CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.200600299

Multi-input–Multi-output Molecular Response System Based on Dynamic Redox Behavior of Hexaphenylethane-type Electron Donors with the Tetrahydrophenanthrazepine Skeleton: Strong Chiroptical Signals through the Transmission of Point Chirality to Helicity

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Abstract: The title heterocyclic donors undergo reversible C−C bond formation/cleavage upon electron transfer (dynamic redox behavior). The helical sense in both neutral and cationic states is interconvertible by facile ring flipping. The π-type asymmetric center on the azepine nitrogen atom induces a significant degree of diasteromeric preference, thus endowing strong CD activity based on exciton coupling. Chiroptical properties could be modified not only by redox reactions but also by heat and protonation. The present redox pairs can serve as unprecedented three-way-input (e, H^+, Δ) and two-way-output (UV/Vis, CD) response systems.

Keywords: chirality · circular dichroism · electrochromism · molecular devices · redox systems

Introduction

Organic redox systems with asymmetric elements have recently attracted considerable attention owing to their unique ability to realize photochirogenetic reactions[1] or their novel physical properties such as chiral magnetism.[2] They are also important components of electrochiroptical systems,[3] which, like advanced electrochromic systems,[4] can transduce electrochemical input into two kinds of spectral output, that is, UV/Vis and circular dichroism (CD). Redox pairs with helicity or axial chirality are especially suitable for constructing this less-explored class of two-way-output response systems. They can give very strong CD signals ($\Delta\varepsilon \approx 50$–$150\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) by an exciton-coupling mechanism,[5] whereas chiral organic molecules with simple point chirality usually exhibit ellipticity that is too weak ($\Delta\varepsilon < 1\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) to be detected as an output signal. When the chiroptical properties of the redox pairs are further modified by external stimuli other than electric potential, they can serve as rare examples of multi-input–multi-output response systems,[6] which offer potential applications in molecular sensing. As multi-input systems are prototypes of molecular-level logic operators,[7] the functional addition of a multi-output response would endow such systems with the ability to act as parallel operating logic elements ("molecular CPU"[8]) when the proper stimuli/spectra are available as input/output signals. We report herein the preparation, chiroptical and redox properties, and X-ray structures of newly designed helical donors **1** with a series of substituents on the azepine nitrogen. We observed an unprecedented three-way-input, two-way-output response with the (*R*)-phenylethyl derivative.

Results and Discussion

Molecular Design

Reversibility and bistability of the electrochemical response are prerequisites for making use of redox couples as molecular devices.[9] In this context, the hexaphenylethane-type electron donor **2** is of interest because it exhibits a drastic change in color from colorless to deep orange upon two-electron oxidation to give the bond-dissociated bis(9-xanthenylium)-type dication $\mathbf{2}^{2+}$ (Scheme 1).[10] This dynamic redox pair exhibits a large enough separation of redox potentials ($\Delta E > 0.85$ V) to warrant electrochemical bistability ($\Delta G_{\mathrm{ET}}^{\neq} > 20\,\mathrm{kcal\,mol^{-1}}$). Furthermore, both components have suitable asymmetric elements of helicity (**2**) and axial

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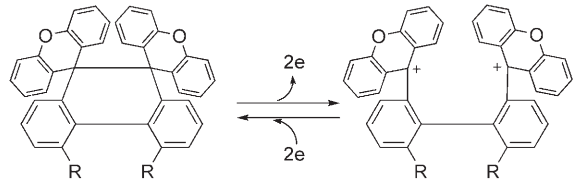
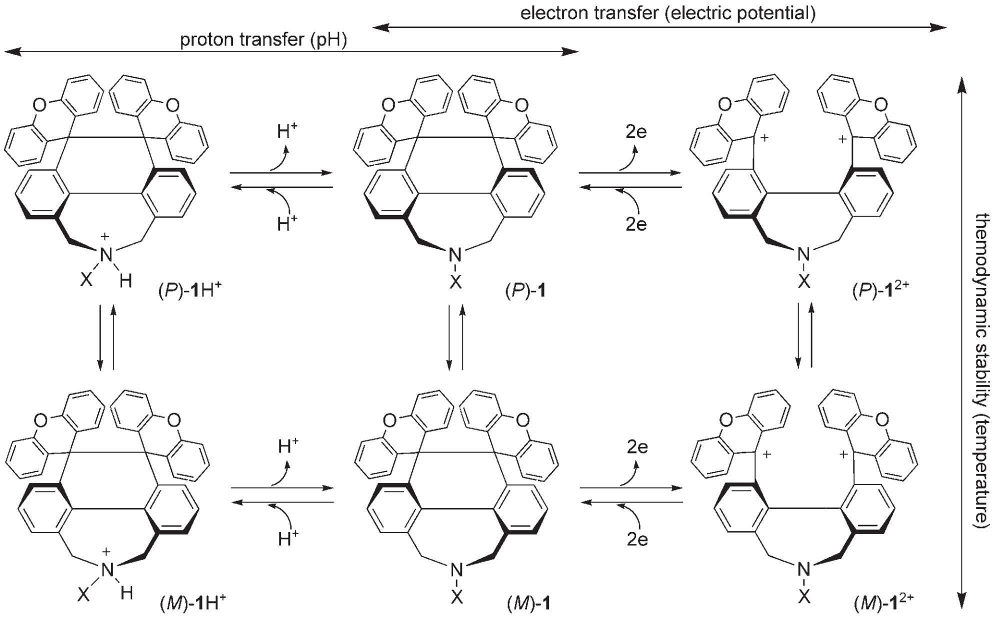


2: R = H; **3**: R = Br; **4**: R = CHO   **2**$^{2+}$: R = H; **3**$^{2+}$: R = Br

Scheme 1. Dispiro(dihydrophenanthrene)-type dynamic redox pairs.

chirality (**2**$^{2+}$) to generate strong chiroptical signals. Although their configurations are so labile that the enantiomers of this electrochromic pair interconvert rapidly ($\Delta G_{\mathrm{rac}}^{\ddagger} < 12.6$ kcal mol^{-1}), the introduction of bulky substituents in the bay region suppresses racemization. Thus, both enantiomers of dibromide **3** and **3**$^{2+}$ were isolated and interconverted without loss of optical purity upon electrolysis to give a huge electrochiroptical response.[3f]

We envisaged that the easily interconvertible helicity in **2** could be biased toward one of two directions if chirality is introduced at a proper point in the molecule. When such a helical donor exhibits a significant diastereomeric preference, strong CD signals would be obtained. Therefore, tetrahydrophenanthr[4,5-cde]azepine derivatives **1**, which may undergo facile ring flipping between two helical structures (Scheme 2), were newly designed with these considerations in mind. The azepine nitrogen atom[11] seems to be the best position for locating the chiral substituent that may induce a diastereomeric preference[12] due to steric requirements or some other weakly attractive force such as π–π interaction. As the ratio of equilibrated diastereomers is a function of the temperature, the chiroptical output could be further modified by heating or cooling the solution of **1**. Protonation of the azepine nitrogen atom may also alter the UV/Vis spectrum as well as the diastereomeric preference, so that pH could be used as a third external stimulus to change the chiroptical signals.



a: X = (*R*)-PhCHMe; *ent*-**a**: X = (*S*)-PhCHMe; **b**: X = (*R*)-1-NapCHMe; **c**: X = (*R*)-*c*HexCHMe; **d**: X = Me; **e**: X = Bn

Scheme 2. Multi-input–multi-output response system based on diastereomeric preference of dispiro(phenanthrazepine)-type donor. *c*Hex = cyclohexyl, Nap = naphthyl.

Abstract in Japanese:

新規な縮合複素環電子供与体である表題化合物は、電子授受に際して可逆なC－C結合の形成と切断を伴う動的酸化還元挙動を示す。中性状態およびジカチオン状態でのヘリシティは環反転により容易に入れ替わるが、アゼピン窒素上にパイ型不斉補助基を導入すると良好なジアステレオ選択性が誘起され、励起子相互作用に基づく強い円二色性を示す。キロオプティカル出力は、酸化還元ばかりでなく温度やプロトン化によっても変化する。これにより、本論文の化合物は前例のない三重入力（電子、プロトン、熱）－二重出力（紫外可視、円二色性）型分子応答系となることが明らかになった。

Preparation and Diastereomeric Preference

Although the title heterocyclic system in **1** is a hitherto unknown skeleton, we were able to construct it by forming the dihydroazepine ring in a manner similar to the Strecker reaction of 2,2′-diformylbiphenyl.[11b,13] Condensation of (±)-dialdehyde **4**[14] derived from (±)-dibromide **3** with primary amines gave diimine intermediates, which underwent reductive cyclization upon treatment with diisobutylaluminum hydride (DIBALH) to afford colorless crystals of **1** in moderate two-step yields of 31–43 %. By these one-pot procedures, not only simple substituents [Me (**d**) and Bn (**e**)] but also chiral auxiliaries such as (*R*)-PhMeCH (**a**), (*S*)-PhMeCH (*ent*-**a**), (*R*)-1-NapMeCH (**b**), and (*R*)-*c*HexMeCH (**c**) could be attached to the azepine nitrogen atom. The ^{1}H NMR spectrum of achiral **1e** is C_{2v}-symmetric at room temperature, indicating rapid ring flipping of the framework. With a decrease in temperature, the broad resonance for the methylene protons of dihydroazepine (3.73 ppm) was separated into two sharp doublets (3.93 and 3.55 ppm). Based on variable-temperature (VT) NMR analyses, the energy barrier for the inversion of helicity in **1e** was estimated to be 13.9 kcal mol^{-1}, which is comparable to that for the methyl derivative (**1d**: 14.1 kcal mol^{-1}). In the case of chiral amine derivatives **1a**–**c**, ^{1}H NMR spectra at −60 °C ($CDCl_3$) consist of two sets of resonances with unequal intensity, which were assigned to the diastereomers of different helicity. The isomer ratios were determined by integrating the Me resonances of the point chirality (e.g., 1.61 and 1.82 ppm for **1a**). The chiral auxiliary with an aromatic ring in **1a** and **1b** induces a significant diastereomeric preference (75:25 and 73:27, respectively),[15] whereas alicyclic substituents that are similar in size to the phenyl group in **1c** does not (55:45), suggesting that π–π interaction is an important factor in biasing the helicity.[16]

A higher helicity preference for **1a** is also observed in the solid state. According to X-ray analyses, all molecules with the (*R*)-PhMeCH group in **1a** have *M* helicity, whereas the helicity is exclusively *P* for the (*S*)-PhMeCH derivative *ent*-**1a**, so that the crystal forms have 100 % de (Figure 1). In contrast, both diastereomers coexist in a 1:1 ratio in a crystal of **1c** (Figure 2), which means 0 % de for the (*R*)-*c*Hex-MeCH derivative. Thus, we realized a significant degree of diastereomeric preference not only in the crystal but also in solution through transmission of point chirality to helicity[19] by choosing the proper asymmetric auxiliary. By comparing the shape and sign of the exciton-type CD couplets (Figure 3) to those of optically resolved dibromide **3**,[3f] the stereochemistries of the preferred helicity in solution were unambiguously determined to be *M* and *P* for the (*R*)- and (*S*)-PhMeCH derivatives **1a** and *ent*-**1a**, respectively,[20] which are the same as those in the crystal. Notably, they exhibit large CD signals ($A = 83$ at 252 nm, +20 °C) that are strong enough for them to be used as electrochiroptical materials.

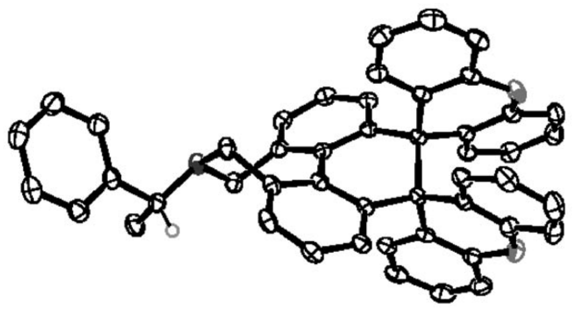


Figure 1. Molecular structure of **1a** determined by X-ray analysis at −120 °C, shown at 50 % ellipsoid probability. The absolute configuration of the point chirality is known to be *R* by chemical correlation. The central C−C bond length is 1.659(2) Å, and the twisting angle of the biphenyl skeleton is 30.8(1)°. Independent analysis of *ent*-**1a** gave parallel results.

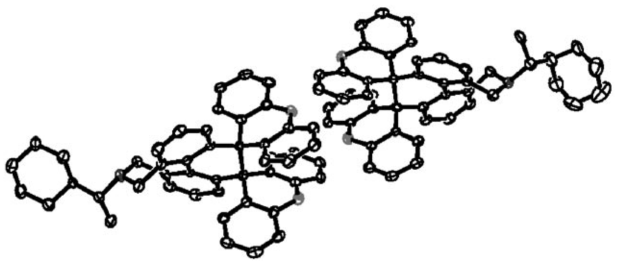


Figure 2. Molecular structure of **1c** determined by X-ray analysis at −120 °C, shown at 50 % ellipsoid probability. The absolute configuration of the point chirality is known to be *R* by chemical correlation. This crystal contains two crystallographically independent molecules in the non-centrosymmetric space group of *P*1. Attempted refinement by assuming the centrosymmetric space group $P\bar{1}$ based on several disordered atoms did not give satisfactory results. The central C−C bond length for molecule 1 (*P* helicity) is 1.630(4) Å, whereas that for molecule 2 (*M* helicity) is 1.642(4) Å. The twisting angles of the biphenyl skeleton in molecules 1 and 2 are 29.7(1) and 31.0(1)°, respectively.

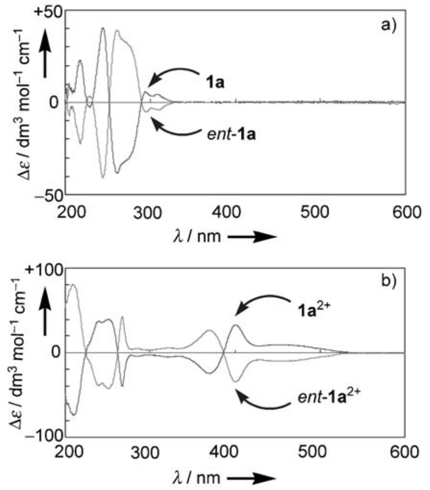


Figure 3. a) CD spectra of neutral donors in MeCN at 20 °C: (*R*)-PhMeCH derivative (**1a**) and (*S*)-PhMeCH derivative (*ent*-**1a**). b) CD spectra of dications in MeCN at 20 °C: (*R*)-PhMeCH derivative ($\mathbf{1a}^{2+}$) and (*S*)-PhMeCH derivative (ent-$\mathbf{1a}^{2+}$).

Three-way-Input, Two-way-Output Response

Upon treatment with 2 equivalents of $(p\text{-}BrC_6H_4)_3N^+\cdot SbCl_6^-$ in CH_2Cl_2, colorless **1a**–**e** afforded deep-orange dication salts $\mathbf{1a}$–$\mathbf{e}^{2+}$ $(SbCl_6^-)_2$ in high yields, which regenerated the starting donors **1a**–**e** through reduction with Zn powder in MeCN (Table 1). As commonly observed in dynamic redox systems that undergo C−C bond formation/cleavage upon electron transfer,[9] there are large separations between the oxidation potentials of **1** ($E_{ox} \approx +1.15$ V vs. saturated calomel electrode (SCE)) and the reduction potentials of $\mathbf{1}^{2+}$

Table 1. Redox potentials[a] of **1** and $\mathbf{1}^{2+}$ and their interconversion yields.

Substituent (X)	$E_{ox}(\mathbf{1})$ [V]	$\mathbf{1}^{2+[b]}$ [%]	$E_{red}(\mathbf{1}^{2+})$ [V]	$\mathbf{1}^{[c]}$ [%]
(*R*)-PhMeCH (**a**)	+1.15	94	+0.41	84
(*R*)-1-NapMeCH (**b**)	+1.19	90	+0.44	92
(*R*)-*c*HexMeCH (**c**)	+1.15	83	+0.41	92
Me (**d**)	+1.12	84	+0.42	83
Bn (**e**)	+1.18	96	+0.42	87

[a] Versus SCE in MeCN. In voltammograms of the oxidation process, we also observed ambiguous oxidation peaks at around +0.9 V in some derivatives, which may be related to electron transfer from the azepine nitrogen atom. Reduction proceeded in a two-stage-one-electron manner, and the second reduction potentials appeared at around +0.5 V. The stepwise reduction process in $\mathbf{1}^{2+}$ suggests the presence of through-space interaction between two xanthenylium units,[14] which are forced to stay in close proximity to induce large coulombic repulsion. [b] Yield of isolated $(\mathrm{SbCl_6}^-)_2$ salts from **1** upon oxidation with 2 equivalents of $(p\text{-}\mathrm{BrC_6H_4})_3\mathrm{N}^{+}\cdot\mathrm{SbCl_6}^-$ in $\mathrm{CH_2Cl_2}$. [c] Yield from $\mathbf{1}^{2+}\cdot(\mathrm{SbCl_6}^-)_2$ isolated upon reduction with excess Zn powder in MeCN.

($E_{red} \approx +0.4$ V), thus confirming the electrochemical bistability of these pairs (Figure 4). The resulting dication salt $\mathbf{1a}^{2+}$ also exhibits strong CD couplets in the visible region ($A = 57$ at 387 nm, +20 °C) (Figure 3b). This is also the case for the (*R*)-1-NapMeCH derivative $\mathbf{1b}^{2+}$, which suggests that a significant helicity preference is also induced for dications by π-type point chirality. The stereochemistry of the major diastereomer of $\mathbf{1a,b}^{2+}$ was determined to be *M* by comparing the CD spectra with those of optically resolved dicationic dibromide $\mathbf{3}^{2+}$.[3f,21]

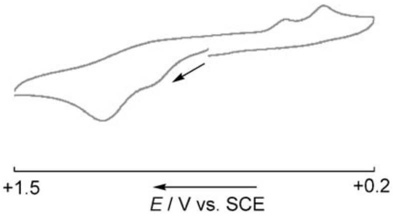


Figure 4. Cyclic voltammogram of **1a** measured in MeCN containing 0.1 M $\mathrm{Et_4NClO_4}$ (Pt electrode, scan rate 100 mV s^{-1}). Under similar conditions, the redox potentials of dibromide **3** and $\mathbf{3}^{2+}$ were +1.06 and +0.42 V, respectively.

The electrochemical response of **1a** was first examined by UV/Vis spectroscopy in MeCN, and a vivid color change occurred in two stages upon oxidation (Figure 5). When a similar electrolysis was followed by CD spectrum analysis, drastic changes in ellipticity ($\Delta\Delta\varepsilon > 30$) were also observed with several isosbestic points, again in two stages (Figure 6). This successfully demonstrates an electrochiroptical response of the present dynamic redox system. When solutions of **1a** and $\mathbf{1a}^{2+}$ were cooled from +20 to −30 °C, a steady increase in ellipticity was observed (Figure 7). Furthermore, addition of 0.5 and 1 equivalent of TsOH to a solution of **1a** in MeCN induced significant changes in the UV/Vis and CD spectra (Figure 8).

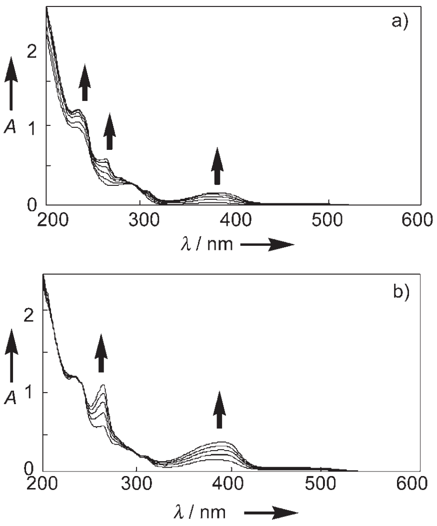


Figure 5. Continuous changes in UV/Vis spectra of **1a** (3.5 mL, 1.9×10^{-5} mol dm^{-3}) upon constant-current electrochemical oxidation (14 μA) in MeCN containing 0.05 mol dm^{-3} $n\mathrm{Bu_4NBF_4}$. a) 0–20 min (every 4 min); b) 20–52 min (every 8 min).

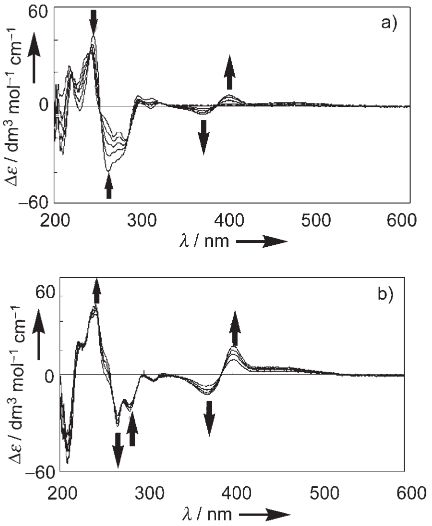


Figure 6. Continuous changes in CD spectra of **1a** (3.5 mL, 1.9×10^{-5} mol dm^{-3}) upon constant-current electrochemical oxidation (14 μA) in MeCN containing 0.05 mol dm^{-3} $n\mathrm{Bu_4NBF_4}$. a) 0–16 min (every 4 min); b) 16–48 min (every 8 min).

Conclusions

The results shown above are the first demonstration of a three-way-input, two-way-output response system. By choosing the proper chiral auxiliary, point chirality is effectively transmitted to helicity to induce strong CD signals that are essential for chiroptical response. We are now planning to attach surface-modifying functionalities so that they can be used as molecular devices.

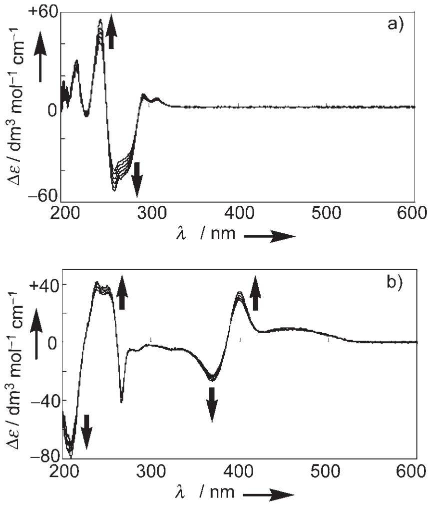


Figure 7. Continuous changes in CD spectra upon changing the solution temperature of a) neutral donor **1a** and b) dication $\mathbf{1a}^{2+}$ from +20 to −30 °C in MeCN.

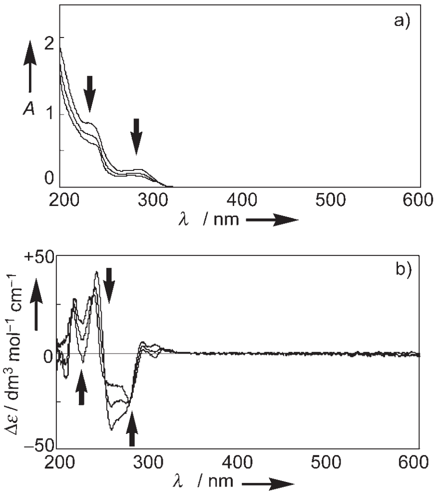


Figure 8. Changes in a) UV/Vis and b) CD spectra of neutral donor **1a** upon the addition of 0.5 and 1 equivalent of TsOH in MeCN at 20 °C.

Experimental Section

Syntheses

1: (*R*)-1-Phenylethylamine (30.5 μL, 237 μmol) and trifluoroacetic acid (2.0 μL, 26 μmol) were added to a solution of **4** (44.7 mg, 78.6 μmol) in benzene (10 mL), and the mixture was stirred under Ar at room temperature for 13 h in the presence of 4-Å molecular sieves (148 mg). After filtration, the mother liquor was concentrated. DIBALH (0.94 M in hexane, 420 μL, 395 μmol) was added to a solution of crude diimine in dry CH_2Cl_2 (2 mL). After the mixture was stirred for 2 h at room temperature, saturated aqueous potassium sodium tartrate (1 mL) was added, and stirring was continued for a further 1 h. The mixture was extracted with CH_2Cl_2, and the combined organic layer was washed with water and brine and dried over $MgSO_4$. Filtration and removal of solvent gave a yellow oil, which was separated by preparative thin-layer chromatography (PTLC; Al_2O_3, benzene). Recrystallization from benzene gave **1a** as colorless crystals (16.7 mg) in 32 % yield. M.p. > 298 °C (decomp.); $[\alpha]_D^{23}$ = −64.7° (c = 0.172, $CHCl_3$); UV/Vis (CH_3CN): λ_{max} (ε) = 232 (50500), 289 (14200), 302 nm (8520 $dm^3 mol^{-1} cm^{-1}$); CD (CH_3CN): λ_{max} ($\Delta\varepsilon$) = 309 (+4.39), 304 (+3.29), 294 (+5.85), 275 (−30.4), 268 (−32.8), 261 (−38.2), 245 (+40.6), 229 (−2.70), 218 nm (+22.7 $dm^3 mol^{-1} cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 3065, 2972, 2791, 1596, 1477, 1442, 1306, 1282, 1242, 1099, 755, 749, 739 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.62 (br d, J = 7.6 Hz, 2H), 7.45 (br dd, J = 7.6, 7.6 Hz, 2H), 7.36 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.20 (dd, J = 7.6, 7.6 Hz, 2H), 7.20–6.93 (br, 4H), 7.03 (d, J = 7.6 Hz, 2H), 7.02–6.40 (br, 10H), 5.80–5.60 (br, 2H), 4.08–3.85 (br, 3H), 3.65–3.40 (br, 2H), 1.85–1.54 ppm (br, 3H); LRMS (FD): m/z = 657 $[M]^+$ (bp = base peak); HRMS (FD): m/z calcd for $C_{48}H_{35}NO_2$: 657.2667; found: 657.2684; elemental analysis: calcd (%) for $C_{48}H_{35}NO_2 \cdot 0.25H_2O$: C 87.05, H 5.40, N 2.11; found: C 87.00, H 5.67, N 2.01.

Other derivatives were prepared by similar procedures using the corresponding primary amines. Physical and spectral data are as follows.

ent-**1a**: Yield: 39 %; $[\alpha]_D^{25}$ = +63.8° (c = 0.186, $CHCl_3$); CD (CH_3CN): λ_{max} ($\Delta\varepsilon$) = 310 (−4.13), 302 (−3.01), 295 (−5.29), 275 (+31.1), 268 (+33.9), 261 (+39.0), 244 (−40.8), 229 (+3.24), 218 nm (−22.5 $dm^3 mol^{-1} cm^{-1}$).

1b: Yield: 31 %; m.p.: 272–275 °C (decomp.); $[\alpha]_D^{23}$ = −116.8° (c = 0.192, $CHCl_3$); UV/Vis (CH_3CN): λ_{max} (ε) = 221 sh (119000), 224 (121000), 238 sh (52500), 275 (20300), 284 (22200), 293 nm (20100 $dm^3 mol^{-1} cm^{-1}$); CD (CH_3CN): λ_{max} ($\Delta\varepsilon$) = 307 (+4.81), 305 (+4.52), 294 (+10.4), 274 (−33.1), 261 (−45.6), 244 (+28.4), 225 (−48.4), 205 ppm (+54.1 $dm^3 mol^{-1} cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 3065, 2967, 1597, 1477, 1442, 1308, 1281, 1242, 1099, 781, 756, 739 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.72 (br, 1H), 7.97 (br, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.73–7.50 (br m, 3H), 7.30 (br d, J = 7.6 Hz, 2H), 7.25–6.92 (br, 4H), 7.18 (dd, J = 7.6, 7.6 Hz, 2H), 7.03 (dd, J = 7.6, 1.4 Hz, 2H), 6.92–6.38 (br m, 10H), 5.74 (br, 2H), 4.76 (br, 1H), 4.08 (br, 2H), 3.55 (br, 2H), 1.73 ppm (br, 3H); LRMS (FD): m/z = 707 $[M]^+$ (bp); elemental analysis: calcd (%) for $C_{52}H_{37}NO_2$: C 88.23, H 5.27, N 1.98; found: C 88.36, H 5.37, N 1.87.

1c: Yield: 43 %; m.p.: 251–257 °C (decomp.); $[\alpha]_D^{22}$ = +10.7° (c = 0.218, $CHCl_3$); UV/Vis (CH_3CN): λ_{max} (ε) = 233 (51400), 279 (15700), 291 nm (13900 $dm^3 mol^{-1} cm^{-1}$); CD (CH_3CN): λ_{max} ($\Delta\varepsilon$) = 277 (+5.77), 262 (+5.76), 244 (−8.11), 230 nm (+3.70 $dm^3 mol^{-1} cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 3065, 2925, 2850, 1598, 1477, 1443, 1308, 1282, 1243, 1099, 749, 739, 707 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (dd, J = 7.7, 1.1 Hz, 2H), 7.19 (dd, J = 7.7, 7.7 Hz, 2H), 7.20–7.00 (br, 6H), 7.02 (dd, J = 7.7, 1.1 Hz, 2H), 6.83–6.30 (br, 10H), 4.15- 3.50 (br, 4H), 2.79 (br, 1H), 2.12–1.67 (m, 6H), 1.44–1.04 (m, 5H), 1.23 (d, J = 6.3 Hz, 3H); LRMS (FD): m/z = 663 $[M]^+$ (bp); HRMS (FD): m/z calcd for $C_{48}H_{41}NO_2$: 663.3138; found: 663.3157; elemental analysis: calcd (%) for $C_{48}H_{41}NO_2 \cdot 0.5H_2O$: C 85.68, H 6.29, N 2.08; found: C 85.59, H 6.24, N 2.04.

1d: Yield: 42 %; m.p.: 220–223 °C; UV/Vis (CH_3CN): λ_{max} (ε) = 231 (64600), 286 nm (17900 $dm^3 mol^{-1} cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 3067, 2945, 2774, 1598, 1570, 1477, 1442, 1308, 1282, 1242, 1098, 750, 739, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (dd, J = 7.5, 1.4 Hz, 2H), 7.21 (dd, J = 7.5, 7.5 Hz, 2H), 7.20–7.00 (br, 6H), 7.06 (dd, J = 7.5, 1.4 Hz, 2H), 6.97–6.42 (br, 10H), 3.70 (br, 4H), 2.72 ppm (s, 3H); LRMS (FD): m/z = 567 $[M]^+$ (bp); elemental analysis: calcd (%) for $C_{41}H_{29}NO_2$: C 86.75, H 5.15, N 2.47; found: C 86.88, H 5.23, N 2.47.

1e: Yield: 37 %; m.p.: 264–268 °C (decomp.); UV/Vis (CH_3CN): λ_{max} (ε) = 231 (52600), 288 nm (14800 $dm^3 mol^{-1} cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 3065, 1598, 1570, 1477, 1442, 1307, 1281, 1242, 1099, 749, 738, 708 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, J = 7.5 Hz, 2H), 7.47 (dd, J = 7.5, 7.5 Hz, 2H), 7.39 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 1H), 7.21 (dd, J = 7.5, 7.5 Hz, 2H), 7.18–7.00 (br, 4H), 7.05 (dd, J = 7.5, 1.1 Hz, 2H), 6.87–6.43 (br, 10H), 6.09–5.48 (br, 2H), 4.01 (s, 2H), 4.00–3.83 ppm (br, 4H); LRMS (FD): m/z = 643 $[M]^+$ (bp); elemental analysis: calcd (%) for $C_{47}H_{33}NO_2$: C 87.69, H 5.17, N 2.18; found: C 87.75, H 5.23, N 2.12.

Oxidation of **1** to $\mathbf{1a}^{2+}$: (p-$BrC_6H_4)_3N^{+\cdot}SbCl_6^-$ (83.3 mg, 0.102 mmol) was added to a solution of **1a** (34.1 mg, 51.8 μmol) in dry CH_2Cl_2 (2.5 mL). After the mixture was stirred for 3 h under Ar, the orange suspension was diluted with diethyl ether (1.5 mL). Filtration of the orange precipitate gave $\mathbf{1a}^{2+\cdot}(SbCl_6^-)_2$ (64.4 mg) in 94 % yield. M.p.: 195–200 °C (decomp.); $[\alpha]_D^{23}$ = +438° (c = 0.182, CH_3CN); UV/Vis (CH_3CN): λ_{max}

(ε)=264 (67000), 389 (27700), 467 (4510), 501 nm (3300 dm^3 mol^{-1} cm^{-1}); CD (CH$_3$CN): $\lambda_{\max}$ ($\Delta\varepsilon$)=452 (+9.34), 429 (+7.69), 401 (+32.7), 371 (−24.7), 336 (−4.11), 321 (−5.39), 300 (−2.54), 285 (−4.46), 277 (−2.89), 267 (−39.6), 251 (+40.0), 243 (+35.3), 240 (+37.5), 209 nm (−74.3 dm^3 mol^{-1} cm^{-1}); IR (KBr): $\tilde{\nu}$=3075, 1621, 1595, 1577, 1537, 1503, 1367, 755 cm^{-1}; ^{1}H NMR (300 MHz, CD$_3$CN): δ=8.62–8.13 (m, 8H), 7.92–7.53 (m, 14H), 7.31 (d, J=8.2 Hz, 1H), 7.26 (d, J=8.2 Hz, 1H), 7.23 (d, J=8.2 Hz, 1H), 6.61 (d, J=8.2 Hz, 1H), 6.55 (d, J=8.2 Hz, 1H), 5.32 (br d, J=13 Hz, 1H), 4.68–4.20 (m, 4H), 2.00 ppm (br, 3H); LRMS (FAB): m/z=658 [M+1] (93%); HRMS (FAB): m/z calcd for $C_{48}H_{36}NO_2$: 658.2746; found: 658.2746.

Other dication salts were generated by similar procedures and obtained in yields shown in Table 1. Physical and spectral data are as follows.

ent-**1a**$^{2+}\cdot(\mathrm{SbCl_6}^-)_2$: $[\alpha]_D^{24}$=+459° (c=0.183, CH$_3$CN); CD (CH$_3$CN): $\lambda_{\max}$ ($\Delta\varepsilon$)=445 (−10.3), 428 (−8.48), 400 (−34.9), 370 (+26.5), 332 (+4.36), 320 (+5.79), 300 (+2.92), 285 (+5.00), 267 (+42.4), 252 (−42.7), 243 (−36.2), 239 (−39.1), 209 nm (+80.8 dm^3 mol^{-1} cm^{-1}).

1b$^{2+}\cdot(\mathrm{SbCl_6}^-)_2$: M.p.: 180–184 °C (decomp.); $[\alpha]_D^{24}$=+71.7° (c=0.151, CH$_3$CN); UV/Vis (CH$_3$CN): $\lambda_{\max}$ (ε)=212 sh (72200), 220 sh (84400), 225 (87000), 264 (59200), 281 sh (19300), 294 sh (12100), 382 (23400), 467 nm (4430 dm^3 mol^{-1} cm^{-1}); CD (CH$_3$CN): $\lambda_{\max}$ ($\Delta\varepsilon$)=215 (−33.8), 224 (−34.9), 226 (−38.6), 238 (+11.0), 250 (+10.1), 254 (+11.6), 267 (−16.6), 297 (+1.54), 331 (−3.09), 369 (−12.9), 397 (+16.8), 422 (+3.39), 468 nm (+5.92 dm^3 mol^{-1} cm^{-1}); IR (KBr): $\tilde{\nu}$=3078, 1621, 1595, 1575, 1547, 1537, 1502, 1486, 1367, 1064, 755 cm^{-1}; ^{1}H NMR (300 MHz, CD$_3$CN): δ=8.80–7.67 (br m, 10H), 8.40 (dd, J=7.6, 7.6 Hz, 2H), 8.16 (d, J=7.6 Hz, 2H), 8.04 (d, J=7.6 Hz, 2H), 7.82 (d, J=7.6 Hz, 2H), 7.67–7.38 (br, 6H), 7.38–7.01 (br, 3H), 6.55 (br, 2H), 5.49 (br, 2H), 4.75–4.28 (br m, 3H), 2.09 ppm (br, 3H); LRMS (FAB): m/z=708 [M+1] (55%); HRMS (FAB): calcd for $C_{52}H_{38}NO_2$: 708.2902; found: 708.2900.

1c$^{2+}\cdot(\mathrm{SbCl_6}^-)_2$: M.p.: 192–197 °C (decomp.); $[\alpha]_D^{23}$=+35.0° (c=0.138, CH$_3$CN); UV/Vis (CH$_3$CN): $\lambda_{\max}$ (ε)=264 (61600), 365 sh (20000), 389 (24700), 464 nm (3890 dm^3 mol^{-1} cm^{-1}); CD (CH$_3$CN): $\lambda_{\max}$ ($\Delta\varepsilon$)=404 (+2.77), 368 (−1.52), 266 (−1.41), 251 (+2.71), 245 (+2.04), 238 (+2.97), 213 nm (−4.06 dm^3 mol^{-1} cm^{-1}); IR (KBr): $\tilde{\nu}$=3079, 2930, 1621, 1596, 1577, 1537, 1503, 1367, 755 cm^{-1}; ^{1}H NMR (300 MHz, CD$_3$CN): δ=8.64–6.35 (br m, 22H), 5.65 (br s, 1H), 5.09 (br d, J=15 Hz, 1H), 4.95 (br t, J=15 Hz, 1H), 4.40 (br d, J=15 Hz, 1H), 4.05 (q, J=7.0 Hz, 1H), 2.00–1.09 ppm (m, 14H); LRMS (FAB): m/z=664 [M+1] (42%); HRMS (FAB): m/z calcd for $C_{48}H_{42}NO_2$: 664.3216; found: 664.3210.

1d$^{2+}\cdot(\mathrm{SbCl_6}^-)_2$: M.p.: 191–192 °C (decomp.); UV/Vis (CH$_3$CN): $\lambda_{\max}$ (ε)=264 (74400), 337 sh (10400), 387 (29800), 467 (5050), 500 nm sh (3680 dm^3 mol^{-1} cm^{-1}); IR (KBr): $\tilde{\nu}$=3077, 1621, 1595, 1576, 1537, 1502, 1368, 755cm^{-1}; ^{1}H NMR (300 MHz, CD$_3$CN): δ=8.53 (dd, J=7.8, 7.8 Hz, 2H), 8.42 (dd, J=7.8, 7.8 Hz, 2H), 8.24 (d, J=7.8 Hz, 2H), 8.16 (dd, J=7.8, 7.8 Hz, 2H), 7.86–7.76 (m, 6H), 7.58 (dd, J=7.8, 7.8 Hz, 2H), 7.54 (d, J=7.8 Hz, 1H), 7.44 (d, J=7.8 Hz, 1H), 7.30 (d, J=7.8 Hz, 1H), 7.25 (d, J=7.8 Hz, 1H), 6.58 (br d, J=7.8 Hz, 2H), 4.91 (br d, J=13 Hz, 1H), 4.64 (br dd, J=13, 13 Hz, 1H), 4.59 (dd, J=13, 13 Hz, 1H), 4.08 (br dd, J=13, 6.9 Hz, 1H), 3.12 ppm (s, 3H); LRMS (FAB): m/z=568 [M+1] (85%), 567 [M]$^+$ (75%); HRMS (FAB): m/z calcd for $C_{41}H_{30}NO_2$: 568.2276; found: 568.2304.

1e$^{2+}\cdot(\mathrm{SbCl_6}^-)_2$: M.p.: 181–185 °C (decomp.); UV/Vis (CH$_3$CN): $\lambda_{\max}$ (ε)=264 (64400), 337 sh (8980), 380 (27000), 465 (5120), 500 nm sh (3720 dm^3 mol^{-1} cm^{-1}); IR (KBr): $\tilde{\nu}$=3076, 1621, 1595, 1577, 1537, 1502, 1367, 755, 739 cm^{-1}; ^{1}H NMR (300 MHz, CD$_3$CN): δ=8.52 (br d, J=7.8 Hz, 2H), 8.42 (br dd, J=7.8, 7.8 Hz, 2H), 8.23 (dd, J=7.8, 4.0 Hz, 2H), 8.15 (d, J=7.8 Hz, 2H), 8.00–7.71 (m, 8H), 7.66–7.48 (m, 6H), 7.39 (d, J=7.8 Hz, 1H), 7.33 (d, J=7.8 Hz, 1H), 7.23 (d, J=7.8 Hz, 1H), 6.57 (br d, J=7.8 Hz, 2H), 4.87 (d, J=12 Hz, 1H), 4.65 (d, J=12 Hz, 1H), 4.60 (br s, 2H), 4.49 (d, J=12 Hz, 1H), 4.18 ppm (br dd, J=12, 12 Hz, 1H); LRMS (FAB): m/z=644 [M+1] (bp); HRMS (FAB): m/z calcd for $C_{47}H_{34}NO_2$: 644.2589; found: 644.2570.

Reduction of **1a**$^{2+}$ to **1**: Dry MeCN (1 mL) was added to a mixture of **1a**$^{2+}\cdot(\mathrm{SbCl_6}^-)_2$ (38.1 mg, 28.7 µmol) and Zn dust (22.4 mg, 0.342 mmol), and the whole mixture was stirred at room temperature for 4 h under Ar. After dilution with water, the product was extracted with benzene. The combined organic layer was washed with water and brine and dried over MgSO$_4$. After filtration and removal of solvent, the residue was purified by chromatography (Al$_2$O$_3$, benzene/hexane) to give **1a** (15.8 mg) in 84% yield.

Other dication salts were reduced by similar procedures and donors **1** were regenerated in yields shown in Table 1.

X-ray Analyses

1a: $C_{48}H_{35}NO_2$, M_r=657.81, orthorhombic, $P2_12_12_1$, a=14.095(1), b=14.193(1), c=16.469(2) Å, V=3294.5(5) Å^3, ρ (Z=4)=1.326 g cm^{-3}, T=153 K, R=2.99%.

ent-**1a**: $C_{48}H_{35}NO_2$, M_r=657.81, orthorhombic, $P2_12_12_1$, a=14.080(2), b=14.191(2), c=16.456(2) Å, V=3288.2(6) Å^3, ρ (Z=4)=1.329 g cm^{-3}, T=153 K, R=3.03%.

1c: $C_{48}H_{41}NO_2$, M_r=663.86, triclinic, $P1$, a=9.888(2), b=12.458(3), c=15.131(3) Å, α=105.385(3), β=91.321(2), γ=107.303(3)°, V=1705.2(6) Å^3, ρ (Z=2; two independent molecules)=1.293 g cm^{-3}, T=153 K, R=5.19%.

CCDC-298636 (**1a**), -298637 (**1c**), and -298638 (*ent*-**1a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the JSPS KAKENHI (No. 15350019).

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[15] Determined in $CDCl_3$. A similar value was obtained in [D$_6$]toluene (78:28).

[16] Preliminary results showed that the introduction of an electron-withdrawing group as in (*R*)-(4-FC$_6$H$_4$)MeCH induces a higher diastereomeric preference (82:18) than in the case of (*R*)-PhMeCH. As electron-deficient and -rich π systems are favored to produce stronger π–π[17] and C–H···π[18] interactions, respectively, the contribution from π–π interaction seems to be more important for the present cases.

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[20] The (*R*)-1-NapMeCH derivative **1b** also exhibits a preference for *M* helicity (Figure S1), whereas the diastereomer with *P* helicity exists in slight excess for the (*R*)-*c*HexMeCH derivative **1c** (Figure S2).

[21] The dication **1c**$^{2+}$ also prefers *M* helicity. Diastereomer ratios for the dications **1a**–**c**$^{2+}$ could not be determined by VT NMR. By assuming a similar amplitude of ellipticity for the present dications compared to that of dibromide **3**$^{2+}$ ($\Delta\varepsilon = \pm 80\,dm^3 mol^{-1} cm^{-1}$ at 400 nm), the ratios of *M*/*P* were estimated to be about 70:30, 60:40, and 52:48 for **1a**–**c**$^{2+}$, respectively.

Received: September 4, 2006