

Electronic Supplementary Information

High efficiency luminescent liquid crystal: aggregation-induced emission strategy and biaxially oriented mesomorphic structure

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Experimental Section

Materials and Instrumentations. THF was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. Dichloromethane (DCM) was distilled under normal pressure over calcium hydride under nitrogen before use. Triethylamine (TEA) was distilled and dried over potassium hydroxide. 4-iodophenol (**4**), 1,12-dibromododecane (**5**), (trimethylsilyl)acetylene (**8**), 1 M tetrabutylammonium fluoride (TBAF) in THF (containing 5% water), copper(I) iodide (CuI), triphenylphosphine (PPh_3), dichlorobis(triphenylphosphine)palladium(II) [$\text{Pd}(\text{PPh}_3)_3\text{Cl}_2$], 4,4'-dihydroxylbenzophenone (**2**), 9,10-diphenylanthracene (DPA), titanium tetrachloride (TiCl_4), zinc dust, potassium carbonate, sodium chloride, magnesium sulfate, sodium sulfate, methanol, acetone, and cyclohexane, were all purchased from Aldrich. 1-iodo-4-(4-pentylcyclohexyl)benzene (**7**) was purchased from Shijiazhuang Chengzhi Yonghua Display Materials Co., Ltd (China). All these materials are analytical grade and used as received.

^1H and ^{13}C NMR spectra were measured on a Bruker ARX 400 spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS, $\delta = 0$) as internal standard. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) high-resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer. Elemental analysis was performed on an Elementar Vario EL equipment (Germany). Absorption spectra were taken on a Milton Roy Spectronic 3000 Array spectrometer. Emission spectra were taken on a Perkin-Elmer spectrofluorometer LS 55. The quantum yields (Φ_{F} 's) in THF solutions were estimated using 9,10-diphenylanthracene ($\Phi_{\text{F}} = 90\%$ in cyclohexane) as standard according to the following equation:

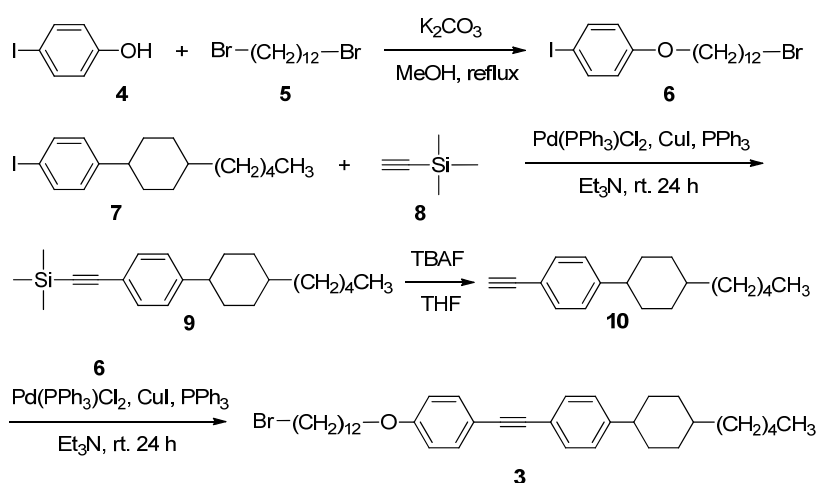
$$\Phi = \Phi_{\text{st}} \left(\frac{A_{\text{st}}}{A} \right) \left(\frac{F}{F_{\text{st}}} \right) \left(\frac{n}{n_{\text{st}}} \right)^2$$

where Φ (Φ_{st}), A (A_{st}), F (F_{st}), and n (n_{st}) are the fluorescence quantum efficiency, the absorbance at the excitation wavelength, the integral over the emission spectrum, and the refractive index of the solvent used for the testing sample (standard), respectively. Different to the comparison technique utilized for the solution quantum efficiency measurement, absolute measurement was adopted for the film photoluminescence quantum efficiency ($\Phi_{\text{F,f}}$) using an integrating sphere^[1] with an error of $\pm 5\%$.

The thermal stability of the resulting compound TPE4Mes was evaluated on a Perkin-Elmer TGA 7 under nitrogen at a heating rate of $20\text{ }^{\circ}\text{C}/\text{min}$. A Perkin-Elmer DSC 7 was employed to measure the phase transition thermograms. An Olympus BX 60 polarized optical microscope (POM) equipped with a Linkam TMS 92 hot stage was used to observe the anisotropic optical textures. One-dimensional wide-angle X-ray diffraction (1D-WAXD) powder experiments were performed on a Philips X'Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu $K\alpha$) and an X'celerator detector. The sample stage was set horizontally and the samples were protected by nitrogen gas during the measurements. The reflection peak positions were calibrated with silicon powder ($2\theta > 15^{\circ}$) and silver behenate ($2\theta < 10^{\circ}$). Background scattering was recorded and subtracted from the sample patterns. A temperature control unit (Paar Physica TCU 100) in conjunction with the diffractometer was utilized to study the

structure evolutions as a function of temperature. Two dimensional (2D) WAXD patterns were obtained using a Bruker D8 Discover diffractometer with general area detector diffraction system (GADDS) as a 2D detector. 2D WAXD experiments were carried out using molecularly oriented sample to identify the mesophase. To obtain the mono-domains oriented liquid crystalline film, TPE4Mes was slowly cooled from its isotropic state to 140 °C, annealed overnight^[2] and then quenched to room temperature.

Scheme S1. Synthetic route to intermediate **3**



Preparation of 1-((12-bromododecyl)oxy)-4-iodobenzene (6). Into a 250 mL round-bottom flask equipped with a reflux condenser was added 3.94 g (12 mmol) of 1,12-dibromododecane and 5.53 g (40 mmol) of potassium carbonate in 100 mL of acetone. 2.20g (10 mmol) of 4-iodophenol (**4**) in 40 mL of acetone was added into the flask dropwise within 4 h under reflux. The mixture was further refluxed for 24 h and then cooled to room temperature. The inorganic salt was filtered and washed with acetone several times. The filtrate was concentrated by a rotary evaporator and then extracted with 200 mL of DCM. The organic phase was washed with 150 mL of water three times and 100 mL of brine twice and then dried over 5 g of magnesium sulfate for 4 h. The crude product was condensed and purified on a silica-gel column using hexane as eluent. A white solid of **6** was obtained in 60.6% yield. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.52 (d, 2H, aromatic protons meta to –O–), 6.68 (d, 2H, aromatic protons ortho to –O–), 3.90 (t, 2H, –OCH₂), 3.41 (t, 2H, –CH₂Br), 1.85 (m, 2H, –OCH₂CH₂), 1.76 (m, 2H,

$-CH_2CH_2Br$), 1.42 (br m, 4H, $-OCH_2CH_2CH_2$ and $-CH_2CH_2CH_2Br$), 1.28 (br m, 12H, $-(CH_2)_6$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 158.99 (aromatic carbon connected to $-O-$), 138.13 (aromatic carbons meta to $-O-$), 116.91 (aromatic carbons ortho to $-O-$), 82.37 (aromatic carbon para to $-O-$), 68.10 ($-OCH_2$), 34.06 ($-CH_2Br$), 32.82, 29.49, 29.40, 29.32, 29.11, 28.74, 28.16, 25.96. HRMS (MALDI-TOF): Calcd. for $C_{18}H_{28}BrIO$ [M^+]: 466.0368. Found: 466.1852.

Preparation of trimethyl((4-(4-pentylcyclohexyl)phenyl)ethynyl)silane (9). Into a 250 mL two-necked round-bottom flask were added 84 mg of $Pd(PPh_3)_2Cl_2$, 23 mg of CuI , 63 mg of PPh_3 , 4.28 g (12 mmol) of 1-iodo-4-(4-pentylcyclohexyl)benzene (**7**), and a mixture of 150 mL of THF/TEA (30:120 v/v) under nitrogen. The mixture was stirred at room temperature for 30 min, then 2 mL (14.4 mmol) of (trimethylsilyl)acetylene (**8**) was injected. After reaction for 24 h, the formed solid was removed by filtration and washed with diethyl ether. The crude product was condensed and purified on a silica-gel column using hexane as eluent. A white solid was obtained in 96.8% yield. 1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.36 (d, 2H, aromatic protons ortho to $C\equiv C$), 7.14 (d, 2H, aromatic protons meta to $C\equiv C$), 2.44 (t, 1H, proton in cyclohexyl connected to aromatic ring), 1.84 (d, 4H, protons in cyclohexyl ortho to phenyl), 1.40 (m, 2H), 1.20~1.34 (m, 9H), 1.10 (m, 2H), 0.89 (t, 3H, $-CH_2CH_3$), 0.23 (s, 9H, $-Si(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 148.56 (aromatic carbon para to $C\equiv C$), 131.89 (aromatic carbons ortho to $C\equiv C$), 126.72 (aromatic carbons meta to $C\equiv C$), 120.38 (aromatic carbon connected to $C\equiv C$), 105.41 ($\equiv CAr$), 93.18 ($SiC\equiv$), 44.57 (carbon in cyclohexyl connected to aromatic ring), 37.33, 37.26, 34.10, 33.49, 32.19, 26.62, 22.70, 14.11 ($-CH_2CH_3$), 0.02 ($-Si(CH_3)_3$).

Preparation of 1-ethynyl-4-(4-pentylcyclohexyl)benzene (10). Into a 100 mL round-bottom flask was placed 30 mL of a THF solution of **9** (3.27 g, 10 mmol) and 15 mL of 1 M TBAF. After stirring for 45 min, 30 mL of water was added. The mixture was extracted with 200 mL of DCM three times and then washed by brine twice. The mixture was then dried over 5 g of anhydrous sodium sulfate for 4 h. The crude product was condensed and purified on a silica-gel column using hexane as eluent. A white solid of **10** was obtained in 97.8% yield. 1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.40 (d, 2H, aro-

matic protons ortho to C≡C), 7.17 (d, 2H, aromatic protons meta to C≡C), 3.02 (s, 1H, HC≡), 2.46 (t, 1H, proton in cyclohexyl connected to aromatic ring), 1.85 (d, 4H, protons in cyclohexyl ortho to phenyl), 1.41 (m, 2H), 1.19~1.34 (m, 9H), 1.05 (m, 2H), 0.89 (t, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 148.87 (aromatic carbon para to C≡C), 132.07 (aromatic carbons ortho to C≡C), 126.85 (aromatic carbons meta to C≡C), 119.36 (aromatic carbon connected to C≡C), 83.88 (≡CAr), 76.68 (HC≡), 44.57 (carbon in cyclohexyl connected to aromatic ring), 37.33, 37.26, 34.10, 33.48, 32.19, 26.62, 22.70, 14.10 (–CH₃). HRMS (MALDI-TOF): Calcd. for C₁₉H₂₆ [(M+H)⁺]: 254.2113. Found: 255.2116.

Preparation of 1-((12-bromododecyl)oxy)-4-((4-(4-pentylcyclohexyl)phenyl)ethynyl)benzene (3).

Into a 250 mL two-necked flask were added 70.1 mg of PdCl₂(PPh₃)₂, 19 mg of CuI, 13 mg of PPh₃, 2.34 g (5 mmol) of **6**, 1.27 g (5 mmol) of **10**, and a mixture of 130 mL of THF/TEA (30:100 v/v) under nitrogen. The mixture was stirred at 50 °C for 24 h. The formed solid was removed by filtration and washed with acetone. The filtrate was concentrated by a rotary evaporator. The crude product was purified on a silica-gel column with hexane as eluent. A white solid was obtained in 80.3% yield. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.43, 7.42 (two overlapped double peaks, 4H, aromatic protons ortho to C≡C), 7.18 (d, 2H, aromatic protons ortho to cyclohexyl), 6.86 (aromatic protons ortho to –O–), 3.96 (t, 2H, –OCH₂), 3.41 (t, 2H, –CH₂Br), 2.46 (t, 1H, proton in cyclohexyl connected to aromatic ring), 1.85 (m, 6H), 1.78 (m, 2H), 1.24~1.51 (m, 27H), 1.06 (m, 2H), 0.90 (t, 3H, –CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 159.06 (aromatic carbon connected to –O–), 147.93 (aromatic carbon connected to cyclohexyl), 132.94 (aromatic carbons meta to –O–), 131.37 (aromatic carbons meta to cyclohexyl), 126.84 (aromatic carbons ortho to cyclohexyl), 120.91 (aromatic carbon para to cyclohexyl), 115.39 (aromatic carbon para to –O–), 114.49 (aromatic carbons ortho to –O–), 88.69 (≡CAr), 88.15 (OArC≡), 68.06 (–OCH₂), 44.56 (carbon in cyclohexyl para to –CH₂), 37.36 (–CH₂ connected to cyclohexyl), 37.29, 34.16, 34.05, 33.53, 32.84, 32.21, 29.51, 29.42, 29.35, 29.19, 28.76, 28.17, 26.64, 26.00, 22.71, 14.11 (–CH₃). HRMS (MALDI-TOF): Calcd. for C₃₇H₅₃BrO: 594.3280. Found:

594.4399 [M⁺]. UV/Vis (THF): λ_{max} (ϵ) = 295 nm ($3.96 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$), 313 nm ($3.39 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$).

Preparation of 1. The synthetic procedure of **1** is similar to that of **3**. Grey-white solid, yield: 95.3%. Characterization data: ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.76 (d, 4H, aromatic protons ortho to –C=O), 7.43, 7.42 (two overlapped double peaks, 8H, aromatic protons ortho to C \equiv C), 7.18 (d, 4H, aromatic protons ortho to cyclohexyl), 6.95 (d, 4H, aromatic protons meta to –C=O), 6.86 (d, 4H, aromatic protons ortho to –O– in –CH₂OArC \equiv), 4.03 (t, 4H, O=CArCH₂O–), 3.96 (t, 4H, –CH₂OArC \equiv), 2.46 (br t, 2H, protons in cyclohexyl connected to aromatic ring), 1.74~1.88 (m, 16H), 1.20~1.51 (m, 54H), 1.06 (m, 4H), 0.90 (t, 6H, –CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 195.39 (C=O), 162.43 (aromatic carbons para to C=O), 159.00, 147.93, 132.94, 132.22, 131.37, 126.84, 120.84, 115.34, 114.47, 113.90, 88.68 (\equiv CAr), 88.16 (OArC \equiv), 68.23, 68.04, 44.45, 37.27, 34.15, 33.52, 32.21, 29.55, 29.36, 29.19, 29.14, 26.65, 26.01, 22.72, 14.13. HRMS (MALDI-TOF): HRMS (MALDI-TOF): Calcd. for C₈₇H₁₁₄O₅ [(M+K)⁺]: 1277.8303. Found: 1277.8550.

Preparation of TPE4Mes. Into a 100 mL two-necked round-bottom flask equipped with a reflux condenser was placed 0.26 g of zinc dust (4 mmol), 619.9 mg (0.5 mmol) of **1**. The flask was evacuated under vacuum and flushed with dry nitrogen three times, after which 60 mL of THF was added. The mixture was cooled to around 0 °C, to which 0.22 mL (2 mmol) of titanium tetrachloride was slowly added. The mixture was slowly warmed to room temperature and then stirred for 24 h under reflux. After being cooled to room temperature again, the reaction mixture was quenched with a 10% potassium carbonate aqueous solution. A large amount of water was added until the solid is turned to grey or white. The mixture was then extracted with DCM three times and the combined organic layer was washed by brine twice. The mixture was dried over 5 g of anhydrous sodium sulfate. The crude product was condensed and purified on a silica-gel column using a mixture of DCM/hexane (1:3 v/v) as eluent. A white solid was obtained in 65.1% yield. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.43, 7.42 (two over-

lapped double peaks, 16H, aromatic protons ortho to $\text{C}\equiv\text{C}$), 7.18 (d, 8H, aromatic protons ortho to cyclohexyl), 6.98 (d, 8H, aromatic protons meta to $-\text{C}=\text{C}-$), 6.85 (d, 8H, aromatic protons ortho to $-\text{O}-$ in $-\text{CH}_2\text{OArC}\equiv$), 6.63 (d, 8H, aromatic protons meta to $-\text{C}=\text{C}-$), 3.95 (t, 8H, $-\text{CH}_2\text{OArC}\equiv$), 3.80 (t, 8H, $-\text{C}=\text{CArOCH}_2$), 2.46 (br t, 4H, protons in cyclohexyl connected to aromatic ring), 1.86 (br d, 16H), 1.77 (m, 8H), 1.68 (m, 8H), 1.21~1.48 (m, 108H), 1.06 (m, 8H), 0.90 (t, 6H, $-\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 159.07 (aromatic carbons connected to $-\text{O}-$ in $-\text{OArC}\equiv$), 156.92 (aromatic carbons para to $-\text{C}=\text{C}-$), 147.91 (aromatic carbons connected to cyclohexyl), 136.23 ($-\text{C}=\text{C}-$), 132.93 (aromatic carbons meta to $-\text{O}-$ in $-\text{OArC}\equiv$), 131.37 (aromatic carbons meta to cyclohexyl, aromatic carbons connected to $-\text{C}=\text{C}-$), 129.26 (aromatic carbons ortho to $-\text{C}=\text{C}-$), 126.83 (aromatic carbons ortho to cyclohexyl), 120.92 (aromatic carbons para to cyclohexyl), 115.38 (aromatic carbons para to $-\text{O}-$ in $-\text{OArC}\equiv$), 114.49 (aromatic carbons ortho to $-\text{O}-$ in $-\text{OArC}\equiv$), 114.05 (aromatic carbons meta to $-\text{C}=\text{C}-$), 88.71 ($\equiv\text{CAr}$), 88.14 ($\text{OArC}\equiv$), 68.06 ($-\text{CH}_2\text{OArC}\equiv$), 67.78 ($-\text{C}=\text{CArOCH}_2$), 44.56 (carbon in cyclohexyl para to $-\text{CH}_2$), 37.36 ($-\text{CH}_2$ connected to cyclohexyl), 37.29, 34.16, 33.53, 32.84, 32.21, 29.53, 29.38, 29.36, 29.32, 29.20, 26.64, 26.05, 26.00, 22.70, 14.10 ($-\text{CH}_3$). HRMS (MALDI-TOF): Calcd. for $\text{C}_{174}\text{H}_{228}\text{O}_8$ $[(\text{M}+\text{H})^+]$: 2447.7546 Found: 2447.8457. Elemental analysis for $\text{C}_{174}\text{H}_{228}\text{O}_8$: Calcd C 85.38%, H 9.39% Found: C 84.97%, H 9.24%. UV/Vis (THF): λ_{max} (ϵ) = 295 nm ($1.34 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$), 313 nm ($1.13 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$).

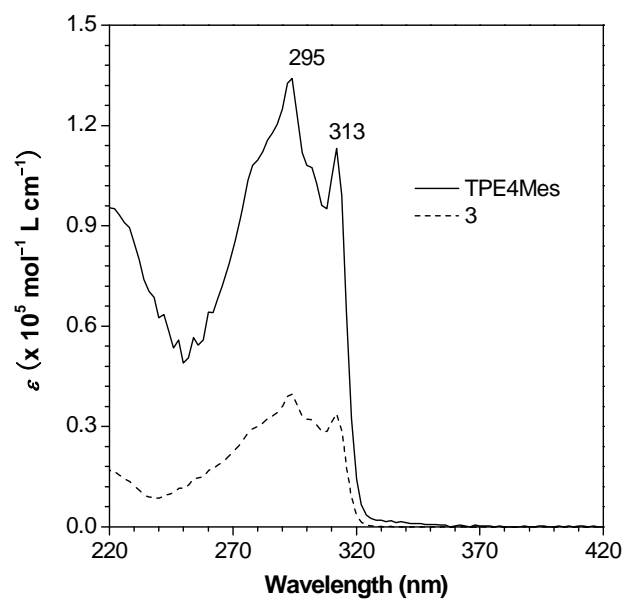


Fig. S1 Absorption spectra of TPE4Mes and compound **3** in THF. ϵ : molar absorptivity; concentration (μM): 4 (TPE4Mes), 20 (**3**).

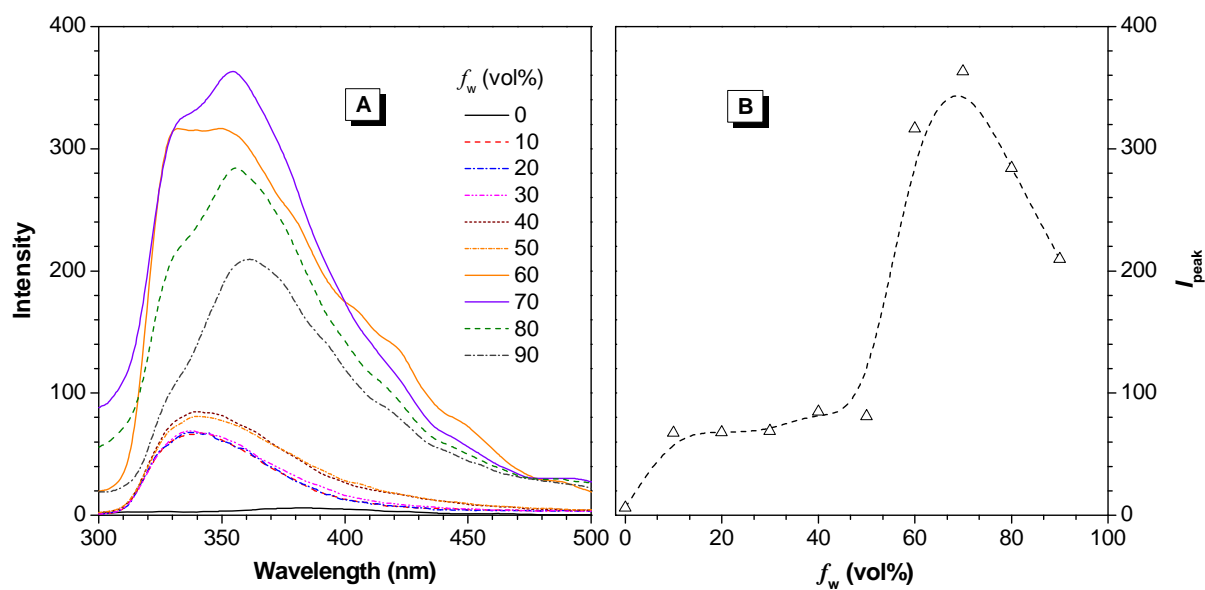


Fig. S2 (A) Emission spectra of **3** in THF and THF/water mixtures; (B) Plots of the emission maxima of **3** in THF and THF/water mixtures versus water fractions (f_w). Concentration = 20 μM . Excitation wavelength = 280 nm.

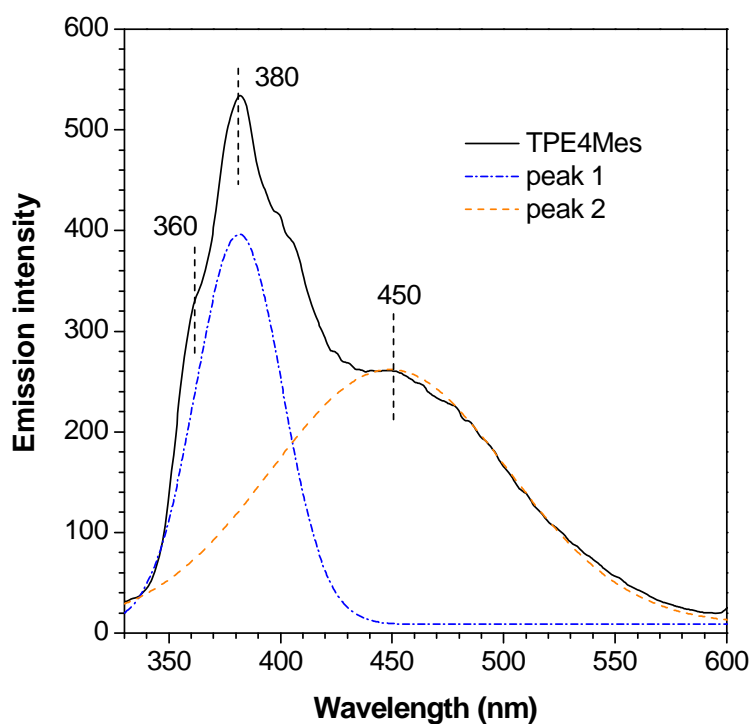


Fig. S3 Emission spectrum of TPE4Mes in 10/90 THF/water aqueous mixture and its fitted divisions with maxima at 380 (peak 1) and 450 nm (peak 2), respectively.

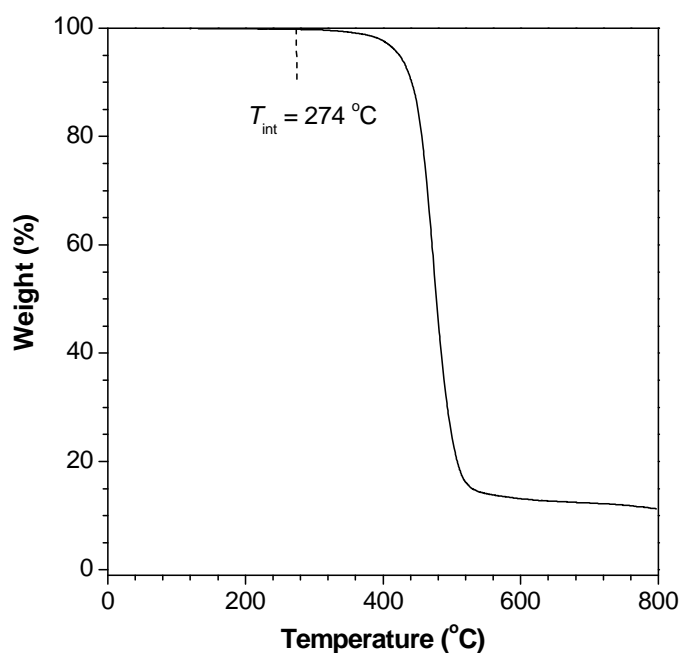


Fig. S4 TGA thermogram of TPE4Mes measured under nitrogen at a heating rate of 20 °C/min.

Table S1. 1D WAXD analysis data of TPE4Mes at varying temperatures

Temperature (°C)	d_1^a	d_2^a	d_3^a
200 ^b	—	1.74	0.50
155 ^c	4.44	2.23	0.47
100 ^c	4.53	2.26	0.45
30 ^c	4.53	2.26	0.43

^a d -spacing (in units of nm). ^b isotropic state. ^c mesomorphic state.

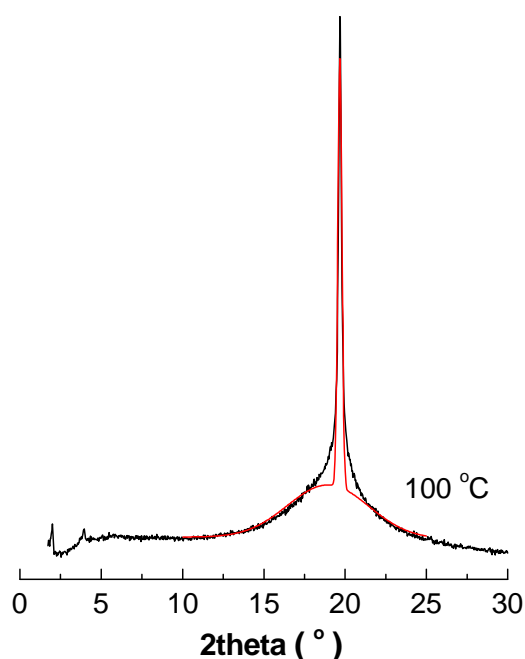


Fig. S5 Peak fitting of the XRD pattern for TPE4Mes recorded at 100 °C during the cooling process.

The sharp diffractions at high angular region imply the presence of a long-range order on the sub-nanometre scale in the low temperature phase, whose correlation length is ~33 nm as estimated from the peak width using Scherrer equation. The calculation detail is listed as bellow:

Scherrer equation:
$$L_{hkl} = \frac{k\lambda}{\beta \cos \theta}$$

where L_{hkl} is the correlation length perpendicular to (hkl), λ is the wavelength of the incident X-ray (0.1548 nm), and β is the full width at half maximum, k is a constant of 0.89.

$$L = \frac{0.89 \times 0.15418}{(19.805 - 19.560) \times 0.017453 \times \cos(19.70^\circ/2)} = 33(\text{nm})$$

In the denominator, 19.805 and 19.560 are the left and right 2θ values at half height of the diffraction peak, 19.70° is the 2θ peak value, and 0.017453 is the factor of exchanging angle into radian.

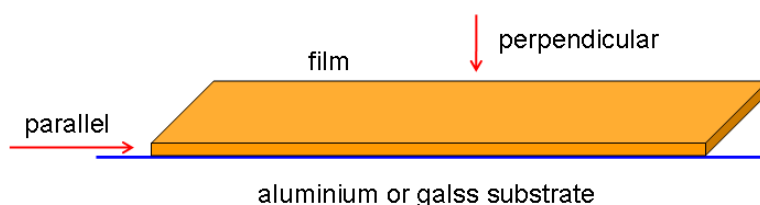


Fig. S6 Schematic illustration of the geometry adopted in 2D WAXD experiments with the X-ray incident beam perpendicular or parallel to the film.

References and Notes

- [1] (a) Kawamura, Y.; Sasabe, H.; Adachi, C. *Jpn. J. Appl. Phys.* **2004**, *43*, 7729. (b) Porrès, L.; Holland, A.; Pålsson, L.-O.; Monkman, A. P.; Kemp, C.; Beeby, A. *J. Fluoresc.* **2005**, *16*, 267.
- [2] It is reported that thermal annealing can be applied to align mono-domains of liquid crystals, particularly for discotic molecules to form face-on alignment. For examples, see: (a) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902. (b) Zhou, X. L.; Kang, S. W.; Kumar, S.; Kulkarni, R. R.; Cheng, S. Z. D.; Li, Q. *Chem. Mater.* **2008**, *20*, 3551. (c) Thiebaut, O.; Bock, H.; Grelet, E. *J. Am. Chem. Soc.* **2010**, *132*, 6886.