Supporting Information

Photoisomerization Locking of Azobenzene by Formation of Self-assembled Macrocycle

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(1) General experimental details

All reactions were performed under a dry nitrogen atmosphere. Organic solvents were purchased as pre-dried solvents and used without any further purification. H₂O was deionised and microfiltered using a Millipore machine, Milli-Q® Integral 3. ¹H and ¹³C NMR spectra were recorded by Bruker AVANCE400 using TMS as an internal reference. ¹¹B and ²³Na NMR spectra were recorded by Bruker AVANCE400 using BF₃·OEt₂ and NaCl as external references, respectively. DOSY spectra were recorded by Bruker AVANCE 600. ESI-TOF Mass spectra were recorded on Applied Biosystems QStar Pulsar i. MALDI-TOF Mass spectra were recorded on AB Sciex TOF/TOF5800. UV-vis spectra were recorded by JASCO Ubest V-660. Melting points were obtained using a Yanaco melting point apparatus and are uncorrected. X-ray diffraction was recorded on Bruker APEXII ULTRA. Photoreactions were performed using a 400 W high-pressure mercury lamp on SEN Light Corporation through a color filter. Molecular dynamics and density functional theory calculations were performed using Spartan09 program.

(2) Synthetic procedure

LH₄ and L′H₂ were synthesized followed by procedure shown in Scheme S1. Starting materials 1,¹ ½,² and 4³ were prepared by a literature method.

Scheme S1. Synthetic procedure for LH₄ and L′H₂
Synthesis of 3

To a mixture of 1 (200.2 mg, 0.589 mmol), 2 (217.1 mg, 1.19 mmol), Na₂CO₃ (253 mg, 2.39 mmol), and Pd[PPh₃]₄ (44.9 mg, 0.021 mmol) were added degassed toluene (5 mL), methanol (1 mL), and water (2 mL). The reaction mixture was refluxed overnight. The mixture was extracted with toluene, and the organic layer was washed with water, dried over MgSO₄, and evaporated. The crude mixture was separated by silica-gel column chromatography using chloroform as an eluent to give orange crystal of 3 (203.6 mg, 72%).

3: orange crystal, mp 185-186 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.64 (s, 6H), 3.93 (s, 6H), 6.98 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.2 Hz, 2H), 7.17 (t, J = 8.2 Hz, 2H), 7.75 (d, J = 8.4 Hz, 4H), 8.00 (d, J = 8.4 Hz, 4H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 55.99 (CH₃), 60.71 (CH₂), 112.02 (CH), 122.47 (CH), 122.64 (CH), 124.21 (CH), 130.08 (CH), 135.09 (C), 141.02 (C), 146.73 (C), 151.73 (C), 153.23 (C); Anal. Calcd for C₂₀H₂₅N₂O₄: 0.2CHCl₃: C, 70.80; H, 5.52; N, 5.86. Found: C, 70.71; H, 5.78; N, 5.76.

Synthesis of LH₄

To a solution of 3 (152.7 mg, 0.336 mmol) in dichloromethane (7.5 mL) was added BBr₃ (1 mL, 0.01 mol) dropwise at 0 °C, and the reaction mixture was stirred at room temperature overnight. Methanol and saturated sodium carbonate solution were successively added to the reaction mixture. The mixture was extracted with AcOEt, and the organic layer was washed with water, dried over MgSO₄, and evaporated. The crude mixture was recrystallized from methanol to give red crystal of LH₄ (101.8 mg, 75%).

LH₄: red crystal, mp 262-264 °C (dec); ¹H NMR (400 MHz, DMSO-d₆) δ 6.76 (dd, J = 8.2 Hz, J = 7.0 Hz, 2H), 6.84 (d, J = 7.0 Hz, 2H), 6.84 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.9 Hz, 4H), 7.94 (d, J = 8.9 Hz, 4H), 8.53 (brs, 2H), 9.61 (brs, 2H); ¹³C{¹H} NMR (100 MHz, DMSO-d₆) δ 115.39 (CH), 119.84 (CH), 120.99 (CH), 122.68 (CH), 127.68 (C), 130.49 (CH), 142.38 (C), 143.33 (C), 146.14 (C), 150.95 (C); Anal. Calcd for C₂₄H₁₀N₂O₄: 0.25MeOH: C, 71.66; H, 4.71; N, 6.89. Found: C, 71.84; H, 4.82; N, 6.87.

Synthesis of [L₄B₄](Et₃NH)₄

To a solution of LH₄ (10.0 mg, 25.1 μmol) and triisopropyl borate (5.8 μL, 25 μmol) in THF (5.0 mL) was added NEt₃ (7.0 μL, 50 μmol), and the reaction mixture was stirred at room temperature overnight. Orange glassy solid was gradually precipitated from reaction mixture. The precipitate was washed with THF and dried under vacuum to give orange solid of [L₄B₄](Et₃NH)₄ (11.1 mg, 88%).

[L₄B₄](Et₃NH)₄: orange glassy solid, mp >300 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 1.44 (t, J = 7.5 Hz, 36H), 3.03 (q, J = 7.5 Hz, 24H), 6.60 (d, J = 8.0 Hz, 8H), 6.67 (t, J = 8.0 Hz, 8H), 6.96 (d, J = 8.0 Hz, 8H), 7.90 (d, J = 8.0 Hz, 16H), 8.09 (d, J = 8.0 Hz, 16H); ¹³C{¹H} NMR (100 MHz, DMSO-d₆) δ 9.58 (CH₃), 34.55 (CH₂), 55.91 (CH₃), 60.71 (CH₂), 112.02 (CH), 122.47 (CH), 122.64 (CH), 124.21 (CH), 130.08 (CH), 135.09 (C), 141.02 (C), 146.73 (C), 151.73 (C), 153.23 (C), 159.95 (C); Anal. Calcd for C₂₄H₁₀N₂O₄: 0.25MeOH: C, 71.66; H, 4.71; N, 6.89. Found: C, 71.84; H, 4.82; N, 6.87.
108.76 (CH), 117.51 (CH), 119.14 (CH), 119.84 (C), 123.48 (CH), 129.10 (CH), 141.94 (C), 150.29 (C), 151.10 (C), 152.97 (C); $^{11}$B\{\text{H}\} NMR (126 MHz, DMSO-$d_6$) $\delta$ 14.4; ESI-TOF-MS (neg) observed $m/z$ 405.1 \([\text{L}_2\text{B}]^{3+}\); Anal. Calcd for C$_{140}$H$_{144}$B$_4$N$_{16}$O$_{18}$thf-4H$_2$O: C, 68.52; H, 6.31; N, 7.73. Found: C, 68.11; H, 5.98; N, 7.80.

Synthesis of \([\text{L}_2\text{Ti}_2]\)Na$_4$

To a solution of LH$_4$ (9.9 mg, 25 µmol) and Ti(O)(acac)$_2$ (4.5 mg, 17 µmol) in methanol (12 mL) was added Na$_2$CO$_3$ (2 mg, 0.02 mmol), and the reaction mixture was stirred at room temperature overnight. The reaction mixture was evaporated and the residue was dissolved into water. The aqueous layer was washed with AcOEt and evaporation of solvent gave orange powder of \([\text{L}_2\text{Ti}_2]\)Na$_4$ (14.0 mg, >99%). \([\text{L}_2\text{Ti}_2]\)Na$_4$: orange powder, mp >300 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.08 (d, $J$ = 7.5 Hz, 6H), 6.38 (t, $J$ = 7.5 Hz, 6H), 6.62 (d, $J$ = 7.5 Hz, 6H), 8.04 (d, $J$ = 8.5 Hz, 12H), 8.45 (d, $J$ = 8.5 Hz, 12H); $^{13}$C\{\text{H}\} NMR (100 MHz, DMSO-$d_6$) $\delta$ 109.94 (CH), 115.32 (CH), 117.25 (CH), 120.74 (C), 122.72 (CH), 129.55 (CH), 144.71 (C), 150.15 (C), 160.89 (C), 161.91 (C); $^{23}$Na\{\text{H}\} NMR (106 MHz, DMSO-$d_6$) $\delta$ -0.2 ($\Delta\nu_{1/2}$ = 162 Hz); MALDI-TOF-MS (neg) observed $m/z$ 1303.1 \([\text{L}_5\text{Ti}_2]+\text{Na}+2\text{H}]^-$; Anal. Calcd for C$_{72}$H$_{142}$Na$_6$O$_{12}$Na$_4$Ti$_2$:18H$_2$O: C, 51.02; H, 4.64; N, 4.96. Found: C, 50.88; H, 4.28; N, 4.53.

Synthesis of 5

To a mixture of 4 (1.00 g, 2.95 mmol), 2 (0.54 g, 3.0 mmol), Na$_2$CO$_3$ (0.69 g, 6.1 mmol), and Pd[PPh$_3$_]$_4$ (0.12 g, 0.10 mmol) were added degassed toluene (25 mL), methanol (5 mL), and water (2 mL). The reaction mixture was refluxed overnight. The mixture was extracted with chloroform, and the organic layer was washed with water, dried over MgSO$_4$, and evaporated. The crude mixture was separated by silica-gel column chromatography using chloroform as an eluent to give orange crystal of 5 (0.76 g, 79%). 5: orange crystal, mp 98-99 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.61 (s, 3H), 3.92 (s, 3H), 6.95 (dd, $J$ = 8.1 Hz, $J$ = 1.2 Hz, 1H), 6.97 (dd, $J$ = 8.1 Hz, $J$ = 1.2 Hz, 1H), 7.13 (t, $J$ = 8.1 Hz, 1H), 7.46-7.54 (m, 3H), 7.71 (d, $J$ = 8.4 Hz, 2H), 7.92 (dd, $J$ = 8.1 Hz, $J$ = 1.2 Hz, 2H), 7.96 (d, $J$ = 8.4 Hz, 2H); $^{13}$C\{\text{H}\} NMR (100 MHz, CDCl$_3$) $\delta$ 55.99 (CH$_3$), 60.69 (CH$_3$), 112.02 (CH), 122.44 (CH), 122.64 (CH), 122.84 (CH), 124.21 (CH), 129.09 (CH), 130.07 (CH), 130.91 (CH), 135.05 (C), 141.09 (C), 146.72 (C), 151.60 (C), 152.79 (C), 153.23 (C); Anal. Calcd for C$_{28}$H$_{16}$N$_2$O$_2$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.15; H, 5.70; N, 8.73.
Synthesis of $\text{L}^\prime\text{H}_2$

To a solution of $\text{5}$ (405.4 mg, 1.27 mmol) in dichloromethane (30 mL) was added $\text{BBr}_3$ (1 mL, 0.01 mol) dropwise at 0 °C, and the reaction mixture was stirred at room temperature overnight. Methanol and saturated sodium carbonate solution were successively added to the reaction mixture. The mixture was extracted with AcOEt, and the organic layer was washed with water, dried over $\text{MgSO}_4$, and evaporated. The crude residue was washed with chloroform and recrystallization from THF gave pale yellow crystal of $\text{L}^\prime\text{H}_2$ (241.0 mg, 65%).

$L^\prime H_2$: pale yellow crystal, mp 114-115 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 5.37 (brs, 1H), 5.38 (brs, 1H), 6.94-6.98 (m, 3H), 7.51-7.57 (m, 3H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.98 (dd, $J = 8.2$ Hz, $J = 1.2$ Hz, 2H), 8.06 (d, $J = 8.0$ Hz, 2H); $^{13}$C{$_1^1$H} NMR (100 MHz, CDCl$_3$) δ 115.01 (C$_1$H), 121.05 (C$_2$H), 121.76 (C$_3$H), 122.92 (C$_4$H), 123.50 (C$_5$H), 127.70 (C$_6$H), 129.13 (C$_7$H), 129.70 (C$_8$H), 131.16 (C$_9$H), 139.72 (C$_{10}$H), 140.40 (C$_{11}$H), 144.22 (C$_{12}$H), 151.93 (C$_{13}$), 152.67 (C$_{14}$H). Anal. Calcd for C$_{18}$H$_{14}$N$_2$O$_2$·0.67H$_2$O: C, 71.51; H, 5.11; N, 9.27. Found: C, 71.61; H, 4.69; N, 9.03.

Synthesis of $[\text{L}^\prime \text{H}_2]\text{B}$(Et$_3$NH)

To a mixture of $\text{L}^\prime\text{H}_2$ (5.0 mM methanol solution, 2.0 mL, 10 µmol), triisopropyl borate (5.0 mM methanol solution, 1.0 mL, 5 µmol), and methanol (2.0 mL) was added NEt$_3$ (14 µL, 100 µmol), and the reaction mixture was stirred at room temperature for 2 hours. After evaporation of solvent, reprecipitation from THF/ether gave orange powder of $[\text{L}^\prime\text{H}_2]\text{B}$(Et$_3$NH) (3.1 mg, 55%).

$[\text{L}^\prime \text{H}_2]\text{B}(\text{Et}_3\text{NH})$: orange powder, mp >300 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.99 (br, 9H), 2.69 (br, 6H), 6.83 (dd, $J = 7.6$ Hz, $J = 2.4$ Hz, 1H), 6.86 (t, $J = 7.6$ Hz, 1H), 6.98 (dd, $J = 7.6$ Hz, $J = 2.4$ Hz, 1H), 7.47-7.55 (m, 3H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.97 (d, $J = 8.0$ Hz, 2H), 8.05 (d, $J = 8.0$ Hz, 2H).

Synthesis of $[\text{L}^\prime \text{H}_2]\text{Ti}\text{Na}_2$

To a solution of $\text{L}^\prime\text{H}_2$ (10.0 mg, 35 µmol) in methanol (10 mL) was added Na$_2$CO$_3$ (1.24 mg, 11.7 µmol) and Ti(O)(acac)$_2$ (3.01 mg, 11.5 µmol), and the reaction mixture was stirred at room temperature overnight. After evaporation of solvent, reprecipitation from THF/ether gave orange powder of $[\text{L}^\prime\text{H}_2]\text{Ti}\text{Na}_2$ (19.0 mg, 57%).

$[\text{L}^\prime \text{H}_2]\text{Ti}\text{Na}_2$: orange powder, mp >300 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 6.08 (dd, $J = 7.5$ Hz, $J = 1.5$ Hz, 3H), 6.37 (t, $J = 7.5$ Hz, 3H), 6.63 (dd, $J = 7.5$ Hz, $J = 1.5$ Hz, 3H), 7.50-7.65 (m, 9H), 7.82-7.94 (m, 12H), 8.06-8.15 (m, 6H); MALDI-TOF-MS (neg) observed $m/z$ 913.2 [L$^\prime$Ti+H].

S5
(3) $^1$H NMR spectra

Figure S1. $^1$H NMR spectrum of LH$_4$ (400 MHz, DMSO-$d_6$)

Figure S2. $^1$H NMR spectrum of [L$_4$B$_4$](Et$_3$NH)$_4$ (400 MHz, DMSO-$d_6$)
Figure S3. $^1$H NMR spectrum of $[\text{L}_3\text{Ti}_2]\text{Na}_4$ (400 MHz, DMSO-$d_6$)

(4) 2D diffusion-ordered NMR spectra

Figure S4. $^1$H DOSY of LH$_4$ (600 MHz, DMSO-$d_6$, 300 K) measured under condition of diffusion time of 90 ms and gradient pulse of 5 ms.
Figure S5. $^1$H DOSY of $[\text{L}_4\text{B}_4](\text{Et}_3\text{NH})_4$ (600 MHz, DMSO-$_d$$_6$, 300 K) measured under condition of diffusion time of 120 ms and gradient pulse of 7 ms.

Figure S6. $^1$H DOSY of $[\text{L}_3\text{Ti}_2]\text{Na}_4$ (600 MHz, DMSO-$_d$$_6$, 300 K) measured under condition of diffusion time of 120 ms and gradient pulse of 7 ms.
(5) Mass spectra

Figure S7. Negative-mode ESI-TOF-MS of $[L_nB_n](\text{HNET}_3)_n$ ($n = 3, 4$).

Figure S8. Negative-mode MALDI-TOF-MS of $[L_3\text{Ti}_2]\text{Na}_4$ using dithranol as a matrix.
(6) X-ray crystallographic analysis

The single crystal of LH₄ was obtained by recrystallization from THF/hexane. CCD area-detector diffractometer data were measured with monochromatic MoKα radiation (λ = 0.71073 Å), and yielded reflections was merged after multi-scan absorption correction. The structure was solved by direct methods and refined by full-matrix least-squares on F² using all the data. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Hydrogen atoms were placed in idealized geometric positions. There are two independent molecules having an inversion point. One of them is shown in Fig S9 because the structural parameters of the two molecules are almost the same. Crystallographic data for LH₄·thf₂: C₃₂H₃₄N₂O₆, Mw = 542.61, triclinic, P-1, a = 8.9085(12), b = 11.6096(15), c = 14.9458(19) Å, α = 69.838(2), β = 74.1440(10), γ = 85.913(2)⁰, V = 1395.4(3) Å³, Z = 2, Dcalc = 1.291 g cm⁻³, λ = 0.71073 Å, µ = 0.089 mm⁻¹, T = 120(2) K, 6662 reflections, 4796 unique (Rint = 0.0109), GOF = 1.015, R₁ = 0.0360 (I > 2σ(I)), wR₂ = 0.1064. CCDC 855272 contains the supplementary crystallographic data for this paper, which can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Figure S9. ORTEP drawing of LH₄·thf₂ (50% probability): Blue: nitrogen, red: oxygen, black: carbon, green: hydrogen atoms. Selected bond lengths, angles, and dihedral angles: N(1)–N(1)* 1.256(2) Å, N(1)–C(1) 1.4288(16) Å, C(1)–C(2) 1.3898(18) Å, N(1)*–N(1)–C(1) 114.33(14)⁰, N(1)–C(1)–C(2) 115.86(11)⁰, N(1)*–N(1)–C(1)–C(2) 178.11(13)⁰.
(7) Photoisomerization

Figure S10. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of a) LH₄, and b) after photoirradiation at 360 nm for 1 hour.

Figure S11. UV-vis spectra (DMSO, [LH₄] = 25 µM) of a) LH₄ before (black) and after (red) photoirradiation at 360 nm for 1 min, and b) LH₄ at PSS at 360 nm (black) and after (red) photoirradiation at 440 nm for 20 min.
Figure S12. $^1$H NMR spectra (400 MHz, CDCl$_3$) of a) [L’$_2$B](HNEt$_3$), and b) after photoirradiation at 360 nm for 1 hour. “tt”, “ct”, and “cc” denotes [(trans-L’)$_2$B], [(cis-L’)(trans-L’)]B, and [(cis-L’)$_2$B], respectively.

Figure S13. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of a) [L’$_3$Ti]Na$_2$, and b) after photoirradiation at 360 nm for 1 hour.
(8) Computational details

An equilibrium conformation was determined by Monte Carlo method at the PM3 level. The optimization of the equilibrium conformer was performed at the BLYP/6-31G* level. There are four isomers of [L₄B₄]⁺ due to the chirality of biscatechlateboron. Here, assuming that azobenzene unit was a liner structure, the symmetry of molecules was determined.

Figure S14. The optimized geometries of two diastereomers of [L₃B₃]²⁻, D₃ and C₁ symmetric isomers.

Figure S15. The optimized geometries of four diastereomers of [L₄B₄]⁺, D₄, D₂d, C₂b, and C₂ symmetric isomers.
Figure S16. The optimized geometries of two diastereomers of $[\text{L}_3\text{Ti}_2]^+$, $D_3$ and $C_{3h}$ symmetric isomers.

References