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Planar Chirality of Twisted *trans*-Azobenzene Structure Induced by Chiral Transfer from Binaphthyls

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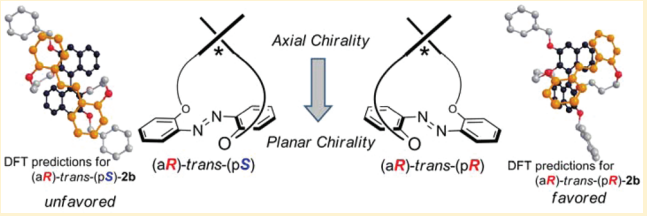
Supporting Information

ABSTRACT: The absolute configuration of a binaphthyl-azobenzene dyad **2b**, which has a chiral axis and a chiral plane, was determined by comparing the experimental circular dichroism (CD) spectra with the theoretical CD spectra calculated by the time-dependent (TD)-DFT method. The CD signals of the *trans*-azobenzene moiety indicated that the two benzene rings of this moiety are twisted unidirectionally. It is suggested that these dyads with shorter linkers may be suitable for use as chiroptical switches.



The *cis* and *trans* forms of the azobenzene skeleton can be easily and reversibly photoisomerized and differ significantly in length. Therefore, azobenzene structures are widely used as the photochromic moiety in many types of molecular switches.[1] Recently, optically active azobenzene adducts have been reported as potential chiroptical switches.[2,3] We have studied the photoswitching of chiroptical properties, such as circular dichroism (CD) and optical rotation,[4] and we reported induced helical chirality of *cis*-azobenzene units in axially chiral binaphthyl-azobenzene dyads,[5,6] mainly **1b** and **2b** (Figure 1). However, questions remain about (1) the origin of the CD activity of *trans*-azobenzene moieties and (2) the effect of linker length between the binaphthyl and azobenzene moieties on the conformation and optical properties. The *trans*-azobenzenes of dyads **1** and **2** are able to take at least three different configurations. The three (a*R*)-*trans*-forms are shown in Figure 2. The linkers of the left structure, (a*R*)-*trans*-achiral form (hereinafter called (a*R*)-*trans*-A form), lie in the same direction. In contrast, the linkers of the other two structures are staggered, so that these structures have planar chirality, (a*R*)-*trans*-(p*R*) form (center) and (a*R*)-*trans*-(p*S*) form (right), respectively. Although inversion of the two benzene rings or the N═N bond of the azobenzene moiety has been reported,[7] we speculated that the *trans*-azobenzene moieties of **1** and **2** would be biased toward the one of the above three configurations due to the cyclic structure with a chiral binaphthyl. Moreover, we focused on the influence of linker length, since this might affect the extent of propagation of chiroptical properties of dyads on photoirradiation. Perhaps shorter would be better? Herein, we investigated the planar chirality of the *trans*-azobenzene moieties, the origin of the CD activity, and the potential chiroptical switching capabilities of dyads **1a**−**e** and **2a**−**e**.

(a*R*)-**1b** and (a*R*)-**2b** are known compounds, as noted above. Novel azobenzene-binaphthyl dyads were synthesized as shown in Scheme 1. Compounds **4a**[8] and **4c**-**e** were prepared by coupling of 2,2′-dihydroxyazobenzene (**3**) and appropriate ω-bromo-α-hydroxyalkanes in moderate yields. Usual dimesylation of **4** gave **5a**[8] and **5c**-**e**. (a*R*)-**1a** and **1c**-**e** were prepared by tandem etherification of (*R*)-BINOL (**6**) and appropriate dimesylates **5**. (a*R*)-**2a** and **2c**-**e** were synthesized similarly using benzylated binol (*R*)-**7**.[9] In the cyclization to dyads (a*R*)-**1** and (a*R*)-**2**, the yields of (a*R*)-**1d** and (a*R*)-**2d** were higher than the others. Therefore, linkers much longer or much shorter than those of (a*R*)-**1d** and (a*R*)-**2d** were unfavorable for the cyclization.

Cis-*trans* reversible photoisomerization of all of these cyclic dyads occurred and could be detected as changes of absorption at around 360 nm, which is derived from the allowed $\pi-\pi^*$ transition of the *trans*-azobenzene. As is typical, *trans*→*cis* isomerization was induced by 365 nm irradiation, whereas *cis*→*trans* isomerization was induced by 436 nm irradiation. The isomerization ratios of all of (a*R*)-**1** and -**2** were ca. 0.8. Absorption spectra of (a*R*)-**2a** and (a*R*)-**2e** after photoirradiation are shown in Figures 3b,c and 3e,f, respectively. Spectral shapes were similar and independent of linker length. However, there were major differences in the CD spectra at longer wavelength (400−600 nm), where only the azobenzene moiety (n-π^*) absorbs, among the compounds (Figures 3a, 3d, and Table 1).[10] In general, dyads possessing longer linkers exhibited a low value of $\Delta\varepsilon$ at this region. These CD data indicated that chiral transfer from the binaphthyl skeleton to the azobenzene moiety is more favorable in both *cis*- and *trans*-azobenzene of dyads with shorter linkers, that is, (a*R*)-**1a**−**b** and -**2a**−**b**.

First, in the *cis*-form, the azobenzene moieties have helical chirality (direction of twisting pattern of the two benzene rings), as previously reported.[5] That is, the negative Cotton effect at longer wavelength induced by (a*R*)-binaphthyls after 365 nm irradiation indicated that helical chirality of *cis*-azobenzenes was (*P*). Second, in

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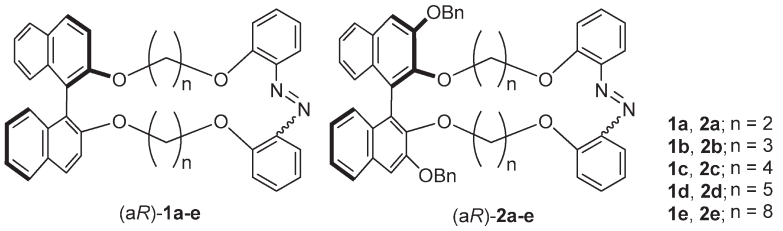
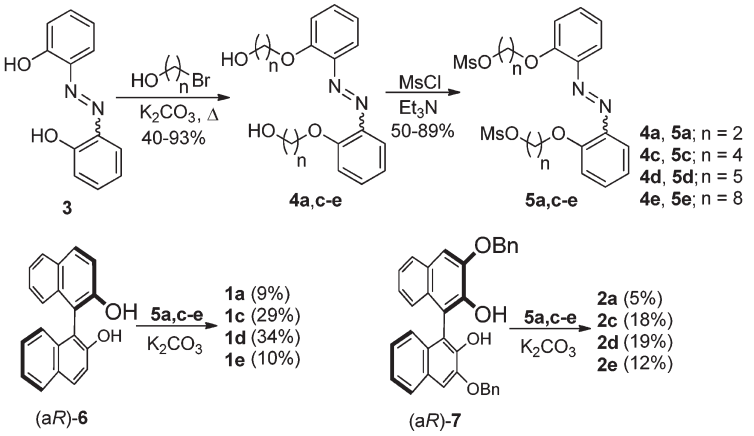


Figure 1. Axially chiral binaphthyl-azobenzene dyads. "a*R*" means that the axial chirality of binaphthyl is *R*.

Scheme 1. Synthesis of Azobenzene-binaphthyl Dyads (a*R*)-1a, 1c−e, 2a, and 2c−e



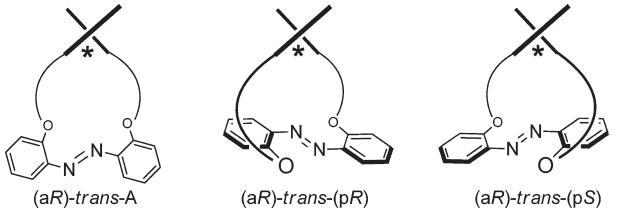


Figure 2. Configurations of binaphthyl-*trans*-azobenzene dyads. "a*R*" means that the axial chirality of binaphthyl is *R*. "p*R*" means that the planar chirality of azobenzene is *R*.

the *trans*-form, it was considered that only one of the three structures shown in Figure 2 was induced. To confirm this, we calculated the optimized conformations and their CD spectra of each of the three configurations of (a*R*)-**1a**, -**1b**, -**2a**, and -**2b**. Figure 4 shows the three optimized geometries and the torsion angles between the two benzene rings of azobenzene in (a*R*)-**2b** obtained by DFT calculation at the B3LYP/6-31G(d) level.[11,12] These structures illustrate the following two points: (1) In all conformations, the azobenzene moieties were not fully planar, but their two benzene rings were twisted. The torsion angles of C(1)−C(2)−C(3)−C(4) were 49.5° (*trans*-A-**2b**), −125.2° (*trans*-(p*R*)-**2b**), and 137.1° (*trans*-(p*S*)-**2b**), respectively as if the binaphthyls pulled on each benzene ring.[13] (2) The azobenzene moiety and benzyl groups of binaphthyl at the 3,3′-positions of *trans*-(p*R*)-**2b** did not interact (side view (Figure 4B)), whereas in *trans*-(p*S*)-**2b**, there is an overlap (side view (Figure 4C)).

Next, by using the optimized geometries, CD signals at 350−500 nm were calculated by means of the TD-DFT method (Figure 5). The Cotton effect patterns of the calculated CD spectra, compared with the experimental spectra, indicated that (a*R*)-*trans*-(p*R*)-**2b** is the preferred configuration. Although we similarly examined the configurations of the other compounds (Figure S7−S9 in the Supporting Information), in addition to prediction of NMR, VCD, and $[\alpha]_D$, it was impossible to make a clear decision as to the predominant structure. However, because CD of the azobenzene moieties of **1a**, **1b** and **2a** were active, it was considered that the azobenzene moieties were also unidirectionally twisted in these compounds. In addition, the CD spectrum of just the azobenzene moiety, *trans*-2,2′-dimethoxyazobenzene, extracted from the optimized (a*R*)-*trans*-(p*R*)-**2b**, was calculated (Figure 6). This CD spectrum in the 350−600 nm region was in excellent agreement with that of (a*R*)-*trans*-(p*R*)-**2b**. The same tendency was also seen in the cases of (a*R*)-*trans*-A-**2b** and (a*R*)-*trans*-(p*S*)-**2b**. Therefore, the CD signal in this region was derived from the unidirectionally twisted benzene rings of the azobenzene moiety and was not induced CD related to the presence of the binaphthyl moiety.[14,15] The relationship between the twisting pattern of the *trans*-azobenzene moiety judged from the crystal structures and the Cotton effect are consistent with those reported by Tamaoki.[3b]

Moreover, we focused on the switching of the optical rotation,[16] which can be detected at an unabsorbed wavelength, so that the target compounds are not degraded during measurements and do not exhibit hysteresis. The column $[\alpha]_D$ in Table 1 shows the values of (a*R*)-**1** and (a*R*)-**2** during photoirradiation, until the values became constant. Shorter linkers tended to be associated with larger changes of $[\alpha]_D$. Actually, $[\alpha]_D$ of (*R*)-**1a** exhibited the largest change (ca. 1500°), and this compound is a good candidate for a switch based on dextro-rotation/levo-rotation. In addition, (a*R*)-**1b** and (a*R*)-**2a** are candidates for switches based on zero-rotation/dextro-rotation. Compounds **1c**−**e** and **2c**−**e** seem to be unsuitable for chiroptical switches because of their small chiroptical changes. Furthermore, at

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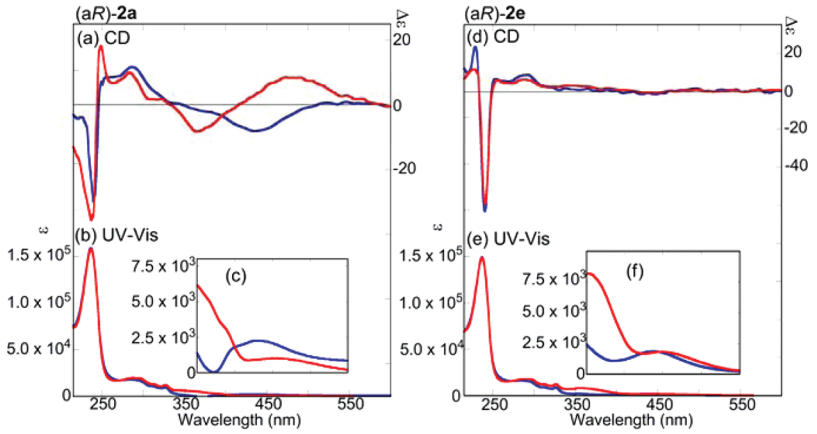

Figure 3. (a) CD spectra of (a*R*)-**2a**, (b,c) absorption spectra of (a*R*)-**2a**, (d) CD spectra of (a*R*)-**2e**, and (e,f) absorption spectra of (a*R*)-**2e** after 365 nm irradiation (blue, rich in *cis*-form) and 436 nm irradiation (red, rich in *trans*-form). Conditions: 1,4-dioxane, 1.0×10^{-5} M, 20 °C, light path length = 10 mm, irradiation 10 mW/cm^2, 100 s).

Table 1. CD[a] Data and $[\alpha]_D$[b] of (a*R*)-1a−2e after Photoirradiation

	after 365 nm irradiation			after 436 nm irradiation		
	CDλ	$\Delta\varepsilon$	$[\alpha]_D$	CDλ	$\Delta\varepsilon$	$[\alpha]_D$
(a*R*)-**1a**	425	−17	−644	468	+12	+839
(a*R*)-**1b**	435	−23	−1318	432	−10	+79
(a*R*)-**1c**	429	−16	−749	429	−9	−454
(a*R*)-**1d**	433	−12	−600	433	−11	−559
(a*R*)-**1e**		0	−63		0	−91
(a*R*)-**2a**	435	−8	−72	472	+9	+845
(a*R*)-**2b**	434	−19	−314	482	+14	+642
(a*R*)-**2c**	435	−8	−507		0	−235
(a*R*)-**2d**	(432)	−10	−456	(448)	−11	−511
(a*R*)-**2e**		0	−81		0	−97

[a] Conditions: 1,4-dioxane, 1.0×10^{-5} M, 20 °C, light path length = 10 mm, irradiation strength = 10 mW/cm^2, 100 s. [b] Conditions: chloroform, *c* = 0.10 g/dL, 20 °C, light path length = 10 cm, irradiation strength = 10 mW/cm^2, 500 s.

298 K, the half-lives of most of these cyclic *cis*-compounds were longer than 100 h, which is extraordinary for azobenzene derivatives (Table S3 in the Supporting Information).

In summary, the absolute configuration of a planar-chiral binaphthyl-*trans*-azobenzene dyad **2b** was determined. The *trans*-azobenzene of **2b** was twisted unidirectionally. It is likely that the azobenzene moieties of **1a**, **1b**, and **2a** are also unidirectionally twisted, though this remains to be confirmed. Huge optical rotation switching was achieved by dyads with short linkers, suggesting that asymmetric azobenzenes are good candidates for chiroptical switches, asymmetric organo catalysts and chiral recognition agents. Further studies aimed at the synthesis of binaphthyl-azobenzene dyads connected by extremely short linkers are under way in our laboratory.

EXPERIMENTAL SECTION

Synthetic Method of 1−4. *2,2′-bis(2-Hydroxyethoxy)azobenzene (**4a**).* A suspension of 2,2′-dihydroxyazobenzene (6.42 g, 30 mmol), 2-bromo-1-ethanol (10.7 mL, 150 mmol, 5.0 equiv), and potassium carbonate (20.7 g, 150 mmol, 5.0 equiv) in DMF

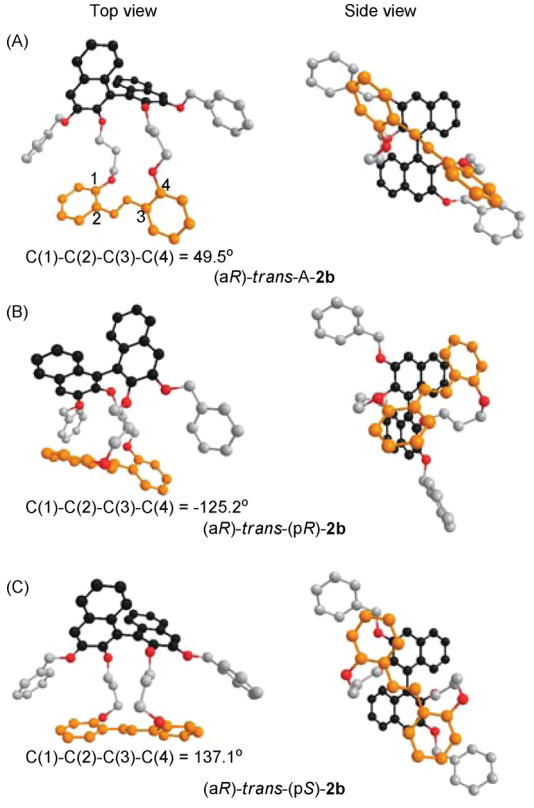

Figure 4. Top view and side view of the optimized structures of the three types of (a*R*)-*trans*-**2b** at the B3LYP/6-31G(d) level. Azobenzene moieties are shown in orange and binaphthyl skeletons in black. Hydrogen atoms are not shown.

(30 mL) was stirred for 24 h at 80 °C. The reaction mixture was poured into the mixed solvent of chloroform and water. The organic layer was separated and washed successively with 0.1 N hydrochloric acid solution, water (twice), and brine. After dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2; chloroform/ethyl acetate = 6/4) to afford **4a** (5.61 g, 18.6 mmol, 62%). **4a** is a known compound although synthetic route is difference from traditional method.[8]

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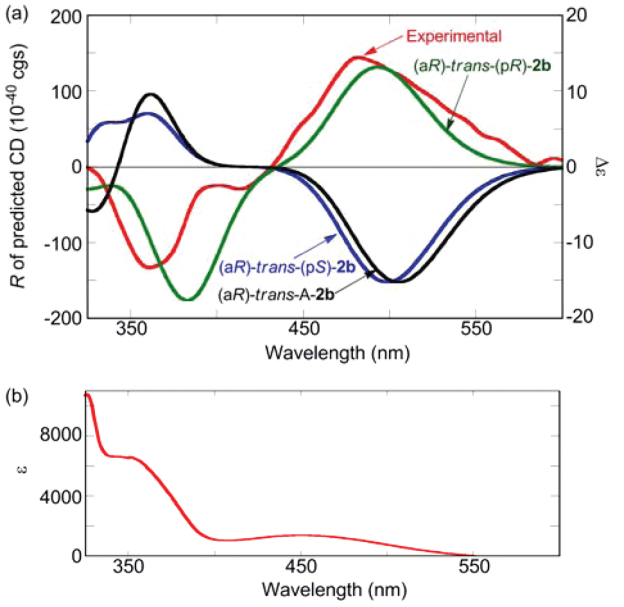

Figure 5. (a) Calculated CD of (a*R*)-*trans*-A-**2b** (black), (a*R*)-*trans*-(p*R*)-**2b** (green), (a*R*)-*trans*-(p*S*)-**2b** (blue) (TD-DFT method at the B3LYP/6-31G(d) level, Gaussian bands with a half-bandwidth of 2500 cm^{-1}), and experimental CD of (a*R*)-**2b** after 436 nm irradiation (1,4-dioxane, 1×10^{-5} M, 20 °C). (b) Absorption spectra of (a*R*)-**2b** after 436 nm irradiation (1,4-dioxane, 1×10^{-5} M, 20 °C).

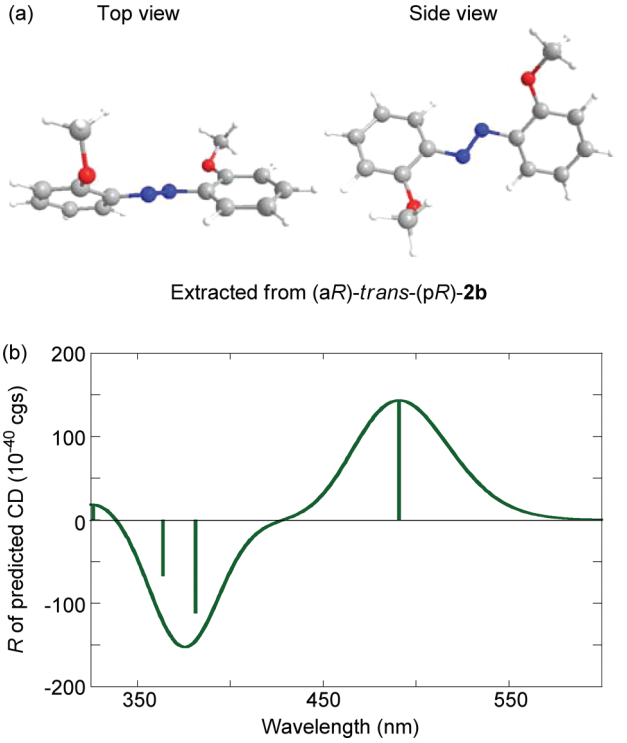

Figure 6. (a) Structure of 2,2′-dimethoxyazobenzene extracted from the optimized (a*R*)-*trans*-(pR)-**2b**. (All hydrogen atoms are hidden.) (b) Calculated CD of 2,2′-dimethoxyazobenzene extracted from the optimized (a*R*)-*trans*-(pR)-**2b**. (TD-DFT method at the B3LYP/6-31G(d) level, Gaussian bands with a half-bandwidth of 2500 cm^{-1}.)

2,2′-bis(4-Hydroxybutoxy)azobenzene (***4c***). **4c** was synthesized in a similar manner to that for **4a** with the exception that 4-bromo-1-butanol was used. 67% yield; Red amorphous; IR (KBr) 3276, 1487, 1467, 1279, 1232, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 1.6−1.9 (m, 4H), 1.9−2.2 (m, 4H), 2.46 (s, 2H), 3.7−4.1 (m, 4H), 4.1−4.4 (m, 4H), 6.5−7.2 (m, 4H), 7.2−7.5 (m, 2H), 7.65, 7.68 (two d, J = 8.4 Hz, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 25.6, 26.1, 30.1, 61.9, 69.4, 69.4, 113.9, 113.9, 117.2, 117.4, 120.1, 121.0, 132.1, 132.3, 142.8, 142.8, 156.2, 156.3 (Some peaks overlapped); LR MS (FAB^+) 359.2 $(M+H)^+$; HR MS (FAB^+) Calcd for $C_{20}H_{27}N_2O_4$ $(M+H)^+$: 359.1971. Found: 359.1966.

2,2′-bis(5-Hydroxypentoxy)azobenzene (***4d***). **4d** was synthesized in a similar manner to that for **4a** with the exception that 5-bromo-1-pentanol was used; 93% yield; Red amorphous; IR (KBr) 3349, 1491, 1474, 1281, 1154, 755, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 1.4−1.8 (m, 8), 1.8−2.0 (m, 4H), 3.63 (br s, 4H), 4.19 (t, J = 6.4 Hz, 4H), 7.00 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm, single isomer) δ 22.4, 28.9, 62.7, 69.6, 114.6, 117.3, 120.9, 131.0, 143.2, 156.5; LR MS (FAB^+) 387.2 $(M+H)^+$; HR MS (FAB^+) Calcd for $C_{22}H_{30}N_2O_4$ (M^+): 386.2206. Found: 386.2196.

2,2′-bis(8-Hydroxyoctoxy)azobenzene (***4e***). **4e** was synthesized in a similar manner to that for **4a** with the exception that 8-bromo-1-octanol was used; 40% yield; Red oil; IR (KBr) 3462, 1489, 1470, 1240, 1155, 1047, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm, major isomer) δ 1.2−1.4 (m, 12H), 1.4−1.6 (m, 8H), 1.8−2.1 (m, 4H), 3.55 (t, J = 6.8 Hz, 4H), 4.16 (t, J = 6.4 Hz, 4H), 6.98 (t, J = 7.2 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm, major isomer) δ 25.5, 25.9, 29.1, 29.2, 29.2, 29.3, 62.6, 69.7, 114.5, 117.1, 120.6, 131.9, 143.7, 156.5; LR MS (FAB^+) 471.3 $(M+H)^+$; HR MS (FAB^+) Calcd for $C_{28}H_{42}N_2O_4$ (M^+): 470.3145. Found: 470.3139.

2,2′-bis(4-Mesyloxypropoxy)azobenzene (***5c***). A suspension of **4c** (780 mg, 2.17 mmol), methanesulfonyl chloride (843 μL, 10.9 mmol, 5.0 equiv), and triethylamine (606 μL, 4.35 mmol, 2.0 equiv) in dichloromethane (40 mL) was stirred for 2 h at r.t. The reaction mixture was poured into the mixed solvent of chloroform and water. The organic layer was separated and washed successively with 0.1 N hydrochloric acid solution, water (twice) and brine. After dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2; chloroform/ethyl acetate = 7/3) to afford **5c** (887 mg, 1.72 mmol, 79%). Red amorphous; IR (KBr) 1487, 1353, 1279, 1173, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm, major isomer) δ 1.9−2.1 (m, 8H), 2.91 (s, 6H), 4.23 (t, J = 5.6 Hz, 4H), 4.36 (t, J = 5.6, 2H), 7.0−7.1 (m, 4H), 7.40 (t, J = 7.2 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 25.3, 26.3, 37.2, 37.3, 68.9, 68.9, 69.9, 70.0, 114.6, 114.6, 117.1, 117.3, 120.9, 121.2, 132.0, 132.2, 143.1, 143.1, 156.3, 156.5; LR MS (FAB^+) 515.1 $(M+H)^+$; HR MS (FAB^+) Calcd for $C_{22}H_{31}N_2O_8S_2$ $(M+H)^+$: 515.1522. Found: 515.1508.

2,2′-bis(5-Mesyloxybutoxy)azobenzene (***5d***). **5d** was synthesized in a similar manner to that for **5c** with the exception that **4d** was used; 50% yield; Red amorphous; IR (KBr) 1488, 1342, 1279, 1171, 939, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.6−1.8 (m, 4H), 1.8−1.9 (m, 4H), 1.9−2.0 (m, 4H), 2.92 (s, 6H), 4.1−4.3 (m, 8H), 6.9−7.1 (m, 4H), 7.3−7.7 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm, major isomer) δ 22.3, 28.5, 28.8, 37.2, 69.3, 69.9, 114.5, 117.1, 120.9, 132.1, 143.1, 156.4; LR MS (FAB^+) 543.2 $(M+H)^+$; HR MS (FAB^+) Calcd for $C_{24}H_{35}N_2O_8S_2$ $(M+H)^+$: 543.1835. Found: 543.1825.

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*2,2′-bis(8-Mesyloxyoctoxy)azobenzene (**5e**).* **5e** was synthesized in a similar manner to that for **5c** with the exception that **4e** was used; 89% yield; Red oil; IR (KBr) 1488, 1342, 1279, 1171, 765 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, ppm, single isomer) δ 1.2−1.5 (m, 12H), 1.54 (quintet, J = 7.5 Hz, 4H), 1.73 (quintet, J = 6.6 Hz, 4H), 1.90 (quintet, J = 6.9 Hz, 4H), 2.98 (s, 6H), 3.67 (s, 4H), 4.18 (t, J = 6.6 Hz, 4H), 7.00 (t, J = 7.8 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 7.39 (dt, J = 7.8 Hz, 1.5 Hz, 2H), 7.65 (dd, J = 7.8 Hz, 1.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm, single isomer) δ 25.1, 25.7, 28.8, 28.9, 29.0, 37.0, 52.4, 69.6, 70.1, 114.5, 117.0, 120.6, 132.0, 142.9, 156.5; LR MS (FAB^+) 627.3 $(M + H)^+$; HR MS (FAB^+) Calcd for $C_{30}H_{47}N_2O_8S_2$ $(M + H)^+$: 627.2774. Found: 627.2778.

General Procedure for the Synthesis of Compounds (a*R*)-1a, (a*R*)-1c−e, (a*R*)-2a and (a*R*)-2c−e. The synthesis of (a*R*)-**1a** is typical.

*(aR)-Binaphthyl-azobenzene Dyad **1a**.* A suspension of (*R*)-BINOL (200 mg, 698 μmol) and **5a** (320 mg, 698 μmol), and potassium carbonate (965 mg, 6.98 mmol, 10 equiv) in DMF (20 mL) was stirred for 24 h at 80 °C. The reaction mixture was poured into the mixed solvent of chloroform and water. The organic layer was separated and washed successively with 0.1 N hydrochloric acid solution, water (twice) and brine. After dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2; *n*-hexane/chloroform/ethyl acetate = 6/3/1) and GPC to afford (a*R*)-**1a** (33 mg, 59.7 μmol, 9%). Red amorphous; IR (KBr) 3056, 1507, 1489, 1241, 1091, 1052, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm, major isomer) δ 4.0−4.2 (m, 4H), 4.2−4.3 (m, 2H), 4.3−4.4 (m, 2H), 6.85 (d, J = 8.4 Hz, 2H), 7.0−7.1 (m, 4H), 7.1−7.4 (m, 8H), 7.58 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 68.0, 68.7, 69.3, 113.7, 115.8, 116.1, 120.1, 121.5, 122.1, 123.6, 123.9, 125.3, 125.4, 126.2, 126.4, 127.9, 127.9, 128.8, 129.3, 129.4, 129.7, 131.0, 134.0, 134.1, 143.4, 144.2, 152.6, 154.4 (Some peaks overlapped.); LR MS (FAB^+) 553.2 $(M + H)^+$; HR MS (FAB^+) Calcd for $C_{36}H_{28}N_2O_4$ $(M)^+$: 552.2049. Found: 552.2061.

*(aR)-Binaphthyl-azobenzene Dyad **1c**.* Yield 29%; Red amorphous; IR (KBr) 3057, 1507, 1467, 1242, 1085, 1044, 1014, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm, major isomer) δ 1.3−1.7 (m, 8H), 3.5−4.0 (m, 8H), 6.86 (d, J = 8.7 Hz, 2H), 7.0−7.5 (m, H), 7.45 (dd, J = 8.1 Hz, 1.5 Hz, 2H), 7.67 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm, major isomer) δ 25.2, 25.5, 25.9, 26.3, 68.6, 69.0, 69.2, 70.0, 112.9, 115.3, 115.4, 119.6, 120.1, 120.6, 121.0, 123.2, 125.3, 125.9, 126.0, 127.7, 128.6, 129.0, 129.0, 129.1, 131.1, 134.0, 143.3, 144.6, 148.5, 153.9, 154.3 (Some peaks overlapped.); LR MS (FAB^+) 609.3 $(M + H)^+$; HR MS (FAB^+) Calcd for $C_{40}H_{36}N_2O_4$ (M^+): 608.2675. Found: 608.2683.

*(aR)-Binaphthyl-azobenzene Dyad **1d**.* Yield 34%; Red amorphous; IR (KBr) 3056, 1507, 1466, 1274, 1242, 1087, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 1.0−1.6 (m, 12H), 3.6−3.7 (m, 2H), 3.7−3.8 (m, 2H), 3.9−4.0 (m, 2H), 4.0−4.1 (m, 2H), 6.7−7.8 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 22.0, 22.3, 28.1, 28.5, 28.7, 29.0, 68.7, 68.8, 69.2, 69.5, 113.0, 114.5, 115.4, 115.5, 119.7, 119.7, 120.4, 120.6, 120.6, 120.7, 123.2, 123.3, 125.4, 125.4, 125.9, 126.1, 127.7, 127.7, 128.6, 128.9, 128.9, 129.1, 129.1, 129.1, 131.1, 134.1, 134.2, 143.1, 144.5, 148.7, 154.2, 154.4; LR MS (FAB^+) 636.3 (M^+); HR MS (FAB^+) Calcd for $C_{42}H_{40}N_2O_4$ (M^+): 636.2988. Found: 636.2991.

*(aR)-Binaphthyl-azobenzene Dyad **1e**.* Yield 10%; Red amorphous; IR (KBr) 3057, 1508, 1488, 1242, 1158 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 0.8−2.0 (m, 24H), 3.5−4.2 (m, 8H), 6.5−8.0 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 25.1, 25.6, 25.8, 25.9, 28.5, 28.6, 28.7, 28.8, 29.0, 29.0, 29.1, 29.2, 29.2, 29.3, 69.3, 69.5, 69.5, 69.8, 112.9, 114.6, 115.6, 115.8, 117.2, 118.8, 119.7, 120.0, 120.5, 120.7, 123.2, 123.2, 125.4, 125.9, 126.0, 127.6, 127.7, 128.9, 129.0, 129.1, 129.1, 131.5, 131.9, 134.1, 134.2, 143.2, 143.5, 143.8, 154.4, 154.4, 155.5, 156.7; LR MS (FAB^+) 721.3 $(M + H)^+$; HR MS (FAB^+) Calcd for $C_{48}H_{52}N_2O_4$ (M^+): 720.3927. Found: 720.3923.

(a*R*)-**2a** and (a*R*)-**2c**−**e** were synthesized in a similar manner to that for (a*R*)-**1a** with the exception that (*R*)-3,3′-dibenzyloxybinaphthol **7** was used.

*(aR)-3,3′-Dibenzyloxybinaphthyl-azobenzene Dyad **2a**.* Yield 5%; Red amorphous; IR (KBr) 3060, 1457, 1438, 1245, 1167, 747 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 3.7−4.0 (m, 2H), 4.1−4.2 (m, 2H), 4.3−4.4 (m, 2H), 4.4−4.5 (m, 2H), 5.04, 5.19 (ABq, ν_{AB} = 18.0 Hz, J_{AB} = 11.4 Hz; s, 4H), 6.40, 6.48 (two d, J = 7.8 Hz, J = 8.4 Hz, 2H), 6.6−7.5 (m, 24H), 7.58, 7.75 (two d, J = 8.1 Hz, 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 68.8, 70.3, 70.5, 71.0, 108.6, 108.7, 113.2, 113.6, 119.7, 120.2, 122.1, 123.8, 124.2, 124.8, 125.0, 125.3, 125.6, 126.0, 126.6, 126.7, 127.3, 127.5, 127.6, 127.7, 127.8, 128.0, 128.3, 128.5, 128.8, 128.9, 130.7, 130.9, 136.5, 136.7, 142.9, 147.2, 151.1, 151.3, 152.4 (Some peaks overlapped); LR MS (FAB^+) 764.4 $(M)^+$; HR MS (FAB^+) Calcd for $C_{50}H_{40}N_2O_6$ $(M)^+$: 764.2886. Found: 764.2913.

*(aR)-3,3′-Dibenzyloxybinaphthyl-azobenzene Dyad **2c**.* Yield 18%; Red amorphous; IR (KBr) 3061, 1507, 1440, 1249, 1169, 1116, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 1.2−1.7 (m, 8H), 3.5−3.7 (m, 2H), 3.7−3.8 (m, 4H), 3.8−3.9 (m, 2H), 5.05, 5.29 (two ABq, ν_{AB} = 12.4 Hz, J_{AB} = 11.4 Hz; ν_{AB} = 16.9 Hz, J_{AB} = 11.4 Hz, 4H), 6.5−8.0 (m, 28H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 25.1, 25.2, 26.0, 26.1, 70.1, 70.2, 71.8, 71.9, 77.2, 77.4, 108.3, 116.0, 120.6, 120.7, 121.1, 123.9, 124.9, 125.8, 126.3, 126.4, 127.4, 127.4, 127.8, 128.3, 128.4, 128.5, 129.1, 130.8, 131.1, 136.6, 144.6, 146.6, 151.5, 154.3 (Some peaks overlapped); LR MS (FAB^+) 820.4 (M^+); HR MS (FAB^+) Calcd for $C_{54}H_{48}N_2O_6$ (M^+): 820.3512. Found: 820.3540.

*(aR)- 3,3′-Dibenzyloxybinaphthyl-azobenzene Dyad **2d**.* 19%Yield ; Red amorphous; IR (KBr) 3061, 1457, 1440, 1376, 1247, 1168, 1115, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 0.9−1.6 (m, 12H), 3.5−4.2 (m, 8H), 5.06, 5.29 (two ABq, ν_{AB} = 5.5 Hz, J_{AB} = 12.0 Hz; ν_{AB} = 7.9 Hz, J_{AB} = 12.0 Hz, 4H), 6.6−6.8 (m, 2H), 6.8−7.8 (m, 26H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 22.1, 22.4, 28.3, 28.5, 29.3, 29.4, 29.4, 69.0, 69.7, 70.3, 70.6, 72.5, 73.0, 108.3, 108.6, 113.1, 114.3, 119.5, 119.7, 120.6, 123.9, 124.0, 124.8, 125.7, 125.9, 126.3, 126.3, 126.4, 126.5, 127.5, 127.6, 127.7, 127.9, 128.4, 128.5, 128.5, 129.2, 129.2, 130.8, 130.7, 130.9, 136.7, 136.8, 143.3, 144.7, 147.0, 147.1, 148.7, 151.6, 151.6, 154.6 (Some peaks overlapped); LR MS (FAB^+) 848.4 (M^+); HR MS (FAB^+) Calcd for $C_{56}H_{52}N_2O_6$ (M^+): 848.3825. Found: 848.3802.

*(aR)- 3,3′-Dibenzyloxybinaphthyl-azobenzene Dyad **2e**.* Yield 12%; Red amorphous; IR (KBr) 3062, 1457, 1440, 1248, 1168, 1115, 747 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 0.7−2.0 (m, 24H), 3.5−4.3 (m, 8H), 5.20, 5.27 (two s, 4H), 6.6−6.8 (m, 2H), 6.8−8.0 (m, 26H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 25.1, 25.5, 25.5, 25.7, 28.6, 28.8, 28.9, 29.1, 29.5, 29.7, 68.8, 69.7, 69.9, 70.4, 70.4, 72.8, 72.9, 108.5, 112.8, 114.8, 119.4, 119.5, 120.3, 120.7, 123.8, 123.9, 124.7, 125.8, 126.4, 127.3, 127.4, 127.8, 127.9, 128.4, 128.5, 129.2, 129.3, 130.8, 130.8, 131.3, 131.9, 136.8, 136.9, 143.3, 144.0, 147.2, 147.2, 148.8, 151.6, 151.6, 155.1 (Some peaks overlapped);

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LR MS (FAB$^+$) 932.5 (M^+); HR MS (FAB$^+$) Calcd for $C_{62}H_{64}N_2O_6$ (M^+): 932.4764. Found: 932.4799.

■ ASSOCIATED CONTENT

Supporting Information. UV−vis spectra, CD spectra, Computational details, thermodynamic parameters, and ^{1}H NMR and ^{13}C NMR spectra of various compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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