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Dynamic redox systems based on bis(spiroxanthene)-type donors with a polycyclic aromatic hydrocarbon: preparation, X-ray structures, and electrochromic response with fluorescence change

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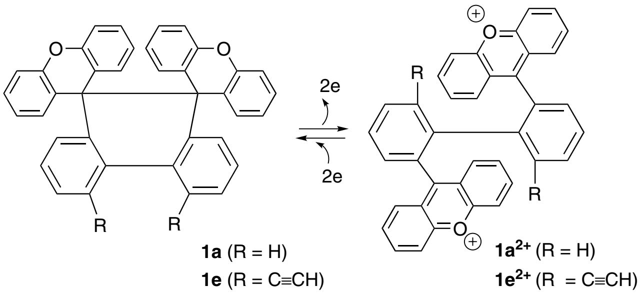
Abstract—The long C–C bonds (1.614(2)–1.630(2) Å) in newly prepared title donors **2**–**6** are cleaved upon two-electron oxidation to afford the bond-dissociated dicationic dyes $\mathbf{2}^{2+}$–$\mathbf{6}^{2+}$, whose electron affinities are stronger than the corresponding biphenyl-2,2′-diyl dications $\mathbf{1}^{2+}$ due to the spatial proximity of two xanthenylium units. Not only UV–vis but also fluorescence spectra changed drastically upon electrolysis since only colorless neutral donors are fluorescent.

Recently much attention has been focused on the organic redox systems in the field of materials chemistry. Electrochromic systems[1] whose optical properties can be controlled electrochemically are attracting special attention for use as molecular memories or switches.[2] We previously found that the 9,9,10,10-tetraaryl-9,10-dihydrophenanthrene-type electron donors (e.g., **1a**) and the corresponding biphenyl-2,2′-diylbis(triarylmethane) dyes (e.g., $\mathbf{1a}^{2+}$) can constitute a unique class of electrochromic systems (Scheme 1),[3] which exhibit large shifts in redox potentials. Such shifts correspond to very high electrochemical bistability thanks to the reversible C–C bond making/breaking upon electron transfer ('dynamic redox properties').[4,5] Due to the rotational freedom around the biaryl axis, the dicationic species adopt quite different geometries from the neutral donors; however, it is still unclear if such a drastic change in geometry is essential to induce the observed high bistability.

With these in mind, we have designed here a series of polycyclic aromatic hydrocarbons (PAHs) **2**–**6** containing two spiroxanthene units as a novel class of electron donors. Upon two-electron oxidation of **2**–**6**, the corresponding dications would be formed by C–C bond fission as in the case of **1a**, but the two xanthenylium chromophores in $\mathbf{2}^{2+}$–$\mathbf{6}^{2+}$ would be forced to remain in a proximity due to the fused aromatic ring (Scheme 2). Beside the perturbation on the redox properties by their rigid nature, the PAH units in **2**–**6** play a role as fluorophores. Thus, the present molecules would function as the multi-output response system, by which the electrochemical input is transduced into two kinds of spectral outputs, that is, UV–vis and fluorescence spectra.[3d,6]



Scheme 1. Dynamic redox system based on bis(spiroxanthene)-type donor with a 9,10-dihydrophenanthrene skeleton.

4,5-Dibromo-9,10-dihydrophenanthrene derivative **1b** was chosen as a common starting material for **2**–**6** and

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Keywords: Redox system; Hexaphenylethane; Xanthene; Electron donor; Electrochromism; Fluorescence; Polycyclic aromatic hydrocarbon; Multi-output response system; Dye; Dication.

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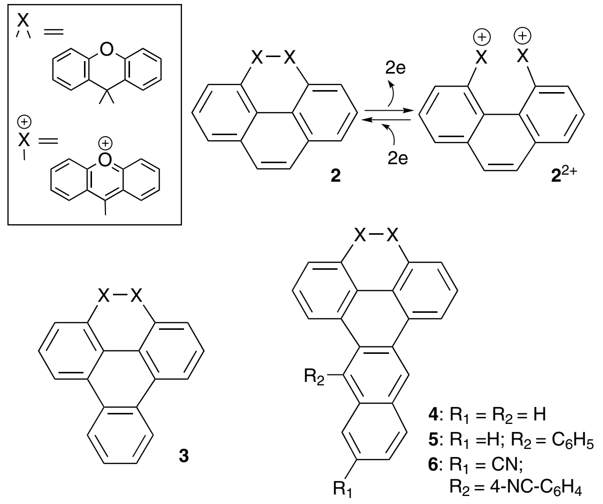
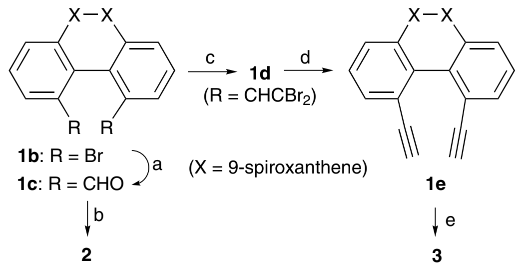
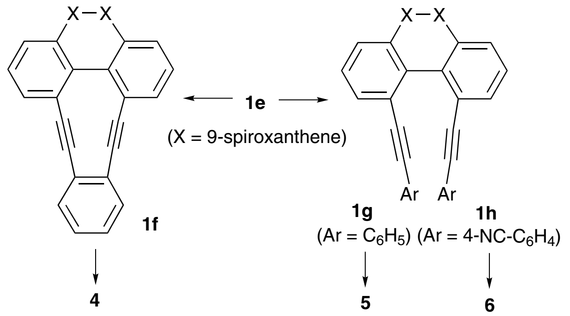


Scheme 2. Dynamic redox properties of dispiro-PAH donors **2**–**6**.



Scheme 3. Reagents and conditions: (a) BuLi, THF, then DMF, 57%; (b) $TiCl_4$–Zn, THF, 22%; (c) CBr_4, PPh_3, CH_2Cl_2, 79%; (d) BuLi, THF, 64%; (e) Ni(0), PPh_3, C_2H_2, THF, 53%.

derived from 2,2′,6,6′-tetrabromobiphenyl[7] according to the reported procedure.[3b] Dispiro-4,5-dihydropyrene **2**[8,9] was prepared by the intramolecular McMurry coupling of dialdehyde **1c**,[8] which was easily obtained from **1b**. Dispiro-4,5-dihydrobenzo[*e*]pyrene **3**[8] was obtained by Ni(0)-catalyzed [2+2+2] co-cyclization[10] of acetylene and diethynyl derivative **1e**,[8,11] which was derived from dialdehyde **1c** via **1d** by applying the Corey–Fuchs protocol (Scheme 3).

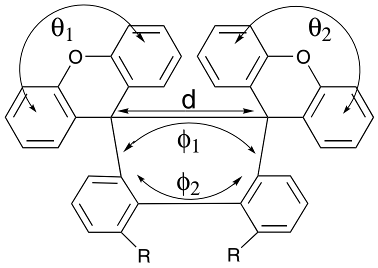


Scheme 4. Intramolecular cyclization of **1f**–**h** to PAHs **4**–**6**.

Inspired by the facile cyclization of 1,5-didehydro-3,4-benz[10]annulene to anthracene,[13] macrocycle **1f** was selected as the precursor of dispiro-4,5-dihydrodibenzo[*de*,*qr*]naphthacene **4** and generated by Sonogashira coupling of **1e** and 1,2-diiodobenzene (Pd(II), CuI, Et_3N–DMF). Spontaneous Masamune–Bergman aromatization[13,14] of **1f** under the reaction conditions afforded colorless crystals of **4** in 7% yield (Scheme 4). The low yield of **4** may be due to the inefficient macrocyclization of **1e** to the strained precursor **1f**. So, we turned our attention to the substituted derivatives **5** and **6**, which might be produced by the intramolecular cyclization[15] of the unstrained precursors, bis(arylethynyl) derivatives **1g** and **1h**. Sonogashira coupling (Pd(II), CuI, Et_3N–THF) of **1e** and iodobenzene afforded a mixture of **1g** and **5**. Although they were difficult to separate, **5** could be isolated in 49% yield after heat treatment since thermally labile **1g** was cleanly converted to **5** ($9.4 \times 10^{-6}\,s^{-1}$ in $CDCl_3$ at 24 °C in the dark). Similarly, dinitrile **6** was obtained in 18% yield starting from **1e** and 4-bromobenzonitrile.

After many efforts, X-ray structural analyses on all the members of PAHs studied here (**2**–**6**) could be accomplished to allow the detailed discussion on their precise

Table 1. Listing of structural data in **1e**,**g**, and **2**–**6** determined by X-ray analyses



Compound	d/Å	ϕ_1/°	ϕ_2/°	θ_1/°	θ_2/°
1e (R = C≡CH)	1.643(3)	49.0(2)	33.3(3)	20.1(1)	21.0(1)
1g (R = C≡CPh)	1.645(6)	51.3(4)	32.6(6)	21.0(2)	27.0(2)
2 (R, R = C_2H_2)	1.625(2)	43.2(1)	8.3(2)	17.6(1)	26.4(1)
3 (R, R = C_6H_4)	1.630(2)	49.7(2)	12.1(2)	14.1(1)	16.1(1)
4 (R, R = $C_{10}H_6$)	1.626(3)	45.4(3)	9.3(4)	18.3(1)	19.1(1)
5 (R, R = $C_{16}H_{10}$)	1.614(2)	41.2(2)	10.8(2)	20.1(1)	22.6(1)
6 (R, R = $C_{18}H_8N_2$)	1.614(6)	48.2(4)	15.0(5)	15.5(2)	22.6(2)

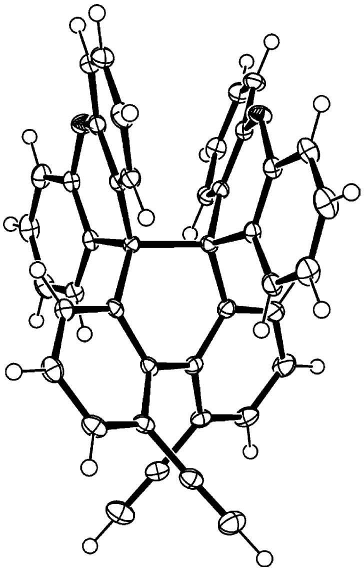


Figure 1. Molecular structure of dispiro-4,5-diethynyl-9,10-dihydrophenanthrene **1e** determined by X-ray analysis at −120 °C.

geometries (Table 1, Figs. 1, 2, and Figs. S1–S5).[16] Crystallographic analyses on 4,5-diethynyl (**1e**) and 4,5-bis(phenylethynyl) (**1g**) substituted 9,10-dihydrophenanthrenes were also conducted for comparisons. Butterfly-shaped folding of spiroxanthene units was observed as one of the common features in seven species with the dihedral angles of θ_1 and θ_2 in the range of 14.1°–27.0°. The elongation of the hexaarylated C–C bond (*d*) is another common feature. Although the long C–C bond is popular in hexaphenylethanes,[3,4,17] the values over 1.6 Å are far beyond the standard (1.54 Å). Such expansion can be accounted for by steric repulsion[18] among bulky aromatic units rather than by any orbital interactions.

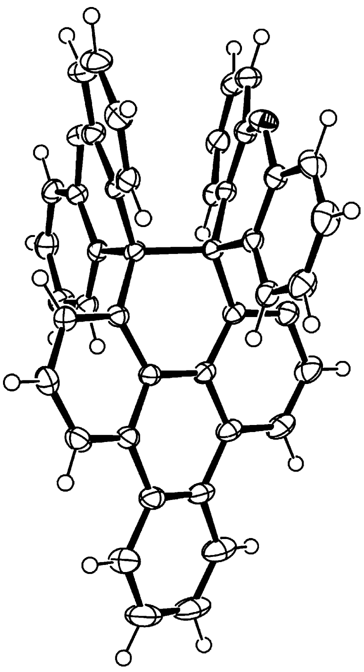


Figure 2. Molecular structure of dispiro-4,5-dihydrobenzo[*e*]pyrene **3** determined by X-ray analysis at −120 °C.

As shown by the large torsion angles of ϕ_1 and ϕ_2, the six-membered ring containing the long C–C bond adopts half-chair conformation in **1e**,**g**, whereas that in **2**–**6** is much flattened (ϕ_2: 8.3°–15.0°) due to the fused PAH unit (Figs. 1 and 2). The marginally shorter bond length (*d*) in **2**–**6** than in **1e**,**g** may be related to such a flattened geometry of this ring, which makes the two spiroxanthene units come closer. Irrespective of the degree of elongation, these weakened bonds of newly prepared donors are proven to be cleaved upon electron transfer.

Redox properties as well as the electrochemical response were first investigated on **1e** with ethynyl substituents at the bay region, which can serve as a nonannelated reference compounds to **2**–**6**. Voltammetric analyses showed that the irreversible oxidation potential (E^{ox}/V vs SCE in MeCN) of diethynyl derivative **1e** (+1.01 V) is close to that of **1a** (+1.02 V) without bay-region substituents. As commonly observed in the dynamic redox systems, the corresponding reduction peak appeared in the far cathodic region, which was assigned to the reduction potential (E^{red}) of the bond-dissociated dication $\mathbf{1e}^{2+}$ (+0.35 V). This value is rather close to E^{red} of 9-phenylxanthenylium (−0.03 V) measured under the same conditions. Upon treatment of **1e** with 2 equiv of $Ar_3N^{+\bullet}SbCl_6^-$ (Ar = 4-BrC$_6$H$_4$), dication salt $\mathbf{1e}^{2+}(SbCl_6^-)_2$ was isolated as an orange powder in 91% yield. This salt regenerated the neutral donor **1e** in quantitative yield by reducing with Zn dust. The high-yield interconversion between **1e** and $\mathbf{1e}^{2+}$ made them possible to function as an electrochromic system (Fig. S6), and the presence of the several isosbestic points indicates the negligible steady-state concentration of the intermediary cation radical $\mathbf{1e}^{+}$ during the interconversion.

The cyclic voltammogram of dihydropyrene **2** (E^{ox} = + 1.10 V, Fig. S7) exhibits the similar irreversible oxidation peak at the potential close to **1e**, suggesting that the long C–C bond is also cleaved in this case upon electron transfer. In fact, phenanthrene-4,5-diylbis(9-xanthenylium) $\mathbf{2}^{2+}$ could be generated upon treatment with $Ar_3N^{+\bullet}SbCl_6^-$ (2 equiv) and isolated as $SbCl_6^-$ salt in quantitative yield. According to the X-ray analysis of this salt (Fig. 3), two xanthenylium units are arranged nearly in paralell (dihedral angle: 5.4°) with the interplanar distance of 3.18 Å. The separation between the two C$_9$ of xanthenylium units (3.06 Å) is one of the smallest values ever reported for $C^+\cdots C^+$ contacts.[19] Close proximity of two xanthenylium units in $\mathbf{2}^{2+}$ must be the main reason for the enhanced electron affinity of $\mathbf{2}^{2+}$ (E^{red} = +0.63 V) compared with $\mathbf{1e}^{2+}$. This salt regenerated **2** in 86% yield upon reduction with Zn.

Other donors **3**–**6** exhibit similar voltammograms to **2** with the separation of redox peaks about ca. 0.5 V.[20,21] Although these values are smaller than those of **1a**,**e** (ca. 0.7 V), the observed potential difference corresponds to pretty high electrochemical bistability. These results clearly show that bistability of dynamic redox systems

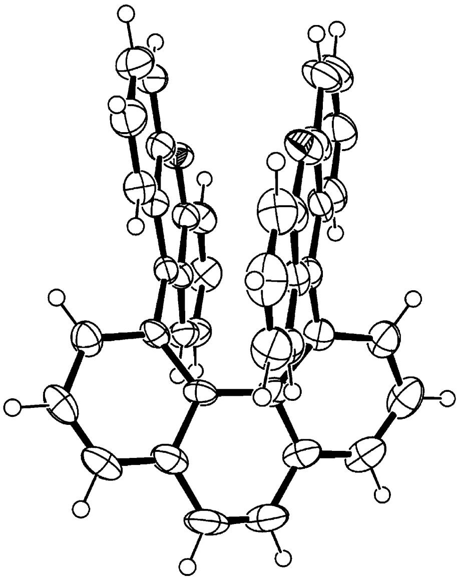


Figure 3. Molecular structure of phenanthrene-4,5-diylbis(9-xanthenylium) $\mathbf{2}^{2+}$ determined by X-ray analysis of $SbCl_6^-$ salt at room temperature.

is induced by reversible C–C bond making/breaking even when they do not undergo drastic geometrical change during the interconversion. It is noteworthy that the present PAH-type donors undergo stepwise electron transfer upon electrolysis. For example, the spectroelectrogram exhibits two-stage continuous changes upon oxidation of **5** (Fig. 4) although only one oxidation wave was observed in the voltammogram. The first stage is assigned to conversion of **5** to $\mathbf{5}^{+\bullet}$, and the intermediary $\mathbf{5}^{+\bullet}$ was transformed into $\mathbf{5}^{2+}$ in the second stage. The final spectrum is identical to that of isolated salt of $\mathbf{5}^{2+}$.[21] These results can be accounted for by the increased Coulombic interaction between two xanthenylium units in the dicationic state, thus making the second oxidation process more difficult than in other dynamic redox systems whose dications adopt quite different geometries from those of neutral donors.

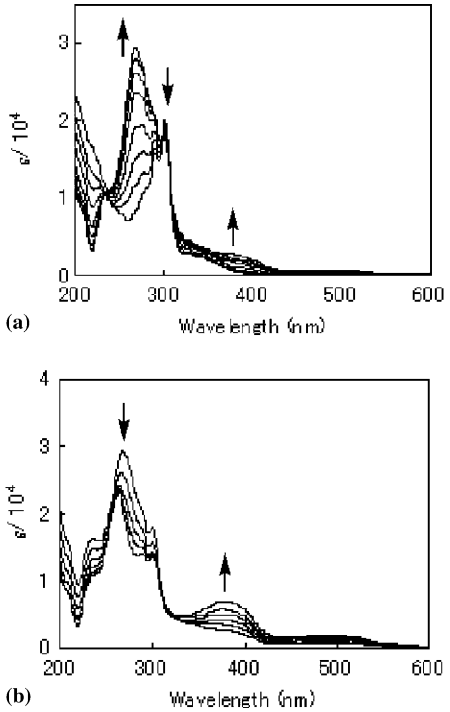


Figure 4. Changes in UV–vis spectra of **5** (3.5 mL, 3.01×10^{-5} mol dm^{-3}) upon constant-current electrochemical oxidation (26 μA): (a) first stage (0–35 min, every 5 min); (b) second stage (40–90 min, every 10 min).

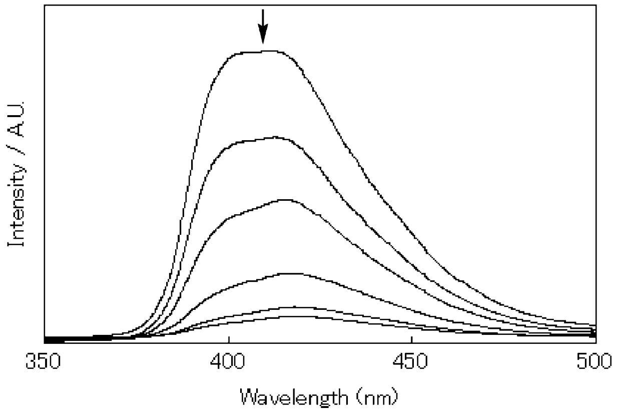


Figure 5. Changes in fluorescence spectra of **5** (3.5 mL, 3.01×10^{-5} mol dm^{-3}) upon constant-current electrochemical oxidation (26 μA, every 10 min).

Another interesting property of the present donors is emission of fluorescence. Although the fluorescence quantum yields are not high (Φ_f: **2**, 0.01; **3**, 0.01; **4**, 0.07; **5**, 0.02; **6**, 0.004),[22] drastic change in fluorescence spectra was observed upon electrolysis as exemplified by Figure 5 since the dications are nearly nonfluorescent. It is concluded that the present donors can serve as a new class of multi-output response systems by which the electrochemical input is transduced into UV–vis and fluorescence spectra.[3d,6b]

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.09.080. 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 244306–244312, and 245423. 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]. ORTEP drawings of **1g** (Fig. S1), **2** (Fig. S2), **4** (Fig. S3), **5** (Fig. S4), and **6** (Fig. S5) as well as spectroelectrogram of **1e** (Fig. S6) and cyclic voltammogram of **2** (Fig. S7) were submitted as electronic supplementary data. Physical data and crystal data are also given.

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20. The values of E^{ox} are +1.10, +1.09, +1.11, and +1.15 V, respectively, for **3**–**6**. The corresponding reduction peaks are appeared in the far cathodic region, from which E^{red} of $\mathbf{3}^{2+}$–$\mathbf{6}^{2+}$ were estimated as +0.63, +0.66, +0.57, and +0.60 V, respectively. All the values shown in this paper were measured under the same conditions (0.1 mol dm^{-3} Et$_4$NClO$_4$ in MeCN, scan rate 100 mV s^{-1}, Pt electrode) and are reported in V versus SCE.
21. Upon treatment of **3**–**6** with 2 equiv of Ar$_3$N$^+$·SbCl$_6^-$, dication salts $\mathbf{3}^{2+}$ (SbCl$_6^-$)$_2$–$\mathbf{6}^{2+}$ (SbCl$_6^-$)$_2$ were isolated in 93%, 96%, 94%, and 91% yield, respectively. These salts regenerated neutral donors **3**–**6** in 94%, 94%, 87%, and 85% yield, respectively, by reducing with Zn powder.
22. Fluorescence quantum yields were determined in MeCN by using 9,10-diphenylanthracene as a standard ($\Phi_{\mathrm{f}} = 1.00$, Ref. 23). The smaller Φ_{f} value of **6** than that in **5** may be related to the quenching by intramolecular charge transfer from the spiroxanthene unit to the cyano-substituted PAH unit.
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