Electronic Supplementary Information

Design of $C_2$-symmetric alkaloidal chiral amphiphiles and configurational effects on self-assembly

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All reactions were performed under nitrogen atmosphere unless otherwise specified. Reactions were monitored by thin layer chromatography using Merck Millipore TLC Silica gel F254 plates (0.25 mm) which were visualized using UV light, phosphomolybdic acid (PMA) stain, PMS stain and p-anisaldehyde strain and cerium ammonium molybdate stain (CAM). Flash column chromatography was performed using Kanto Silica Gel 60N. The medium pressure liquid chromatography (MPLC) purifications were performed on a YAMAZEN YFLC-AI-580 and Biotage® Isolera. \(^1\)H and \(^{13}\)C nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-ECA 500 spectrometer (\(^1\)H/500 MHz, \(^{13}\)C/125 MHz), JEOL JNM-ECX 400 spectrometer (\(^1\)H/400 MHz, \(^{13}\)C/100 MHz) JEOL JNM-ECP 300 (\(^1\)H/300 MHz, \(^{13}\)C/75 MHz) spectrometer. Chemical shifts are reported in \(\delta\) (ppm) using chloroform and dimethyl sulfoxide as an internal standard of \(\delta\; 7.26, 2.50\) and \(77.16, 39.52\) for \(^1\)H and \(^{13}\)C-NMR, respectively. Data for \(^1\)H-NMR are reported as follows: chemical shift (number of hydrogens, multiplicity, coupling constant). Multiplicity is abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), br (broad). Electrospray ionization time-of-flight mass (ESI-TOF MS) spectra were recorded on Bruker Daltonics micrOTOF-QII. UV-vis absorption spectra were recorded on a JASCO V-650 spectrometer. Fluorescence spectra were recorded on JASCO FP-6500 and Shimadzu RF-6000 spectrometers. 11-Bromo-1-undecene (15) was purchased from FUJIFILM Wako Pure Chemical Co. or Tokyo Chemical Industry Co., Ltd. (TCI). Tris(2,2'-bipyridyl)ruthenium(II) hexafluorophosphate was obtained from TCI. Pd(PPh\(_3\))\(_4\) was purchased from Sigma-Aldrich or TCI. All of reagents and commercial solvents were used as received.
Molecular models of 4–7

Figure S1  Molecular models of 4–7 calculated by the semi-empirical molecular orbital PM3 method. Top views: a) 4, b) 5, c) 6 and d) 7. Side views: e) 4 and f) 6. In the models, the alkyl links in 5 and 7 have Z geometries. Gray, blue and red parts depict carbon, nitrogen and oxygen atoms, respectively. Hydrogen atoms are omitted for clarity. The phenylacetylene (PA) units are drawn in a ball and stick style. The dihedral angles between the PA units: a) 40.3° for 4, c) 36.7° for 6.
UV-vis absorption spectra of 4–7

Figure S2  UV-vis absorption spectra of a) 4, b) 5, c) 6 and d) 7 in the mixtures of THF and water with various ratios at 20 °C. [4–7] = 20 µM.
Spectroscopic analyses of 19

**Figure S3**  a) UV-vis absorption, b) circular dichroism and c) fluorescence spectra of 19 in THF at 20 °C. Excitation wavelength: 272 nm. [19] = 20 µM.
Fluorescence spectra of 4–7

Figure S4  Fluorescence spectra of a) 4, b) 5, c) 6 and d) 7 in THF (black lines) and a mixture of THF and water at 10/90 (blue lines) at 20 °C. [4–7] = 20 µM. Excitation wavelengths: a) 272, b) 278, c) 272 and d) 278 nm in THF, a) 273 b) 269, c) 274 and d) 271 nm in the mixture of THF and water.
Synthetic procedures

Synthesis of $C_2$ dimer 10

**Compound 9:**$^1$ To a solution of 8 (9.00 g, 21.5 mmol) in CH$_2$Cl$_2$ (200 mL, 0.11 M) were successively added PPTS (5.40 g, 21.5 mmol, 1.0 eq.) and NBS (3.83 g, 21.5 mmol, 1.0 eq.) at room temperature. After being stirred for 30 min at room temperature, the resulting mixture was treated with brine. The organic layer was separated, washed with aqueous solutions of NaHCO$_3$, Na$_2$SO$_3$, and brine, and dried over Na$_2$SO$_4$. After filtration and concentration in vacuo, the residue was purified by silica-gel chromatography (hexane/AcOEt) to afford 9 (9.49 g, 19.1 mmol, 89%).

9: $R_f = 0.44$ (Hex–AcOEt = 3 : 1); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.55 (1H, br-s), 7.37–7.29 (2H, m), 7.12 (1H, dd, $J = 8.1$, 7.4 Hz), 6.40 (1H, s), 3.89 (1H, dd, $J = 10.4$, 6.3 Hz), 3.75 (3H, s), 3.21 (1H, dd, $J = 12.6$, 6.3 Hz), 2.82 (1H, dd, $J = 12.6$, 10.4 Hz), 1.59 (9H, s), 1.40 (9H, br-s).

**Compound 10:**$^2$ A mixture of 9 (5.00 g, 10.1 mmol), DPPE (602 mg, 1.51 mmol, 15 mol%), NiI$_2$ • 6H$_2$O (634 mg, 1.51 mmol, 15 mol%) in DMA (8.2 mL, 1.23 M) was degassed by four cycles of gentle pumping and argon replacement. After addition of manganese (762 mg, 11.6 mmol, 1.15 eq.), the mixture was then degassed by four cycles in the almost identical manner. The mixture was then allowed to be stirred for 12 h at room temperature under argon. The mixture was diluted with AcOEt, treated with 1 M HCl and then extracted with AcOEt. The organic extracts were washed with 1 M HCl, H$_2$O, saturated aqueous solution of Na$_2$SO$_3$ and brine, and then dried over Na$_2$SO$_4$. Drying agent was filtered off and the solvent was removed under reduced pressure. During the concentration, white solid was precipitated and filtered off. The resulting residue was purified by silica-gel chromatography (hexane/AcOEt) to afford 10 (2.73 g, 3.27 mmol, 65%).

10: $R_f = 0.42$ (Hex–AcOEt = 2 : 1); $^1$H NMR (400 MHz, DMSO-$_d_6$, 95 °C): $\delta$ 7.37 (2H, d, $J = 8.0$ Hz), 7.21–7.11 (4H, m), 6.91 (2H, m), 6.09 (2H, s), 3.70 (2H, m), 3.68 (6H, s), 2.64 (2H, dd, $J = 12.7$, 7.0 Hz), 2.25 (2H, dd, $J = 12.7$, 9.5 Hz), 1.57 (18H, s), 1.33 (18H, s).

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Syntheses of enyne 14

![Chemical structures and reactions](image)

**Compound S2:** To a stirred solution of 11-bromo-1-undecene (15) (3.06 g, 13.1 mmol) in acetone (10 mL, 1.3 M) was added NaI (2.42 g, 16.1 mmol, 1.2 eq.) and the resulting solution was refluxed for 5 h. The resulting mixture was treated with H2O (40 mL) and extracted with CH2Cl2 (25 mL × 4). The combined organic extracts were washed with saturated aqueous solution of Na2SO3, dried over Na2SO4, filtered and concentrated *in vacuo* to afford S1 (3.92 g) as a colorless liquid, which was used without further purification. To a solution of trimethylsilylacetylene (2.75 mL, 19.9 mmol, 1.5 eq.) in THF (5 mL) was added n-BuLi (1.55 M in hexane, 11.0 mL, 17.1 mmol, 1.3 eq.) over 5 min at −78 °C. After being stirred for 30 min, HMPA (10.4 mL) was added to the mixture. A solution of S1 (3.92 g) in THF (13 mL) was added dropwise at −78 °C and then mixture was allowed to warm up to room temperature. After being stirred for 5 h, saturated aqueous solution of NH4Cl (50 mL) was added to the resulting mixture. The layers were separated, and the aqueous layer was extracted with AcOEt (130 mL × 3). The combined organic extracts were washed with brine (150 mL), dried over Na2SO4, filtered and concentrated *in vacuo*. The crude residue was purified by silica-gel column chromatography (hexane) to afford S2 (3.03 g, 12.1 mmol, 92% for 2 steps) as a colorless liquid.

S2: $^4$ Rf = 0.41 (Hex); $^1$H NMR (500 MHz, CDCl3): $\delta$ 5.81 (1H, ddt, J = 18.1, 10.6, 6.8 Hz), 4.99 (1H, ddt, J = 18.1, 2.3, 1.7 Hz), 4.93 (1H, br-d, J = 10.6 Hz), 2.21 (2H, t, J = 7.2 Hz), 2.04 (2H, dt, J = 7.5, 7.2 Hz), 1.54–1.48 (2H, m), 1.41–1.32 (4H, m), 1.31–1.26 (8H, m), 0.14 (9H, s).

**Compound 14:** To a solution of S2 (3.56 g, 14.2 mmol) in MeOH (284 mL, 0.05 M) was added potassium carbonate (5.90 g, 42.7 mmol, 3.0 eq.) at room temperature. The suspension was stirred at room temperature for 10.5 h and then solvent was evaporated under reduced pressure. The resulting mixture was treated with brine (60 mL) and H2O (40 mL) extracted with Et2O (160 mL × 3). The combined organic extracts were washed with brine, dried over Na2SO4, filtered, and concentrated *in vacuo* to afford 14 (2.41 g, 13.5 mmol, 95%) as a colorless liquid.

14: $^5$ Rf = 0.59 (Hex); $^1$H NMR (500 MHz, CDCl3): $\delta$ 5.81 (1H, ddt, J = 17.2, 10.3, 6.8 Hz), 4.99 (1H, ddt, J = 17.2, 2.3, 1.7 Hz), 4.94–4.92 (1H, m), 2.18 (2H, td, J = 7.2, 2.7 Hz), 2.04 (2H, dt, J = 7.5, 6.8 Hz), 1.94 (1H, t, J = 2.7 Hz), 1.56–1.49 (2H, m), 1.40-1.34 (4H, m), 1.28 (8H, s).

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Syntheses of enyne 19

**Compound S3:** To a stirred solution of 9 (314 mg 0.631 mmol) in DMF (6.3 mL, 0.10 M) was successively added Ru cat. (tris(2,2’-bipyridyl)ruthenium(II) hexafluorophosphate) (14.1 mg, 16.4 µmol, 2.6 mol%), ethyldiisopropylamine (DIPEA) (1.08 mL, 6.31 mmol, 10 eq.) and HCO₂H (0.240 mL, 6.31 mmol, 10.0 eq.) at room temperature. The resulting mixture was placed at a distance of ~10 cm from a 15 W fluorescent lamp. After being stirred at room temperature for 4 h, the resulting mixture was poured into a separatory funnel containing 80 mL of Et₂O and 80 mL of H₂O. The layers were separated and the aqueous layer was extracted with Et₂O (100 mL × 2). The combined organic extracts were dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude residue was purified by silica-gel column chromatography (hexane/AcOEt) to afford S3 (160 mg, 0.382 mmol, 61%) as a white solid.

δ ~1H NMR (500 MHz, CDCl₃): δ 7.54 (1H, br-s), 7.22 (1H, dd, J = 7.5, 7.5 Hz), 7.15 (1H, d, J = 7.5 Hz), 7.04 (1H, dd, J = 7.5, 7.5 Hz), 6.37 (1H, d, J = 6.3 Hz), 3.97–3.94 (2H, m), 3.72 (3H, s), 2.53–2.46 (1H, m), 2.30–2.24 (1H, m), 1.56 (9H, s), 1.39 (9H, s);

**Compound S4:** To a stirred solution of S3 (80.2 mg 0.192 mmol) in MeCN (0.80 mL, 0.24 M) was added NIS (104 mg, 0.462 mmol, 2.4 eq.) and PPTS (25.8 mg, 0.103 mmol, 54 mol%) at room temperature. After being stirred at room temperature for 11.5 h, the mixture was diluted with AcOEt, washed with saturated aqueous solution of NaHCO₃ (10 mL), Na₂SO₄ (25 mL) and then brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude residue was purified by silica-gel column chromatography (hexane/AcOEt) to afford S4 (88.7 mg, 0.163 mmol, 85%) as a white solid.

δ ~1H NMR (500 MHz, CDCl₃, 50 ºC): δ 7.52 (1H, d, J = 8.3 Hz), 7.44 (1H, d), 7.36 (1H, br-d, J = 8.3 Hz), 6.32 (1H, d, J = 5.7 Hz), 4.00 (1H, dd, J = 9.5, 7.2 Hz), 3.95–3.91 (1H, m), 3.73 (3H, s), 2.50–2.46 (1H, m), 2.30–2.24 (1H, m), 1.56 (9H, s), 1.39 (9H, s);

δ ~1H NMR (125 MHz, CDCl₃, 50 ºC): δ 173.09, 152.27, 142.63, 137.49, 135.03, 132.63, 119.67, 86.10, 82.13, 81.04, 59.20, 52.19, 44.74, 33.06, 28.46, 28.38; HR-MS (ESI): calcd. for C₂₂H₂₃IN₂O₆Na [M+Na]⁺ 567.0962, found 567.0945.

Compound 19: Pd(PPh₃)₄ (21.7 mg, 18.8 μmol, 17 mol%) and Cul (4.60 mg, 24.2 μmol, 22 mol%) were placed in a flask, and a solution of the iodide S₄ (58.7 mg, 0.108 mmol), enyne 12 (61.0 mg, 0.342 mmol, 3.2 eq.) and Et₃N (2.7 mL) in DMF (1.35 mL) was added. The mixture was heated at 90 °C with stirring for 3 h. After being cooled to 0 °C, the resulting mixture was treated with saturated aqueous solution of NH₄Cl (10 mL) and extracted with Et₂O (50 mL × 3). The combined organic extracts were washed with H₂O (40 mL × 3) and brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude residue was purified by silica-gel column chromatography (hexane/AcOEt) to afford 19 (48.2 mg, 81.0 μmol, 75%) as a pale brown amorphous. 19: Rf = 0.63 (Hex–AcOEt = 2 : 1); ¹H NMR (500 MHz, CDCl₃): δ 7.47 (1H, br-s), 7.27 (1H, br d, J = 8.0 Hz), 7.19 (1H, s), 6.35 (1H, d, J = 5.7 Hz), 5.81 (1H, ddt, J = 17.2, 10.3, 6.8 Hz), 5.01–4.97 (1H, m), 4.94–4.91 (1H, m), 3.96 (1H, dd, J = 9.7, 6.9 Hz), 3.92 (1H, br-t, J = 6.3 Hz), 3.72 (3H, s), 2.51 (1H, dd, J = 12.7, 7.2 Hz), 2.38 (2H, t, J = 7.2 Hz), 2.26 (1H, ddd, J = 12.7, 9.7, 7.2 Hz), 2.04 (2H, dt, J = 7.1, 7.1 Hz), 1.62–1.25 (14H, m), 1.56 (9H, s), 1.39 (9H, s); ¹³C-NMR (125 Hz, CDCl₃): δ 173.22, 152.38, 141.87, 139.38, 132.33, 132.12, 126.73, 119.24, 117.48, 114.26, 89.87, 81.95, 80.98, 80.39, 59.11, 52.27, 44.75, 33.95, 33.04, 29.85, 29.62, 29.31, 29.28, 29.09, 28.96, 28.45, 28.36, 19.57; HR-MS (ESI): calcd for C₃₅H₅₀N₂O₆Na [M+Na]⁺ 617.3561, found 617.3544.

Figure S5  $^1$H-NMR spectrum (500 MHz) of 11 in DMSO-$d_6$ at 90 ºC.
Figure S6  $^{13}$C-NMR spectrum (125 MHz) of 11 in DMSO-$d_6$ at 90 °C.
Figure S7  $^1$H-NMR spectrum (500 MHz) of 12 in CDCl$_3$ at 50 ºC.
Figure S8  \(^{13}\)C-NMR spectrum (125 MHz) of 12 in DMSO-\(d_6\) at 90 °C.
Figure S9  $^1$H-NMR spectrum (500 MHz) of 13 in DMSO-_$d_6$ at 90 °C.
**Figure S10**  $^{13}$C-NMR spectrum (125 MHz) of 13 in DMSO-$d_6$ at 90 ºC.
Figure S11  $^1$H-NMR spectrum (500 MHz) of 4 in DMSO-$d_6$ at 90 ºC.
Figure S12  $^{13}$C-NMR spectrum (500 MHz) of 4 in DMSO-$d_6$ at 90 ºC.
Figure S13  $^1$H-NMR spectrum (500 MHz) of 5 in DMSO-$d_6$ at 90 °C.
Figure S14  $^{13}$C-NMR spectrum (125 MHz) of 5 in DMSO-$d_6$ at 90 °C.
Figure S15 $^1$H-NMR spectrum (500 MHz) of the aryl bromide (obtained through bromination of 10) in CDCl$_3$ at 50 ºC.
Figure S16. $^{13}$C-NMR spectrum (125 MHz) of the aryl bromide (obtained through bromination of 10) in CDCl$_3$ at 50 ºC.
Figure S17  $^1$H-NMR spectrum (500 MHz) of 17 in DMSO-$d_6$ at 90 °C.
Figure S18  $^{13}$C-NMR spectrum (125 MHz) of 17 in DMSO-$d_6$ at 90 ºC.
Figure S19: $^1$H-NMR spectrum (500 MHz) of 6 in DMSO-$d_6$ at 90 ºC.
Figure S20  $^{13}$C-NMR spectrum (125 MHz) of 6 in DMSO-$d_6$ at 90 ºC.
Figure S21  $^1$H-NMR spectrum (500 MHz) of 7 in DMSO-$d_6$ at 90 °C.
Figure S22  $^{13}$C-NMR spectrum (125 MHz) of 7 in DMSO-$d_6$ at 90 °C.
Figure S23  $^1$H-NMR spectrum (500 MHz) of S4 in CDCl$_3$ at 50 $^\circ$C.
Figure S24  $^{13}$C-NMR spectrum (125 MHz) of S4 in CDCl$_3$ at 50 °C.
Figure S25  $^1$H-NMR spectrum (500 MHz) of 19 in CDCl$_3$. 
Figure S26  $^{13}$C-NMR spectrum (125 MHz) of 19 in CDCl$_3$.