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Fluorescent solvent-free lignin ionic complexes with thermostability toward to luminescent hydrophobic coating material

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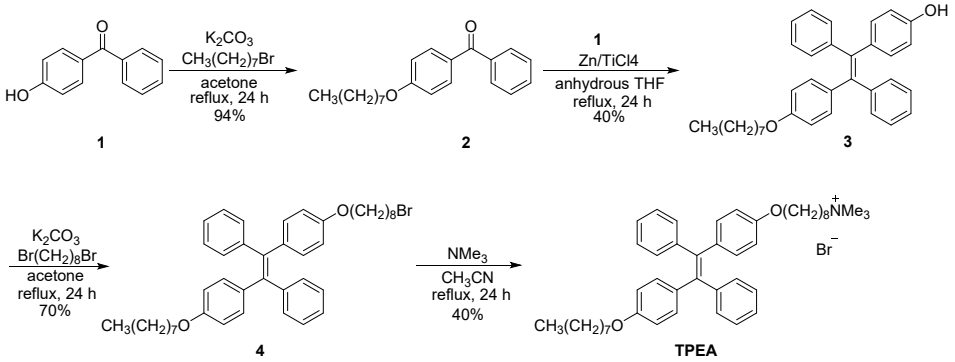
1. General remarks

Meterials: sodium ligninsulfonate (LS-Na) used for the preparation of lignin complexes was purchased from Saihan Tech. (Shanghai) Co., Ltd., with the chemical formula: $[C_{20}H_{24}Na_2O_{10}S_2]_n$, which equals to 2 negative charges per 534.51 g/mol. All the chemicals used for the synthesis of TPEA were purchased and used directly. All the aqueous solutions were prepared using ultrapure water through a Millipore Milli-Q 185 water purification system (Millipore, USA).

Characterizations of TPEA and LS-TPEA: ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker Avance 500 (500 and 125 MHz, respectively) or Bruker Avance 400 (400 and 100 MHz, respectively) with $CDCl_3$ as solvent. Chemical shifts were determined relative to the residual solvent peaks ($CHCl_3$, δ = 7.26 ppm for ^{1}H NMR, δ = 77.0 ppm for ^{13}C-NMR). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Mass spectra were recorded on a Thermo Scientific LTQ Orbitrap XL machine. TGA was carried out using a Netzsch STA 449C thermal analyzer in a nitrogen atmosphere and with a heating/cooling rate of 10 ^oC min^{-1}. DSC was performed by a Netzsch DSC204F1 machine with a heating rate of 5 ^oC min^{-1}. POM was conducted on a Nikon ECLIPSE LV100NPOL machine with a computational controlled heating plate. SAXS was performed by employing a conventional X-ray source with radiation wavelength of λ = 1.54 Å. The sample holder is a metal plate with a small hole (diameter ≈ 0. 5 cm, thickness ≈ 0. 5 cm), where the X-ray beam passes through and the sample-to-detector distance was 18 cm. The scattering vector q is defined as $q = 4\pi \sin\theta/\lambda$ with 2θ being the scattering angle. Fluorescence spectra were recorded by using an F-4600 fluorescence spectrophotometer from Hitachi, Japan. PL quantum yields and lifetimes were measured by using FLS1000 from Edinburgh Instruments, UK. The excitation source is 365 nm UV light. All spectral scans were saved as ACS II files and further processed in OriginLab software to produce all graphs shown.

2. Synthesis of surfactant TPEA and LS-TPEA ionic complexes



Scheme S1. Synthesis of TPEA.

(4-(octyloxy)phenyl)(phenyl)methanone (2)[1]: to a solution of **1** (1.00 g, 5.04 mmol) in acetone (25 mL) were added the 1-bromooctane (0.83 mL, 5.5 mmol) and K_2CO_3 (2.07 g, 15.00 mmol), and the resulting mixture was refluxed over 24 h. After cooling to room temperature, the solid of mixture was filtered off, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5 : 1) to afford **2** (1.46 g, 94% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d，J = 8.0 Hz, 2 H)，7.75 (d，J = 7.5 Hz, 2 H)，7.56 (t，J = 7.0 Hz, 1 H)，7.47 (t，J = 7.5 Hz, 2 H)，6.95 (d，J = 8.5 Hz, 2 H），4.03 (t，J = 6.0 Hz, 2 H)，1.84-1.79 (m，2H)，1.48-1.44 (m，2H)，1.35-1.30 (m，8H)，0.89-0.88 (m，3H).

4-(2-(4-(octyloxy)phenyl)-1,2-diphenylvinyl)phenol (3)[2]: to a solution of **2** (1.25 g, 4.00 mmol), **1** (0.80 g, 4.00 mmol) and Zn (1.31 g, 20.00 mmol) in anhydrous tetrahydrofuran (30 mL) were added $TiCl_4$ (1.32 mL, 13.00 mmol) slowly, and the resulting mixture was refluxed over 24 h. After cooling to room temperature, the reaction mixture was quenched by ice-water, which was adjusted to pH 7 with saturated Na_2CO_3 (aq). The obtained mixture was extracted with CH_2Cl_2, and the combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 3 : 2) to afford **3** (0.76 g, 40% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13-7.08 (m，10 H)，6.94-6.86 (m，4 H)，6.66-6.54 (m，4 H)，3.90-3.85（m，2 H），1.78-1.70 (m，2 H)，1.45-1.39 (m，2 H)，1.32-1.26 (m, 8 H)，0.90-0.88 (m，3 H).

(1-(4-((8-bromooctyl)oxy)phenyl)-2-(4-(octyloxy)phenyl)ethene-1,2-diyl)dibenzene (4): to a solution of **3** (487 mg, 1.00 mmol) in acetone (25 mL) were added the 1,8-dibromooctane (0.20 mL, 1.27 mmol) and K_2CO_3 (406 mg, 3.00 mmol), and the resulting mixture was refluxed over 24

h. After cooling to room temperature, the solid of mixture was filtered off, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 9 : 1) to afford **4** (466 mg, 70% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14-7.02 (m, 10 H)，6.94(dd，J_1 = 19.5, J_2 = 8.5 Hz, 4 H)，6.64 (dd，J_1 = 16.5, J_2 = 8.5 Hz, 4 H)，3.91-3.86 (m，4H)，3.42 (td, J_1 = 8.5, J_2 = 2.0 Hz, 1 H)，3.21 (td, J_1 = 8.5, J_2 = 2.0 Hz, 1 H)，1.89-1.81 (m, 2H)，1.79-1.72 (m, 4 H), 1.46-1.31 (m, 18H)，0.92-0.89 (m，3H).

***N,N,N*-trimethyl-8-(4-(2-(4-(octyloxy)phenyl)-1,2-diphenylvinyl)phenoxy)octan-1-aminium bromide (TPEA):** to a solution of **4** (168 mg, 0.25 mmol) in CH_3CN (15 mL) was added trimethylamine (4.2 M in ethanol, 0.10 mL). After being stirred under reflux overnight, the mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (MeOH/EtOAc = 1 : 1) to afford TPEA (74 mg, 40% yield) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-6.98 (m, 10 H)，6.92-6.86 (m, 4 H)，6.62-6.59 (m, 4 H), 3.86-3.84 (m, 4 H)，3.53-3.52 (m, 2 H)，3.43 (s, 9 H)，1.71 (t, J = 8.5 Hz, 6 H)，1.36-1.26 (m, 18 H)，0.88-0.85(m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$), δ 157.6, 157.5, 144.4, 139.7, 139.6, 136.34, 136.25, 132.53, 131.46, 129.4, 128.5, 128.2, 127.7, 127.6, 126.2, 114.2, 113.68, 113.66, 113.57, 67.9, 67.7, 67.0, 53.7, 31.9, 29.8, 29.44, 29.38, 29.29, 29.24, 26.22, 26.13, 26.05, 23.24, 22.71, 14.19; HRMS (ESI) calcd. for $C_{45}H_{60}NO_2$ $[M - Br]^+$ 646.4619, found 646.4612.

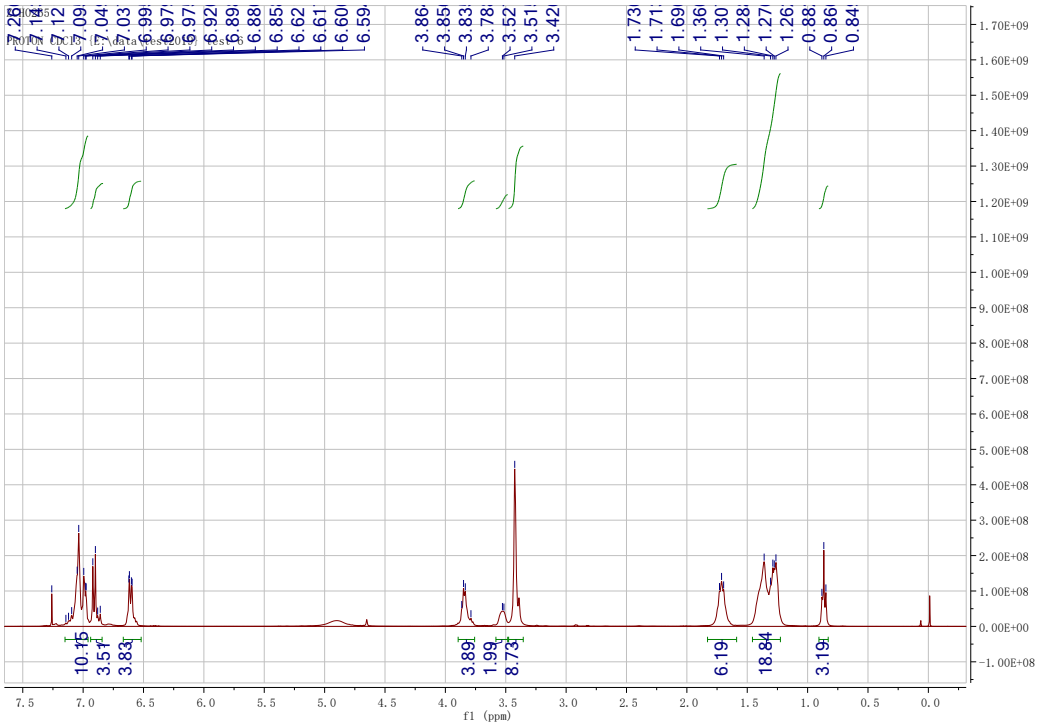


Figure S1. ^{1}H NMR of TPEA.

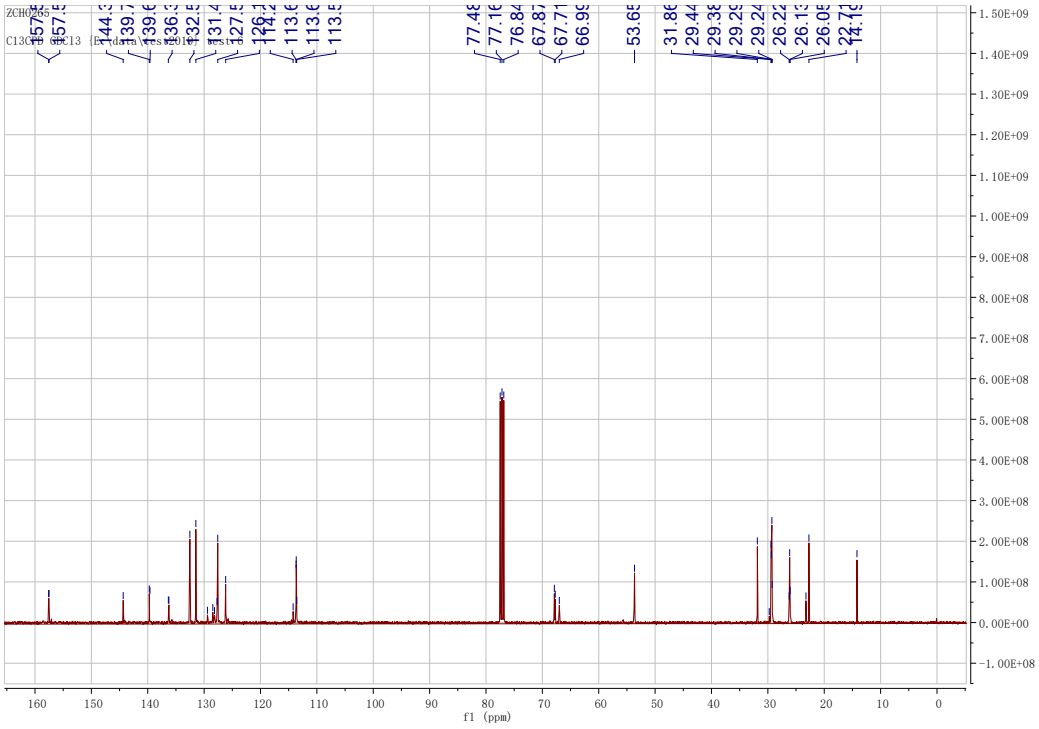


Figure S2. ^{13}C NMR of TPEA.

3. Synthesis of LS-TPEA complexes

The aqueous solution of TPEA was added into the aqueous LS-Na solution using a pipette with the needed stoichiometric charge ratio, which led to the precipitate of LS-TPEA complex. The precipitate was purified by washing-centrifugation-water removing over three times and lyophilization to afford the solvent-free LS-TPEA complex.

4. Characterizations of surfactant TPEA and LS-TPEA complexes

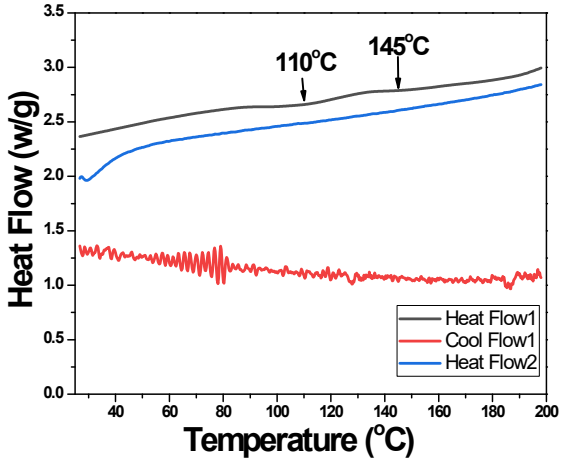


Figure S3. DSC profiles of TPEA, indicating the gradually slow phase change processes in both heating and cooling conditions. Heating/cooling rate: 5 °C/min.

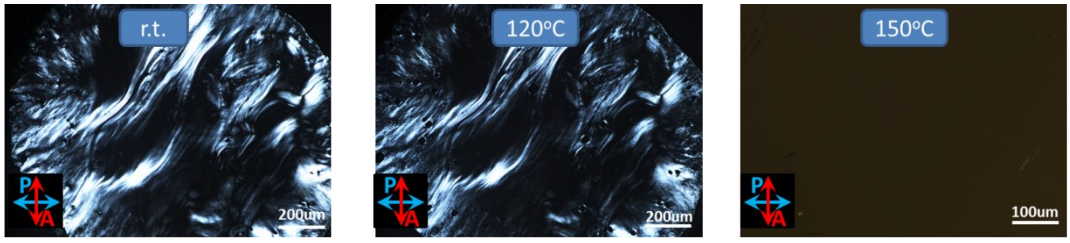


Figure S4. Temperature-dependent POM analysis on TPEA, indicating the thermotropic liquid crystal property of TPEA.

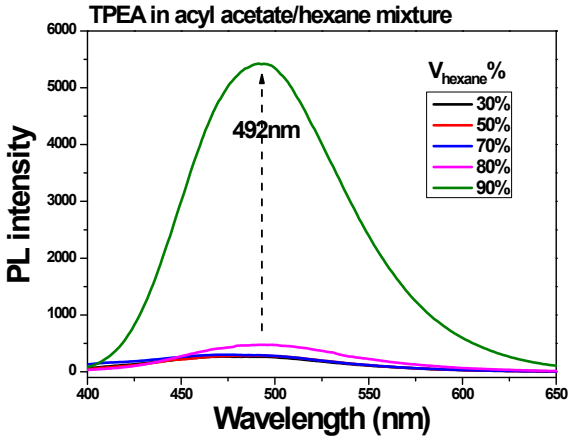


Figure S5. Fluorescence spectra of TPEA (4.50 mM) in ethyl acetate/hexane mixture with different volume fractions of hexane ranging from 30% to 90%. λ_{ex} = 365 nm. TPEA could only give very weak fluorescent emission when the volume fraction of hexane is lower than 80%. Upon increasing the volume fraction of hexane up to 90%, a significant enhanced fluorescent emission is observed.

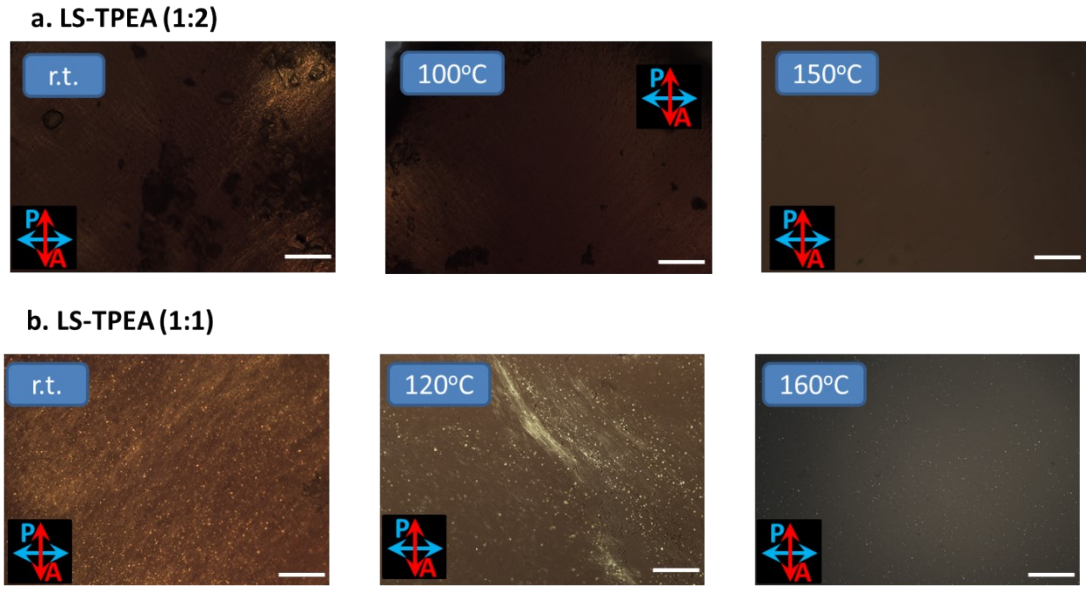


Figure S6. Temperature-dependent POM analyses on the phase changes of a) LS-TPEA (1:2) and b) LS-TPEA (1:1). Scale bar: 50 μm. Upon heating condition, LS-TPEA (1:2) and LS-TPEA (1:1) exhibit thermotrpic liquid crystal property by disappearing the birefringent textures. In this test, these two samples did not give distinct difference on thermal property.

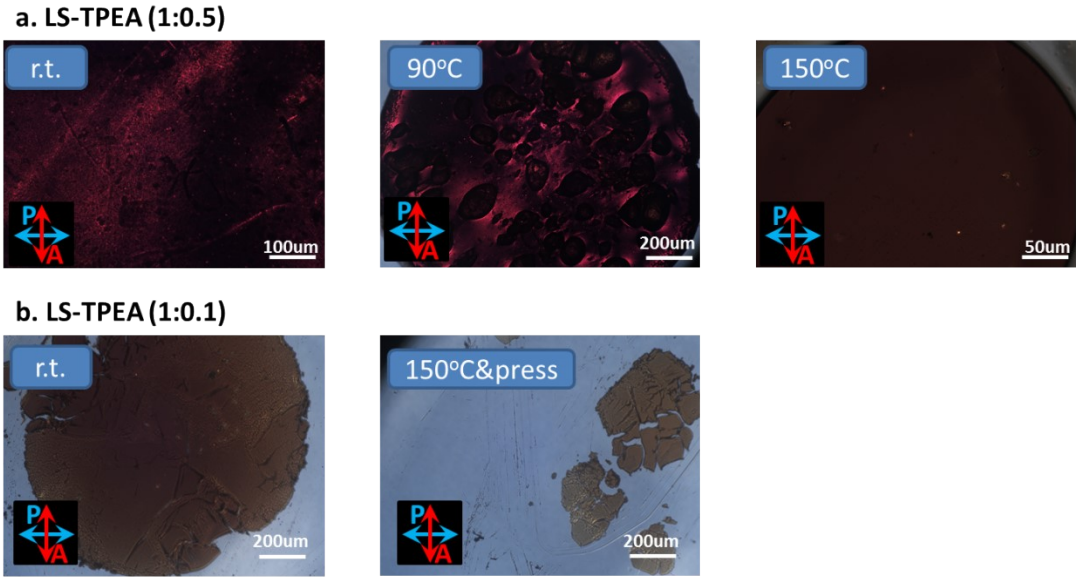


Figure S7. Temperature-dependent POM analyses on the phase changes of a) LS-TPEA (1:0.5) and b) LS-TPEA (1:0.1). Upon heating, LS-TPEA (1:0.5) could exhibit thermotropic liquid crystal property, while, LS-TPEA (1:0.1) could not. LS-TPEA (1:0.1) is a brittle material either at room temperature or at high temperature.

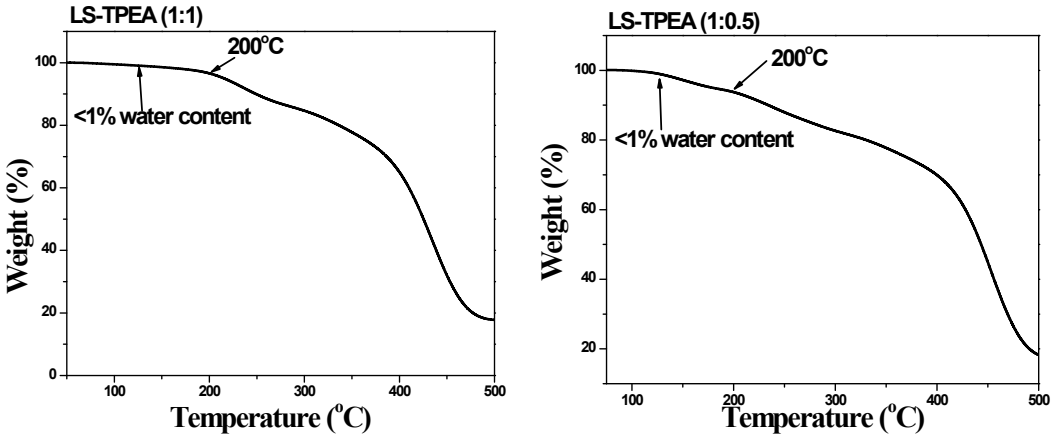


Figure S8. TGA profiles of LS-TPEA (1:1) and LS-TPEA (1:0.5), indicating the water contents less than 1% and thermal integrities up to ~200°C.

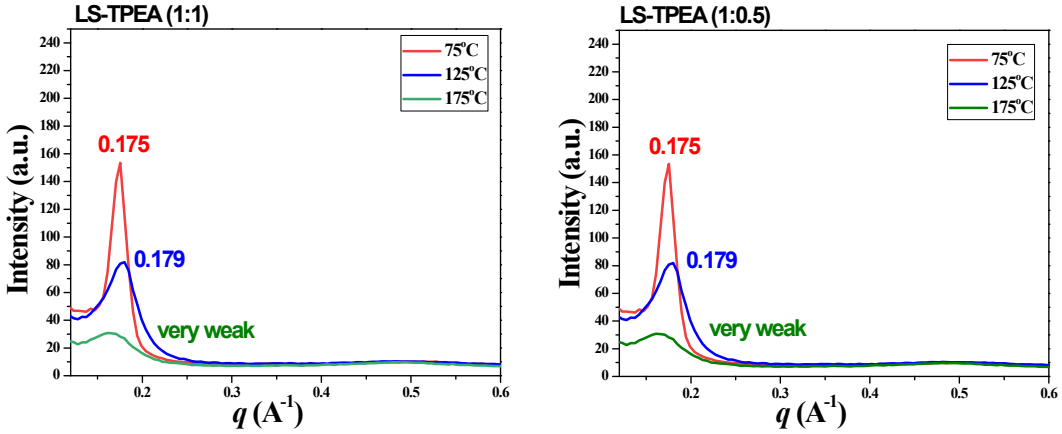


Figure S9. Temperature-dependent SAXS analyses on LS-TPEA (1:1) and LS-TPEA (1:0.5), indicating the slow phase changes from ordered state to isotropic liquid by showing decreased diffraction peaks upon heating condition.

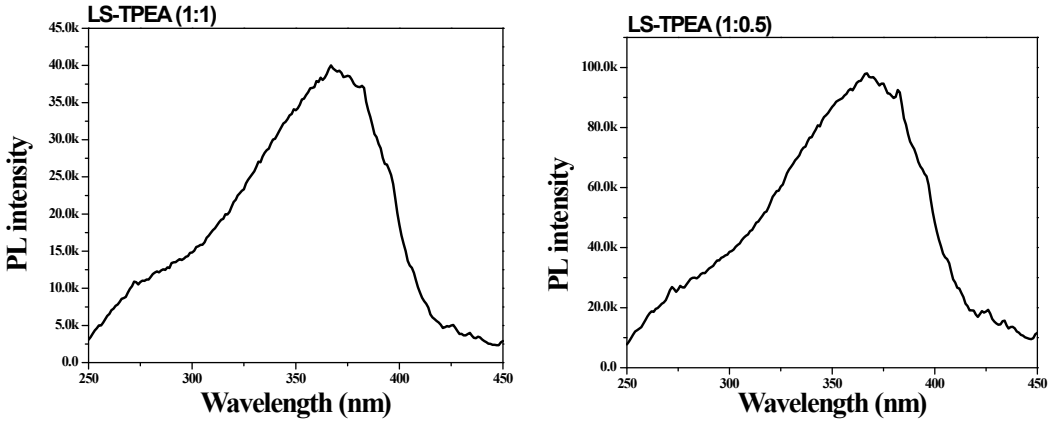


Figure S10. The excitation spectra of solvent-free LS-TPEA (1:1) and LS-TPEA (1:0.5), indicating the commonly used UV light is an effective excitation source for the fluorescent emission of LS-TPEA complexes.

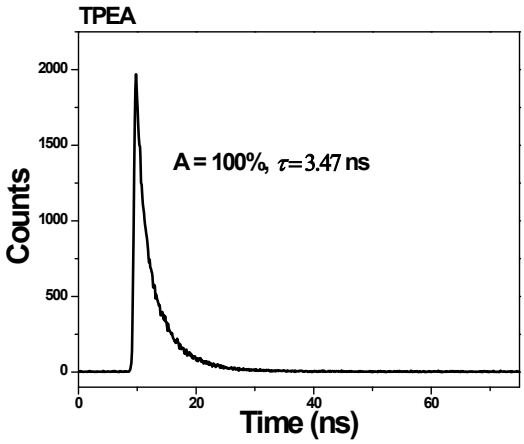


Figure S11. Fluorescence decay of solid-state TPEA, fitting to the single-exponential function as $I = Ae^{-t/\tau 1}$, which means TPEA molecules are in same environment.

References

[1] M.P. Aldred, C. Li, M.-Q. Zhu, Optical Properties and Photo-Oxidation of Tetraphenylethene-Based Fluorophores, Chemistry – A European Journal, 18 (2012) 16037-16045.

[2] W. Guan, W. Zhou, C. Lu, B.Z. Tang, Synthesis and Design of Aggregation-Induced Emission Surfactants: Direct Observation of Micelle Transitions and Microemulsion Droplets, Angewandte Chemie International Edition, 54 (2015) 15160-15164.