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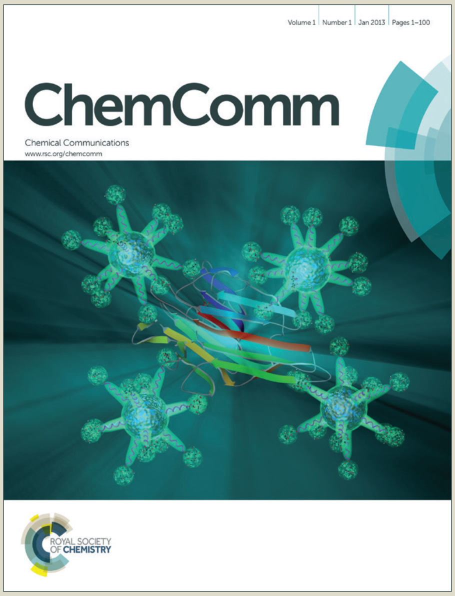

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Cite this: DOI: 10.1039/c0xx00000x

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Communication

Two-way chromic interconversion of 2,2'-biphenol-6,6'-diyl dication with 5*H*,10*H*-dioxapyrene or 9*H*,10*H*-4,5-dihydroxyphenanthrene: Concomitant two-proton or two-electron transfer accompanied by drastic structural changes

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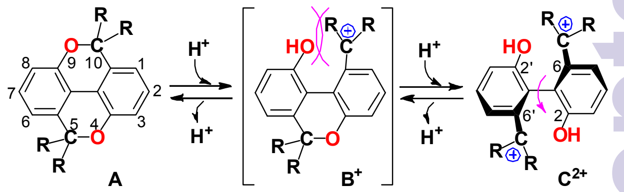
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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).

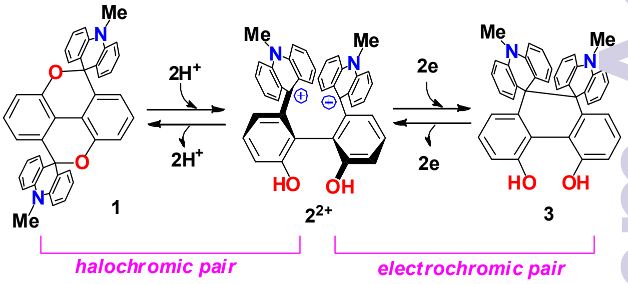
5*H*,10*H*-Dioxapyrene (diopy; 5*H*,10*H*-[1]benzopyrano[5,4,3-*cde*][1]benzopyran) is a less-studied heterocyclic skeleton[1] in contrast to its 5,10-dione analogue. We envisaged that the flattened framework of diopy provides a unique opportunity for the development of new bistable molecular response systems, in which an external stimulus induces the cleavage of two C(sp$_3$)–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 hydroxyl 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 two-state halochromic interconversion between **1** and **2**$^{2+}$. Another interesting point is that, upon reduction, dication **2**$^{2+}$ would be transformed into dihydrophenanthrene (DHP) derivative **3** accompanied by C(sp$_3$)–C(sp$_3$) 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 chromic behavior during the interconversion between **1** and **2**$^{2+}$ (halochromic[3] pair) as well as **2**$^{2+}$ and **3** (electrochromic[8] pair).

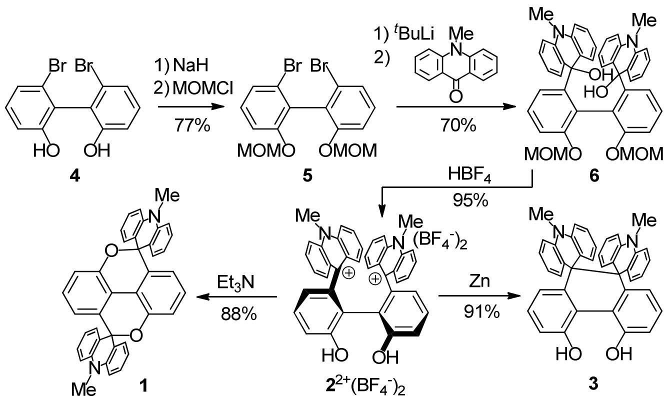


Scheme 1. Interconversion of diopy **A** and biphenolic dication **C**$^{2+}$ upon double protonation/deprotonation via intermediate **B**$^+$



Scheme 2. Multi-input chromic behavior of diopy **1**, biphenolic dication **2**$^{2+}$, and DHP **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. Dilithio derivative derived from **5** and 4 equiv. of *t*BuLi in THF was then reacted with 10-methyl-9(10*H*)-acridone to give bis(hydroxy)base **6**[10] in 70% yield. Upon treatment of **6** with HBF$_4$ in MeOH-CHCl$_3$ at reflux afforded desired **2**$^{2+}$(BF$_4^-$)$_2$[10] as yellow-orange crystals in 95% yield. Reaction of **2**$^{2+}$(BF$_4^-$)$_2$ with Et$_3$N in MeCN gave colorless crystals of diopy **1**[10] in 88% yield (Scheme 3).



Scheme 3. Preparation scheme for **1**, $\mathbf{2}^{2+}(\mathrm{BF_4}^-)_2$ salt, and **3**.

Based on the results of an X-ray analysis[11] 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 (Figures 1 and S1). The two benzene rings are coplanar (dihderal angle: 0º). 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)º], as found in other structurally-related molecules.[12] In contrast, the two molecular halves in dication $\mathbf{2}^{2+}$ are largely twisted in the crystal of $(\mathrm{BF_4}^-)_2$ salt[11] (Figures 2 and S2). The dihedral angle of biphenyl unit is 68.8(1)º (*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 3.050(2) Å, intermolecular H-bonding is not effective in $\mathbf{2}^{2+}$ (typical distance for 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 (Figures S2 and S3),[13] and thus the chromophores are stacked nearly in parallel [dihedral angle: 3.92(3)º] 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 $\mathrm{CH_2Cl_2}$], whereas $\mathbf{2}^{2+}$ exhibits a yellow-orange color [358 (3.92) in MeCN] due to the characteristic absorptions of acridinium (Figure 3a). Although 10-methylacridinium itself is highly fluorescent, $\mathbf{2}^{2+}$ is non-fluorescent due to 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**, clean conversion to $\mathbf{2}^{2+}$ was observed (Figure S4). The resulting spectra showed the presence of only two species (**1** and $\mathbf{2}^{2+}$), 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 microL) to a DMSO solution of **1** (1.2×10^{-5} M), followed by the addition of $\mathrm{Et_3N}$ (200 microL) to the solution of as-generated $\mathbf{2}^{2+}$. By monitoring the color change by UV-Vis spectroscopy, we could confirm the reversibility of the present halochromism (Figures 3b and S5).

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 $\mathrm{CH_2Cl_2}$/MeCN (4:1) vs SCE (Figure S6a). The return peak was observed in the far cathodic region (E_{pc} = –0.23 V), which corresponds to the reduction process of dication $\mathbf{2}^{2+}$ (Figure S6b). In fact, Zn-reduction of $\mathbf{2}^{2+}(\mathrm{BF_4}^-)_2$ 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 $\mathrm{CH_2Cl_2}$] were isolated in 91% yield, and regenerated $\mathbf{2}^{2+}(\mathrm{BF_4}^-)_2$ in 87% yield upon treatment with 2 equiv. of ferrocenium tetrafluoroborate in $\mathrm{CH_2Cl_2}$/MeCN. In this way, reversible redox interconversion between $\mathbf{2}^{2+}$ 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, which was confirmed by the negligible steady-state concentration of intermediary cation radical upon the electrochemical conversion of **3** to $\mathbf{2}^{2+}$ (Figure 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.

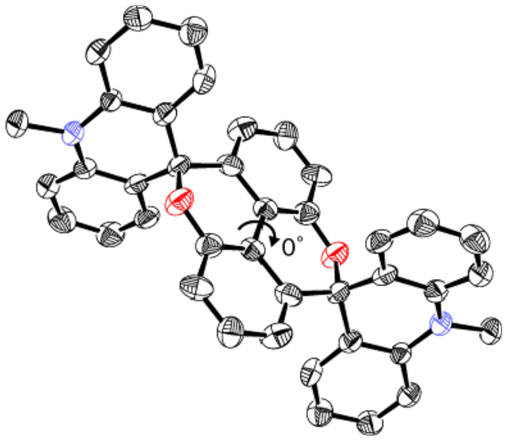


Figure 1. ORTEP drawing of diopy **1** determined by X-ray analysis at 150 K.

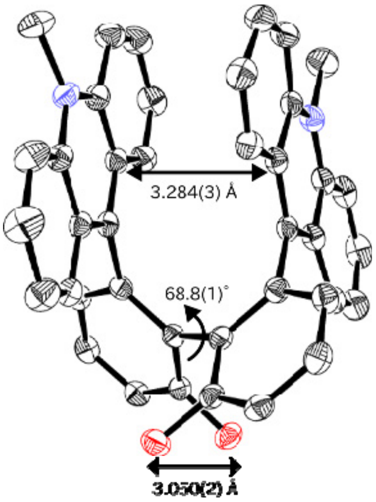


Figure 2. ORTEP drawing of $\mathbf{2}^{2+}$ in $\mathbf{2}^{2+}(\mathrm{BF_4}^-)_2$ salt determined by X-ray analysis at 150 K.

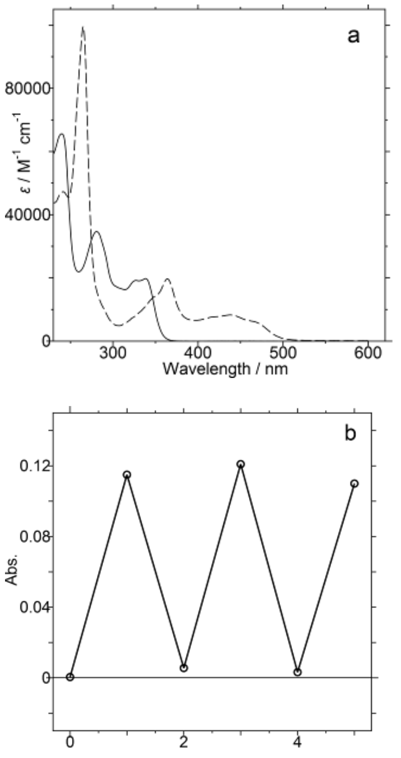


Figure 3. (a) UV-Vis spectra of **1** (solid line) in CH_2Cl_2 and $\mathbf{2}^{2+}(BF_4^-)_2$ (dashed line) in MeCN. (b) UV-Vis spectral changes at 440 nm for halochromic switching from **1** [1.2 x 10^{-5} M; 3 mL] to $\mathbf{2}^{2+}$ by addition of TfOH (100 microL) in DMSO. The reverse conversion was accomplished by addition of Et_3N (200 microL). The halochromic cycles could be repeated without significant loss of response.

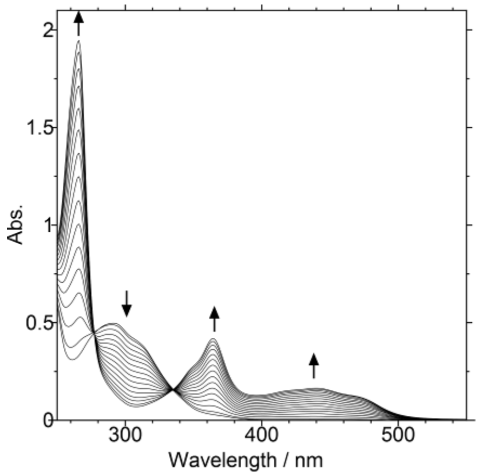


Figure 4. A continuous change in UV-Vis spectra of **3** [2.1 x 10^{-5} M; 3 mL] to $\mathbf{2}^{2+}$ in CH_2Cl_2/MeCN (4:1) containing 0.05 M Bu_4NBF_4 upon constant-current electrochemical oxidation on Pt electrode (30 microA, every 1 min)

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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.] See DOI: 10.1039/c000000x/

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10 Experimental detail and selected spectral data are given in supporting information

11 CCDC deposition numbers are as follows: **1** [*P*21/c, *Z* = 2] 1061368; $\mathbf{2}^{2+}(BF_4^-)_2$ [*P*bca, *Z* = 8] 1061367; MOM-$\mathbf{2}^{2+}(BF_4^-)_2$ $(CH_3CN)_{0.5}$ [*P*21/c, *Z* = 8] 1061369.

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13 A quite similar molecular geometry was observed in the structurally-related dication salt of MOM-$\mathbf{2}^{2+}(BF_4^-)_2$,[11,] which was selectively obtained upon treatment of diol **6** with HBF_4 in MeOH-$CHCl_3$ at ambient temperature. The crystal of MOM-$\mathbf{2}^{2+}$ salt contains two independent molecules (mol-1, -2), in which main difference is the geometry around the MOM groups. The torsion angle of biphenyl unit is 64.7(1)º or 63.2(1)º in mol-1 and -2 respectively. In both molecules, the two acridinium chromophores are stacked nearly in parallel [dihedral angle: 2.04(7)º or 4.99(7)º] with the shortest C -- C contact of 3.315(6) Å or 3.266(6) Å, respectively.

14 Cyclic voltammetry was conducted in CH_2Cl_2/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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