2</sub>.

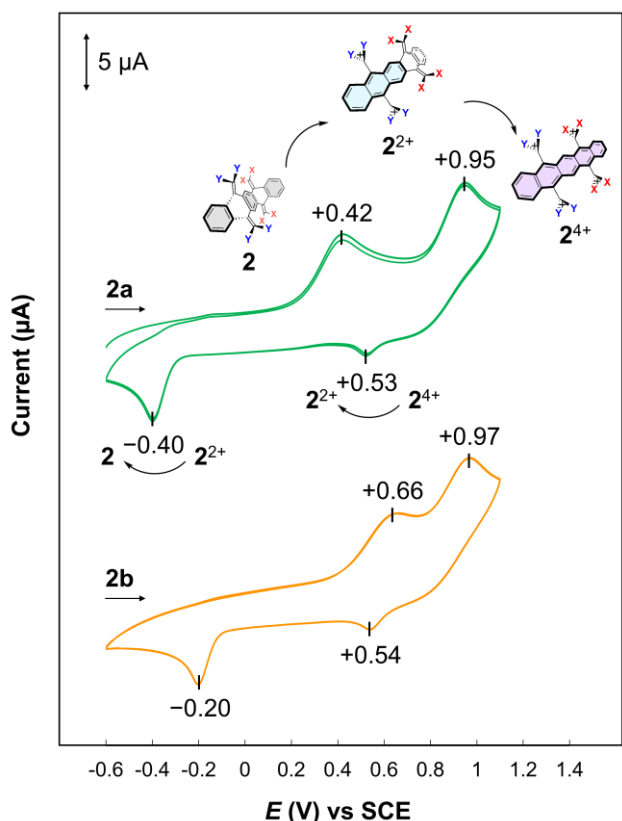
|                                                                                        | Substituents                                                                                                                    | $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon$ ) |
|----------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|
| <b>II</b> <sup>4+</sup> (SbCl <sub>6</sub> <sup>-</sup> ) <sub>4</sub> <sup>[42]</sup> | Ar = 4-MeOC <sub>6</sub> H <sub>4</sub>                                                                                         | 922 (4.06), 517 (5.30)                          |
| <b>1a</b> <sup>4+</sup> (I <sub>3</sub> <sup>-</sup> ) <sub>4</sub>                    | X = Y = 4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>                                                                        | 780 <sup>[a]</sup> , 592 <sup>[a]</sup>         |
| <b>1b</b> <sup>4+</sup> (I <sub>3</sub> <sup>-</sup> ) <sub>4</sub>                    | X = Y = 4-O(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>                                         | 830 (4.13), 600 (5.29)                          |
| <b>2a</b> <sup>4+</sup> (SbCl <sub>6</sub> <sup>-</sup> ) <sub>4</sub>                 | X = 4-MeOC <sub>6</sub> H <sub>4</sub> ,<br>Y = 4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>                                | 1025 (3.71), 656 (4.97),<br>532 (5.23)          |
| <b>2b</b> <sup>4+</sup> (SbCl <sub>6</sub> <sup>-</sup> ) <sub>4</sub>                 | X = 4-MeOC <sub>6</sub> H <sub>4</sub> ,<br>Y = 4-O(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | 1000 (3.71), 659 (5.01),<br>534 (5.22)          |

<sup>[a]</sup> The molar extinction coefficients were not determined due to low solubility.

### Redox Properties of BQDs and Their Cationic States

To investigate the redox behavior of newly synthesized BQDs, cyclic voltammetry (CV) measurements were performed in CH<sub>2</sub>Cl<sub>2</sub> with ferrocene as an external standard. BQDs **1a** and **1b** with eight aminophenyl groups exhibit voltammograms as shown in

Figure S20 that are quite similar to that of methoxyphenyl analogue **II**. Thus, one-wave 4e-electron oxidation peak as well as two-stage 2e-reduction peaks were observed. The anodic peak potential ( $E_{\text{peak}}^{\text{ox}}/\text{V}$  vs SCE: +0.50 for **1a** and +0.68 for **1b**, respectively) is less positive than that for **II** (+1.12), which corresponds to the electron-donating ability of aryl groups.<sup>[45]</sup> The DFT calculations show that, for BQDs **1** with the same eight aryl groups, the HOMO is widely delocalized over the same two units of tetraarylquinodimethane, so that the oxidation process apparently proceeds as a one-wave 4e process to produce the corresponding tetracationic states. Accordingly, the dicationic states **1**<sup>2+</sup> are short-lived during the oxidation process and could be generated only upon 2e-reduction of the tetracations **1**<sup>4+</sup> (Figure S20).



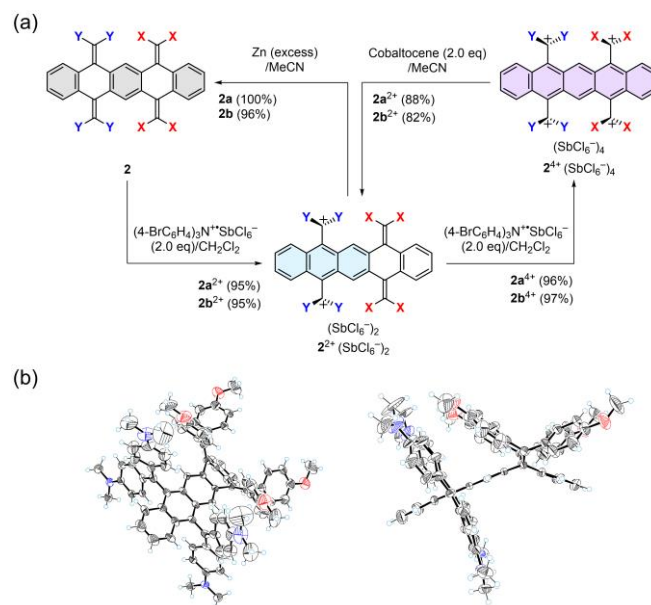
**Figure 4.** Cyclic voltammograms of neutral donors **2a** and **2b** measured at 297 K in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $\text{Bu}_4\text{NBF}_4$  as a supporting electrolyte (scan rate 0.1  $\text{V s}^{-1}$ , Pt electrodes). [**2a**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; **2b**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-O(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>]

In contrast, the redox behavior of hybrid BQDs **2a** and **2b** is quite different from that of simple BQDs **1** shown above, due to the different electronic natures of the two kinds of aryl substituents (Figure 4). Thus, two-stage 2e-processes occur in both oxidation and reduction waves. The two-stage oxidation processes were also supported by differential pulse voltammetry (DPV) measurements (Figure S22). Thus, the dications **2a**<sup>2+</sup> and **2b**<sup>2+</sup> would be generated not only by 2e-reduction of the tetracations, but also by 2e-oxidation of the neutral forms. The oxidation peaks of **2a** ( $E_{\text{peak}}^{\text{ox}}/\text{V}$  vs SCE: +0.42 and +0.95) can be characterized by considering the combination of AQDs with dimethylaminophenyl groups (+0.50) and methoxyphenyl groups (+1.03), respectively, suggesting that the 2e-oxidation of **2a** proceeds at the more easily oxidized dimethylaminophenyl units,

followed by oxidation of the methoxyphenyl units. As a result of the dynamic change in structure between the zigzag for the neutral state and planar pentacene for the tetracation, return peaks appeared in the far cathodic region ( $E_{\text{peak}}^{\text{red}}/\text{V}$ : +0.53 and -0.40), where two-step 2e-reduction occurs with a negligible steady-state concentration of intermediate open-shell species (**2a**<sup>•+</sup> or **2a**<sup>3•+</sup>). This holds true for another hybrid compound **2b**, with a slight change of redox potentials ( $E_{\text{peak}}^{\text{ox}}/\text{V}$ : +0.66 and +0.97;  $E_{\text{peak}}^{\text{red}}/\text{V}$ : +0.54 and -0.20), which were tuned by the electronic properties of the amino substituents. The energies of the HOMO and LUMO levels of each redox state were qualitatively reproduced by DFT calculations (Figures S14 and S15).

### Isolation and Structure of Dications of BQDs

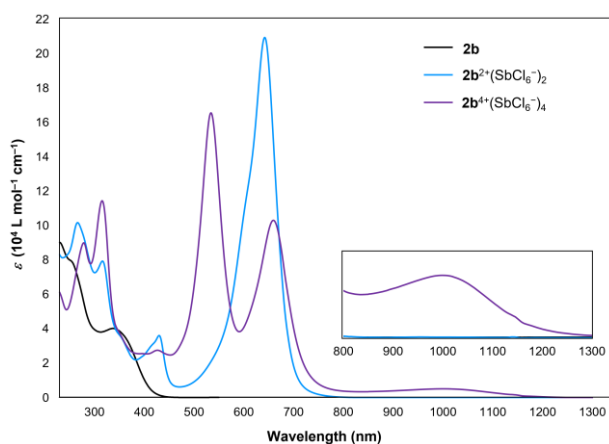
Based on the stepwise redox processes observed in the voltammograms of hybrid BQDs **2a** and **2b**, their dications would be isolated not only upon 2e-reduction of the tetracations, but also upon 2e-oxidation of neutral BQDs under preparative conditions. In fact, treatment of neutral **2a** and **2b** with two equivalents of Magic Blue allowed isolation of the dicationic salts **2a**<sup>2+</sup>( $\text{SbCl}_6^-$ )<sub>2</sub> and **2b**<sup>2+</sup>( $\text{SbCl}_6^-$ )<sub>2</sub> in respective yields of 95% and 95%. Meanwhile, treatment of the tetracation salts **2a**<sup>4+</sup>( $\text{SbCl}_6^-$ )<sub>4</sub> and **2b**<sup>4+</sup>( $\text{SbCl}_6^-$ )<sub>4</sub> with two equivalents of cobaltocene as a reducing agent gave the same dicationic salts in respective yields of 88% and 82%. In addition, the obtained dicationic salts can be oxidized to the tetracationic salts **2a**<sup>4+</sup>( $\text{SbCl}_6^-$ )<sub>4</sub> and **2b**<sup>4+</sup>( $\text{SbCl}_6^-$ )<sub>4</sub> in yields of 96% and 97%, whereas Zn-reduction regenerated **2a** and **2b** in yields of 100% and 96% yields. Therefore, the dication of hybrid BQDs is the isolable intermediate in a three-state redox interconversion in both the oxidation and reduction cycles (Figure 5a).



**Figure 5.** (a) Isolation of dication salts **2a**<sup>2+</sup>( $\text{SbCl}_6^-$ )<sub>2</sub> and **2b**<sup>2+</sup>( $\text{SbCl}_6^-$ )<sub>2</sub> and redox interconversion among dicationic states **2a**<sup>2+</sup> and other redox states **2a**<sup>4+</sup>. (b) X-ray crystal structures (ORTEP drawings) of **2a**<sup>2+</sup>( $\text{SbCl}_6^-$ )<sub>2</sub> determined at 150 K. The counterions solvent molecules, and disordered atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. #One of the two crystallographically independent molecules. [**2a**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; **2b**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-O(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>]

The  $^1\text{H}$  NMR spectra of  $\mathbf{2a}^{2+}(\text{SbCl}_6^-)_2$  and  $\mathbf{2b}^{2+}(\text{SbCl}_6^-)_2$  indicate that positive charges are located on the aminophenyl moieties, based on a comparison of the chemical shifts to those of AQD derivatives,<sup>[45]</sup> which is in accord with the expectation based on voltammetric analyses. There were no signs of a contribution from the open-shell species for the dications. Finally, X-ray analysis of the dicationic salt  $\mathbf{2a}^{2+}(\text{SbCl}_6^-)_2$  revealed that it consists of an anthracene skeleton attached to two bis(dimethylaminophenyl)methylm units, to which tetrakis(methoxyphenyl)quinodimethane unit is annulated (Figure 5b). Thus, the dicationic states of hybrid BQDs with two kinds of electrophores of different donating properties are closed-shell species with localized positive charges on the diarylmethylm moieties with more strongly donating aryl groups.

As expected from the X-ray structure of  $\mathbf{2a}^{2+}(\text{SbCl}_6^-)_2$ , the absorption band based on bis(methoxyphenyl)methylm units would disappear for both dicationic salts. Indeed, only the absorption bands attributed to bis(aminophenyl)methylm units were observed [ $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ) in  $\text{CH}_2\text{Cl}_2$ : 640 (5.37) for  $\mathbf{2a}^{2+}$  and 642 (5.32) for  $\mathbf{2b}^{2+}$ , respectively]. The NIR absorption band is absent in dications  $\mathbf{2a}^{2+}$  and  $\mathbf{2b}^{2+}$  because the intramolecular CT bands overlap the local absorption bands of bis(aminophenyl)methylms. The blue-shift of the CT bands can be accounted for by the higher LUMO level of these dications due to the lower electron-accepting ability of the bis(aminophenyl)methylm groups and by the lower HOMO level by changing the acene unit from pentacene in the tetracations to anthracene in the dications. In this way, a sharp difference in the absorption band for the three interconvertible closed-shell states is realized for **2** (only UV),  $\mathbf{2}^{2+}$  (blue without NIR), and  $\mathbf{2}^{4+}$  (violet with NIR) (Figures 6 and S18).



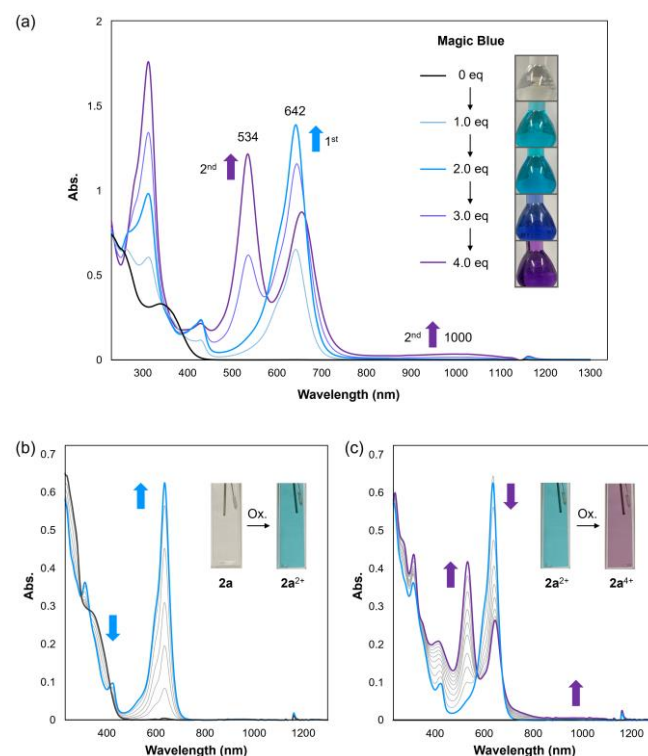
**Figure 6.** UV/Vis/NIR spectra of **2b** (black),  $\mathbf{2b}^{2+}(\text{SbCl}_6^-)_2$  (light blue), and  $\mathbf{2b}^{4+}(\text{SbCl}_6^-)_4$  (violet) in  $\text{CH}_2\text{Cl}_2$ . [**2b**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-O(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>]

### Tricolor Electrochromism in the UV/Vis/NIR Region

To demonstrate the redox-dependent color changes of hybrid BQDs, a titration experiment was conducted for **2b** by using Magic Blue in  $\text{CH}_2\text{Cl}_2$ , which was monitored by UV/Vis/NIR spectroscopy (Figure 7a). Upon the addition of several aliquots of oxidant, sequential and drastic spectral changes were observed. First, a strong band at 642 nm grew to give blue solution with an isosbestic point at 389 nm (1<sup>st</sup> stage), and then strong absorption at 534 nm gradually grew to give a purple solution with several isosbestic points at 663, 577, 435, and 266 nm (2<sup>nd</sup> stage). Such a spectral change can be accounted for by considering the quantitative conversion to **2b** to  $\mathbf{2b}^{2+}$  in the 1<sup>st</sup> stage until the

addition of 2 equivalents of Magic Blue, whereas the 2<sup>nd</sup> stage shows the quantitative conversion of  $\mathbf{2b}^{2+}$  to  $\mathbf{2b}^{4+}$  with concomitant growth of the NIR band. In both stages, steady-state concentrations of open-shell intermediates ( $\mathbf{2b}^{\cdot+}$  and  $\mathbf{2b}^{3\cdot+}$ ) are negligible.

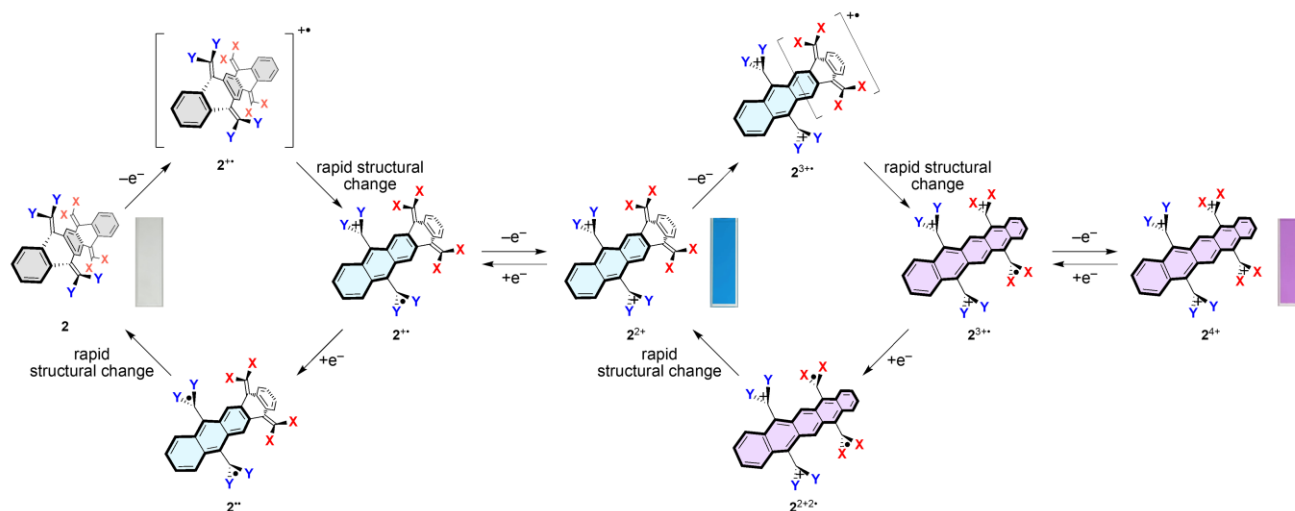
In addition to the titration experiments, the constant-current electrochemical oxidation of **2a** in  $\text{CH}_2\text{Cl}_2$  was conducted, and this was monitored by UV/Vis/NIR spectroscopy. The 1<sup>st</sup>-stage spectroelectrogram with isosbestic points showed that the spectrum could be accounted for simply by considering the presence of **2a** and  $\mathbf{2a}^{2+}$  (Figure 7b). The 2<sup>nd</sup>-stage spectroelectrogram also exhibits the isosbestic points, indicating only the presence of  $\mathbf{2a}^{2+}$  and  $\mathbf{2a}^{4+}$  with an increase in NIR absorption (Figure 7c). During the electrochemical reduction of as-generated  $\mathbf{2a}^{4+}$ , sequential spectral changes were observed; initially, the bands at 534 nm and those in the NIR region disappeared to give a blue solution of  $\mathbf{2a}^{2+}$ , and then the absorption at 640 nm gradually faded to give a colorless solution of **2a** (Figure S19).



**Figure 7.** (a) Change in UV/Vis/NIR spectrum of **2b** (8.00  $\mu\text{M}$ ) upon the addition of several aliquots of Magic Blue in  $\text{CH}_2\text{Cl}_2$  [**2b**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-O(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>]. Changes in UV/Vis/NIR spectra upon constant-current electrochemical oxidation of (b) **2a** (7.23  $\mu\text{M}$ , 30  $\mu\text{A}$ , every 2 min) and (c) as-prepared  $\mathbf{2a}^{2+}$  (30  $\mu\text{A}$ , every 8 min) in  $\text{CH}_2\text{Cl}_2$  containing 0.05 M  $\text{Bu}_4\text{NBF}_4$  as a supporting electrolyte. [**2a**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>]

Thus, by using the hybrid BQDs **2a** and **2b**, reversible interconversion among the three closed-shell species (neutral, dicationic, and tetracationic states) can demonstrate tricolor UV/Vis/NIR electrochromism in both oxidation and reduction processes, for which apparent 2e-transfer is accompanied by a change in color. In addition, no change was observed in the cyclic voltammograms during measurement for dozens of consecutive

## BQD-based Tricolor-electrochromic Dyrex Systems



**Scheme 1.** Dynamic redox interconversion among **2** (colorless), **2<sup>2+</sup>** (blue), and **2<sup>4+</sup>** (violet with NIR). Photographs show the CH<sub>2</sub>Cl<sub>2</sub> solutions of **2a**, **2a<sup>2+</sup>**(SbCl<sub>6</sub><sup>−</sup>)<sub>2</sub>, and **2a<sup>4+</sup>**(SbCl<sub>6</sub><sup>−</sup>)<sub>4</sub>. [**2a**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; **2b**: X = 4-MeOC<sub>6</sub>H<sub>4</sub>, Y = 4-O(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>]

cycles (Figure S21), which supports the electrochemical stability of the present electrochromic systems.

Compared to the previously reported tricolor electrochromic systems in which the intermediary state is an open-shell species that undergoes disproportionation,<sup>[47]</sup> all of the neutral, dicationic, and tetracationic states in the present systems exhibit thermodynamic stability, as demonstrated by isolation and X-ray analysis of each state including the intermediary dicationic state. Drastic geometrical changes among the redox states are another characteristic that facilitates the apparent 2e-transfer (Scheme 1). In the oxidation process, as-generated **2<sup>2+</sup>** and **2<sup>3+</sup>** are more easily oxidized than **2** and **2<sup>2+</sup>** due to the rapid structural change. In the reduction process, cation radical species **2<sup>3+</sup>** and **2<sup>2+</sup>** can be generated upon the reduction of **2<sup>4+</sup>** and **2<sup>2+</sup>**, however, they rapidly disproportionate into **2<sup>4+</sup>**/**2<sup>2+</sup>** and **2<sup>2+</sup>**/**2<sup>0</sup>**, respectively, under ambient conditions. The structural change of the resulting diradical species is very fast, and thus a steady-state concentration of intermediate open-shell species is negligibly small in both oxidation and reduction processes. Geometrical changes would be also associated with high electrochemical bistability, as suggested by CV measurements, between the neutral and dicationic states as well as between the dicationic and tetracationic states. Thus, the neutral and dicationic states can coexist without mutual electron exchange in the potential region from −0.40 to +0.42 V for **2a**/**2a<sup>2+</sup>** and from −0.20 to +0.66 V for **2b**/**2b<sup>2+</sup>**. Similarly, the dicationic and tetracationic states can coexist without mutual electron exchange in the potential region from +0.53 to +0.95 V for **2a<sup>2+</sup>**/**2a<sup>4+</sup>** and from +0.54 to +0.97 V for **2b<sup>2+</sup>**/**2b<sup>4+</sup>**. Such bistability also favors reversible conversion among the closed-shell states by reducing the concentration of open-shell intermediates.

## Conclusion

In summary, we have designed and synthesized hybrid BQDs **2**, which consist of two types of aryl groups with different electron-donating abilities on each quinodimethane unit. Electrochemical measurements revealed that they undergo stepwise interconversion among the neutral, dicationic, and tetracationic states in both oxidation and reduction processes via apparent 2e-transfer, which supports clean tricolor chromism because the

steady-state concentration of the open-shell species is negligibly small due to a proper molecular design. Indeed, we have isolated and carried out spectroscopic and X-ray measurements for the three closed-shell redox states of different colors: **2** (colorless) / **2<sup>2+</sup>** (blue) / **2<sup>4+</sup>** (violet with NIR). Compared to the BQD tetracations with the same eight aryl groups such as **1<sup>4+</sup>**, a red-shift of all of the Vis-NIR bands is induced for hybrid tetracations **2a<sup>4+</sup>** and **2b<sup>4+</sup>**, indicating that attaching two different electrophores to the pentacene scaffold is a versatile way not only to modify the tricolor-chromic behavior but also to fine-tune the absorption bands through intramolecular interactions. Meanwhile, the absence or presence of the CT band in the NIR region is regulated electrochemically by interconversion between the dicationic and tetracationic states. Thus, the present tricolor electrochromicity is endowed with an ON/OFF function regarding NIR absorption.

Furthermore, in these tricolor-electrochromic systems, a dynamic change in structure occurs twice with an apparent 2e-transfer in both steps. Such "double dyrex" systems can exhibit unprecedented electrochemical bistability between neutral and dicationic states and between dicationic and tetracationic states due to the large difference in redox potentials based on the structural change. Thus, they are expected to be used for the development of blur-free displays, molecular memories, redox switches, and other applications.

In conclusion, the successful demonstration of tricolor electrochromism in this study could lead to studies on a new class of multi-stage electrochromic molecules, for which all of the color states are long-lived and/or can be isolated as stable entities.

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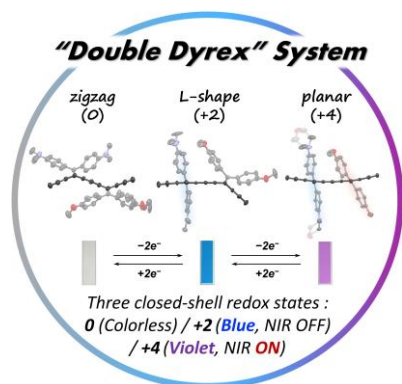
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- [48] Deposition numbers <https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/chem.202301476> 2247038 (for **1a**), 2247039 (for **1b**), 2247040 (for **1a**<sup>4+</sup>(I<sub>3</sub><sup>−</sup>)<sub>4</sub>), 2247041 (for **1b**<sup>4+</sup>(I<sub>3</sub><sup>−</sup>)<sub>4</sub>), 2247042 (for **2a**), 2247043 (for **2b**), 2247044 (for **2a**<sup>2+</sup>(SbCl<sub>6</sub><sup>−</sup>)<sub>2</sub>), and 2247045 (for **2b**<sup>4+</sup>(SbCl<sub>6</sub><sup>−</sup>)<sub>4</sub>) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe [Access Structures](#) service.

## Entry for the Table of Contents

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Tricolor electrochromic systems were constructed by realizing a double dynamic structural change that facilitates an apparent 2e<sup>-</sup> transfer in both oxidation and reduction processes. Therefore, redox interconversion cleanly proceeds among neutral (zigzag), dicationic (L-shape), and tetracationic (planar) states, accompanied by a drastic change in color and near infrared (NIR)-absorption.

Institute and/or researcher Twitter usernames: Takashi Harimoto (@ZhangBen\_dyrex), Yusuke Ishigaki (@ysk\_isgk), and Laboratory (@Yuuichi\_Hokudai)