

ChemComm

Chemical Communications

www.rsc.org/chemcomm



ISSN 1359-7345



COMMUNICATION

Takanori Suzuki *et al.*

Two-way chromic interconversion of the 2,2'-biphenol-6,6'-diyl dication with 5*H*,10*H*-dioxapyrene or 9*H*,10*H*-4,5-dihydroxyphenanthrene



Cite this: *Chem. Commun.*, 2015, 51, 14303

Received 29th July 2015,
Accepted 10th August 2015

DOI: 10.1039/c5cc06338h

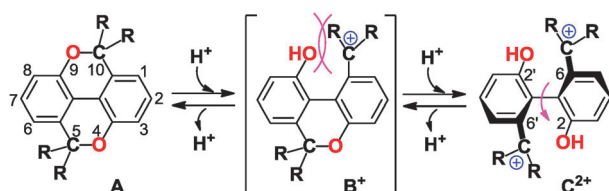
www.rsc.org/chemcomm

Two-way chromic interconversion of the 2,2'-biphenol-6,6'-diyl dication with 5*H*,10*H*-dioxapyrene or 9*H*,10*H*-4,5-dihydroxyphenanthrene†

Yuto Sakano, Ryo Katoono, Kenshu Fujiwara and Takanori Suzuki*

Two-proton or two-electron transfer of the title biphenolic dication proceeds nearly simultaneously to induce 2,6'/2',6- or 6,6'-bond formation to give dioxapyrene or dihydrophenanthrene derivatives, respectively, with vivid changes in color (halochromism and electrochromism).

5*H*,10*H*-Dioxapyrene (diopy; 5*H*,10*H*-[1]benzopyrano[5,4,3-*cde*][1]-benzopyran) is a less-studied heterocyclic skeleton¹ in contrast to its 5,10-dione analogue. We envisaged that the flattened framework of diopy provides a unique opportunity for the development of new bistable molecular response systems, in which an external stimulus induces the cleavage of two C(sp₃)-O bonds to transform into the corresponding biphenyl derivatives with a twisted conformation (Scheme 1). Upon acid treatment of diopy (**A**) with cation-stabilizing substituents at 5,10-positions, the biphenolic dication (**C**²⁺) would be generated *via* the monocationic intermediate (**B**⁺). When **B**⁺ suffers from severe steric repulsion at the bay-region, this amphiprotic species easily undergoes acid–base disproportionation to **A** and **C**²⁺, so that double protonation/deprotonation between **A** and **C**²⁺ would occur nearly simultaneously. Such a simplified pseudo-two-state switching is favored



Scheme 1 Interconversion of diopy **A** and biphenolic dication **C**²⁺ upon double protonation/deprotonation *via* intermediate **B**⁺.

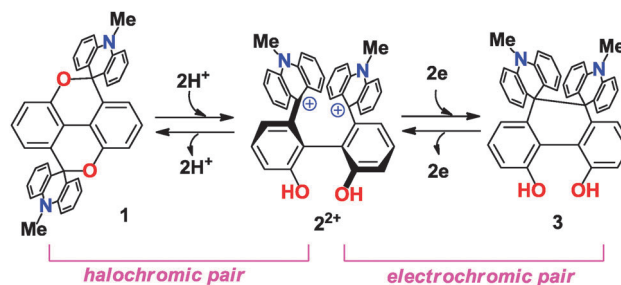
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan. E-mail: tak@sci.hokudai.ac.jp; Fax: +81-11-706-2714; Tel: +81-11-706-2714

† Electronic supplementary information (ESI) available: Experimental procedure and characterization data. Supplementary figures of X-ray single-crystal structure analyses, halochromic titration, and cyclic voltammograms. CCDC 1061367, 1061368 and 1061369. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/c5cc06338h

for the construction of promising molecular response systems with a sharp ON/OFF threshold.² When the cationic part in **C**²⁺ is endowed with a strong absorption in the visible region, interconversion between **A** and **C**²⁺ is accompanied by halochromism,³ since diopy **A** shows absorptions only in the UV region.

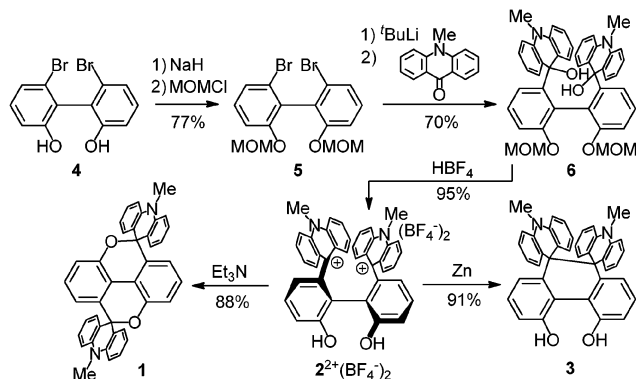
To generate and isolate the dicationic state as a stable entity despite the presence of hydroxy groups within the molecule, the cationic subunit should have a large *pK_R*⁺ value, which prompted us to select the 10-methylacridinium chromophore^{4,5} (Scheme 2). Due to the bulkiness of the chromophore, the biphenol skeleton in **2**²⁺ would have a large torsion angle, whereas the diopy skeleton in **1** would be nearly planar, since the spiro(10-methylacridan) units do not induce any steric hindrance. Such a drastic structural change would realize the two-state halochromic interconversion between **1** and **2**²⁺. Another interesting point is that, upon reduction, dication **2**²⁺ would be transformed into a dihydrophenanthrene (DHP) derivative **3** accompanied by C(sp₃)-C(sp₃) bonding through “dynamic redox (dyrex)” behavior,⁶ and the interconversion between **2**²⁺ and **3** would also exhibit characteristic color and structural changes. Thus, **1**, **2**²⁺ and **3** can serve as a novel motif for multi-input molecular response systems.⁷

Here we report the preparation and X-ray structures of **1** and **2**²⁺ along with their chromic behavior during the interconversion between **1** and **2**²⁺ (halochromic³ pair) as well as **2**²⁺ and **3** (electrochromic⁸ pair).



Scheme 2 Multi-input chromic behavior of diopy **1**, biphenolic dication **2**²⁺, and DHP **3**.





Scheme 3 Preparation scheme for **1**, $2^{2+}(\text{BF}_4^-)_2$ salt, and **3**.

6,6'-Dibromo-2,2'-biphenol **4**⁹ was first reacted with methoxymethyl (MOM) chloride/NaH in DMF to give MOM-protected biphenol **5**¹⁰ in 77% yield. The dilithio derivative derived from **5** and 4 equiv. of ^tBuLi in THF was then reacted with 10-methyl-9(10H)-acridone to give bis(hydroxy)base **6**¹⁰ in 70% yield. Upon treatment of **6** with HBF₄ in MeOH–CHCl₃ at reflux afforded the desired $2^{2+}(\text{BF}_4^-)_2$ ¹⁰ as yellow-orange crystals in 95% yield. The reaction of $2^{2+}(\text{BF}_4^-)_2$ with Et₃N in MeCN gave colorless crystals of diopy **1**¹⁰ in 88% yield (Scheme 3).

Based on the results of an X-ray analysis¹¹ at 150 K, the diopy core in **1** is nearly planar (largest deviation of an atom from the mean plane: 0.23 Å), although the pyran rings adopt a very shallow twist-chair form (Fig. 1 and Fig. S1, ESI[†]). The two benzene rings are coplanar (dihedral angle: 0°). To this core are attached the spiro(10-methylacridan) units, which are slightly deformed into a butterfly-shape [dihedral angle between two benzene nuclei of acridan: 21.3(2)°], as found in other structurally-related molecules.¹² In contrast, the two molecular halves in dication 2^{2+} are largely twisted in the crystal of (BF₄⁻)₂ salt¹¹ (Fig. 2 and Fig. S2, ESI[†]). The dihedral angle of the biphenyl unit is 68.8(1)° (*syn*-form), and there are no signs to indicate coordination of the hydroxy groups to the acridinium chromophores. If we consider that the two oxygen atoms at the 2,2'-positions are separated by a distance of 3.050(2) Å, intermolecular H-bonding is not effective in 2^{2+} (typical distance for

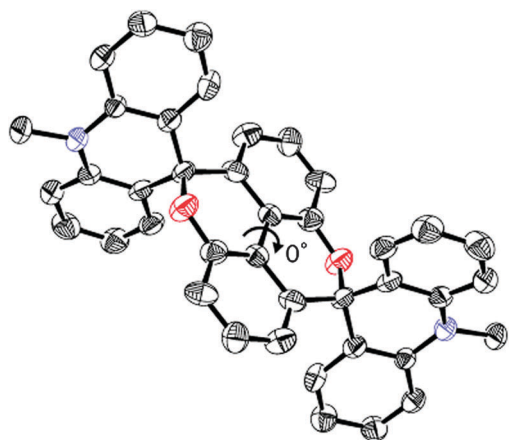


Fig. 1 ORTEP drawing of diopy **1** determined by X-ray analysis at 150 K.

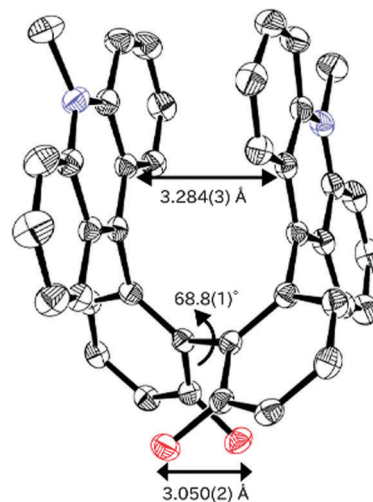


Fig. 2 ORTEP drawing of 2^{2+} in $2^{2+}(\text{BF}_4^-)_2$ salt determined by X-ray analysis at 150 K.

the H-bonded O...O: 2.75 ± 0.2 Å). The π–π interaction between two acridinium units must be the major directing force to give the observed *syn*-form (Fig. S2 and S3, ESI[†]),¹³ and thus the chromophores are stacked nearly in parallel [dihedral angle: 3.92(3)°] with the shortest C...C contact of 3.284(3) Å (sum of van der Waals radii: 3.40 Å).

Diopy **1** is colorless, with absorptions only in the UV region [$\lambda_{\text{max}}/\text{nm}$: 339 (4.30) in CH₂Cl₂], whereas 2^{2+} exhibits a yellow-orange color [358(3.92) in MeCN] due to the characteristic absorptions of acridinium (Fig. 3a). Although 10-methylacridinium itself is highly fluorescent, 2^{2+} is non-fluorescent due to the charge-shift-type quenching of the excited state by the electron-donating biphenyl unit. Upon the aliquot addition of TFOH to a DMSO-*d*₆ solution of **1**, a clean conversion to 2^{2+} was observed (Fig. S4, ESI[†]). The resulting spectra showed the presence of only two species (**1** and 2^{2+}), which demonstrated that the steady-state concentration of the intermediary monocationic derivatives is negligible. The halochromic response was examined by the repeated addition of TFOH (100 µL) to a DMSO solution of **1** (1.2 × 10⁻⁵ M), followed by the addition of Et₃N (200 µL) to the solution of as-generated 2^{2+} . By monitoring the color change using UV-vis spectroscopy, we could confirm the reversibility of the present halochromism (Fig. 3b and Fig. S5, ESI[†]).

According to the results of a voltammetric analysis,¹⁴ **3** undergoes irreversible two-electron oxidation at an anodic peak potential (E_{pa}) of +0.32 V in CH₂Cl₂/MeCN (4:1) vs. SCE (Fig. S6a, ESI[†]). The return peak was observed in the far cathodic region ($E_{\text{pc}} = -0.23$ V), which corresponds to the reduction process of dication 2^{2+} (Fig. S6b, ESI[†]). In fact, Zn-reduction of $2^{2+}(\text{BF}_4^-)_2$ induced C(sp₃)–C(sp₃) bonding at the C6 and C6' positions to give DHP **3**. Colorless crystals of **3** [$\lambda_{\text{max}}/\text{nm}$: 285 (4.37) in CH₂Cl₂] were isolated in 91% yield, and regenerated $2^{2+}(\text{BF}_4^-)_2$ in 87% yield upon treatment with 2 equiv. of ferrocenium tetrafluoroborate in CH₂Cl₂/MeCN. In this way, reversible redox interconversion between 2^{2+} and **3** accompanied by C–C bond formation/cleavage (“dyrex” behavior) was confirmed. Due to the dynamic geometrical changes,¹⁵ two-electron transfer occurs nearly simultaneously,



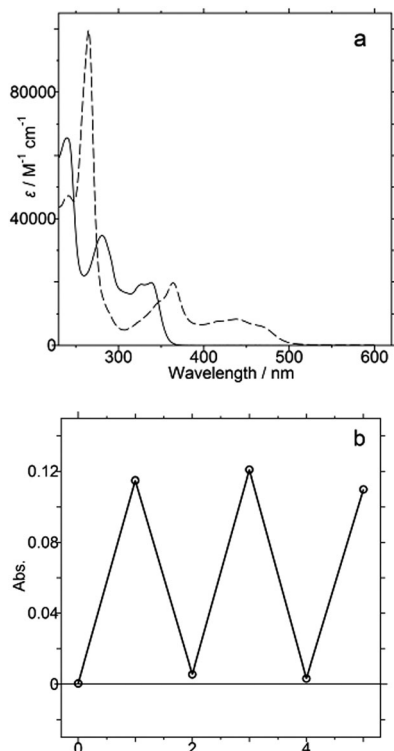


Fig. 3 (a) UV-vis spectra of **1** (solid line) in CH_2Cl_2 and $2^{2+}(\text{BF}_4^-)_2$ (dashed line) in MeCN. (b) UV-vis spectral changes at 440 nm for halochromic switching from **1** [1.2×10^{-5} M; 3 mL] to 2^{2+} upon addition of TfOH (100 μmol) in DMSO. The reverse conversion was accomplished upon addition of Et_3N (200 μmol). The halochromic cycles could be repeated without significant loss of response.

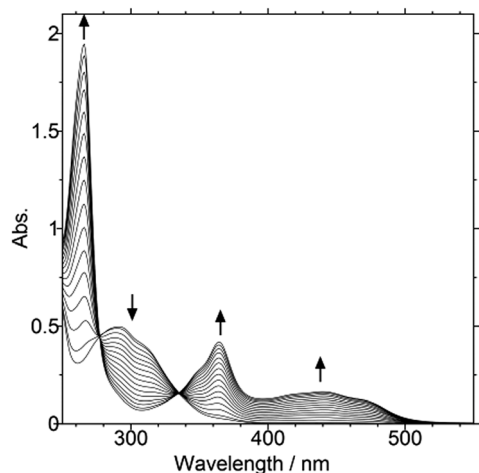


Fig. 4 A continuous change in the UV-vis spectra of **3** [2.1×10^{-5} M; 3 mL] to 2^{2+} in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (4:1) containing 0.05 M Bu_4NBF_4 upon constant-current electrochemical oxidation on a Pt electrode (30 μA , every 1 min).

which was confirmed by the negligible steady-state concentration of the intermediary cation radical upon the electrochemical conversion of **3** to 2^{2+} (Fig. 4).

In this work, we have demonstrated the reversible halochromic and electrochromic interconversion of 2,2'-biphenyl-6,6'-diyl dication with two kinds of neutral molecules (diopy and DHP).

This is the first example of concomitant but independent two-proton or two-electron transfer with a negligible concentration of the intermediates. A drastic structural change is the key to this novel feature, which may represent a new molecular design concept for multi-input response systems with advanced features.

Notes and references

- (a) P. S. Dewar, A. R. Forrester and R. H. Thomson, *J. Chem. Soc. C*, 1971, 3950–3959; (b) A. M. Costero and M. Pitarch, *J. Chem. Res., Miniprint*, 1994, 761–769; (c) M. Mazzega, F. Fabris, S. Cossu, O. De Lucchi, V. Lucchini and G. Valle, *Tetrahedron*, 1999, **55**, 4427–4440.
- Reviews: (a) M. Takeuchi, M. Ikeda, A. Sugasaki and S. Shinkai, *Acc. Chem. Res.*, 2001, **34**, 865–873; (b) L. Kovbasyuk and R. Krämer, *Chem. Rev.*, 2004, **104**, 3161–3187; (c) N. C. Gianneschi, M. S. Masar, III and C. A. Mirkin, *Acc. Chem. Res.*, 2005, **38**, 825–837; (d) Y. Kubo and Y. Ishii, *J. Nanosci. Nanotechnol.*, 2006, **6**, 1489–1509; (e) C. Kremer and A. Luetzen, *Chem. – Eur. J.*, 2013, **19**, 6162–6196; (f) H. Kawai, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 399–409.
- P. Bamfield and M. G. Hutchings, *Chromic Phenomena: Technological Applications of Colour Chemistry*, RSC, Cambridge, 2nd edn, 2010.
- The $\text{p}K_{\text{R}^+}$ value of 10-methyl-9-phenylacridinium is 11.0: J. W. Bunting and W. G. Meathrel, *Can. J. Chem.*, 1973, **51**, 1965–1972.
- T. Suzuki, T. Takeda, E. Ohta, K. Wada, R. Katoono, H. Kawai and K. Fujiwara, *Chem. Rec.*, 2015, **15**, 280–294.
- Review on “dyrex” systems undergoing drastic structural changes upon electron transfer: T. Suzuki, E. Ohta, H. Kawai, K. Fujiwara and T. Fukushima, *Synlett*, 2007, 851.
- (a) F. M. Raymo, *Adv. Mater.*, 2002, **14**, 401–414; (b) T. Suzuki, S. Tanaka, H. Kawai and K. Fujiwara, *Chem. – Asian J.*, 2007, **2**, 171–177; (c) T. Suzuki, T. Iwai, E. Ohta, H. Kawai and K. Fujiwara, *Tetrahedron Lett.*, 2007, **48**, 3599–3603; (d) T. Suzuki, K. Ohta, T. Nehira, H. Higuchi, E. Ohta, H. Kawai and K. Fujiwara, *Tetrahedron Lett.*, 2008, **49**, 772–776; (e) V. Luxami and S. Kumar, *New J. Chem.*, 2008, **32**, 2074–2079; (f) T. Suzuki, Y. Ishigaki, T. Iwai, H. Kawai, K. Fujiwara, H. Ikeda, Y. Kano and K. Mizuno, *Chem. – Eur. J.*, 2009, **15**, 9434–9441; (g) T. Suzuki, Y. Umezawa, Y. Sakano, H. Tamaoki, R. Katoono and K. Fujiwara, *Chem. Lett.*, 2015, **44**, 905–907.
- (a) P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism: Fundamentals and Applications*, VCH, Weinheim, 1995; (b) P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism and Electrochromic Devices*, Cambridge Univ. Press, Cambridge, 2007.
- Y. Zou, H. Geng, W. Zhang, S. Yu and X. Zhang, *Tetrahedron Lett.*, 2009, **50**, 5777–5779.
- Experimental details and selected spectral data are given in the ESI†.
- CCDC deposition numbers are as follows: **1** [P21/c, Z = 2] 1061368; $2^{2+}(\text{BF}_4^-)_2$ [Pbca, Z = 8] 1061367; MOM- $2^{2+}(\text{BF}_4^-)_2 \cdot (\text{CH}_3\text{CN})_{0.5}$ [P21/c, Z = 8] 1061369.
- (a) T. Suzuki, A. Migita, H. Higuchi, H. Kawai, K. Fujiwara and T. Tsuji, *Tetrahedron Lett.*, 2003, **44**, 6837–6840; (b) K. Wada, T. Takeda, H. Kawai, R. Katoono, K. Fujiwara and T. Suzuki, *Chem. Lett.*, 2013, **42**, 1194–1196.
- A quite similar molecular geometry was observed in the structurally related dication salt of MOM- $2^{2+}(\text{BF}_4^-)_2$,¹¹ which was selectively obtained upon treatment of diol **6** with HBF_4 in $\text{MeOH}-\text{CHCl}_3$ at ambient temperature. The crystal of the MOM- 2^{2+} salt contains two independent molecules (mol-1, -2), in which the main difference is the geometry around the MOM groups. The torsion angle of the biphenyl unit is $64.7(1)^\circ$ or $63.2(1)^\circ$ in mol-1 and -2, respectively. In both molecules, the two acridinium chromophores are stacked nearly in parallel [dihedral angle: $2.04(7)^\circ$ or $4.99(7)^\circ$] with the shortest C...C contact of 3.315(6) Å or 3.266(6) Å, respectively.
- Cyclic voltammetry was conducted in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (4:1) containing 0.1 M Bu_4NBF_4 as a supporting electrolyte (E/V vs. SCE, Pt electrode, scan rate 100 mV s^{-1}). Ferrocene undergoes 1e-oxidation at +0.53 V under similar conditions.
- (a) M. R. Bryce, A. J. Moore, M. Hasan, G. J. Ashwell, A. T. Fraser, W. Clegg, M. B. Hursthouse and A. I. Karaulov, *Angew. Chem., Int. Ed.*, 1990, **29**, 1450–1452; (b) K. Hu and D. H. Evans, *J. Phys. Chem.*, 1996, **100**, 3030–3036; (c) M. Guerro, R. Carlier, K. Boubekeur, D. Lorcé and P. Hapiot, *J. Am. Chem. Soc.*, 2003, **125**, 3159–3167.

