

Supplementary Data

Distinct Bulk Emission Properties of the Hexacatenar Molecules by Varying the Polarity of Peripheral Chains

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Materials and Methods: Thionyl chloride (SOCl₂, 1 M solution in methylene chloride) and *p*-toluenesulfonyl chloride were purchased from Alfa aesar. *N,N'*-Dicyclohexylcarbodiimide (DCC), propyl gallate, and 4-dimethylaminopyridine (DMAP) were purchased from Sigma-Aldrich Chemical. Tri(ethylene glycol) monomethyl ether, 1-bromodecane, hydrazine monohydrate (N₂H₄·H₂O), *n*-butanol, and 1,4-naphthalene dicarboxylic acid were purchased from Tokyo Chemical Industry. Potassium carbonate (K₂CO₃), hydrochloric acid (HCl), sodium hydroxide (NaOH), nitric acid (HNO₃), magnesium sulfate (MgSO₄), methylene chloride (MC), *N,N*-dimethylformamide (DMF), *n*-hexane (HX), tetrahydrofuran (THF), methyl ethyl ketone (MEK), ethyl acetate (EA), cyclohexane (CycloHX), glycerol, and toluene were purchased from Duksan Pure Chemical, Korea. THF and MC were distilled from calcium hydride (CaH₂) and stored over 4-Å molecular sieves.

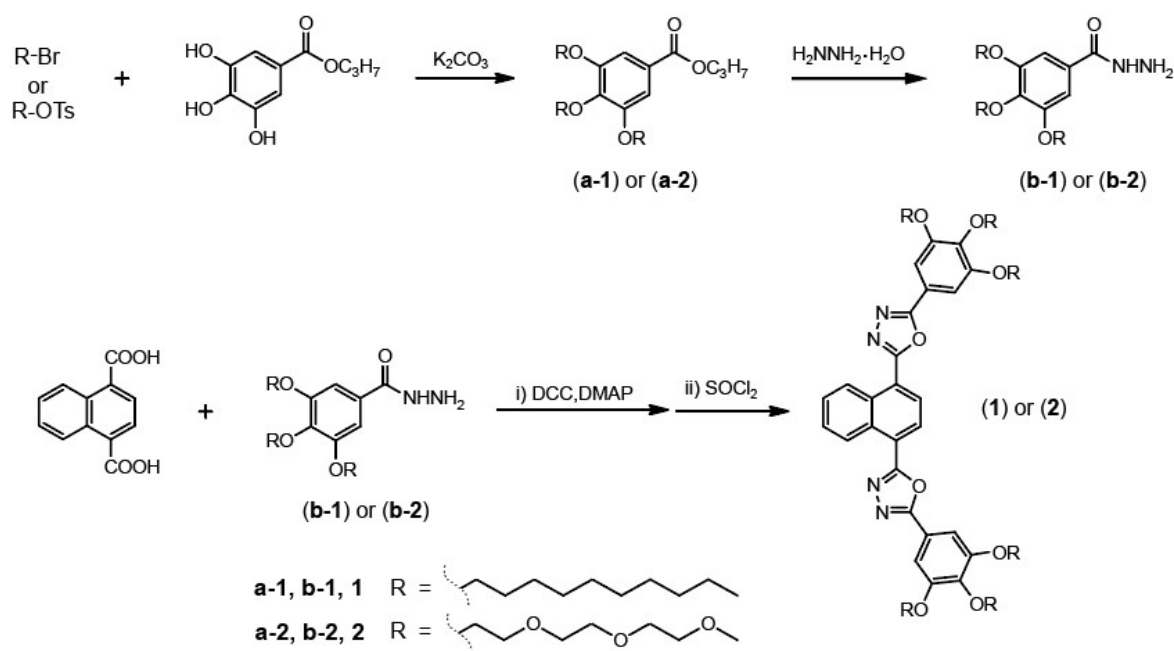
The purity of the synthesized compounds was checked by thin-layer chromatography (TLC; Merck, silica gel 60). Gel permeation chromatography (GPC) measurements were conducted in THF and *N,N'*-dimethylacetamide (99.9%) (40:1 volume ratio) using a Waters 401 instrument equipped with Styragel HR 2,3 columns and a Shodex AT-8045 at a flow rate of 1.0 mL/min. ¹H- and ¹³C-NMR spectra were recorded from CDCl₃ solutions using Bruker Ascend™ 500 spectrometer. Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at the Organic Chemistry Research Center, Sogang University, Korea. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q2000 thermal analysis system. Indium (melting temperature = 429 K and ΔH = 28.45 J/g) was used as a calibration standard. A Nikon Eclipse LV100 optical polarized microscope equipped with a Linkam TMS 94 heating system was used to observe the thermal transitions and to analyze the anisotropic texture.

All X-ray scattering experiments were conducted at the UNIST-PAL 6D beamline of the Pohang Accelerator Laboratory (PAL), South Korea. Temperature-variable X-ray diffraction (XRD) measurements were performed in transmission mode. The sample was held in an aluminum sample holder with polyimide (PI) films on both sides. For the grazing incidence X-ray diffraction (GIXRD) experiments, surface-aligned samples were prepared by spin-casting the sample solutions (dissolved in THF, ~5 wt%) on piranha solution-treated Si-wafers. The aligned samples were held in a vacuum chamber with a temperature-controlled heating stage and the diffraction patterns were recorded with a 2D imaging detector. The X-ray spectra were plotted against the *q* value ($q = 4\pi\sin\theta/\lambda$). Dielectric relaxation spectroscopy (DRS) measurements were performed at frequencies ranging from 0.1 to 10⁵ Hz using a Solartron Impedance Analyzer (SI 1260). The sample was measured in a 5 μm-thick indium tin oxide (ITO) liquid crystal cell coated with PI (Instec, United States). The LC cell was placed on a homemade heating block connected to a Test & Probe Hot Chuck Controller. The DRS measurements were performed between 30 and 100 °C. From the measured capacitance and loss tangent (tanδ), ε' (dielectric constant), and ε'' (dielectric loss) were obtained using the following equations: $\epsilon' = C/C_0$ and $\tan\delta = \epsilon''/\epsilon'$. UV-vis absorption spectra were obtained using a Perkin Elmer Lambda 950 UV/Vis/NIR spectrometer. Emission spectra were obtained using a Hitachi F-7000 fluorescence spectrophotometer equipped with a heating holder. The emission spectra were obtained during heating, with the sample annealed at each temperature for 3 min. Time-resolved fluorescence (TRF) study was performed using a fluorescence confocal microscope (MicroTime-200, Picoquant, Germany) at the Korea Basic Science Institute (KBSI), Daegu Center, Korea. A single-mode

pulsed diode laser (375 nm with 30 ps pulse width and average power of ~ 0.6 nW operating in 5 MHz repetition rate) was used as an excitation source. The pulsed laser line was focused on samples through a $10\times$ (air) objective. The emission photon was directed to a dichroic mirror (Z375RDC, AHF), a long-pass filter (HQ405lp, AHF), a $150\ \mu\text{m}$ pinhole, and a mirror, and finally collected by an avalanche photodiode detector (PDM series, MPD). A time-correlated single-photon counting system (PicoHarp300, PicoQuant GmbH, Germany) was used to count emission photons. Exponential function fitting for the obtained fluorescence decays was performed using the Symphotime-64 software (Ver. 2.2) by the exponential decay model; $I(t) = \sum A_i e^{-t/\tau_i}$, where $I(t)$ is the time-dependent fluorescence intensity, A is the amplitude, and τ is the fluorescence lifetime. Absolute quantum yield measurements were carried out using an absolute photoluminescence (PL) quantum yield measurement system (C11347, Hamamatsu Photonics, Hamamatsu, Japan) equipped with a 150-W xenon lamp (Hamamatsu Photonics, Hamamatsu, Japan).

All simulations were performed using the ORCA 5.0.3 software with the B3LYP functional and the 6-31G(d,p) basis set. Before each simulation, the structures were optimized using the DFT method. The HOMO-LUMO orbitals and their energy gap were calculated using the optimized structures, which were employed for visualizing the molecular orbitals. For the dihedral angle-dependent energy simulations, the total energy of each conformer was determined using single-point calculations. The energy gap between the HOMO and LUMO was calculated for each dihedral angle (α , β).

Synthesis of hexacatenar molecules **1** and **2**.



Scheme S1. Synthetic procedure for **1** and **2**.

Synthesis of a-1. Propyl gallate (5.8 g, 27 mmol), 1-bromodecane (30 g, 136 mmol) and K_2CO_3 (18.8 g, 136 mmol) were dissolved in a mixture of MEK (80 mL) and DMF (20 mL). The reaction mixture was heated to reflux for 24 h under nitrogen atmosphere. After cooling to room temperature (RT), the solvents were removed using a rotary evaporator. The obtained mixture was extracted with 1 M HCl and MC. The organic layer was further washed with deionized water several times and dried over MgSO_4 . After removing MC using a rotary evaporator, the resulting mixture was purified by sequential column chromatographies

(silica gel) from HX to MC as the eluents, to yield 16.5 g (96.5%) of a colorless liquid. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 7.25 (s, 2H, Ar-H), 4.25 (t, 2H, $J = 6.8$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 4.01 (t, 6H, $J = 6.6$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$), 1.84-1.71 (m, 8H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$), 1.50-1.27 (m, 42H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$), 1.02 (t, 3H, $J = 7.4$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.88 (t, 9H, $J = 6.9$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$).

Synthesis of b-1. Compound **a-1** (16 g, 25.3 mmol) and hydrazine monohydrate (18 mL, 368 mmol) were dissolved in *n*-butanol (20 mL). The reaction mixture was heated to reflux for 72 h. After removing the solvent using a rotary evaporator, the mixture was extracted with MC and deionized water. The organic layer was washed several times with deionized water and dried over MgSO_4 . After removing MC using a rotary evaporator, 14.7 g (93.5 %) of a white solid was obtained. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 6.94 (s, 2H, Ar-H), 4.01-3.94 (m, 6H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$), 1.83-1.69 (m, 6H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$), 1.48-1.20 (m, 42H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$), 0.88 (t, 9H, $J = 6.9$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$).

Synthesis of 1. 1,4-Naphthalene dicarboxylic acid (0.6 g, 2.8 mmol) and DMAP (0.14 g, 1.1 mmol) were dissolved in a mixture of anhydrous MC (10 mL) and DMF (10 mL). The mixture was stirred for 30 mins at RT under a nitrogen atmosphere. Then, the solution of DCC (1.2 g, 5.8 mmol) in MC (10 mL) was injected into the solution and stirred for another 30 min at RT. Subsequently, a solution of compound **b-1** (3.36 g, 5.6 mmol) in MC (10 mL) was injected and stirred for 4 h at RT. After the reaction, the precipitate was filtered through filter paper, and the solvent of the filtered solution was evaporated using a rotary evaporator. The resulting mixture was extracted with MC and deionized water. The organic layer was washed several times with deionized water and dried over MgSO_4 . After removing MC using a rotary evaporator, 2.5 g of the amide intermediate was obtained. The amide intermediate and SOCl_2 (15 mL) were heated to reflux for 12 h under nitrogen atmosphere. Then, deionized water was slowly added to the reaction mixture to quench the SOCl_2 . The organic layer was separated using a separatory funnel with distilled water and MC, then dried over anhydrous MgSO_4 . After evaporating the solvent using a rotary evaporator, the resulting mixture was purified by sequential column chromatographies (silica gel) from MC to MC:EA = 20:1 as the eluents, yielding 1.8 g (47.5%) of a green solid. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 9.41 (d, 2H, $J = 5.8$ Hz, Ar-H), 8.36 (s, 2H, Ar-H), 7.83 (d, 2H, $J = 5.8$ Hz, Ar-H), 7.39 (s, 4H, Ar-H), 4.11-4.07 (m, 12H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$), 1.87-1.28 (m, 96H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$), 0.88 (m, 18H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ , ppm): 164.85, 164.73, 153.72, 141.78, 130.63, 128.83, 127.04, 126.82, 124.14, 118.17, 105.72, 73.71, 69.49, 31.93, 30.37, 29.76, 29.61, 29.44, 29.37, 26.13, 22.70, 14.12. Anal. Calcd for $\text{C}_{86}\text{H}_{136}\text{N}_4\text{O}_8$: C, 76.29; H, 10.12; N, 4.14. Found: C, 76.35; H, 10.13; N, 4.10.

Synthesis of a-2. Propyl gallate (4.7 g, 22 mmol), tosylated TEO (TEO-Ots, 35.3 g, 111 mmol), and K_2CO_3 (15.3 g, 111 mmol) were dissolved in a mixture of MEK (80 mL) and DMF (20 mL). The reaction mixture was heated to reflux for 24 h under a nitrogen atmosphere. After cooling to RT, the solvents were removed using a rotary evaporator. The resulting mixture was extracted with 1 M HCl and MC. The organic layer was further washed several times with deionized water and dried over MgSO_4 . After removing MC using a rotary evaporator, the resulting mixture was purified by column chromatography (silica gel) using EA:MC = 1:1 as the eluent, to yield 11.7 g (82.2%) of a yellow liquid. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 7.28 (s, 2H, Ar-H), 4.25-4.18 (m, 8H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{OCH}_3$), 3.87-3.52 (m, 30H, $\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{OCH}_3$), 3.36 (s, 9H, $\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{OCH}_3$), 1.80-1.73 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.01 (t, 3H, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$).

Synthesis of b-2. Compound **a-2** (11 g, 16.9 mmol) and hydrazine monohydrate (17.4 mL, 338 mmol) were dissolved in *n*-butanol (20 mL). The reaction mixture was heated to reflux for 72 h. After removing the solvent using a rotary evaporator, the mixture was extracted with MC and deionized water. The organic layer was washed several times with deionized water and dried over MgSO_4 . After removing MC using a rotary evaporator, 10.0 g (95.3 %) of a yellow liquid was obtained. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm):

7.09 (s, 2H, Ar-H), 4.19 (t, 6H, $J = 4.9$ Hz, $\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{OCH}_3$), 3.84-3.52 (m, 30H, $\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{OCH}_3$), 3.35 (s, 9H, $\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{OCH}_3$).

Synthesis of 2. 1,4-Naphthalene dicarboxylic acid (0.6 g, 2.8 mmol) and DMAP (0.14 g, 1.1 mmol) were dissolved in anhydrous MC (10 mL) and DMF (10 mL). The mixture was stirred for 30 min at RT under a nitrogen atmosphere. Then, the solution of DCC (1.2 g, 5.8 mmol) in MC (10 mL) was injected into the solution and stirred for another 30 min at RT. Subsequently, a solution of compound **b-2** (3.46 g, 5.6 mmol) in MC (10 mL) was injected and stirred for 4 h at RT. After the reaction, the precipitate was filtered through filter paper, and the solvent of the filtrate was evaporated using a rotary evaporator. The resulting mixture was extracted with MC and deionized water. The organic layer was washed several times with deionized water and dried over MgSO_4 . After removing MC using a rotary evaporator, 2.0 g of the amide intermediate was obtained. The amide intermediate was then heated to reflux with SOCl_2 (15 mL) under a nitrogen atmosphere for 12 h. Then, deionized water was slowly added to the reaction mixture to quench the SOCl_2 . The organic layer was separated using a separatory funnel with deionized water and MC, and dried over anhydrous MgSO_4 . After evaporating the solvent using a rotary evaporator, the resulting mixture was purified by column chromatography (silica gel) using MC to MC:MeOH = 10:1 as eluent, yielding 1.0 g (25.7%) of a viscous liquid. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 9.40 (d, 2H, $J = 6.7$ Hz, Ar-H), 8.38 (s, 2H, Ar-H), 7.83 (d, 2H, $J = 6.7$ Hz, Ar-H), 7.45 (s, 4H, Ar-H), 4.31-4.27 (m, 12H, $\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{OCH}_3$), 3.93-3.53 (m, 60H, $\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{OCH}_3$), 3.36 (s, 18H, $\text{OCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{OCH}_3$). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ , ppm): 164.53, 163.84, 153.24, 142.02, 130.62, 128.87, 127.16, 126.80, 124.10, 118.47, 105.84, 72.60, 71.95, 70.73, 70.60, 69.69, 69.20, 59.04. Anal. Calcd for $\text{C}_{68}\text{H}_{100}\text{N}_4\text{O}_{26}$: C, 58.78; H, 7.25; N, 4.03. Found: C, 58.78; H, 7.19; N, 4.02.

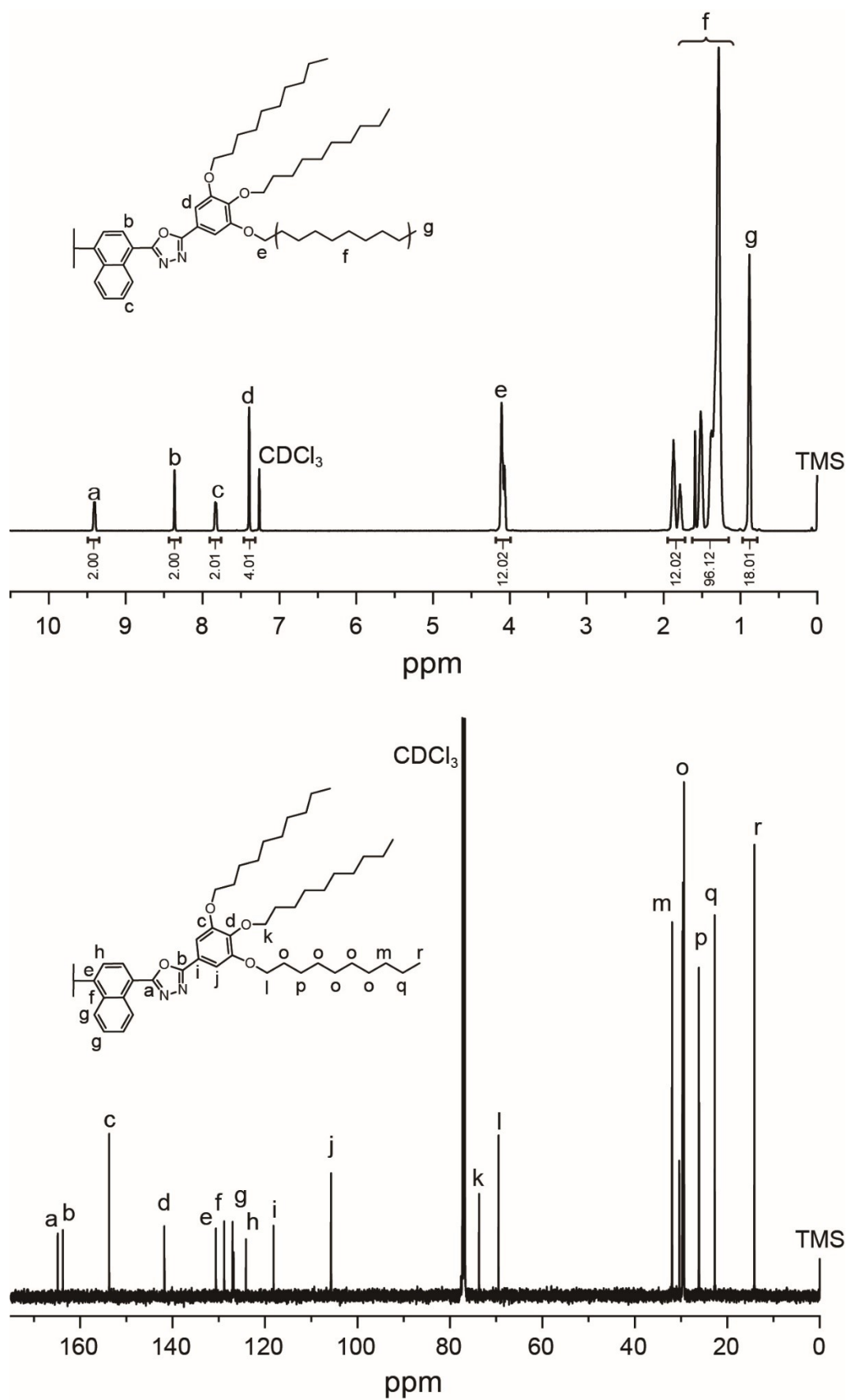


Fig. S1 ^1H - and ^{13}C -NMR spectra of compound 1.

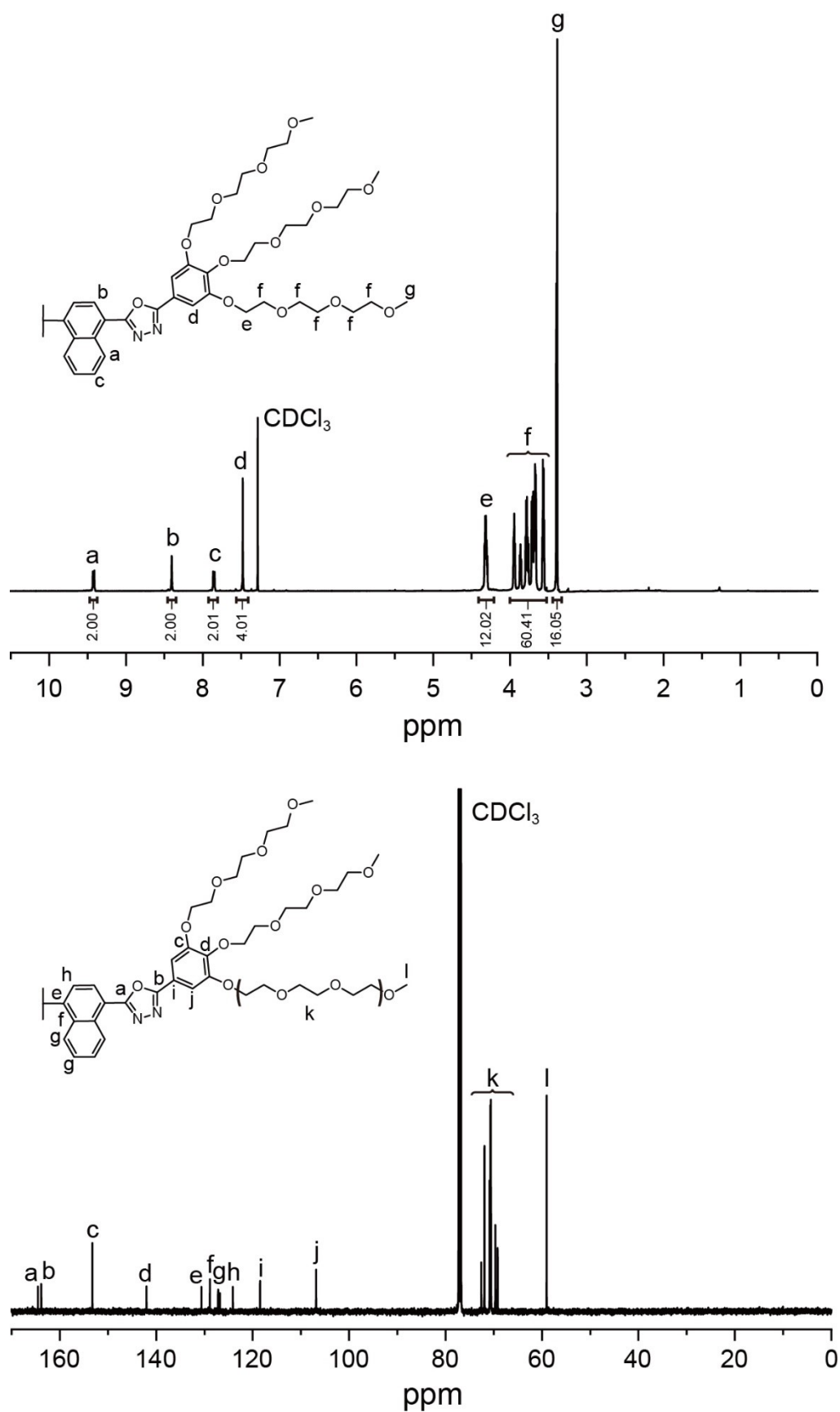


Fig. S2 ^1H - and ^{13}C -NMR spectra of compound 2.

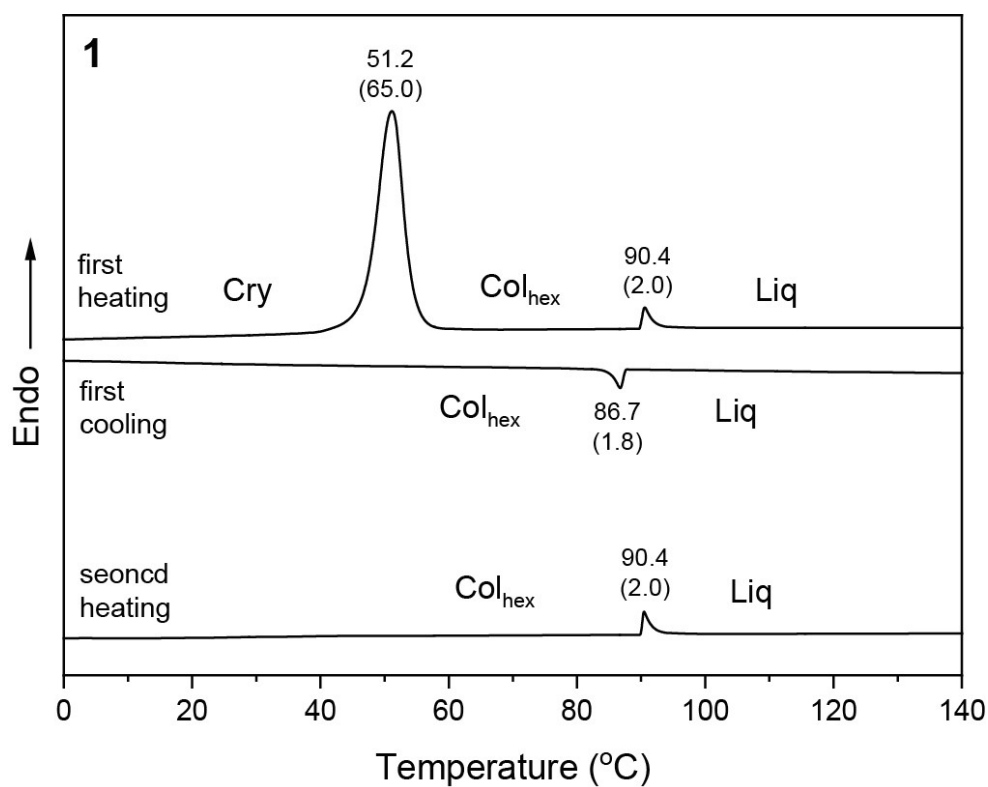


Fig. S3 DSC thermograms of **1**. Temperatures are given in °C. The parentheses values indicate each transition's enthalpy change (kJ/ mol). Cry, crystalline; Col_{hex}, hexagonal columnar; Liq, liquid phase.



Fig. S4 POM image of **2** at 30 °C.

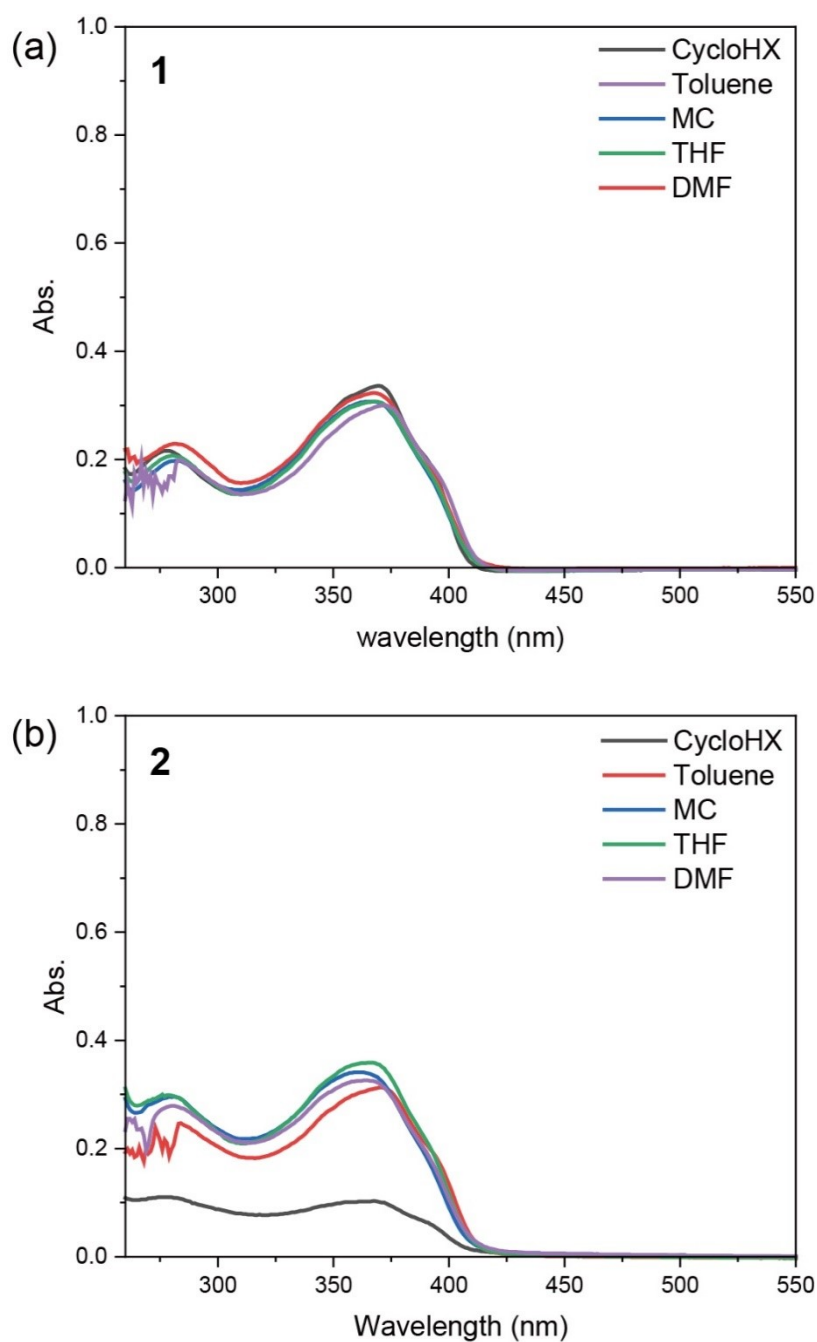


Fig. S5 UV-vis absorption spectra of the various solutions (concentration: 10^{-5} M) of (a) **1** and (b) **2**. The lower absorption of **2** in the CycloHX solution is due to its poor solubility. The undissolved liquid adheres to the walls and bottom of the sample cell.

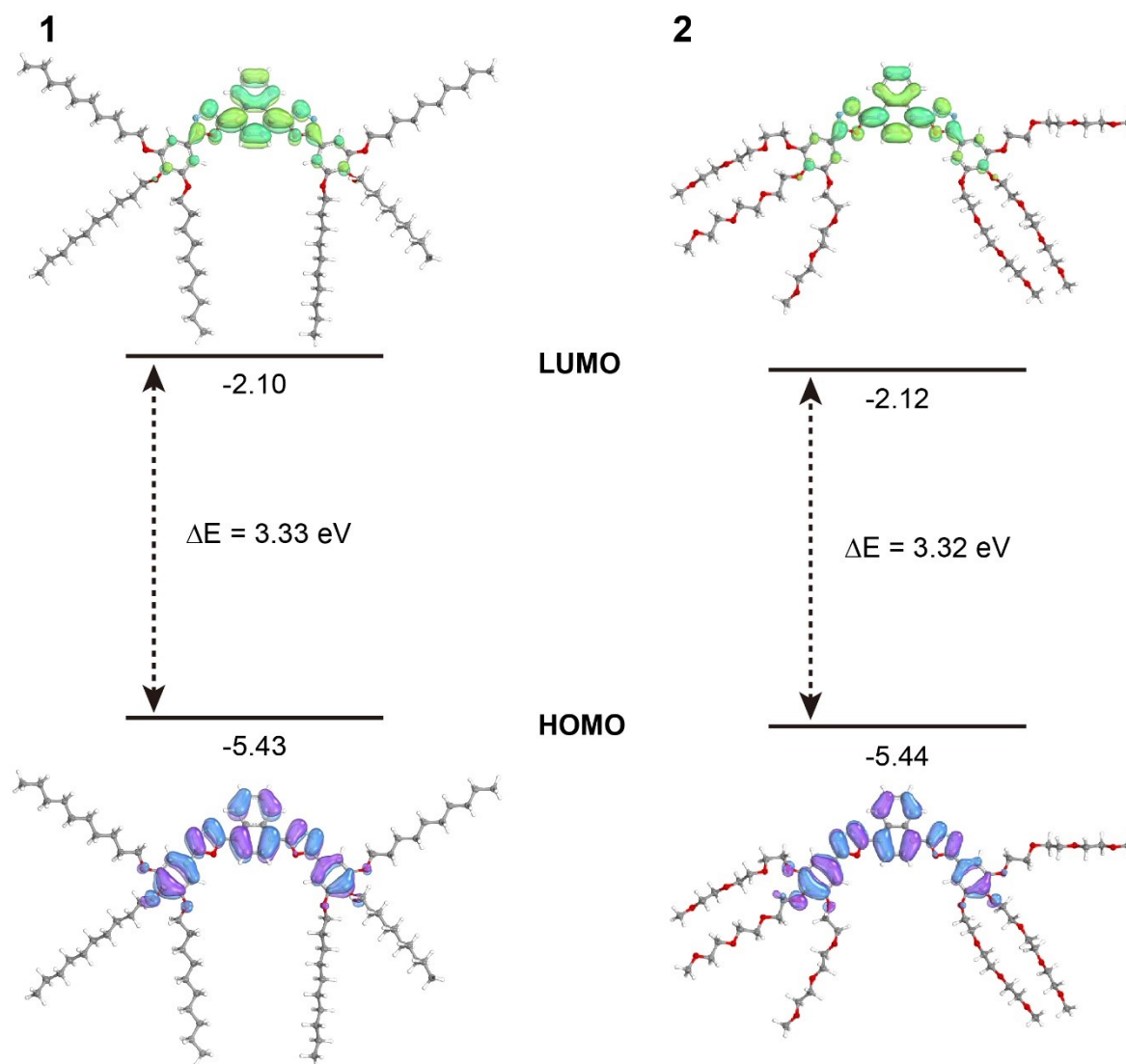


Fig. S6 DFT simulation data of the HOMO and LUMO energy levels for **1** and **2**.

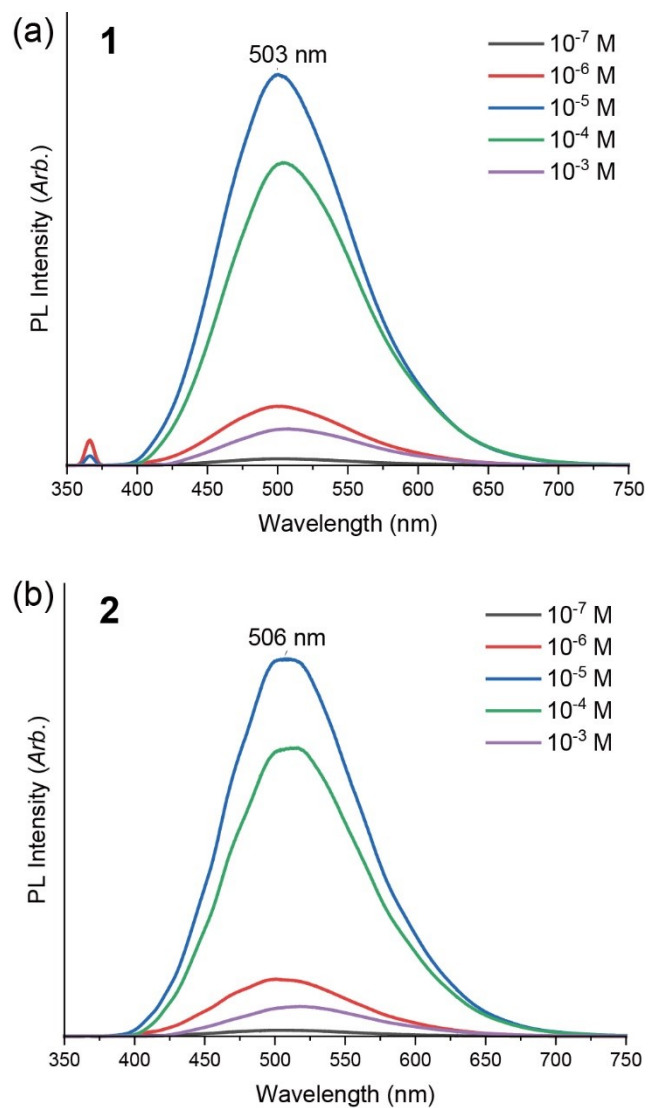


Fig. S7 Emission spectra of the THF solutions of (a) **1** and (b) **2** at different concentrations. The spectra were obtained after excitation at 365 nm.

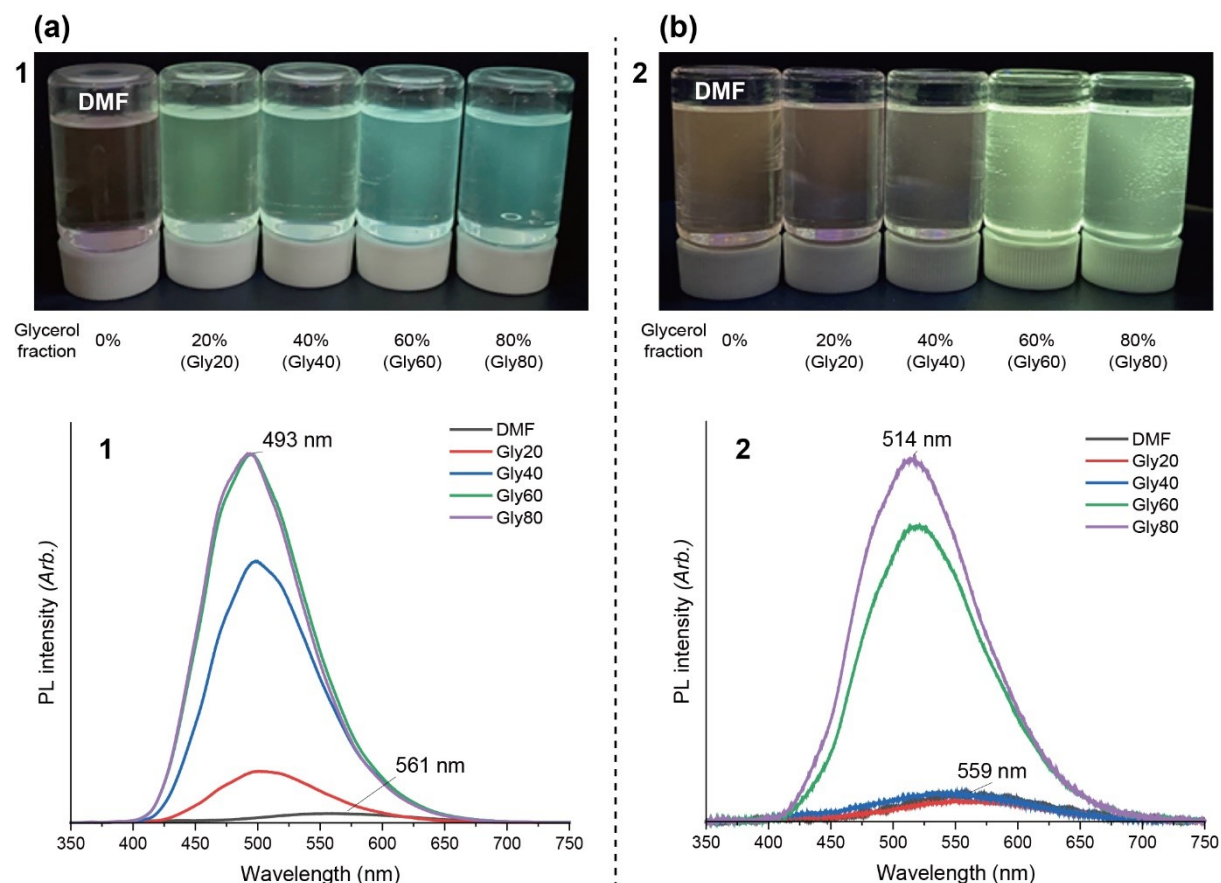


Fig. S8 Emission images and emission spectra of the solutions of (a) **1** and (b) **2** as a function of glycerol fraction. Emission images were obtained under UV irradiation at 365 nm. The spectra were obtained after excitation at 365 nm.

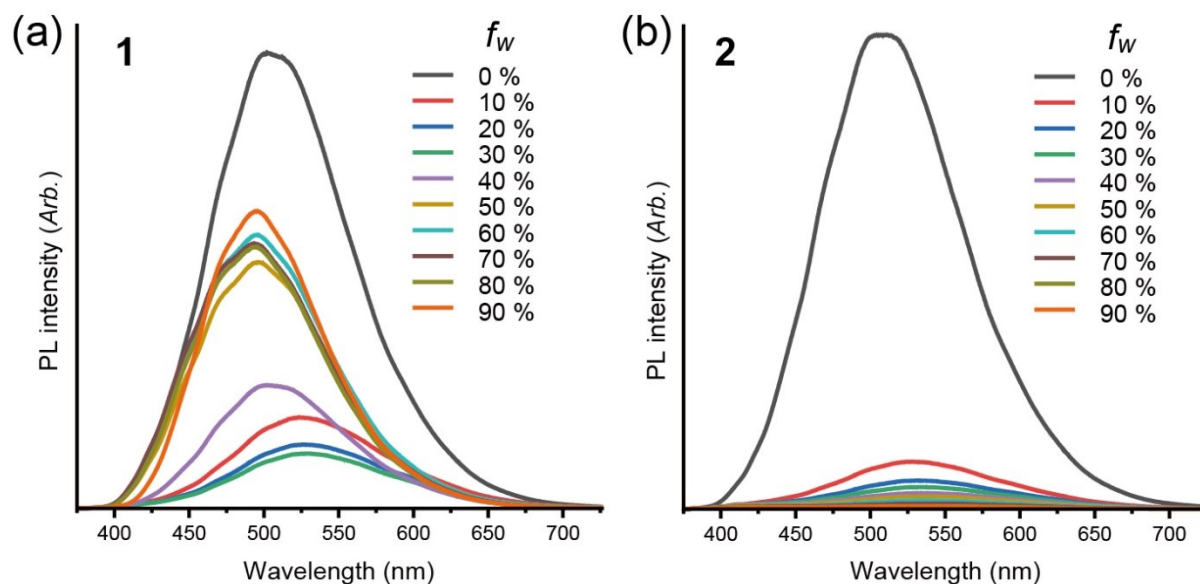


Fig. S9 Emission spectra of the THF/water solutions of (a) **1** and (b) **2** as a function of f_w . The spectra were obtained after excitation at 365 nm.

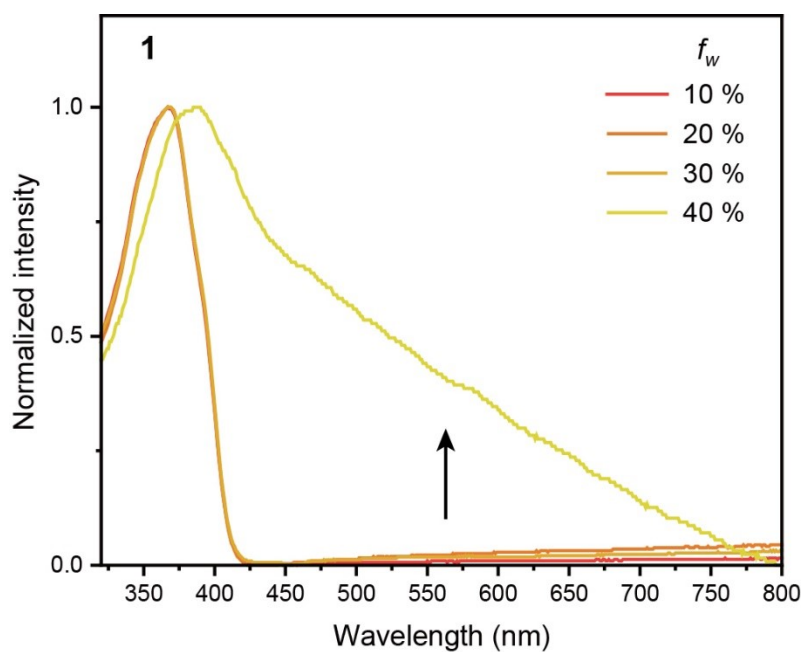


Fig. S10 UV-vis absorption spectra of the THF/water solutions of **1** at different f_w s.

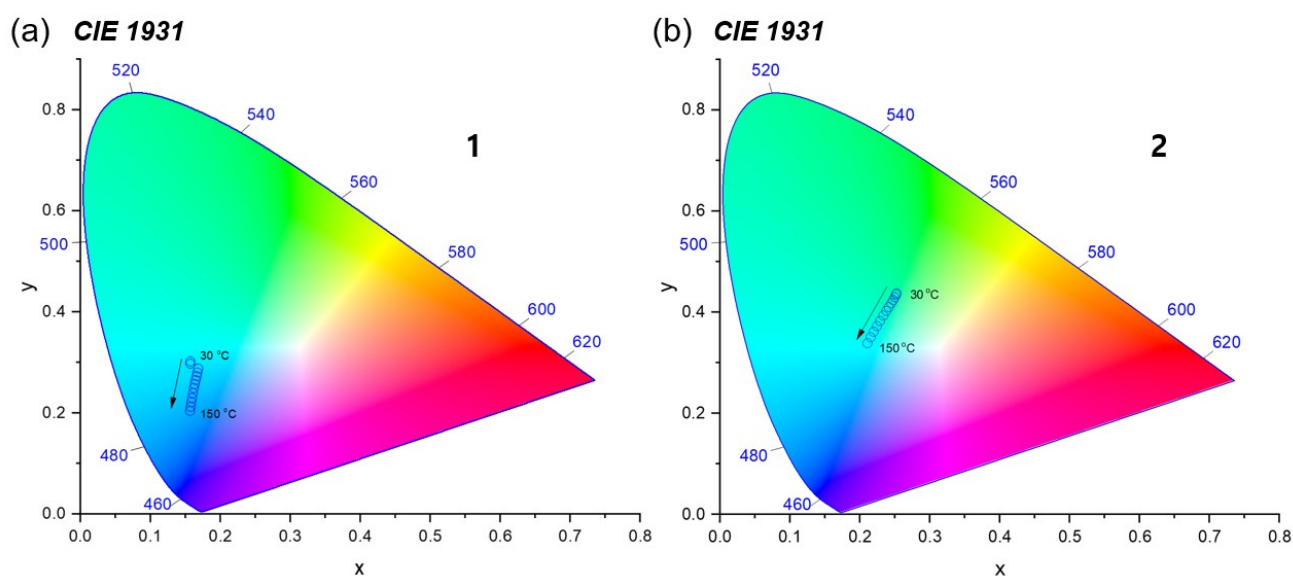


Fig. S11 Variation in the 1931 CIE chromaticity of (a) **1** and (b) **2** upon heating. The arrow indicates the heating direction.

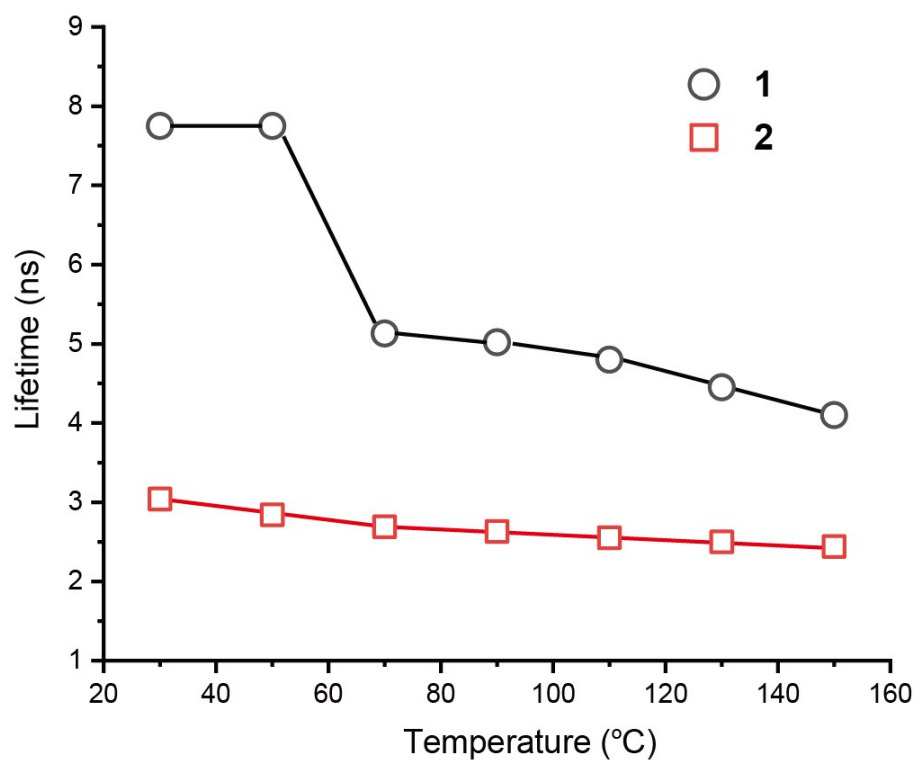


Fig. S12 Variation in lifetime values of bulk samples **1** and **2** as a function of temperature.