

Supporting Information

Design, Synthesis and Ordering Enhanced Emission of Luminescent Liquid Crystalline Polymers based on “Jacketing” Effect

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Materials. 1-Bromo-*n*-butane, 4-bromobenzophenone, 4,4'-dihydroxybenzophenone, zinc powder, titanium tetrachloride, benzoic acid pinacol ester, potassium acetate, bis(triphenylphosphine) palladium dichloride, tetra(triphenylphosphine), palladium methyl trioctyl ammonium chloride and trichloromethane were purchased from Energy Chemical and directly used. THF was refluxed over sodium and distilled before use. Potassium carbonate, acetone, potassium iodide, 1,4-epoxycyclohexane, toluene, dichloromethane, ethyl acetate, and petroleum ether were purchased from Guangdong

Guanghua Sci-Tech Co, Ltd., and were used directly. 3-bromostyrene and 3,5-dibromostyrene were synthesized according the previous work.

Instruments and Measurements. ^1H NMR and ^{13}C NMR experiments were operated by a Bruker ARX400 spectrometer, where deuterated chloroform (CDCl_3) was employed as the solvent and tetramethylsilane (TMS) as the internal standard. Mass spectral was carried out on Autoflex III. A GPC (Waters GPC1515) experiment was executed to determine the apparent number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n), where THF was utilized as the eluent and the linear polystyrene as standard was used to calibrate the standard curve.

UV–vis absorption spectra were recorded on a Cary 100 using the Flashing xenon lamp as the light source. Emission spectra were measured on a spectrofluorometer QM40 in the right-angle geometry with 1 cm quartz cuvettes. The wavelength of the excitation light fixed was $\lambda_{\text{ex}} = 350$ nm, and the slit width of 5 nm was used for both monochromators. The quantum yields ($\Phi_{\text{F's}}$) in the solid state were determined by using an integrating sphere on a NanologR FluoroLog-3-2-iHR320 infrared fluorescence spectroscopy equipped with R928 photo-multiplier as detector.

Thermogravimetric analysis (TGA) was carried out on a TA SDT2960 instrument under a nitrogen atmosphere at a heating rate of 20 °C/min. DSC experiment was performed on a TA DSC Q100 calorimeter with a programmed heating procedure in nitrogen. The LC texture of the samples was investigated under PLM (Leica DM-LM-P), which was equipped with a Mettler FP82HT hot stage. 1D-WAXD powder curves

were recorded on a Bruker D8 advance diffraction equipped with a temperature control unit (Paar Physica TCU 100). In WAXD experiment, the sample was set horizontally on the stage and the silver behenate ($2\theta < 10^\circ$) was used to calibrate the reflection peak position.

Synthesis of 4''-bromo-4,4'-dihydroxytetraphenylethylene. A mixture of 4,4'-dihydroxybenzophenone (10.0 g, 0.047 mol), 4-bromobenzophenone (13.4 g, 0.051 mol) and zinc powder (12.8 g, 0.197 mol) was added to a three-necked flask. Subsequently, the flask was evacuated under vacuum and flushed with N₂ for three times. Then, the purified THF (350 mL) was injected by a syringe and the reaction mixture was stirred at 0 °C for 0.5 h under an atmosphere of N₂. TiCl₄ (19.5 g, 0.103 mol) was then slowly added into the reaction mixture and these starting materials were stirred in salt-ice bath conditions for another 0.5 h. Then the intermediate reaction was allowed to react at room temperature for 1 h. Finally, it was placed and kept stirring in an oil bath for 12 h. When the reaction mixture was cooled to 25 °C, 10% aqueous K₂CO₃ solution was added into the reaction system to precipitate. After filtration, THF was evaporated and the mixture was then extracted three times with ethyl acetate. The crude product was dried over anhydrous MgSO₄ and then the product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 4:1). Yield: 60%. ¹H NMR (DMSO-*d*₆) δ (ppm): 9.68 (s, 2H, -OH), 7.2 (d, 2 H, Ar-H), 7 (d, 7 H, Ar-H), 6.85 (m, 4 H, Ar-H), 6.55 (m, 4 H, Ar-H).

Synthesis of 4''-bromo-4,4'-dibutyloxytetraphenylethylene. A mixture of 4''-bromo-4,4'-dihydroxytetraphenylethylene (1.5 g, 3.4 mmol), 1-bromo-butane (1.9 g, 13.6 mmol), K₂CO₃ (1.9 g, 33.3 mmol), KI (0.1 g, 0.6 mmol) and acetone (200 mL) was added to a one-necked flask. The mixture was then stirred in an oil bath at 68 °C for 12 h to afford the crude product. The crude product was filtered to remove the insoluble white solid. The filtrate was dried and purified by column chromatography on silica gel using dichloromethane: petroleum ether = 1:3 (v/v) as eluent. Yield: 95%. ¹H NMR (CDCl₃) δ (ppm): 7.22 (d, 2 H, Ar-H), 7.00 (d, 7 H, Ar-H), 6.88 (m, 4 H, Ar-H), 6.63 (m, 4 H, Ar-H), 3.89(m, 4 H, -OCH₂-), 1.73 (s, 4 H, -CH₂-), 1.46 (s, 4 H, -CH-), 0.98 (s, 6 H, -CH₃).

Synthesis of 4',4''-dibutyloxy-tetraphenylethylene-4-borate. A mixture of 4''-bromo-4,4'-dibutyloxytetraphenylethylene (2.0 g, 3.60 mmol), boronic acid pinacol ester (1.3 g, 5.10 mmol), Bis(triphenylphosphine)palladium dichloride (0.1 g, 0.14 mmol), and potassium acetate (1.06 g, 10.80 mmol) was added into a 250 mL three-necked flask. The mixture was evacuated firstly and then bubbled through N₂ for three consecutive times. Then 1,4-epoxycyclohexane (60 mL) was injected into the mixture as the reaction solvent, and the flask was stirred in an oil bath at 85 °C for 24 h. Afterward, the crude product was extracted for three times using DCM/H₂O (v/v = 1:2), dried over anhydrous MgSO₄, and then purified by column chromatography on silica gel (petroleum ether/DCM = 4:1).Yield:85%.¹H NMR (CDCl₃)δ(ppm): 7.22 (d, 2 H, Ar-H), 7.00 (d, 7 H, Ar-H), 6.88 (m, 4 H, Ar-H), 6.63 (m, 4 H, Ar-H), 3.89 (m, 4 H, -

OCH₂-), 1.73 (s, 4 H, -CH₂-), 1.46 (s, 4 H, -CH₂-), 1.32 (s, 12 H, -CH₃), 0.98 (s, 6 H, -CH₃).

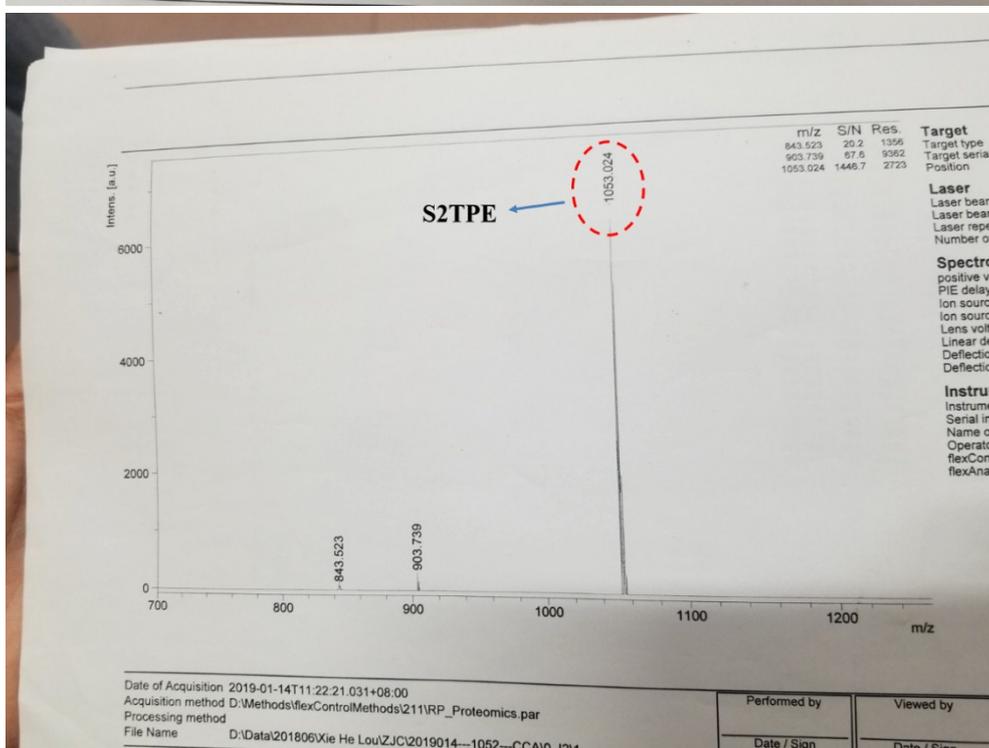
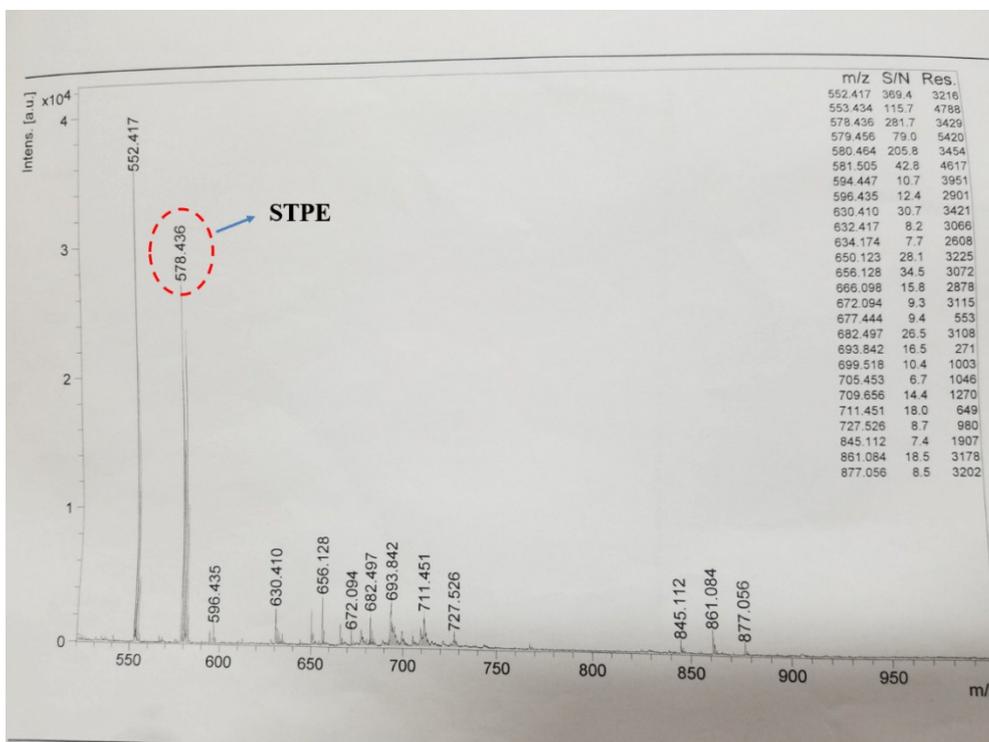


Figure S1. MALDI-TOF spectra of STPE (up) and S2TPE (below).

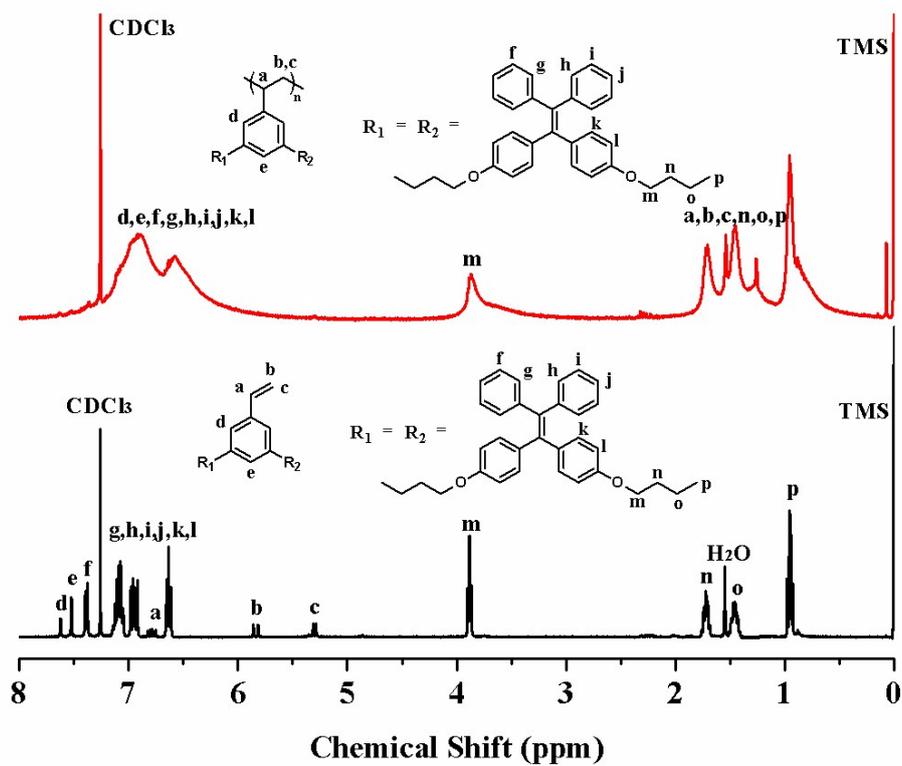


Figure S2. ^1H NMR spectra of S2TPE and PS2TPE

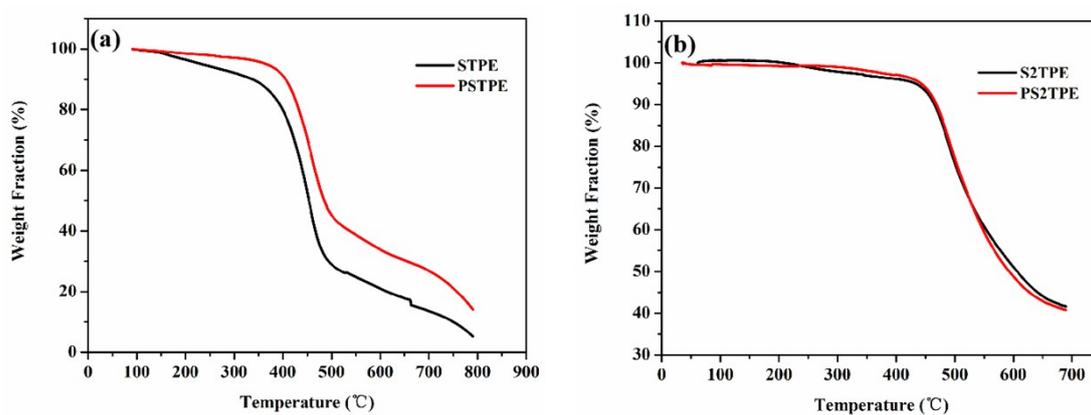


Figure S3. Thermogravimetric analysis results of STPE and PSTPE (a) and those of S2TPE and PS2TPE (b).

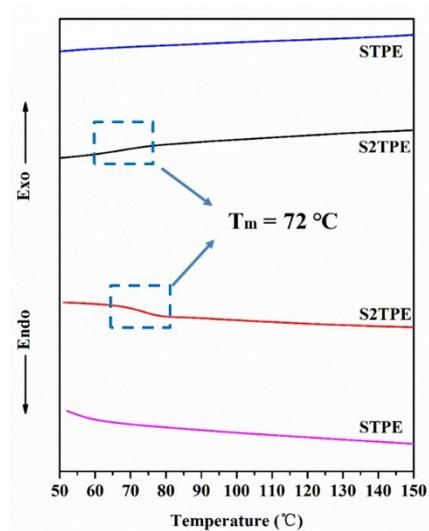


Figure S4. DSC thermograms of STPE and S2TPE recorded under nitrogen at a rate 10 °C/min during the first cooling cycle and the second heating cycle.

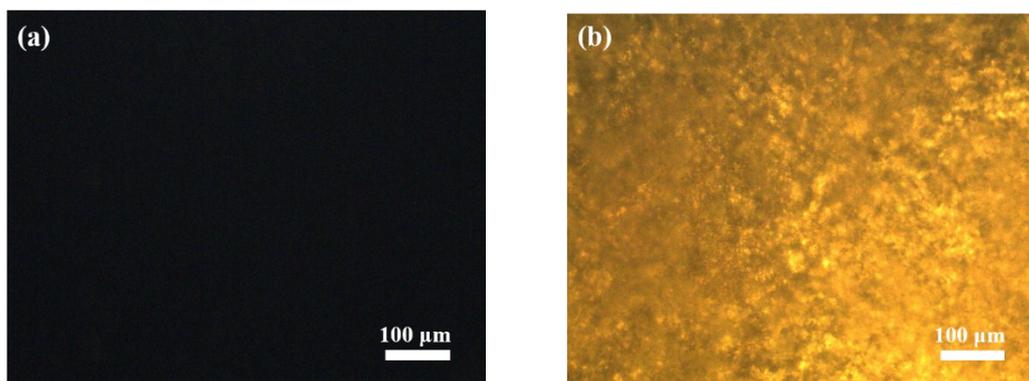


Figure S5. Representative PLM images of STPE (a) and S2TPE (b) at 80 °C. (200× magnification).

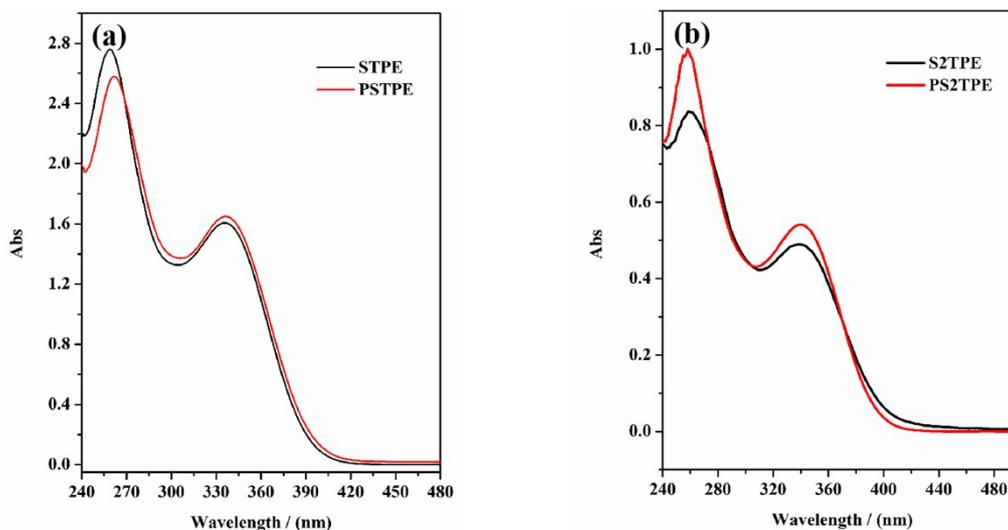


Figure S6. Absorption spectra of STPE, S2TPE, PSTPE and PS2TPE in THF. Solution concentration: 10^{-5} M.

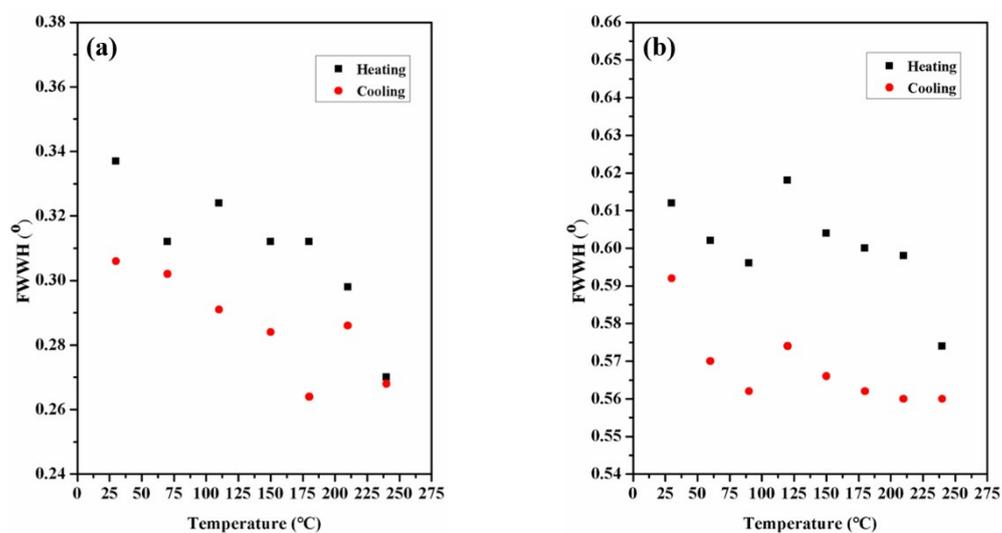


Figure S7. Full width of half-height (FWWH) of the high-angle diffraction/scattering as functions of temperature of PSTPE(a) and PS2TPE(b).