

# Bispyrene based chiroptical molecular redox switch

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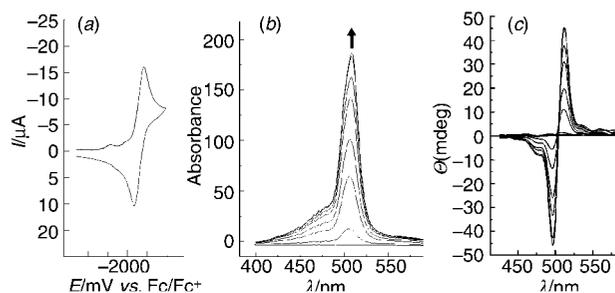
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Received (in Cambridge, UK) 14th September 1999, Accepted 28th October 1999

The chiral *trans*-cyclohexanediol bispyrene esters (**1R,2R**)-**1a** and (**1S,2S**)-**1b** are reversibly reduced to the corresponding bisradical anions **1a**<sup>2-</sup> and **1b**<sup>2-</sup> which show strong absorption bands at 510 nm exhibiting exciton-split circular dichroism (CD) with opposite signs, whereas the radical anions of the bisamides **2a** and **2b** failed to show split CD signals.

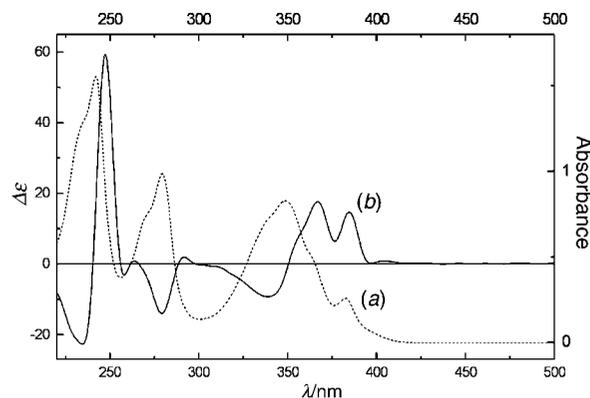
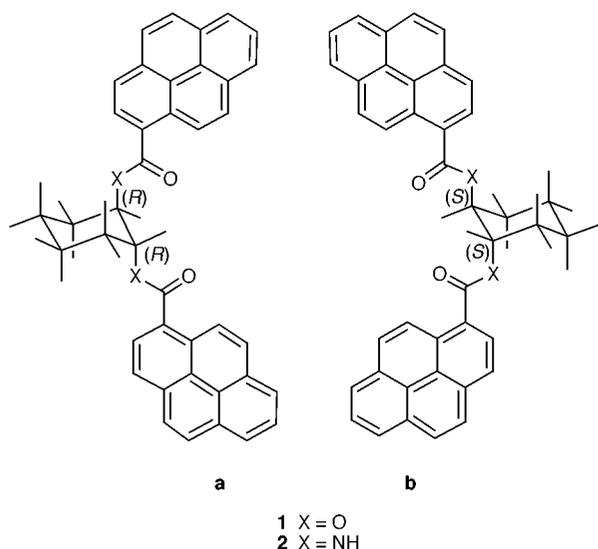
Molecular switches are intensively studied due to their potential applications in molecular devices and optical data storage systems.<sup>1</sup> In this context, much attention has been given to photochemically and electrochemically induced switching processes (photochromic and electrochromic compounds) which lead to significant optical spectra changes. Pyrene derivatives are one of the well-exploited probes for the design of fluorescent molecular switches due to their monomer–excimer emission characteristics.<sup>2</sup> Surprisingly, pyrene based chiroptical molecular redox switches have not received any attention. However, the use of chiroptical molecular switches based on photochromic chiral ethenes has been demonstrated recently by Feringa and co-workers.<sup>3</sup> Circular dichroism spectroelectrochemistry (CD spectroelectrochemistry) is a recent technique that we have introduced to study molecular switches.<sup>4,5</sup> Here the characteristic optical absorption and reversible redox behaviour of pyrene are integrated with the optical activity of *trans*-cyclohexanediol for the design of novel redox active chiroptical molecular switches. The redox switching between the neutral and radical ion states is monitored by both UV–VIS–NIR and circular dichroism (CD) spectroelectrochemical methods.

The requirements for the design of an efficient chiroptical molecular redoxswitch are: (i) stability of the optical active forms, (ii) chemical reversibility of the redox processes, (iii) high sensitivity of the chiroptical response and (iv) potential application in multimode switching. During the process of screening several systems we found that pyrene functionalized *trans*-1,2-substituted cyclohexanes appear to be excellent



**Fig. 1** (a) Cyclic voltammogram of **1a**  $\rightleftharpoons$  **1a**<sup>2-</sup>, and (b) UV–VIS–NIR spectroelectrochemistry and (c) CD spectroelectrochemistry of **1a**  $\rightleftharpoons$  **1a**<sup>2-</sup> obtained by scanning over the reduction wave at  $E_{1/2} = -2120$  mV (vs. Fc<sup>+</sup>/Fc) in THF,  $\nu = 250$  mV s<sup>-1</sup>.

candidates for chiroptical redox switching due to intramolecular exciton coupling which leads to split CD.<sup>6</sup> Bis-esters **1a,b** and bis-amides **2a,b** were synthesized in the optically active forms (**1R,2R**)-**1a** [mp 208 °C,  $[\alpha]_D^{20}$  115.0, (*c* 0.42 in CH<sub>2</sub>Cl<sub>2</sub>)] and (**1S,2S**)-**1b** [mp 208 °C,  $[\alpha]_D^{20}$  -111.6 (*c* 0.40 in CH<sub>2</sub>Cl<sub>2</sub>)], and (**1R,2R**)-**2a** [mp 379–380 °C,  $[\alpha]_D^{20}$  114.3 (*c* 0.01 in THF)] and (**1S,2S**)-**2b** [mp 379–380 °C,  $[\alpha]_D^{20}$  -111.4 (*c* 0.012 in THF)], starting from the corresponding optically active *trans*-cyclohexane-1,2-diols and *trans*-1,2-diaminocyclohexanes respectively. Compounds **1a** and **1b** show reversible reduction (Fig. 1) to the bis-radical anions in a ‘one-wave-two-electron transfer’ cyclic voltammogram [ $E_{1/2}(\text{reduction}) = -2120$  mV (vs. Fc<sup>+</sup>/Fc)] leading to the appearance of an intense absorption at 510 nm [Fig. 2(a)]. Formation of radical anions of both pyrene units was established by comparison with the cyclic voltammetric data of analogous model compounds.<sup>7</sup> Obviously, the two redox active pyrene groups in **1a** and **1b** are weakly coupled in the ground state and can be classified as Robin/Day class I systems. The stationary absorption and CD spectra of the *R,R* isomer **1a** are illustrated in Fig. 2. The CD spectra of **1a** and **1b** show the expected mirror-image features. CD spectroelectrochemistry of **1a** on reduction leads to a split CD with a positive sign at 504 nm [Fig. 1(c)]. The band formation is reversible and the process can be repeated continuously. Compound (*S,S*)-**1b**



**Fig. 2** (a) UV–VIS absorption and (b) CD spectra of (*R,R*)-**1a** (*c* = 10<sup>-5</sup> mol dm<sup>-3</sup> in THF).

behaves identically with a negative sign for the couplet at 504 nm.

It is also interesting to briefly refer on the fluorescence spectra of **1a** and **1b** since these compounds may be of interest for fluorescence-detected circular dichroism<sup>6c</sup> and circularly polarized luminescence. Bis-esters **1a** and **1b** show the typical pyrene emissions at 387, 409 and 432 nm and in addition an excimer emission at 517 nm ( $c = 10^{-6} \text{ mol l}^{-1}$ ). The excimer emission depends strongly on concentration, which is characteristic of the intermolecular association of the pyrene moieties. At  $10^{-4} \text{ mol l}^{-1}$  a three-fold increase in the intensity of the excimer emission is observed.

We also investigated the redox switching behaviour of bis-amides (1*R*,2*R*)-**2a** and (1*S*,2*S*)-**2b**. Both bis-amides **2a** and **2b** are reversibly reduced to their radical anions ( $E_{1/2} = -2420 \text{ mV vs. Fc/Fc}^+$ ) leading to an absorption for the pyrene radical anion at 510 nm. The chiroptical behaviour of **1** and **2** is however different. Even though the neutral compounds **2a** and **2b** showed the expected mirror-image CD spectra, reduction to the radical anions does not lead to a split-CD signal around 500 nm. On reoxidation, the original CD spectrum is restored. Even though at this point the exact reason for this observation is not clear, we assume that proton transfer from the amide linkage at the radical anion stage or possible hydrogen bonding inhibits the appearance of a CD couplet.

In summary, we found that  $C_2$ -symmetric pyrene conjugated cyclohexanes **1** are well-suited as reversible chiroptical redox switches, which behave differently from bisamides **2a** and **2b**. The circular dichroism spectroelectrochemical method has been successfully employed for the monitoring of the switching behaviour. Work to apply compounds **1a** and **1b** as probes for molecular sensing is in progress. Also investigations to correlate the sign of the Cotton effects with the molecular structure of the pyrene-linked cyclohexanes are under way.

C. W. and M. K. are grateful to the Stiftung Stipendien-Fonds des Verbands der Chemischen Industrie, Frankfurt for doctoral

fellowships. The authors thank Dr A. Ajayaghosh for stimulating comments, Mrs M. Lutz for synthetic work and Professor O. S. Wolfbeis for making the spectropolarimeter available.

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Communication 9/07454F