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Reversible Three-State Switching of Luminescence: A New Twist to Electro- and Photochromic Behavior

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Efficient regulation of photonic [luminescence] output in molecular systems is a key goal in the development of molecular based photonic devices.[1] Effecting changes in the luminescence properties of molecules through external control is challenging due to the sensitivity of luminescence quantum yields to very minor changes in molecular structure. Nevertheless, a number of elegant examples of efficient reversible on/off or color switching of luminescence in molecular systems have been reported,[2] through ion binding,[3] photo-[4] and electro-chemical[5] control. Although two-color electroluminescence was demonstrated in a metal complex-based electrochemiluminescent device,[6] the ability to engage in both reversible on/off and color switching of a single-component molecular system has, to our knowledge, not been reported.

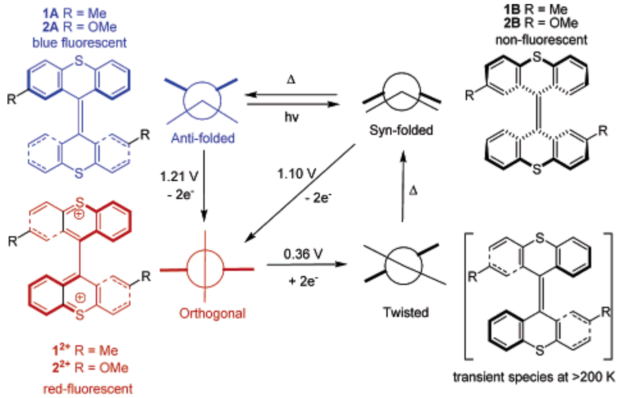
Here we describe a three-state luminescence switch where an organic luminophore (i.e., dimethyl- (**1A**), dimethoxy-bis-thiaxanthylidene (**2A**), Scheme 1)[7] can be switched reversibly between a red ($\lambda_{max} \approx 585$ nm) and blue ($\lambda_{max} \approx 440$ nm) luminescent state and a nonluminescent state through the subtle interplay of photochemical, thermal, and electrochemical stimuli. A combination of steps provides for control of photonic output, where the full completion of each individual step allows for both on/off and color switching (Scheme 1).

Overcrowded alkenes have captured the imagination of chemists for over 100 years,[8,9] both for their thermo-, photo-, electro-, and piezochromic behavior and their dynamic stereochemistry. The potential of this class of compound toward application in functional molecular materials is demonstrated elegantly in the bistricyclic aromatic enylidenes (BEA)[10] and phenanthrylidenes,[11] which were the basis for unidirectional light-driven molecular motors developed within our own group.[11b,d]

BEAs, such as bis-thiaxanthylidenes **1A** and **2A** (Scheme 1), adopt a stable nonplanar anti-folded geometry due to steric overcrowding of the upper and lower aromatic rings.[9d] Although thermally stable to both *cis*−*trans* and conformational isomerization, changes in molecular structure can be effected through both redox-[12] and photochemistry[8] as reported for bis-thiaxanthylidene (**3A**, R = H). A photochemically inactive syn-folded conformational isomer (**1B** and **2B**, Scheme 1) of **1A** and **2A**, is formed quantitatively upon near-UV irradiation ($\lambda_{exc} = 365$ nm). Both **1B** and **2B** are nonfluorescent and undergo complete thermal reversion to **1A** and **2A**, respectively (Figure 1 and Figures S1−4).[13]

Cyclic voltammetry of **1A** shows an irreversible oxidation to form $\mathbf{1}^{2+}$ at $E_{p,a} \approx 1.21$ V (vs SCE). Under thin layer conditions at 298 K, the reduction of $\mathbf{1}^{2+}$ at $E_{p,c} \approx 0.36$ V (vs SCE) is observed with quantitative reformation of **1A** (Figure 2). The structure of the air-stable dication $\mathbf{1}^{2+}$, isolated from bulk anodic oxidation, shows unique, near-perpendicular (87°) orientation of the aromatic moieties upper and lower tricyclic aromatic moieties.[14] The large geometrical changes, which accompany the interconversion between the anti-folded **1A** and the orthogonal $\mathbf{1}^{2+}$, are responsible for the hysteresis observed in the **1A**/$\mathbf{1}^{2+}$ redox system (Figure 2). Similar electrochemical behavior is observed for **2A**.

Scheme 1. Changes in Conformation in BEAs[a] between the **1/2A** (anti-folded) and **1/2B** (syn-folded) States and the Orthogonal and Dicationic State ($\mathbf{1/2}^{2+}$)



[a] Only trans isomers are shown for clarity. Note that some of the compounds are present as a mixture of stereoisomers.

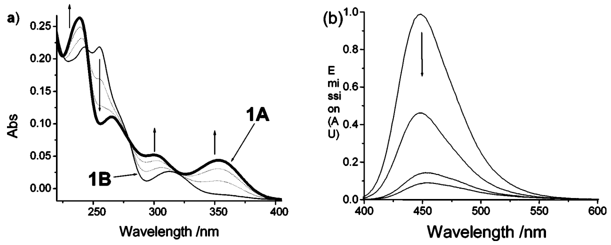


Figure 1. (a) UV/vis spectrum showing thermal reversion of photochemically generated **1B** to **1A**. (b) Changes in the fluorescence spectrum of **2A** ($\lambda_{exc} = 320$ nm) upon photochemical conversion to **2B**.

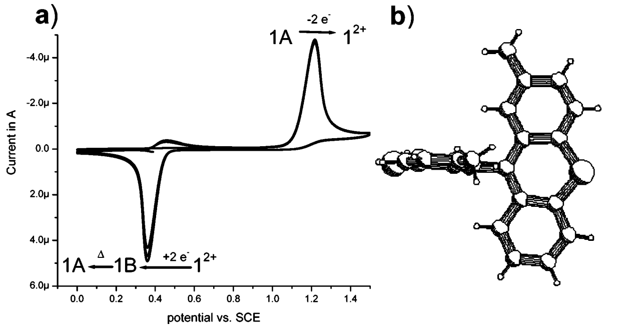


Figure 2. (a) Thin-layer cyclic voltammetry of **1A** (CH_3CN/0.1 M TBAP, 10 mV s^{-1}). (b) Ortep plot of $\mathbf{1}^{2+}$ (PF_6^- anions not shown).

The electrochromic behavior of **1A** and **2A** is characterized by an increase in visible absorption and the appearance of two intense absorptions at ~280 and 400 nm upon oxidation to the dication (Figure 3a). The spectra of **1A** and **2A** are very similar to that

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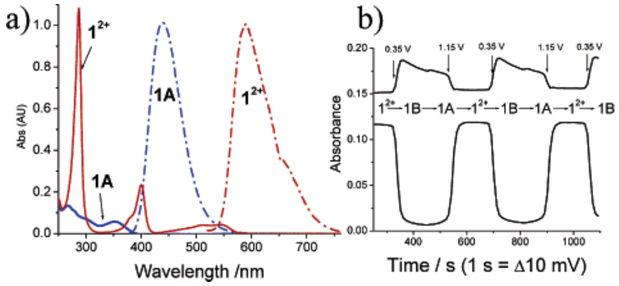

Figure 3. (a) UV/vis absorption and emission spectra of **1A** (blue) and **1**$^{2+}$ (red) in CH_3CN/0.1M KPF_6. (b) Changes in absorption intensity of **1**$^{2+}$ at 254 (blue) and 400 nm (black) upon cycling between 1.4 and −0.2 V vs SCE, at 0.01 V s^{-1}.

observed for the thiaxanthylidium cation.[12] Oxidation of **1A** to **1**$^{2+}$ results in a dramatic change in luminescence (λ_{exc} = 365 nm), with the blue (λ_{max} = 440 nm) fluorescence of **1A** being replaced by the red (λ_{max} = 600 nm) fluorescence of **1**$^{2+}$ (Figures 3a and S8). This remarkable behavior is in marked contrast to structurally related molecules,[5d,15] where a change in redox state results in a change in fluorescence intensity only.

At 293 K under thin layer conditions, rapid electrochemical reduction of **1**$^{2+}$ to the neutral state is observed (by UV/vis spectroscopy). The reformation of the spectrum of **1A** is, however, a thermally activated process, and hence the reduction does not lead directly to the reformation of **1A** (Figures 3b, S11). At 263 K, reduction of **1**$^{2+}$ results, initially, in the formation of meta-stable **1B** (Figures S1, S5, and S11).[16] Oxidation of **1B** ($E_{p,a}$ 1.10 V, ~110 mV less anodic than **1A**) leads to the quantitative reformation of **1**$^{2+}$ (Figure S9). As with **1B**, generated photochemically, quantitative conversion to **1A** occurs upon warming to ambient temperatures. The observation that both irradiation of **1A** and electrochemical reduction of **1**$^{2+}$ leads to the same metastable species **1B** (confirmed by ^{1}H NMR spectroscopy, Figure S1) provides compelling evidence that **1B** is indeed in the syn-folded conformational state.[8b] Furthermore, in contrast to the blue fluorescence observed for the anti-folded **1A**, the syn-folded **1B** is nonfluorescent (Figure 1b); thus, on/off switching of fluorescence is achieved both photo- and electrochemically. A similar pattern of fully reversible (three cycles are shown for **1A** in Figure 3b) changes are observed for **2A**.

Photochemically and thermally driven changes in molecular structure, either through intramolecular isomerizations or changes in conformation,[17] allow for external control of optical properties of molecular materials. We demonstrate that **1A** and **2A** behave as three-state luminescent switches, where reversible interconversion between blue, red, and nonfluorescent states can be addressed individually through irradiation, redox changes, and control of temperature. The ability to switch luminescence on and off with external control and also to change luminescence energy holds considerable potential toward application in future responsive molecular based photonic devices.

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Supporting Information Available: Experimental details, preparation of **1**$^{2+}$, UV/vis and emission spectra, and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Thermal reversion from the syn form was reported for **3A**;[8c] however, in addition to this process, photochemically driven *cis* → *trans* isomerization (see Figures S3 and S4) is observed for **1A** and **2A** also.

(14) Although, the 90° twist around the axial C−C bond in **3**$^{2+}$ has been proposed[12] on the basis of UV/vis spectroscopy and cyclic voltammetry, in the present study, the isolation of the dication **1**$^{2+}$ via preparative anodic oxidation unequivocally demonstrates by X-ray analysis that the dication adopts a perpendicular structure (Figure 2).

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(16) The reduction of **1**$^{2+}$ proceeds via a transient twisted state[8d] (Scheme 1), the reversion of which to the syn-folded form (**1B**) is fast on the electrochemical time scale >200 K.

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