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# Electrochiroptical Response of 2,2'-(2,2-Diarylethenyl)binaphthyl-Type Electron Donors That Undergo Reversible C–C Bond Formation/Breaking upon Two-Electron Transfer

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2,2'-[2,2-Bis(4-dimethylaminophenyl)ethenyl]biphenyl (1) is a strong electron donor that undergoes oxidative C–C bond formation to give a stable dication  $rac \cdot 2^{2+}$ , the 9,10-dihydrophenanthrene derivative substituted with two bis(4-dimethylaminophenyl)methylium chromophores. This dication salt regenerates the starting diolefin 1 by reductive C–C bond breaking, thus realizing a new electrochromic system with high electrochemical bistability and a vivid change in color from yellow to deep blue. Similarly, the binaphthylic diolefin  $rac \cdot 3$  and the helicene-type dication  $rac \cdot 4^{2+}$  are interconvertible upon two-electron transfer. Both the UV–vis and CD spectra changed drastically upon electrochemical transformation between optically pure 3 and  $4^{2+}$ , which represents a new electrochiroptical system.

Electrochiroptical materials are a novel class of multioutput response systems, by which electrochemical input is transduced into two kinds of spectral output, i.e., UV-vis and circular dichroism (CD). They are promising candidates for use as chiral redox memories.<sup>1</sup> Compared with extensive studies on electrochromic materials that give UV-vis spectral changes as a sole output,<sup>2</sup> there have been only a few successful examples reported so far of those involving changes in CD spectra.<sup>3,4</sup> During the course of our continuing study on new electrochromic materials, we found that  $\beta$ , $\beta$ -bis(4-dimethylaminophenyl)styrene (5) undergoes oxidative dimerization to give a stable salt of 1,4-dication  $6^{2+}$  in quantitative yield<sup>2c</sup> (Scheme 1). This result prompted us to design novel bichromophoric redox pairs containing a biaryl skeleton, where the oxidative C-C bonding to the dication is an intramolecular process. In this way, the neutral donors and the dications are endowed with an asymmetric element of axial chirality and helicity, respectively, to realize the chiroptical response.

We report here the preparation and redox properties of biphenylic diolefin **1** and binaphthylic diolefin **3**, as

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well as their electrochromic behavior based on their reversible interconversion with the bridged dications  $\mathbf{2}^{2+}$ 

#### **SCHEME 1**



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**FIGURE 1.** Solid-state geometries of diolefins **1** and **3** determined by low-temperature X-ray analyses.

and  $4^{2+}$ , respectively. Large changes in the CD spectrum were observed during the electrolysis of enantiomerically pure binaphthylic donor **3**, which demonstrates that the optically active (*P*),(*M*)-**3** and (*P*),(*M*)-**4**<sup>2+</sup> are new electrochiroptic materials.<sup>5</sup>

### **Results and Discussion**

**Preparation and X-ray Structures of New Electron Donors, 1 and 3.** The reaction of 2,2'-bitolyl with *n*-BuLi in the presence of TMEDA gave 2,2'-bis(lithiomethyl)biphenyl,<sup>6</sup> which was then reacted with 4,4'-bis-(dimethylamino)benzophenone. The resulting diol was treated with a catalytic amount of TsOH in refluxing benzene under dehydrating conditions (Dean–Stark) to give diolefin **1** in 62% yield.<sup>7</sup> Similarly, *rac*-2,2'-dimethylbinaphthyl was converted to the racemic diolefin **3** in two steps in 63% yield. Optically pure (*P*)- and (*M*)-**3** were obtained by starting with (*S*)- and (*R*)-dimethylbinaphthyl, respectively, in 72% and 87% yield. Under these conditions, no signs of racemization were observed for (*P*)- and (*M*)-**3**, or for their synthetic intermediates.

According to the X-ray analysis, diolefin **1** adopts a pseudo- $C_2$  symmetry with a twisting angle of 57.6(1)° around the biphenyl axis (Figure S1). Two olefinic units overlap nearly in parallel [dihedral angle 22.2(1) Å] with a short atomic distance of 3.21(1) Å between the benzylidene carbons (Figure 1). In the case of binaphthyl derivative *rac*-**3**, the twisting angle of two molecular halves is 83.1(1)°, which is much larger than that in **1** due to the increased steric demand of the fused benzene rings (Figure S2). Accordingly, the dihedral angle between the two olefinic parts [29.2(2)°] and the intra-

SCHEME 2



molecular distance between benzylidene carbons [3.69-(1) Å] are marginally larger than those for **1**. These solidstate structures are quite suitable for C–C bond formation upon 2e-oxidation to give dications ( $2^{2+}$  and  $4^{2+}$ ) with 9,10-dihydrophenanthrene or dihydro[5]helicene skeletons, respectively, although the structures in solution may differ to some extent due to the high mobility of olefin units.

Redox Reactions of 1 and rac-2<sup>2+</sup>. Upon treatment of a yellow solution of 1 with 3 equiv of  $I_2$  in  $CH_2Cl_2$ , a deep blue  $I_3^-$  salt of 1,4-dication  $rac-2^{2+}$  was obtained in 98% isolated yield, and its structure was deduced from spectral data. A noteworthy feature in the <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN is the sharp singlet at 5.68 ppm, which is assigned to the two methine protons at C<sub>9</sub> and  $C_{10}$  attached in a trans orientation.  $^{9}\,As$  in the case of the previously studied 1,4-dication  $6^{2+}$ , this species is a peculiar type of carbenium ion, which has been postulated as a reactive intermediate but has not previously been isolated or even detected spectroscopically due to its instability by rapid deprotonation to the corresponding diene. For example, the structurally related electron donor 7 was reported to give the fully conjugated dication **8**<sup>2+</sup> in one pot by sequential 2e-oxidation, 2H<sup>+</sup>-detachment, and further 2e-oxidation (Scheme 2).<sup>10</sup> In the case of the surprisingly stable 1,4-dications  $2^{2+}$  and  $6^{2+}$ , the acidic methine protons are sterically shielded by several aryl groups to suppress their abstraction by base. Another factor that impairs deprotonation seems to be the nearly perpendicular arrangement of the C–H  $\sigma$  orbital and the vacant p orbital of the carbenium center, which was experimentally verified by X-ray in the case of  $4^{2+}$ with a binaphthyl moiety (vide infra). Both factors that stabilize 1,4-dications arise from the steric bulkiness of

<sup>(5)</sup> Although the chirality of binaphthyl derivatives is commonly designated by (R)/(S), the stereochemistry of **3** is shown as (P) or (M), which indicates that the configuration corresponds to the binaphthyl framework of the (P)- or (M)-dihydro[5]helicene skeleton in  $4^{2+}$ . On the basis of the (R)/(S) designation, (P)-**3** and (P)- $4^{2+}$  are assigned as (S)-**3** (axial chirality) and (S,S)- $4^{2+}$  (two asymmetric centers), respectively. Similarly, (S,S)- and (R,R)- $2^{2+}$  are shown as (P)- and (M)- $2^{2+}$ , respectively.

<sup>(6)</sup> Stavinoha, J. L.; Phillips, G. W.; Puckette, T. A.; Devon, T. J. Eur. Pat. 326268, 1989 (cf. *Chem. Abstr. 112*, 98823z).

<sup>(7)</sup> This procedure follows the reported preparation of olefin 5 (ref 8) and gives a better yield of 1 than the Wittig-Horner reaction of 2,2'-diformylbiphenyl with Ar<sub>2</sub>CHPO(OMe)<sub>2</sub>/*n*-BuLi.

<sup>(8)</sup> Matsui, M.; Tsuge, M.; Shibata, K.; Muramatsu, H. Bull. Chem. Soc. Jpn. **1994**, 67, 1753.

<sup>(9)</sup> The stereochemistry was finally confirmed by an X-ray study of a single crystal of  $2^{2+}(I_3^{-})_2$ , although the analysis is considered to be unsatisfactory due to the difficulty of obtaining complete reflection data with c > 40 Å in lattice P as well as the low quality of the crystal specimen. Crystal data:  $C_{48}H_{50}I_6N_4$ , M1444.38, tetragonal  $P4_{12}I_2$  (No. 92), a = 11.3853(6) Å, c = 41.963(2) Å, V = 5439.5(5) Å<sup>3</sup>,  $\rho(Z=4) = 1.764$  g cm<sup>-1</sup>. A total of 9671 unique data points ( $2\theta_{max} = 53.5^{\circ}$ ) were measured at T = 123 K by a Rigaku Mercury CCD apparatus (Mo K $\alpha$  radiation,  $\lambda = 0.71069$  Å). Absorption correction was applied ( $\mu = 34.61$  cm<sup>-1</sup>). The final R and Rw values are 0.122 and 0.166 for 2070 reflections with  $I > 3\sigma I$  and 262 parameters.

<sup>(10)</sup> Ohta, A.; Yamashita, Y. J. Chem. Soc., Chem. Commun. 1995, 1761.





aryl groups, which also destabilizes the deprotonated diene **9** by steric repulsion. Thus, the hindered methine protons of **2**<sup>2+</sup> could be detached by treatment with F<sup>-</sup>, a small base; however, the intense yellow diene was too susceptible to oxygen to isolate in a pure form.<sup>11</sup> Therefore, formation of **9** by treatment of **2**<sup>2+</sup> with TBAF in THF was suggested by in situ oxidation with I<sub>2</sub> to afford the I<sub>3</sub><sup>-</sup> salt of fully conjugated dication **10**<sup>2+</sup> in moderate yield (Scheme 3).

Upon treatment of  $rac \cdot 2^{2+}(I_3^-)_2$  with Zn powder in MeCN, the starting diolefin 1 was regenerated in quantitative yield. Such a high yield of interconversion shows that the pair of 1 and  $2^{2^+}$  can be considered a type of reversible redox couple, although C-C bond formation/ breaking accompanies 2e-transfer ("dynamic redox behavior"<sup>12</sup>). One option for the dynamic redox system is high electrochemical bistability, which can be measured by the difference between the irreversible redox potentials of the pair. For this couple, diolefin 1 undergoes electrochemical oxidation at +0.41 V vs SCE in MeCN, whereas the bridged dication  $2^{2+}$  is reduced at -0.41 V (Figure 2). Thus, the present couple can coexist at any proportion within a potential range of +0.41 to -0.41 V without mutual electron exchange. Another option is the negligible steady-state concentration of the intermediary cation radical during the interconversion between 1 and  $2^{2+}$ . Thus, several isosbestic points were obtained in the electrospectrogram when electrochemical oxidation was monitored by UV-vis spectroscopy (Figure 3). A very low concentration of the cation radical favors reversibility of the electrochemical response<sup>13</sup> by reducing the chance of side reactions from the reactive open-shell species. There are large differences in the spectra of yellow 1 [ $\lambda_{max}$ /nm  $(\log \epsilon)$ : 347 (sh) (4.57) ] and deep blue  $2^{2+}$  [588 (4.98)], which makes it easy to follow the progress of the reaction visually. In this way, 1 and  $2^{2+}$  were proven to represent a novel electrochromic system that exhibits a vivid change in color and high electrochemical bistability.

Although racemization between (*P*)- and (*M*)- $2^{2+}$  seems impossible,<sup>5</sup> easy rotation around the central biphenyl axis in **1** prevented us from conducting the optical



**FIGURE 2.** Cyclic voltammogram of **1** in MeCN (*EV* vs SCE, Pt electrode, scan rate 100 mV  $s^{-1}$ ).



**FIGURE 3.** Changes in the UV–vis spectrum of **1** (3.0 mL,  $2.4 \times 10^{-5}$  mol dm<sup>-3</sup> in MeCN containing 0.05 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>-NBF<sub>4</sub>) to **2**<sup>2+</sup> upon constant-current electrochemical oxidation (30  $\mu$ A, 4-min interval).

resolution of **1** as well as further studying the chiroptical response using this couple. We now turn our attention to the couple **3** and  $4^{2+}$ , which contain a binaphthyl skeleton, and in which racemization does not proceed under ambient conditions for both the neutral and dicationic species.

**Redox Reactions of Racemic and Chiral Pairs of** 3 and 4<sup>2+</sup>. According to the voltammetric measurement, binaphthylic diolefin 3 undergoes irreversible 2e-oxidation at +0.44 V, and a new peak was observed in the far cathodic region in the return cycle of the voltammogram. These features resemble the redox properties of 1 and  $2^{2+}$ , and thus the latter peak was assigned to the reduction process of the bridged dication  $4^{2+}$  (-0.40 V). In fact, the dihydro[5]helicene-type dication salt  $rac-4^{2+}$ - $(I_3)_2$  was isolated in 95% yield when *rac*-**3** was treated with 3 equiv of  $I_2$  in  $CH_2Cl_2$ . Upon treatment of this salt with Zn powder in MeCN, the starting diolefin *rac*-3 was isolated in quantitative yield. Optically active (P), (M)-3 and  $(P), (M)-4^{2+}$  were also interconvertible with a high isolated yield (>95%). All of the spectral data of the dication were in agreement with the assigned structure  $4^{2+}$ , and the two methine protons appeared at 5.72 ppm in the <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN. These protons are arranged in a trans manner over the newly formed C-C bond, as confirmed by X-ray analysis (Figure S3). This dication is also a stable species and does not lose acidic C-H protons under ambient conditions. The reluctant deprotonation can be partly accounted for by the largely twisted arrangement of the C–H  $\sigma$  orbital and the vacant p orbital of the carbenium center (62 and 70°), as observed in the solid-state structure of  $4^{2+}$ .

The sharp contrast in the UV–vis spectra of **3** [ $\lambda_{max}$ / nm (log  $\epsilon$ ): 365 (sh) (4.60)] and **4**<sup>2+</sup> [588 (5.09)] again induces a drastic change in color upon electrolysis, and the presence of several isosbestic points in the electrospectrogram from *rac*-**3** to *rac*-**4**<sup>2+</sup> indicates clean and

<sup>(11)</sup> Spectral data of **9**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm 7.78 (2H, broad d, J = 7.5 Hz), 7.23 (2H, ddd, J = 7.5, 7.5, 1.2 Hz), 7.10 (2H, dd, J = 7.5, 1.2 Hz), 7.02 (2H, broad dd, J = 7.5, 7.5 Hz), 6.81 (4H, broad AA'XX'), 6.75 (4H, broad AA'XX'), 6.59 (4H, broad AA'XX'), 6.55 (4H, broad AA'XX'), 2.94 (12H, broad s), 2.84 (12H, broad s); ESI-HRMS calcd for C<sub>48</sub>H<sub>48</sub>N<sub>4</sub> 680.3879, found 680.3881. Spectral data for **10**<sup>2+</sup>: <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN)  $\delta$ /ppm 9.02 (2H, d, J = 8.1 Hz), 7.90– 7.80 (2H, m), 7.60–7.55 (4H, m), 7.19 (8H, broad AA'XX'), 6.68 (8H, broad AA'XX'), 3.17 (24H, s); FD-MS *m*/z 680 (M<sup>+</sup>, BP), 340 (M<sup>2+</sup>). (12) Suzuki, T.; Higuchi, H.; Tsuji, T.; Nishida, J.; Yamashita, Y.;

<sup>(12)</sup> Suzuki, T.; Higuchi, H.; Tsuji, T.; Nishida, J.; Yamashita, Y.; Miyashi, T. Dynamic Redox Systems: Toward the Realization of Unimolecular Memory. In *Chemistry of Nanomolecular Systems*; Nakamura, T., Matsumoto, T., Tada, H., Sugiura, K., Eds.; Springer-Verlag: Heidelberg, Germany, 2003; Chapter 1, p 3 and references therein.

<sup>(13)</sup> Hünig, S.; Kemmer, M.; Wenner, H.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Gescheid, G. *Chem. Eur. J.* **1999**, *5*, 1969.



**FIGURE 4.** (a) Changes in the UV–vis spectrum of *rac*-**3** (3.5 mL,  $3.9 \times 10^{-5}$  mol dm<sup>-3</sup> in MeCN containing 0.05 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NBF<sub>4</sub>) to *rac*-**4**<sup>2+</sup> upon constant-current electrochemical oxidation (30  $\mu$ A, 4-min interval). (b) Changes in the CD spectrum of (*M*)-**3** (3.5 mL,  $2.1 \times 10^{-5}$  mol dm<sup>-3</sup> in MeCN containing 0.05 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NBF<sub>4</sub>) upon constant-current electrochemical oxidation (30  $\mu$ A, 4-min interval). (c) Changes in the CD spectrum of (*M*)-**4**<sup>2+</sup>(I<sub>3</sub>-)<sub>2</sub> (3.5 mL, 5.9  $\times 10^{-6}$  mol dm<sup>-3</sup> in MeCN containing 0.05 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NBF<sub>4</sub>) upon constant-current electrochemical reduction (30  $\mu$ A, 5-min interval).



**FIGURE 5.** (a) CD spectra of (*P*)- and (*M*)-**3** in MeCN; (b) CD spectra of (*P*)- and (M)-**4**<sup>2+</sup>( $I_3$ <sup>-</sup>)<sub>2</sub> in MeCN.

quantitative conversion (Figure 4a). Enantiomerically pure (*P*),(*M*)-**3** [ $\Delta \epsilon = \pm 81$  at 356 nm] and (*P*),(*M*)-**4**<sup>2+</sup> [ $\Delta \epsilon = \pm 206$  at 256 nm] exhibit very strong CD signals (Figure 5) due to exciton-coupling<sup>14</sup> between two identical chromophores, and the shapes of the neutral and dicationic species are quite different. Very large changes in the CD spectrum were observed<sup>15</sup> when a similar electrolysis was conducted with use of a chiral compound (Figure 4b,c). This pair represents a successful new entry into an electrochiroptical response system, and a noteworthy feature is that the axial chirality in binaphthyl **3** and central chiralities in dihydro[5]helicene  $4^{2+}$  can be reversibly converted<sup>16</sup> by applying an external electrochemical input.

## Conclusions

The present results show that dramatic UV–vis spectral output can be obtained by electrochemical input to new electrochromic systems (**1** and **2**<sup>2+</sup>; **3** and **4**<sup>2+</sup>) based on a biaryl skeleton with a pair of electron-donating diarylethenyl moieties<sup>17</sup>at the 2,2'-positions. A striking feature is the strong absorption maxima at 588 nm (log  $\epsilon$ , ca. 5) for the dications (**2**<sup>2+</sup> and **4**<sup>2+</sup>) thanks to the Ar<sub>2</sub>-CH<sup>+</sup> moieties. This chromophore also endows the chiral binaphthylic dications (*P*),(*M*)-**4**<sup>2+</sup> with CD output at 657 nm ( $\Delta \epsilon = \pm 18$ ), which appears at a far longer wavelength region than previously reported electrochiroptical systems containing xanthenylium-type chromophores.<sup>4</sup> Further studies on related compounds are now underway to realize electrochiroptical materials that can be fixed to a metal surface.<sup>18</sup>

### **Experimental Section**

Preparation of 2,2'-Bis[2,2-bis(4-dimethylaminophenyl)ethenyl|biphenyl (1). To a solution of 2,2'-bitolyl (311 mg, 1.7 mmol) in dry TMEDA (540 µL) was added dropwise n-BuLi (1.52 mol dm<sup>-3</sup> in *n*-hexane, 2.35 mL, 3.6 mol) at 23 °C under Ar, and the mixture was stirred for 1 h at 65 °C. Then, to the resultant suspension of 2,2'-bis(lithiomethyl)biphenyl was added a suspension of 4,4'-bis(dimethylamino)benzophenone (1.03 g, 3.8 mmol) in dry THF (15 mL) at -20 °C, and the suspension was kept at this temperature for 1 h. The whole mixture was allowed to warm and then stirred for 1 h at 23 °C. After addition of 1.0 mL of water and evaporation of solvent, the remaining solid was suspended in water and extracted with 1,2-dichloroethane. The organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Yellow solid containing 2,2'-bis[2,2-bis(4-dimethylaminophenyl)-2-hydroxyethyl]biphenyl (1.47 g) was obtained by evaporation of solvent, which was directly used for the further transformation.

To a solution of crude diol in toluene (50 mL) was added a catalytic amount of TsOH (10 mg). After the mixture was refluxed for 2 h under dehydrating conditions (Dean–Stark), evaporation of solvent and chromatographic separation on Al<sub>2</sub>O<sub>3</sub> (benzene) gave 1 (719 mg) as a yellow solid in 62% yield over two steps from 2,2'-bitolyl. An analytical sample was obtained by recrystallization from benzene. Data for 1: mp 274–280 °C dec; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm 7.21 (2H, d, J = 7.3 Hz), 7.08–7.06 (2H, m), 7.07 (4H, AA'XX'), 6.94–6.92 (4H, m), 6.91 (4H, AA'XX'), 6.59 (4H, AA'XX'), 6.37 (2H, s), 6.28 (4H, AA'XX'), 2.92 (12H, s), 2.84 (12H, s); IR (KBr) 1610, 1588, 1520, 1360, 816 cm<sup>-1</sup>; FD-MS *m/z* 682 (M<sup>+</sup>, BP);

(18) Shipway, A. N.; Willner, I. Acc. Chem. Res. 2001, 34, 421.

<sup>(14)</sup> In *Circular Dichroism: Principles and Application*; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley-VCH: New York, 2000; p 337 and references therein.

<sup>(15)</sup> Careful examination of the CD spectrum of as-prepared  $4^{2+}$  with that of isolated  $I_3^-$  salt indicated the slight difference in their shapes. This can be rationalized by assuming that as-prepared  $4^{2+}$  adopts a metastable conformation, which takes hours to transform into the relaxed form in  $4^{2+}$  of the isolated salt. In fact, the CD spectrum of (M)- $4^{2+}$  obtained by electrolysis showed gradual changes that obeyed slow first-order kinetics ( $k = 1.3 \times 10^{-5} \, \mathrm{s}^{-1}$ ) to give the final spectrum after 56 h, which is identical with that of the isolated (M)- $4^{2+}$  salt (Figure S4). Furthermore, both the as-prepared and isolated species of  $4^{2+}$  could be transformed into diolefin **3** upon electrochemical reduction, which also supports this explanation.

<sup>(16)</sup> Ohmori, K.; Kitamura, M.; Suzuki, K. Angew. Chem., Int. Ed. 1999, 38, 1226.

<sup>(17)</sup> Suzuki, T.; Yoshino, T.; Nishida, J.; Ohkita, M.; Tsuji, T. J. Org. Chem. **2000**, 65, 5514.

 $\begin{array}{l} UV-vis~(CH_{3}CN)~\lambda_{max}~347~sh~(log~\epsilon~4.57),~321~(4.65),~262~(4.61)\\ nm.~Anal.~Calcd~for~C_{48}H_{50}N_{4}:~C,~84.42;~H,~7.38;~N,~8.20.\\ Found:~C,~84.67;~H,~7.53;~N,~8.18.\\ \end{array}$ 

**Oxidation of Diolefin 1 to Dication Salt**  $2^{2+}(I_3^{-})_2$ . To a solution of diolefin **1** (50 mg, 73  $\mu$ mol) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added iodine (56 mg, 0.22 mmol) under Ar, and the mixture was stirred overnight at 23 °C. Addition of dry ether (5 mL) and removal by filtration of dark brown powder gave dication salt  $2^{2+}(I_3^{-})_2$  in 98% yield. Data for  $2^{2+}(I_3^{-})_2$ : mp 128–139 °C dec; <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN)  $\delta$ /ppm 8.09 (2H, dd, J = 7.8, 1.2 Hz), 7.50 (2H, ddd, J = 7.8, 7.8, 1.2 Hz), 7.34–7.16 (8H, br AA'XX'), 7.25 (2H, ddd, J = 7.8, 7.8, 1.2 Hz), 6.72 (8H, br AA'XX'), 3.27 (12H, br s), 3.17 (12H, br s); IR (KBr) 1584, 1408, 1376, 1166 cm<sup>-1</sup>; FD-MS m/z 682 (M<sup>+</sup>, BP), 341 (M<sup>2+</sup>); UV–vis (CH<sub>3</sub>CN)  $\lambda_{max}$  588 (log  $\epsilon$  4.98), 418 sh (4.34), 365 (4.66), 292 (4.96) nm. Anal. Calcd for C<sub>48</sub>H<sub>50</sub>N<sub>4</sub>I<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 38.48; H, 3.43; N, 3.66. Found: C, 38.20; H, 3.40; N, 3.30.

**Reduction of Dication Salt**  $2^{2+}(I_3^{-})_2$  **to Diolefin 1.** To a suspension of  $2^{2+}(I_3^{-})_2$  (30 mg, 21  $\mu$ mol) in CH<sub>3</sub>CN (20 mL) was added Zn powder (14 mg, 0.21 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 Na<sub>2</sub>SO<sub>4</sub>. Evaporation of solvent gave a yellow solid of diolefin **1** (14 mg) in quantitative yield.

Preparation of Racemic 2,2'-Bis[2,2-bis(4-dimethylaminophenyl)ethenyl]binaphthyl (rac-3). To a solution of rac-2,2'-dimethylbinaphthyl (600 mg, 2.1 mmol) in dry TMEDA (660  $\mu$ L) was added dropwise *n*-BuLi (1.57 mol dm<sup>-3</sup> in n-hexane, 2.80 mL, 4.4 mol) at 23 °C under Ar, and the mixture was stirred for 1 h at 80 °C. Then, to the resultant suspension of 2,2'-bis(lithiomethyl)binaphthyl was added a suspension of 4,4'-bis(dimethylamino)benzophenone (1.14 g, 4.6 mmol) in dry THF (15 mL) at -15 °C, and the suspension was kept at this temperature for 1 h. The whole mixture was allowed to warm and then stirred for 1 h at 23 °C. After addition of 1.0 mL of water and evaporation of solvent, the remaining solid was suspended in water and extracted with 1,2-dichloroethane. The organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. A yellow solid containing rac-2,2'-bis[2,2-bis(4-dimethylaminophenyl)-2-hydroxyethyl]binaphthyl (1.89 g) was obtained by evaporation of solvent, which was directly used for the further transformation.

To a solution of crude diol in benzene (50 mL) was added a catalytic amount of TsOH (10 mg). After the mixture was refluxed for 4 h under dehydrating conditions (Dean-Stark), evaporation of solvent and chromatographic separation on  $Al_2O_3$  (benzene) gave rac-3 (1.05 g) as a yellow solid in 63% yield over two steps from rac-2,2'-dimethylbinaphthyl. An analytical sample was obtained by recrystallization from benzene. Data for rac-3: mp 275-280 °C dec; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm 7.74 (2Ĥ, d, J = 7.8 Hz), 7.47 (2H, d, J =8.7 Hz), 7.35 (2H, ddd, J = 7.8, 7.8, 1.5 Hz), 7.19 (2H, ddd, J = 7.8, 7.8, 1.5 Hz), 7.15 (2H, d, J = 8.7 Hz), 7.12 (2H, d, J = 7.8 Hz), 7.03 (4H, AA'XX'), 7.01 (4H, AA'XX'), 6.53 (4H, AA'XX'), 6.28 (2H, s), 6.22 (4H, AA'XX'), 2.89 (12H, s), 2.83 (12H, s); IR (KBr) 1610, 1520, 1352, 824 cm<sup>-1</sup>; FD-MS *m*/*z* 782 (M<sup>+</sup>, BP), 783 (M<sup>+</sup> + 1); UV-vis (CH<sub>3</sub>CN)  $\lambda_{max}$  352 sh (log  $\epsilon$ 4.55), 330 (4.56), 260 (4.82), 207 (5.04) nm. Anal. Calcd for C<sub>56</sub>H<sub>54</sub>N<sub>4</sub>: C, 85.90; H, 6.95; N, 7.16. Found: C, 86.16; H, 7.20; N, 6.86.

**Preparation of Chiral 2,2'-Bis[2,2-bis(4-dimethylaminophenyl)ethenyl]binaphthyl ((P)- and (M)-3).** Chiral (P)and (M)-3 were obtained from (S)- and (R)-2,2'-dimethylbinaphthyl by the similar procedure to *rac*-3 in 72% and 87% yield, respectively. To confirm that the heat treatment in the above procedure induces no racemization of the products and synthetic intermediates, lithiation and dehydration processes were conducted below room temperature in other experiments as follows. The resulting products exhibit the identical optical activities to those obtained through the heated processes.

To a solution of (S)-2,2'-dimethylbinaphthyl (430 mg, 1.5 mmol) in dry TMEDA (500 µL) was added dropwise n-BuLi (1.57 mol dm<sup>-3</sup> in *n*-hexane, 2.10 mL, 3.4 mol) at 23 °C under Ar, and the mixture was stirred for 20 h at this temperature. Then, to the resultant suspension of (S)-2,2'-bis(lithiomethyl)binaphthyl was added a suspension of 4,4'-bis(dimethylamino)benzophenone (1.02 g, 3.8 mmol) in dry THF (15 mL) at -15<sup>o</sup>C, and the suspension was kept at this temperature for 1 h. The whole mixture was allowed to warm and then stirred for 1 h at 23 °C. After addition of 2.0 mL of water and evaporation of solvent, the remaining solid was suspended in water and extracted with 1,2-dichloroethane. The organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. A yellowish brown solid containing (S)-2,2'-bis[2,2-bis(4-dimethylaminophenyl)-2-hydroxyethyl]binaphthyl (2.79 g) was obtained by evaporation of solvent, which was directly used for the further transformation. Dehydration was carried out by passing a solution of crude diol in benzene through a SiO<sub>2</sub> column. Reprecipitaion from benzene solution by adding methanol at 23 °C gave (P)-3 (285 mg) as a yellow solid in 24% yield over two steps from (P)-2,2'-dimethylbinaphthyl. Similarly, (R)-2,2'dimethylbinaphthyl was transformed into (*M*)-**3** in 31% yield. Data for (P)-3: mp 178-190 °C dec; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) is identical with that for *rac*-**3**;  $[\alpha]^{25}_{D}$  –1048 (*c* 0.92 in CH<sub>3</sub>CN); CD (CH<sub>3</sub>CN)  $\lambda$  404 ( $\Delta \epsilon$  +44), 357 (-83), 307 (-44), 293 (-41), 262 (+27), 231 (-70), 213 (-78) nm. Data for (M)-3: mp 177-185 °C dec; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) is identical with that for *rac*-**3**;  $[\alpha]^{25}_{D}$  –1024 (*c* 0.81 in CH<sub>3</sub>CN); CD (CH<sub>3</sub>-CN)  $\lambda$  404 ( $\Delta \epsilon$  -41), 355 (+81), 309 (+42), 294 (+40), 262 (-26), 231 (+71), 212 (+75) nm.

**Oxidation of Diolefin 3 to Dication Salt 4<sup>2+</sup>(I<sub>3</sub><sup>-</sup>)**<sub>2</sub>. To a solution of diolefin rac-3 (50 mg, 64  $\mu$ mol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added iodine (54 mg, 0.21 mmol) under Ar, and the mixture was stirred overnight at 23 °C. Addition of dry ether (10 mL) and removal by filtration of dark brown powder gave dication salt rac- $4^{2+}(I_3^-)_2$  in 95% yield. Similarly, (P)- and (M)-3 were transformed into (*P*)- and (*M*)- $\mathbf{4}^{2+}(\mathbf{I}_3^{-})_2$ , respectively, in 95% and 95% yield. Data for rac-4<sup>2+</sup>(I<sub>3</sub><sup>-</sup>)<sub>2</sub>: mp 218 °C dec; <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN)  $\delta$ /ppm 8.03 (2H, d, J = 8.1 Hz), 7.92 (2H, d, J = 8.6 Hz), 7.56 (2H, ddd, J = 8.1, 6.7, 1.2 Hz), 7.52(2H, d, J = 8.6 Hz), 7.45 (4H, AA'XX'), 7.37 (2H, ddd, J = 8.1, 6.7, 1.2 Hz), 7.18 (2H, d, J = 8.1 Hz), 7.03 (4H, AA'XX'), 6.79 (4H, AA'XX'), 6.63 (4H, AA'XX'), 5.73 (2H, s), 3.31 (12H, s), 3.01 (12H, s); IR (KBr) 1580, 1406, 1378, 1194, 1168 cm<sup>-1</sup>; FD-MS m/z 782 (M<sup>+</sup>, BP), 783 (M<sup>+</sup> + 1), 342 (M<sup>2+</sup>); UV-vis (CH<sub>3</sub>-CN)  $\lambda_{\text{max}}$  588 (log  $\epsilon$  5.04), 411 sh (4.52), 358 (4.85), 293 (5.11), 241 (4.77), 221 (5.10) nm. Anal. Calcd for C48H50N4I6.0.5CH2-Cl<sub>2</sub>: C, 42.76; H, 3.49; N, 3.57. Found: C, 42.84; H, 3.56; N, 3.49. Data for (*P*)- $4^{2+}(I_3^{-})_2$ : mp 152–161 °C dec; <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN) is identical with that of  $rac-4^{2+}(I_3^{-})_2$ ; CD (CH<sub>3</sub>-CN)  $\lambda$  658 (  $\Delta\epsilon$  +19), 584 (+35), 422 (+20), 389 (–14), 337 (–22), 256 (+207), 236 (-20), 227 (+57), 220 (-216) nm. Data for (M)-**4**<sup>2+</sup>(I<sub>3</sub><sup>-</sup>)<sub>2</sub>: mp 152–160 °C dec; <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>-CN) is identical with that of *rac*- $4^{2+}(I_3^-)_2$ ; CD (CH<sub>3</sub>CN)  $\lambda$  656  $(\Delta \epsilon - 18)$ , 585 (-32), 424 (-20), 388 (+15), 338 (+24), 256 (-206), 236 (+22), 227 (-51), 220 (+218) nm.

**Reduction of Dication Salt**  $4^{2+}(I_3^{-})_2$  **to Diolefin 3.** To a suspension of  $rac \cdot 4^{2+}(I_3^{-})_2$  (50 mg, 32 µmol) in CH<sub>3</sub>CN (20 mL) was added Zn powder (21 mg, 0.32 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 Na<sub>2</sub>SO<sub>4</sub>. Evaporation of solvent gave a yellow solid of diolefin **3** (25 mg) in quantitative yield. Similarly, (*P*)- and (*M*)- $4^{2+}(I_3^{-})_2$  were transformed into (*P*)- and (*M*)-**3**, respectively, in 98% and 95% yield.

**Redox Potential Measurements.** Redox potentials ( $E^{\text{tx}}$  and  $E^{\text{red}}$ ) were measured by cyclic voltammetry in dry MeCN containing 0.1 mol dm<sup>-3</sup> Et<sub>4</sub>NClO<sub>4</sub> as a supporting electrolyte. Ferrocene undergoes 1e-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, and the half-wave potentials

were estimated from the anodic peak potentials ( $E^{\text{pa}}$ ) as  $E^{\text{bx}} = E^{\text{pa}} - 0.03$  or the cathodic peak potentials ( $E^{\text{pc}}$ ) as  $E^{\text{red}} = E^{\text{pc}} + 0.03$  V.

**X-ray Analyses.** Crystal data for 1:  $C_{48}H_{50}N_4$ , *M* 682.95, yellow rod,  $0.5 \times 0.35 \times 0.25$  mm<sup>3</sup>, triclinic *P*1, *a* = 10.215(4) Å, *b* = 12.474(4), *c* = 16.820(6) Å,  $\alpha$  = 86.39(1)°,  $\beta$  = 72.333-(1)°,  $\gamma$  = 65.84(1)°, *V* = 1858(1) Å<sup>3</sup>,  $\rho(Z=2)$  = 1.220 g cm<sup>-1</sup>. A total of 6364 unique data ( $2\theta_{max}$  = 55°) were measured at *T* = 123 K by a Rigaku Mercury CCD apparatus (Mo K $\alpha$  radiation,  $\lambda$  = 0.71069 Å). Absorption correction was applied ( $\mu$  = 0.71 cm<sup>-1</sup>). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on *F* with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final *R* and *Rw* values are 0.046 and 0.047 for 6364 reflections with *I* > 3 $\sigma$ I and 469 parameters. Estimated standard deviations are 0.002–0.003 Å for bond lengths and 0.1–0.2° for bond angles.

Črystal data for *rac*-**3**: C<sub>56</sub>H<sub>54</sub>N<sub>4</sub>, *M* 783.07, yellow plate, 0.2 × 0.2 × 0.03 mm<sup>3</sup>, triclinic *P*1, *a* = 9.715(4) Å, *b* = 11.188-(4) Å, *c* = 21.364(8) Å, *α* = 77.92(2)°, *β* = 84.80(2)°, *γ* = 71.50-(2)°, *V* = 2152(1) Å<sup>3</sup>, *ρ*(*Z*=2) = 1.208 g cm<sup>-1</sup>. A total of 9323 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). Absorption correction was applied ( $\mu$  = 0.70 cm<sup>-1</sup>). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on *F* with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final *R* and *Rw* values are 0.074 and 0.091 for 4517 reflections with *I* > 3 $\sigma$ I and 541 parameters. Estimated standard deviations are 0.007–0.009 Å for bond lengths and 0.4–0.6° for bond angles. Crystal data for  $rac 4^{2^+}(I_3^-)_2$ :  $C_{56}H_{54}I_6N_4$ , M1544.50, black rod,  $0.2 \times 0.03 \times 0.03$  mm<sup>3</sup>, monoclinic C2/c, a = 43.83(4) Å, b = 9.686(7), c = 29.76(2) Å,  $\beta = 117.71(1)^\circ$ , V = 11187(15) Å<sup>3</sup>,  $\rho(Z=8) = 1.834$  g cm<sup>-1</sup>. A total of 12326 unique data ( $2\theta_{max} = 55^\circ$ ) were measured at T = 153 K by a Rigaku Mercury CCD apparatus (Mo K $\alpha$  radiation,  $\lambda = 0.71069$  Å). Absorption correction was applied ( $\mu = 33.72$  cm<sup>-1</sup>). The structure was solved by the direct method (SIR92) and refined by the fullmatrix least-squares method on F with anisotropic temperature factors only for iodine atoms. Hydrogen atoms were located at the calculated positions. The final R and Rw values are 0.069 and 0.077 for 3438 reflections with  $I > 3\sigma I$  and 297 parameters. Estimated standard deviations are 0.001–0.02 Å for bond lengths and 0.07–1° for bond angles.

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**Supporting Information Available:** ORTEP drawings (Figures S1–S3) and CIF data for the X-ray analyses of 1, *rac*-**3**, and *rac*-**4**<sup>2+</sup>(I<sub>3</sub><sup>-</sup>)<sub>2</sub>. Time-course of the CD spectrum of asprepared (*M*)-**4**<sup>2+</sup> changing into its relaxed conformer (Figure S4), and <sup>1</sup>H NMR spectrum of **4**<sup>2+</sup> (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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