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A new type of tricolor electrochromic system based on the dynamic redox properties of hexaarylethane derivatives

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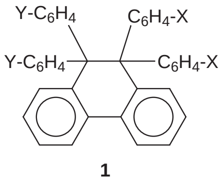
Electrochemical interconversion between 9,9,10,10-tetraaryldihydrophenanthrene 1 and 2,2′-bis(triarylmethylium) 2^{2+} has been proven to proceed *via* open form cation radical $2^{+\cdot}$ as a stable intermediate; using these three species, a novel tricolor electrochromic system that exhibits hysteretic color change (color 1 → color 2 → color 3 → color 1) is formed.

Molecular systems whose properties can be controlled electrochemically are attracting much attention because they might be applicable to the construction of molecular devices such as redox switches.[1] From this point of view the redox couples of hexaarylethanes **1d**,**e** and bis(triarylmethane) dyes **2d**,**e**$^{2+}$ are interesting;[2] their noteworthy features include electrochromic behaviour with vivid changes in color and very high bistability due to reversible C–C bond making/breaking[3] upon two-electron transfer (dynamic redox properties). During the course of our mechanistic investigation on the interconversion between **1** and **2**$^{2+}$, we have found that a unique tricolor electrochromic system could be achieved using **1a**,**b** and **2a**,**b**$^{2+}$ possessing two different triarylmethane moieties, whose properties are reported herein. Although several multi-color electrochromic systems have been reported (color 1 ↔ color 2 ↔ color 3 ↔ *etc.*),[4] the hysteretic chromicity of the present systems (color 1 → color 2 → color 3 → color 1) is unprecedented.



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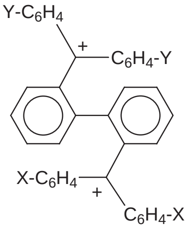
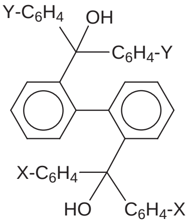


2^{2+}



3

a X = p-Me$_2$N; Y = p-MeO
b X = p-Me$_2$N; Y–Y = o-O-o
c X–X = Y–Y = o-O-o
d X = Y = p-Me$_2$N
e X = Y = p-MeO

Unsymmetric diols **3a**‡ and **3b**‡ were prepared in 12 and 8% yield, respectively, by the reaction of 2,2′-dilithiobiphenyl[5] with a mixture of the corresponding two ketones followed by chromatographic separation on SiO_2 from the symmetric diols **3c–e**. Deeply colored dication salts **2a**$^{2+}(BF_4^-)_2$‡ [λ_{max}(MeCN)/nm (log ε) 632 (4.93), 519 (4.72), 319 (4.25), 272 (4.24)] and **2b**$^{2+}(BF_4^-)_2$‡ [632 (4.92), 488 sh (3.76), 425 (4.22), 377 (4.46), 321 (4.23), 261 (4.63)] were obtained in 91 and 93% yield, respectively, by treating these diols with 42% HBF_4–$(EtCO)_2O$. Reduction of the dication salts with SmI_2 in THF gave colorless ethanes **1a**‡ [λ_{max}(MeCN)/nm (log ε) 268 (4.61)] and **1b**‡ [270 (4.58)] in 97 and 78% yield. X-Ray analysis§ has revealed that **1b** has a very long C–C bond [1.643(6) Å] (Fig. 1).¶ Thus, oxidation of **1a**,**b** with 2 equiv. of $(p\text{-}BrC_6H_4)_3N^{+\cdot}SbCl_6^-$ in CH_2Cl_2 led to the fission of the weak bonds to regenerate the dications **2a**,**b**$^{2+}$, which were isolated as $SbCl_6^-$ salts‡ in 82 and 79% yield, respectively. C_2-Symmetric ethane **1c**‡ [λ_{max}(MeCN)/nm (log ε) 282 (4.27), 230 sh (4.71)] and orange-colored **2c**$^{2+}(BF_4^-)_2$‡ [495 sh (3.62), 460 (3.79), 382 (4.56), 263 (4.82)] containing two xanthene moieties were also prepared from diol **3c**‡ for comparisons.

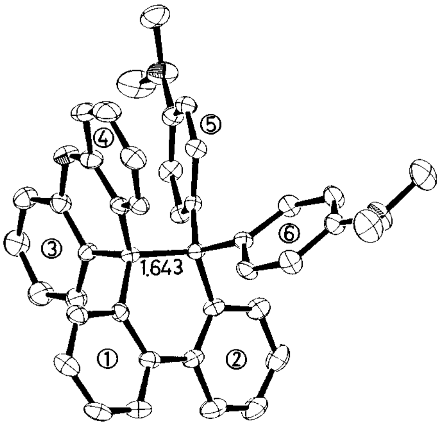


Fig. 1 Molecular geometry of ethane **1b** determined by X-ray analysis. The bipheny skeleton is nearly planar (the dihedral angle between planes 1 and 2: 16.2°), and the central six-membered ring adopts a pseudo-half chair conformation (planes 3 and 6: axial; 4 and 5: equatorial). The xanthene moiety is deformed slightly into the butterfly shape (the dihedral angle between planes 3 and 4: 15.2°). There is no disorder around the ethane bond in **1b**, unlike the symmetric ethane **1e** (ref. 2).

The cyclic voltammogram of **1c** is quite similar to those of **1d**,**e**; it shows irreversible 2e oxidation peak at +1.42 V, and the corresponding cathodic peak is largely shifted to +0.50 V, which was assigned to the 2e reduction peak of **2c**$^{2+}$ (Table 1). In contrast, unsymmetric ethanes **1a**,**b** behave rather differently from **1c–e**. Although their oxidation potentials are close to that of the tetrakis(dimethylamino) derivative **1d**, in the return cycle of the voltammograms there appeared two cathodic peaks (Fig. 2). From independent measurements on **2a**,**b**$^{2+}$ it was confirmed that these peaks are due to two-stage 1e reduction

Table 1 Redox potentials of ethanes **1** and dications **2**$^{2+}$ in CH_2Cl_2[a]

	E/V *vs.* SCE		
Compound	E^{ox} (**1**)	E_1^{red} (**2**$^{2+}$)	E_2^{red}(**2**$^{2+}$)
a X = p-Me$_2$N, Y = p-MeO	+0.83[b,c]	+0.10	−0.45[c]
b X = p-Me$_2$N, Y–Y = o-O-o	+0.76[b,c]	+0.24	−0.19[c]
c X–X = Y–Y = o-O-o	+1.39[b,c]	+0.53[b,c]	
d[d] X = Y = p-Me$_2$N	+0.74[b,c]	−0.42[b,c]	
e[d] X = Y = p-MeO	+1.44[b,c]	+0.21[b,c]	

[a] 0.1 mol dm^{-3} Bu$^n_4$NBF$_4$, Pt electrode, scan rate 100 mV s^{-1}. [b] Two-electron process. [c] Irreversible wave, values were calculated as $E^{ox} = E_{peak} - 0.03$ and $E^{red} = E_{peak} + 0.03$, respectively. [d] Ref. 2.

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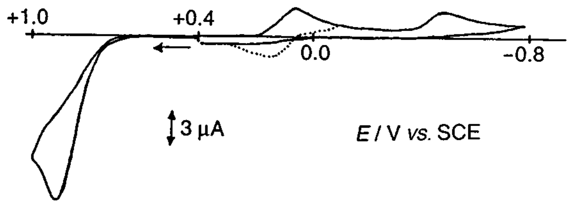
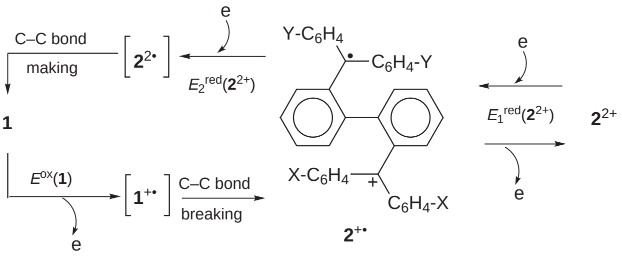


Fig. 2 Cyclic voltammogram of ethane **1a** (10^{-3} mol dm^{-3}) in CH_2Cl_2 (*E*/V *vs*. SCE 0.1 mol dm^{-3} $Bu^n_4NBF_4$, Pt electrode, scan rate 500 mV s^{-1}). The reduction peaks are absent when the voltammogram is first scanned cathodically. As shown by the dotted line, the first reduction wave at +0.07 V is reversible when the scanning was reversed at −0.10 V.

processes of the dications; the first one corresponding to the Y-C_6H_4-C^+-C_6H_4-Y moiety is completely reversible. Furthermore, the anodic peak due to the oxidation of **1a**,**b** appears in the voltammograms of **2a**,**b**$^{2+}$ after scanning the irreversible second 1e reduction wave. Such redox properties can be accounted for only by assuming the reaction mechanism shown in Scheme 1, in which the weakened C–C bond of hexaarylethane **1** is cleaved after 1e oxidation‖ to **1**$^{+\cdot}$ whereas two-fold 1e reduction of **2**$^{2+}$ to **2**$^{2\cdot}$ is necessary before the ring closure to **1**. It should be noted that **2**$^{+\cdot}$ produced from **1**$^{+\cdot}$ is more easily oxidized than **1** [E^{ox}(**1a**,**b**) is much more positive than E^{ox}(**2a**,**b**$^{+\cdot}$) = E_1^{red}(**2a**,**b**$^{2+}$)], thus the steady-state concentration of **2**$^{+\cdot}$ is negligible during the electrochemical oxidation of **1**, although the same specimen is a long-lived intermediate in the reduction process of **2**$^{2+}$.



Scheme 1

Thanks to the hysteretic interconversion between **1**, **2**$^{+\cdot}$ and **2**$^{2+}$, novel tricolor electrochromic systems could be constructed using the unsymmetric derivatives. Thus, upon electrochemical oxidation of colorless **1a**, both the blue (X = *p*-Me_2N) and red (Y = *p*-MeO) triarylmethylium chromophores grow simultaneously to develop the violet color of **2a**$^{2+}$ [Fig. 3(*a*)]. On the other hand, the red chromophore disappears first upon reduction of **2a**$^{2+}$ [Fig. 3(*b*), stage 1], and next the blue cation radical **2a**$^{+\cdot}$ is converted to colorless **1a** [Fig. 3(*c*), stage 2] even under the constant-current electrolytic conditions. Similar behaviour but with a different color was observed for the interconversion of **2b**$^{2+}$ (green) (isosbestic points: 248, 270, 300 nm) ⟶ **2b**$^{+\cdot}$ (blue) (296 nm) ⟶ **1b** (colorless) (309 nm) ⟶ **2b**$^{2+}$ (green), showing the generality of the unprecedented pattern of color change.

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Notes and References

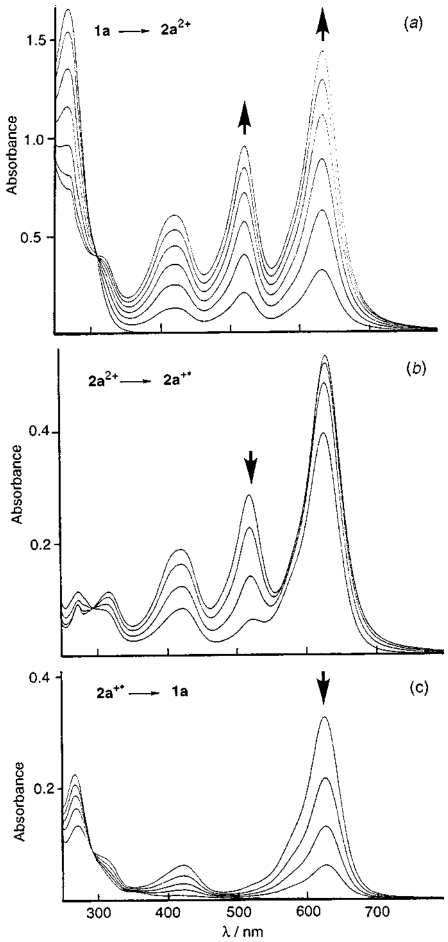

Fig. 3 Changes in the UV–VIS spectra of (*a*) **1a** (3.6 ml; 4.1 × 10^{-5} mol dm^{-3} in MeCN containing 0.04 mol dm^{-3} $Bu^n_4NBF_4$) upon electrochemical oxidation (15 μA) at 10 min intervals, and **2a**$^{2+}$ (3.6 ml soln; 6.6 × 10^{-6} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} $Bu^n_4NBF_4$) upon electrochemical reduction (70 μA): (b) stage 1, at 0.5 min intervals; (c) stage 2, at 1 min intervals

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‡ All new compounds gave satisfactory spectral data and analytical values.

§ *Crystal Data* for **1b**: $C_{42}H_{36}N_2O$, *M* 584.76, *P*212121, *a* = 14.216(4), *b* = 20.806(6), *c* = 10.483(3) Å, *V* = 3100(1) Å^3, D_c (Z = 4) = 1.253 g cm^{-1}, *Rw* = 0.025. CCDC 182/1003.

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