

Electronic Supplementary Information For:

Photoresponsive double-stranded helices composed of complementary strands

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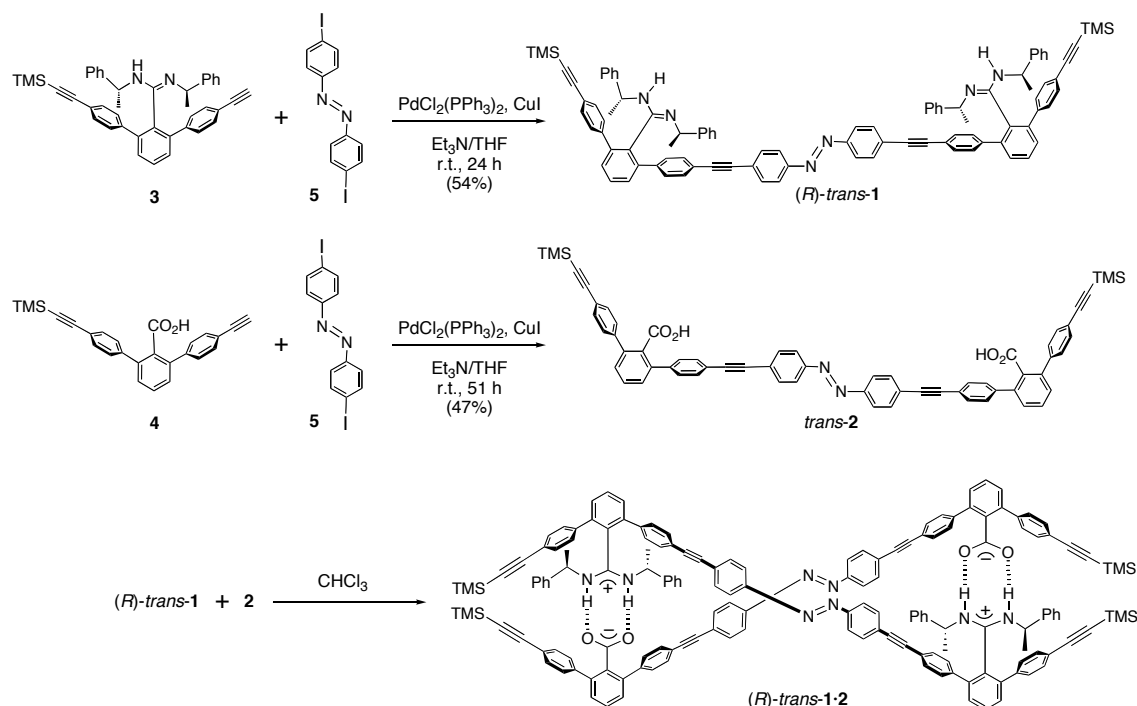
1. Materials.

All starting materials and dehydrated solvents were purchased from Sigma-Aldrich (Milwaukee, WI), Wako Pure Chemical Industry (Osaka, Japan), or Tokyo Chemical Industry (Tokyo, Japan) unless otherwise noted. The monosilylamidine **3**¹, monosilylcarboxylic acid **4**¹, and 4,4'-diiodoazobenzene **5**² (Scheme S1) were synthesized according to the previously reported methods. The silica gels used for column chromatography, the normal silica gel BW-300 (SiO₂) and the aminopropyl-modified silica gel Chromatorex NH-DM1020 (NH-SiO₂), were purchased from Fuji Silysia Chemical (Kasugai, Japan). The neutral alumina (Al₂O₃) employed for column chromatography, Aluminium oxide 90 active neutral, was purchased from Merck & Co., Inc. (NJ, USA).

2. Instruments.

The melting points were measured on a Yanaco MP-500D micro melting point apparatus and are uncorrected. The NMR spectra were taken on a Varian UNITY INOVA 500AS spectrometer operating at 500 MHz for ¹H and 125 MHz for ¹³C in CDCl₃ using a solvent residual peak as the internal standard. The IR spectra were recorded on a JASCO Fourier Transform IR-680 Plus spectrophotometer. The absorption and CD spectra were measured in a 1-, 5- or 10-mm quartz cell on a JASCO V-570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The temperature was controlled with a liquid nitrogen-controlled quartz cell (5.0 mm) in a cryostat (+25 to -45 °C). The electron spray ionization mass spectra (ESI-MS) were recorded using a JEOL JMS-T100CS spectrometer (Akishima, Japan). The photoirradiation for *trans/cis* photoisomerization was performed on a JASCO FP-770 spectrofluorometer with a 150 W xenon lamp. The slit width used in the experiment was 20 nm. The elemental analyses were performed by the Nagoya University Analytical Laboratory in the Graduate School of Bioagricultural Sciences. Molecular modeling and molecular mechanics calculations were performed using the Compass Force Field as implemented in the Materials Studio software (version 3.0; Accelrys Inc.).

3. Synthetic Procedures



Scheme S1

Diamidine strand (*R*)-*trans*-1. To a mixture of 4,4'-diiodoazobenzene **5**² (21.7 mg, 0.050 mmol), PdCl₂(PPh₃)₂ (1.75 mg, 0.0025 mmol), and CuI (0.47 mg, 0.0025 mmol) in Et₃N/THF (1/1 (v/v), 2.0 mL) was added monosilylamidine **3**¹ (60.0 mg, 0.100 mmol). After being stirred under Ar at ambient temperature for 24 h, the resultant mixture was evaporated to dryness. The residue was purified by column chromatography (NH-SiO₂ (*n*-hexane/diethyl ether = 1/1 (v/v), then neutral Al₂O₃ (*n*-hexane/ether = 4/1 to 1/1 (v/v))) to afford 37 mg of (*R*)-*trans*-1 in 54% yield as an orange solid: M.p. = 120–122 °C; ¹H NMR (500 MHz, CDCl₃, (*R*)-*trans*-1 (1.0 mM), CH₃CO₂H (32 mM), 25 °C): δ 13.06 (br s, 4H, N–H), 7.94 (d, *J* = 8.3 Hz, 4H, ArH), 7.77 (t, *J* = 7.8 Hz, 2H, ArH), 7.68 (d, *J* = 8.3 Hz, 4H, ArH), 7.55 (d, *J* = 7.6 Hz, 2H, ArH), 7.52 (d, *J* = 7.6 Hz, 2H, ArH), 7.36–7.20 (m, 16H, ArH), 7.05 (m, 8H, ArH), 6.74 (d, *J* = 8.3 Hz, 4H, ArH), 6.67 (d, *J* = 8.1 Hz, 4H, ArH), 3.94 (m, 4H, CHN), 2.10 (s, 97H, CH₃CO₂), 0.73 (d, *J* = 7.6 Hz, 6H, CH₃CHN), 0.72 (d, *J* = 7.3 Hz, 6H, CH₃CHN), 0.26 (s, 18H, TMS); ¹³C NMR (125 MHz, CDCl₃, (*R*)-*trans*-1 (1.0 mM), CH₃CO₂H (32 mM), 25 °C): δ 177.97, 162.50, 151.94, 142.91, 142.83, 141.65, 141.52, 138.43, 138.22, 138.05, 132.51, 132.24, 131.98, 131.79, 130.60, 130.50, 129.03, 129.01, 128.67, 128.45,

127.92, 126.60, 126.56, 125.90, 124.52, 123.32, 123.10, 122.62, 104.19, 96.04, 91.73, 90.76, 55.42, 23.49, 22.29, -0.10; FT-IR (KBr): $\nu = 3427$ ($\nu_{\text{N-H}}$), 2213 ($\nu_{\text{C}\equiv\text{C}}$), 2157 ($\nu_{\text{C}\equiv\text{C}}$), 1636 ($\nu_{\text{C}=\text{N}}$) cm^{-1} ; Anal. Calcd for $\text{C}_9\text{H}_8\text{N}_6\text{Si}_2$: C, 83.56; H, 6.28; N, 6.09. Found: C, 83.57; H, 6.13; N, 6.13.

Dicarboxylic acid strand *trans*-2. To a mixture of 4,4'-diiodoazobenzene **5**² (21.7 mg, 0.050 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (1.75 mg, 0.0025 mmol), and CuI (0.47 mg, 0.0025 mmol) in $\text{Et}_3\text{N}/\text{THF}$ (1/1 (v/v), 2.0 mL) was added monosilylcarboxylic acid **4**¹ (39.4 mg, 0.100 mmol). After being stirred under Ar at ambient temperature for 51 h, the resultant mixture was partitioned between EtOAc (20 mL) and 0.5 M HCl (20 mL). The organic layer was separated, washed with H_2O (10 mL) and then brine (10 mL), dried over anhydrous MgSO_4 , and evaporated to dryness. The residue was purified by column chromatography (SiO_2 ($\text{CHCl}_3/\text{EtOAc} = 1/0$ to $0/1$ (v/v))) to afford 23 mg of *trans*-**2** in 47% yield as an orange solid: M.p. = 176–178 °C; ^1H NMR (500 MHz, CDCl_3 , 2.0 mM, 25 °C): δ 7.86 (d, $J = 8.5$ Hz, 4H, ArH), 7.66 (d, $J = 8.2$ Hz, 4H, ArH), 7.63 (d, $J = 8.2$ Hz, 4H, ArH), 7.56–7.52 (m, 6H, ArH), 7.44 (d, $J = 8.0$ Hz, 4H, ArH), 7.41–7.34 (m, 8H, ArH), 0.26 (s, 18H, TMS); ^{13}C NMR (125 MHz, CDCl_3 , 2.0 mM, 25 °C): δ 151.79, 145.41, 140.50, 140.30, 139.85, 139.64, 132.46, 131.98, 131.76, 130.07, 129.71, 129.10, 128.65, 128.42, 126.10, 123.03, 122.68, 122.48, 104.76, 95.23, 91.82, 90.11, -0.02; FT-IR (KBr): $\nu = 3445$ ($\nu_{\text{O-H}}$), 2213 ($\nu_{\text{C}\equiv\text{C}}$), 2157 ($\nu_{\text{C}\equiv\text{C}}$), 1737 ($\nu_{\text{C}=\text{O}}$), 1703 ($\nu_{\text{C}=\text{O}}$) cm^{-1} ; Anal. Calcd for $\text{C}_{64}\text{H}_{50}\text{N}_2\text{O}_4\text{Si}_2$: C, 79.47; H, 5.21; N, 2.90. Found: C, 79.49; H, 5.28; N, 3.09.

Double helix (*R*)-*trans*-1·2. (*R*)-*trans*-**1** (10.88 mg, 0.00788 mmol) and *trans*-**2** (7.63 mg, 0.00788 mmol) were dissolved in CHCl_3 (5.0 mL), and the solution was filtered through a membrane filter (0.45 μm). The filtrate was evaporated to afford the duplex (*R*)-*trans*-**1·2** as an orange solid in quantitative yield: M.p. > 300 °C; ^1H NMR (500 MHz, CDCl_3 , 0.5 mM, 25 °C): δ 13.51 (br s, 2H, N-H), 13.45 (br s, 2H, N-H), 7.74 (t, $J = 7.7$ Hz, 2H, ArH), 7.71–7.57 (m, 8H, ArH), 7.57–7.35 (m, 42H, ArH), 7.22–7.15 (m, 8H, ArH), 7.11 (m, 4H, ArH), 6.80 (d, $J = 7.8$ Hz, 4H, ArH), 6.77–6.70 (m, 8H, ArH), 6.60 (d, $J = 7.8$ Hz, 4H, ArH), 3.90 (m, 2H, CHN), 3.81 (m, 2H, CHN), 0.71 (d, $J = 6.8$

Hz, 6H, CH_3CHN), 0.68 (d, $J = 6.6$ Hz, 6H, CH_3CHN), 0.31 (s, 18H, TMS), 0.28 (s, 18H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 1.4 mM, 25 °C): δ 162.24, 151.48, 151.47, 151.30, 142.70, 142.65, 142.48, 142.35, 141.57, 140.99, 138.15, 138.10, 137.34, 132.30, 132.24, 132.15, 131.75, 131.65, 131.43, 131.17, 130.39, 130.26, 129.17, 129.09, 129.04, 129.01, 128.84, 128.83, 128.77, 128.55, 128.44, 127.76, 127.65, 126.89, 126.46, 126.26, 126.15, 125.43, 123.49, 123.34, 122.74, 122.72, 122.68, 121.69, 121.39, 105.83, 104.13, 96.39, 94.55, 92.38, 91.16, 91.06, 89.60, 55.63, 55.58, 22.61, 22.55, 0.23, -0.02; FT-IR (KBr): $\nu = 3430$ (ν_{N-H}), 2211 ($\nu_{C=C}$), 2156 ($\nu_{C=C}$), 1635, 1595 cm^{-1} ; Anal. Calcd for $C_{160}H_{136}N_8O_4Si_4(CHCl_3)_{0.4}$: C, 81.87; H, 5.84; N, 4.77. Found: C, 81.90; H, 5.82; N, 4.75.

4. Structural Analysis of Double Helical (*R*)-*trans*-1·2

4-1. ESI-MS Spectrum of (*R*)-*trans*-1·2

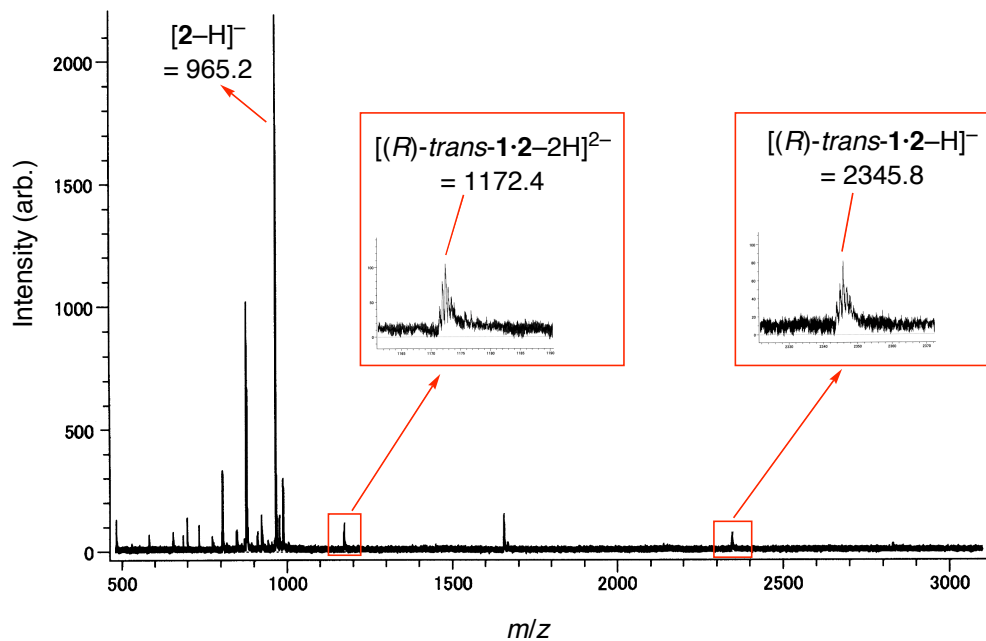


Fig. S1. Negative mode ESI-MS ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 1/1$ as a solvent) spectrum of (*R*)-*trans*-1·2.

4-2. Molecular Modeling and Calculations

Molecular modeling and molecular mechanics calculations were performed using the Compass Force Field as implemented in the Materials Studio software (version 3.0; Accelrys Inc.). The initial structures of the double helical (*R*)-*trans*- and (*R*)-*cis*-**1·2** were constructed using the crystal structure of an analogous double helical molecule bearing diacetylene linkers¹ using Materials Visualizer in the Materials Studio. The geometry optimization of (*R*)-*trans*- and (*R*)-*cis*-**1·2** was carried out by the steepest descent, conjugated gradient, and finally Quasi-Newton methods (smart algorithm) with the Forcite program using the Universal force field. The energy minimization was continued until the root-mean-square (rms) value became less than $0.0001 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$.

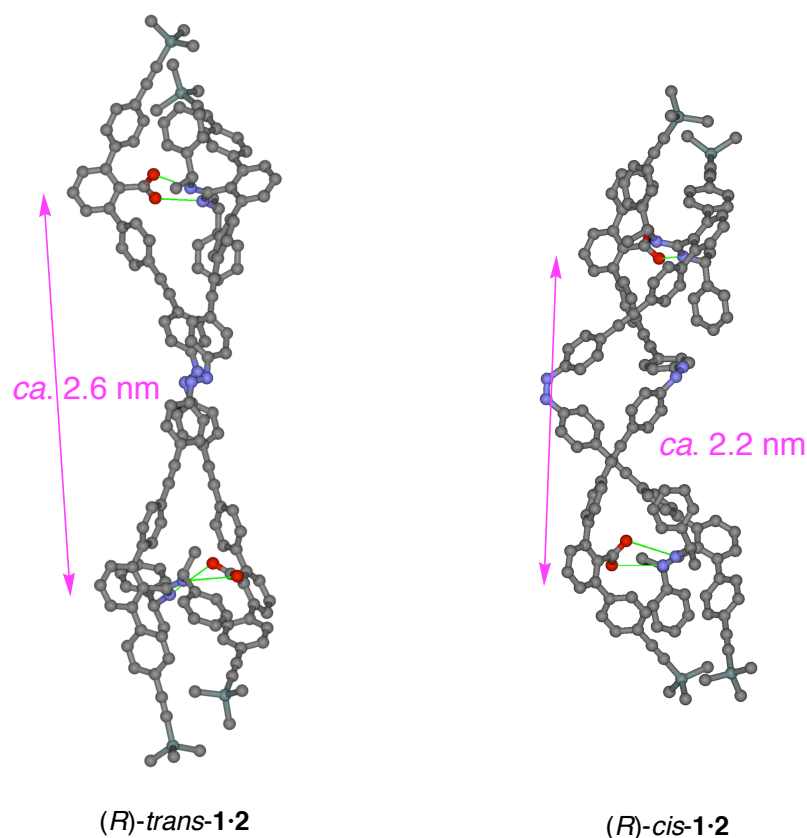


Fig. S2. Capped-stick drawings of the molecular-mechanics calculated structures of (*R*)-*trans*-**1·2** (left) and (*R*)-*cis*-**1·2** (right). Carbon, grey; oxygen, red; nitrogen, blue. The intermolecular hydrogen bonds are shown by green solid lines. Hydrogen atoms are omitted for clarity.

4-3. CD Spectra of (*R*)-*trans*-1·2 at Various Concentrations

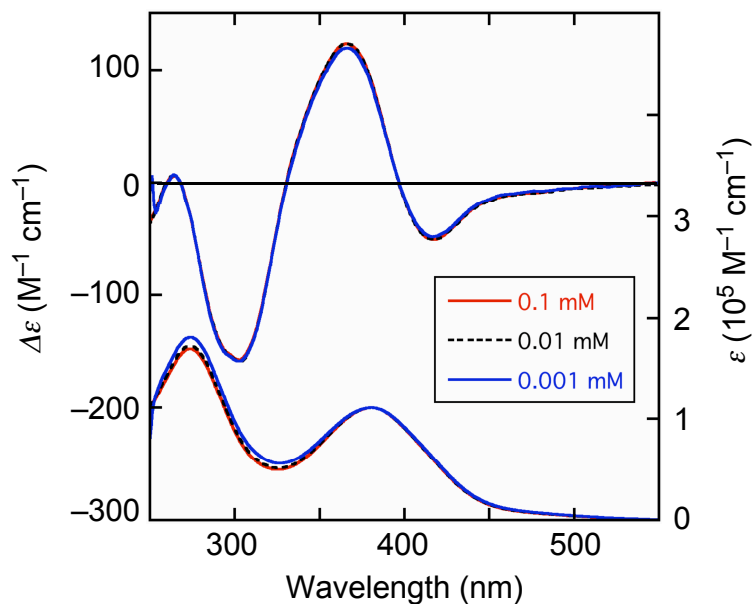


Fig. S3. CD and absorption spectra of (*R*)-*trans*-1·2 in $CDCl_3$ at 25 °C at 0.1 (red solid line), 0.01 (black dotted line), and 0.001 (blue solid line) mM.

4-4. CD Spectra of (*R*)-*trans*-1·2 at Various Temperatures

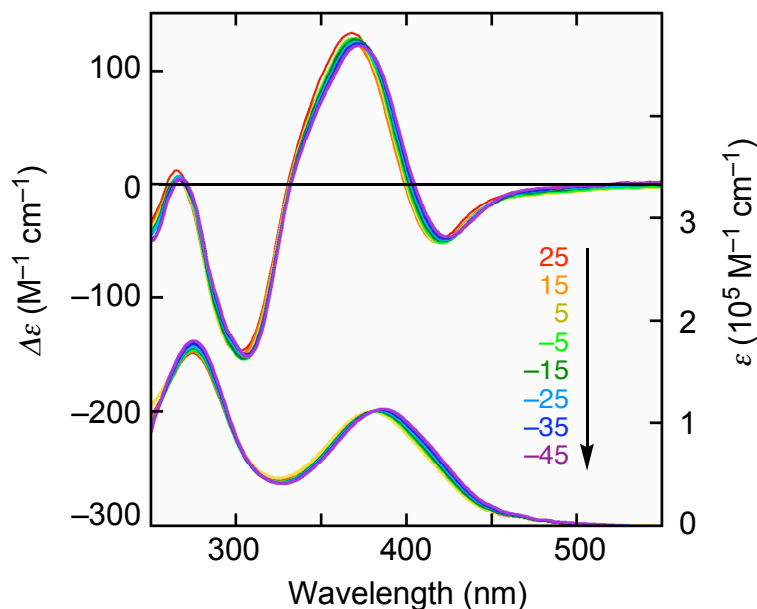


Fig. S4. CD and absorption spectra of (*R*)-*trans*-1·2 in $CDCl_3$ at 0.1 mM at 25, 15, 5, -5, -15, -25, -35, and -45 °C.

4-5. ^1H NMR Spectra of (*R*)-*trans*-1·2 at Various Temperatures

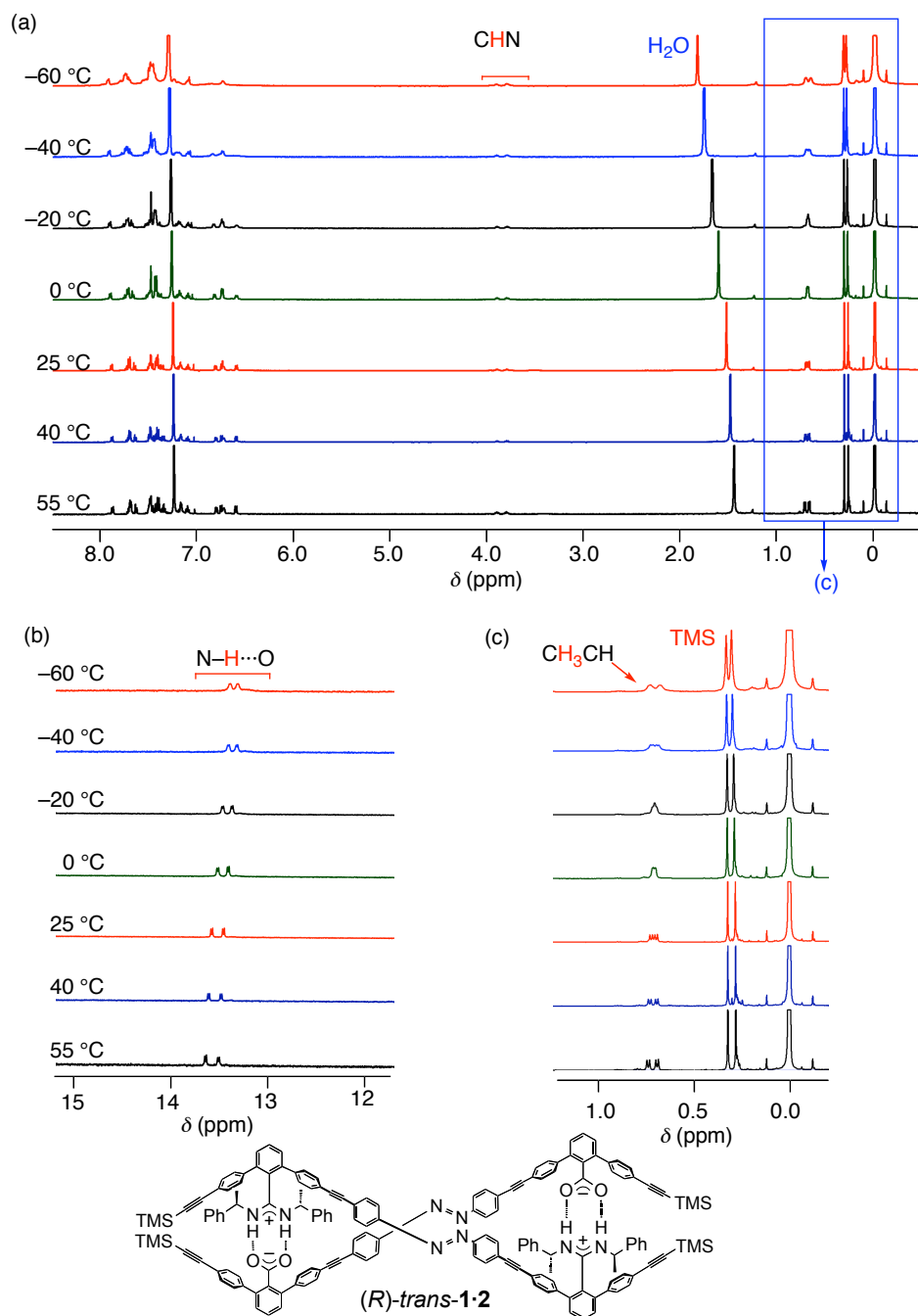


Fig. S5. Partial ^1H NMR (500 MHz, CDCl_3 , 0.1 mM) spectra of (*R*)-*trans*-1·2 at -60, -40, -20, 0, 25, 40, and 55 °C.

5. ^1H NMR Spectra of (*R*)-*trans*-1·2 after Photoirradiation

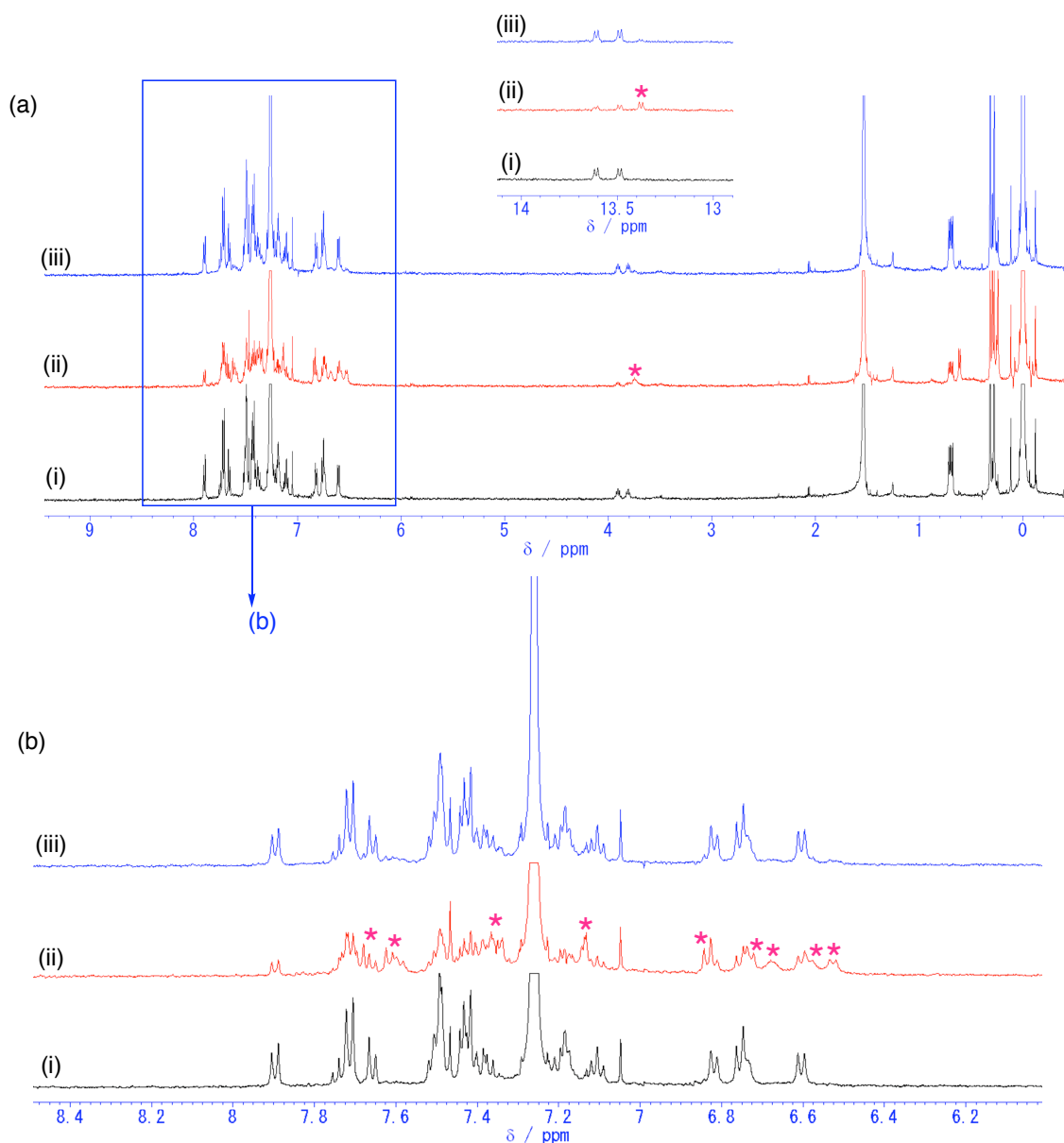


Fig. S6. (a) Full and (b) partial ^1H NMR spectra (500 MHz, CDCl_3 , 25 °C) of (*R*)-*trans*-1·2 (i) before and (ii) after irradiation of UV light (390 nm) for 30 min, and (iii) after further irradiation of visible light (490 nm) for 20 min.

6. References

- 1 Y. Tanaka, H. Katagiri, Y. Furusho and E. Yashima, *Angew. Chem., Int. Ed.*, 2005, **44**, 3867–3870.
- 2 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.