CHEMCOMM
Communication
www.rsc.org/chemcomm

Dual-mode electrochromism switched by proton transfer: dynamic redox properties of bis(diarylmethylenium)-type dyes†

Takanori Suzuki,* Hiroki Higuchi, Masakazu Ohkita and Takashi Tsuji

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan.
E-mail: tak@sci.hokudai.ac.jp

Received (in Cambridge, UK) 31st May 2001, Accepted 28th June 2001
First published as an Advance Article on the web 3rd August 2001

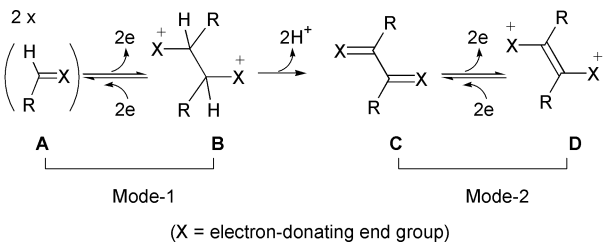
Upon oxidative dimerization of pale yellow $Ar_2C{=}CHPh$ 1 ($Ar = 4\text{-}Me_2NC_6H_4$), deep blue 1,4-dication 2^{2+} was obtained as a stable salt, which was transformed into 1 by reductive C–C bond fission; deprotonation of 2^{2+} gave intense yellow diene 3, which was interconvertible with violet dication 4^{2+} by two-electron transfer, thus exhibiting two distinct modes of electrochromism before and after proton transfer.

Recently, much attention has been focused on electrochromic dyes[1,2] for use as optical memories or electrochemical switches.[3] The representative examples are a series of open-chain violenes[4] shown by the redox couple of **C** and **D** in Scheme 1. Diene **C** can be prepared by oxidative dimerization of olefin **A**,[2*a*] and the similar procedure has been widely used to synthesize novel TTF vinylogues.[5,6] Although the oxidation reactions are believed to proceed *via* unconjugated 1,4-dication **B**, this intermediate has never been isolated nor even detected spectroscopically probably due to its instability by rapid deprotonation to **C** under the reaction conditions.

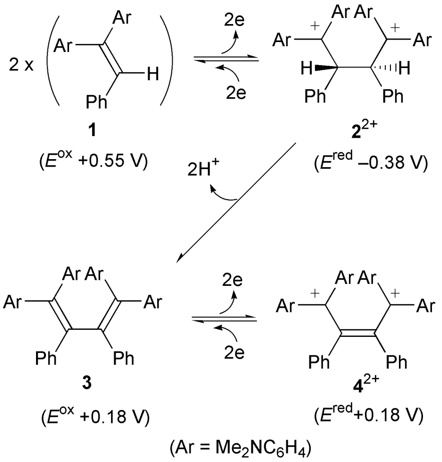
In our continuing efforts to develop new electrochromic systems endowed with bistability by reversible C–C bond making/breaking[7] or drastic structural changes[8] upon electron transfer (dynamic redox properties), we have found here that the dication **B** possessing two dye chromophores [X = $(4\text{-}Me_2NC_6H_4)_2C$] and two aryl groups (R = aryl) can be isolated as stable salts. By the selective transformation of **B** to **A** by reduction and **B** to **C** by deprotonation, novel dual-mode electrochromism shown in Scheme 1 could be realized, where proton transfer alters the mode from one to another.

The voltammetric analysis‡ indicated that olefin **1**§ undergoes irreversible oxidation at +0.55 V *vs.* SCE in MeCN. The corresponding reduction wave appeared in the far cathodic region (−0.38 V), which is rather close to the reduction potential of $(4\text{-}Me_2NC_6H_4)_2CH^+$ (−0.54 V). Such a large shift of redox peaks can be accounted for by assuming oxidative dimerization of **1** (Scheme 2).

In fact, dication $\mathbf{2}^{2+}$ was isolated as deep blue I_3^- salt§ in 97% yield by the reaction of yellow olefin **1**§ with 1.5 eq. of I_2 in CH_2Cl_2. Mechanistically, there can be two pathways to produce $\mathbf{2}^{2+}$ from **1**: (a) dimerization of $\mathbf{1}^{+\cdot}$ to $\mathbf{2}^{2+}$, and (b) reaction of $\mathbf{1}^{+\cdot}$ with neutral **1** to form $\mathbf{2}^{+\cdot}$ followed by further one-electron oxidation. In the present case, path (a) is plausible because $\mathbf{2}^{2+}$ $(I_3^-)_2$ was obtained in 92% yield by the reaction of **1** with 1.5 eq. I_2 under the presence of $Ph_2C{=}CHPh$ (2 eq.) which remained intact and was recovered quantitatively.



Scheme 1



Scheme 2

The 1,4-dication $\mathbf{2}^{2+}$ is surprisingly stable with no sign of spontaneous deprotonation; its methine proton appears at 6.02 ppm as a sharp singlet in the ^{1}H NMR spectrum measured in CD_3CN. Upon reduction of this salt with Zn powder in MeCN, olefin **1** was regenerated in 100% yield. Such high-yield interconversion indicates that **1** and $\mathbf{2}^{2+}$ can be considered as a 'reversible' redox pair even though C–C bond making and breaking are accompanied by two-electron transfer.[7,10]

When $\mathbf{2}^{2+}$ $(I_3^-)_2$ was treated with Bu^n_4NF in THF–MeCN, deprotonation proceeded smoothly to give intense yellow diene **3**§ in 75% yield, which is a stronger donor [E^{ox} +0.18 V (2e, rev.)]‡ than **1**. Attempted deprotonation of $\mathbf{2}^{2+}$ $(I_3^-)_2$ with Et_3N [E^{ox} +0.85 V (irrev.)] resulted in formation of olefin **1** in quantitative yield by electron transfer, and deprotonation with pyridine was very slow.

Upon treatment of **3** with 3 eq. of I_2 in CH_2Cl_2, deep violet dication salt $\mathbf{4}^{2+}$ $(I_3^-)_2$§ was obtained in 98% yield, which regenerated diene **3** in 100% yield upon reduction with Zn in MeCN. According to the X-ray analyses,¶ the diene unit in **3** adopts a nonplanar geometry with a large torsion angle of 59.1° around the C^2–C^3 bond (Fig. 1a), which is undoubtedly due to steric congestion among six aryl groups. It is likely that lack of effective conjugation in diene **3** as well as steric shielding against the base in the hindered C–H acid $\mathbf{2}^{2+}$ are the reasons for reluctant deprotonation of $\mathbf{2}^{2+}$ to **3**. On the other hand, all of the diene carbons lie nearly on the same plane in $\mathbf{4}^{2+}$ (Fig. 1b), thus confirming drastic geometrical changes by twisting motions[2,6,8] during interconversion between **3** and $\mathbf{4}^{2+}$.

In this way, two types of dynamic structural changes are presented by the redox couples of **1**–$\mathbf{2}^{2+}$ and **3**–$\mathbf{4}^{2+}$, which can be switched by proton transfer. Furthermore, the novel dual-mode electrochromism can be realized by these couples since each pair exhibits distinct spectral changes upon electrolyses

---

† Electronic supplementary information (ESI) available: spectral data for new compounds. See http://www.rsc.org/suppdata/cc/b1/b104742f/

DOI: 10.1039/b104742f

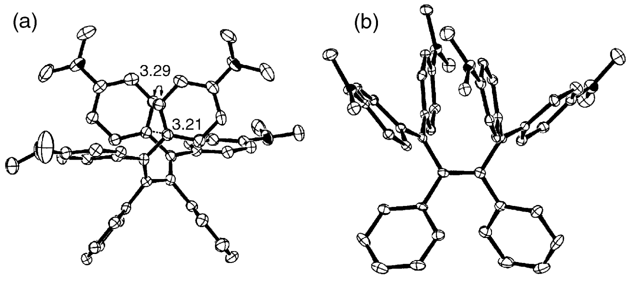


Fig. 1 (a) ORTEP drawing of diene **3** determined by X-ray at −163 °C. Torsion angle of diene unit is 59.1°. Two aryl groups are arranged in a face-to-face manner (dihedral angle 7.9°). Short intramolecular C···C contacts (3.21 and 3.29 Å) are shown by dotted line. (b) ORTEP drawing of dication **4**$^{2+}$ determined by X-ray at −176 °C on I_3^- salt. The four carbon atoms of $C^+–C=C–C^+$ lie nearly on the same plane (the largest deviation from the least-squares plane, 0.09 Å).

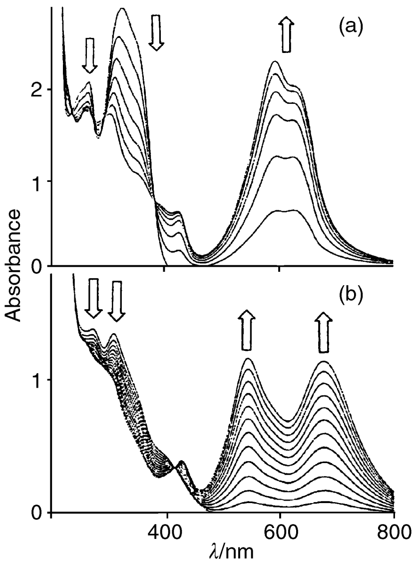


Fig. 2 Two modes of electrochromism. a) Mode-1; changes in the UV-VIS spectrum of **1** (3.5 mL, 1.1 × 10^{-4} mol dm^{-3} in MeCN) upon constant-current electrochemical oxidation (32 μA, 4 min interval) to **2**$^{2+}$. (b) Mode-2; changes in the UV-VIS spectrum of **3** (3.5 mL, 2.6 × 10^{-5} mol dm^{-3} in MeCN) upon constant-current electrochemical oxidation (31 μA, 2 min interval) to **4**$^{2+}$. Note the presence of isosbestic points in both transformation.

(Fig. 2), which opens up a way to construct a molecular device where two independent inputs (e^- and H^+) are transduced into a unified two-dimensional output (ε *vs.* λ in UV-VIS).

This work has revealed that the 1,4-dication **B** in Scheme 1 can exist as stable species (as in **2**$^{2+}$)‖ when deprotonation is not feasible due to steric shielding in **B** and/or prohibited full-conjugation in diene **C** by twisted geometry. In such an appropriate case, all of the species of **A**–**D** (as in **1**–**4**$^{2+}$) are stable enough to realize the dual-mode optical response. The present electrochromism modulated by proton transfer provides a new successful entry into the proton–electron cooperating functions.[11]

This work was supported by the Ministry of Education, Science, and Culture, Japan (No. 13440184). Financial support from the Iwatani Naoji Foundation is gratefully acknowledged. We thank Professor Tamotsu Inabe (Hokkaido University) for use of the X-ray structure analysis system.

Notes and references

‡ All of the redox potentials shown in the text were measured under the same conditions: E/V *vs.* SCE, 0.1 mol Et_4NClO_4 in MeCN, Pt electrode, scan rate 100 mV s^{-1}. Values for E^{ox} and E^{red} were calculated as $E_p - 0.03$ and $E_p + 0.03$ V, respectively, in the cases of irreversible processes.

§ Olefin **1** was prepared in 95% yield by Wittig–Horner reaction of PhCHO and Ar_2CH-PO(OMe)$_2$/Bu^{n}Li in THF, and its physical data are identical to those reported in ref. 9. Stereochemistry of **2**$^{2+}$ was determined to be *dl* by X-ray analysis of I_3^- salt.¶ All new compounds show satisfactory analytical values. λ_{max} (MeCN)/nm (log ε): **1**, 345 sh (4.38), 322 (4.43), 266 (4.30), 255 (4.28); **2**$^{2+}$ (I_3^-)$_2$, 619 (4.83), 595 (4.84), 423 (4.47), 361 (4.80), 293 (5.04); **3**, 397 sh (4.27), 345 sh (4.59), 312 (4.71), 277 (4.65); **4**$^{2+}$ (I_3^-)$_2$, 679 (4.86), 545 (4.91), 426 (4.48), 358 (4.83), 292 (5.14).†

¶ *Crystal data* for **2**$^{2+}$ (I_3^-)$_2$: $C_{48}H_{52}N_4I_6$, M 1446.39, monoclinic, $P2_1/n$, a = 10.054(2), b = 17.393(3), c = 28.880(5) Å, β = 92.970(9)°, U = 5043(1) Å^3, D_c (Z = 4) = 1.905 g cm^{-3}, μ(Mo-Kα) = 37.43 cm^{-1}, T = 123 K. The final R value is 0.062 for 4842 independent reflections with $I > 3\sigma I$ and 263 parameters. For **3**: $C_{48}H_{50}N_4$, M 682.95, monoclinic, $P2_1/c$, a = 14.612(3), b = 16.076(2), c = 17.1807(7) Å, β = 91.792(1)°, U = 4034.0(10) Å^3, D_c (Z = 4) = 1.124 g cm^{-1}, μ(Mo-Kα) = 0.66 cm^{-1}, T = 110 K. The final R value is 0.065 for 3614 independent reflections with $I > 3\sigma I$ and 469 parameters. For **4**$^{2+}$ (I_3^-)$_2$: $C_{48}H_{50}N_4I_6$, M 1444.38, monoclinic, $P2_1/n$, a = 9.6884(8), b = 23.432(1), c = 22.8948(4) Å, β = 107.5794(4)°, U = 4954.9(5) Å^3, D_c (Z = 4) = 1.936 g cm^{-1}, μ(Mo-Kα) = 37.99 cm^{-1}, T = 97 K. The final R value is 0.026 for 7707 independent reflections with $I > 3\sigma I$ and 526 parameters. CCDC/164961–164963. See http://www.rsc.org/suppdata/cc/b1/b104742f/ for electronic files in .cif or other electronic format.

‖ Similarly, 2,2′-bis[2,2-bis(4-dimethylaminophenyl)ethenyl]biphenyl undergoes oxidative cyclization to give another isolable 1,4-dication framed in a 9,10-dihydrophenanthrene skeleton, which will be reported in a full paper.

1 P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism: Fundamentals and Applications*, VHC, Weinheim, 1995.

2 (*a*) S. Hünig, M. Kemmer, H. Wenner, F. Barbosa, G. Gescheidt, I. G. Perepichka, P. Bäuerle, A. Emge and K. Peters, *Chem. Eur. J.*, 2000, **6**, 2618; (*b*) S. Hünig, M. Kemmer, H. Wenner, I. F. Perepichka, P. Bäuerle, A. Emge and G. Gescheid, *Chem. Eur. J.*, 1999, **5**, 1969.

3 V. Balzani, M. Gómez-López and J. F. Stoddart, *Acc. Chem. Res.*, 1998, **31**, 405; J.-P. Sauvage, *Acc. Chem. Res.*, 1998, **31**, 611; P. L. Boulas, M. Gómez-Kaifer and L. Echegoyen, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 216.

4 K. Deuchert and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 875.

5 R. Mayer and K. Kröber, *J. Prakt. Chem.*, 1974, **316**, 907; U. Schöberl, J. Salbech and J. Daub, *Adv. Mater.*, 1992, **4**, 41; D. Lorcy, R. Carlier, A. Robert, A. Tallec, P. Le Maguerés and L. Ouahav, *J. Org. Chem.*, 1995, **60**, 2443; P. Hapiot, D. Lorcy, A. Tallec, R. Carlier and A. Robert, *J. Phys. Chem.*, 1996, **100**, 14 823; A. Benahmed-Gasmi, P. Frére, J. Roncali, E. Elandaloussi, J. Ordun, J. Garin, M. Jubault and A. Gorgues, *Tetrahedron Lett.*, 1995, **36**, 2983; A. J. Moore, M. R. Bryce, P. J. Skabara, A. S. Datsanov, L. M. Goldenberg and J. A. K. Howard, *J. Chem. Soc., Perkin Trans. 1*, 1997, 3443; P. Hascoat, D. Lorcy, A. Robert, R. Carlier, A. Tallec, K. Boubekeur and P. Batail, *J. Org. Chem.*, 1997, **62**, 6086.

6 A. Ohta and Y. Yamashita, *J. Chem. Soc., Chem. Commun.*, 1995, 1761; Y. Yamashita, M. Tomura, M. B. Zaman and K. Imaeda, *Chem. Commun.*, 1998, 1657.

7 T. Suzuki, J. Nishida and T. Tsuji, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1329; *Chem. Commun.*, 1998, 2193; T. Suzuki, H. Takahashi, J. Nishida and T. Tsuji, *Chem. Commun.*, 1998, 1331; T. Suzuki, M. Kondo, T. Nakanura, T. Fukushima and T. Miyashi, *Chem. Commun.*, 1997, 2325; T. Suzuki, T. Yoshino, M. Ohkita and T. Tsuji, *J. Chem. Soc., Perkin Trans. 1*, 2000, 3417; T. Suzuki, J. Nishida, M. Ohkita and T. Tsuji, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 1804.

8 T. Suzuki, H. Shiohara, M. Monobe, T. Sakimura, S. Tanaka, Y. Yamashita and T. Miyashi, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 455; T. Suzuki, Y. Yoshino, J. Nishida, M. Ohkita and T. Tsuji, *J. Org. Chem.*, 2000, **65**, 5514.

9 M. Matsui, M. Tsuge, K. Shibata and H. Muramatsu, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1753.

10 M. Horner and S. Hünig, *J. Am. Chem. Soc.*, 1977, **99**, 6122; R. Rathore, P. Le Magueres, S. V. Lindeman and J. K. Kochi, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 809.

11 K. Nakasuji, K. Sugiura, J. Toyoda, Y. Morita, H. Okamoto, K. Okaniwa and T. Mitani, *Mol. Cryst. Liq. Cryst.*, 1992, **216**, 213; G. De Santis, L. Fabbrizzi, M. Licchelli and P. Pallavicini, *Inorg. Chim. Acta*, 1994, **225**, 239; V. A. Ozeryanskii, A. F. Pozharskii, G. R. Milgizina and S. T. Howard, *J. Org. Chem.*, 2000, **65**, 7707.