Electrochiroptical response of a hexaarylethane derivative with a helical π-skeleton: drastic UV–Vis and CD spectral changes upon electrolysis of 4′,5′-dibromodispiro[xanthene-9,9′(9′H,10′H)-phenanthrene-10′,9″-xanthene]

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Upon two-electron oxidation of the title electron donor **1a**, the elongated central C_9–C_{10} bond [1.656(5) Å (X-ray)] is cleaved to give the biphenyl-2,2′-diyl bis(xanthenylium) dye **2a^{2+}**, which regenerates the colorless dispiro compound **1a** by two-electron reduction. The presence of isosbestic points in the UV–Vis spectra during the electrochemical oxidation of **1a** to **2a^{2+}** indicates the negligible steady-state concentration of the intermediate cation radical. Interconversion between optically resolved **1a** and **2a^{2+}** is accompanied by drastic changes in the CD spectra again with several isosbestic points, and racemization of (*P*)- and (*M*)-**1a** and (*S*)- and (*R*)-**2a^{2+}** does not occur at ambient conditions. This redox pair represents a new motif for the multi-output response system, where the electrochemical input is transduced into two independent spectral outputs.

Introduction

Electrochiroptical materials are a novel class of multi-output response systems, in which an electrochemical input is transduced into two kinds of spectral outputs, *i.e.*, UV–Vis and circular dichroism (CD). Although they are promising candidates for use as chiral redox memory materials, there have been only a few successful examples reported so far.[1–3] One reason for this shortage is that optically active redox systems are rare, and another reason is that only a small amplitude CD output is available for chiral molecules with a simple asymmetric center ($\Delta\varepsilon < 5$). The latter is a more significant difficulty to overcome in constructing electrochiroptical systems. In this connection, the redox pair of the dihydro[5]helicene **3** and binaphthylic dication **4^{2+}** shown in Scheme 1 is interesting[3] since not only

(*P*)-**3**: Δε (264 nm) = +97   (*S*)-**4^{2+}**: Δε (255 nm) = -45
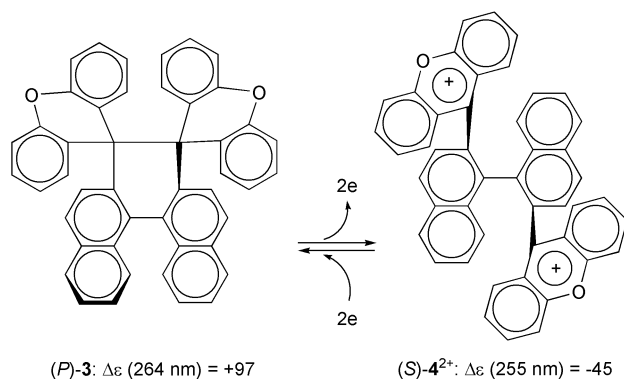
Scheme 1

UV–Vis but also CD outputs could be detected with no difficulty during the electrolysis of a very dilute solution of 10^{-5} M. The high amplitude of the CD signals in that pair comes from the helicene-type twisted π-system[4] for **3** and the exciton coupling[5] of the two dye moieties in **4^{2+}**.

During the course of our continuing study on chiral redox switches as well as the electrochromic systems based on hexaarylethanes,[6] we have found that the redox pair of 9,10-dihydrophenanthrene-type donor **1** and biphenylic dication **2^{2+}** can be optically resolved as in the case of **3** and **4^{2+}** when the appropriate substituents are introduced at the bay region to retard racemization (Scheme 2). Here we report a new successful example of electrochiroptics based on the interconversion between **1a** and **2a^{2+}** containing two Br groups. Because the Br group could be replaced by other substituents through subsequent reactions, optically active **1a** can serve as a new useful synthon for further electrochiroptical studies.
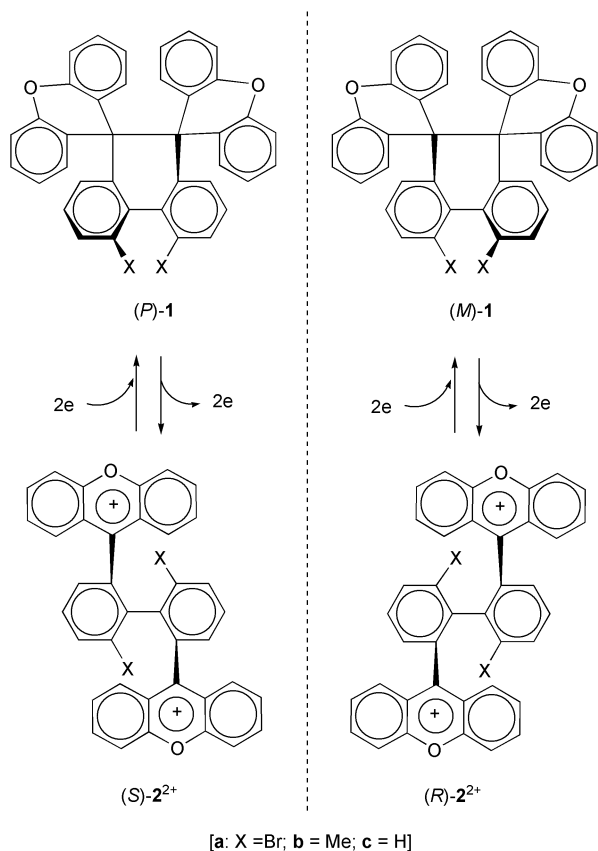
Results and discussion

Preparation and properties of the racemic redox pair, 1a and 2a^{2+}

2,2′,6,6′-Tetrabromobiphenyl[7] was chosen as a starting material, and was efficiently converted to the 2,2′-dibromo-6,6′-dilithio derivative by treating with excess BuLi in THF at −78 °C. Successive reaction with xanthone gave racemic diol *rac*-**5** in 68% yield (Scheme 3). Upon treatment of *rac*-**5** with HBF$_4$ in (EtCO)$_2$O, racemic dication salt *rac*-**2a^{2+}**(BF$_4^-$)$_2$ was isolated as an orange powder in 87% yield. This salt was converted to colorless crystals of dispiro-dihydrophenanthrene *rac*-**1a** in 71% yield by the reaction with Zn powder in MeCN. The high-yield transformation of **2a^{2+}** to **1a** shows that the repulsive interaction between the two Br groups in the bay region in **1a** is not too severe to prevent the cyclization of **2a$^{2•}$**.†

To investigate the detailed geometrical features of **1a**, X-ray analysis on the racemate was carried out at −120 °C. Although the hexaphenylethane skeleton is notorious for giving severely

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† The reaction mechanism for the redox process was elucidated for a system structurally related to **1a**, namely, the 9,10-dihydrophenanthrene derivative substituted with two different aryl groups at the 9,10-positions (ref. 6).

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Scheme 2

(P)-1   (M)-1

2e   2e   2e   2e

(S)-2²⁺   (R)-2²⁺

[**a**: X = Br; **b** = Me; **c** = H]

Scheme 2

Scheme 3

BuLi

TsOH

rac-5

SiO₂

(S)-6   (R)-6

HBF₄   HBF₄

(S)-2a²⁺ (BF₄⁻)₂   (R)-2a²⁺ (BF₄⁻)₂

Zn   Zn

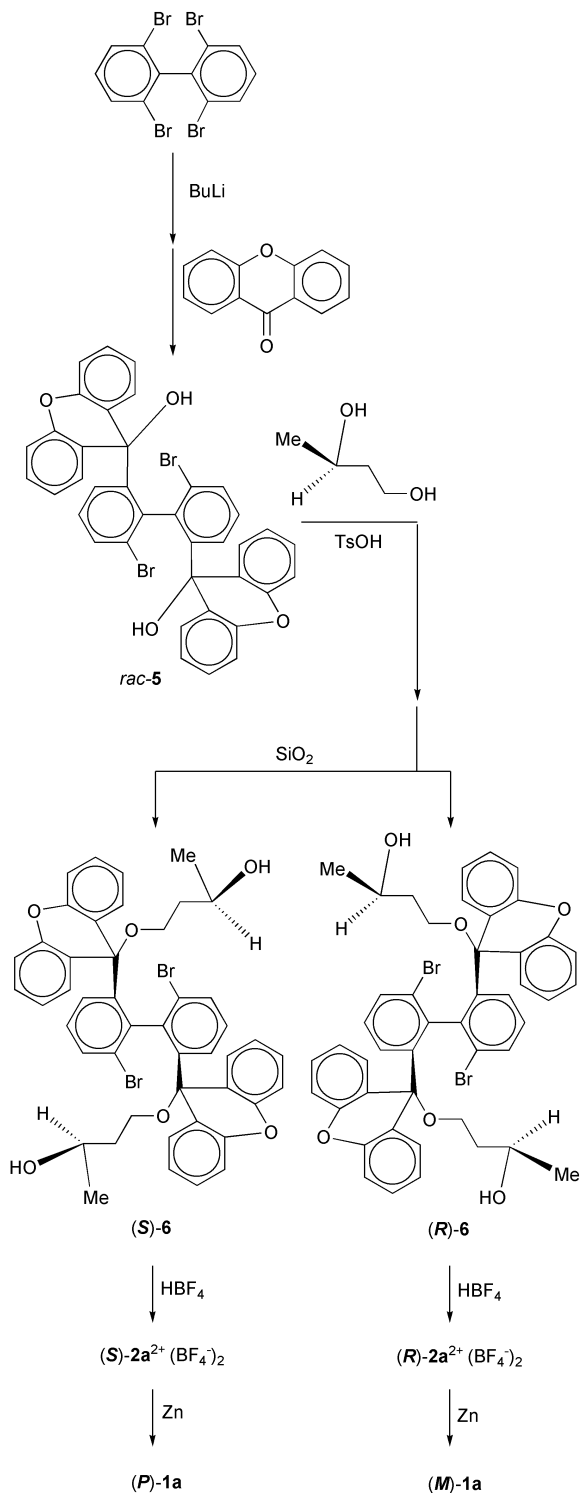(P)-1a   (M)-1a

Scheme 3

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disordered crystal structures,[8] this is not the case. The structural parameters for **1a** could be obtained with high accuracy. The most outstanding feature is the very long central $C_9–C_{10}$ bond [1.656(5) Å]. Such elongation partly comes from the steric hindrance between the aryl groups ("front strain").[9] Another factor may be the repulsion between two Br groups [3.423(1) Å] as shown by the relatively large twisting angle [41.4(1)°] around the $C_{4a}–C_{4b}$ bond (Fig. 1). Despite the strained geometry, **1a** is a stable compound with no signs of decomposition or oxygenation under the ambient conditions, suggesting that the $C_9–C_{10}$ bond in **1a** is robust enough against its homolytic rupture.

Upon electrochemical oxidation, however, this weakened bond is cleaved easily as indicated by the cyclic voltammogram of **1a** shown in Fig. 2. The oxidation peak appears at +1.45 V as an irreversible wave. A noteworthy feature is the large negative shift of the corresponding cathodic peak (+0.51 V), which is indicative of the dynamic redox properties involving C–C bond breaking upon electron transfer.[3,6,10] In fact, upon oxidation of *rac*-**1a** with 2 equiv. of $(4\text{-}BrC_6H_4)_3N^{+\bullet} SbCl_6^-$, the dication salt of *rac*-**2a²⁺**$(SbCl_6^-)_2$ was isolated in 95% yield. These results indicate that **1a** and **2a²⁺** can be considered as a "reversible" redox pair although the C–C bond making/breaking accompanies their interconversion.

Conversion of racemic dibromide 1a to dimethyl derivative 1b

Upon reaction of dibromide *rac*-**1a** with BuLi followed by MeI, colorless crystals of 4,5-dimethyl-9,10-dihydrophenanthrene *rac*-**1b** were obtained in 85% yield. This result indicates that the dibromide **1a** can serve as a useful synthon for further functionalization of the redox pairs of **1** and **2²⁺** by modifying the substituents at the C_4 and C_5 positions.

The X-ray analysis of dimethyl derivative *rac*-**1b** shows that its molecular structure is quite similar to that of **1a**. The bond distance for the central $C_9–C_{10}$ bond is 1.652(4) Å, and the twisting angle around the $C_{4a}–C_{4b}$ bond is 40.2(1)° in **1b**. Such resemblance is in accord with the similar van der Waals radii[11] of Br (1.95 Å) and Me (2.0 Å) groups. According to the vol-

tammetric analysis, **1b** (E^{ox}_{peak} +1.35 V) shows slightly stronger donating properties than dibromide **1a** or **1c** without bay region substituents (+ 1.42 V)[6] due to the electron-releasing effects of the Me groups. This oxidation process is also irreversible with the cathodic peak appearing in the far cathodic region (+0.45 V), suggesting that dimethyl derivative **1b** also undergoes dynamic redox properties with the bond making/breaking phenomenon. Due to the close similarity of the geometrical features and redox properties between **1a** and **1b**, further studies on chiroptics were carried out only for the dibromide **1a**.

Preparation of optically pure dibromides, 1a and 2a²⁺

The ¹H NMR spectra of **1a** and **2a²⁺** are C_2-symmetric whereas the parent skeletons without Br groups (**1c** and **2c²⁺**) exhibit
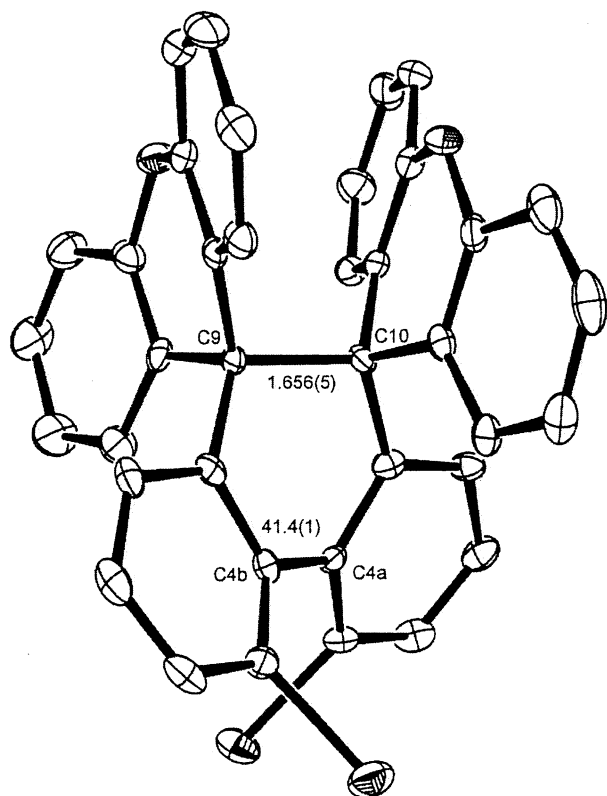
Fig. 1 Molecular structure of **1a** determined by X-ray analysis on the racemate at −120 °C. The bridging bond length and twisting angle of **1a** are close to those of the previously analyzed binaphthyl derivative **3** (1.651 Å, 37.1°).
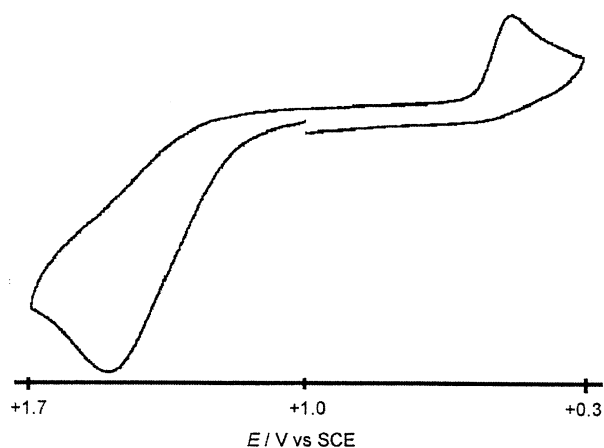
**Fig. 2** Cyclic voltammogram of **1a** in CH$_2$Cl$_2$ (E/V vs. saturated calomel electrode). The scan rate of 500 mV s^{-1} was adopted to show the reduction peak more clearly than in the voltammogram with a 100 mV s^{-1} scan rate).

C_{2v}-symmetric spectra. The higher symmetry in the latter comes from the rapid ring-flip in **1c** and free rotation around the biphenyl axis in **2c^{2+}** since lowering the temperature caused broadening of the signals for the spiroxanthene units in **1c** (CDCl$_3$). In the case of **2c^{2+}**, the xanthenylium protons were split into two sets of signals to give a C_2-symmetric spectrum at −40 °C in CD$_3$CN. The energy barrier for the dynamic behavior in **2c^{2+}** was estimated to be about 12.5 kcal mol^{-1} based on the coalescence temperature (−15 °C) and the Δδ value (0.215 ppm at 300 MHz). On the other hand, the spectrum of dibromide **1a** is essentially temperature-independent up to 60 °C (CDCl$_3$). The spectrum of **2a^{2+}** in CD$_3$CN became broad at 80 °C, yet this was well before the coalescence of signals. These results suggest that their configurations are stable enough under the ambient conditions to conduct optical resolution of the enantiomers based on the helicity for **1a** and the axial chirality for **2a^{2+}**.

Reaction of *rac*-**1a** with (R)-butane-1,3-diol in the presence of a catalytic amount of TsOH gave two isomers of the 9,9′-bis[(3R)-3-hydroxybutoxy]-9,9′-(biphenyl-2,2′-diyl)dixanthene, (R)- and (S)-**6**, which are diastereomeric due to the axial chirality of the biphenyl moiety (Scheme 3). They could be isolated by repeated chromatographic separation though in variable yields (30–68%), and their configurations were unambiguously determined based on the X-ray structure of (R)-**6**.

Treatment of (R)-**6** with HBF$_4$ in (EtCO)$_2$O gave the chiral dication salt (R)-**2a^{2+}**(BF$_4^-$)$_2$ in 96% yield, which was further transformed into the chiral dispiro compound (M)-**1a** ([a]$_D^{23}$ −402, c = 0.43 in CHCl$_3$) in 77% yield. Similarly, (S)-**6** was converted to (P)-**1a** ([a]$_D^{23}$ +413, c = 0.47 in CHCl$_3$) via (S)-**2a^{2+}**(BF$_4^-$)$_2$. The large optical rotations for (P)- and (M)-**1a** may be due to the helical arrangement of π-electron systems as in the helicenes. Similar to the redox pair of dihydrohelicene **3** and binaphthylic dication **4^{2+}** (see ref. 3), the optically resolved **1a** and **2a^{2+}** are strongly CD active as shown in Fig. 3. Large
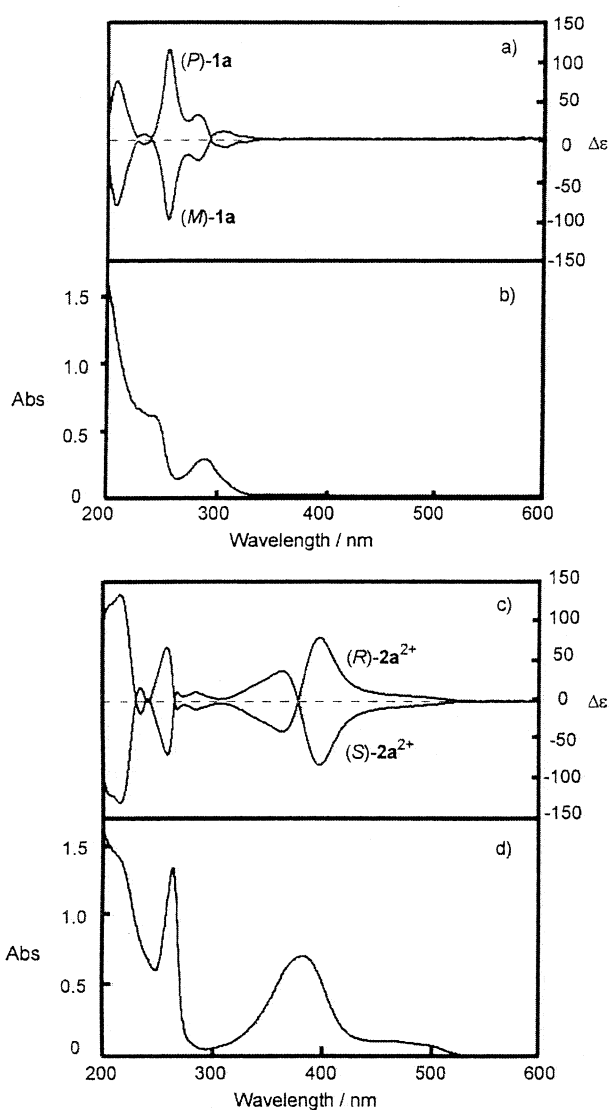

Fig. 3 CD (a) and UV–Vis (b) spectra of **1a** in MeCN; and CD (c) and UV–Vis (d) spectra of **2a^{2+}**(BF$_4^-$)$_2$ in MeCN.

couplets suggest exciton coupling[5] between two identical chromophores in **1a** and **2a^{2+}**. The spectral shapes and amplitude were unchanged after allowing to stand for 40 h at room temperature, confirming that their racemization does not occur under the ambient conditions.

Electrochemical response

The response of the present redox pair against the electrical input was first examined by UV–Vis spectroscopy (Fig. 4a). The
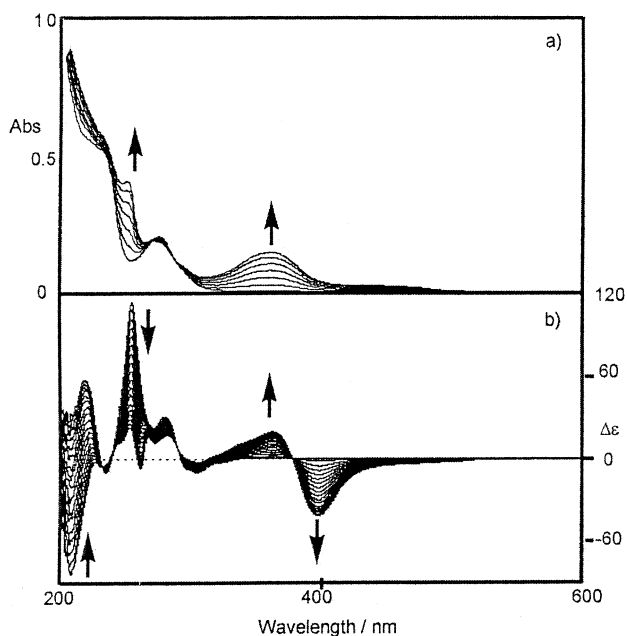
Fig. 4 (a) Changes in the UV–Vis spectrum of (*P*)-**1a** (1.28×10^{-5} mol dm^{-3} in MeCN) upon constant-current electrochemical oxidation (26 μA at 10 min interval) to (S)-**2a**$^{2+}$; (b) Changes in the CD spectrum of (*P*)-**1a** (3.92×10^{-5} mol dm^{-3} in MeCN) upon constant-current electrochemical oxidation (27 μA at 10 min interval) to (S)-**2a**$^{2+}$. The electrochemical reduction of the resulting dication solutions induced the reverse spectral changes.

oxidation of **1a** to **2a**$^{2+}$ caused a vivid color change since **1a** shows absorption only in the UV region [λ_{max} 290 nm (ε 16200 dm^3 mol^{-1} cm^{-1})] whereas the absorption bands occur in the visible region for the dicationic dye **2a**$^{2+}$ [467 (4680), 455 (4580)]. The isosbestic points observed in the spectra are indicative of a clean transformation between **1a** and **2a**$^{2+}$ as well as of the negligible steady-state concentration of the intermediate cation radical. †

When the electrochemical study was followed by CD spectroscopy, drastic change was again observed with several isosbestic points (Fig. 4b). Upon electrolysis of (*P*)-**1a**, the large negative couplet appears gradually around the 320–420 nm region, which is assigned to the exciton coupling between the two xanthenylium chromophores in (*S*)-**2a**$^{2+}$. Larger changes in $\Delta\varepsilon$ are observed in the UV region because of the different signs of the CD signals for the interconvertible pair, such as (*P*)-**1a** [$\Delta\varepsilon = -82$ at 208 nm, $+114$ at 255 nm] and (*S*)-**2a**$^{2+}$ [$\Delta\varepsilon = +136$ at 217 nm, -68 at 260 nm] (Fig. 3). Due to such contrasts in the CD spectra before and after electrolysis, detection of the chiroptical output for the present system is quite easy especially around 215 ($\Delta\Delta\varepsilon$ 182) and 255 ($\Delta\Delta\varepsilon$ 167) nm.

Conclusion

This work has revealed that a large chiroptical output is available for the redox pair of **1a** and **2a**$^{2+}$ based on a dihydrophenanthrene-type skeleton. This example demonstrates a new route into an electrochiroptical system, which still is an undeveloped category among molecular response systems. Compared with previously studied molecules with a binaphthyl moiety,[3] the dihydrophenanthrene derivatives are advantageous in terms of easier functionalization of the compounds for further exploration; *e.g.* chiroptical materials that can be fixed on the metal surface.[12] Studies in this vein are now under way by

using the Br group in **1a** as a means to introduce appropriate substituents.

Experimental

Preparation of 4′,5′-dibromodispiro[xanthene-9,9′(9′*H*,10′*H*)-phenanthrene-10′,9″-xanthene] 1a

To a solution of dication salt *rac*-**2a**$^{2+}$ (BF$_4^-$)$_2$ (100 mg, 0.118 mmol) in dry MeCN (2.5 mL) was added activated Zn powder (273 mg, 4.17 mmol). After stirring for 2 h under Ar at room temperature, the mixture was diluted with benzene (5 mL) and insoluble material was removed by filtration. Chromatographic separation on Al$_2$O$_3$ (benzene) and trituration with hot EtOH gave *rac*-**1a** as a colorless powder (79 mg) in 71% yield. Similarly, (*S*)-**2a**$^{2+}$ (BF$_4^-$)$_2$ and (*R*)-**2a**$^{2+}$ (BF$_4^-$)$_2$ were transformed into (*P*)-**1a** and (*M*)-**1a**, respectively, in 78% and 77% yields.

Data for *rac*-**1a**: mp > 300 °C (Found: C, 67.9; H, 3.55; Br, 23.9; Calcd. for C$_{38}$H$_{22}$O$_2$Br$_2$: C, 68.1; H, 3.3; Br, 23.85%); λ_{max} (MeCN)/nm 290 (ε 16200), 243 (42500); δ_H (300 MHz; CDCl$_3$; TMS) 7.68 (2H, dd, $J = 8.0$, 1.5 Hz), 7.19 (2H, ddd, $J = 8.0$, 8.0, 1.5 Hz), 7.10–7.00 (6H, m), 6.88 (2H, dd, $J = 8.0$, 1.5 Hz), 6.78 (2H, dd, $J = 8.0$, 1.5 Hz), 6.75 (2H, ddd, $J = 8.0$, 8.0, 1.5 Hz), 6.60 (2H, dd, $J = 8.0$, 1.5 Hz), 6.46 (2H, ddd, $J = 8.0$, 8.0, 1.5 Hz), 5.61 (2H, dd, $J = 8.0$, 1.5 Hz); ν_{max} (KBr)/cm^{-1} 1478, 1442, 1308, 1246, 752; *m/z* (FD) 672 (M$^+$, 75), 670 (M$^+$, 100), 668 (M$^+$, 61).

Data for (*P*)-**1a**: mp > 300 °C; δ_H (300 MHz; CDCl$_3$) is identical to that of *rac*-**1a**; CD λ (CH$_3$CN)/nm 305 ($\Delta\varepsilon$ −10), 281 (+31), 271 (+23), 255 (+114), 232 (−5.8), 227 (−2.2), 208 (−82).

Data for (*M*)-**1a**: mp > 300 °C; δ_H (300 MHz; CDCl$_3$) is identical to that of *rac*-**1a**; CD λ (CH$_3$CN)/nm 304 ($\Delta\varepsilon$ + 11), 281 (−31), 272 (−22), 255 (−115), 232 (+8.1), 226 (+3.8), 208 (+86).

Preparation of racemic 4′,5′-dimethyldispiro[xanthene-9,9′(9′*H*,10′*H*)-phenanthrene-10′,9″-xanthene] *rac*-1b

To a solution of *rac*-**1a** (270 mg, 0.403 mmol) in 15 mL dry THF was added dropwise BuLi (1.56 M in *n*-hexane, 0.77 mL, 1.20 mmol) at −78 °C under Ar. After stirring for 2 h at this temperature, MeI (180 mg, 1.27 mmol) was added, and the temperature was gradually raised to room temperature. After addition of water, the mixture was extracted with CH$_2$Cl$_2$. The organic layer was washed with water and brine, and dried over Na$_2$SO$_4$. Evaporation of solvent gave the crude product, which was purified by thick layer chromatography (SiO$_2$, CHCl$_3$, $R_f =$ 0.75) to give 185 mg of colorless crystals of **1b** in 85% yield: mp > 300 °C (Found: C, 87.15; H, 5.25; Calcd. for C$_{40}$H$_{28}$O$_2$·½H$_2$O: C, 87.4; H, 5.3); δ_H (300 MHz; CDCl$_3$; TMS) 7.29 (2H, br d, $J = 8.0$ Hz), 7.16 (2H, ddd, $J = 8.0$, 8.0, 1.5 Hz), 7.09 (2H, dd, $J = 8.0$, 8.0 Hz), 7.00 (2H, $J = 8.0$, 8.0, 1.5 Hz), 6.89 (2H, br d, $J = 8.0$ Hz), 6.80 (2H, dd, $J = 8.0$, 1.5 Hz), 6.78 (2H, dd, $J = 8.0$, 1.5 Hz), 6.63 (2H, ddd, $J = 8.0$, 8.0, 1.5 Hz), 6.57 (2H, dd, $J = 8.0$, 1.5 Hz), 6.43 (2H, ddd, $J = 8.0$, 8.0, 1.5 Hz), 5.68 (2H, dd, $J = 8.0$, 1.5 Hz), 2.61 (6H, s); ν_{max} (KBr)/cm^{-1} 1478, 1440, 1306, 1238, 748; *m/z* (FD) 540 (M$^+$, 100).

Preparation of 2,2′-dixanthenylium-9-yl-6,6′-dibromobiphenyl bis(tetrafluoroborate) 2a^{2+}(BF$_4^-$)$_2$

To a solution of racemic diol *rac*-**5** (200 mg, 0.284 mmol) in (EtCO)$_2$O (5 mL) was added 42% aqueous HBF$_4$ (0.10 mL, 0.71 mmol), and the mixture was stirred overnight at room temperature. Addition of dry ether (5 mL) and removal by filtration of the orange powder gave *rac*-**2a**$^{2+}$(BF$_4^-$)$_2$ (209 mg) in 87% yield. Similarly, (*R*)- and (*S*)-9,9′-bis[(3*R*)-3-hydroxybutoxy]-9,9′-(biphenyl-2,2′-diyl)dixanthene **6** were transformed into (*R*)- and (*S*)-**2a**$^{2+}$(BF$_4^-$)$_2$, respectively, in 96% and 79% yields.

Data for *rac*-**2a**$^{2+}$(BF$_4^-$)$_2$: mp 184–188 °C (decomp.) (Found: C, 54.1; H, 2.8; Br, 18.6; Calcd. for C$_{38}$H$_{22}$O$_2$Br$_2$B$_2$F$_8$: C, 54.05;

H, 2.65; Br, 18.95%); λ_{max} (MeCN)/nm 467 (ε 4680), 455 (4580), 383 (31700), 264 (60200), 216 sh (50200); δ_H (300 MHz; CD$_3$CN; TMS) 8.62 (2H, br.d), 8.51 (2H, br.d), 8.40–8.35 (4H, m), 8.24 (2H, d, J = 8.0 Hz), 7.99 (2H, dd, J = 8.0, 8.0 Hz), 7.85 (2H, d, J = 8.0 Hz), 7.56 (2H, dd, J = 8.0 Hz), 7.46 (2H, dd, J = 8.0, 8.0 Hz), 7.08 (2H, d, J = 8.0 Hz), 6.45 (2H, br.d); ν_{max} (KBr)/cm^{-1} 1598, 1510, 1058, 758; m/z (FAB) 672 (M$^+$, 31), 670 (M$^+$, 46), 668 (M$^+$, 26), 591 (M$^+$ − Br, 97), 589 (M$^+$ − Br, 88), 511 (M$^+$ − 2Br, 100).

Data for (*R*)-2a^{2+}(BF$_4$$^-$)$_2$: mp 190–193 °C (decomp.); δ_H (300 MHz; CD$_3$CN) is identical to that of *rac*-2a^{2+} salt; CD λ (CH$_3$CN)/nm 398 ($\Delta\varepsilon$ +81), 366 (−39), 309 (−2.8), 287 (−10), 275 (−4.6), 269 (−11), 259 (+70), 243 (−1.3), 236 (+17), 206 (−130).

Data for (*S*)-2a^{2+}(BF$_4$$^-$)$_2$: mp 189–191 °C (decomp.); δ_H (300 MHz; CD$_3$CN) is identical to that of *rac*-2a^{2+} salt; CD λ (CH$_3$CN)/nm 399 ($\Delta\varepsilon$ −82), 364 (+39), 307 (+2.4), 286 (+11), 274 (+5.9), 269 (+12), 260 (−68), 243 (+3.0), 236 (−15), 217 (+136).

Preparation of racemic 2,2′-dixanthenylium-9-yl-6,6′-dibromo-biphenyl bis(hexachloroantimonate) *rac*-2a^{2+}(SbCl$_6$$^-$)$_2$

To a solution of racemic dihydrophenanthrene *rac*-1a (110 mg, 0.164 mmol) in dry CH$_2$Cl$_2$ (3 mL) was added (4-BrC$_6$H$_4$)$_3$-N$^{+\bullet}$SbCl$_6$$^-$ (295 mg, 0.361 mmol), and the mixture was stirred for 2 h under Ar. Addition of dry ether (20 mL) and removal by filtration of the orange powder gave *rac*-2a^{2+}(SbCl$_6$$^-$)$_2$ (210 mg) in 95% yield: mp 224–227 °C (decomp.) (Found: C, 34.05; H, 1.8; Br, 11.6; Calcd. for C$_{38}$H$_{22}$O$_2$Br$_2$Sb$_2$Cl$_{12}$: C, 34.1; H, 1.65; Br, 11.95%); δ_H (300 MHz; CD$_3$CN; TMS) 8.62 (2H, br d, J = 8.0 Hz), 8.51 (2H, br d, J = 8.0 Hz), 8.40–8.35 (4H, m), 8.24 (2H, d, J = 8.0 Hz), 7.99 (2H, dd, J = 8.0, 8.0 Hz), 7.85 (2H, d, J = 8.0 Hz), 7.56 (2H, dd, J = 8.0, 8.0 Hz), 7.46 (2H, dd, J = 8.0, 8.0 Hz), 7.08 (2H, d, J = 8.0 Hz), 6.45 (2H, br d, J = 8.0 Hz); ν_{max} (KBr)/cm^{-1} 1598, 1506, 758; m/z (FAB) 672(M$^+$, 13), 670 (M$^+$, 25), 668 (M$^+$, 16), 591(M$^+$ − Br, 100), 589 (M$^+$ − Br, 93), 511 (M$^+$ − 2Br, 41).

Preparation of racemic 6,6′-dibromo-2,2′-bis(9-hydroxyxanthen-9-yl)biphenyl *rac*-5

To a solution of 2,2′,6,6′-tetrabromobiphenyl[7] (2.00 g, 4.26 mmol) in dry THF (60 mL) was added dropwise BuLi (1.56 M in *n*-hexane, 13.6 mL, 21.3 mmol) at −78 °C under Ar. The mixture was stirred for 2 h at this temperature, during which time a fine precipitate of 2,2′-dibromo-6,6′-dilithiobiphenyl gradually separated out. To this mixture was added xanthone (4.18 g, 21.3 mmol) under Ar at −78 °C, and the temperature was slowly raised to room temperature. After addition of water, the mixture was extracted with CH$_2$Cl$_2$, and the organic layer was washed with brine and dried over Na$_2$SO$_4$. Evaporation of solvent and recrystallization from 1,2-dichloroethane–*n*-hexane gave colorless crystals of *rac*-5 as a 1,2-dichloroethane solvate (2.20 g) in 68% yield: mp 183–186 °C (Found: C, 62.4; H, 3.55; Calcd. for C$_{38}$H$_{24}$O$_4$Br$_2$·½C$_2$H$_4$Cl$_2$: C, 62.1; H, 3.5%); δ_H (300 MHz; CDCl$_3$; TMS) 7.69 (2H, dd, J = 7.8, 1.5 Hz), 7.52 (2H, dd, J = 7.8, 1.5 Hz), 7.35–7.15 (10H, m), 7.05 (2H, dd, J = 7.8, 7.8 Hz), 7.03 (2H, ddd, J = 7.8, 7.8, 1.5 Hz), 6.93 (2H, ddd, J = 7.8, 7.8, 1.5 Hz), 6.84 (2H, dd, J = 7.8, 1.5 Hz), 4.19 (2H, s); ν_{max} (KBr)/cm^{-1} 3424, 2944, 1464, 744; m/z (FD) 706 (M$^+$, 72), 704 (M$^+$, 100), 702 (M$^+$, 65).

Preparation of (*R*)- and (*S*)-9,9′-bis[[(3*R*)-3-hydroxybutoxy]-9,9′-(biphenyl-2,2′-diyl)dixanthene 6

To a suspension of racemic diol *rac*-5 (391 mg, 0.555 mmol) and (*R*)-butane-1,3-diol (200 mg, 2.22 mmol) in benzene (40 mL) was added TsOH (10 mg), and the mixture was refluxed for 3 h under dehydrating conditions (Dean–Stark). After cooling, the resulting solution was washed with water and brine, and

dried over Na$_2$SO$_4$. Evaporation of solvent and chromatographic separation on Al$_2$O$_3$ (1,2-dichloroethane–EtOAc) gave a mixture of diastereomers, (*R*)- and (*S*)-6, which were separated by thick layer chromatography (SiO$_2$, *n*-hexane : EtOAc = 2 : 1; elution 5 times). Stereochemical assignment was done based on the X-ray structure of (*R*)-6.

Data for (*R*)-6 (R_f = 0.73, yield 48% based on (*R*)-5): pale tan solid, mp 195–196 °C (decomp.) (Found: C, 65.35; H, 4.8; Br, 18.7; Calcd. for C$_{46}$H$_{40}$O$_6$Br$_2$: C, 65.1; H, 4.75; Br, 18.85.%); δ_H (300 MHz; CDCl$_3$; TMS) 7.99 (2H, d, J = 8.0 Hz), 7.55 (4H, m), 7.36 (2H, dd, J = 8.0, 8.0 Hz), 7.22 (2H, d, J = 8.0 Hz), 7.15–7.08 (6H, m), 6.92 (2H, dd, J = 8.0, 8.0 Hz), 6.86 (2H, d, J = 8.0 Hz), 3.42–3.40 (2H, m), 2.84–2.78 (4H, m), 0.85 (6H, d, J = 6.3 Hz), 0.76–0.72 (2H, m), 0.65–0.62 (2H, m), 0.53 (2H, br.s); ν_{max} (KBr)/cm^{-1} 1478, 1446, 1316, 1240, 760; m/z (FD) 850 (M$^+$, 67), 848 (M$^+$, 100), 846 (M$^+$, 46).

Data for (*S*)-6 (R_f = 0.66, yield 68% based on (*S*)-5): pale yellow wax, mp 186–187 °C (decomp.) (Found: C, 64.85; H, 4.7; Br, 18.7; Calcd. for C$_{46}$H$_{40}$O$_6$Br$_2$: C, 65.1; H, 4.75; Br, 18.85%); δ_H (300 MHz; CDCl$_3$; TMS) 7.91 (2H, d, J = 7.5 Hz), 7.61 (2H, d, J = 7.5 Hz), 7.55 (2H, d, J = 7.5 Hz), 7.34 (2H, dd, J = 7.5, 7.5 Hz), 7.19 (2H, d, J = 7.5 Hz), 7.15–7.10 (4H, m), 7.08 (2H, dd, J = 7.5, 7.5 Hz), 6.95 (2H, dd, J = 7.5, 7.5 Hz), 6.85 (2H, d, J = 7.5 Hz), 6.35–6.30 (2H, m), 3.35–3.29 (2H, m), 2.80–2.70 (4H, m), 0.95 (2H, br.s), 0.81–0.73 (4H, m), 0.65 (6H, d, J = 6.0 Hz); ν_{max} (KBr)/cm^{-1} 1478, 1446, 1316, 1240, 760; m/z (FD) 850 (M$^+$, 65), 848 (M$^+$, 100), 846 (M$^+$, 47).

Crystallographic study ‡

Data collection was conducted on a Rigaku Mercury CCD apparatus with Mo-Kα radiation at 153 or 123 K (a liquid N$_2$ flow method). Crystallographic data are as follows.

rac-1a: C$_{38}$H$_{22}$Br$_2$O$_2$, M 670.40, monoclinic $P2_1/c$, a = 12.462(6), b = 15.613(7), c = 15.042(7) Å, β = 111.35(1)°, U = 2725(2) Å^3, D_c (Z = 4) = 1.633 g cm^{-1}, T = 153 K, μ = 30.19 cm^{-1}. The final R value is 0.036 for 3567 independent reflections with $I > 3\sigma I$ and 379 parameters.

rac-1b: C$_{40}$H$_{28}$O$_2$, M 540.66, monoclinic, $P2_1/n$, a = 10.059(5), b = 14.309(7), c = 19.109(10) Å, β = 97.049(7)°, U = 2729(2) Å^3, D_c (Z = 4) = 1.315 g cm^{-1}, T = 153 K, μ = 0.79 cm^{-1}. The final R value is 0.057 for 2925 independent reflections with $I > 3\sigma I$ and 379 parameters.

(*R*)-6: C$_{46}$H$_{40}$Br$_2$O$_6$, M 848.63, monoclinic, C2, a = 21.614(2), b = 9.8916(8), c = 9.6740(4) Å, β = 113.459(2)°, U = 1897.3(2) Å^3, D_c (Z = 2) = 1.485 g cm^{-1}, T = 123 K, μ = 21.93 cm^{-1}. The final R value is 0.032 for 1777 independent reflections with $I > 3\sigma I$ and 245 parameters. Stereochemistry of axial chirality was determined to be (*R*) on the basis of known configuration at the side chains.

Redox potentials and spectroelectrochemical measurements

Oxidation potentials (E^{ox}) were measured by cyclic voltammetry in dry CH$_2$Cl$_2$ containing 0.1 mol dm^{-3} Bu$_4$NBF$_4$ as a supporting electrolyte. Ferrocene undergoes reversible one-electron oxidation at +0.53 V under the same conditions. All the values shown in the text are the peak potentials in E/V *vs.* SCE measured at the scan rate of 100 mV s^{-1}. A Pt disk electrode (diameter, 1.6 mm) and a Pt wire electrode were used as the working and counter electrodes, respectively. The working electrode was polished using a water suspension of Al$_2$O$_3$ (0.05 µm) before use.

Spectroelectrochemical measurements were carried out on a 3.5 mL MeCN solution containing 0.05 M Bu$_4$NBF$_4$ in a quartz cell (10 × 10 × 40 mm) equipped with a Pt mesh as a working

electrode and a salt bridge. A Pt wire was placed in the latter as a counter electrode. Electrical current was monitored by a microampere meter.

Acknowledgements

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