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Butane-1,4-diyl dications stabilized by steric factors: electrochiroptical response systems based on reversible interconversion between dihydro[5]helicene-type electron acceptors and electron-donating 1,1′-binaphthyls

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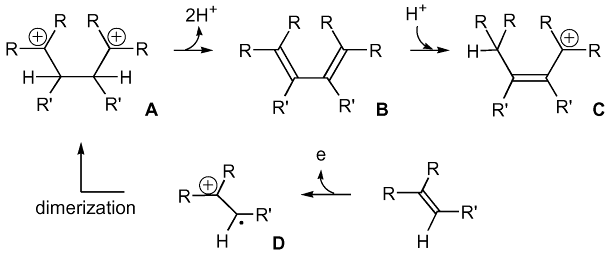
Incorporation in the dihydro[5]helicene framework prevents deprotonation of the title dications by steric factors, thus allowing their isolation as deeply colored stable salts. Based on the reversible interconversion with the electron-donating binaphthylic diolefins, they constitute a new class of electrochromic systems, in which C–C bond making/breaking is accompanied by two-electron transfer. Optically pure (*R*)-binaphthylic donors are interconvertible with the 1,4-dications with the *R*,*R*-configuration. The very large molar ellipticity makes it possible for them to be used as electrochiroptical response systems, by which the electrochemical input is transduced into two spectral outputs, *i.e.* UV-Vis and circular dichroism. Structurally related push–pull-type bis(quinonemethide)s also exhibit a similar multi-output electrochemical response.

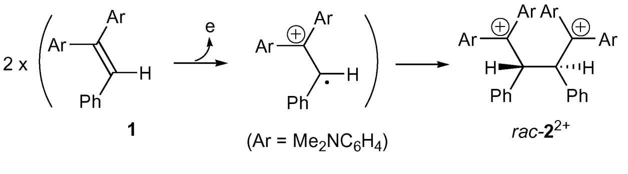
Introduction

The butane-1,4-diyl dications (**A**) belong to a peculiar class of carbocations that have been postulated as reactive intermediates[1,2] but not isolated or even detected spectroscopically due to their instability against rapid deprotonation to give the corresponding 1,3-dienes (**B**) (Scheme 1). Since protonation of dienes generally affords allyl cations (**C**),[3] dimerization of the olefin cation radicals (**D**) seems the only effective way to produce these intriguing species.

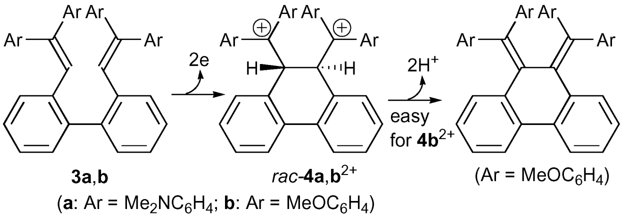


Scheme 1

During the course of our continuing studies[4] on novel electrochromic systems[2,5] that undergo reversible C–C bond making/breaking upon electron transfer,[6] we found that strong electron-donating groups such as the dimethylaminophenyl group stabilize this type of dication effectively. Thus, upon oxidative dimerization of $(4\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{C=CHPh}$ **1**, the salt of 1,4-dication $\mathbf{2}^{2+}$ was obtained as the first isolable member of the general formula **A** (Scheme 2).[4a] Similarly, another dication $\mathbf{4a}^{2+}$ with the 9,10-dihydrophenanthrene skeleton was isolated upon two-electron oxidation of the biphenyl-type donor **3a** with two bis(4-dimethylaminophenyl)ethenyl units (Scheme 3).[4b] In contrast, the less electron-donating methoxyphenyl group is not effective enough to stabilize $\mathbf{4b}^{2+}$ against deprotonation, which was thus transformed into the conjugated diene derivative *in situ* upon oxidation of **3b**.[7] The different behavior between $\mathbf{4a}^{2+}$ and $\mathbf{4b}^{2+}$ is in line with the much smaller $\mathrm{p}K_{\mathrm{R}^+}$ value of $(4\text{-MeOC}_6\text{H}_4)_2\text{CPh}^+$ (−1.24)[8a] than $(4\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{CPh}^+$ (6.90).[8b]

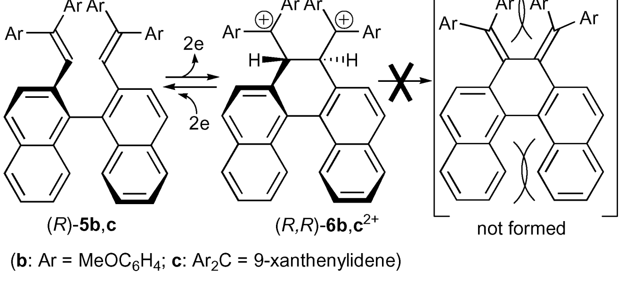


Scheme 2



Scheme 3

We envisaged that deprotonation from 1,4-dications (**A**) could be suppressed not only by electronic effects but also by steric factors. That is, the bulky substituents may kinetically protect the acidic C–H groups against the base. Furthermore, the deprotonated dienes may be thermodynamically destabilized by severe deformation due to steric repulsion between substituents. We have succeeded here in isolating new members of stable butane-1,4-diyl dications incorporated in the dihydro[5]helicene skeleton having two bis(4-methoxyphenyl)methylium ($\mathbf{6b}^{2+}$) or two xanthenylium ($\mathbf{6c}^{2+}$) units (Scheme 4). Here we report the preparation, redox properties, and X-ray structure of $\mathbf{6b,c}^{2+}$ and the electron-donating binaphthylic precursors **5b,c**. It is noteworthy that the optically active (*R*)-**5b,c** and (*R*,*R*)-$\mathbf{6b,c}^{2+}$ can



Scheme 4

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constitute novel electrochiroptical response systems, by which the electrochemical input can be transduced into two different spectroscopic outputs, *i.e.* UV-Vis and circular dichroism (CD).

Results and discussion

Preparation and X-ray structures of new electron donors 5b,c

The reaction of *rac*-2,2′-dimethyl-1,1′-binaphthyl with BuLi in the presence of TMEDA gave 2,2′-bis(lithiomethyl) derivative,[4b] which was then reacted with 4,4′-dimethoxybenzophenone to give diol *rac*-**7b**. Dehydration to *rac*-**5b** proceeded smoothly by treating with a catalytic amount of TsOH in refluxing benzene (Dean–Stark) in a two-step yield of 78%. By starting with optically pure (*R*)-dimethylbinaphthyl, (*R*)-**5b** was obtained as a colorless solid by the same procedures in 66% yield over two steps.

According to the X-ray analysis on *rac*-**5b** (Fig. 1a), the binaphthyl skeleton is twisted by 81.1(2)°, and the two bis(4-methoxyphenyl)ethenyl moieties are arranged close to each other. The intramolecular separation between methine carbons of the 2,2-diarylethenyl units is 3.77 Å, which is marginally larger than the sum of van der Waals radii (3.40 Å).[9] Optically pure (*R*)-**5b** exhibits a strong negative couplet ($A = 173$) around 340 nm in the CD spectrum (Fig. 2a), which can be accounted for by assuming the similar conformation in solution to realize effective exciton coupling[10] between diarylethenyl chromophores.

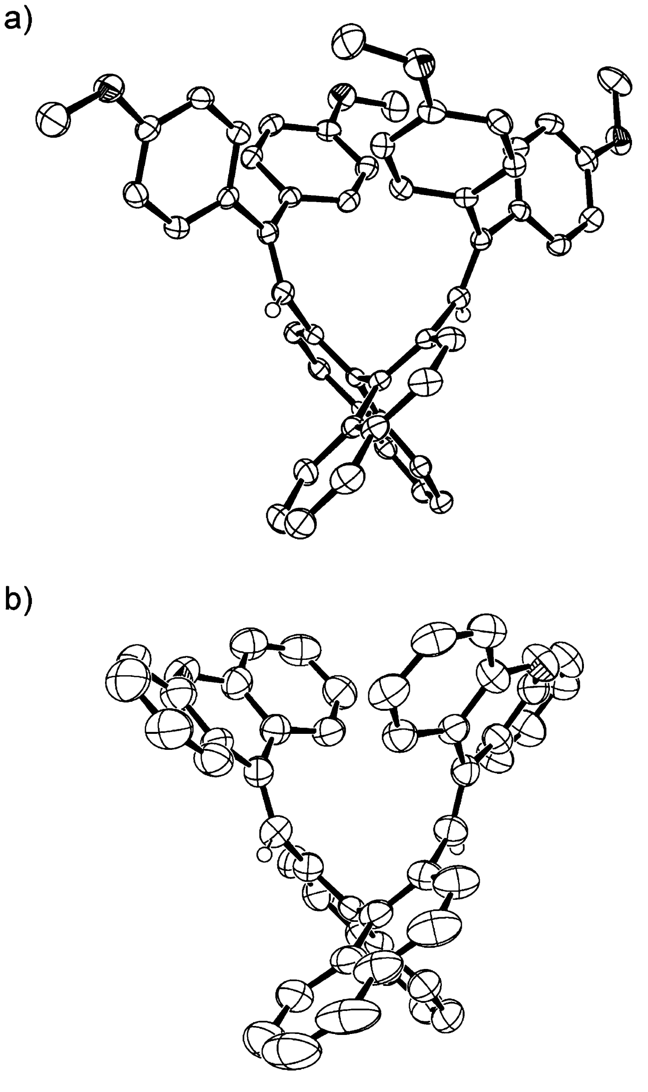


Fig. 1 (a) X-Ray structure of **5b** determined on the benzene solvate at 153 K. (b) X-Ray structure of **5c** determined at 300 K.

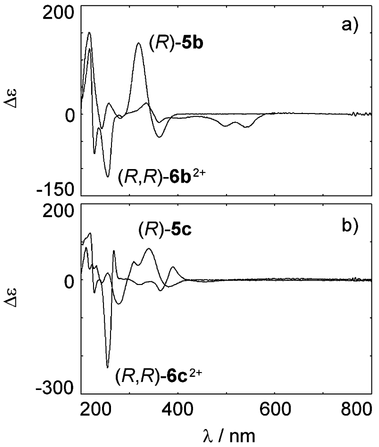
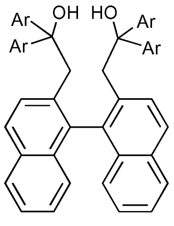


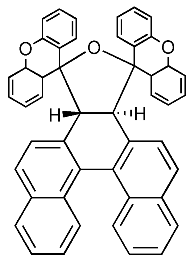
Fig. 2 (a) CD spectra of (*R*)-**5b** and (*R*,*R*)-**6b**$^{2+}$ measured in MeCN. (b) CD spectra of (*R*)-**5c** and (*R*,*R*)-**6c**$^{2+}$ measured in MeCN.

Compound *rac*-**5c** with two 9-xanthenylidene units as electron-donating groups was prepared from *rac*-dimethylbinaphthyl and xanthone *via* diol *rac*-**7c** in 80% overall yield as sparingly soluble pale yellow crystals. Solubility is much higher for (*R*)-**5c** prepared from (*R*)-dimethylbinaphthyl in 43% yield. The X-ray structure determined on *rac*-**5c** has several common features to **5b**: the binaphthyl skeleton is twisted almost perpendicularly (dihedral angle 91.5(1)°), and the separation of two methine carbons is 3.79 Å (Fig. 1b). This solid-state structure is also suitable for exciton coupling to induce strong CD signals as observed (Fig. 2b).



rac-**7b**,**c**

(**b**: Ar = MeOC$_6$H$_4$;
c: Ar$_2$C = 9-xanthenylidene)



rac-**9c**

Redox properties of 5b and reversible interconversion with 1,4-dication 6b^{2+}

According to the voltammetric study in MeCN (Fig. 3), the binaphthylic donor **5b** with four 4-methoxyphenyl groups undergoes electrochemical oxidation at a peak potential of +1.07 V, which is close to that of biphenyl analogue **3b** (E_p^{ox} +1.03 V).[7] The corresponding reduction wave appeared in the far cathodic region (E_p^{red} +0.25 V). Such a large shift of redox peaks is indicative of the chemical process such as C–C bond making that follows electron transfer.

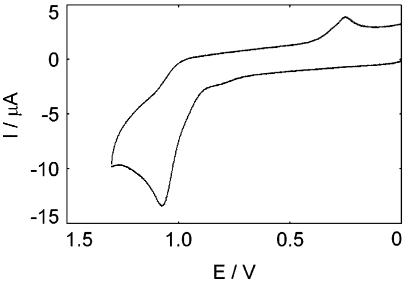


Fig. 3 Cyclic voltammogram of **5b** measured in MeCN containing 0.1 mol dm^{-3} Et$_4$NClO$_4$ (E/V *vs* SCE, scan rate 300 mV s^{-1}, Pt electrode).

Upon treatment of colorless *rac*-**5b** with 2 equivalents of (4-BrC$_6$H$_4$)$_3$N$^{+\bullet}$ SbCl$_6^-$ in CH$_2$Cl$_2$, a deep red solid was obtained in 82% isolated yield, which was assigned to the 1,4-dication salt of *rac*-**6b**$^{2+}$ on the basis of the ^{1}H NMR spectrum with a sharp singlet at δ 6.16 for acidic methine protons. Its structure was finally confirmed by the X-ray analysis (*vide infra*). Treatment of this salt with Zn dust in MeCN gave the starting diolefin *rac*-**5b** in quantitative yield. Such a high-yield interconversion indicates that **5b** and **6b**$^{2+}$ can be considered as a sort of reversible redox pair (dynamic redox pair),[6] for which the C–C bond making/breaking is accompanied by 2e-transfer.

X-Ray structure of dication 6b^{2+} and alkaline hydrolysis to bis(quinonemethide) 8b

The dication **6b**$^{2+}$ is located on the crystallographic 2-fold axis, and the newly formed central 6-membered ring adopts the half-chair conformation (Fig. 4a). The bulky diarylmethylium units are located on the pseudo-equatorial positions. Absence of *meso*-isomer of **6b**$^{2+}$ upon oxidation of **5b** can be accounted for by its larger steric hindrance caused by positioning one of the two bulky dye units at the pseudo-axial position. The acidic methine protons of **6b**$^{2+}$ are located at the pseudo-axial positions and concealed deeply inside the aryl π cloud. So that, the bases are prevented from approaching these protons. At the same time, the largely twisted arrangement of the C–H σ orbital and the vacant p orbital of the methylium center (dihedral angle of *ca.* 60°) also disfavors deprotonation of **5b** to the conjugated diene.

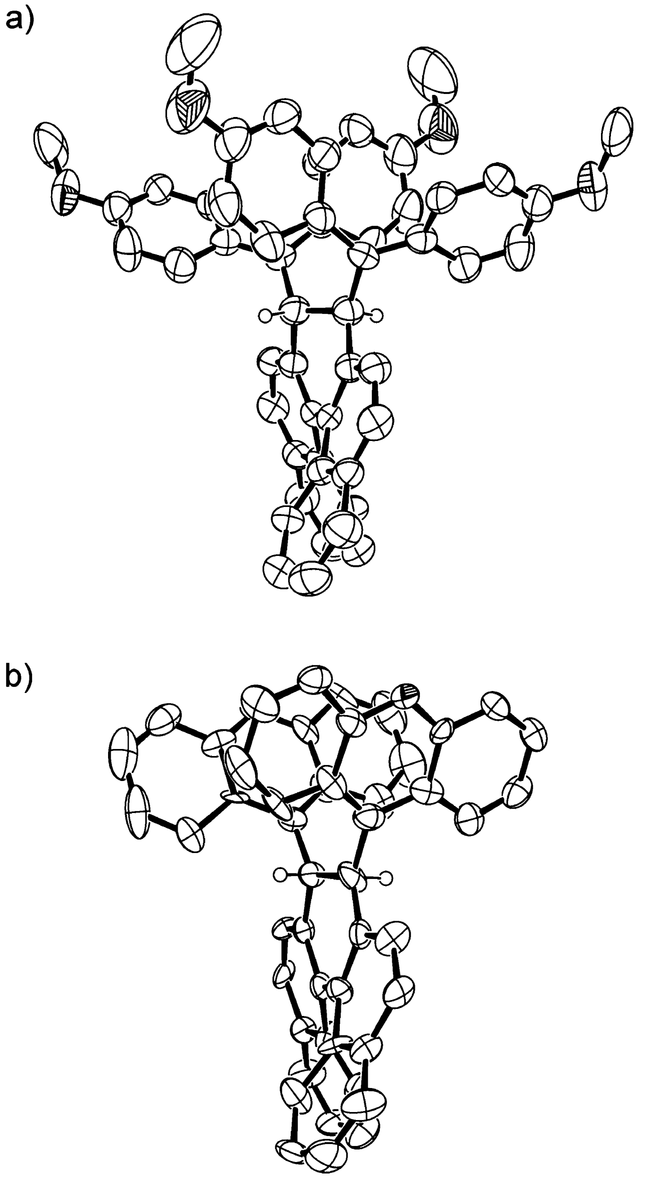
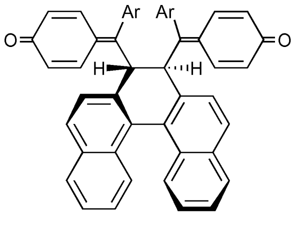
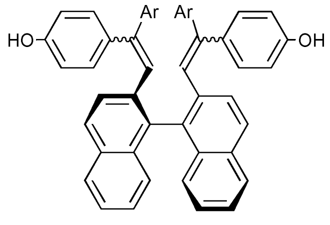


Fig. 4 (a) X-Ray structure of **6b**$^{2+}$ determined on the SbCl_6^- salt at 300 K. (b) X-Ray structure of **6c**$^{2+}$ determined on the SbCl_6^- salt (dichloromethane solvate) at 153 K.

In fact, the 1,4-dication **6b**$^{2+}$ is definitely stable under ambient conditions, and several attempts at deprotonation even by using small bases such as F$^-$ or H$^-$ caused recovery of **6b**$^{2+}$ or formation of intractable material. When the salt of *rac*-**6b**$^{2+}$ was treated with aqueous NaOH solution, the bis(quinonemethide) derivative *rac*-**8b** was obtained in quantitative yield, which is the hydrolysis product at the methoxy terminus of the diarylmethylium dyes.[11a] These results clearly show that steric bulkiness[11b,c] by the dihydro[5]helicene framework in **6b**$^{2+}$ suppresses nucleophilic attack on the methylium centers or abstraction of acidic C–H protons by base, showing the validity of our molecular design concept for the sterically stabilized 1,4-dications. Upon similar alkaline hydrolysis of *rac*-**6a**$^{2+}$ with quadruple 4-dimethylamino substitution[4b] *rac*-**8a** was also obtained in quantitative yield.



(*S*,*S*)-**8a**,**b**



(*R*)-**10a**,**b**

(**a**: Ar = $\text{Me}_2\text{NC}_6\text{H}_4$; **b**: Ar = MeOC_6H_4)

Redox properties of 5c and reversible interconversion with 1,4-dication 6c^{2+}

In view of the success in isolating the 1,4-dication **6b**$^{2+}$ with four 4-methoxyphenyl groups, less sterically hindered **6c**$^{2+}$ with two xanthenylium units was chosen as the next target. As shown by comparisons of the pK_{R^+} values of 9-phenylxanthenylium (0.81)[8c] and $(4\text{-MeOC}_6\text{H}_4)_2\text{CPh}^+$, the former is the thermodynamically more stable cation. Thus, **6c**$^{2+}$ may still have a chance to be a persistent species despite the lesser degree of kinetic protection than for **6b**$^{2+}$.

The oxidation potential of diolefin **5c** ($E_\mathrm{p}^{\mathrm{ox}}$ +0.94 V) is slightly less positive than that of **5b**, and the corresponding reduction peak was again observed in the far cathodic region ($E_\mathrm{p}^{\mathrm{red}}$ +0.22 V). Upon treatment of pale yellow *rac*-**5c** with 2 equivalents of $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{+\bullet}$ SbCl_6^- in CH_2Cl_2, a greenish yellow solid of the 1,4-dication salt *rac*-**6c**$^{2+}$ $(\text{SbCl}_6^-)_2$ was obtained in good isolated yield of 82%, which regenerated the starting diolefin *rac*-**5c** in 97% yield upon treatment with Zn dust in MeCN. The X-ray analysis of the salt indicates that **6c**$^{2+}$ adopts a similar geometry to **6b**$^{2+}$ (Fig. 4b).

In this way, we could demonstrate that the 1,4-dication with xanthenylium units is also a stable and persistent species that does not undergo facile deprotonation. When *rac*-**6c**$^{2+}$ $(\text{SbCl}_6^-)_2$ was treated with aqueous NaHCO_3 in MeCN, tetrahydrofuran derivative *rac*-**9c** was obtained in 84% yield. Its structure was unambiguously determined by X-ray analysis (Fig. 5), and the two methine protons are located in the *trans* manner at the pseudo-axial positions. In contrast to the reaction of tetrakis(4-methoxyphenyl) derivative **6b**$^{2+}$, hydroxide ion did attack the cationic center of **6c**$^{2+}$. This is in accord with the less hindered structure of **6c**$^{2+}$ than **6b**$^{2+}$. It is noteworthy that the adjacent methine protons remain intact. These results indicate that the E1 process of **6c**$^{2+}$ to form the corresponding diene is completely suppressed due to the severe steric hindrance in the deprotonated product.

Electrochiroptical response of chiral redox pairs: (*R*)-5b,c and 6b,c^{2+}

The high yield interconversion between **5b**,**c** and **6b**,**c**$^{2+}$ indicates that they can be considered as a sort of reversible redox pair. The C–C bond making/breaking accompanied by electron

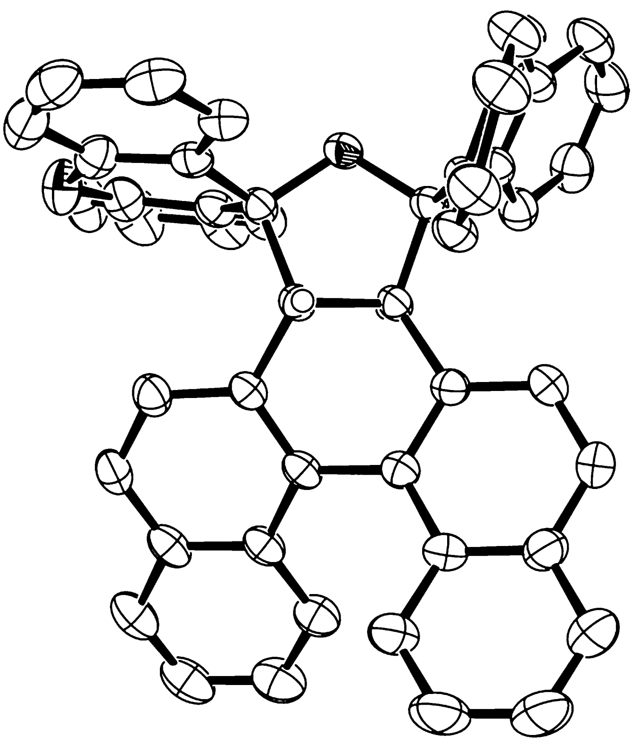


Fig. 5 X-Ray structure of **9c** determined on the chloroform solvate at 300 K. The dihedral angle of two naphthalene units is 48.3(1)°. The central 6-membered ring adopts the half-chair conformation, to which the tetrahydrofuran ring is fused in a *trans* fashion.

transfer (dynamic redox properties)[6] endows the pairs with high electrochemical bistability. A drastic color difference between **5b,c** and **6b,c**$^{2+}$ prompted us to explore their electrochemical response in solution, which was first followed by UV-Vis spectroscopy.

When the electrolysis of *rac*-**5b** [λ_{max} 325 nm (log ε 4.63)] was monitored, smooth and clean oxidation to *rac*-**6b**$^{2+}$ [506 (4.81)] was observed with a vivid change in color from colorless to deep red. The spectroelectrogram exhibits several isosbestic points, indicating the negligible concentration of the intermediary cation radical (Fig. 6a). Such behavior has been commonly observed in dynamic redox pairs,[6] and provides favorable conditions to realize molecular response systems with high reversibility by reducing the chance of side reactions from the labile open-shell species.[2b]

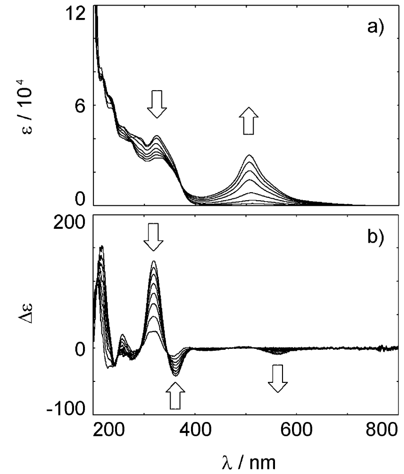


Fig. 6 (a) Changes in the UV-Vis spectrum of *rac*-**5b** (3 mL, 3.94 × 10^{-5} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} Bu_4NBF_4 as a supporting electrolyte) to *rac*-**6b**$^{2+}$ upon constant-current electrochemical oxidation (30 μA, 5 min intervals). (b) Changes in the CD spectrum of optically pure (*R*)-**5b** (3 mL, 1.07 × 10^{-5} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} Bu_4NBF_4 as a supporting electrolyte) to (*R*,*R*)-**6b**$^{2+}$ upon constant-current electrochemical oxidation (30 μA, 5 min intervals).

When a similar electrochemical oxidation was conducted by using optically pure (*R*)-**5b** and followed by CD spectroscopy, drastic changes with several isosbestic points were observed as shown in Fig. 6b. Thus, the redox pair of (*R*)-**5b** and (*R*,*R*)-**6b**$^{2+}$ provides a new entry into electrochiroptical systems,[4b,12] the less well-developed category of multi-output response systems. In the preparative scale experiments, (*R*)-**5b** was converted to the salt of (*R*,*R*)-**6b**$^{2+}$ in 82% yield, which regenerated (*R*)-**5b** in quantitative yield. These transformations did not cause any deterioration of optical purity.

Compared with bis(4-methoxyphenyl)methylium, the xanthenylium chromophore does not exhibit strong absorption in the long-wavelength region. So that, the electrolysis of *rac*-**5c** [λ_{max} 346 (log ε 4.57)] to *rac*-**6c**$^{2+}$ [363 (4.61), 457 (3.80), 597 (3.37)] did not induce spectacular changes in the UV-Vis spectrum (Fig. 7a). However, huge changes were observed in the CD spectrum again with several isosbestic points. For example, molar ellipticity at 255 nm is +18 for (*R*)-**5c** which becomes −231 in the oxidized form (*R*,*R*)-**6c**$^{2+}$, thus the electrochemical input causes $\Delta\Delta\varepsilon$ of *ca.* 250 for the electrochiroptical pair of (*R*)-**5c** and (*R*,*R*)-**6c**$^{2+}$ at this wavelength. This is one of the largest CD outputs ever reported upon redox reactions. In the preparative scale experiments, (*R*)-**5c** and (*R*,*R*)-**6c**$^{2+}$ could be interconverted without decrease in optical activity.

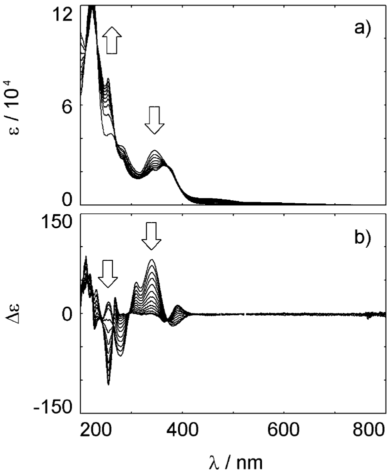
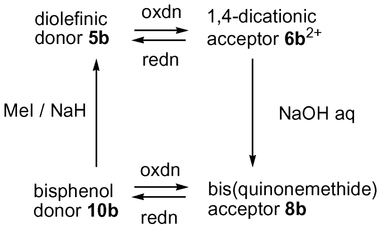


Fig. 7 (a) Changes in the UV-Vis spectrum and (b) the CD spectrum of optically pure (*R*)-**5c** (3 mL, 1.12 × 10^{-5} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} Bu_4NBF_4 as a supporting electrolyte) to (*R*,*R*)-**6c**$^{2+}$ upon constant-current electrochemical oxidation (30 μA, 5 min intervals).

Electrochiroptical response of bis(quinonemethide) 8a,b

As in the cases of *p*-quinonemethide derivatives substituted with the electron-donating unit at C7 position,[2b,11b,c] **8a** [λ_{max} 460 (log ε 4.53); E_p^{red} −1.08 V] and **8b** [375 (4.69); −1.14] exhibit remarkable absorption in the visible region. Although they are weaker electron acceptors than the corresponding dications **6a**$^{2+}$ (E_p^{red} −0.43 V) or **6b**$^{2+}$ (+0.25), their reduction may induce C–C bond cleavage to give the binaphthylic bisphenol **10a,b** (Scheme 5). In fact, treatment of *rac*-**8a,b** with SmI_2 in THF gave the bisphenol *rac*-**10a,b** in respective isolated



Scheme 5

yields of 85 and 91% (isomer mixture), which regenerated *rac*-**8a,b** upon oxidation with DDQ in 67% and quantitative yield, respectively. In this way, **8a,b** and **10a,b** are shown to constitute the interconvertible redox pair[13] that undergo C–C bond making/breaking upon 2e-transfer.

Since bisphenols are only faintly colored, interconversion between **8a,b** and **10a,b** causes a vivid color change. Fig. 8 shows the spectroelectrogram obtained upon electrochemical reduction of the quinonemethide *rac*-**8a,b**. It is evident that absorption bands in the visible region for the push–pull compound **8a,b** diminished gradually with isosbestic point. Furthermore, optically pure (*S*,*S*)-**8a,b** obtained by hydrolysis of (*R*,*R*)-**6a,b**$^{2+}$ exhibited drastic changes in CD spectrum upon electrochemical reduction to (*R*)-**10a,b** (Fig. 9). These results indicate that newly prepared bis(quinonemethide)s **8a,b** can also serve as electrochiroptical materials.

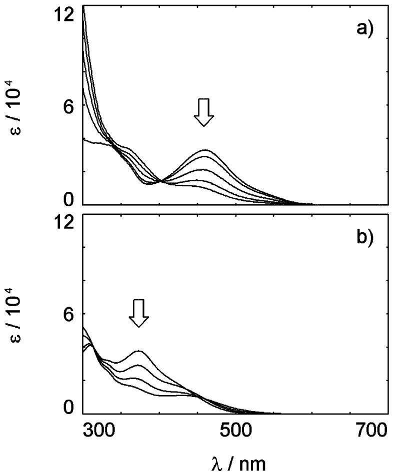


Fig. 8 (a) Changes in the UV-Vis spectrum of *rac*-**8a** (3 mL, 2.71 × 10^{-6} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} Bu_4NBF_4 as a supporting electrolyte) upon constant-current electrochemical reduction (0.1 mA, 5 min intervals). (b) Changes in the UV-Vis spectrum of *rac*-**8b** (3 mL, 6.87 × 10^{-6} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} Bu_4NBF_4 as a supporting electrolyte) upon constant-current electrochemical reduction (0.1 mA, 5 min intervals).

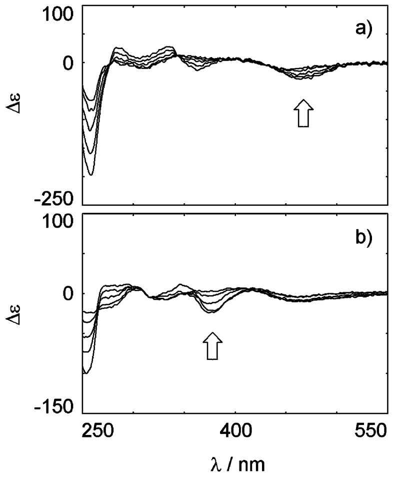


Fig. 9 (a) Changes in the CD spectrum of optically pure (*S*,*S*)-**8a** (3 mL, 2.71 × 10^{-6} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} Bu_4NBF_4 as a supporting electrolyte) upon constant-current electrochemical reduction (0.1 mA, 5 min intervals). (b) Changes in the CD spectrum of optically pure (*S*,*S*)-**8b** (3 mL, 5.89 × 10^{-6} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} Bu_4NBF_4 as a supporting electrolyte) upon constant-current electrochemical reduction (0.1 mA, 5 min intervals).

It is interesting to note that bisphenol *rac*-**10b** was easily reconverted into the tetramethoxy derivative *rac*-**5b** in 76% yield by treatment with NaH–MeI in THF. In this way, the two redox pairs, **5b**–**6b**$^{2+}$ and **8b**–**10b**, can be coupled by chemical transformation. This example provides unique a prototype to study the multi-input response systems.

Conclusion

As described in this paper, we have succeeded in stabilizing the intrinsically labile butane-1,4-diyl dication (**A**) by incorporation into the dihydro[5]helicene framework. The newly isolated dications **6b,c**$^{2+}$ are interesting dyes that serve as electrochromic systems on the basis of reversible interconversion with the binaphthylic donors **5b,c**. Configurational stability in terms of axial chirality of **5b,c** as well as point chiralities (helicity) of **6b,c**$^{2+}$ endow the present systems with the controllable chiroptical properties by electron transfer. Electrochiroptical response was also realized upon electrolysis of novel push–pull-type quinonemethides-type acceptors **8a,b**.

Experimental

Preparation of 2,2′-bis[2,2-bis(4-methoxyphenyl)ethenyl]-binaphthyl (5b)

To a solution of *rac*-2,2′-dimethylbinaphthyl (959 mg, 3.4 mmol) in dry TMEDA (1.70 mL) was added dropwise BuLi (1.58 mol dm^{-3} in *n*-hexane, 4.73 mL, 7.5 mmol) at 23 °C under Ar, and the mixture was stirred for 20 h at 70 °C. Then, to the resultant suspension of 2,2′-bis(lithiomethyl)binaphthyl was added a suspension of 4,4′-dimethoxybenzophenone (1.81 g, 7.5 mmol) in dry THF (100 mL) at −20 °C, and the suspension was kept at this temperature for 2 h. The whole mixture was allowed to warm and stirred for 4 h at 23 °C. After addition of 30 mL of water, the suspension was extracted with 1,2-dichloroethane. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of solvent followed by chromatographic separation (Al_2O_3, benzene–EtOAc) gave *rac*-2,2′-bis[2,2-bis(4-methoxyphenyl)-2-hydroxyethyl]binaphthyl *rac*-**7b** (2.19 g) as a yellow solid.

To a solution of *rac*-**7b** in benzene (150 mL) was added a catalytic amount of TsOH (17.5 mg). After the mixture was refluxed for 5 h under dehydrating conditions (Dean–Stark), the mixture was washed with water and brine, and dried over $MgSO_4$. Evaporation of solvent and chromatographic separation on Al_2O_3 (benzene) gave *rac*-**5b** (1.96 g) as a pale yellow solid in 78% yield over two steps from *rac*-2,2′-dimethylbinaphthyl. An analytical sample was obtained by recrystallization from benzene as a solvated crystal (**5b**·benzene).

Optically pure (*R*)-**5b** was similarly obtained in 66% yield over two steps by starting with (*R*)-2,2′-dimethylbinaphthyl.

Data for *rac*-5b. Mp 248–251 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.77 (2H, d, $J = 7.8$ Hz), 7.49 (2H, d, $J = 8.7$ Hz), 7.40 (2H, ddd, $J = 7.8, 7.8, 1.5$ Hz), 7.22 (2H, ddd, $J = 7.8, 7.8, 1.5$ Hz), 7.09 (2H, d, $J = 7.8$ Hz), 7.05 (2H, d, $J = 8.7$ Hz), 6.99 (4H, AA′XX′), 6.72 (4H, AA′XX′), 6.36 (4H, AA′XX′), 6.36 (2H, s), 3.76 (6H, s), 3.67 (6H, s); IR (KBr) 1604, 1510, 1249, 1173, 1033, 833, 680 cm^{-1}; FD-MS *m*/*z* 730 (M$^+$, BP), 731 (M$^+$ + 1); UV-vis (CH_3CN) λ_{max} 325 (log ε 4.63), 285 sh (4.61), 255 sh (4.68), 238 (4.77), 215 (4.91) nm. Anal. Calcd. for $C_{52}H_{42}O_4$: C, 85.45; H, 5.79. Found: C, 85.62; H, 6.00%. Data for (*R*)-**5b**: mp 143–153 °C (decomp.); $[\alpha]_{\mathrm{D}}^{27}$ +792 (*c* 0.114 in CH_3CN); CD (CH_3CN) λ 361 ($\Delta\varepsilon$ −42), 319 (131), 282 (−8), 258 (21), 243 (−26), 217 (150) nm.

Preparation of 2,2′-bis(9-xanthenylidenemethylidene)binaphthyl (5c)

To a solution of *rac*-2,2′-dimethylbinaphthyl (554 mg, 2.0 mmol) in dry TMEDA (1.5 mL) was added dropwise BuLi (1.59 mol dm^{-3} in *n*-hexane, 3.00 mL, 4.8 mol) at 24 °C under Ar, and the mixture was stirred for 20 h at 70 °C. Then, to the resultant suspension of 2,2′-bis(lithiomethyl)binaphthyl was added a solution of xanthone (935 mg, 4.8 mmol) in dry THF (50 mL) at −20 °C, and the suspension was kept at this temperature for 2 h. The whole mixture was allowed to warm and stirred for 1 h at 24 °C. After addition of 30 mL of water, the suspension was extracted with 1,2-dichloroethane. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of solvent followed by chromatographic separation (Al_2O_3, hexane–EtOAc) gave *rac*-2,2′-bis(9-hydroxy-9-xanthenylmethyl)binaphthyl **7c** (1.13 g) as a pale yellow solid.

To a solution of the diol **7c** in benzene (100 mL) was added a catalytic amount of TsOH (10.0 mg). After refluxing for 13 h under dehydrating conditions (Dean–Stark), the mixture was washed with water and brine, and dried over $MgSO_4$. Evaporation of solvent and chromatographic separation on SiO_2 ($CHCl_3$) gave *rac*-**5c** (856 mg) as a pale yellow solid in 80% yield over two steps from *rac*-2,2′-dimethylbinaphthyl. An analytical sample was obtained by recrystallization from benzene.

Optically pure (*R*)-**5c** was similarly obtained in 43% yield over two steps by starting with (*R*)-2,2′-dimethylbinaphthyl.

Data for *rac*-5c. Mp 282 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.95 (2H, d, J = 8.4 Hz), 7.82 (2H, d, J = 8.7 Hz), 7.55 (2H, d, J = 8.7 Hz), 7.51–7.46 (4H, m), 7.29–7.26 (4H, m), 7.17–7.12 (2H, m), 7.04 (2H, ddd, J = 8.4, 7.8, 1.5 Hz), 7.01 (2H, d, J = 8.7 Hz), 6.97 (2H, dd, J = 8.4, 1.2 Hz), 6.91–6.89 (4H, m), 6.52 (2H, s) 6.42 (2H, ddd, J = 7.5, 7.2, 1.5 Hz); IR (KBr) 1452, 1281, 1248, 766, 754 cm^{-1}; FD-MS m/z 638 (M$^+$, BP), 639 (M$^+$ + 1); UV-vis (CH_3CN) λ_{max} 346 (log ε 4.57), 284 (4.51), 222 (5.16) nm. Anal. Calcd. for $C_{48}H_{30}O_2$: C, 90.17; H, 4.61. Found: C, 90.38; H, 4.70%. Data for (*R*)-**5c**: mp 160 °C (decomp.); $[\alpha]_D^{22}$ +657 (c 0.0310 in CH_3CN); CD (CH_3CN) λ 381 ($\Delta\varepsilon$ −18), 340 (82), 310 (48), 277 (−64), 256 (18), 232 (38), 223 (41), 211(86) nm.

Oxidation of diolefin 5b to dication salt $6b^{2+}(SbCl_6^-)_2$

To a solution of diolefin *rac*-**5b** benzene solvate (74.4 mg, 92 μmol) in dry CH_2Cl_2 (10 mL) was added $(4\text{-}BrC_6H_4)_3N^{+\bullet}$ $SbCl_6^-$ (149 mg, 0.18 mmol) under Ar, and the mixture was stirred for 14 h at 23 °C. Addition of dry ether (30 mL) and removal by filtration of dark green powder gave dication salt *rac*-**6b**$^{2+}$($SbCl_6^-$)$_2$ in 82% yield. Similarly, (*R*)-**5b** was transformed into (*R*,*R*)-**6b**$^{2+}$($SbCl_6^-$)$_2$ in 82% yield.

Data for *rac*-6b^{2+}(SbCl$_6^-$)$_2$. Mp 189–190 °C; ^{1}H NMR (300 MHz, CD_3CN) δ/ppm 8.07 (2H, d, J = 8.1 Hz), 7.96 (2H, d, J = 8.1 Hz), 7.83 (4H, AA′XX′), 7.63 (2H, ddd, J = 8.1, 6.6, 1.2 Hz), 7.57 (2H, d, J = 8.4 Hz), 7.43 (2H, ddd, J = 8.1, 6.6, 1.2 Hz), 7.32 (4H, AA′XX′), 7.20 (4H, AA′XX′), 7.02 (4H, AA′XX′), 7.01 (2H, d, J = 8.4 Hz), 6.16 (2H, s), 4.17 (6H, s), 3.95 (6H, s); IR (KBr) 1606, 1576, 1399, 1314, 1284, 1161 cm^{-1}; FD-MS m/z 730 (M$^+$, BP), 731 (M$^+$ + 1); UV-vis (CH_3CN) λ_{max} 506 (log ε 4.81), 339 (4.43), 316 (4.43), 272 (4.77), 220 (5.01) nm. Anal. Calcd. for $C_{52}H_{42}O_4Cl_{12}Sb_2$: C, 44.62; H, 3.02; Cl, 30.39. Found: C, 45.30; H, 3.23; Cl, 29.69%. Data for (*R*,*R*)-**6b**$^{2+}$($SbCl_6^-$)$_2$: mp 169–171 °C; CD (CH_3CN) λ 538 ($\Delta\varepsilon$ −24), 497 (−22), 362 (−15), 334 (+21), 256 (−115), 228 (−72), 218 (121) nm.

Reduction of dication salt $6b^{2+}(SbCl_6^-)_2$ to diolefin 5b

To a solution of *rac*-**6b**$^{2+}$($SbCl_6^-$)$_2$ (30 mg, 21 μmol) in CH_3CN (5 mL) was added Zn powder (20 mg, 0.31 mmol), and the mixture was stirred overnight at 24 °C. The mixture was diluted with water and extracted with benzene. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of solvent gave a pale yellow solid of diolefin *rac*-**5b** (16 mg) in quantitative yield. Similarly, (*R*,*R*)-**6b**$^{2+}$($SbCl_6^-$)$_2$ was transformed into (*R*)-**5b** in quantitative yield.

Oxidation of diolefin 5c to dication salt $6c^{2+}(SbCl_6^-)_2$

To a solution of diolefin *rac*-**5c** (103 mg, 0.16 mmol) in dry CH_2Cl_2 (70 mL) was added $(4\text{-}BrC_6H_4)_3N^{+\bullet}$ $SbCl_6^-$ (263 mg, 0.32 mmol) under Ar, and the mixture was stirred for 26 h at 23 °C. Addition of dry ether (70 mL) and removal by filtration of a dark brown powder gave dication salt *rac*-**6c**$^{2+}$($SbCl_6^-$)$_2$ in 82% yield. Similarly, (*R*)-**5c** was transformed into (*R*,*R*)-**6c**$^{2+}$($SbCl_6^-$)$_2$ in 72% yield.

Data for *rac*-6c^{2+}(SbCl$_6^-$)$_2$. Mp 183 °C (decomp.); ^{1}H NMR (300 MHz, CD_3CN) δ/ppm 8.58 (2H, dd, J = 8.7, 1.2 Hz), 8.52 (2H, dd, J = 8.7, 1.2 Hz), 8.38 (2H, ddd, J = 8.7, 6.9, 1.2 Hz), 8.31 (2H, ddd, J = 8.7, 6.9, 1.2 Hz), 8.07 (2H, dd, J = 8.7, 1.2 Hz), 8.07 (2H, dd, J = 8.7, 1.2 Hz), 8.03 (2H, dd, J = 8.7, 1.2 Hz), 7.85 (2H, d, J = 8.4 Hz), 7.73–7.62 (8H, m), 7.51 (2H, ddd, J = 8.7, 6.9, 1.5 Hz), 7.39 (2H, s) 6.85 (2H, d, J = 8.4 Hz); IR (KBr) 1596, 1576, 1538, 1512, 1365, 750 cm^{-1}; FD-MS m/z 635 (M$^+$ − 3, BP); UV-vis (CH_3CN) λ_{max} 597 (log ε 3.37), 457 (3.80), 363 (4.61), 255 (5.08), 222 (5.15) nm. Anal. Calcd. for $C_{48}H_{30}O_2Cl_{12}Sb_2$: C, 44.09; H, 2.31; Cl, 32.53. Found: C, 44.20; H, 2.56; Cl, 32.35%. Data for (*R*,*R*)-**6c**$^{2+}$($SbCl_6^-$)$_2$: mp 174 °C (decomp.); CD (CH_3CN) λ 389 ($\Delta\varepsilon$ +34), 364 (−29), 323 (−13), 268 (+78), 255 (−231), 228 (−34), 219 (+123) nm.

Reduction of dication salt $6c^{2+}(SbCl_6^-)_2$ to diolefin 5c

To a suspension of *rac*-**6c**$^{2+}$($SbCl_6^-$)$_2$ (7.7 mg, 5.9 μmol) in CH_3CN (5 mL) was added Zn powder (7.7 mg, 0.12 mmol), and the mixture was stirred overnight at 23 °C. The mixture was diluted with water and extracted with benzene. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of solvent gave a pale yellow solid of diolefin *rac*-**5c** (3.7 mg) in 97% yield. Similarly, (*R*,*R*)-**6c**$^{2+}$($SbCl_6^-$)$_2$ was transformed into (*R*)-**5b** in quantitative yield.

Hydrolysis of dication salt $6a^{2+}(I_3^-)_2$ to quinonemethide 8a

To a solution of *rac*-**6a**$^{2+}$(I_3^-)$_2$[4b] (92 mg, 60 μmol) in CH_3CN (50 mL) was added aqueous NaOH (0.1 mol dm^{-3}, 5.0 mL, 0.5 mmol), and the mixture was stirred for 6 h at 23 °C. The mixture was diluted with aqueous $Na_2S_2O_3$ and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. Filtration through an Al_2O_3 column and evaporation of solvent gave deep red solid of quinonemethide *rac*-**8a** (43 mg) in quantitative yield. An analytical sample was obtained by recrystallization from CH_3CN. Similarly, (*R*,*R*)-**6a**$^{2+}$(I_3^-)$_2$ was transformed into (*S*,*S*)-**8a** in 96% yield.

Data for *rac*-8a. Mp 223 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.94 (2H, d, J = 8.4 Hz), 7.85 (2H, d, J = 8.7 Hz), 7.52 (2H, ddd, J = 8.4, 7.8, 0.9 Hz), 7.51 (2H, d, J = 8.7 Hz), 7.42 (2H, dd, J = 9.9, 3.0 Hz), 7.36 (2H, d, J = 8.4 Hz), 7.31 (2H, ddd, J = 8.4, 7.8, 0.9 Hz), 6.77 (4H, AA′XX′), 6.73 (2H, dd, J = 10.2, 3.0 Hz), 6.43 (4H, AA′XX′), 6.34 (2H, dd, J = 9.9, 2.1 Hz), 5.94 (2H, dd, J = 10.2, 2.1 Hz), 5.18 (2H, s), 2.92 (12H, s); IR (KBr) 3429, 1629, 1595, 1503, 1172 cm^{-1}; FD-MS m/z 728 (M$^+$ + 1, BP); UV-vis (CH_3CN) λ_{max} 460 (log ε 4.53), 331 (4.51), 246 (4.73), 221 (5.00) nm. Anal. Calcd. for $C_{52}H_{42}N_2O_2 \cdot H_2O$: C, 83.84; H, 5.95, N; 3.76. Found: C, 83.55; H, 5.88; N, 3.76%. Data for (*S*,*S*)-**8a**: mp 209 °C (decomp.); CD (CH_3CN) λ 465 ($\Delta\varepsilon$ −29), 365 (−14), 336 (+31), 285 (+28), 258 (−210), 226 (−58), 216 (180) nm.

Hydrolysis of dication salt $6b^{2+}(SbCl_6^-)_2$ to quinonemethide 8b

To a solution of *rac*-**6b**$^{2+}$($SbCl_6^-$)$_2$ (130 mg, 86 μmol) in CH_3CN (100 mL) was added aqueous NaOH (0.1 mol dm^{-3}, 5.0 mL, 0.5 mmol), and the mixture was stirred for 5 min at 23 °C. The mixture was diluted with water and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. Filtration through a SiO_2 column and evaporation of solvent gave a deep yellow solid of quinonemethide *rac*-**8b** (60.6 mg) in quantitative yield. An analytical sample was obtained by recrystallization from CH_3CN as a solvated crystal (**8b**·CH_3CN). Similarly, (R,R)-**6b**$^{2+}$($SbCl_6^-$)$_2$ was transformed into (S,S)-**8b** in quantitative yield.

Data for *rac*-8b. Mp 207 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.96 (2H, d, $J = 8.1$ Hz), 7.88 (2H, d, $J = 8.4$ Hz), 7.54 (2H, dd, $J = 8.1$, 7.8 Hz), 7.47 (2H, d, $J = 8.4$ Hz), 7.37–7.29 (6H, m), 6.82 (4H, br), 6.70 (4H, AA′XX′), 6.64 (2H, dd, $J = 9.9$, 3.0 Hz), 6.35 (2H, dd, $J = 10.2$, 2.1 Hz), 6.06 (2H, dd, $J = 9.9$, 2.1 Hz), 5.05 (2H, s) 3.73 (6H, s); IR (KBr) 3438, 1632, 1604, 1505, 1254, 1168 cm^{-1}; FD-MS m/z 700 (M^+, BP), 701 ($M^+ + 1$); UV-vis (CH_3CN) λ_{max} 375 (log ε 4.69), 310 (4.51), 240 (4.69), 221 (5.01) nm. Anal. Calcd. for $C_{50}H_{36}O_4 \cdot CH_3CN$: C, 84.19; H, 5.30. Found: C, 84.55; H, 5.25%. Data for (S,S)-**8b**: mp 197 °C (decomp.); CD (CH_3CN) λ 419 ($\Delta\varepsilon$ + 20), 375 (−70), 344 (+10), 292 (+21), 255 (−180), 228 (−125), 218 (+138) nm.

Hydrolysis of dication salt 6c^{2+}($SbCl_6^-$)$_2$ to tetrahydrofuran derivative 9c

To a solution of *rac*-**6c**$^{2+}$($SbCl_6^-$)$_2$ (32.0 mg, 24 µmol) in CH_3CN (25 mL) was added 0.5 mL of saturated aqueous $NaHCO_3$, and the mixture was stirred for 30 min at 23 °C. The mixture was diluted with water and extracted with benzene. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of solvent and chromatographic separation on SiO_2 (hexane–$CHCl_3$) gave *rac*-**9c** (13.4 mg) as a colorless solid in 84% yield. An analytical sample was obtained by recrystallization from benzene–hexane as a solvated crystal (**9c**·benzene).

Data for *rac*-9c. Mp 261–264 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.79 (2H, d, $J = 8.1$ Hz), 7.60 (2H, d, $J = 8.4$ Hz), 7.42–7.29 (12H, m), 7.27–7.12 (8H, m), 7.06 (2H, ddd, $J = 7.1$, 7.0, 1.8 Hz), 6.82 (2H, ddd, $J = 7.5$, 7.5, 1.1 Hz), 5.18 (2H, s); IR (KBr) 3427, 1598, 1477, 1448, 1321, 1302, 1261, 1246, 1230, 905, 820, 761, 751, 744, 685 cm^{-1}; FD-MS m/z 654 (M^+, BP), 655 ($M^+ + 1$); UV-vis (CH_3CN) λ_{max} 355 (log ε 4.08), 341 (4.14), 327 (4.02), 287 (4.15), 243 sh (4.82), 224 (5.20) nm. Anal. Calcd. for $C_{48}H_{30}O_3 \cdot C_6H_6$: C, 88.50; H, 4.95. Found: C, 88.28; H, 4.91%.

Reduction of quinonemethide 8a to bisphenol 10a

A solution of *rac*-**8a** (29 mg, 39 µmol) in dry THF (40 mL) was degassed by bubbling with Ar, then a solution of SmI_2 in THF (0.1 mol dm^{-3}, 5 mL, 0.5 mmol) was added at 23 °C. After stirring at this temperature for 2 h, the mixture was diluted with water and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. Filtration through a Florisil column and evaporation of solvent gave a pale yellow solid of bisphenol **10a** (25 mg) in 91% yield. This material is an inseparable mixture of three isomers in terms of E- and Z-diarylethenyl units.

Data for 10a. ^{1}H NMR of major isomer (300 MHz, $CDCl_3$) δ/ppm 7.75 (2H, d, $J = 7.8$ Hz), 7.45 (2H, d, $J = 8.7$ Hz), 7.37 (2H, dd, $J = 7.8$, 7.8 Hz), 7.17 (2H, dd, $J = 7.8$, 7.8 Hz), 7.00 (2H, d, $J = 7.8$ Hz), 7.00 (2H, d, $J = 8.7$ Hz), 6.83 (4H, AA′XX′), 6.79 (4H, AA′XX′), 6.32 (2H, s), 6.27 (4H, AA′XX′), 6.23 (4H, AA′XX′), 4.62 (2H, s), 2.78 (12H, s); IR (KBr) 3417, 1608, 1510, 1356, 1261, 1225, 1197, 1168, 817 cm^{-1}; FD-HR-MS Calcd. for $C_{54}H_{44}N_2O_2$: 728.3403 Found: 728.3403.

Oxidation of bisphenol 10a to quinonemethide 8a

To a solution of *rac*-**10a** (8.2 mg, 11 µmol) in CH_2Cl_2 (5.0 mL) and water (1.0 mL) was added DDQ (11 mg, 48 µmol), and the mixture was stirred for 5 min at 23 °C. The mixture was diluted with water and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. Filtration through an Al_2O_3 column and evaporation of solvent gave 5.5 mg of quinonemethide *rac*-**8a** in 67% yield.

Reduction of quinonemethide 8b to bisphenol 10b

A solution of *rac*-**8b** CH_3CN solvate (36 mg, 48 µmol) in dry THF (20 mL) was degassed by bubbling with Ar, then a solution of SmI_2 in THF (0.1 mol dm^{-3}, 100 mL, 10 mmol) was added at 23 °C. After stirring at this temperature for 5 h, the mixture was diluted with water and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. Filtration through a Florisil column and evaporation of solvent gave a pale yellow solid of bisphenol **10b** (31 mg) in 91% yield. This material is an inseparable mixture of three isomers in terms of E- and Z-diarylethenyl units.

Data for 10b. ^{1}H NMR of major isomer (300 MHz, $CDCl_3$) δ/ppm 7.77 (2H, d, $J = 7.5$ Hz), 7.49 (2H, d, $J = 8.7$ Hz), 7.40 (2H, ddd, $J = 7.5$, 7.5, 1.2 Hz), 7.22 (2H, ddd, $J = 7.5$, 7.5, 1.2 Hz), 7.08 (2H, d, $J = 7.5$ Hz), 7.02 (2H, d, $J = 8.7$ Hz), 6.78 (4H, AA′XX′), 6.95 (4H, AA′XX′), 6.64 (4H, AA′XX′), 6.37 (4H, AA′XX′), 6.35 (2H, s), 3.68 (6H, s); IR (KBr) 3413, 1606, 1510, 1245, 1171, 1105, 1032, 833, 820 cm^{-1}; FD-HR-MS Calcd. for $C_{50}H_{38}O_4$: 702.2770 Found: 702.2771.

Oxidation of bisphenol 10b to quinonemethide 8b

To a solution of *rac*-**10b** (1.1 mg, 1.4 µmol) in CH_2Cl_2 (1.0 mL) and water (1.0 mL) was added DDQ (1.2 mg, 5.3 µmol), and the mixture was stirred for 5 min at 23 °C. The mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. Filtration through a SiO_2 column and evaporation of solvent gave 1.1 mg of quinonemethide *rac*-**8b** in quantitative yield.

Methylation of bisphenol 10b to tetrakis(methoxyphenyl) derivative 5b

To a solution of *rac*-**10b** (2.4 mg, 3.4 µmol) in dry THF (5.0 mL) was added NaH (60% oil dispersion, 1.0 mg, 25 µmol) under Ar at 0 °C, and the mixture was stirred at this temperature for 30 min. CH_3I (50 µL, 0.80 mmol) was added to the mixture. Then, the resultant mixture was allowed to warm and stirred for 30 min at 23 °C. After addition of 8 mL of water, the suspension was extracted with benzene. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of solvent followed by chromatographic purification (SiO_2, benzene) gave 1.9 mg of *rac*-**5b** in 76% yield.

Redox potential measurements

Redox potentials (E^{ox} and E^{red}) were measured by cyclic voltammetry in dry MeCN containing 0.1 mol dm^{-3} Et_4NClO_4 as a supporting electrolyte. Ferrocene undergoes one-electron oxidation at +0.38 V under the same conditions. All of the values shown in the text are in E/V *vs* SCE. All the voltammograms are irreversible because of the redox switching of single bonds, so that, the peak potentials (E_p) were given in the text.

Crystallographic study†

Crystal data for *rac*-5b benzene solvate. $C_{58}H_{48}O_4$, M 809.01, colorless prism, 0.2 × 0.2 × 0.2 mm, monoclinic $P21/c$, $a = 10.54(2)$, $b = 25.92(2)$, $c = 16.25(1)$ Å, $\beta = 100.15(2)$, $V = 4367.7(6)$ Å^3, $\rho(Z = 4) = 1.230$ g cm^{-1}. A total of 9960 unique data ($2\theta_{max} = 55°$) were measured at $T = 153$ K by a Rigaku Mercury CCD apparatus (Mo-Kα radiation, $\lambda = 0.71069$ Å, 50 kV 50 mA). Absorption correction was applied ($\mu = 0.76$ cm^{-1}). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F^2 (all data) with anisotropic temperature factors for non-hydrogen atoms.

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† CCDC reference numbers 270835–270838 and 273466. See http://dx.doi.org/10.1039/b506435j for crystallographic data in CIF or other electronic format.

Hydrogen atoms were located at the calculated positions. The final *R* and *Rw* values are 0.044 and 0.109 for 7473 reflections with $I > 2\sigma I$ and 559 parameters. Estimated standard deviations are 0.002–0.003 Å for bond lengths and 0.1–0.2° for bond angles.

Crystal data for *rac*-5c. $C_{48}H_{30}O_2$, *M* 638.76, yellow needle, 0.1 × 0.03 × 0.03 mm, monoclinic *P*21/n, $a = 11.977(3)$, $b = 24.465(6)$, $c = 12.250(4)$ Å, $\beta = 110.328(2)$, $V = 3365.8(1)$ Å^3, $\rho(Z = 4) = 1.260$ g cm^{-1}. A total of 7457 unique data ($2\theta_{max} = 55°$) were measured at $T = 293$ K by a Rigaku Mercury CCD apparatus (Mo-Kα radiation, $\lambda = 0.71069$ Å, 50 kV, 200 mA). Absorption correction was applied ($\mu = 0.75$ cm^{-1}). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F^2 (all data) with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final *R* and *Rw* values are 0.062 and 0.164 for 2329 reflections with $I > 2\sigma I$ and 451 parameters. Estimated standard deviations are 0.005–0.01 Å for bond lengths and 0.4–0.7° for bond angles.

Crystal data for *rac*-6b^{2+}(SbCl$_6^-$)$_2$. $C_{52}H_{42}Cl_{12}O_4Sb_2$, *M* 1399.84, red platelet, 0.2 × 0.2 × 0.05 mm, monoclinic *C*2/m, $a = 18.425(7)$, $b = 34.50(1)$, $c = 10.674(4)$ Å, $\beta = 115.457(3)$, $V = 6125.4(3)$ Å^3, $\rho(Z = 4) = 1.518$ g cm^{-1}. A total of 7050 unique data ($2\theta_{max} = 55°$) were measured at $T = 293$ K by a Rigaku Mercury CCD apparatus (Mo-Kα radiation, $\lambda = 0.71069$ Å, 50 kV, 200 mA). Absorption correction was applied ($\mu = 14.43$ cm^{-1}). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F^2 (all data) with the anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final *R* and *Rw* values are 0.054 and 0.160 for 1874 reflections with $I > 2\sigma I$ and 322 parameters. Estimated standard deviations for **6b**$^{2+}$ are 0.008–0.010 Å for bond lengths and 0.4–0.9°.

Crystal data for *rac*-6c^{2+}(SbCl$_6^-$)$_2$ dichloromethane solvate. $C_{50.5}H_{30}Cl_{15}O_2Sb_2$, *M* 1444.09, black platelet, 0.2 × 0.05 × 0.01 mm, orthorhombic *F*dd2, $a = 57.17(1)$, $b = 35.880(9)$, $c = 10.483(3)$ Å, $V = 21504(8)$ Å^3, $\rho(Z = 16) = 1.789$ g cm^{-1}. A total of 6324 unique data ($2\theta_{max} = 55°$) were measured at $T = 153$ K by a Rigaku Mercury CCD apparatus (Mo-Kα radiation, $\lambda = 0.71069$ Å, 50 kV, 200 mA). Absorption correction was applied ($\mu = 17.89$ cm^{-1}). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F^2 (all data) with the anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final *R* and *Rw* values are 0.056 and 0.2134 for 1582 reflections with $I > 2\sigma I$ and 611 parameters. Estimated standard deviations for **6c**$^{2+}$ are 0.02–0.03 Å for bond lengths and 1–2°.

Crystal data for *rac*-9c chloroform solvate. $C_{50}H_{32}N_3Cl_6$, *M* 893.52, colorless rod, 0.3 × 0.3 × 0.3 mm, triclinic $P\bar{1}$, $a = 11.209(4)$, $b = 12.480(5)$, $c = 16.557(7)$ Å, $\alpha = 86.02(1)$, $\beta = 89.83(1)$, $\gamma = 64.63(1)°$, $V = 2088.6(1)$ Å^3, $\rho(Z = 2) = 1.421$ g cm^{-1}. A total of 8353 unique data ($2\theta_{max} = 55°$) were measured at $T = 293$ K by a Rigaku Mercury CCD apparatus (Mo-Kα radiation, $\lambda = 0.71069$ Å, 50 kV, 200 mA). Absorption correction was applied ($\mu = 4.55$ cm^{-1}). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F^2 (all data) with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final *R* and *Rw* values are 0.068 and 0.176 for 5013 reflections with $I > 2\sigma I$ and 532 parameters. Estimated standard deviations for *rac*-**9c** are 0.003–0.005 Å for bond lengths and 0.2–0.3° for bond angles.

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