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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†

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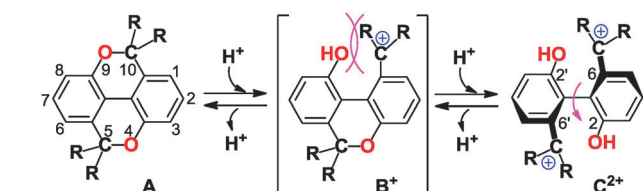
Two-proton or two-electron transfer of the title biphenolic dication proceeds nearly simultaneously to induce 2,6'/2',6- or 6,6'-bond formation to give dioxapyrene or dihydrophenanthrene derivatives, respectively, with vivid changes in color (halochromism and electrochromism).

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

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

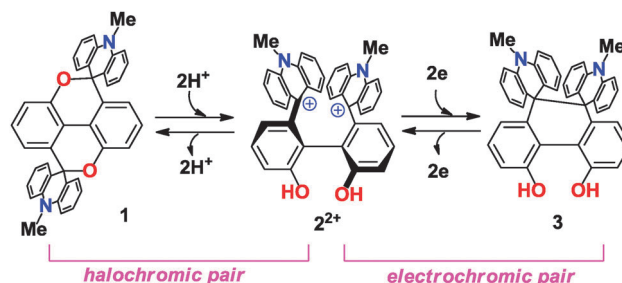
Here we report the preparation and X-ray structures of **1** and **2**²⁺ along with their chromic behavior during the interconversion between **1** and **2**²⁺ (halochromic³ pair) as well as **2**²⁺ and **3** (electrochromic⁸ pair).



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

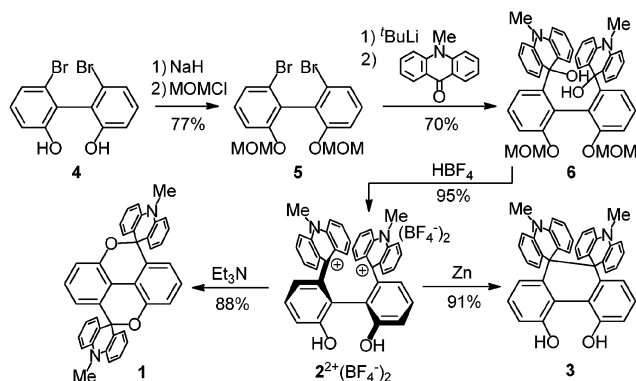
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† Electronic supplementary information (ESI) available: Experimental procedure and characterization data. Supplementary figures of X-ray single-crystal structure analyses, halochromic titration, and cyclic voltammograms. CCDC 1061367, 1061368 and 1061369.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



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





Scheme 3 Preparation scheme for **1**, **2²⁺**(BF₄[−])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 **2²⁺**(BF₄[−])₂¹⁰ as yellow-orange crystals in 95% yield. The reaction of **2²⁺**(BF₄[−])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 **2²⁺** 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 **2²⁺** (typical distance for

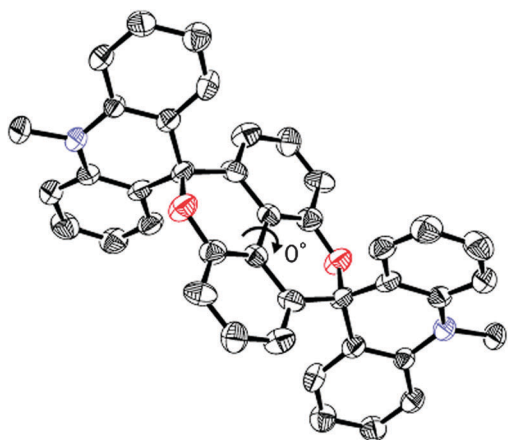


Fig. 1 ORTEP drawing of diopy **1** determined by X-ray analysis at 150 K.

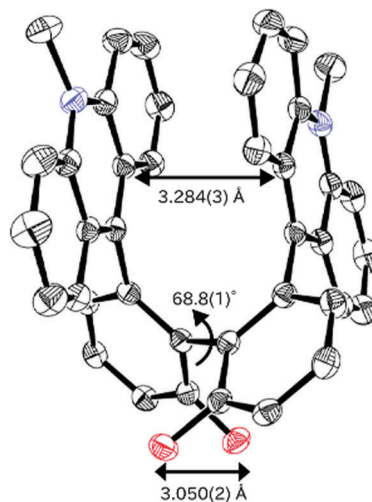


Fig. 2 ORTEP drawing of **2²⁺** in **2²⁺**(BF₄[−])₂ salt determined by X-ray analysis at 150 K.

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 [λ_{max} /nm: 339 (4.30) in CH₂Cl₂], whereas **2²⁺** 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, **2²⁺** is non-fluorescent due to the charge-shift-type quenching of the excited state by the electron-donating biphenol unit. Upon the aliquot addition of TFOH to a DMSO-*d*₆ solution of **1**, a clean conversion to **2²⁺** was observed (Fig. S4, ESI†). The resulting spectra showed the presence of only two species (**1** and **2²⁺**), 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 **2²⁺**. 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_{pc} = −0.23 V), which corresponds to the reduction process of dication **2²⁺** (Fig. S6b, ESI†). In fact, Zn-reduction of **2²⁺**(BF₄[−])₂ induced C(sp₃)–C(sp₃) bonding at the C6 and C6' positions to give DHP **3**. Colorless crystals of **3** [λ_{max} /nm: 285 (4.37) in CH₂Cl₂] were isolated in 91% yield, and regenerated **2²⁺**(BF₄[−])₂ in 87% yield upon treatment with 2 equiv. of ferrocenium tetrafluoroborate in CH₂Cl₂/MeCN. In this way, reversible redox interconversion between **2²⁺** 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,



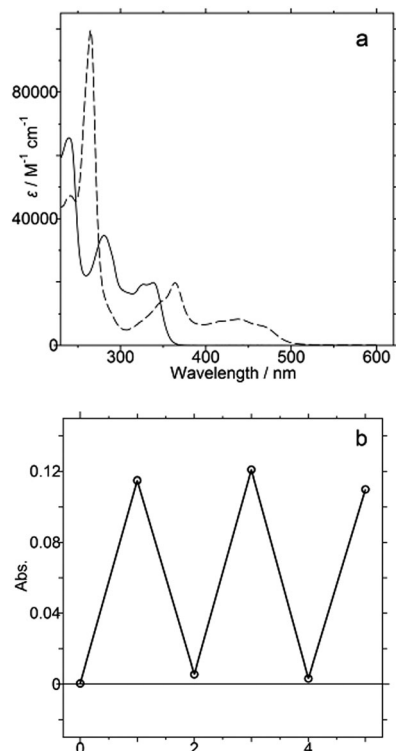


Fig. 3 (a) UV-vis spectra of **1** (solid line) in CH_2Cl_2 and $2^{2+}(\text{BF}_4^-)_2$ (dashed line) in MeCN. (b) UV-vis spectral changes at 440 nm for halochromic switching from **1** [1.2×10^{-5} M; 3 mL] to 2^{2+} upon addition of TfOH (100 μL) in DMSO. The reverse conversion was accomplished upon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

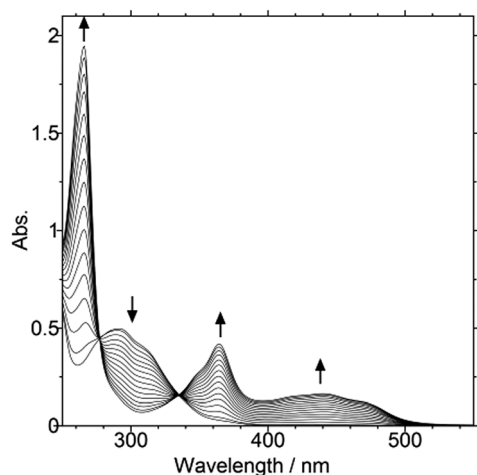


Fig. 4 A continuous change in the UV-vis spectra of **3** [2.1×10^{-5} M; 3 mL] to 2^{2+} in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (4:1) containing 0.05 M Bu_4NBF_4 upon constant-current electrochemical oxidation on a Pt electrode (30 μA , every 1 min).

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.

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- 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.
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- 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.
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