Supplementary Material

Drastic Change in Racemization Barrier upon Redox Reactions: Novel Chiral-memory Units Based on Dynamic Redox Systems

Takanori Suzuki,* Kazuhisa Wada, Yusuke Ishigaki, Yasuyo Yoshimoto, Eisuke Ohta, Hidetoshi Kawai, and Kenshu Fujiwara

<<< Spectral Data of New compounds >>>

10,10,11,11-Tetrakis(4-methoxyphenyl)-4,5,10,11-tetrahydrophenanthr[4,5-*cde*]oxepin 1a

cm.p. 243-244 °C; ^{1}H NMR (300MHz, C_6D_6, 10 °C) δ 3.09 (6H, s), 3.28 (6H, s), 4.21 (2H, d, *J*= 8.9 Hz), 4.54 (2H, d, *J*= 8.9 Hz), 6.37 (2H, br-s), 6.72 (2H, br-s), 6.98 (4H, d, *J*= 8.9 Hz) 7.01 (2H, dd, *J*= 7.3 Hz, 7.3 Hz), 7.08 (2H, d, *J*= 7.3 Hz), 7.33 (2H, br-s), 7.48 (2H, d, *J*= 7.3 Hz), 7.60 (2H, br-s); IR (KBr) ν 2999, 2950, 2833, 1606, 1579, 1509, 1460, 1437, 1372, 1291, 1254, 1184, 1146, 1120, 1083, 1037, 919, 895, 854, 826, 810, 771, 741, 688, 598, 569 cm^{-1}; LR-MS (FD) *m/z* = 648 (14), 647 (49), 646 (M^+, bp), 324 (15), 323 (M^{2+}, 34).

5,7-Dihydrodibenz[*c*,*e*]oxepin-1,11-diylbis[bis(4-methoxyphenyl)methylium] 2a^{2+} (BF_4^-)$_2$

m.p. 230-232 °C; ^{1}H NMR (300MHz, CD_3CN) δ 3.97 (6H, s), 4.13 (6H, s), 4.30 (2H, d, *J*=12.5 Hz), 4.56 (2H, d, *J*=12.5 Hz), 6.99 (4H, d, *J*=9.2 Hz), 7.04 (2H, dd, *J*=2.7 Hz, 9.1 Hz), 7.16 (4H, br-d, *J*=9.2 Hz) 7.29 (4H, br-d, *J*=7.0 Hz), 7.47 (2H, dd, *J*=2.7 Hz, 9.1 Hz), 7.53 (4H, d, *J*=7.0 Hz), 7.69 (2H, dd, *J*=2.7 Hz, 9.2 Hz); IR (KBr) ν 1761, 1609, 1577, 1507, 1461, 1373, 1276, 1159, 1083, 1056, 999, 914, 855, 762, 541 cm^{-1}; LR-MS (FAB) *m/z* = 555 ([M-2BF_4-anisole]$^+$, 8); UV-Vis (CH_2Cl_2): λ_{max} / nm (ε / M^{-1} cm^{-1}) 525 (50864), 449 (24042), 405 (24611), 272 (19262); CD spectrum of optically pure (*M*)-**2a**$^{2+}$(BF_4^-)$_2$ derived from diol (-)-**6**: λ_{ext} / nm ($\Delta\varepsilon$ / M^{-1} cm^{-1}) 559 (+182), 518 (-133), 476 (-13.0), 452 (-16.7), 404 (+37.9), 264 (+34.9)

1,11-Bis[bis(4-methoxyphenyl)hydroxymethyl]-5,7-dihydrodibenz[*c*,*e*]oxepin *rac*-4

m.p. 300-303 °C; ^{1}H NMR (300MHz, $CDCl_3$) δ 2.89 (2H, d, *J*= 11.4 Hz), 3.72 (2H, d, *J*=11.4 Hz), 3.73 (6H, s), 3.81 (6H, s), 5.17 (2H, s), 6.60 (4H, d, *J*=8.9Hz), 6.69 (4H, d, *J*=8.9Hz), 6.86 (4H, d, *J*=8.9 Hz), 6.89 (2H, dd, *J*=1.1 Hz, 7.4 Hz), 7.00 (2H, dd, *J*=1.1 Hz, 7.4 Hz), 7.17 (2H, dd, *J*=7.4 Hz, 7.4 Hz), 7.28 (4H, d, *J*=8.9 Hz); IR (KBr) ν 3329, 3306, 3007, 2933, 2835, 1606, 1580, 1508, 1466, 1442, 1421, 1296, 1246, 1113, 1033, 1001, 958, 922, 902, 863, 836, 820, 807, 799, 775, 750, 725, 670, 620, 608, 585, 558 cm^{-1}; LR-MS (FD) *m/z* = 682 (18), 681 (55), 680 (M+, bp), 663 (24), 662 (39).

Dispiro[(10-methylacridan)-9,10'(4'*H*,5'*H*,10'*H*,11'*H*)-phenanthr[4',5'-*cde*]oxepin-11',9''-(10''-methyl-acridan) 1b

m.p. 292-296 °C (decomp.); ^{1}H NMR (300MHz, $CDCl_3$) δ 2.73 (6H, s), 4.64 (4H, s), 6.13-6.39 (4H, br), 6.33 (4H, dd, *J*= 7.0 Hz, 7.0 Hz), 6.51 (4H, d, *J*= 8.2 Hz), 6.98 (4H, ddd, *J*= 1.5 Hz, 7.0 Hz, 8.2 Hz), 7.11 (2H, dd, *J*= 1.3 Hz, 7.3 Hz), 7.22 (2 H, dd, *J*= 7.3 Hz, 7.3 Hz), 7.45 (2H, dd, J= 1.3 Hz, 7.3 Hz); IR (KBr) ν 3059, 2956, 2871, 2848, 1591, 1476, 1362, 1323, 1292, 1272, 1167, 1135, 1084, 1070, 1058, 901, 868, 791, 755, 737, 697 cm^{-1}; LR-MS (FD) *m/z* = 582 (13), 581 (49), 580 (M^+, bp), 291 (6.9), 290 (M^{2+}, 15).

5,7-Dihydrodibenz[*c*,*e*]oxepin-1,11-diylbis(10-methyl-9-acridinium) $2b^{2+}$ $(OTf^-)_2$

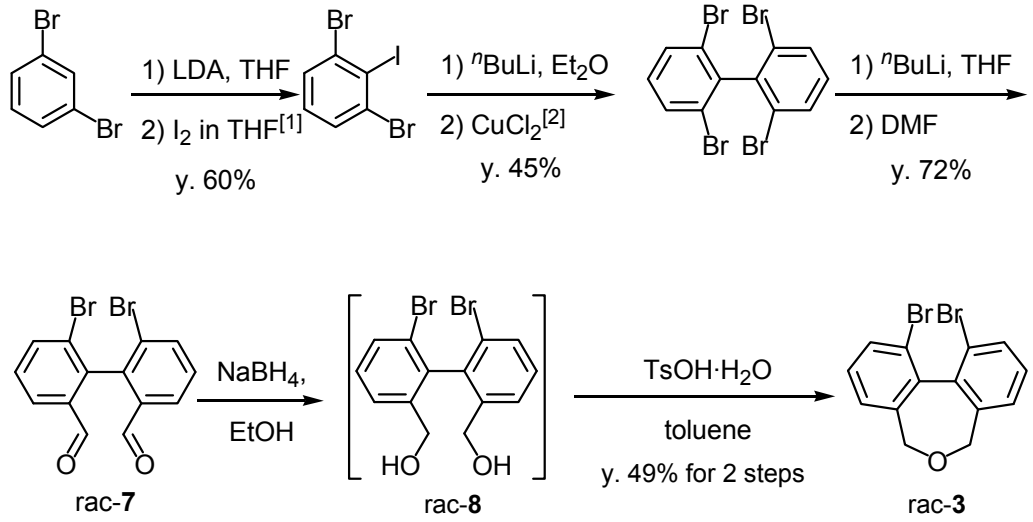
m.p. 270-279 °C (decomp.); ^{1}H NMR (300MHz, CD_3CN) δ 4.39 (6H, s), 4.61 (2H, d, *J*= 11.8 Hz), 5.01 (2H, d, *J*= 11.8 Hz), 6.25 (2H, dd, *J*= 1.4 Hz, *J*= 8.9 Hz), 6.95 (2H, dd, *J*= 1.3 Hz, 7.6 Hz), 7.24 (2H, ddd, *J*= 0.9 Hz, 6.7 Hz, 8.9 Hz), 7.59 (2H, dd, *J*= 7.6 Hz, 7.6 Hz), 7.54-7.67 (4H, m), 7.89 (2H, dd, *J*= 1.3 Hz, 7.6 Hz), 7.97 (2H, d, *J*= 9.0 Hz), 8.12 (2H, ddd, *J*=1.3 Hz, 6.4 Hz, 9.0 Hz), 8.23 (2.0 Hz, 6.4 Hz, 9.4 Hz), 8.40 (2H, d, J= 9.4 Hz); IR (KBr) ν 3110, 2926, 2868, 1609, 1579, 1549, 1460, 1374, 1275, 1224, 1159, 1030, 862, 766, 745, 709, 637, 571, 518 cm^{-1}; LR-MS (FAB) *m/z* = 580 (M^+, 7.3), 565 ($[M-CH_3]^+$, 4.9), 391 (11), 281 (12), 220 (15), 207 (17), 149 (96), 74 (bp); HR-MS (FAB) Calcd. for $C_{42}H_{32}N_2O$: 580.2517, Found : 580.2526; CD spectrum of optically pure (*M*)-$\mathbf{2b}^{2+}(OTf^-)_2$ derived from diacridine (*M*)-**5**: λ_{ext} / nm ($\Delta\varepsilon$ / M^{-1} cm^{-1}) 422 (+3.73), 390 (+0.818), 270 (-36.4), 258 (+33.0), 210 (-30.0).

5,7-Dihydrodibenz[*c*,*e*]oxepin-1,11-diylbis(10-methyl-9-acridinium) $2b^{2+}$ $(SbCl_6^-)_2$

m.p. 239-244 °C (decomp.); 1H NMR in CD_3CN was identical to that of $\mathbf{2b}^{2+}(OTf^-)_2$; IR (KBr) ν 3104, 2969, 2926, 2864, 1608, 1577, 1545, 1457, 1372, 1276, 1123, 1061, 1038, 765, 743, 709, 604 cm^{-1}, LR-MS (FAB) *m/z* = 580 (M^+, 14), 329 (5.0), 290 (M^{2+}, 1.4).

<<< Another route to dibromide **3** >>>

Scheme S1



[1] F. Lenoux, M. chlosser, *Angew. Chem. Int. Ed.*, **2002,** *41,* 4272
[2] A. Rajca, A. Safronov, S. Rajca, C. R. Ross, II, J. J. Stezowski, *J. Am. Chem.Soc.*, **1996,** *118,* 7272

2,6-Dibromo-2',6'-diformylbiphenyl 7

m.p. 128-130°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 (2H, s), 8.03 (2H, dd, *J*=8.1, 1.2 Hz), 7.98 (2H, dd, *J*=8.1, 1.2 Hz), 7.55 (2H, dd, *J*=8.1, 8.1 Hz); IR (KBr) ν 2844, 2739, 1698, 1585, 1556, 1432, 1389, 1237, 1212, 1178, 1131, 1119, 1093, 886, 851, 785, 730, 701, 677, 665 cm^{-1}; FD-MS *m/z* 368 (M^+, bp).

2,6-Dibromo-2',6'-bis(hydroxymethyl)biphenyl 8

m.p. 115-117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (2H, dd, *J*=7.8, 1.2 Hz), 7.66 (2H, dd, *J*=7.8, 1.2 Hz), 7.33 (2H, dd, *J*=7.8, 7.8 Hz), 4.31 (4H, dd, *J*=16.5, 12.0 Hz); IR (KBr) ν 3264, 2949, 2894, 1557, 1477, 1425, 1321, 1216, 1173, 1129, 1015, 996, 863, 788, 749, 672 cm^{-1}; FD-MS *m/z* 373 ($M+1^+$, bp).

<<< Racemization barrier for **1a** >>>

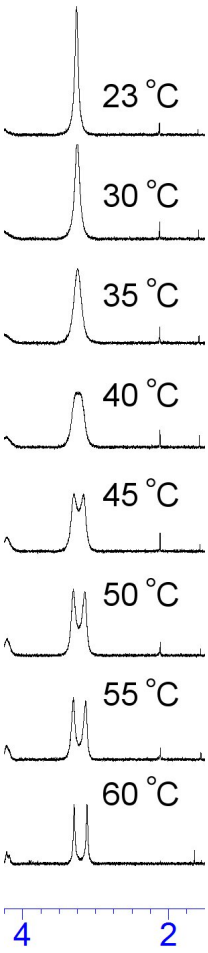


Fig. S1 VT-NMR analysis on **1a** in C_6D_6.

<<X-ray structure of dispiro donor>>

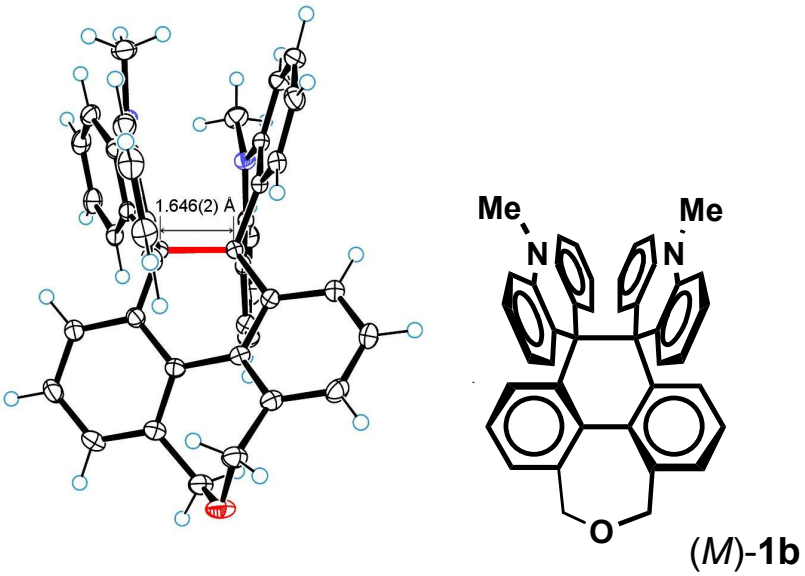


Fig. S2 ORTEP drawing of (*M*)-**1b** in *rac*-**1b** crystal determined by X-ray

<<< Optical resolution of diol **4** >>>

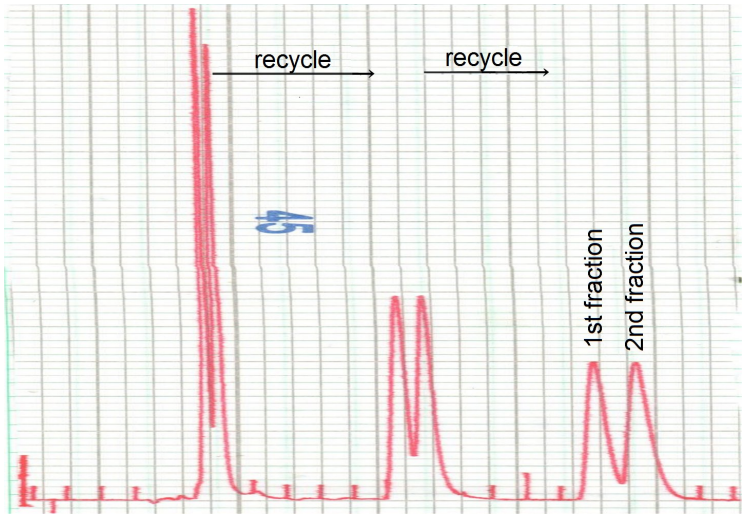


Fig. S3 Chromatogram of *rac*-**4** on Sumichiral OA-2000.
(AcOEt : CH_2Cl_2 : hexane = 1 : 2 : 4 with 0.5 % Et_3N)

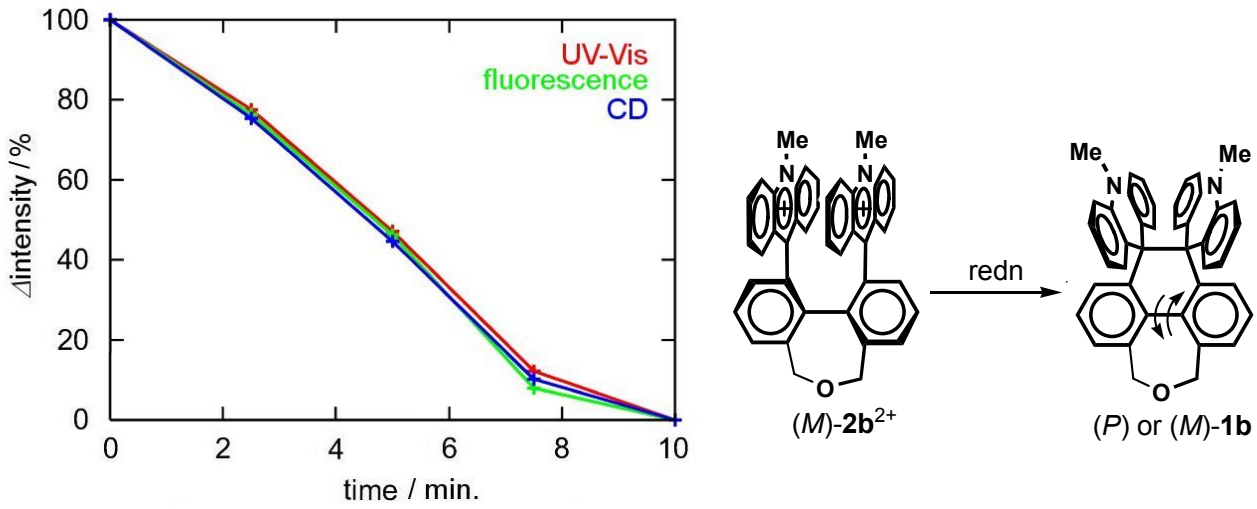


Fig. S4 Time-courses of UV-Vis (changes of ε at 264.5 nm), fluorescence (changes of intensity at 524 nm), and CD (changes of Δε at 259 nm) spectra upon electrochemical reduction of (*M*)-**2b**$^{2+}$ salt (for conditions, see the legend of Figure 3).