

Supporting Information

Title: Molecular Folding Screens: Reversible Folding and Unfolding of 1,8-Anthrylene–Ethyne Oligomers by Photochemical Cycloaddition and Thermal Cycloreversion

Author: Shinji Toyota,* Makoto Kuga, Akiko Takatsu, and Michio Goichi

Department of Chemistry, Faculty of Science, Okayama University of Science,
Ridaicho 1-1, Okayama, 700-0005 (Japan)

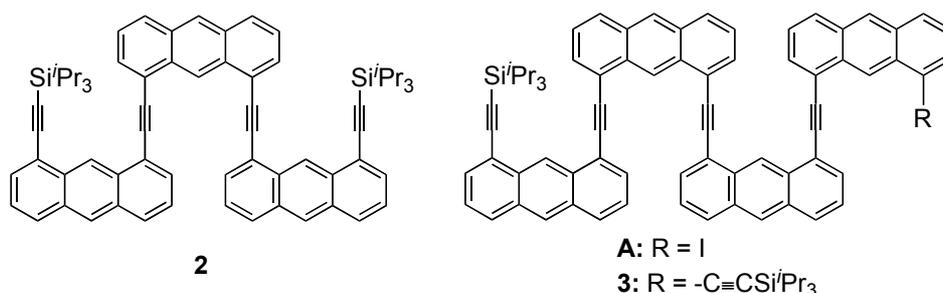
Fax : (+81)-86-256-9457 E-mail : stoyo@chem.ous.ac.jp

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Experimental Details

NMR spectra were measured on a Varian Gemini-300 (^1H : 300 MHz, ^{13}C : 75 MHz), a JEOL GSX-400 (^1H : 400 MHz, ^{13}C : 100 MHz), or a JEOL Lambda-500 (^1H : 500 MHz, ^{13}C : 125 MHz) spectrometer. High-resolution FAB mass spectra were measured on a JEOL MStation-700 spectrometer. UV spectra were measured on a Hitachi U-3000 spectrometer with a 10 mm cell. Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer with a 10 mm cell. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter with a $3.5\phi \times 100$ mm cell. CD spectra were measured on a JASCO J-810 polarimeter with a 10 mm cell. Acyclic trimer **2** and tetrameric monoiodide **A** were prepared by the known method.

S. Toyota, M. Goichi, M. Kotani, and M. Takezaki, *Bull. Chem. Soc. Jpn.* 2005, **78**, 2214.



Acyclic Tetramer 3. To a degassed solution of **A** (44 mg, 41 μ mol) and (triisopropylsilyl)ethyne (45 mL, 0.20 mmol) in triethylamine (10 mL) were added [Pd(PPh₃)₄] (4.7 mg, 4.1 μ mol) and CuI (0.8 mg, 4 μ mol). The solution was refluxed for 48 h under Ar atmosphere. After the solvent was removed by evaporation, the residue was chromatographed on silica gel (NH) with hexane/chloroform (4:1) as eluent. The desired compound was obtained as yellow powder. Yield 27 mg (61%); mp 290–293 °C (dec.); ¹H NMR (300 MHz, CDCl₃): δ = 0.38 (6H, septet, J = 7.8 Hz), 0.59 (36H, d, J = 7.3 Hz), 6.53 (2H, dd, J = 6.8, 8.3 Hz), 6.81 (2H, dd, J = 6.8, 8.8 Hz), 7.13 (2H, d, J = 5.9 Hz), 7.27 (2H, dd, J = 6.8, 8.3 Hz), 7.36 (2H, dd, J = 6.8, 8.3 Hz), 7.49–7.51 (4H, m), 7.56–7.59 (4H, m), 7.72 (2H, dd, J = 5.9 Hz), 7.80 (2H, d, J = 8.8 Hz), 7.85 (2H, d, J = 8.8 Hz), 8.05 (2H, s), 8.09 (2H, s), 9.22 (2H, s), 9.58 (2H, s); ¹³C NMR (100 MHz, CDCl₃): δ = 11.24, 18.32, 92.35, 92.62, 92.91, 96.22, 104.77, 120.92, 121.28, 121.74, 122.08, 123.56, 124.28, 124.33, 124.47, 124.53, 126.46, 126.98, 127.67, 128.11, 128.49, 128.67, 129.50, 129.56, 130.53, 130.71, 130.75, 130.79, 130.93, 131.00, 131.20, 131.36; UV (CHCl₃) λ_{max} (ϵ) 262 (47400), 303 (2900), 391 (930), 411 (1070), 434 (750) nm; FL (CHCl₃) λ_{em} 450, 474 nm (λ_{ex} 393 nm); HR FAB MS: m/z 1138.5305 [M^+]; calcd for C₈₄H₇₄Si₂; m/z 1138.5329 [M^+].

Photoreaction of trimer 2. A solution of **2** (37.6 mg, 40 μ mol) in benzene (40 mL) was degassed by bubbling Ar gas for 30 min. This solution was irradiated with a high-pressure Hg lamp through a L42 filter for 8 h under Ar atmosphere. After the solvent was evaporated, the crude product was purified by chromatography on silica gel with hexane:chloroform 4:1 eluent to give the desired photoproduct as yellow powder. **4a**: yield 34 mg (90%); mp 280–282 °C; ¹H NMR (400 MHz, CDCl₃): δ = –0.41 (6H, septet, J = 7.3 Hz), 0.44 (18H, d, J = 7.3 Hz), 0.49 (18H, d, J = 7.3 Hz), 4.59 (2H, s), 6.77 (2H, s), 6.80–6.94 (8H, m), 7.07 (2H, d, J = 7.3 Hz), 7.21 (2H, d, J = 7.3 Hz), 7.46 (2H, dd, J = 7.3, 8.3 Hz), 7.86 (2H, d, J = 6.8 Hz), 8.03 (2H, d, J = 8.8 Hz), 8.51 (1H, s), 10.09 (1H, s); ¹³C NMR (100 MHz, CDCl₃): δ = 11.80, 18.45, 18.48, 48.37, 53.76, 92.68, 93.88, 97.17, 107.19, 121.61, 123.06, 123.18, 125.39, 125.45, 125.60, 126.11, 127.32, 127.69, 128.06, 128.70, 132.18, 132.28, 132.66, 133.18, 142.50, 142.60, 144.13, 145.98; UV (CHCl₃) λ_{max} (ϵ) 271 (90500), 296 (17400), 367 (2400), 386 (9100), 408 (20500), 432 (23200) nm; FL (CHCl₃) λ_{em} 438, 464 nm (λ_{ex} 393 nm); HR FAB MS: m/z 938.4704 [M^+]; calcd for C₆₈H₆₆Si₂; m/z 938.4703 [M^+].

Photoreaction of tetramer 3. The reaction was similarly carried out with **3** (8.0 mg, 7.0 μmol). The solution was irradiated for 21 h. The crude product was purified by chromatography on silica gel with hexane:chloroform 4:1 eluent to give the photoproduct as yellow powder. **5**: yield 5.9 mg (73%); mp 285–288 °C (dec.); ^1H NMR (500 MHz, CDCl_3): $\delta = -0.01$ (6H, septet, $J = 7.8$ Hz), 0.51 (18H, d, $J = 7.3$ Hz), 0.57 (18H, d, $J = 7.3$ Hz), 4.42 (2H, d, $J = 10.7$ Hz), 4.57 (2H, d, $J = 10.7$ Hz), 6.47 (2H, d, $J = 10.7$ Hz), 6.63 (2H, d, $J = 10.7$ Hz), 6.72 (2H, d, $J = 6.8$ Hz), 6.78 (2H, t, $J = 6.8$ Hz), 6.79 (2H, t, $J = 6.8$ Hz), 6.82 (2H, t, $J = 6.8$ Hz), 6.84–6.88 (4H, m), 6.91 (2H, t, $J = 6.8$ Hz), 6.95 (2H, dd, $J = 6.8, 1.2$ Hz), 7.04 (2H, dd, $J = 6.8, 1.2$ Hz), 7.15–7.19 (6H, m); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 12.04, 18.68, 18.91, 48.91, 49.52, 53.73, 54.55, 91.85, 93.14, 94.98, 97.23, 107.39, 121.49, 122.22, 123.26, 123.82, 125.09, 125.24, 125.41, 125.67, 125.73, 125.84, 126.69, 127.33, 127.82, 129.87, 132.70, 132.87, 141.82, 142.10, 142.43, 143.85, 144.13, 146.85$; UV (CHCl_3) λ_{max} (ϵ) 294 (35000), 331 (9400), 391 (930), 411 (1070), 434 (750); FL (CHCl_3) λ_{em} 441, 468, 497 nm (λ_{ex} 393 nm); HR FAB MS: m/z 1138.5294 [M^+]; calcd for $\text{C}_{84}\text{H}_{74}\text{Si}_2$; m/z 1138.5329 [M^+]. The singly cyclized product could not be isolated in a pure form. Selected ^1H NMR (400 MHz, CDCl_3): $\delta = -0.58$ (6H, septet, $J = 7.1$ Hz), 4.66 (2H, s), 7.61 (1H, d, $J = 6.4$ Hz), 7.71 (1H, d, $J = 6.4$ Hz), 7.83 (1H, d, $J = 8.6$ Hz), 7.92 (1H, s), 8.40 (1H, s), 9.61 (1H, s). Other signals were overlapped with those of **5**.

Thermal Cycloreversion. A solid sample of **4a** (3.0 mg) was heated on a hot-plate at 180 °C for 30 min to give acyclic trimer **2**. When the reaction was monitored by ^1H NMR, only the signals of **2** were observed after the thermal reaction. The solvent was evaporated, and the residue was practically pure acyclic trimer **2**. The isolated yield was >95%. The reaction of **5** was similarly carried out to give acyclic trimer **3**, and the isolated yield was ca. 90%.

Fluorescence measurement. Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer with a 10 mm cell. Measurements were made at room temperature on solutions in chloroform of $1.0 \times 10^{-5} - 1.0 \times 10^{-6}$ mol L^{-1} , which were degassed by Ar gas immediately before measurements. The spectra were measured upon excitation at 393 nm. The spectra in the solid state were measured with a film prepared between quartz plates. The fluorescence lifetimes were measured on a Spectra-Physics time-resolved spectrofluorometer system with a Ti:Sapphire laser (Tsunami 3960/50-M2S).

DSC measurement. Differential scanning calorimetry was measured with a Mac Science DSC 3100 calorimeter. The temperature was raised at a rate of $10.0\text{ }^{\circ}\text{C min}^{-1}$ with 1.5 mg of a sample.

Chiral HPLC and CD spectra. Enantiomeric resolution was carried out with a Daicel Chiralcel OD column (10 mm ϕ \times 250 mm) with hexane: 2-propanol 100:1 eluent. About 2 mg of **4a** was dissolved in the eluent (4 mL), and 0.5 mL of solution was injected into the column in each batch. Enantiomers were eluted at 22.5 and 24.1 min with partial separation. Further separation afforded practically pure enantiomers as pale yellow solid. Chiroptical data of the resolved samples are as follows. First eluted isomer: $[\alpha]_{\text{D}}^{25} -232$ (*c* 0.031, CHCl_3), CD (CHCl_3 , 1.2×10^{-4} mol L^{-1}) λ ($\Delta\epsilon$) 252 (+6.3), 261 (-11.7), 270 (-0.9), 278 (-28.0), 298 (+2.1), 314 (+1.4), 337 (-8.0), 353 (-17.3), 390 (-0.6), 405 (+1.7), 430 nm (+2.6). Second eluted isomer: $[\alpha]_{\text{D}}^{25} +222$ (*c* 0.039, CHCl_3), CD (CHCl_3 , 1.2×10^{-4} mol L^{-1}) λ ($\Delta\epsilon$) 251 (-5.9), 262 (+10.9), 272 (+0.3), 278 (+32.0), 298 (-2.5), 314 (-1.6), 337 (+9.1), 353 (+20.2), 388 (+0.7), 406 (-1.9), 429 nm (-3.2). Enantiomers of **5** could not be resolved with Chiralcel OD, Chiralpak AD, and Chiralpak IA columns under various conditions.

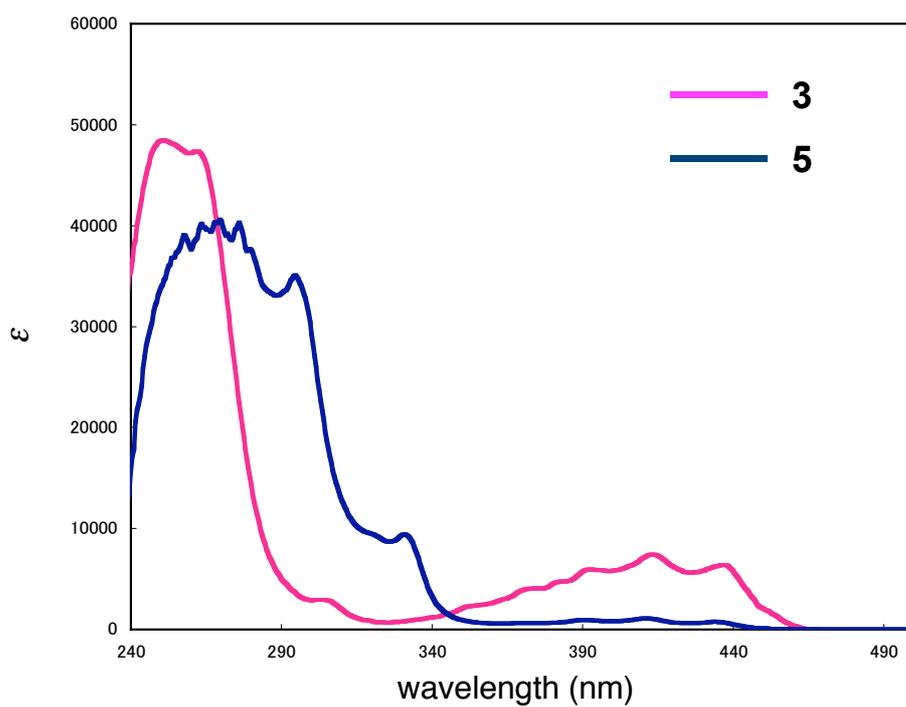
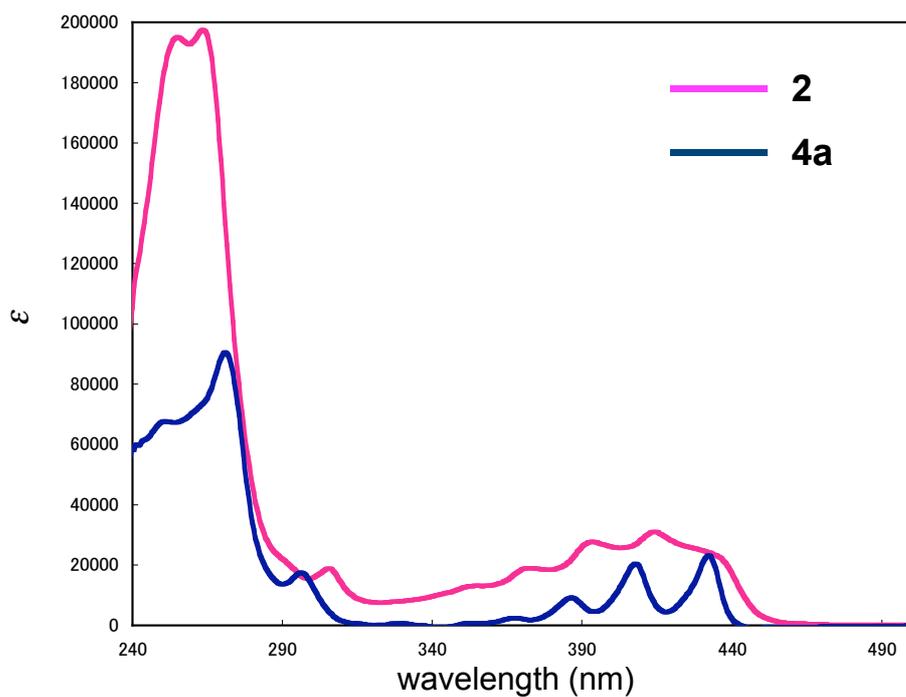


Fig. S1. UV-vis spectra of acyclic oligomers and their photoproducts in chloroform.

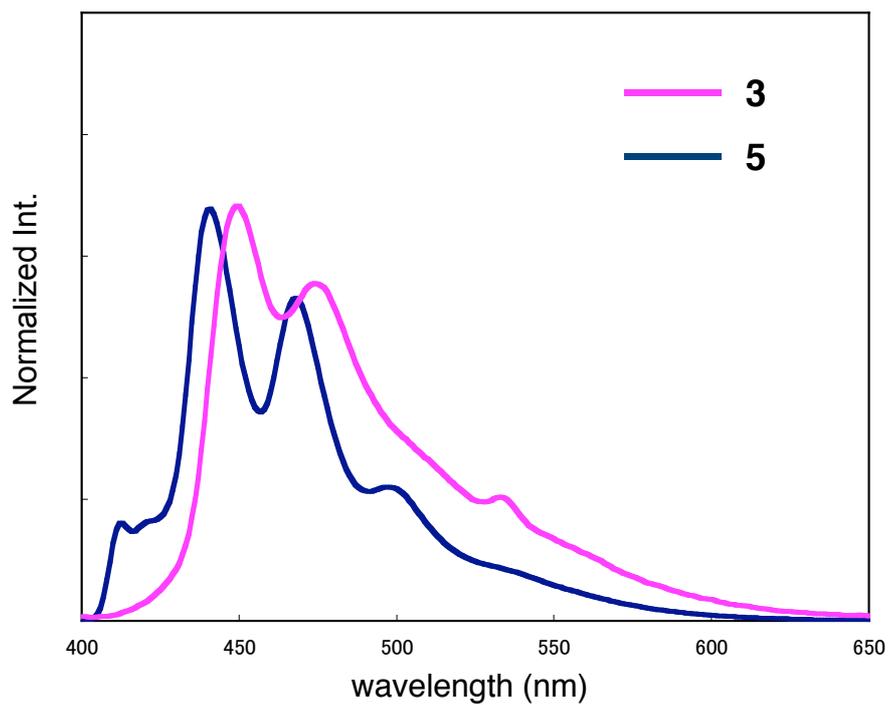
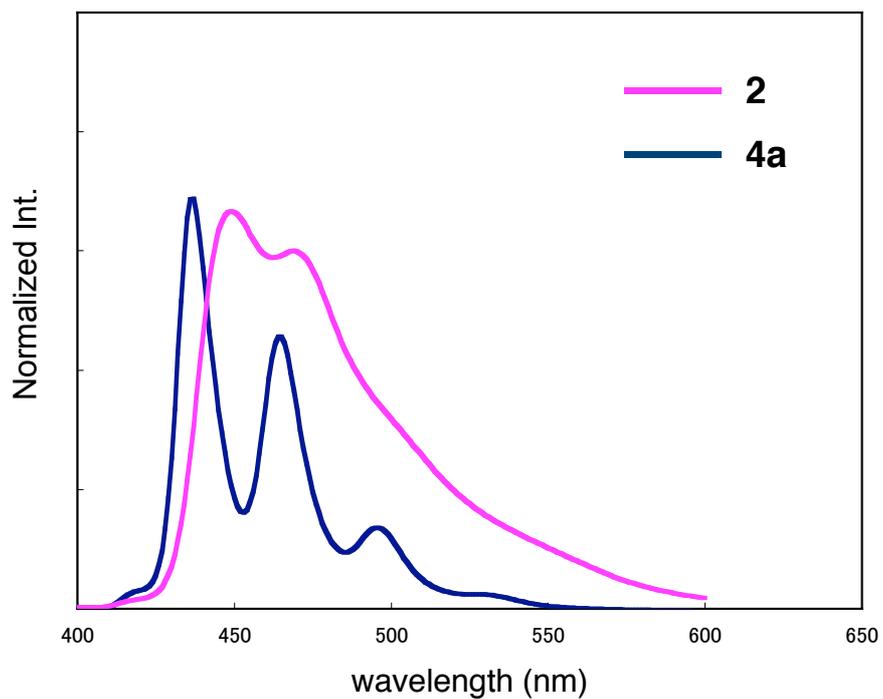


Fig. S2. Fluorescence spectra of acyclic oligomers and their photoproducts in chloroform. Excited at 393 nm.

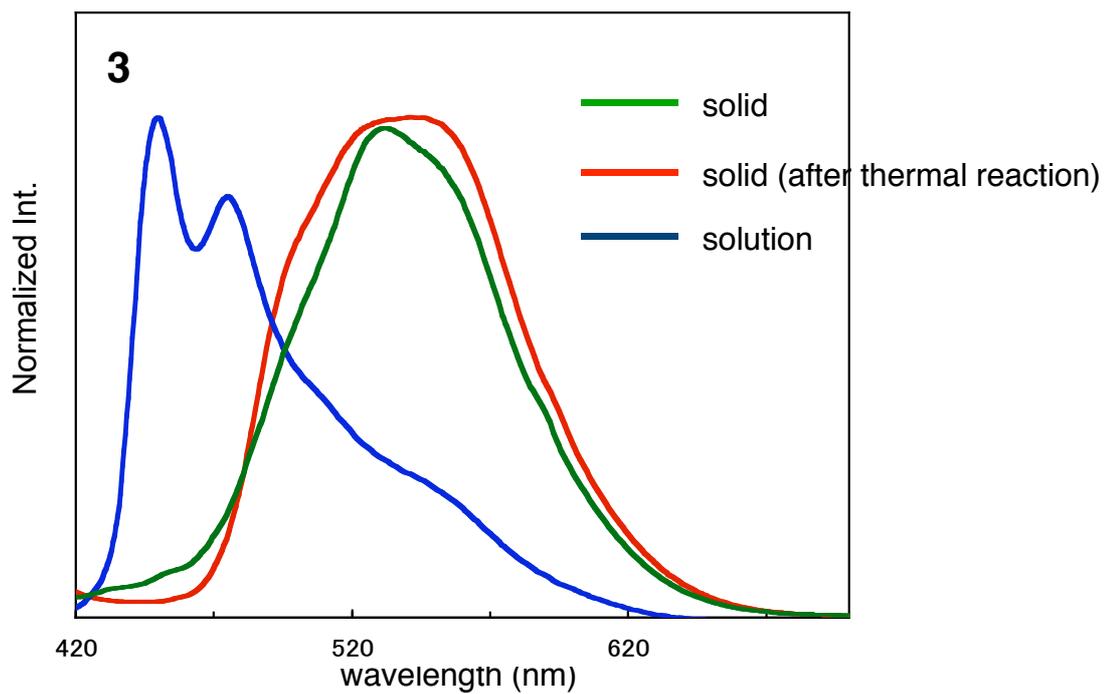
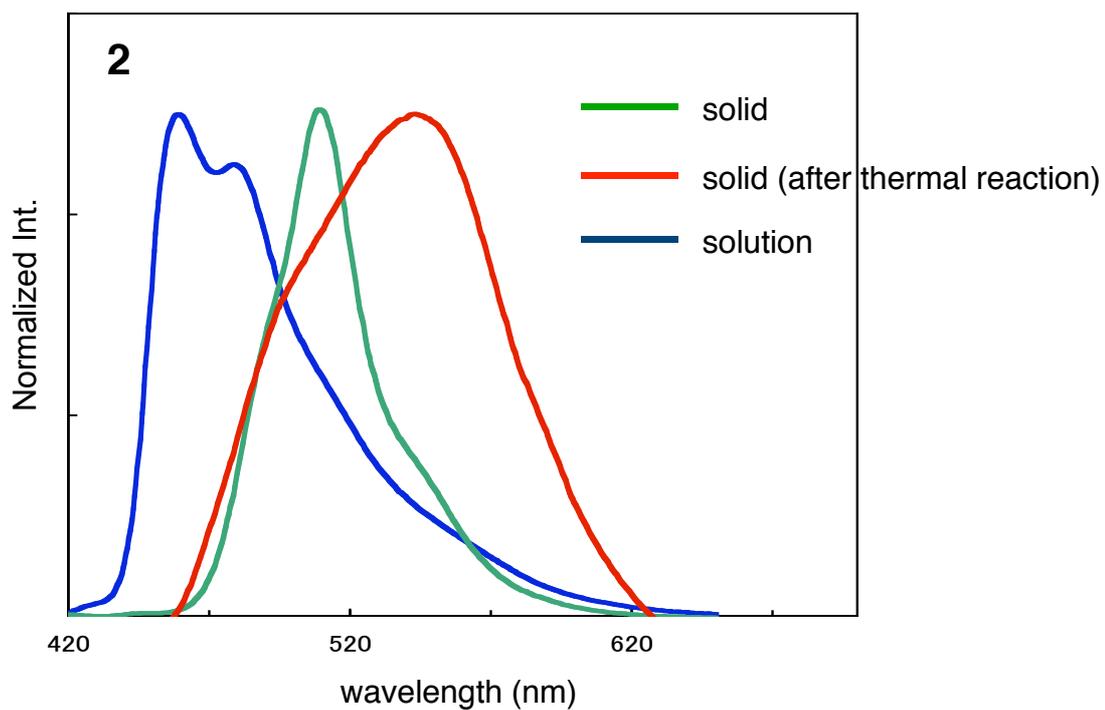


Fig. S3. Fluorescence spectra of **2** and **3** in the solid state. Excited at 393 nm.

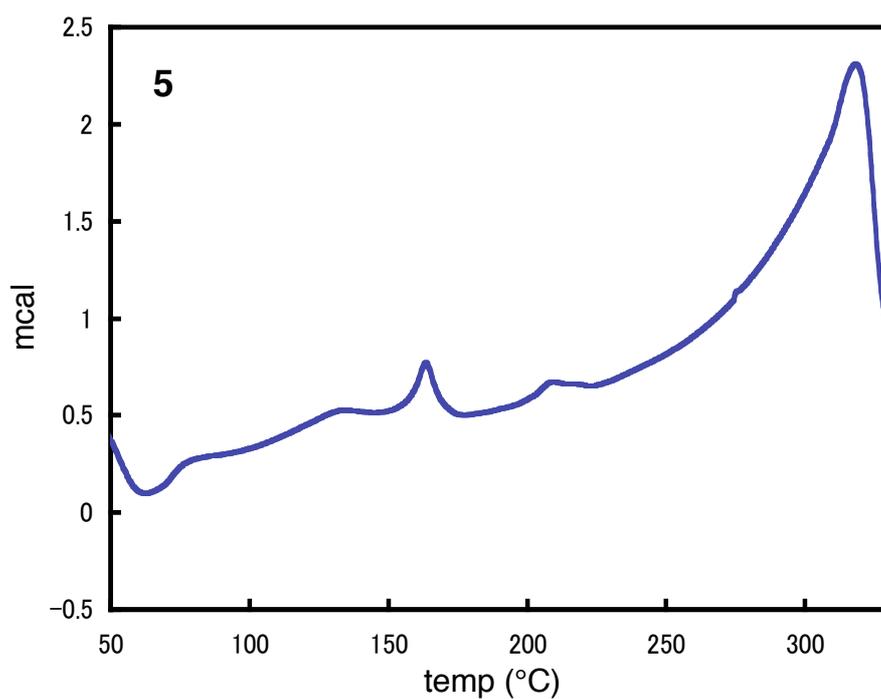
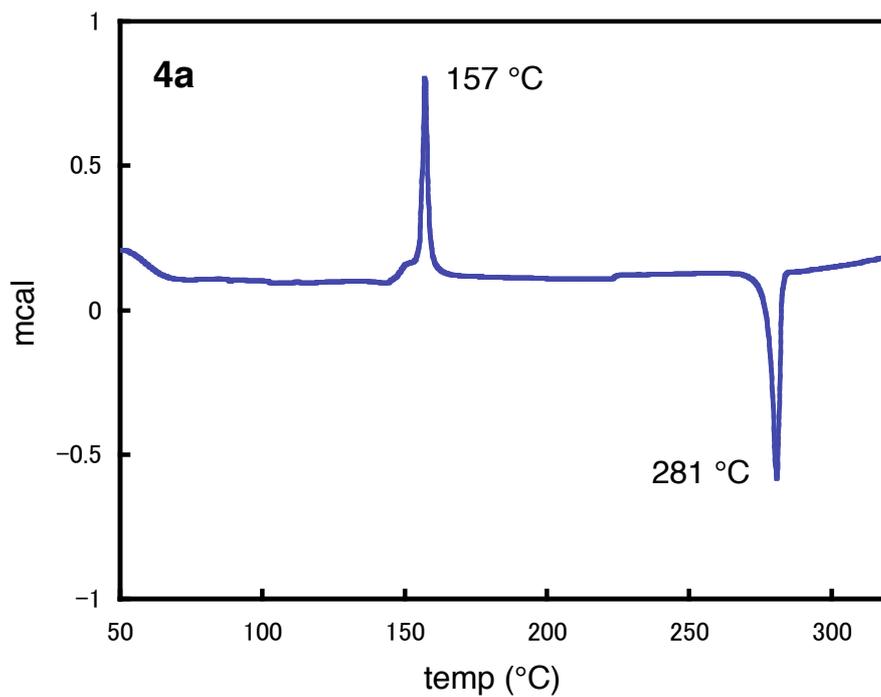


Fig. S4. DSC charts of **4a** (Top) and **5** (Bottom).