Supporting Information

A chiral trianglular coordination complex derived from (*S*,*S*)-2,3-dimethoxy-di-4-(2′-carboxyl-5′-pyridyl)phenyl butane by Self-assembly

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General. Unless otherwise noted, all materials were obtained from commercial suppliers, Aldrich and TCI, and used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl prior to use. Toluene was distilled from calcium hydride and stored over 4 Å molecular sieve. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (0.25 mm thickness, Merck, Darmstadt) and visualized by ultraviolet light and treatment with acidic *p*-anisaldehyde stain followed by gentle heating. Flash chromatography was carried out using silica gel 60 (230–400 mesh). ^{1}H NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. ^{13}C NMR spectra were recorded on a Varian Mercury 75 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS as the internal reference ($CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ 77.7 ppm). High performance liquid chromatography (HPLC) was conducted using a Waters 600 system with a 2487 ultraviolet detector at 254 nm. Infrared (IR) spectra were recorded on a

Bomem 102 FT-IR spectrometer. Optical rotations were measured at the 589 nm sodium D-Line from RUDOLPH AUTOPOL automatic polarimeter. Low- and high-resolution FAB mass spectra were obtained on a JEOL JMS-AX505WA mass spectrometer. Melting points were measured by capillary melting point apparatus of Thomas Hoover and are uncorrected.

***trans*-4,4′-Dibromostilbene** To a stirred suspension of zinc powder (19.9 g, 302 mmol) in dry THF (300 mL) added $TiCl_4$ (16.5 mL, 151 mmol) slowly at −10 ^{0}C. Then, a solution of 4-bromobenzaldehyde (10.0 g, 54 mmol) in dry THF (250 mL) was added dropwise while the mixture was refluxed and stirred for 5 h. The solution was quenched with saturated aqueous $NaHCO_3$ solution and extracted with EtOAc. The extract was washed with brine, dried over $MgSO_4$, and concentrated. The residue was washed with hexane to give **2** as a white solid (8.84 g, 97%). TLC (hexane/EtOAc = 5:1) $R_f = 0.62$; mp = 183–185 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (s, 2H), 7.37 (d, $J = 8.7$ Hz, 4H), 7.49 (d, $J = 8.7$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.62, 127.99, 128.10, 131.84, 135.88; FT-IR (KBr, cm^{-1}) 3055. Element analysis of $C_{14}H_{10}Br_2$: calcd C 49.74, H 2.98, Br 47.28, found C 49.33, H 2.94.

(*S*,*S*)-1,2-Bis(4-bromophenyl)-ethane-1,2-diol AD-mix-α (0.7 g, 1.4 g per mmol) was stirred in two phases of *t*-butyl alcohol (2.5 mL) and H_2O (2.5 mL) at rt After the two phases were clearly formed, $CH_3SO_2NH_2$ (48 mg, 0.5 mmol) was added to the AD-mix-α solution at 0 °C. *trans*-4,4′-Dibromostilbene (120 mg, 0.5 mmol) was added to the reaction mixture at 0 °C. The resultant reaction mixture was stirred at 0 °C for 20 h. After completion of the reaction, the mixture was quenched with a saturated aqueous Na_2CO_3 solution and extracted with EtOAc three times. The combined extract was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting pale yellow precipitate was purified by flash chromatography (hexane/EtOAc = 1:1) to afford **3** (103 mg, 75%) as a white solid. TLC (hexane/EtOAc = 1:1) $R_f = 0.45$; mp = 112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.27 (s, 2H), 4.48 (s, 2H), 6.90 (d, $J = 8.4$ Hz, 4H), 7.34 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 78.42, 122.02, 128.62, 131.31, 138.38; FT-IR (KBr, cm^{-1}) 3379, 3055, 2933; Element analysis of $C_{14}H_{12}Br_2O_2$: calcd C 45.20, H 3.25, Br 42.95, O 8.60, found C 45.14, H 3.23; $[\alpha]_D^{18} = -1434$ (c = 0.0052 g/mL, $CHCl_3$, 99.9% ee); HPLC (Daicel Chiralpak AD-H, *n*-hexane/isopropanol = 9:1, flow 0.5 mL/min, detection at 254 nm), $\tau_R = 20.25$ min.

(*S,S*)-1,2-Bis(4-bromophenyl)-1,2-dimethoxyethane (3). A solution of (*S,S*)-1,2-bis(4-bromophenyl)-ethane-1,2-diol (1.00 g, 2.69 mmol) was slowly added to a suspension of NaH (60% in oil, 533 mg, 13.4 mmol) in dry THF (20 mL) at 0 °C under argon atmosphere. After completion of gas evolution (ca. 10 min), a solution of iodomethane (0.58 mL, 9.4 mmol) in THF (1 mL) was added to the reaction mixture at rt. After stirring for 24 h, the reaction was quenched with H_2O carefully and partitioned between H_2O and EtOAc. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting white solid was purified by flash chromatography (hexane/EtOAc = 5:1) to afford **3** (1.08 g, 100%) as a white solid. TLC (hexane/EtOAc = 5:1) $R_f = 0.43$; mp = 73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.23 (s, 6H), 4.24 (s, 2H), 6.87 (d, $J = 8.4$ Hz, 4H), 7.33 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.25, 86.44, 121.76, 129.50, 131.10, 136.88; FT-IR

(KBr, cm^{-1}) 3059, 2916; Element analysis of $C_{16}H_{16}Br_2O_2$: C 48.03, H 4.03, Br 39.94, O 8.00, found C 48.13, H 4.22; $[\alpha]_D^{17} = -153$ (c = 0.005 g/mL, $CHCl_3$).

(*S,S*)-1,2-Bis(4-tributylstannyl-phenyl)-1,2-dimethoxyethane (4). A solution of *n*-butyllithium (12.50 mL of 1.6 M solution in hexane, 20 mmol) was added slowly to a solution of **3** (4.00 g, 10.0 mmol) in dry THF (50 mL) at −78 °C under argon atmosphere. After stirring for 2 h at −78 °C, tributyltinchloride (5.43 mL, 20 mmol) was added, and the reaction mixture was allowed to warm to rt with stirring for 3 h. The reaction was quenched with 1 M aqueous KF solution (20 mL) and extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting brown oil was purified by flash chromatography to provide **4** (8.12 g, 99%) as a transparent oil. TLC (hexane/EtOAc = 10:1) $R_f = 0.7$; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, J =7.7 Hz, 4H), 6.90(d J =7.7 Hz, 4H), 4.23(s, 2H), 3.27 (s, 6H), 0.84–1.58 (m, 54H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.45, 13.69, 27.29, 29.03, 57.21, 87.76, 127.32, 135.77, 137.85, 141.02; FT-IR (KBr, cm^{-1}) 2919, 1465, 1124; $[\alpha]_D^{20} = -105.71$ (c = 0.0035 g/mL, $CHCl_3$).

(*S,S*)-1,2-Bis-(4-(pyridine-2-carboxylic acid methyl ester)-phenyl)-1,2-dimethoxy-ethane $(CH_3)_2$**-5.** Compound **4** (2.50 g, 3.04 mmol), 5-bromo-pyridine-2-carboxylic acid methyl ester (2.60 g, 12.2 mmol) and tetrakis(triphenylphosphino)palladium (561 mg, 0.486 mmol) were added into toluene (30 mL) and the reaction mixture was heated under argon atmosphere at 120 °C for 5 h. Solvent was evaporated in vacuo and the residue was dissolved in EtOAc. Then the organic layer was washed with brine, separated and dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography to afford the corresponding product $(CH_3)_2$-**5** (1.20 g, 77%). TLC (hexane/EtOAc =1:1) $R_f = 0.1$; mp =340 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.3 (s, 6H), 4.0 (s, 6H), 4.4 (s, 2H), 7.2 (m, 4H), 7.5 (d, J =8.2 Hz, 4H), 8.0 (dd, J = 8.1, 2.1 Hz, 2H), 8.2 (d, J = 8.2 Hz, 2H), 8.9 (d, J = 1.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.1, 57.7, 86.9, 125.4, 127.1, 129.1, 135.2, 136.2, 139.4, 139.5, 146.7, 148.4, 165.8; FT-IR (KBr, cm^{-1}) 1702, 1592; HRMS (FAB+) for $C_{30}H_{28}N_2NaO_6$ (MNa$^+$), calcd 535.1845, found 535.1844; $[\alpha]_D^{24} = -297$ (c = 0.0055 g/mL, $CHCl_3$).

(S,S)-1,2-Bis-(4-(2-nicotinic acid)-phenyl)-1,2-dimethoxy-ethane (H_2-**5).** A solution of $(CH_3)_2$-**5** (500 mg, 0.98 mmol) and 6 M ^{aq}KOH (10 mL) in EtOH/H_2O (10mL/10mL) were stirred at room temperature for 5 h. The reaction mixture was acidified to pH 2.0 with 1 N HCl and then partitioned between EtOAc and H_2O. The organic layer was washed with aqueous NaCl solution and then dried over anhydrous $MgSO_4$, and concentrated in vacuo. The solid residue was recrystallized from EtOAc with n-hexane to afford **(**H_2-**5)** (350 mg, 74%) as a white solid. TLC (CH_2Cl_2/MeOH = 10:1) $R_f = 0.35$; mp = 242 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.2 (s, 6H), 4.5 (s, 2H), 7.3 (d, J = 5.8 Hz, 4H), 7.7 (d, J = 6.0 Hz, 4H), 8.1 (d, J = 6.3 Hz, 2H), 8.2 (s, 2H), 9.0 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 56.8, 85.5, 125.0, 126.6, 128.9, 134.9, 135.4, 138.0, 139.3, 146.6, 147.1, 165.8; FT-IR (KBr, cm^{-1}) 3424, 3006, 2905, 1666; HRMS (FAB+) for $C_{28}H_{24}N_2O_6Na$ (MNa$^+$), calcd 507.1532, found 507.1522; $[\alpha]_D^{24} = +257$ (c = 0.0053 g/mL, DMSO).