Biphenyl-type electron acceptors exhibiting dynamic redox properties: a novel electrochromic system with 'write protect' option

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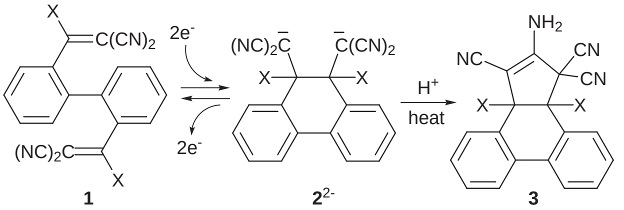
A novel redox pair undergoing reversible C–C bond making/breaking has been constructed based on a bis(dicyanovinyl)biphenyl derivative and a dianion with the dihydrophenanthrene skeleton; further cyclization of the latter to an enaminonitrile endows the 'write protect' option to its electrochromic response.

Recently much attention has been focused on molecules whose geometry and properties can be controlled by the external stimuli.[1] From this point of view redox systems undergoing reversible C–C bond making/breaking upon electron transfer (ET) are interesting[2] and might be applicable to the construction of electrochemical switches or molecular devices[3] based on their optical response and bistability. We have designed the novel redox pair shown in Scheme 1 which has the following interesting features: (*i*) 2,2′-bis(dicyanovinyl)biphenyls **1** are expected to undergo facile ring closure to dihydrophenanthrene-type dianions **2**$^{2-}$ upon two-electron reduction; (*ii*) the resulting dianions are sterically congested molecules and will regenerate the starting material **1** by C–C bond cleavage upon oxidation; (*iii*) in the case of *p*-dimethylaminophenyl derivatives **1a** and **2a**$^{2-}$, a sharp change in color is expected during ET because only the former shows strong absorption in the visible region due to the *p*-(dicyanovinyl)aniline skeleton; (*iv*) besides the reversible interconversion between **1** and **2**$^{2-}$, further cyclization to **3** induced by protonation of **2**$^{2-}$ endows the system with the 'write protect' option in its response (Scheme 2). Here, we report the preparation and unique redox properties of the title acceptors and their reduction products.



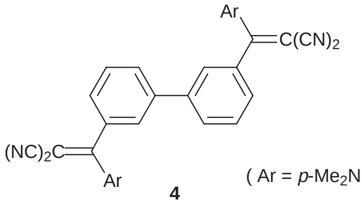
(**a**: X = *p*-Me$_2$NC$_6$H$_4$; **b**: X = H)

Scheme 1

Scheme 2

Condensation reaction of 2,2′-diformylbiphenyl with malononitrile in the presence of TiCl$_4$ and pyridine[4] gave **1b**‡ (mp 224–226 °C) as colorless crystals in 54% yield. Dye **1a**‡ (mp 333–334 °C) was prepared from 2,2′-diiodobiphenyl *via* its 2,2′-dilithio derivative[5] by successive reactions with *p*-dimethylaminobenzonitrile and malononitrile,[6] and obtained as orange plates [λ_{max} (MeCN): 455 nm (log ε 4.24), 279 (4.02)] in 7% yield.

Voltammetric analyses have revealed quite different behavior of **1a** compared with the *m,m*-isomer **4**.§ The redox behaviour of **4** is nearly identical to that of reference compound **5**,[6] which undergoes reversible one-electron reduction to **5**$^{\cdot-}$ (E^{red} = −1.28 V) and oxidation to **5**$^{\cdot+}$ (E^{ox} = +1.08 V). By contrast the reduction process of **1a** (E^{red} = −1.29 V) is irreversible in the sense that the corresponding anodic peak is absent in its cyclic voltammogram (Fig. 1). Instead, a new peak appeared in the anodic region (+0.04 V). This was assigned to the oxidation peak of **2a**$^{2-}$ by independent measurement, and a new cathodic peak corresponding to the reduction of **1a** was observed after the oxidation of **2a**$^{2-}$. Such hysteresis in redox waves is characteristic of 'dynamic' redox systems that undergo reversible and drastic structural change upon ET.[1b,2] Electrochromic behaviour was shown by spectrophotometric monitoring of the electrochemical reduction of **1a**, and the isosbestic point at 380 nm is indicative of the quantitative conversion to **2a**$^{2-}$ (Fig. 2).



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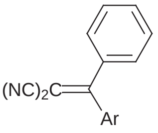
(Ar = *p*-Me$_2$NC$_6$H$_4$)



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The stereospecific nature of the ring closure was evidenced by product analysis on the mixture obtained by the reaction of **1a** with SmI$_2$ then with acid.¶ Thus, *trans*-H$_2$**2a**‡ (mp 221–223 °C) was formed free from the *cis*-isomer and isolated in 64% yield as the sole product. Only by heating in EtOH, does this material isomerize quantitatively to *trans*-**3a**‡ (mp 198–200 °C) by Thorpe condensation[8] which no longer regenerates **1a** upon oxidation, suggesting that 'write protection' can be performed very easily.

Thorpe condensation occurred more rapidly in the absence of dimethylaminophenyl groups. Thus, the enaminonitrile *trans*-**3b**‡ (mp 276–278 °C; $^3J_{HH}$ 13.2 Hz) was obtained as the major

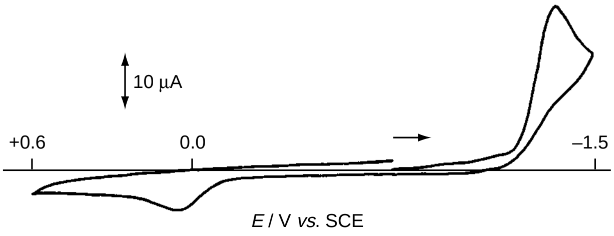

Fig. 1 Cyclic voltammogram of dye **1a** in MeCN (*E*/V *vs.* standard calomel electrode, 0.1 mol dm^{-3} NEt$_4$ClO$_4$, Pt electrode, scan rate 500 mV s^{-1}). The oxidation peak at +0.04 V is absent when the voltammogram was first scanned anodically. Another oxidation peak at +1.07 V was also observed but not shown, which corresponds to the oxidation of dimethylaniline moieties as in **4** and **5**.

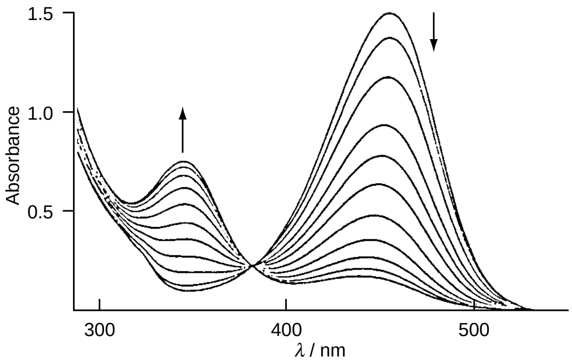

Fig. 2 Changes in UV–VIS spectrum of **1a** (3 ml soln., 7.34 × 10^{-5} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} NEt_4ClO_4) upon electrochemical reduction (480 μA) at 1 min intervals

product when **1b** [E^{red} = −0.87 V (irrev.)] was reduced with SmI_2. Although *trans*-H_2**2b**‡ (decomp. 250–270 °C) could be isolated as a primary product, the ratio of *trans*-H_2**2b** to *trans*-**3b** varied run-by-run depending on the work-up conditions, and in one case *trans*-**3b** free from *trans*-H_2**2b** was obtained in 83% yield. Careful examination of the mixture showed that *cis*-**3b**‡ (mp 281–282 °C; $^3J_{HH}$ 8.3 Hz) was also formed as a minor component [(*trans*-H_2**2b** + *trans*-**3b**): *cis*-**3b** = 10 : 1], which was separated and purified by reverse phase HPLC. These results indicate that the bulkiness of aryl groups in **1a** plays an important role in confining the stereochemical course of the reductive cyclization of **1**. At the same time, the aryl groups retard isomerization to **3**, thus preventing unintended ‘write protection’.

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Notes and References

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‡ All new compounds gave satisfactory analytical values.

§ Compound **4**‡ (mp 202–204 °C) was also formed in 0.5% yield when the dilithiobiphenyl was generated from biphenyl and Bu^nLi–TMEDA[7] and used for the preparation of **1a**. This result suggests tht the direct lithiation of biphenyl affords a small amount of 3,3′-dilithio derivative.

¶ Similar reduction of *m,m*-isomer **4** with SmI_2 did not induce cyclization but instead hydrogenation of two vinyl groups thus giving the tetrahydro derivative H_4**4**‡ (mp 110–112 °C).

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