Supporting Information

Tetraphenylethene-based Chiral Polymer: An AIE Luminogen with High and Tunable CPL Dissymmetry Factor

Xunhua Liu, Jiemin Jiao, Xiaoxiang Jiang, Junfeng Li, Yixiang Cheng*, Chengjian Zhu*

Key Lab of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University,
Nanjing 210093, China.
E-mail: yxcheng@nju.edu.cn and cjzhu@nju.edu.cn

Experimental section

Measurements

^{1}H and ^{13}C NMR spectra measurements (all in $CDCl_3$) were recorded on a Bruker 75 spectrometer with tetramethylsilane as the reference. Fourier transform infrared (FT-IR) spectra were taken on a Nexus 870 FT-IR spectrometer. UV-vis spectra were obtained from a Perkin-Elmer Lambda 35 spectrometer. Fluorescent spectra were obtained with a Perkin-Elmer LS 55 spectrometer. Thermogravimetric analyses (TGA) was performed on a Perkin-Elmer Pyris-1 instrument under N_2 atmosphere. Molecular weight was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. Quantum yields were determined by the optically dilute relative method using the following equation:

$$\Phi_s = \Phi_R * [(I_s * A_R)/(I_R * A_s)]\ [(n_s)^2/(n_R)^2]$$

Where Φ_s is the quantum yield of our **TPETyr** or **TPEBr** sample, Φ_R is the quantum yield of the reference, A is the absorbance at the excitation wavelength, I is the relative intensity of the excitation light at the same wavelength, n is the refractive index, and the subscripts "S" and "R" refer to sample and reference, respectively. In this case, quinine sulfate in 0.5 M sulfuric acid was used as reference (Φ_R = 0.55). DLS measurements were conducted on a Brookheaven BI-200SM. Circular dichroism spectra (CD) were recorded on Jasco J-810 spectropolarimeter. Circularly polarized luminescence (CPL) spectra were recorded on an instrument according to literature procedures.[1] Specific rotations ($[\alpha]_D^{20}$) were measured on a Autopol IV-T/V automatic polarimeter. C, H and N of elemental analyses were performed on an Elementar Vario MICRO analyzer.

Materials

Et_3N used for polymerization was distilled and dried over potassium hydroxide prior to use and THF was used after distillation over Na/benzophenone. All other reagents were commercially obtained, and used as received without purification.

Synthesis

4-(2-Trimethylsilylethynyl)benzophenone (1). 442.60 mg (0.38 mmol) of $Pd(PPh_3)_4$, 72.90 mg (0.38 mmol) of CuI and 1.00 g (3.83 mmol) of 4-bromobenzophenone were added into a 100 mL two-necked round-bottom flask. The flask was evacuated under vacuum and flushed with dry nitrogen three times. Then THF (20 mL) and TEA (30 mL) were injected into it. After the solid mixture was completely dissolved, 1.08 mL (7.66 mmol) of (trimethylsilyl)acetylene was injected into the flask and the mixture was stirred at 70 ℃ for 24 h. After the completion of the reaction, the formed solid was filtered and the solvent was removed by rotary evaporation. The resulting crude product was purified on a silica-gel column using a mixture of chloroform/hexane (1:5 by volume) as eluent. A white solid **1** was obtained in 84.4% yield. ^{1}H NMR (300M, $CDCl_3$), δ (TMS, ppm): 7.78 (m, 4H), 7.60 (m, 3H), 7.51 (m, 2H) (aromatic protons), 0.30 [s, 9H, $Si(CH_3)_3$].

1,2-Bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-1,2-diphenylethene (2). To a 40 mL dry THF solution of **1** (0.90 g, 3.23mmol) and zinc dust (0.85 g, 12.93 mmol) was added titanium(IV) chloride (1.23 g, 6.47 mmol) dropwise under nitrogen at -78 ℃. The mixture was slowly warmed to room temperature and stirred for 0.5 h. Then it was heated to reflux overnight. 10% aqueous K_2CO_3 and a large amount of water were added to quench the reaction. After filtration of the forming solid, the mixture was extracted with DCM for three times. The DCM solution was washed with brine twice and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was subjected to a column chromatography (silica:hexane) to give **2** as a yellow solid in 24.3% yield. ^{1}H NMR (300M, $CDCl_3$), δ (TMS, ppm): 7.26 (m, 4H), 7.14 (m,6H), 7.01 (m, 8H) (aromatic protons), 0.27 and 0.28 [18H, $Si(CH_3)_3$].

1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene (M-1). To a solution of **2** (156.00 mg, 0.30 mmol) in 5 mL dry THF was added 1M THF solution of TBAF (1.19 mL). After stirred for 45 min, the reaction was quenched with 20 mL of water. The mixture was extracted with DCM for three times and then the combined organic layer was washed with brine twice. After solvent evaporation, the crude product was purified on a silica-gel column using hexane as eluent to obtain **M-1** as a light yellow solid in 76.1% yield. ^{1}H NMR (300M, $CDCl_3$), δ (TMS, ppm): 7.28 (m, 4H), 7.15 (m, 6H), 7.04 (m, 8H) (aromatic protons), 3.07 and 3.08 (2H, HC≡). ^{13}C NMR (300M, $CDCl_3$), δ (TMS, ppm): 144.11, 144.01, 142.90, 142.81, 140.86, 131.59, 131.45, 131.22, 127.90, 127.74, 126.87, 126.76, 120.18, 120.03, 83.67 and 83.59 (Ar-C≡), 77.47 and 77.34 (≡CH). Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.72; H, 5.28.

***N*-α-tert-butoxycarbonyl-L-tyrosine methyl ester (3).** L-Tyrosine (10.00 g, 55.19 mmol) was suspended in MeOH (200 mL). $SOCl_2$ (7.3

mL,100.99 mmol) was added to the suspension dropwise at 0 ℃. The mixture was slowly warmed to room temperature and stirred overnight. Most of the solvent was removed by rotary evaporation to concentrate. The residue was dropped into ether. After filtration, L-tyrosine methyl ester was obtained as a white solid in 99% yield. To a solution of L-tyrosine methyl ester (10.67 g, 54.66 mmol) and $NaHCO_3$ (6.88 g, 81.90 mmol) in 70 mL H_2O was added $(Boc)_2O$ (14.32 g, 65.59 mmol) dissolved in 70 mL 1,4-dioxane at 0 ℃. After stirred for 2 h, the mixture was slowly warmed to room temperature and stirred overnight. After completion of the reaction (which was monitored by TLC), the mixture was acidified with 2M HCl to approximately pH = 2. Then it was extracted with EtOAc for three times. The combined organic layer was washed with water and brine, respectively. After solvent evaporation, the residue was purified on a silica-gel column using a mixture of EtOAc/petroleum ether (1:5 by volume) as eluent. **3** was obtained as a white solid in 97%. ^1H NMR (300M, $CDCl_3$), δ (TMS, ppm): 6.98 (d, J = 8.3Hz, 2H), 6.75 (d, J = 8.3Hz, 2H), 5.04 (d, J = 7.8Hz, 1H), 4.55(m, J = 7.8Hz, 1H), 3.73(s, 3H), 3.02(m, 2H), 1.44(s, 9H).

3′,5′-diiodo-*N*-α-tert-butoxycarbonyl-L-tyrosine methyl ester (4). To a solution of **3** (5.81 g, 19.67 mmol), NaCl (4.59 g, 78.69 mmol) and $NaIO_4$ (4.19 g, 19.69 mmol) in $AcOH/H_2O$ (9/1, *v*/*v*, 60 mL) was added KI (9.80 g, 59.02 mmol) portionwise at 0 ℃. The resulting mixture was stirred at room temperature overnight. After completion of the reaction (which was monitored by TLC), the mixture was quenched with water and extracted with CH_2Cl_2 three times. The combined organic layer was washed with 1M aqueous $Na_2S_2O_3{\cdot}5H_2O$ and brine, respectively. After removal of most solvent by rotary evaporation, the residue was dropped into petroleum ether. The resulting precipitate was filtered to obtain **4** as a white solid in 70% yield. ^1H NMR (300M, $CDCl_3$), δ (TMS, ppm): 7.46 (s, 2H), 5.7 (s, 1H), 5.04 (d, J = 7.6Hz, 1H), 4.51 (m, J = 7.6Hz, 1H), 3.76 (s, 3H), 3.04 (dd, J = 14.1Hz, 5.8Hz,1H), 2.91 (dd, J = 14.1Hz, 5.8Hz, 1H), 1.46 (s, 9H).

3′,5′-diiodo-*N*-α-tert-butoxycarbonyl-*O*-octyl-L-tyrosine methyl ester (M-2). To a mixture of **4** (4.19 g, 7.65 mmol) and freshly ground K_2CO_3 (1.59 g, 11.48 mmol) in 40 mL DMF was added $C_8H_{17}Br$ (2.22 g, 11.48 mmol) in 16 mL DMF. The mixture was stirred at room temperature overnight. After the filtration of K_2CO_3, solvent was removed by rotary evaporation. The crude product was purified on a silica-gel column using a mixture of EtOAc/petroleum ether (1:7 by volume) as eluent. **M-2** was obtained as a white solid in 90.7% yield. ^1H NMR (300M, $CDCl_3$), δ (TMS, ppm): 7.54 (s, 2H), 5.04 (d, J = 7.4Hz, 1H), 4.52 (m, J = 7.4Hz, 1H), 3.95 (t, J = 6.6Hz, 2H), 3.76 (s, 3H), 3.05 (dd, J = 13.8Hz, 5.8Hz, 1H), 2.91 (dd, J = 13.8Hz, 5.8Hz, 1H), 1.92 (m, 2H), 1.61-1.32 (m, 10H), 1.46 (s, 9H), 0.91 (t, J=6.8Hz, 3H). ^{13}C NMR (300M, $CDCl_3$), δ (TMS, ppm): 171.66, 157.02, 154.77, 140.50, 135.69, 90.73, 80.13, 73.38, 54.17, 52.33, 36.44, 31.78, 29.93, 29.39, 29.18, 28.22, 25.87, 22.59, 14.03. Anal. Calcd for $C_{23}H_{35}I_2NO_5$: C, 41.90; H, 5.35; N, 2.12. Found: C, 41.86; H, 5.33; N, 2.16.

***N*-α-tert-butoxycarbonyl-*O*-octyl-L-tyrosine methyl ester (model 2).** To a mixture of **3** (1.00 g, 3.39 mmol) and freshly ground K_2CO_3 (0.70 g, 5.08 mmol) in 15 mL DMF was added $C_8H_{17}Br$ (0.98 g, 5.08 mmol) in 6 mL DMF. The mixture was stirred at room temperature overnight. After the filtration of K_2CO_3, solvent was removed by rotary evaporation. The crude product was purified on a silica-gel column using a mixture of EtOAc/petroleum ether (1:15 by volume) as eluent. was obtained as a white solid in 84.5% yield. ^1H NMR (300M, $CDCl_3$), δ (TMS, ppm): 7.04 (d, J = 8.6Hz, 2H), 6.83 (d, J = 8.6Hz, 2H), 4.97 (d, J = 8.2Hz, 1H), 4.56 (m, J = 8.2Hz, 1H), 3.94 (t, J = 6.6Hz, 2H), 3.73 (s, 3H), 3.04 (m, 2H), 1.78 (m, 2H), 1.44 (s, 9H), 1.49-1.27 (m, 10H), 0.91 (t, J = 7.3Hz, 3H). ^{13}C NMR (300M, $CDCl_3$), δ (TMS, ppm): 172.36, 158.16, 155.04, 130.14, 127.57, 114.47, 67.89, 54.34, 52.07, 37.73, 31.73, 29.28. 29.21, 29.16, 28.22, 25.98, 22.58, 14.02. Anal. Calcd for $C_{23}H_{37}NO_5$: C, 67.78; H, 9.15; N, 3.44. Found: C, 67.80; H, 9.18; N, 3.42.

TPETyr. The monomer **M-1** (60.60 mg, 0.16 mmol), **M-2** (105.01 mg, 0.16 mmol), $Pd(PPh_3)_4$ (18.41 mg, 0.016 mmol) and CuI (6.07 mg, 0.032 mmol) were added into Schlenk tube. The tube was evacuated under vacuum and flushed with dry nitrogen three times. Then THF (10 mL) and TEA (10 mL) were injected into it. After stirred at 70 ℃ for 3 d, it was filtered through a short silica gel column in methanol (100 mL) to precipitate the polymer. The resulting polymer was filtered and washed with methanol several times and dried under vacuum to obtain **TPETyr** as a yellow solid in 81.7%. M_w 11680; M_n 7780; PDI 1.5. ^1H NMR (300M, $CDCl_3$), δ (TMS, ppm): 7.57 (m, 3H), 7.02-7.28 (m, 40H), 5.04 (m, 1H), 4.55 (m, 1H), 4.22 (m, 2H), 3.76 (s,3H), 3.01 (m, 2H), 1.86 (m, 2H), 1.24-1.55 (m, 10H), 1.46 (s, 9H), 0.88 (m, 3H). FT-IR (KBr, cm^{-1}): 3418, 3055, 2925, 2854, 2362, 2200,1746, 1717, 1651, 1504, 1443, 1365, 1261, 1165, 1103, 1020, 839, 815, 764, 700, 630, 573.

Reference

[1] Y. Haketa, S. Sakamoto, K. Chigusa, T. Nakanishi and H. Maeda, *J. Org. Chem.*, 2011, **76**, 5177-5184.

Solution NMR spectra

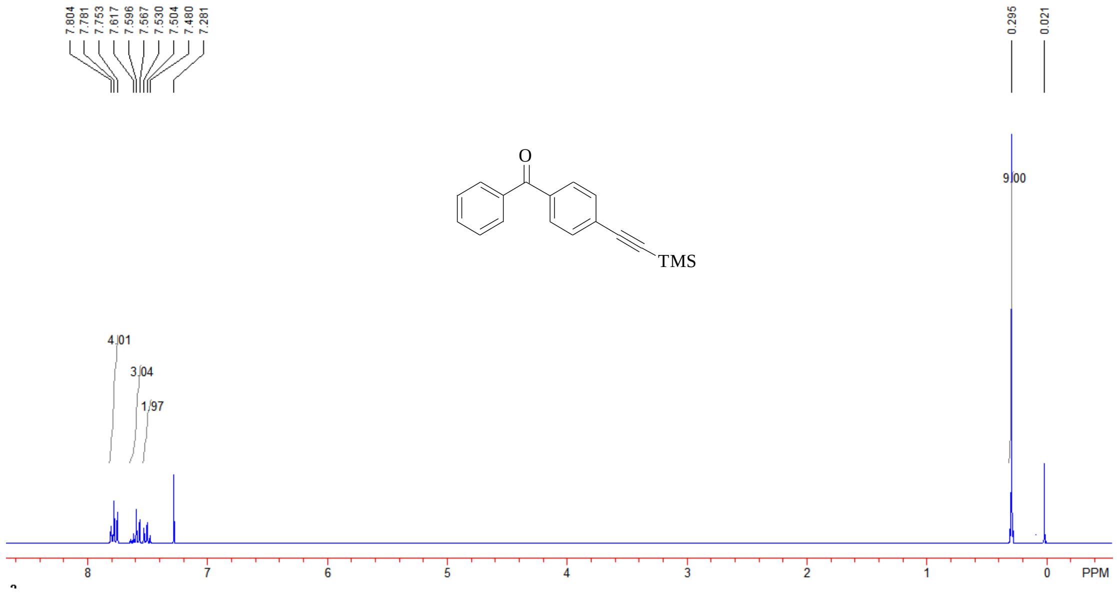

Fig S1. ^{1}H-NMR spectrum of **1** in $CDCl_3$

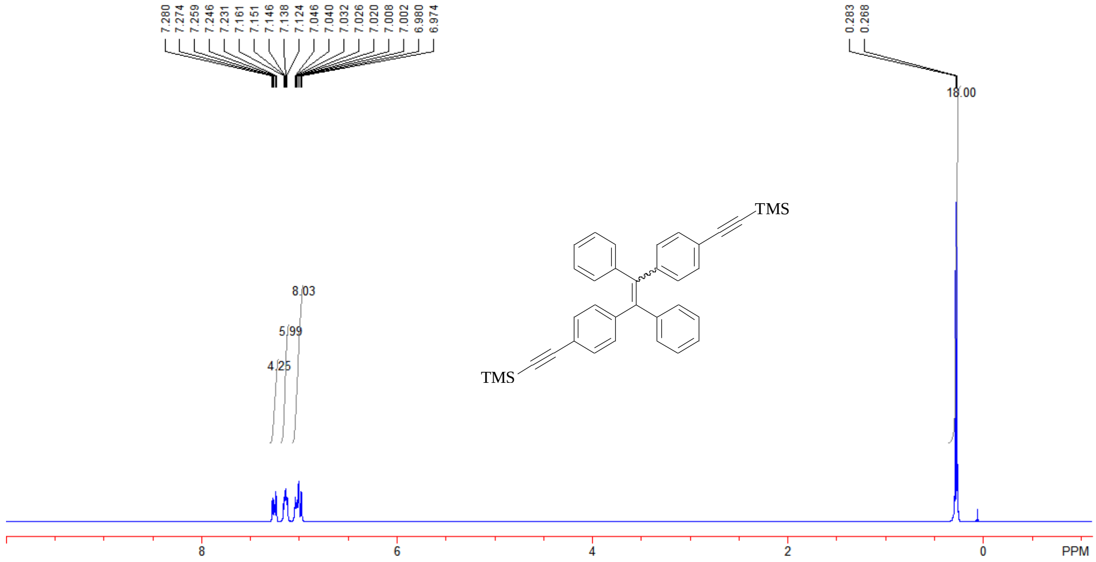

Fig S2. ^{1}H-NMR spectrum of **2** in $CDCl_3$

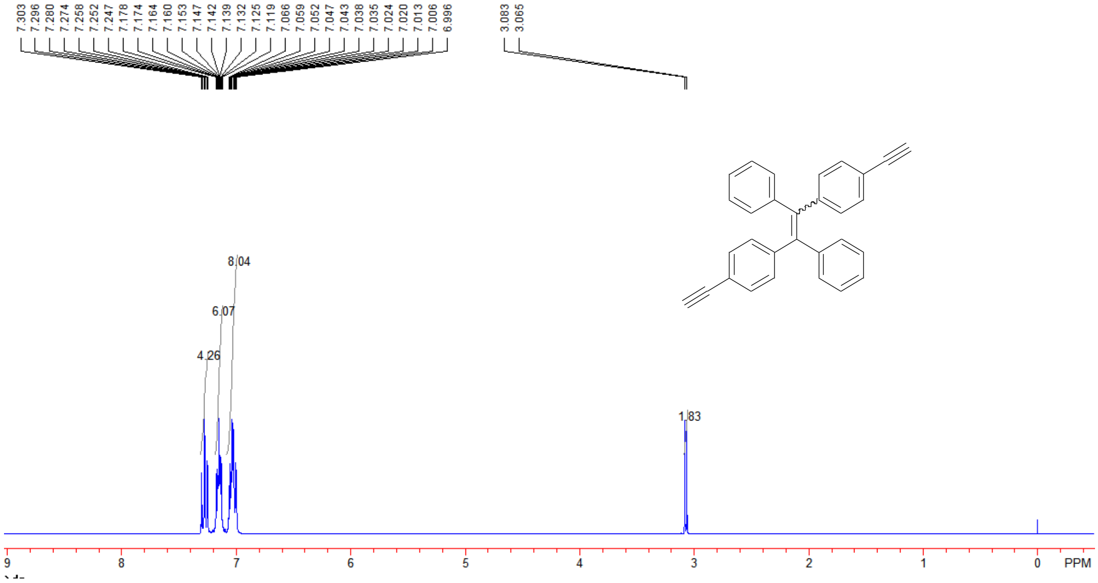

Fig S3. ^{1}H-NMR spectrum of **M-1** in $CDCl_3$

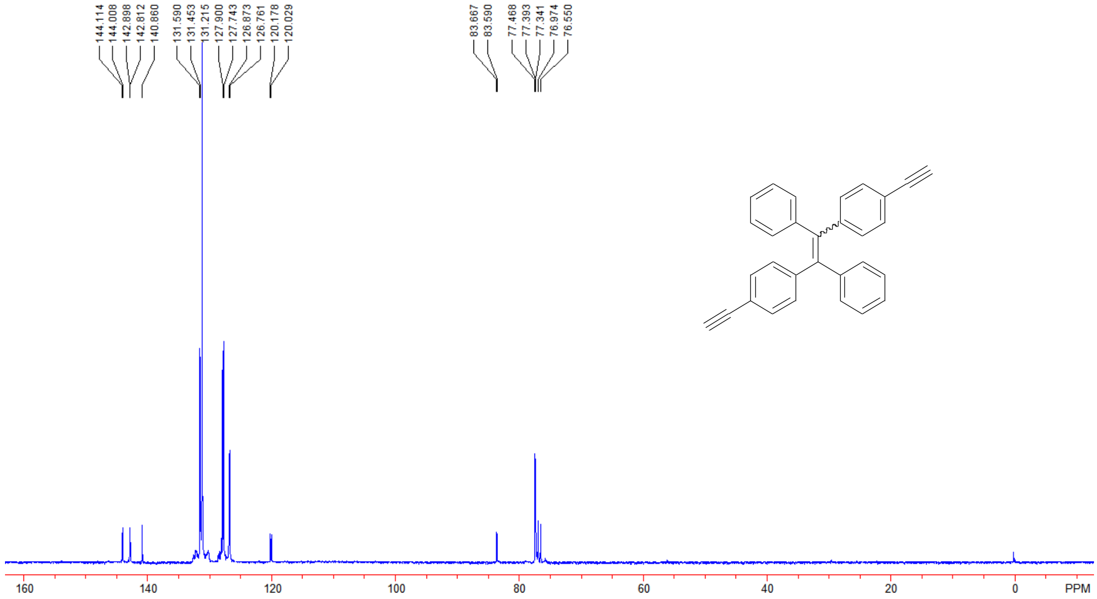

Fig S4. ^{13}C-NMR spectrum of **M-1** in $CDCl_3$

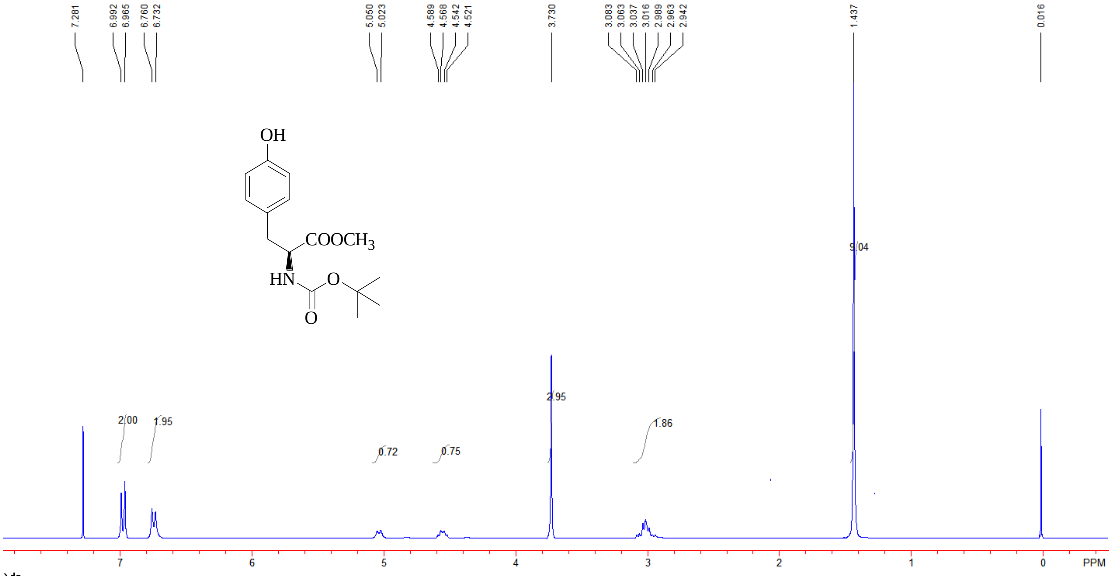

Fig S5. ^{1}H-NMR spectrum of **3** in $CDCl_3$

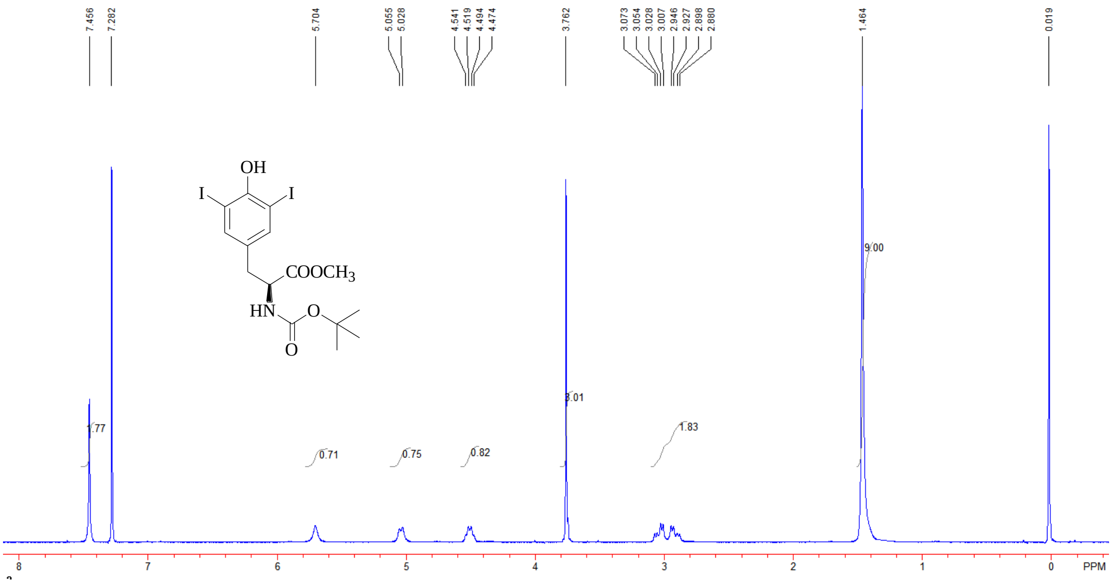

Fig S6. ^{1}H-NMR spectrum of **4** in $CDCl_3$

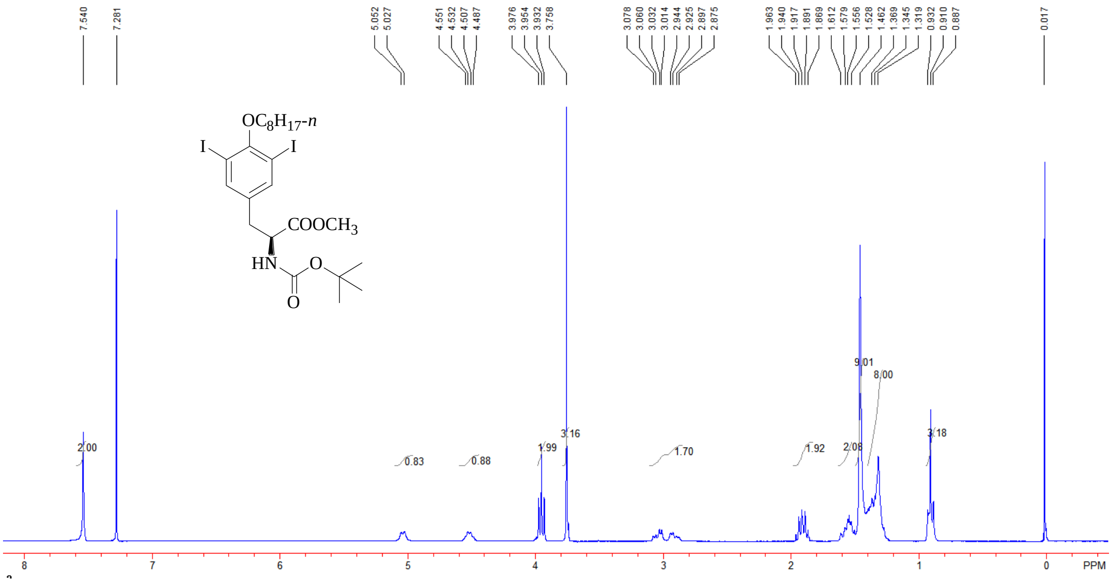

Fig S7. ^{1} H-NMR spectrum of **M-2** in $CDCl_3$

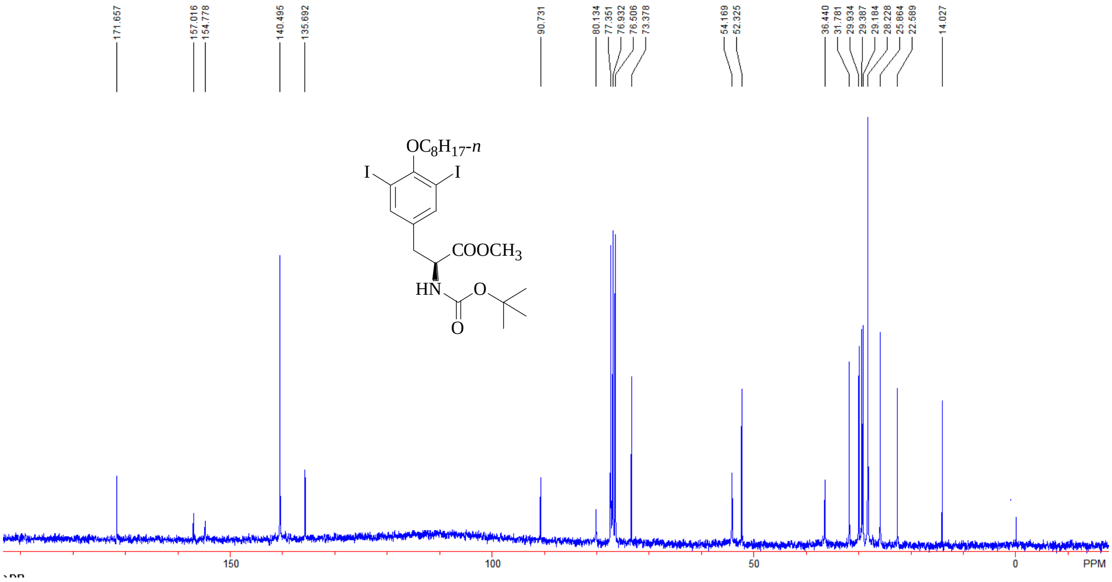

Fig S8. ^{13}C-NMR spectrum of **M-2** in $CDCl_3$

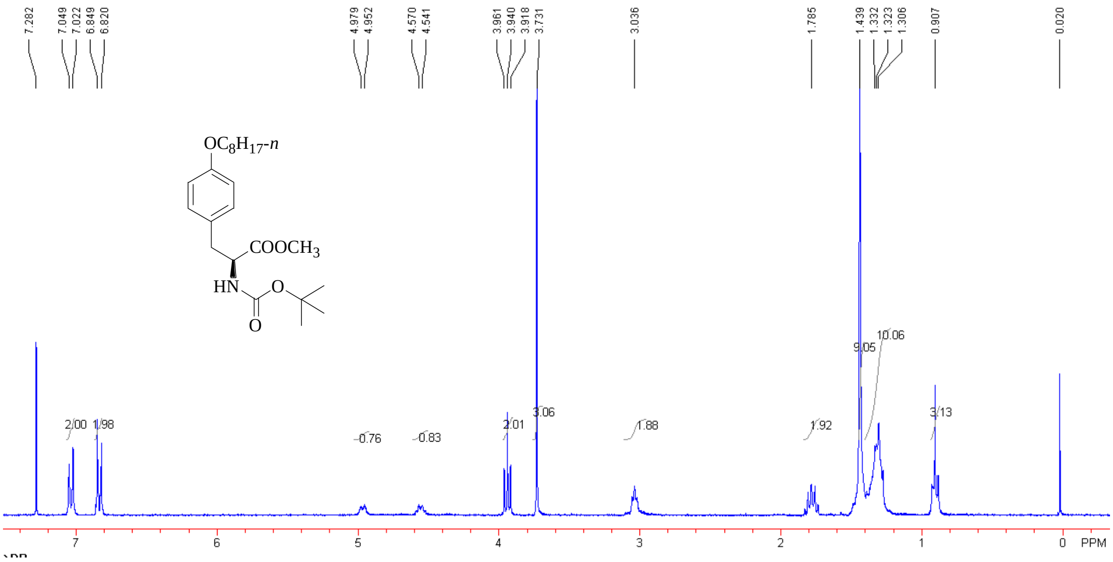

Fig S9. ^{1} H-NMR spectrum of model 2 in $CDCl_3$

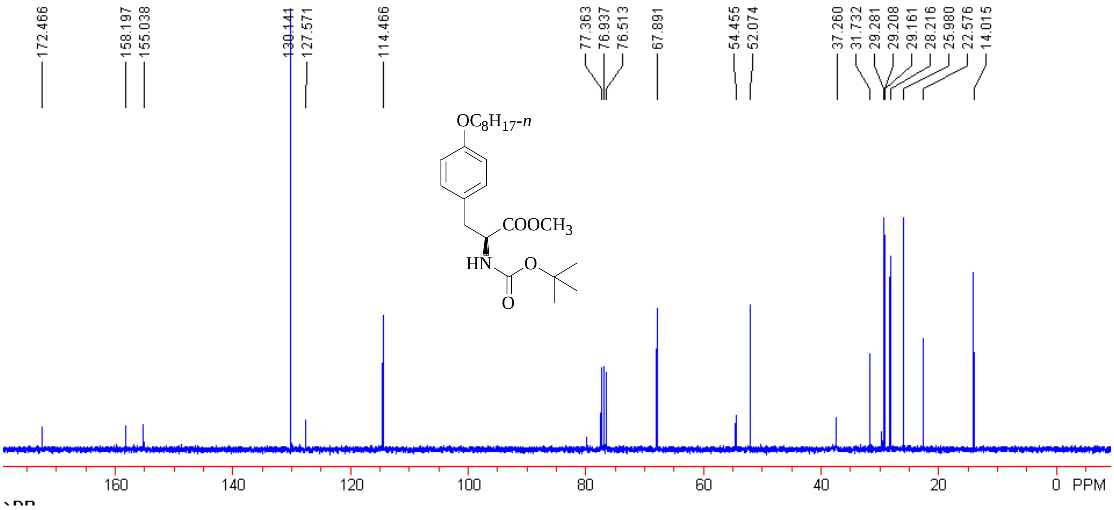

Fig S10. ^{13}C-NMR spectrum of model 2 in $CDCl_3$

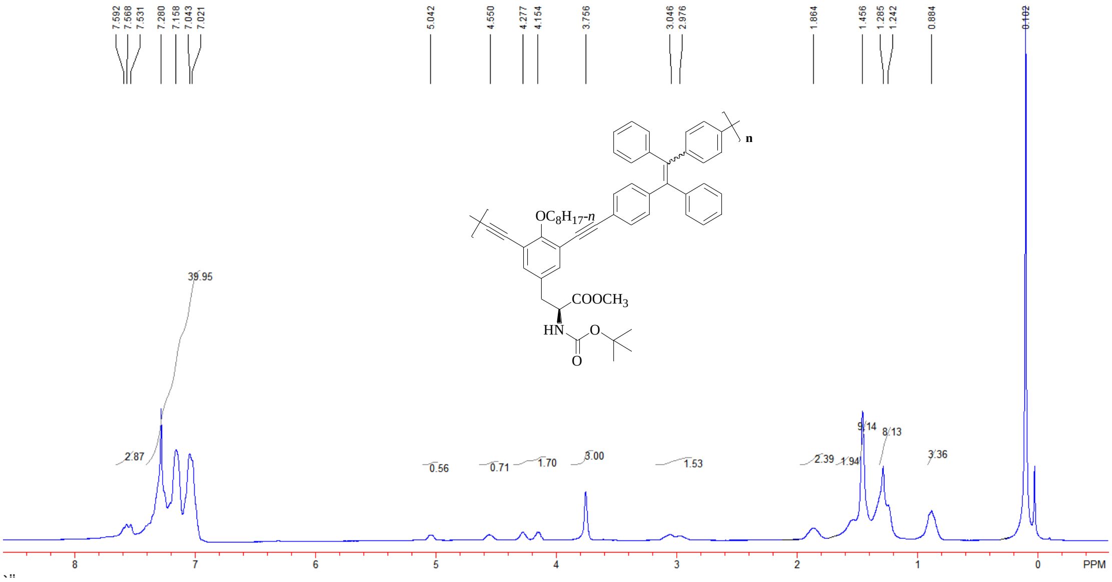

Fig S11. ^{1}H-NMR spectrum of **TPETyr** in $CDCl_3$

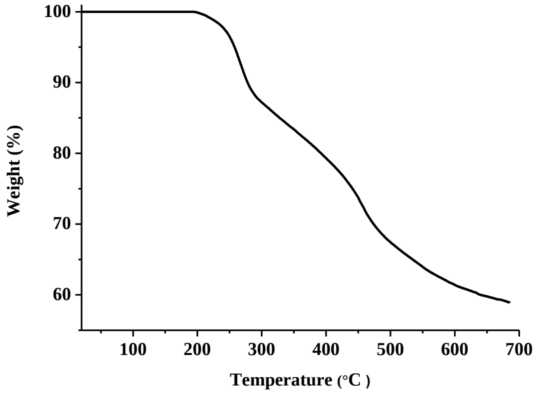

Fig S12. TGA curve of **TPETyr**.

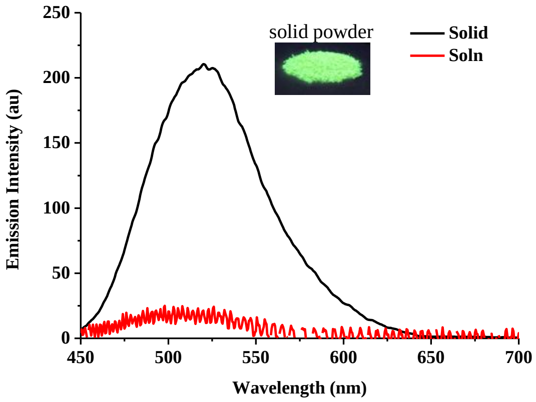

Fig S13. Emission spectra of **TPETyr** in solid and solution (soln) states. Inset: Photograph of solid powder of **TPETyr** taken under UV irradiation (365 nm). Solution concentration: 10μM; excitation wavelength: 380 nm.

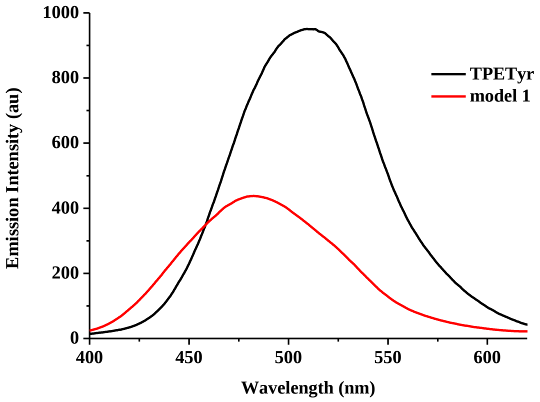

Fig S14. Emission spectra of **TPETyr** and model 1 in THF/water mixture (5/95 *v*/*v*). Solution concentration: 10 μM.

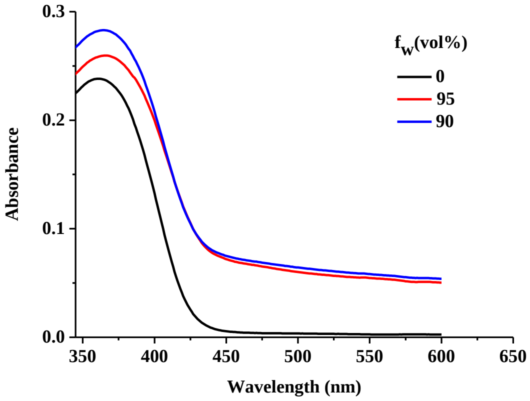

Fig S15. Absorption spectra of **TPETyr** in THF and THF/water mixtures. Solution concentration: 10 μM

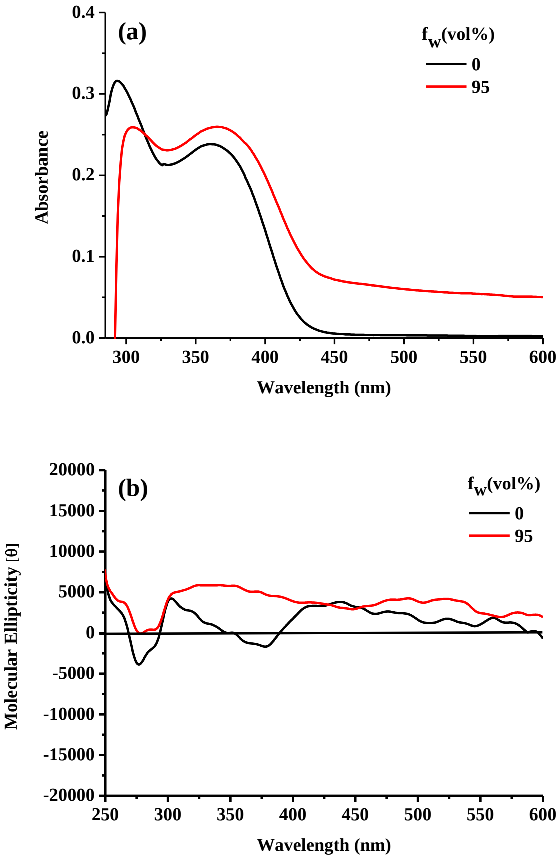

Fig S16 (a) UV-vis and (b) CD spectra of **TPETyr** in THF and THF/water mixture (5/95 *v*/*v*). Solution concentration: 10 μM.

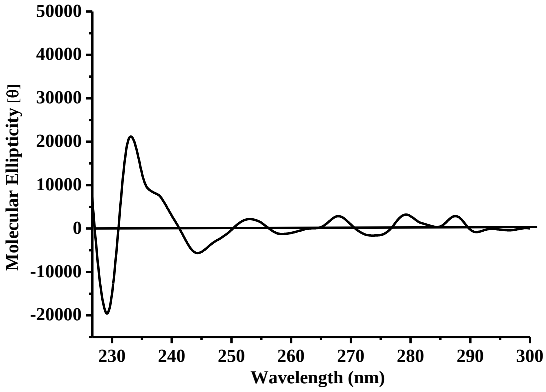

Fig S17 The CD spectrum of model 2 in THF. Solution concentration: 10 μM.

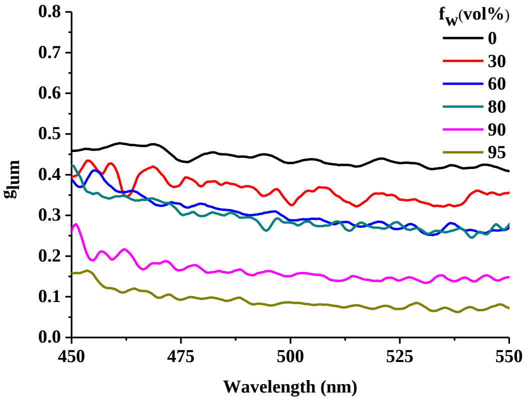

Fig S18. CPL dissymmetry factor g_{lum} *versus* wavelength for **TPETyr** in THF/water mixtures with different fractions of water (f_w). Solution concentration: 10 μM; excitation wavelength: 371 nm.