Electronic Supplementary Information for:

Photocontrolled template-directed synthesis of complementary double helices assisted by amidinium-carboxylate salt bridge formation

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1. Materials

All starting materials and dehydrated solvents were purchased from Aldrich (Milwaukee, WI), Wako Pure Chemical Industries (Osaka, Japan), and Tokyo Chemical Industry (Tokyo, Japan) unless otherwise noted. Silica gel (SiO₂) and aminopropyl-modified silica gel (NH-SiO₂) for the flash chromatography were purchased from Merck (Darmstadt, Germany) and Fuji Silysia Chemical Ltd. (Kasugai, Japan), respectively. Bio-Beads SX-1 for the SEC was purchased from Bio-Rad Laboratories. Compounds 1_{C} ,¹ 2_{C} ,¹ 4_{A} ,² 4_{C} ,³ T_{AA} ,⁴ A-H,² C-H,³ and 5^5 were prepared according to the previously reported methods.

2. Instruments

The melting points were measured using a Yanaco MP-500D melting point apparatus (Kyoto, Japan) and were uncorrected. The NMR spectra were obtained using a Varian UNITY INOVA 500AS spectrometer operating at 500 MHz for ¹H and 125 MHz for ¹³C. Chemical shifts are reported in parts per million (δ) downfield from tetramethysilane (TMS) as the internal standard in CDCl₃. The recycling preparative HPLC was performed with an LC-928R liquid chromatograph (Japan Analytical Industry, Tokyo, Japan) equipped with two SEC columns (JAIGEL-1H (1 × 60 cm) and JAIGEL-2H (1 × 60 cm)) in series and a UV-visible detector (254 nm, JAI UV-310), and chloroform was used as the eluent. The ESI-MS spectra were recorded on a JEOL JMS-T100CS spectrometer (Akishima, Japan). The IR spectra were recorded using a JASCO Fourier Transform IR-680 spectrophotometer (Hachioji, Japan). The absorption and CD spectra were measured in a 0.1-mm quartz cell on a JASCO V-570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The optical rotations were taken using a JASCO P-1030 polarimeter in a 2-cm quartz cell equipped with a temperature controller (EYELA NCB-2100). The photoirradiation for *trans/cis* isomerization of **T**_{CC} was performed on a JASCO FP-6500 spectrofluorometer with a 150 W xenon lamp. The slit width used in the experiments was 20 nm.

3. Synthetic procedures

The optically active amidine monomers 1_A and 2_A bearing a formyl and an amino group at one end, respectively, and the azobenzene-linked carboxylic acid dimer T_{CC} were synthesized according to Scheme S1.



Scheme S1 Synthesis of chiral amidine monomers (1_A and 2_A) and achiral carboxylic acid template (T_{CC}). Reagents and conditions: (a) *p*-bromobenzaldehyde for 1_A and *p*-bromobenzylamine hydrochloride for 2_A , Pd(PPh₃)₄, CuI, toluene-diisopropylamine, 65 °C. (b) Pd(PPh₃)₄, CuI, THF-Et₃N, ambient temperature.

Amidine monomer $\mathbf{1}_{A}$. Copper (I) iodide (2.38 mg, 12.5 µmol) was added to a solution of \mathbf{A} -H² (150)mg, 0.250 mmol), *p*-bromobenzaldehyde (50.8)mg, 0.275 mmol). and tetrakis(triphenylphosphine)palladium(0) (14.4 mg, 12.5 µmol) in toluene-diisopropylamine (7/3 (v/v), 15 mL) and the mixture was stirred at 65 °C for 13 h. After evaporating the solvents, the residue was purified by column chromatography (NH-SiO₂, CHCl₃/Et₂O = 5/1 to 5/3 (v/v)) and Bio-Beads (SX-1, CHCl₃) to give pure $\mathbf{1}_A$ (69.4 mg, 39.3% yield) as a white solid. Mp = 87.0-90.2 °C; $[a]_D^{20}$ -104 (c = 0.1 in CHCl₃). ¹H NMR (500 MHz, CDCl₃, 25 °C, as 1_{A} (CH₃CO₂H)): δ 12.84 (br, 2H, NH), 10.03 (s, 1H, CHO), 7.88 (d, J = 8.3 Hz, 2H, ArH), 7.78 (t,

J = 7.8 Hz, 1H, ArH), 7.68 (d, J = 8.3 Hz, 2H, ArH), 7.56–7.51 (m, 2H, ArH), 7.35–7.20 (m, 10H, ArH), 7.07–7.00 (m, 4H, ArH), 6.73 (d, J = 8.3 Hz, 2H, ArH), 6.66 (d, J = 8.3 Hz, 2H, ArH), 3.93 (q, J = 6.7 Hz, 2H, PhCHN), 2.10 (s, CH₃CO₂), 0.72 (d, J = 6.7 Hz, 3H, CH₃CHN), 0.71 (d, J = 6.7 Hz, 3H, CH₃CHN), 0.26 (s, 9H, TMS); ¹³C NMR (125 MHz, CDCl₃, 25 °C, as 1_A·(CH₃CO₂H)): δ 191.55, 178.69, 162.64, 143.03, 141.84, 141.56, 138.73, 138.13, 135.73, 132.40, 132.30, 132.21, 131.99, 130.83, 130.63, 129.76, 129.39, 129.18, 128.87, 128.59, 128.10, 128.06, 126.75, 126.69, 123.51, 122.80, 122.76, 104.32, 96.24, 92.75, 90.16, 55.7, 24.0, 22.4, 0.14; IR (KBr, cm⁻¹): 3423 (v_{N-H}), 2157 (v_{C-C}), 1702 (v_{C-O}), 1636 (v_{C-N}); HRMS(ESI): m/z calcd for [M(C₄₉H₄₄N₂OSi)+H]⁺, 705.3301; found 705.3278.

Amidine monomer 2_A . Copper (I) iodide (0.76 mg, 4.0 µmol) was added to a solution of $A-H^2$ (120 mg, 0.199 mmol), p-bromobenzylamine hydrochloride (223 mg, 1.00 mmol), and tetrakis(triphenylphosphine)palladium(0) (4.62 mg, 4.00 µmol) in toluene-diisopropylamine (7/3 (v/v), 10 mL). After the mixture was stirred at 65 °C for 20 h, the solvents were evaporated to dryness. The residue was purified by column chromatography (NH-SiO₂, hexane/CHCl₃ = 3/1 to 1/1 (v/v)) and Bio-Beads (SX-1, CHCl₃) to give pure 2_A (34.6 mg, 24.5% yield) as a white solid. Mp = 92.0-94.0 °C; $[a]_{D}^{20}$ -104 (c = 0.1 in CHCl₃). ¹H NMR (500 MHz, CDCl₃, 25 °C, as 2_{A} ·(CH₃CO₂H)): δ 13.15 (br, 2H, NH), 7.76 (t, J = 7.5 Hz, 1H, ArH), 7.55–7.49 (m, 6H, ArH), 7.33–7.21 (m, 6H, ArH), 7.07–7.01 (m, 6H, ArH), 6.71 (d, J = 8.0 Hz, 2H, ArH), 6.68–6.64 (m, 4H, ArH), 3.95-3.90 (m, 4H, PhCHN, CH_2NH_2), 2.08 (s, CH_3CO_2), 0.72 (d, J = 5.0 Hz, 3H, CH₃CHN), 0.71 (d, J = 5.0 Hz, 3H, CH₃CHN), 0.25 (s, 9H, TMS); ¹³C NMR (125 MHz, CDCl₃, 25 °C, as **2**_A·(CH₃CO₂H)): δ 176.65, 162.77, 142.8, 142.75, 141.74, 138.13, 137.93, 132.34, 132.13, 132.03, 130.70, 130.62, 129.20, 129.19, 128.73, 128.66, 128.63, 128.56, 128.13, 127.60, 126.74, 126.71, 123.62, 123.50, 123.44, 122.61, 104.30, 96.23, 90.92, 88.98, 55.6, 22.3, 21.8, 0.14; IR (KBr, cm⁻¹): 3422 (v_{N-H}), 2157 ($v_{C=C}$), 1637 ($v_{C=N}$); HRMS(ESI): m/z calcd for [M(C₄₉H₄₇N₃Si)+H]⁺, 706.3617; found 706.3627.

Dicarboxylic acid template T_{CC} . To a mixture of 4,4'-diiodoazobenzene 5⁵ (21.7 mg, 50.0

μmol), copper (I) iodide (0.47 mg, 2.5 μmol), and tetrakis(triphenylphosphine)palladium(0) (2.89 mg, 2.50 μmol) in Et₃N/THF (1/1 (v/v), 2.0 mL) was added C-H³ (50.3 mg, 0.100 mmol). After the mixture was stirred at ambient temperature for 20 h, the solvents were evaporated to dryness. The residue was dissolved in chloroform, and the solution was washed with 1N HCl, water, and brine. The organic layer was dried over Na₂SO₄. After evaporating the solvent, the residue was purified by column chromatography (SiO₂, CHCl₃/EtOAc = 20/1 to 10/1 (v/v)) and recycling preparative HPLC (CHCl₃) to give pure T_{CC} (38.5 mg, 65.1% yield) as an orange solid. Mp = 242.0–243.6 °C; ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 7.85 (d, *J* = 8.4 Hz, 4H, ArH), 7.65 (d, *J* = 8.4 Hz, 4H, ArH), 7.61 (d, *J* = 8.3 Hz, 4H, ArH), 7.52 (d, *J* = 8.3 Hz, 4H, ArH), 7.43–7.37 (m, 8H, ArH), 7.32 (d, *J* = 8.2 Hz, 4H, ArH), 2.42 (t, *J* = 7.0 Hz, 4H, C=CCH₂), 1.64–1.57 (m, 4H, CH₂), 1.49–1.41 (m, 4H, CH₂), 1.36–1.28 (m, 8H, CH₂), 0.90 (t, *J* = 7.0 Hz, 6H, CH₃), 0.25 (s, 18H, TMS); ¹³C NMR (125 MHz, CDCl₃, 25 °C) δ 151.95, 140.16, 140.07, 139.94, 139.88, 132.63, 132.14, 132.05, 131.92, 130.60, 128.70, 128.49, 126.23, 126.05, 123.19, 122.98, 122.79, 104.9, 95.52, 93.26, 91.95, 90.4, 79.6, 31.5, 28.8, 28.7, 22.7, 19.6, 14.2, 0.12; IR (KBr, cm⁻¹): 3449 (v₀–_H), 2157 (v_{C=C}), 1701 (v_{C=O}); HRMS(ESI): m/z calcd for [M(C₈₀H₇₄ N₂O₄Si₂)–H]⁻, 1181.5109; found 1181.5156.

4. Time-dependent 1H NMR spectral changes of the mixtures of 1_A and 2_A in the absence and presence of T_{CC} or 4_C



Fig. S1 Time-dependent ¹H NMR (500 MHz, CDCl₃) spectral changes of the mixtures of 1_A (0.50 mM) and 2_A (0.50 mM) in the presence of T_{CC} (0.50 mM) at 25 °C.



Fig. S2 Time-dependent ¹H NMR (500 MHz, CDCl₃) spectral changes of the mixtures of $\mathbf{1}_{A}$ (0.50 mM) and $\mathbf{2}_{A}$ (0.50 mM) in the presence of $\mathbf{4}_{C}$ (1.0 mM) at 25 °C.



Fig. S3 Time-dependent ¹H NMR (500 MHz, CDCl₃) spectral changes of the mixtures of $\mathbf{1}_{A}$ (0.50 mM) and $\mathbf{2}_{A}$ (0.50 mM) at 25 °C.

5. ESI-MS spectrum of 3_{AA}·T_{CC}



Fig. S4 Negative mode ESI-MS (CHCl₃/MeOH = 1/1 (ν/ν) as a solvent) spectrum of 3_{AA} ·T_{CC}.





Fig. S5 Time-dependent ¹H NMR (500 MHz, CDCl₃) spectral changes of the mixtures of 1_C (0.50 mM) and 2_C (0.50 mM) in the presence of T_{AA} (0.50 mM) at 25 °C.



Fig. S6 Time-dependent ¹H NMR (500 MHz, CDCl₃) spectral changes of the mixtures of $\mathbf{1}_{C}$ (0.50 mM) and $\mathbf{2}_{C}$ (0.50 mM) in the presence of $\mathbf{4}_{A}$ (1.0 mM) at 25 °C.



7. Acceleration of the imine-bond forming reaction between 1_C and 2_C in the presence of 4_A

Fig. S7 Possible mechanism for the imine-bond forming reaction between 1_A (0.50 mM) and 2_A (0.50 mM) or 1_C (0.50 mM) and 2_C (0.50 mM) in the presence of (a) 4_C (1.0 mM) or (b) 4_A (1.0 mM), respectively, in CDCl₃ at 25 °C.

The terminal amino groups of amidine (2_A) and carboxylic acid (2_C) monomers may form acid-base complexes with the carboxy groups of monomeric carboxylic acid (4_C) and carboxylic acid monomer (1_C) as shown in (a) and (b), respectively. The complex formation of 2_A-4_C will inhibit the imine-bond forming reaction, whereas the complexation of 2_C-1_C may induce a self-catalyzed imine-bond forming reaction, since it is well know that imine-bond forming reaction between aldehydes and amines is catalyzed by acids. Therefore, the imine-bond forming reaction in the presence of 4_A underwent faster than that in the presence of 4_C .





Fig. S8 ¹H NMR (500 MHz, CDCl₃, 25 °C) spectral changes of the mixtures of $\mathbf{1}_{A}$ (1.0 mM) and $\mathbf{2}_{A}$ (1.0 mM) in the presence of (a) *trans*- \mathbf{T}_{CC} (1.0 mM) and (b) *trans/cis*- \mathbf{T}_{CC} (*cis* % = 47) (1.0 mM) during the initial stage of the reaction (top) and after reaching equilibrium (bottom).

9. Time-dependent ¹H NMR spectral changes of the mixtures of 1_A and 2_A in the presence of *trans/cis*-T_{CC}



Fig. S9 Time-dependent ¹H NMR (500 MHz, CDCl₃) spectral changes of the mixtures of $\mathbf{1}_{A}$ (1.0 mM) and $\mathbf{2}_{A}$ (1.0 mM) in the presence of *trans/cis*- \mathbf{T}_{CC} (1.0 mM) upon irradiation with UV light (390 nm) at 25 °C. \mathbf{T}_{CC} (*cis* % = 47) was used as the template, but partial *cis*-to-*trans* thermal isomerization (*ca.* 4-5%) took place at each ¹H NMR measurement.

10. Time-dependent ¹H NMR spectral changes of the mixtures of 1_A and 2_A in the presence of T_{CC} upon alternative irradiation at 390 and 490 nm



Fig. S10 Time-dependent ¹H NMR (500 MHz, CDCl₃) spectral changes of the mixtures of 1_A (1.0 mM) and 2_A (1.0 mM) in the presence of *trans/cis*- T_{CC} (1.0 mM) upon alternative irradiation with UV (390 nm) and visible (490 nm) light at 25 °C. T_{CC} (*cis* % = 43) was used as the template during the initial stage.

11. Supporting references

- 1 H. Yamada, Y. Furusho, H. Ito and E. Yashima, *Chem. Commun.*, 2010, 46, 3487–3489.
- 2 Y. Tanaka, H. Katagiri, Y. Furusho and E. Yashima, *Angew. Chem., Int. Ed.*, 2005, 44, 3867–3870.
- 3 T. Maeda, Y. Furusho, S.-i. Sakurai, J. Kumaki, K. Okoshi and E. Yashima, *J. Am. Chem. Soc.*, 2008, **130**, 7938–7945.
- 4 Y. Furusho, Y. Tanaka, T. Maeda, M. Ikeda and E. Yashima, *Chem. Commun.*, 2007, 3174–3176.
- 5 D. Grebel-Koehler, D. Liu, S. De Feyter, V. Enkelmann, T. Weil, C. Engels, C. Samyn, K. Müllen and F. C. De Schryver, *Macromolecules*, 2003, **36**, 578–590.