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General methods and materials

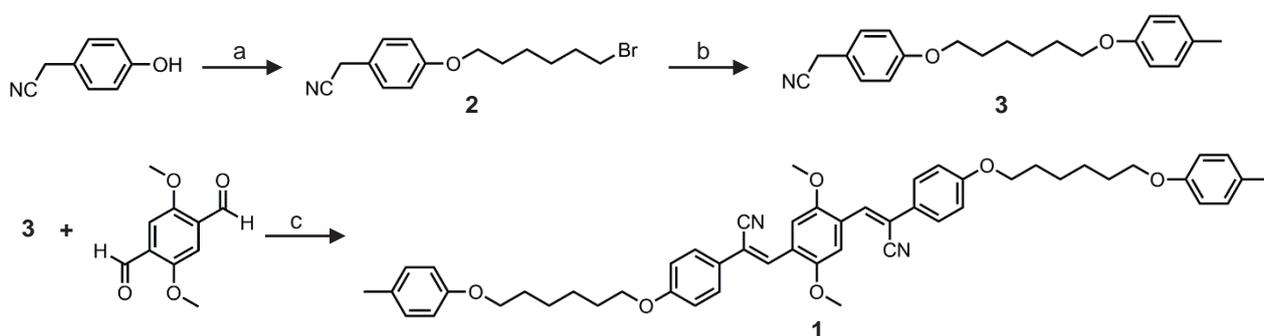
All reagents and solvents were purchased from Aldrich and Tokyo Kasei. Unless otherwise noted, all reactions were carried out under argon atmosphere in dry solvents. Silica gel column chromatography was carried out with a Biotage Isolera Flash system. ¹H and ¹³C NMR spectra were obtained using a Bruker Avance III HD Spectrometer at 400 and 100 MHz, respectively. Chemical shifts of ¹H and ¹³C NMR signals are referred to signals of residual CHCl₃ and expressed in ppm (δ) relative to the signal of tetramethylsilane (0 ppm), with multiplicity, coupling constant (Hz), and relative intensity. Electrospray ionization (ESI) mass spectra were obtained on a Bruker esquireHCT Ion-Trap. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker ultrafleXtreme MALDI-TOF. Elemental analysis was carried out with an Exeter Analytical CE440 Elemental Analyzer. Thermogravimetric analyses were conducted under nitrogen atmosphere using a Mettler-Toledo Stare system thermogravimetric analyzer in the with a heating rate of 10 °C/min. Melting temperatures and enthalpies were calculated from the differential scanning calorimeter measurements. The experiments were conducted using a Mettler-Toledo STAR system modulated differential scanning calorimeter in the range from -70 to 220 °C with a heating/cooling rate of 10 °C min⁻¹. Powder X-ray diffraction measurements were carried out with a Rigaku SmartLab. Steady-state fluorescence spectra were recorded on a Hitachi F-7000 spectrofluorometer. Time-resolved fluorescence measurements were carried out with a Hamamatsu Photonics Quantaaurus-Tau. Absolute quantum efficiencies were measured with a Hamamatsu Photonics Quantaaurus-QY. A circular quartz sample holder was used for measurements of quantum efficiencies for solid samples, which were placed at the bottom of an integrating sphere and were excited with 405 nm light. Single crystal data was collected with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 297 K using a Stoe IPDS-II diffractometer. The crystal was mounted on a

loop and all geometric and intensity data were taken from this crystal. The structure was solved and refined by full-matrix least-squares techniques on F2 with the SHELX-2014 package. All atoms (except hydrogen atoms) were refined anisotropically. Hydrogen atoms were introduced as fixed contributors if a residual electronic density was observed near their expected positions. The X-ray crystallographic file for **1** in the O-form was deposited in the Cambridge Crystallographic Data Centre (CCDC) (deposition code: CCDC 1435841). The CIF file can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of compound **1**

The synthetic route used to prepare compound **1** is shown in Scheme S1.

Scheme S1



Conditions: (a) 1,6-dibromohexane, K_2CO_3 , DMF, 60 °C, 3 h; (b) 4-methylphenol, K_2CO_3 , DMF, 60 °C, 18 h; (c) *t*-BuOK, *n*-Bu₄NOH, *n*-BuOH, THF, 45 °C, 1 h.

4-(6-Bromohexyloxy)benzyl cyanide (2). A mixture of 4-hydroxybenzyl cyanide (3.00 g, 22.5 mmol), 1,6-dibromohexane (22.0 g, 90.0 mmol), and K_2CO_3 (7.78 g, 56.3 mmol) in DMF (150 mL) was vigorously stirred for 3 h at 60 °C, before it was cooled to room temperature and poured into ethyl acetate. The organic phase was washed with saturated aqueous NH_4Cl solution (4 × 150 mL) followed by saturated aqueous NaCl solution (1 × 100 mL) and subsequently dried over Na_2SO_4 , before the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 9:1 to hexane/ethyl acetate = 4:1) to afford compound **2** (4.97 g, 16.8 mmol) as a white solid in 75% yield.

¹H NMR (400 MHz, $CDCl_3$): δ = 1.49–1.54 (m, 4H), 1.80 (quint, J = 6.8 Hz, 2H), 1.90 (quint, J = 6.8 Hz, 2H), 3.42 (t, J = 6.8 Hz, 2H), 3.68 (s, 2H), 3.95 (t, J = 6.4 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H).
¹³C NMR (100 MHz, $CDCl_3$): δ = 22.94, 25.38, 28.01, 29.13, 32.77, 33.89, 67.97, 115.20, 118.33, 121.77, 129.18, 158.94. MS (ESI): m/z : 318.1 (calcd. $[M + Na]^+ = 318.05$).

4-(6-(4-Methylphenoxy)hexyloxy)benzyl cyanide (3). A mixture of **2** (4.50 g, 15.2 mmol), 4-methylphenol (1.81 g, 16.7 mmol) and K_2CO_3 (5.25 g, 38.0 mmol) in DMF (150 mL) was vigorously stirred for 18 h at 60 °C, before it was cooled to room temperature and poured into ethyl acetate. The resulting mixture was washed with saturated aqueous NH_4Cl solution (4 × 150 mL) followed by saturated aqueous NaCl solution (1 × 100 mL) and

subsequently dried over Na₂SO₄, before the solvent was evaporated. The crude product was purified by re-precipitation (chloroform/hexane) to afford compound **3** (3.66 g, 11.3 mmol) as a white powder in 74% yield.

¹H NMR (400 MHz, CDCl₃): δ = 1.52–1.56 (m, 4H), 1.79–1.83 (m, 4H), 2.29 (s, 3H), 3.68 (s, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 20.59, 22.97, 25.99, 26.02, 29.29, 29.41, 68.00, 68.12, 114.51, 115.25, 118.36, 121.72, 129.19, 129.88, 130.00, 157.09, 159.03. MS (ESI): *m/z*: 346.2 (calcd. [M + H]⁺ = 346.18).

1,4-Bis(α-cyano-4-(6-(4-methylphenoxy)hexyloxystyryl))-2,5-dimethoxybenzene (1). A suspension of **3** (800 mg, 2.47 mmol) and 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (234 mg, 1.21 mmol) in THF (50 mL) and *n*-BuOH (100 mL) was stirred at 45 °C. Then, *n*-Bu₄NOH (2.4 mL of 1M solution in methanol) and *t*-BuOK (0.24 mL of 1M solution in THF) were quickly added and the reaction mixture was stirred for 1 h at the same temperature. Methanol (30 mL) was added, the reaction mixture was cooled to room temperature, and the resulting precipitate was filtered off. The crude product was washed with methanol (2 × 100 mL) containing several drops of acetic acid and pure methanol (2 × 100 mL) before it was purified by re-precipitation (chloroform/hexane) to afford compound **1** (663 mg, 0.824 mmol) as a yellow powder in 68% yield.

¹H NMR (400 MHz, CDCl₃): δ = 1.54–1.58 (m, 8H), 1.80–1.87 (m, 8H), 2.29 (s, 6H), 3.95 (s, 6H), 3.95 (t, *J* = 6.4 Hz, 4H), 4.02 (t, *J* = 6.8 Hz, 4H), 6.80 (d, *J* = 8.4 Hz, 4H), 6.96 (d, *J* = 9.2 Hz, 4H), 7.08 (d, *J* = 8.8 Hz, 4H), 7.64 (d, *J* = 9.2 Hz, 4H), 7.88 (s, 2H), 7.89 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 20.60, 26.00, 26.04, 29.29, 29.42, 56.52, 68.01, 68.23, 110.37, 111.73, 114.53, 115.12, 118.74, 125.60, 127.15, 127.65, 129.90, 130.02, 133.87, 152.03, 157.11, 160.24. MS (MALDI): *m/z*: 804.40 (calcd. [M]⁺ = 804.41). Elemental analysis (%) calcd. for C₅₂H₅₆N₂O₆: C 77.58, H 7.01, N 3.48; found: C 77.51, H 6.96, N 3.48.

Procedures used to create the various forms of compound 1

G-form: Almost all of the solvent of a concentrated dichloromethane solution of **1** was slowly evaporated using a rotary evaporator. After the appearance of a green-emissive solid (before complete evaporation of dichloromethane), the latter was filtrated off using a membrane filter and washed with a small amount of cold dichloromethane (3 mL) on the filter. The product was dried in vacuum to afford **1** in the G-form.

Y-form: A mixture of as-prepared compound **1** and toluene/methanol (9:1 v/v) was heated until the solid had completely dissolved. After slowly cooling the mixture to room temperature, a yellow-emissive powder precipitated, which was filtrated off using a membrane filter and washed with methanol several times on the filter. The product was dried in vacuum to afford **1** in the Y-form.

O-form: A mixture of as-prepared compound **1** and 1,4-dioxane was heated until the solid had completely dissolved. Needle crystals appeared upon cooling the mixture to room temperature and the resulting mixture was kept at 0 °C overnight. The resulting needle-like, orange-emissive crystals were filtrated off using a membrane filter and washed with methanol several times on the filter. The product was dried in vacuum to afford **1** in the O-form.

RO-form: A concentrated chloroform solution of as-prepared compound **1** was rapidly poured into a large amount of methanol at room temperature. Red-orange emissive crystals precipitated immediately, which were filtrated off using a membrane filter, washed with methanol several times, and dried in vacuum to afford **1** in the RO-form.

TGA analysis

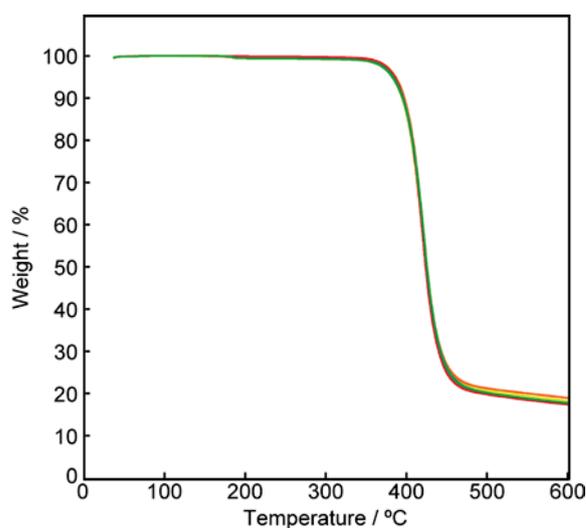


Figure S1. TGA curves acquired for the G-, Y-, O-, and RO-form.

XRD patterns of the O-form, RO-form and annealed RO-form

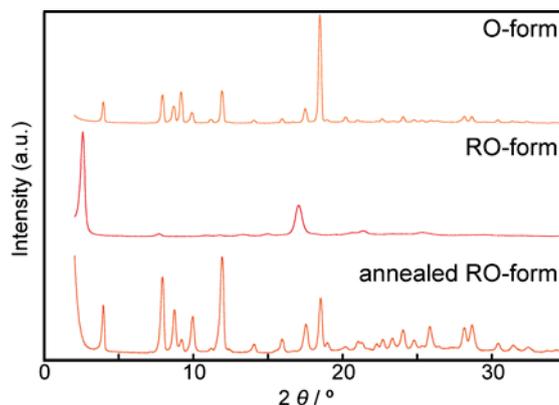


Figure S2. XRD patterns of the O-form, RO-form and a sample that was obtained by annealing the RO-form for 10 min at 150 °C. All measurements were carried out at room temperature.

DSC traces of the crystalline forms of compound 1

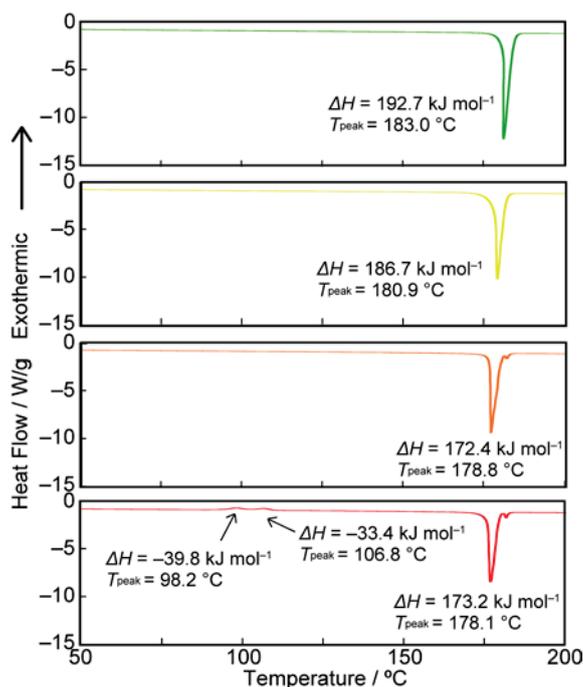


Figure S3. First heating DSC curves of the G- (green line), Y- (yellow line), O- (orange line), and RO-form (red line) of **1**. The small endothermic peaks at 183 °C apparent in the DSC traces of the O- and RO-form are interpreted as melting of small amounts of the G-form, which is assumed to form *in situ* through partial crystallization of the melt formed by melting of the O-form.

Changes in XRD patterns upon annealing ground amorphous forms

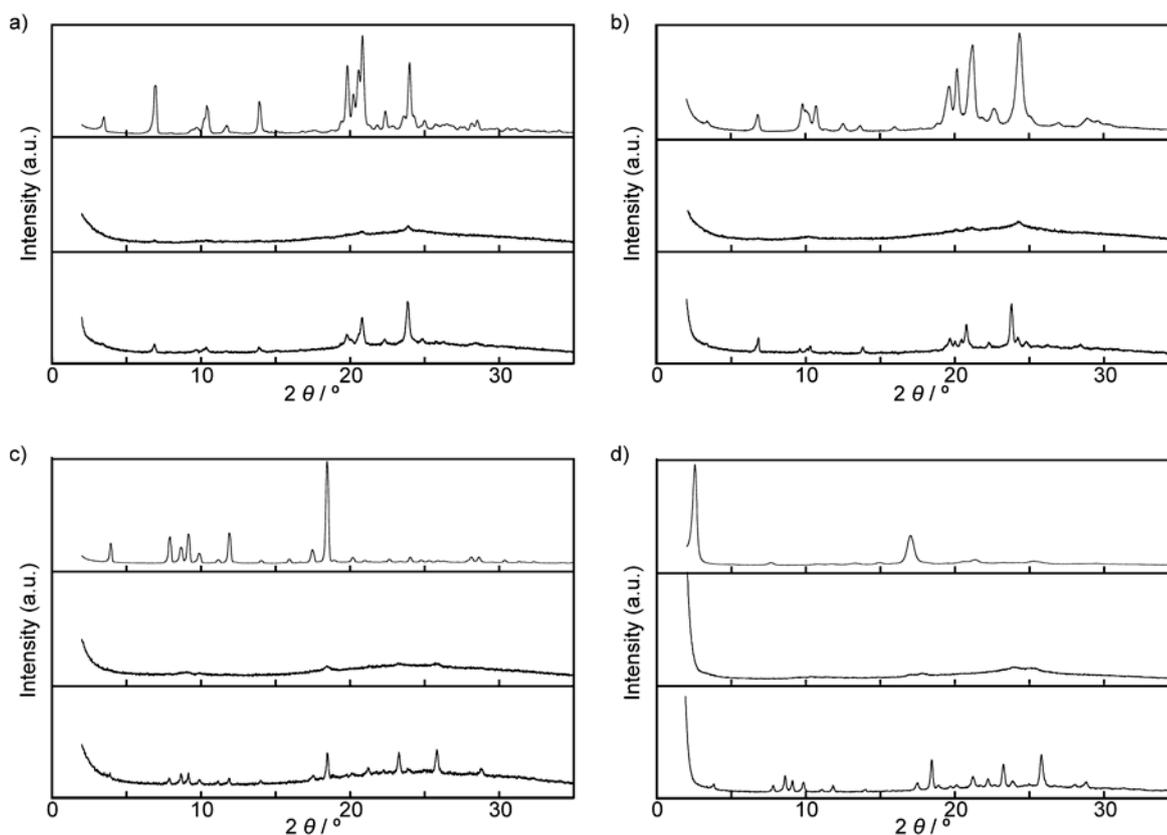


Figure S4. XRD patterns for a) G-, b) Y-, c) O-, and d) RO-form before (top) and after grinding at room temperature (middle) and subsequent annealing at 150 °C for 10 min (bottom). All measurements were carried out at room temperature.

DSC trace of the Am_G-form

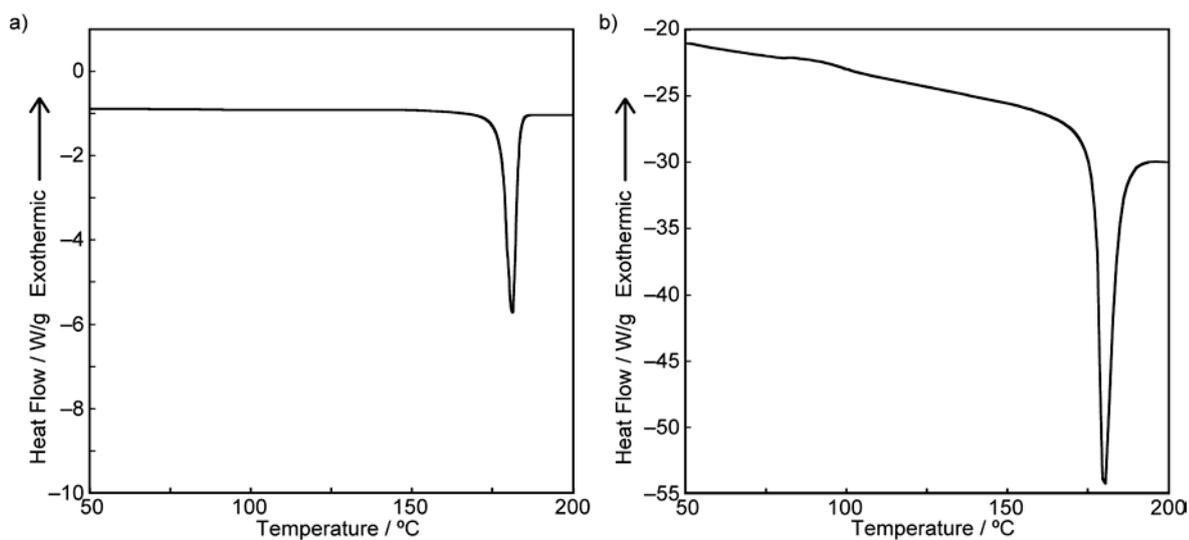


Figure S5. DSC trace (first heating) of the Am_G-form at normal heating rate (a, 10 °C min⁻¹) and fast heating rate (b, 60 °C min⁻¹).

Absorption spectrum of compound **1**

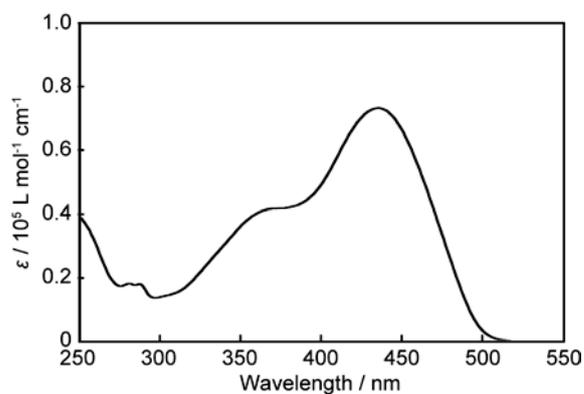


Figure S6. Absorption spectrum of compound **1** in chloroform ($1 \cdot 10^{-5}$ M).

Emission decay profiles

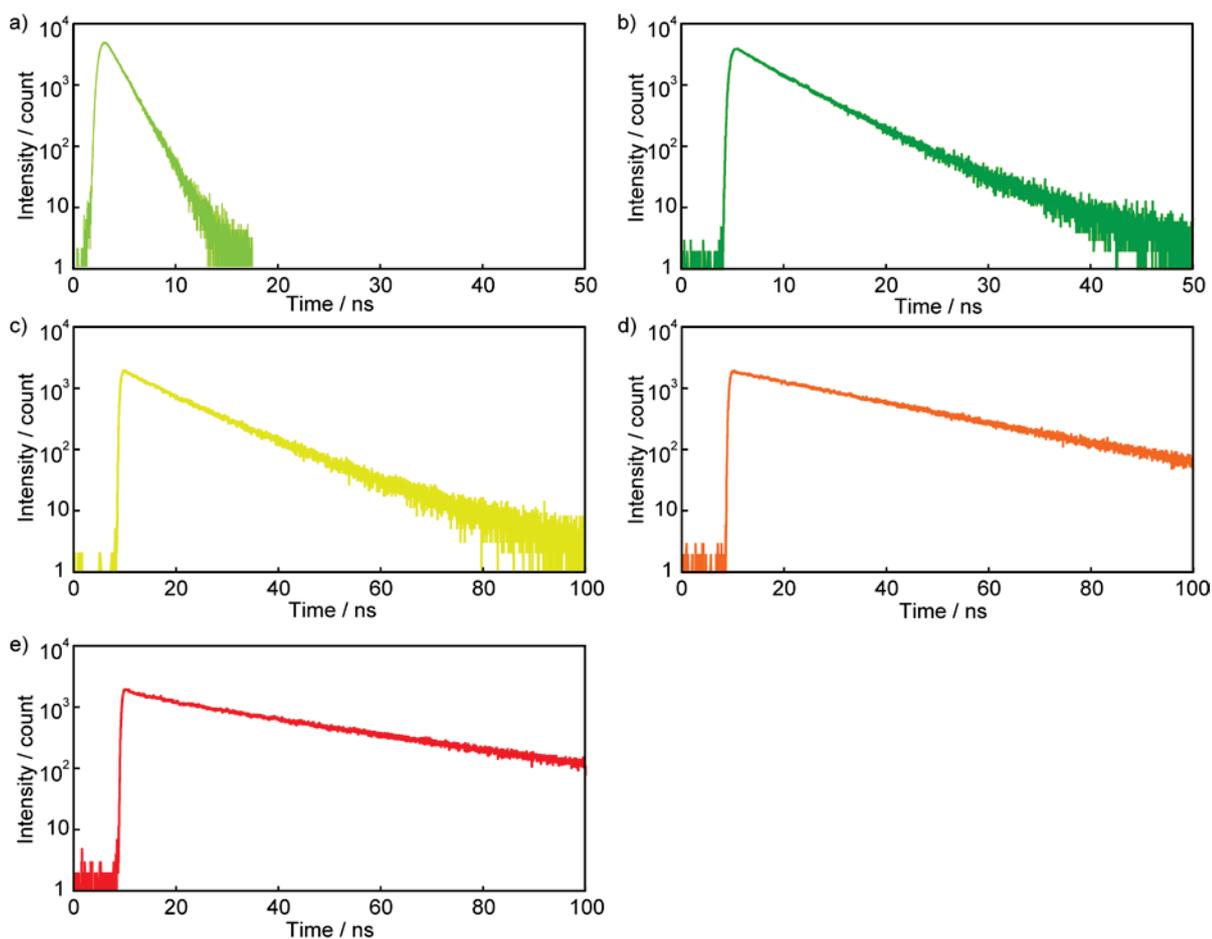


Figure S7. Emission decay curves of a dilute chloroform solution (a, monitored at 515 nm), the G-form (b, monitored at 545 nm), Y-form (c, monitored at 560 nm), O-form (d, monitored at 605 nm), and RO-form (e, monitored at 625 nm) of compound **1**. All measurements were carried out at room temperature. $\lambda_{\text{ex}} = 405$ nm.

Changes of the emission spectrum of the RO-form upon thermal treatment

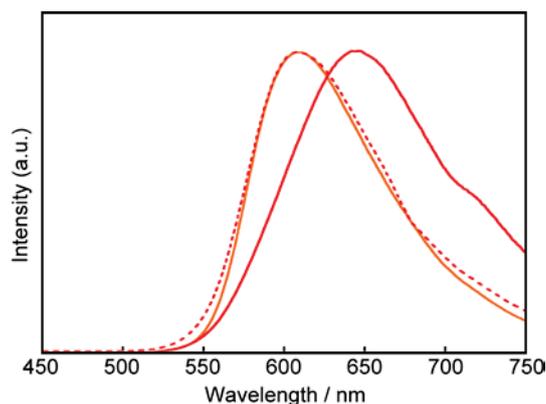


Figure S8. Photoluminescence spectra of the O-form (orange solid line), RO-form (red solid line) and a sample obtained by annealing the RO-form for 10 min at 150 °C (red dashed line). All measurements were carried out at room temperature. $\lambda_{\text{ex}} = 400$ nm.

Emission spectra of annealed Am_Y-form, Am_O-form, and Am_{RO}-form

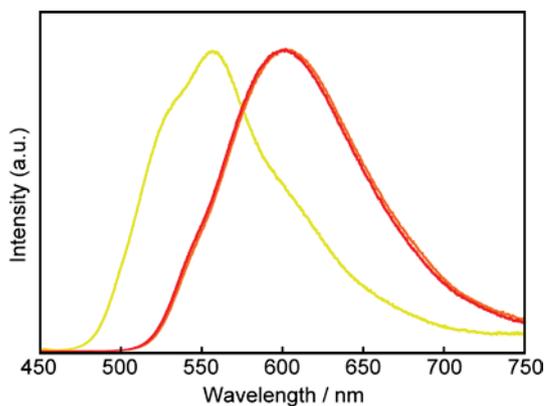


Figure S9. Photoluminescence spectra of annealed Am_Y-form (yellow line), Am_O-form (orange line), and Am_{RO}-form (red line). All measurements were carried out at room temperature. $\lambda_{\text{ex}} = 400$ nm.

Emission spectrum of the Am_G-form after exposure to dichloromethane vapor

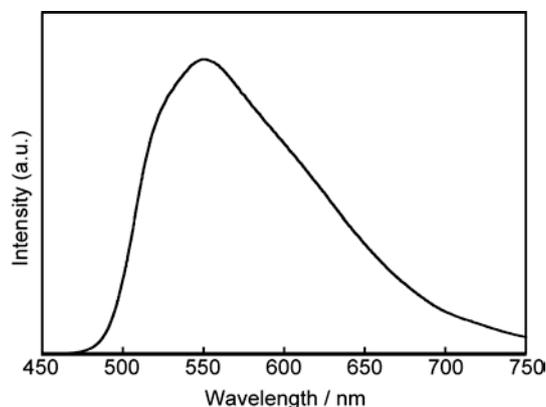


Figure S10. Photoluminescence spectrum of the Am_G-form exposed to dichloromethane vapor. The measurement was carried out at room temperature. $\lambda_{\text{ex}} = 400$ nm.

Single crystal structure of **1** in the O-form

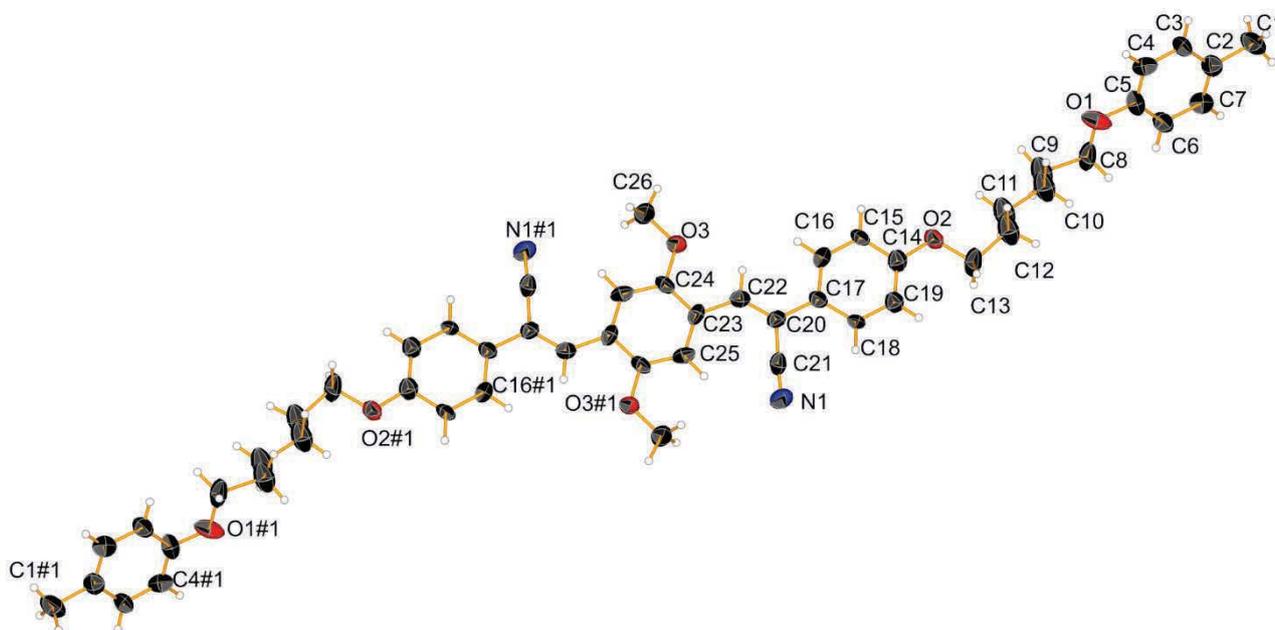


Figure S11. Molecular view of **1** in the O-form; Ellipsoids are drawn at 30 % of probability; #1: $-x-2, -y+1, -z+1$.

Table S1. Crystal data and structure refinement for **1** in the O-form.

| | | |
|---------------------------------|--|-----------------------------|
| Empirical formula | $C_{52} H_{56} N_2 O_6$ | |
| Formula weight | 804.98 | |
| Temperature | 297(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | $P-1$ | |
| Unit cell dimensions | $a = 4.9278(7)$ Å | $\alpha = 83.520(13)^\circ$ |
| | $b = 10.2411(17)$ Å | $\beta = 83.941(12)^\circ$ |
| | $c = 22.357(4)$ Å | $\gamma = 82.523(13)^\circ$ |
| Volume | $1106.8(3)$ Å ³ | |
| Z | 1 | |
| Density (calculated) | 1.208 Mg/m ³ | |
| Absorption coefficient | 0.078 mm ⁻¹ | |
| $F(000)$ | 430 | |
| Crystal size | 0.150 x 0.077 x 0.020 mm ³ | |
| Theta range for data collection | 1.841 to 25.000° | |
| Index ranges | $-5 \leq h \leq 5, -12 \leq k \leq 12, -26 \leq l \leq 26$ | |
| Reflections collected | 14303 | |

| | |
|---|--|
| Independent reflections | 3883 [$R(\text{int}) = 0.4127$] |
| Completeness to $\theta = 25.000^\circ$ | 99.9 % |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3883 / 0 / 249 |
| Goodness-of-fit on F^2 | 0.537 |
| Final R indices [$I > 2\sigma(I)$] | $R1 = 0.0580$, $wR2 = 0.0800$ |
| R indices (all data) | $R1 = 0.4179$, $wR2 = 0.1347$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.234 and $-0.280 \text{ e.}\text{\AA}^{-3}$ |