

Electronic Supplementary Information

Design, synthesis and properties of hemiphasmidic luminescent liquid crystal polymers with AIEE effect

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Materials

Anhydrous tetrahydrofuran (THF) was re-distilled under the nitrogen atmosphere by adding sodium tablets. Dichloromethane was dried over magnesium sulfate anhydrous. MnO₂ were placed in the muffle furnace and activated at 220 °C for 12 hours. All other reagents and solvents were used as received without further purification.

Instruments and Measurements

Nuclear magnetic resonance (NMR). ¹H/¹³C NMR measurements were performed using a Bruker ARX400 MHz spectrometer using CDCl₃ as solvents, with tetramethylsilane (TMS) as internal standard at ambient temperature.

Gel permeation chromatography (GPC). Apparent number average molecular weight (M_n) and polydispersity index ($PDI = M_w/M_n$) of all polymers were measured using a GPC (Waters 1515) with a set of HT3, HT4, HT5 columns. μ -styragel columns were employed with THF as eluent. The flow rate was set at 1.0 mL/min at 30 °C. The GPC data were calibrated with polystyrene standards.

Thermogravimetric analysis (TGA). TGA was performed using a TA SDT 2960 instrument at a heating rate of 20 °C/min in a nitrogen atmosphere.

Differential scanning calorimetry (DSC). DSC traces of all polymers were obtained using a TA-Q10 DSC instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc) at cooling and heating rates of 10 °C/min. Ca. 6 mg samples were encapsulated in sealed aluminum pans.

Polarizing optical microscopy (POM). LC textures and change in light intensity curve of all the polymers during the heating and cooling process were examined by POM (Leica DM-LM-P) equipped with a Mettler Toledo hot stage (FP82HT). The change in

light intensity curve was recorded by Linksys 32.

One-dimensional wide-angle X-ray diffraction (1D WAXD). 1D WAXD experiments were performed using a Bruker AXS D8 Advance diffractometer with a 40 KV FL tubes as the X-ray source (Cu K α) and a LYNXEYE_XE detector. The heating and cooling rates in the 1D WAXD experiments were 10 °C/min.

Small-angle X-ray Scattering. Small-angle X-ray scattering experiments were performed using a high-flux X-ray instrument (SAXSess mc², Anton Paar) equipped with Kratky block collimation system and a GE ID3003 sealed-tube X-ray generator (Cu K α). The wavelength is 0.1542 nm. Samples were wrapped into aluminum foils and sandwiched in a steel sample holder. The X-ray scattering patterns were recorded in vacuum on an imaging-plate (IP) which extended to high-angle range (the q range covered from 0.06 to 10 nm⁻¹, $q = 4\pi(\sin \theta)/\lambda$, where the λ is the wavelength of 0.1542 nm and 2θ is the scattering angle). The scattering peak positions were calibrated with silver behenate.

UV-vis Absorption Spectroscopy: The UV-vis spectra were collected on Agilent spectrum Carry 100 spectrophotomete.

Fluorescence Spectroscopy: Fluorescence spectra were collected on a F-4600 fluorescence spectrometer (HITACH), the excitation wavelength are 350 nm (P2-m), 360 nm (P1-m) and 370 nm (P3-m), respectively.

Fluorescence Quantum Yield: Fluorescence quantum yields were obtained on a FLS980 fluorescence spectrometer (Edinburgh Instrument) equipped with integrating sphere.

Synthesis of the monomers and polymers

Synthesis of 3,4,5-tris(octyloxy)benzaldehyde (3,4,5-tris (octyloxy)phenyl)methanol was reported elsewhere[x] and the other experimental details are described as follows. (3,4,5-tris(octyloxy)phenyl)methanol(30.00g, 60.98 mmol), activated MnO₂ (102.44 g, 1219.51 mmol) and CH₂Cl₂ (300 mL) were charged in a 500 mL round-bottomed flask and stirred at 42 °C. The mixture was heated at 40 °C for 12 h, then the mixture was filtered to remove the MnO₂ and the solvent was evaporated under reduced pressure to get crude product. The product was purified using silica gel column chromatography with CH₂Cl₂ as eluent and the resultant product was a pale yellow liquid with a yield of 80%. ¹H NMR (δ , ppm, CDCl₃): 9.98-9.72 (s, -CHO, 1H), 7.07 (s, Ar-H 2H), 4.03 (m, -CH₂OPh, 6H), 1.94-1.68 (m, -CH₂CH₂OPh 6H), 1.57-1.17 (m, -(CH₂)₅CH₃, 30H), 0.87 (t, -CH₃, 9H).

Synthesis of (Z)-2-(4-hydroxyphenyl)-3-(3,4,5-tris(octyloxy)phenyl) acrylonitrile The mixture of 2-

(4-hydroxyphenyl)acetonitrile (5.54 g, 41.65 mmol), potassium tert-butoxide (9.72 g, 86.77 mmol) and 300 mL tert-Butanol were charged in a 500 mL three-necked flask. The mixture was refluxed for 0.5h. Subsequently, 3,4,5-tris(octyloxy)benzaldehyde (17.01g, 34.71 mmol) was dissolved in 75 mL of tert-Butanol and added dropwise to the above three-necked flask. After the drop is finished, the mixture should continue to stir the 12h at the refluxed temperature. Then the reaction mixture was filtered and the solvent was evaporated under reduced pressure. Afterward, the crude product was extracted with ethyl acetate and hydrochloric acid aqueous solution three times. Combining the organic layer and drying by MgSO₄ for about 1h. Ethyl acetate was distilled off by evaporation under reduced pressure, and the product was further purified using silica gel column chromatography with CH₂Cl₂, petroleum ether and ethyl acetate (v : v : v = 10 : 10 : 1) as eluent, condensed eluent to get resultant product as a yellow solid with a yield of 58%. ¹H NMR (δ, ppm, CDCl₃): 7.53 (d, Ar-**H**, 2H), 7.27 (s, **CH**=CCN, 1H), 7.13 (s, Ar-**H**, 2H), 6.88 (d, Ar-**H**, 2H), 5.18 (s, -**OH**, 1H), 4.02 (t, -**CH**₂OPh, 6H), 1.98-1.67 (m, -**CH**₂CH₂OPh, 6H), 1.42-1.16(m, -(**CH**₂)₄CH₃, 24H), 0.87 (t, -**CH**₃, 9H).

Synthesis of (Z)-4-(1-cyano-2-(3,4,5-tris(octyloxy)phenyl)vinyl)phenyl methacrylate(MTCN-8)
 (Z)-2-(4-hydroxyphenyl)-3-(3,4,5-tris(octyloxy) phenyl) acrylonitrile (5.00 g, 8.26 mmol), triethylamine (4.17g, 41.30 mmol) and 100 mL dried THF were charged in a 250 mL round-bottomed flask and stirred at 0 °C. Subsequently, methacryloyl chloride (2.58 g, 24.78 mmol) was dissolved in 50 mL of THF and added dropwise to the above round bottom flask. After the drop is finished, the mixture should continue to stir for 2h at room temperature. Then the reaction mixture was filtered and the solvent was evaporated under reduced pressure. Afterward, the crude product was extracted with ethyl acetate. The extracts were dried over anhydrous MgSO₄, and condensed to remove the solvent. Finally, the product was purified using silica gel column chromatography with petroleum ether and ethyl acetate (v : v = 10 : 1) as eluent, condensed eluent to get resultant product as a yellow solid with a yield of 75%. ¹H NMR (δ, ppm, CDCl₃): 7.68 (d, Ar-**H**, 2H), 7.39 (s, -**CH**=CCN, 1H), 7.20 (d, Ar-**H**, 2H), 7.15 (s, Ar-**H**, 2H), 6.36 (s, -**CH**=C, 1H), 5.80 (s, **CH**=C, 1H), 4.04 (t, -**CH**₂OPh, 6H), 2.07 (d, CH₂=C**CH**₃, 3H), 1.92-1.66 (m, -**CH**₂CH₂OPh, 6H), 1.55-1.44 (m, -**CH**₂CH₂CH₂OPh, 6H), 1.14-1.39 (m, -(**CH**₂)₄CH₃, 24H), 0.89 (t, -**CH**₃, 9H). ¹³C NMR (CDCl₃, δ, ppm, TMS): 14.18 (-CH₂CH₃), 18.33 (-C(CH₃)=CH₂), 22.73 (-CH₂CH₃), 26.15 (-CH₂CH₂CH₂O-Ph), 29.39 (-CH₂CH₂CH₂CH₃ and -CH₂CH₂CH₂CH₂CH₃), 30.44 (-CH₂CH₂O-Ph), 31.97 (-CH₂CH₂CH₃), 69.09 (-CH₂O-Ph), 73.54 (-CH₂O-Ph), 107.86 (-C-CN), 108.61 (aromatic C), 118.29 (-CN), 122.21 (aromatic C), 126.86 (aromatic C), 127.58 (-C(CH₃)=CH₂), 128.51 (-C(CH₃)=CH₂), 132.20 (aromatic C-C-CN), 135.63 (-C(CH₃)=CH₂), 140.48 (aromatic C-O), 142.51 (-CH=C(CN)-Ph), 151.35 (aromatic C-O-CO), 153.13 (aromatic C-O),

165.41(aromatic C-O). Mass spectrometry (MS) (m/z) [M] calcd for C₄₃H₆₃NO₅,673.47; found, 672.64

Preparation of poly {1,4-bis-(α -cyano-4-tetradecanoyloxy) styrene } (PMTCN-8). Free radical solution polymerization carrying 2-azobisisobutyronitrile (AIBN) as the initiator was employed to prepare the target polymers. A typical polymerization procedure is summarized as the following. 1 g (1.49 mmol) of MTCN-8, 122.18 μ L of chlorobenzene solution of 0.02 g/mL AIBN, 1.69 mL dry THF and a magnetic stir bar were transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed off under vacuum. The polymerization reaction was carried out in an oil bath at 75 °C for about 12h. It was stopped by dipping the tube in ice/water, and the tube was broken. Subsequently, 6 mL of THF were added to the polymerization tube in order to dissolve the polymer, then the solution was slowly dropped into a solvent mixture composed of THF and CH₃OH (v : v = 3 : 1) to precipitate the polymer. The precipitation process would repeat for the 3 times until no peak was observed at the elution time of the monomer in gel permeation chromatography (GPC). Yield : 62%.

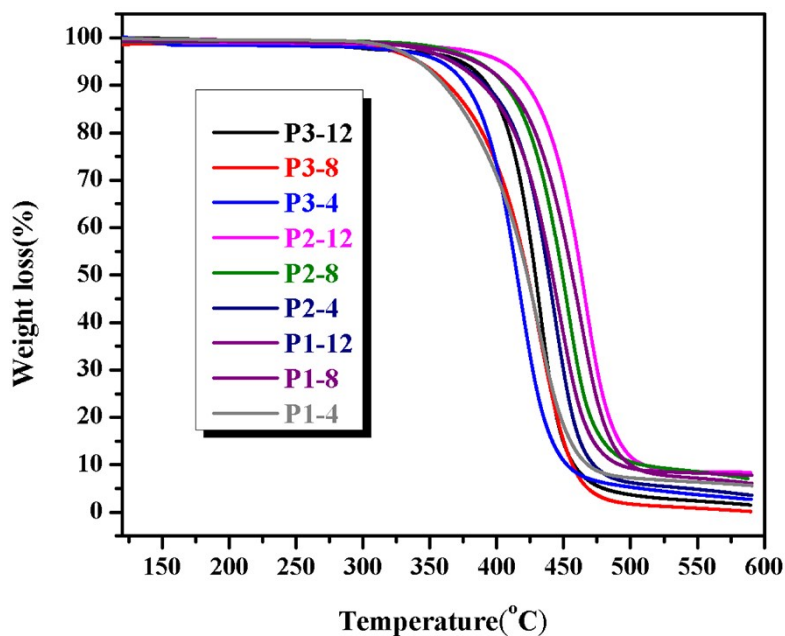


Fig. S1 The TGA diagrams of polymers in N₂ at a rate of 20 °C/min.

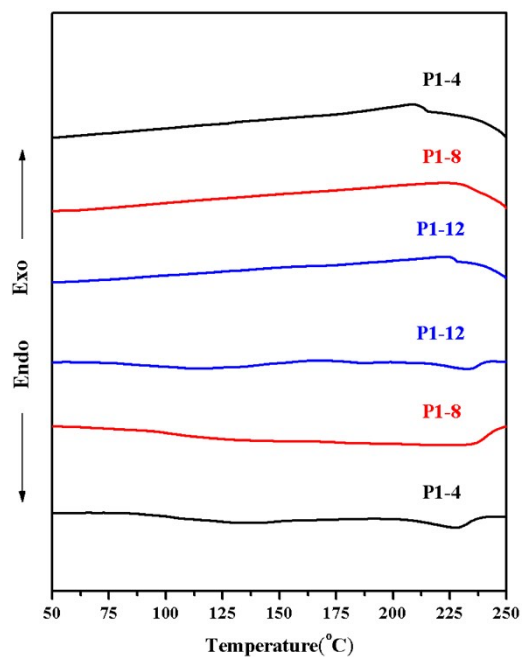


Fig. S2 Differential scanning calorimetry thermograms of P1-m at a rate of 10 °C /min during the first cooling and second heating process.

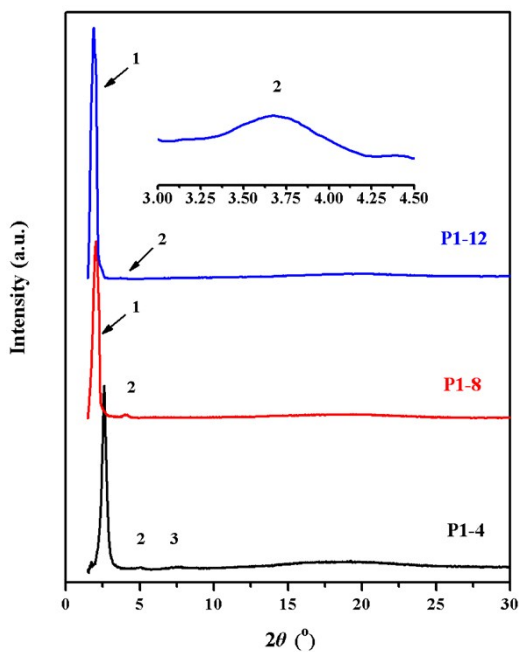


Fig. S3 1D WAXD patterns of P1-m at 30 °C.

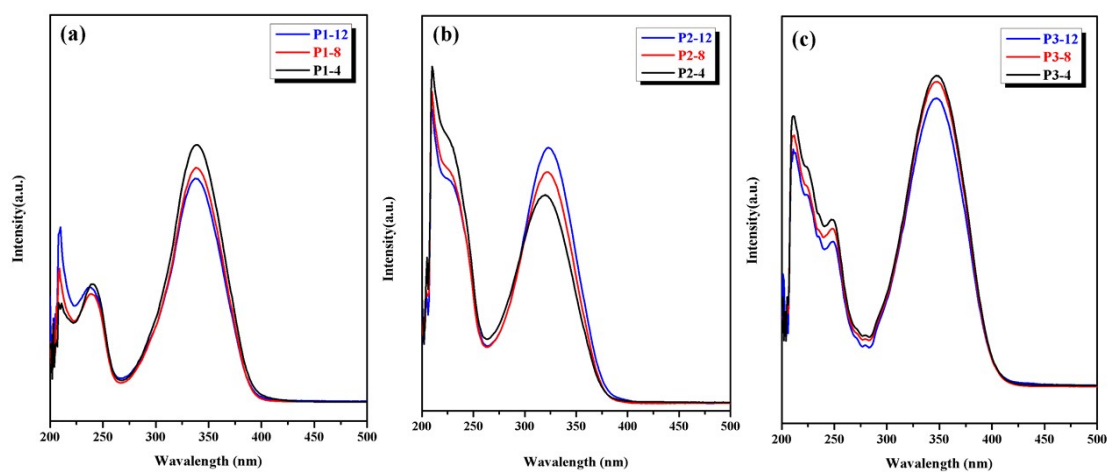
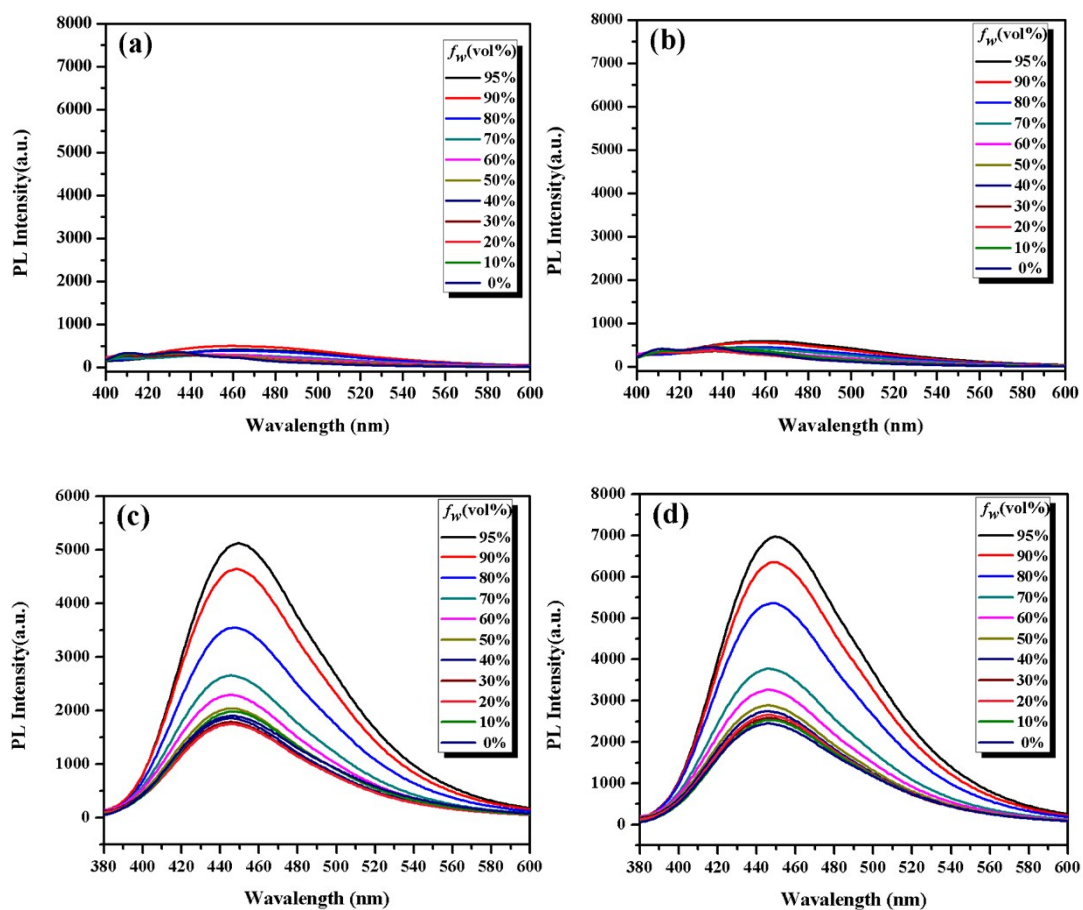


Fig. S4 UV spectra of (a) P1-m, (b) P2-m and (c) P3-m in THF solution



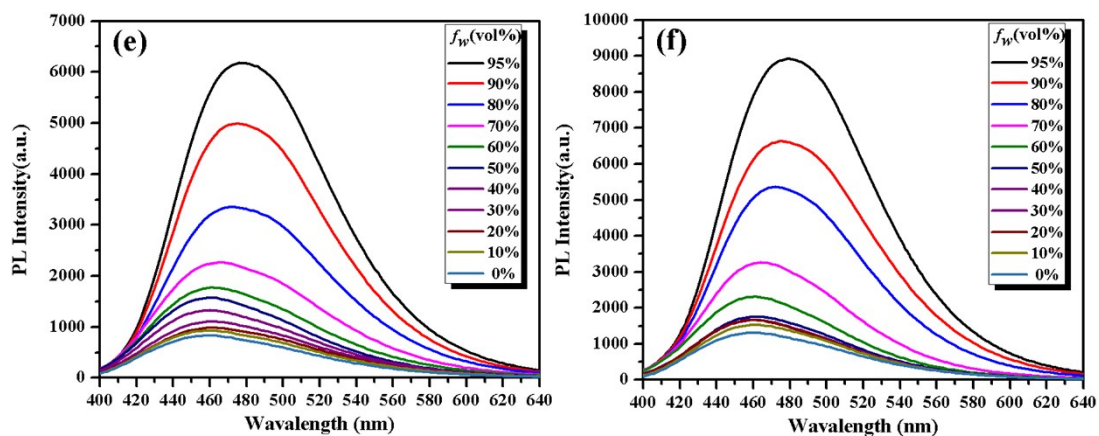


Fig. S5 FL Emission spectra of (a) P1-4, (b) P1-12, (c) P2-4, (d) P2-12, (e) P3-4 and (f) P3-12 in THF/water with varied water content.