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A novel redox switch for fluorescence: drastic UV–vis and fluorescence spectral changes upon electrolysis of a hexaphenylethane derivative of 10,10′-dimethylbiacridan

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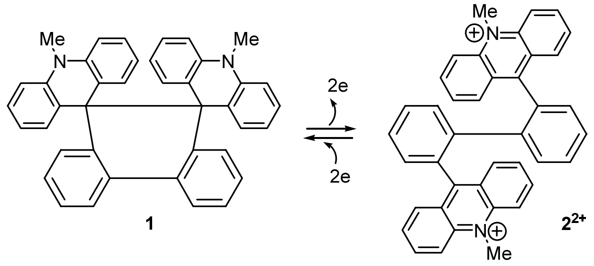
Abstract—The newly prepared title donor **1** has a very long C–C bond [1.635(2) Å], which was readily cleaved upon oxidation to give dication $\mathbf{2}^{2+}$ containing two 10-methylacridinium chromophores. Colorless donor **1** (E^{ox} +0.18 V) is non-fluorescent whereas orange dication $\mathbf{2}^{2+}$ (E^{red} −0.27 V) emits strong green fluorescence, so that, this pair can be considered as a novel redox switch for fluorescence with high electrochemical bistability.

Molecular switches for fluorescence have been attracting considerable recent attention,[1] especially because of high sensitivity of luminescence signals.[2] Redox-dependency of fluorescence has been mainly studied by using metal-centered redox couples,[3] where the communication between the redox-active site (transition metal complex) and the light-emitting-fragment (fluorophore) plays an important role for the ON/OFF mechanism. Pure organic switches without metal ions are rare although an excellent example was reported very recently by using tetrathiafulvalene (TTF) as a redox center and free-base porphyrin as a fluorophore.[4] In the course of our continuing efforts to develop novel molecular switches based on the 'dynamic redox' systems,[5] we have succeeded in constructing a novel fluorescence switch that works under the different mechanism from those of metal-centered complexes (Scheme 1). Here, the 10,10′-dimethylbiacridan unit in **1** and 10-methylacridinium units in $\mathbf{2}^{2+}$ act as redox-active sites.[6] At the same time, the acridinium units in $\mathbf{2}^{2+}$ emit very strong fluorescence.[7] Thus, the redox reaction directly modifies the light-emitting properties of the chromophores in this system. Noteworthy feature is very high electrochemical bistability endowed by reversible C–C bond formation/breaking during the redox reaction.[5] Furthermore, not only fluorescence but also UV–vis spectra change drastically during interconversion between **1** and $\mathbf{2}^{2+}$. So that, this pair can be also served as a new type of multi-output response systems, where one external input is transduced into two spectral outputs.

Biphenyl-2,2′-diylbis(magnesium iodide) was generated in situ from 2,2′-diiodobiphenyl[8] and Mg. Reaction of this Grignard reagent with 10-methylacridinium triflate[9] in THF gave colorless needles of leuco dye $\text{H}_2\mathbf{2}$[10] in 25% yield based on diiodobiphenyl (Scheme 2). When 2,2′-dilithiobiphenyl was used instead of the Grignard reagent, a considerable amount of 10,10′-dimethyl-9,9′-biacridan **3**[11] was formed, probably because electron transfer[6] from aryllithium to acridinium is much easier than in the case of Grignard reagent. Oxidation of leuco dye $\text{H}_2\mathbf{2}$ with 4 equiv. of NOBF_4 gave an orange powder of stable salt of biphenylic dication $\mathbf{2}^{2+}(\text{BF}_4^-)_2$[10]



Scheme 1.

Keywords: redox switch; fluorescence; electrochromism; electron donor; biacridan; dication; acridinium.

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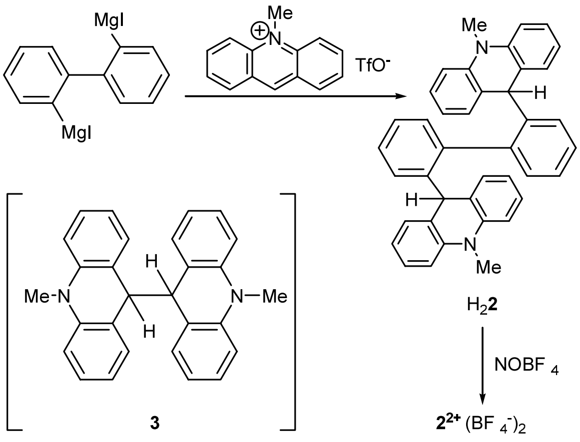

Scheme 2.

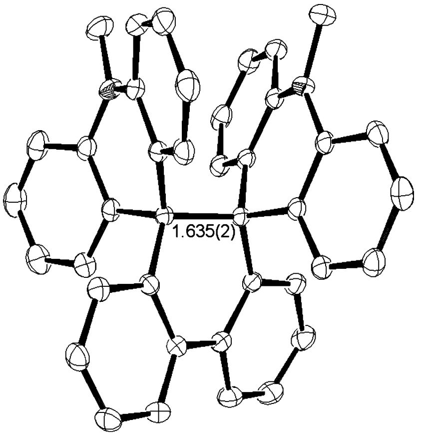

Figure 1. Molecular structure of **1** determined by X-ray analysis at 153 K.

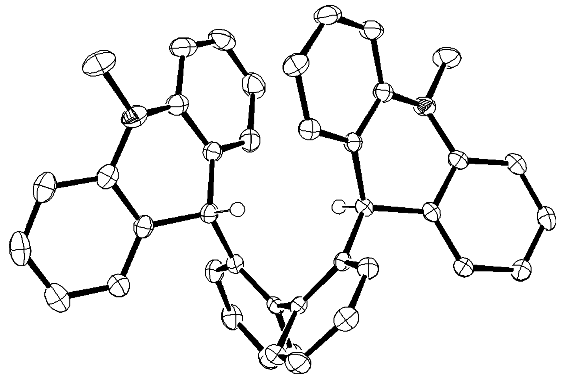

Figure 2. Molecular structure of H_2**2** determined by X-ray analysis at 153 K.

in 98% yield. Upon reduction of this salt with Zn powder in THF–Et_3N, the hexaphenylethane derivative **1**[10] with the 10,10′-dimethylbiacridan skeleton was isolated as colorless crystals in 60% yield.

According to the X-ray analysis at −120°C,[12] the newly formed central C_{sp3}–C_{sp3} bond in **1** [1.635(2) Å; standard, 1.54 Å] is elongated due to the steric interaction[13] between bulky acridan units (Fig. 1). This bond is much longer than the reported values for **3** with the *anti*-conformation [1.580–1.583 (5) Å],[14] so that, the 'front' strain[15] inherited from the hexaphenylethane skeleton increases the steric interaction in **1**. The dihedral angle of the biphenyl moiety in **1** is only 19.5(1)°, which is much smaller than the value in H_2**2**[12] [69.2(1)°] with a deeply twisted conformation (Fig. 2). On the other hand, butterfly-shaped deformation of the spiro-acridan units in **1** [dihedral angles between two benzene nuclei of acridan: 28.6(1) and 21.1(1)°] is not due to the steric effects because the acridan units in H_2**2** also adopt similar folded geometry [31.9(1) and 31.5(1)°].

According to the voltammetric analysis, the oxidation potential of **1** (E^{ox}, +0.18 V versus SCE in MeCN, scan rate 100 mV s^{-1}) is less positive than that of TTF (+0.31 V), showing the stronger electron-donating properties of **1** than TTF. The oxidation wave is irreversible with the return peak being shifted in the far cathodic region, which was assigned to the reduction process of $\mathbf{2}^{2+}$ (E^{red}, −0.27 V). These results suggest that the elongated C–C bond of **1** undergoes facile mesolysis[16] upon oxidation. In fact, dication salt $\mathbf{2}^{2+}$ was regenerated upon treatment of **1** with 2 equiv. of $(p\text{-BrC}_6H_4)_3N^{+\cdot}SbCl_6^-$ and isolated as $SbCl_6^-$ salt in 85% yield. Large separation of redox peaks in **1** and $\mathbf{2}^{2+}$ (ΔE, 0.51 V) indicates high electrochemical bistability for this redox pair, which is hardly attained by usual organic redox systems,[5] but essential to construct promising molecular switches or response systems.

Neutral donor **1** is colorless [λ_{max} (log ε) 282 (4.27), 305 (3.99), 323sh (3.85), 366sh (3.14) nm in MeCN] and almost non-fluorescent.[17] In contrast, dication $\mathbf{2}^{2+}$ shows absorption in the visible region [265 (4.84), 354sh (4.09), 369 (4.23), 438 (3.83), 464sh (3.66)] and strong green fluorescence [λ_{em} 519 nm in MeCN].[18] By comparisons with 10-methylacridinium (λ_{em} 489 nm; $\Phi = 0.87$),[7] fluorescence quantum yield of $\mathbf{2}^{2+}$ was estimated to be 0.3–0.4. Although this value is reduced to about one-third of the reference cation, it is much higher than 10-methyl-9-phenylacridinium ($\Phi = 0.07$).[19] It is also high enough for fluorescence signaling as follows.

The response of the present redox pair against the electrochemical input was first examined by UV–vis spectroscopy (Fig. 3). The oxidation of **1** to $\mathbf{2}^{2+}$ caused a vivid color change from colorless to orange. The isosbestic points observed in the spectra are indicative of a clean transformation from **1** to $\mathbf{2}^{2+}$ as well as of the negligible steady-state concentration of the intermediate cation radical. The latter comes from the dynamic redox properties of the present pair: the facile bond fission of $\mathbf{1}^{+\bullet}$ to $\mathbf{2}^{+\bullet}$ and much easier oxidation of $\mathbf{2}^{+\bullet}$ to $\mathbf{2}^{2+}$ than **1** to $\mathbf{1}^{+\bullet}$.[20] When the electrochemical transformation was followed by fluorescence spectrum, rapid and steady increase was observed as shown in Figure 4. By using a very diluted solution of 7×10^{-6} mol dm^{-3}, intense green light emission could be still observed upon electrolysis. This is a new example of successful execution for redox dependency of fluorescence, thus demonstrating that not only metal complexes or

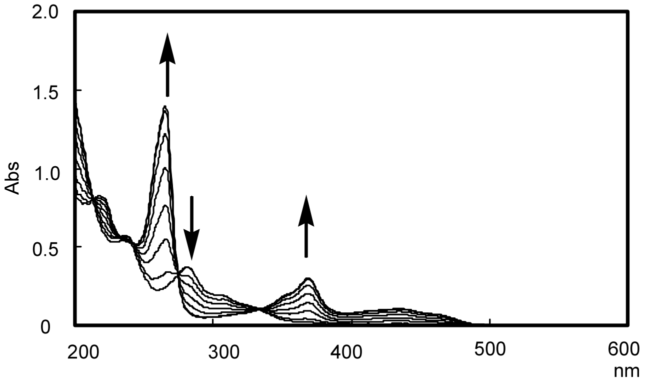

Figure 3. Changes in the UV–vis spectrum of **1** (2.15×10^{-5} mol dm^{-3} in MeCN) upon constant-current electrochemical oxidation (30 μA at 2 min interval) to $\mathbf{2}^{2+}$.

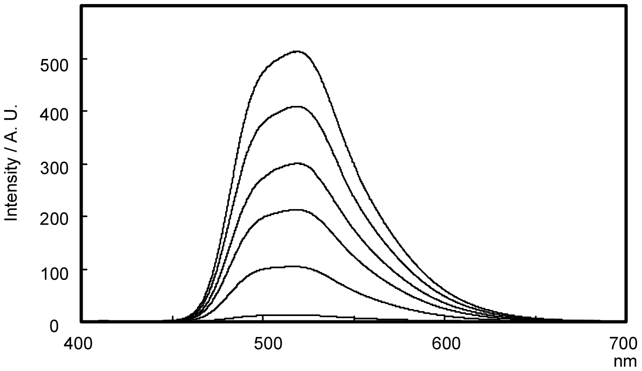

Figure 4. Changes in the fluorescence spectrum of **1** (7.43×10^{-6} mol dm^{-3} in MeCN) upon constant-current electrochemical oxidation (25 μA at 2 min interval) to $\mathbf{2}^{2+}$.

polymers[21] but also pure-organic materials with a low molecular weight can be considered as promising candidates for fluorescence switches.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 212377–212378. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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10. ^{1}H NMR spectrum for **1** ($CDCl_3$): δ 8.12 (dd, 2H, $J=7.5$, 1.0 Hz), 7.38 (ddd, 2H, $J=7.5$, 7.5, 1.0 Hz), 7.13 (ddd, 2H, $J=7.5$, 7.5, 1.0 Hz), 7.02 (dd, 2H, $J=7.5$, 1.0 Hz), 7.00–6.94 (m, 4H), 6.94 (d, 4H, $J=8.0$ Hz), 6.38–6.34 (m, 8H), 2.74 (s, 6H). For $\mathbf{2}^{2+}$ $(BF_4^-)_2$ (CD_3CN): δ 8.35–8.00 (br, 12H), 8.05 (dd, 2H, $J=7.5$, 1.5 Hz), 7.74 (ddd, 2H, $J=7.5$, 7.5 1.5 Hz), 7.50–7.40 (br. 4H), 7.47 (ddd, 2H, $J=7.5$, 7.5, 1.5 Hz), 6.93 (dd, 2H, $J=7.5$, 1.5 Hz), 4.59 (s, 6H). For H_2**2** ($CDCl_3$): δ/ppm: 7.36–7.24 (m, 8H), 7.17 (br. dd, 2H, $J=7.5$, 7.5 Hz), 7.00 (br. dd, 2H, $J=7.5$, 7.5 Hz), 6.87 (br. d, 2H, $J=7.5$ Hz), 6.84 (ddd, 2H, $J=7.5$, 7.5, 1.0 Hz), 6.77 (br. d, 2H, $J=7.5$ Hz), 6.73 (br. d, 2H, $J=7.5$ Hz), 6.51 (br. d, 2H, $J=7.5$ Hz), 6.37 (ddd, 2H, $J=7.5$, 7.5, 1.0 Hz), 5.06 (s, 2H), 3.36 (s, 6H).
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12. Crystal data of **1**: $C_{40}H_{30}N_2$, M 538.69, monoclinic, $P21/n$, $a=13.094(3)$, $b=13.376(3)$, $c=15.540(4)$ Å, $\beta=92.231(3)°$, $U=2719(1)$ Å^3, D_{calcd} $(Z=4)=1.316$ g cm^{-1}, $\mu=0.76$ cm^{-1}, $T=153$ K. The final R value is 0.046 for 4832 independent reflections with $I>3\sigma I$ and 379 parameters. Crystal data of H_2**2**: $C_{40}H_{32}N_2$, M 540.71, monoclinic, $P21/c$, $a=16.722(4)$, $b=7.489(2)$, $c=22.927(6)$ Å, $\beta=95.787(4)°$, $U=2856(1)$ Å^3, D_{calcd} $(Z=4)=1.257$ g cm^{-1}, $\mu=0.73$ cm^{-1}, $T=153$ K. The final R value is 0.041 for 4995 independent reflections with $I>3\sigma I$ and 379 parameters.
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17. Non-fluorescent nature of **1** is intriguing by considering the violet emission observed for **3** with the similar chromophores. This can be possibly accounted for by rapid ring-flip of the central six-membered ring in **1** that may facilitate non-radiative decay of ^{1}**1***.
18. The red-shifted fluorescence in $\mathbf{2}^{2+}$ may be due to aryl-substitution at the 9-position since 10-methyl-9-phenylacridinium (λ_{em} 510 nm) exhibits the similar red shift (Ref. 19).
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