Electronic Supplementary Information for:

Complementary double helix formation through template synthesis

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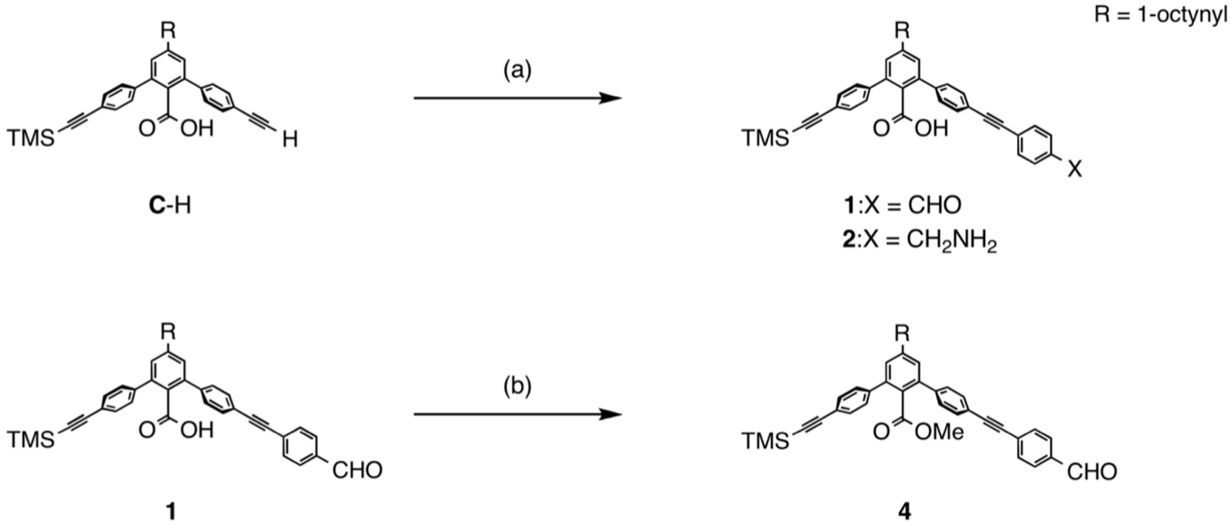
Materials

All starting materials and dehydrated solvents were purchased from Aldrich (Milwaukee, WI), Wako Pure Chemical Industries (Osaka, Japan), or Tokyo Chemical Industry (Tokyo, Japan) unless otherwise noted. Silica gel (SiO_2) for the flash chromatography was purchased from Merck (Darmstadt, Germany). Compounds **A**,[1] **T**,[2] and **C**-H[3] were prepared according to the previously reported methods.

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 ^{1}H and 125 MHz for ^{13}C. The recycling preparative HPLC was performed with an LC-928R liquid chromatograph (Japan Analytical Industry, Tokyo, Japan) equipped with two SEC columns (JALGEL-1H (1 × 60 cm) and JALGEL-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-mass spectra were recorded on a JEOL JMS-T100CS spectrometer (Akishima, Japan). The elemental analyses were performed by the laboratory of elemental analyses in the Department of Agriculture, Nagoya University. The IR spectra were recorded using a JASCO Fourier Transform IR-680 spectrophotometer (Hachioji, Japan). The absorption and CD spectra were measured using a JASCO V-570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively, in a 0.1-mm quartz cell equipped with a temperature controller (EYELA NCB-1200). Molecular modeling and molecular mechanics calculations were performed using the Merck molecular force field (MMFF94) as implemented in *Spartan '08* package (Wavefunction, Inc., Irvine, CA). The initial structures of the right and left-handed double helical **3·T** were constructed based on the crystal structure of an analogous double helical molecule bearing diacetylene linkers.[1] The geometries were further refined by using the restricted Hartree-Fock (RHF) method. The 1-octynyl chains at the *m*-terphenyl groups were substituted with hydrogen atoms for simplifying the calculations.

Synthetic Procedures



Scheme S1. Reagents and conditions: (a) *p*-bromobenzaldehyde for **1** and *p*-bromobenzylamine hydrochloride for **2**, $Pd(PPh_3)_4$, CuI, toluene-diisopropylamine, 65 °C. (b) CH_2N_2/Et_2O, r.t.

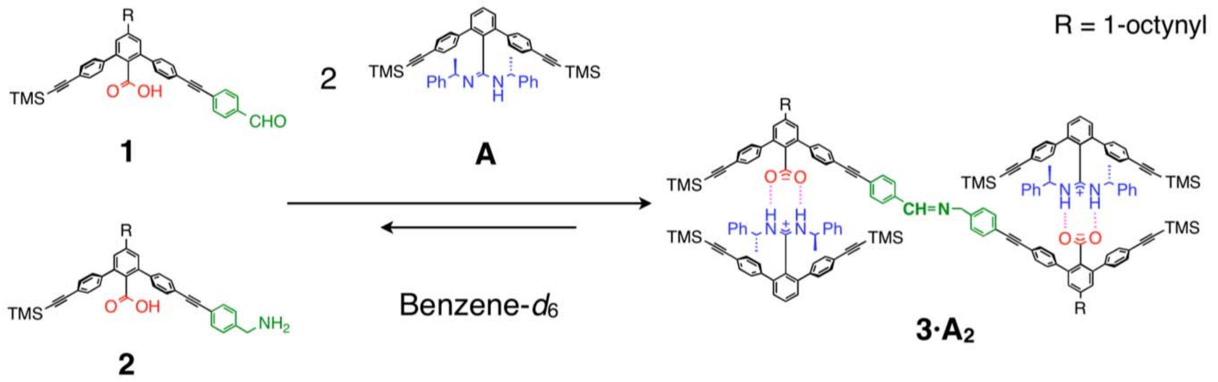
Carboxylic acid 1. Copper (I) iodide (0.95 mg, 5.0 μmol) was added to a solution of **C**-H[3] (126 mg, 0.251 mmol), *p*-bromobenzaldehyde (50.9 mg, 0.275 mmol), and tetrakis(triphenylphosphine)palladium(0) (5.78 mg, 5.00 μmol) in toluene-diisopropylamine (7/3 (v/v), 15 mL) and the mixture was stirred at 65 °C for 13 h. After evaporating the solvent, the residue was dissolved in chloroform, and the solution was washed with 1N HCl, water, and brine. The organic layer was dried over Na_2SO_4. After evaporating the solvent, the residue was purified by column chromatography (SiO_2, hexane/EtOAc = 1/0 to 4/1 (v/v)) and recycling preparative HPLC to give pure **1** (92.7 mg, 61% yield) as a yellow solid. Mp = 81.0–82.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 10.01 (s, 1H, CHO), 7.86 (d, J = 8.4 Hz, 2H, ArH), 7.69 (d, J = 8.4 Hz, 2H, ArH), 7.59 (d, J = 8.4 Hz, 2H, ArH), 7.51 (d, J = 8.4 Hz, 2H, ArH), 7.41–7.38 (m, 4H, ArH), 7.32 (d, J =

8.4 Hz, 2H, ArH), 2.42 (t, *J* = 7.2 Hz, 2H, C≡CCH$_2$), 1.62–1.57 (m, 2H, CH$_2$), 1.49–1.41 (m, 2H, CH$_2$), 1.38–1.30 (m, 4H, CH$_2$), 0.90 (t, *J* = 7.0 Hz, 3H, CH$_3$), 0.25 (s, 9H, TMS); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C) δ 191.520, 191.516, 140.3, 139.9, 139.72, 139.70, 135.4, 132.2, 131.9, 131.8, 129.6, 129.5, 128.58, 128.55, 128.29, 125.9, 122.8, 122.1, 104.7, 95.4, 93.18, 93.17, 89.5, 79.4, 31.3, 28.6, 28.5, 22.5, 19.4, 14.0, –0.1; IR (KBr, cm^{-1}): 2217 (ν_{C-C}), 2157 (ν_{C-C}), 1732 (ν_{C-O}), 1701 (ν_{C-O}); HRMS(ESI): m/*z* calcd for [M($C_{41}H_{38}O_3Si$)–H]$^-$, 605.2512; found 605.2510; Anal. Calcd for $C_{41}H_{38}O_3Si$: C, 81.15; H, 6.31. Found: C, 80.88; H, 6.19.

Carboxylic acid 2. Copper (I) iodide (0.76 mg, 4.00 μmol) was added to a solution of **C**-H[3] (100 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 22 h, the solvent was evaporated to dryness. The residue was purified by column chromatography (SiO$_2$, CHCl$_3$/MeOH = 1/0 to 9/1 (v/v)) to give pure **2** (41.6 mg, 34% yield) as a yellow solid. Mp = 199–201 °C; ^{1}H NMR (500 MHz, CDCl$_3$/CD$_3$OD=8/2 (v/v), 25 °C): δ 7.59–7.53 (m, 4H, ArH), 7.49–7.45 (m, 4H, ArH), 7.41–7.38 (m, 2H, ArH), 7.37–7.34 (m, 2H, ArH), 7.11 (d, *J* = 8.3 Hz, 2H, ArH), 3.53 (s, 2H, CH_2NH$_2$), 2.42 (t, *J* = 7.1 Hz, 2H, C≡CCH$_2$), 1.65–1.57 (m, 2H, CH$_2$), 1.57–1.42 (m, 2H, CH$_2$), 1.36–1.28 (m, 4H, CH$_2$), 0.90 (t, *J* = 6.9 Hz, 3H, CH$_3$), 0.26 (s, 9H, TMS); ^{13}C NMR (125 MHz, CDCl$_3$/CD$_3$OD=8/2 (v/v), 25 °C): δ 175.5, 141.5, 141.1, 139.1, 137.4, 137.2, 132.8, 131.9, 131.7, 131.4, 131.3, 130.9, 128.8, 128.6, 128.3, 123.5, 122.7, 121.7, 121.6, 104.9, 94.1, 90.8, 89.7, 89.1, 79.7, 42.2, 31.1, 28.39, 28.35, 22.3, 19.1, 13.7, –0.5; IR (KBr, cm^{-1}): 2229 (ν_{C-C}), 2157 (ν_{C-C}), 1562 (ν_{COO}-), 1405 (ν_{COO}-) ; HRMS(ESI): m/*z* calcd for [M($C_{41}H_{41}NO_2Si$)–H]$^-$, 606.2828; found 606.2856; Anal. Calcd for $C_{41}H_{41}NO_2Si$: C, 81.01; H, 6.80; N, 2.30. Found: C, 80.99; H, 6.93; N, 2.23.

Methyl ester 4. Carboxylic acid **1** (50 mg, 0.083 mmol) was converted with CH_2N_2 in diethyl ether into the methyl ester **4** (48.7 mg, 95%). Mp = 49.5–50.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 10.03 (s, 1H, CHO), 7.88 (d, J = 8.5 Hz, 2H, ArH), 7.69 (d, J = 8.5 Hz, 2H, ArH), 7.58 (d, J = 8.5 Hz, 2H, ArH), 7.50 (d, J = 8.5 Hz, 2H, ArH), 7.41–7.38 (m, 4H, ArH), 7.32 (d, J = 8.5 Hz, 2H, ArH), 3.40 (s, 3H, OCH_3), 2.42 (t, J = 7.0 Hz, 2H, $C{\equiv}CCH_2$), 1.62–1.57 (m, 2H, CH_2), 1.49–1.41 (m, 2H, CH_2), 1.38–1.30 (m, 4H, CH_2), 0.90 (t, J = 7.0 Hz, 3H, CH_3), 0.26 (s, 9H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 191.4, 169.1, 140.5, 140.0, 139.9, 139.8, 135.5, 132.1, 132.0, 131.9, 131.78, 131.77, 131.4, 129.6, 129.5, 128.5, 128.2, 125.7, 122.7, 122.0, 104.7, 95.2, 93.1, 92.9, 89.3, 79.5, 52.0, 31.3, 28.61, 28.55, 22.5, 19.4, 14.0, –0.1; IR (KBr, cm^{-1}): 2217 ($\nu_{C\equiv C}$), 2158 ($\nu_{C\equiv C}$), 1733 ($\nu_{C=O}$), 1702 ($\nu_{C=O}$); HRMS(ESI): m/*z* calcd for $[M(C_{42}H_{40}O_3Si)+Na]^+$, 643.2644; found 643.2617; Anal. Calcd for $C_{42}H_{40}O_3Si$: C, 81.25; H, 6.49. Found: C, 81.28; H, 6.67.

Time-dependent ^{1}H NMR spectra of the mixture of 1, 2, and A



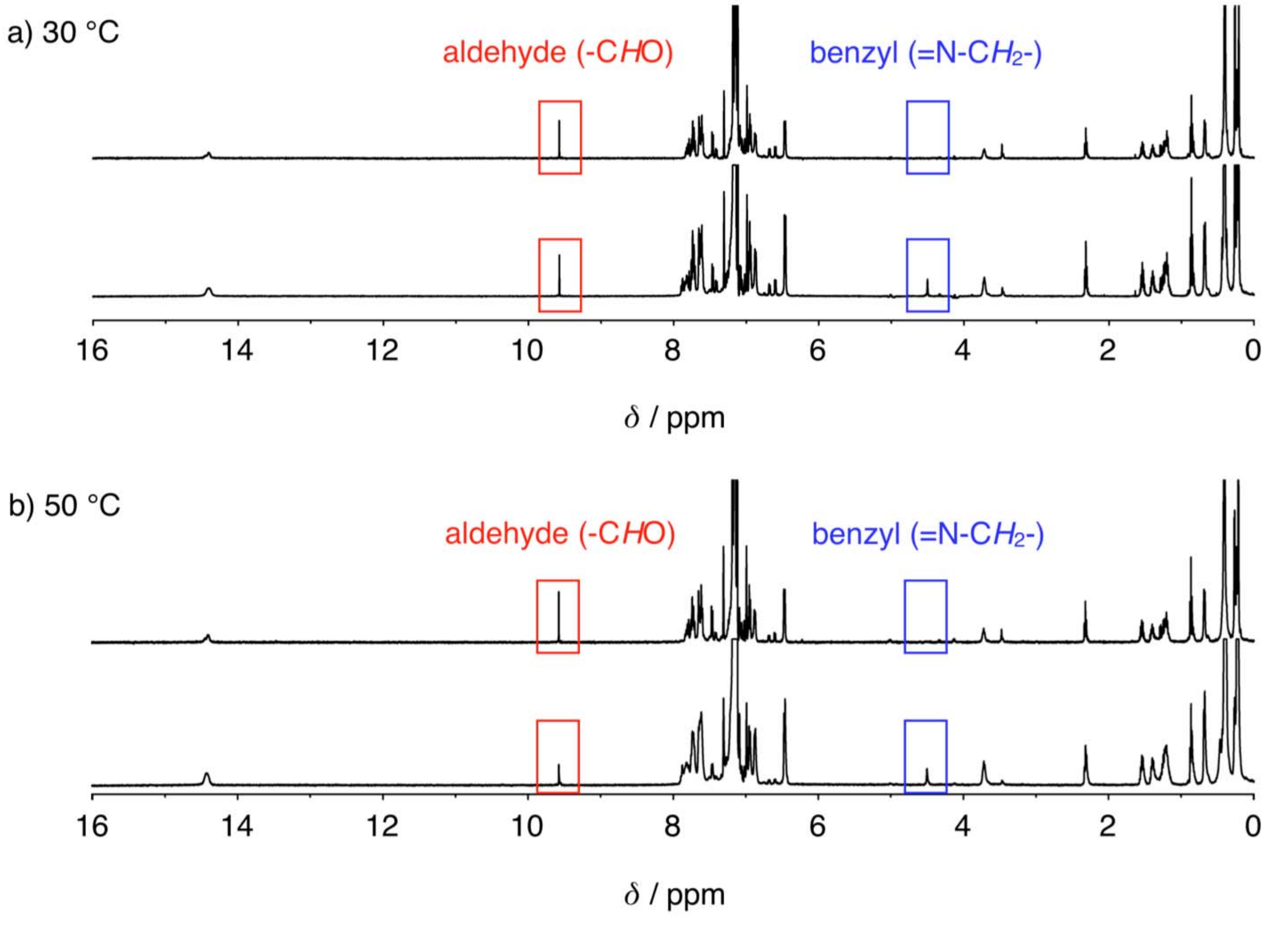


Fig. S1. ^{1}H NMR (500 MHz, benzene-d_6) spectra of the mixture of **1** and **2** (0.5 mM) in the presence of **A** (1.0 mM) at 30 (a) and 50 °C (b) at the initial stage of the reaction (top) and after reaching equilibrium (bottom).

Time-dependent ^{1}H NMR spectra of the mixture of 1, 2, and T

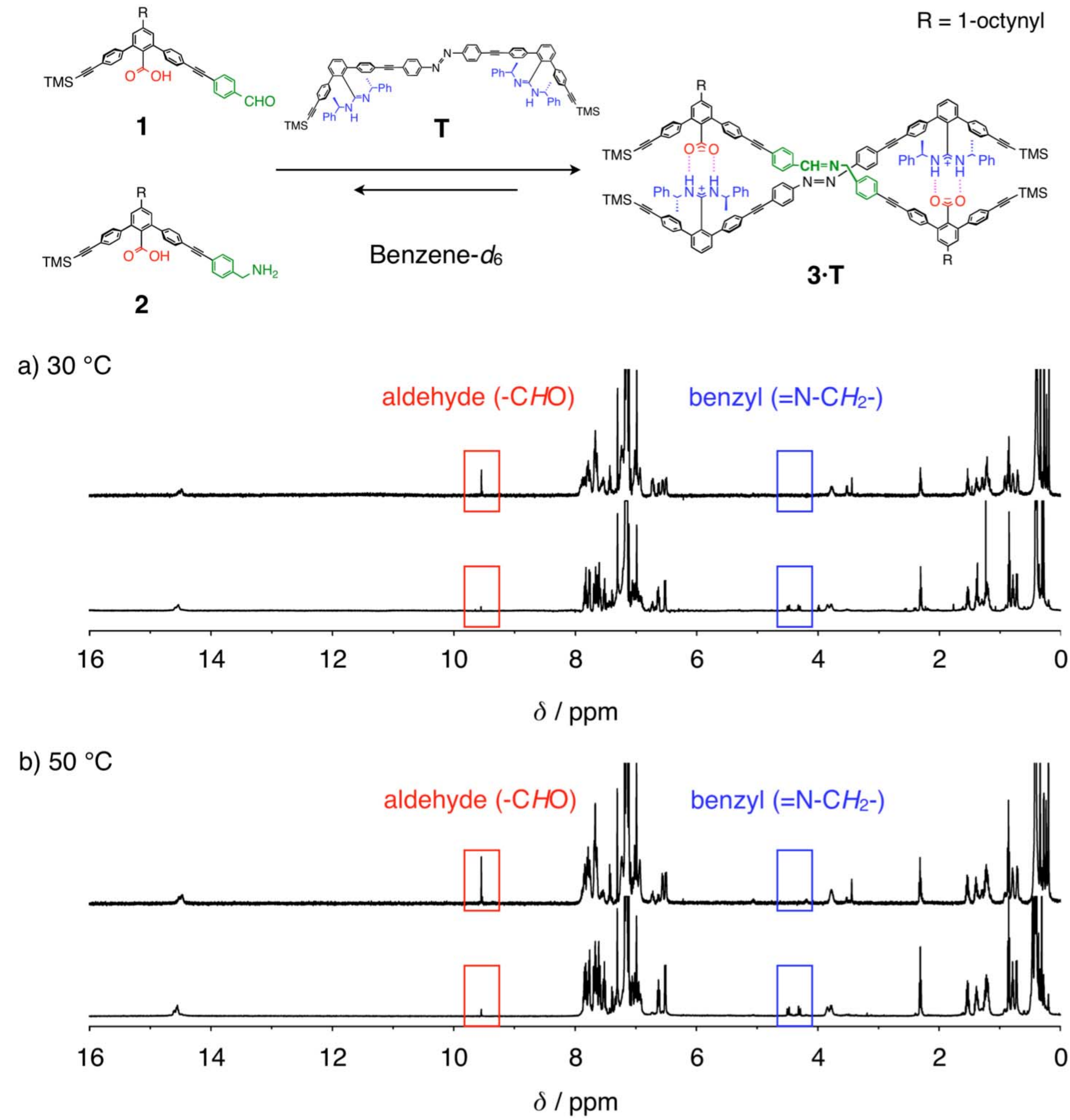


Fig. S2. ^{1}H NMR (500 MHz, benzene-d_6) spectra of the mixture of **1** and **2** (0.5 mM) in the presence of **T** (0.5 mM) at 30 (a) and 50 °C (b) at the initial stage of the reaction (top) and after reaching equilibrium (bottom).

ESI-MS spectrum of 3·T

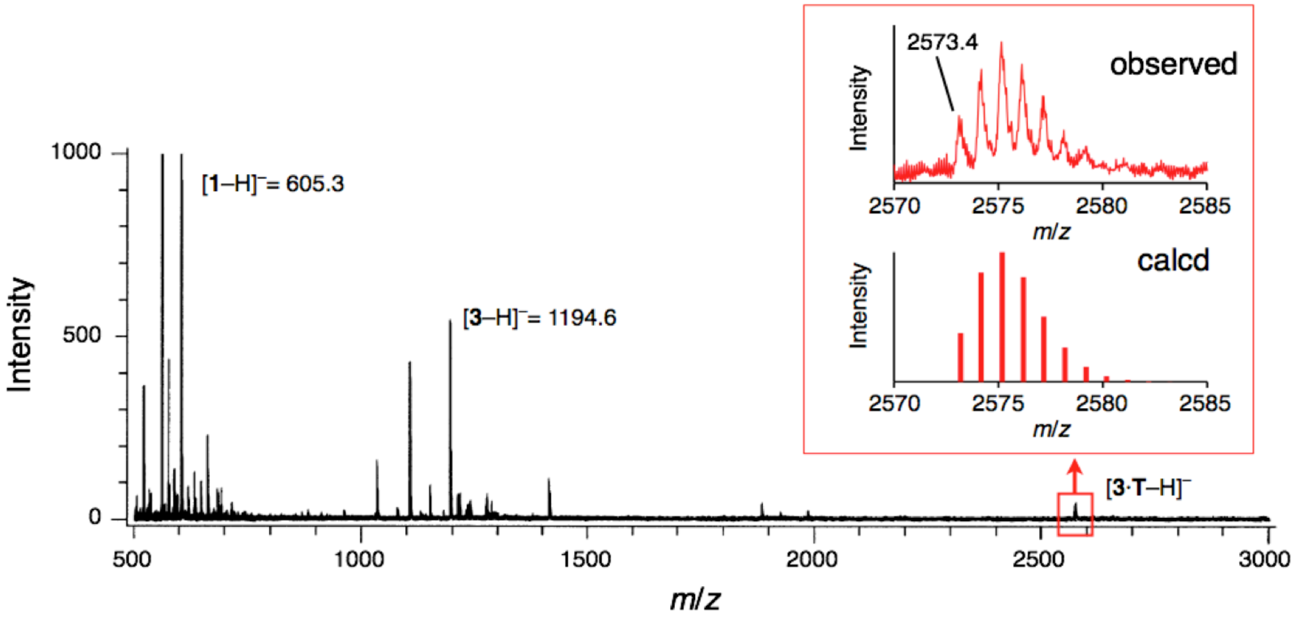


Fig. S3. Negative mode ESI-MS ($CHCl_3$/MeOH = 1/1 as a solvent) spectrum of **3·T**.

Time-dependent CD and absorption spectra

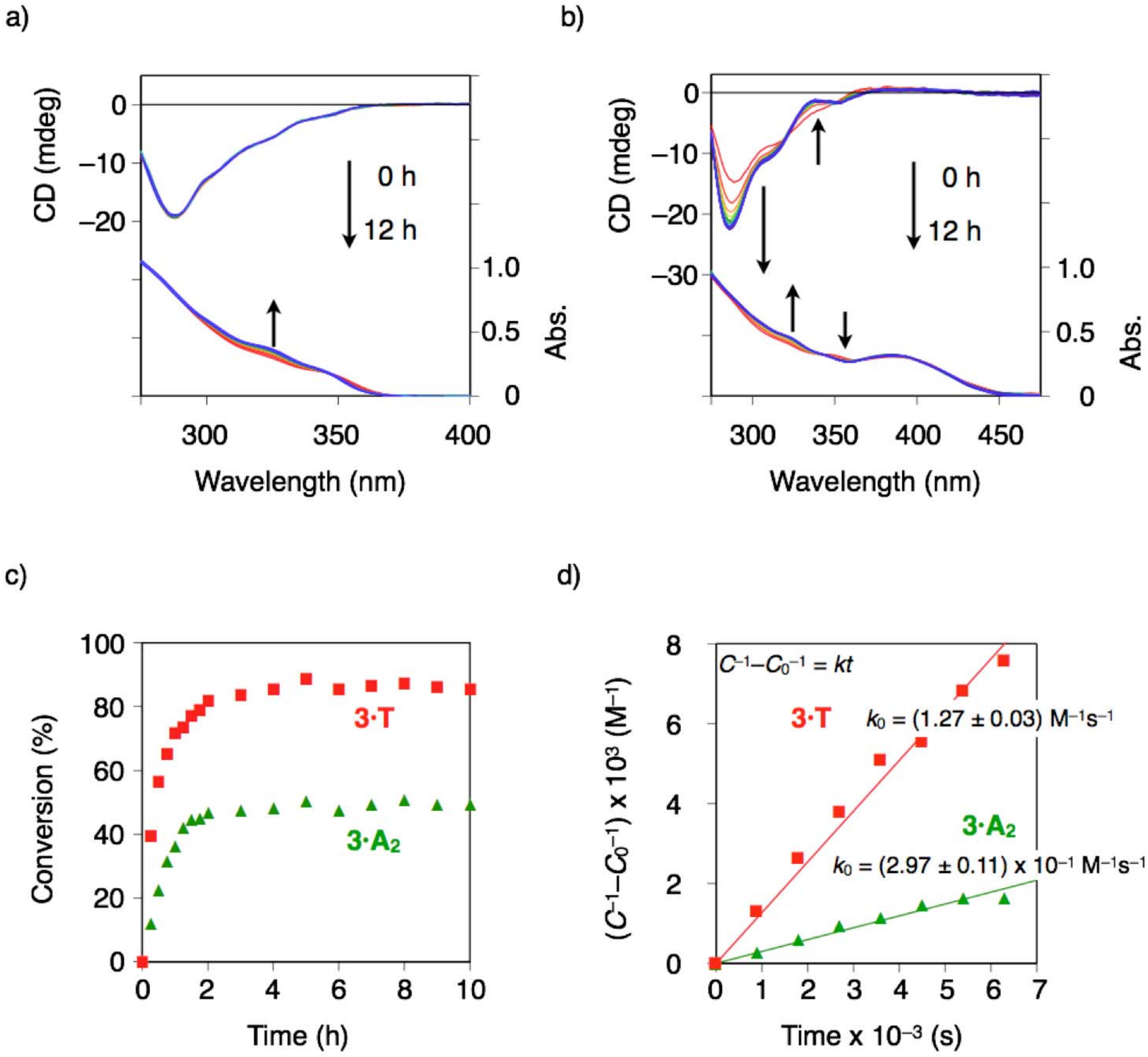


Fig. S4. The imine-bond forming reaction between **1** and **2** (0.5 mM) in benzene-d_6 at 50 °C. Time-dependent CD and absorption spectra of **1** and **2** in the presence of **A** (1.0 mM) (a) and **T** (0.5 mM) (b). Time–conversion relationships (c) and kinetic plots (d) are also shown.

Molecular modeling and calculations

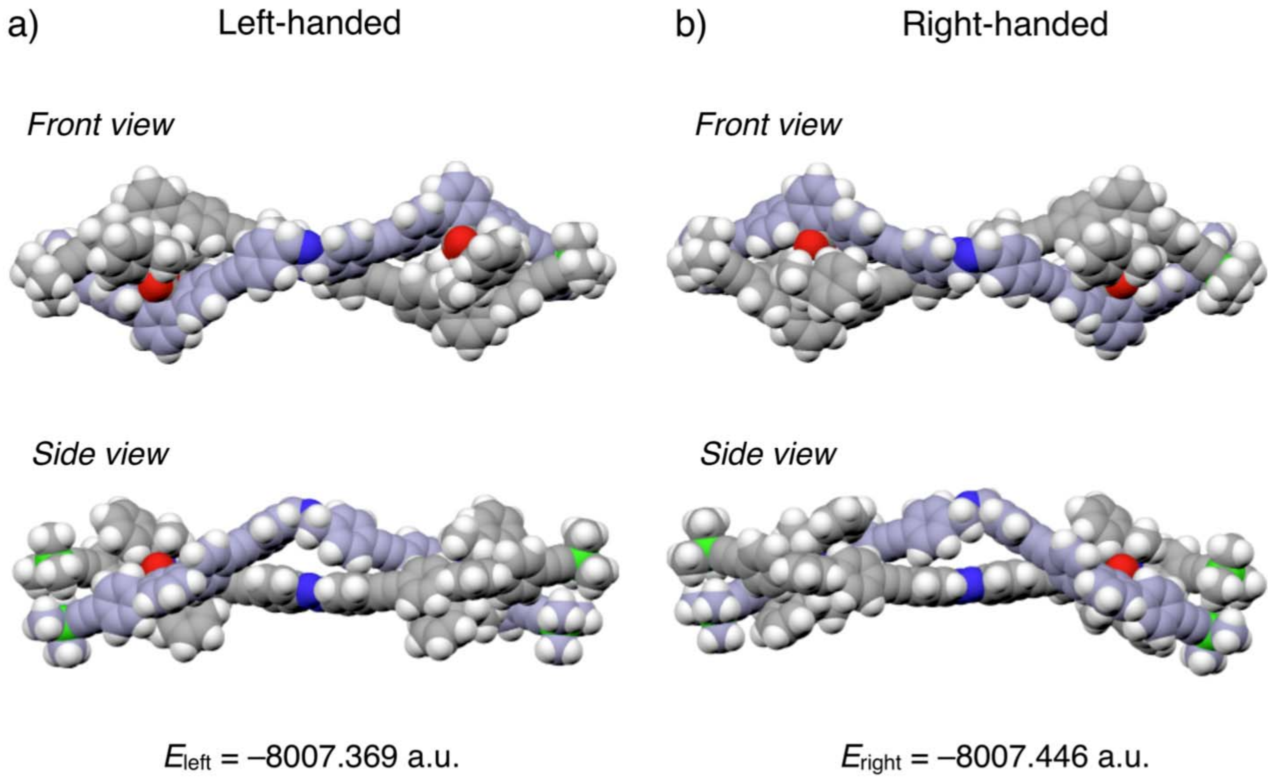


Fig. S5. Space-filling drawings of the structures of left-handed (a) and right-handed (b) double helical **3**·**T** optimized by RHF calculations. The 1-octynyl chains at the *m*-terphenyl groups were substituted with hydrogen atoms for simplifying the calculations. RHF calculated energies for the left-handed and right-handed double helical **3**·**T** are also shown in the bottom.

^{1}H NMR spectra of the reference materials

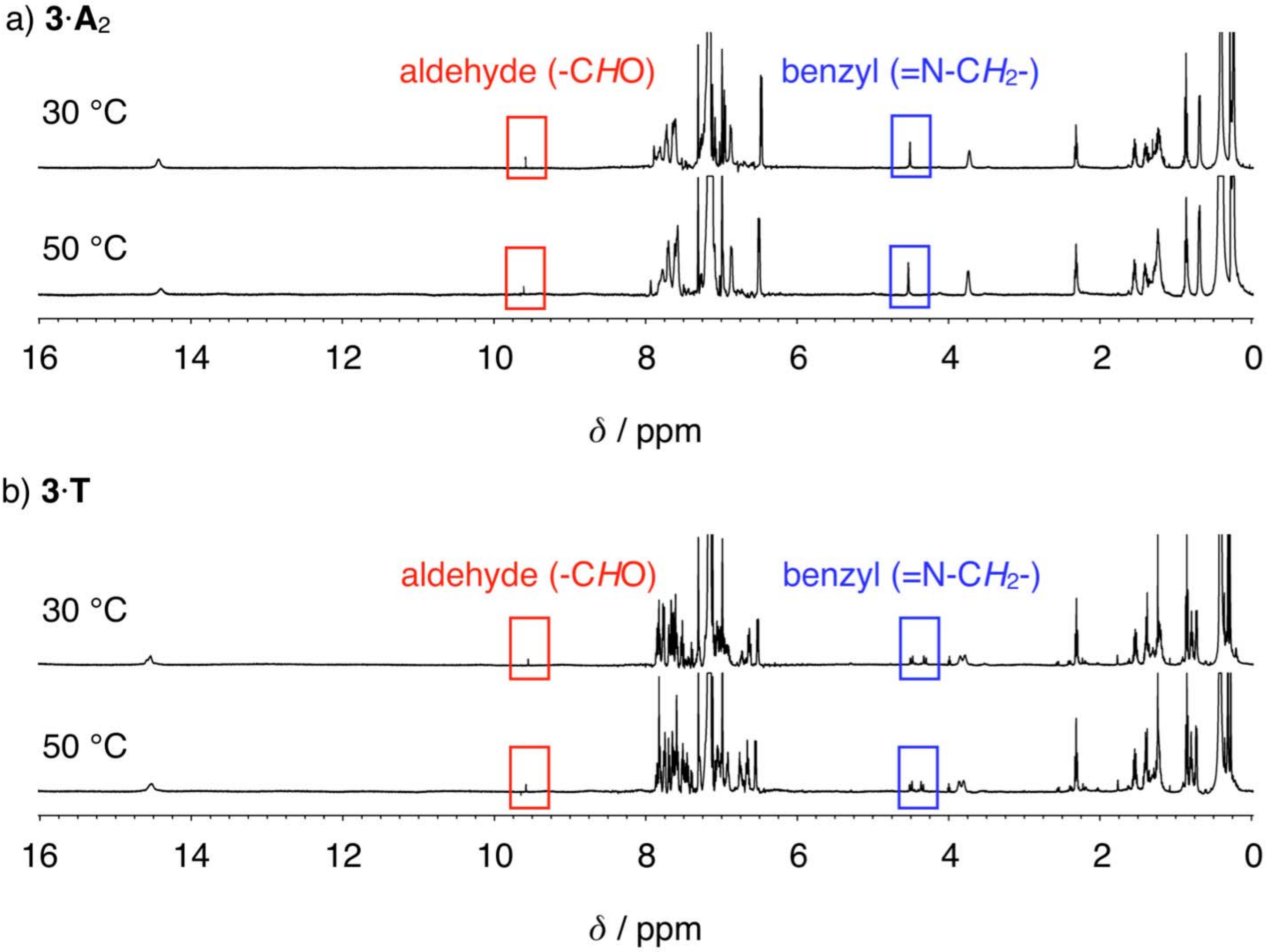


Fig. S6. ^{1}H NMR (500 MHz, 0.5 mM, benzene-d_6) spectra of the reference materials for **3**·**A**$_2$ (a) and **3**·**T** (b) at 30 (top) and 50 °C (bottom). Because of the reversible nature of the imine bond formation, **3**·**T** and **3**·**A**$_2$ could not be obtained as pure forms. Hence, **3**·**T** and **3**·**A**$_2$ were synthesized with relatively high conversion as reference materials by using molecular sieves (MS4A). The conversions were calculated by the integral ratios between the aldehyde peak (*ca*. 9.5 ppm) and benzyl peak (*ca*. 4.5 ppm).

CD and absorption spectra of the reference materials

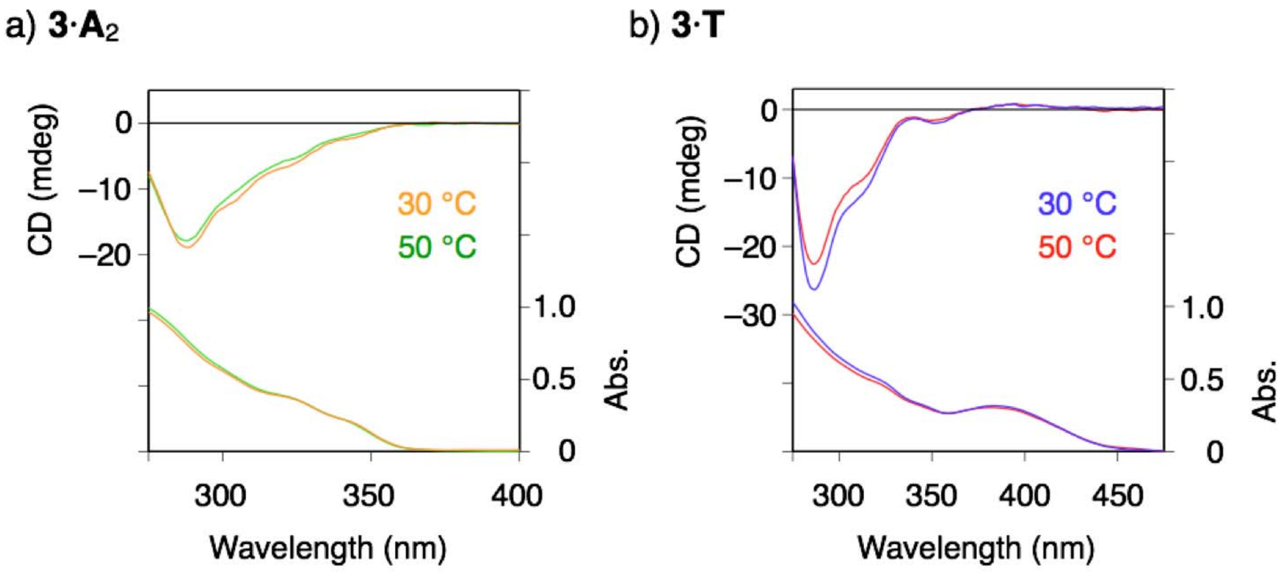


Fig. S7. CD and absorption spectra of the reference materials for (a) **3·A**$_2$ (0.5 mM) and (b) **3·T** (0.5 mM). Because of the reversible nature of the imine bond formation, **3·T** and **3·A$_2$** could not be obtained as pure forms. Hence, **3·T** and **3·A$_2$** were synthesized with relatively high conversion as reference materials by using MS4A.

The determination of the values of the thermodynamic parameters

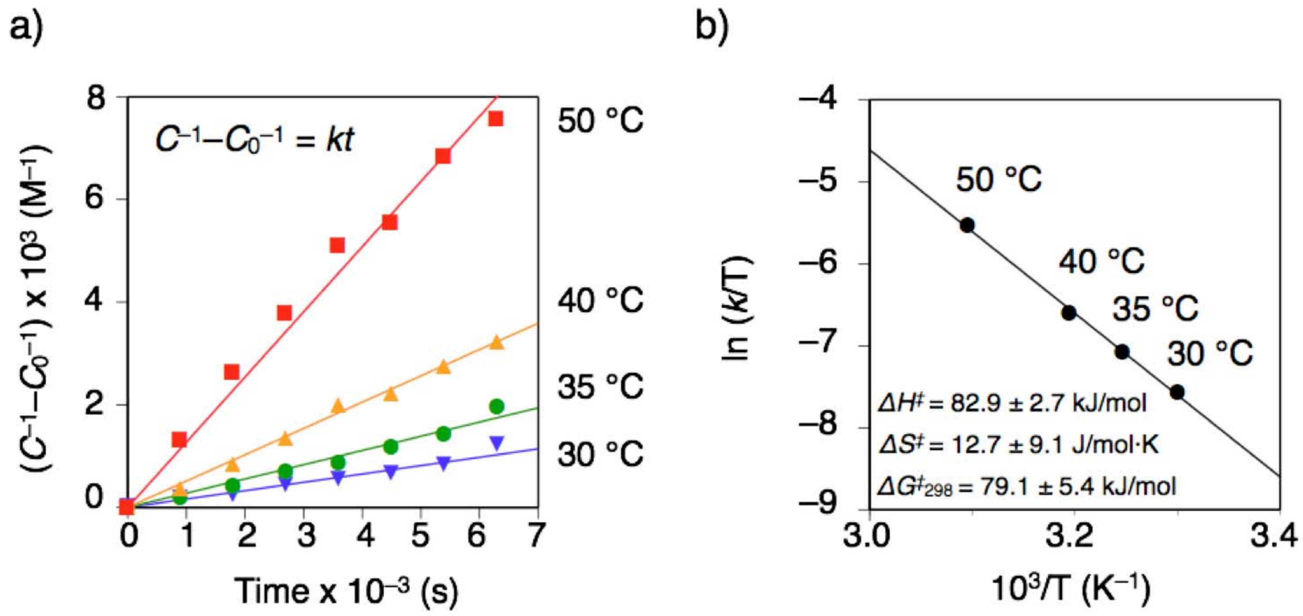


Fig. S8. (a) Kinetic plots of the imine-bond forming reaction between **1** and **2** (0.5 mM) in the presence of **T** (0.5 mM) in benzene-d_6 at the various temperatures (30–50 °C). The solid lines represent the curve-fitting results by using the pseudo-second-order rate equation. (b) The Eyring plots of the temperature dependence of the pseudo-second-order rate constants estimated at 30 to 50 °C, where the thermodynamic parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}_{298}$) were estimated according to the equation, $\ln k/\mathrm{T} = -\Delta H^{\ddagger}/\mathrm{R}\cdot 1/\mathrm{T} + \ln k_B/h + \Delta S^{\ddagger}/\mathrm{R}$.

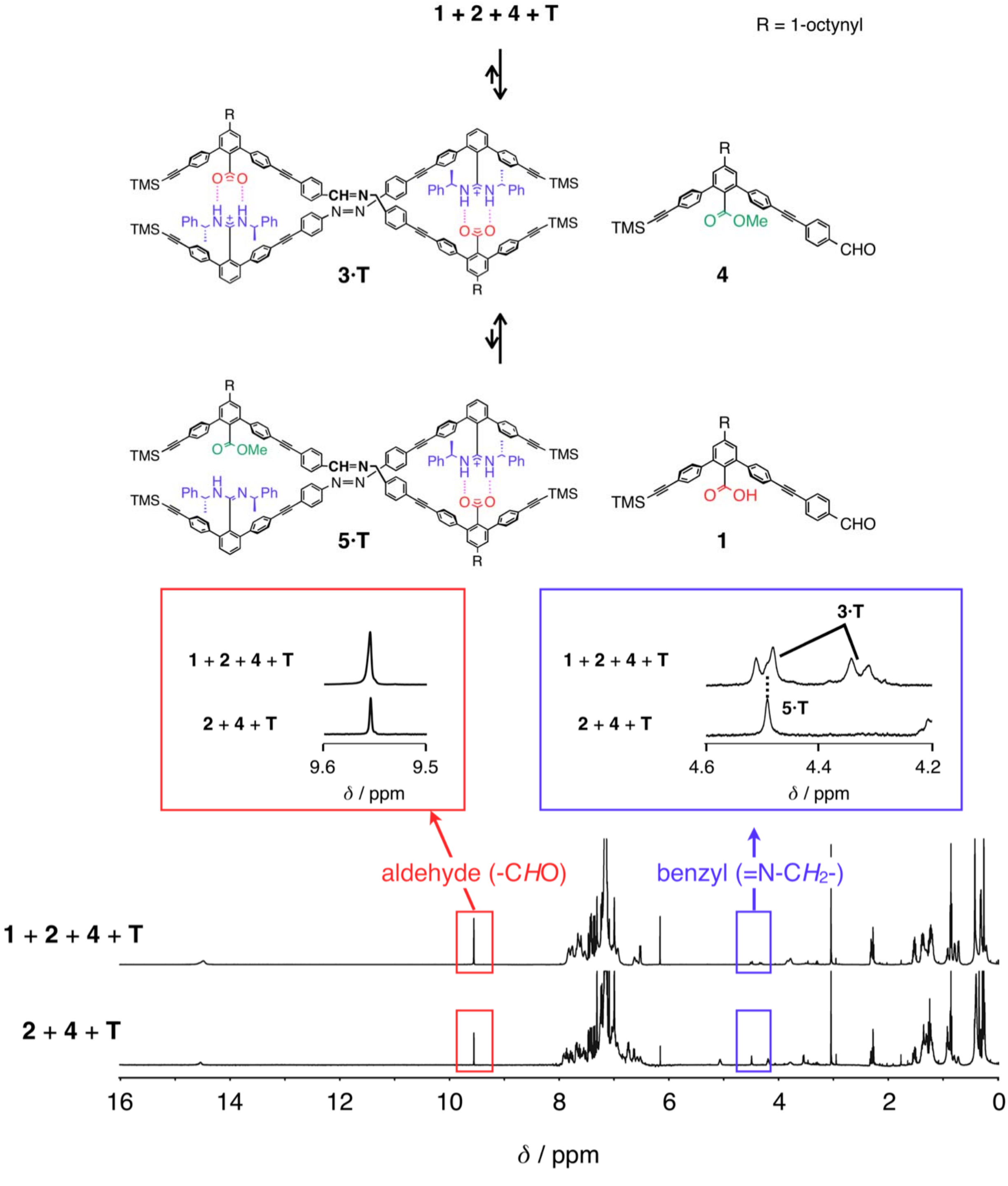


Fig. S9. ^{1}H NMR (500 MHz, benzene-d_6, 0.5 mM for each) spectra of the mixtures of **1**, **2**, **4**, and **T** (top) and **2**, **4**, and **T** (bottom) at 30 °C at equilibrium.

Supporting References

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2 Y. Furusho, Y. Tanaka, T. Maeda, M. Ikeda and E. Yashima, *Chem. Commun.*, 2007, 3174–3176.

3 T. Maeda, Y. Furusho, S.-i. Sakurai, J. Kumaki, K. Okoshi and E. Yashima, *J. Am. Chem. Soc.*, 2008, **130**, 7938–7945.