

Supporting Information

Enhanced Fluorescence Quantum Yield in Syndiotactic Side-Chain TPE Polymers via Rh-Catalyzed Carbene Polymerization: Influence of Substitution Density and Spacer Length

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1. Synthesis of (L-prolinate)Rh^I(1,5-cyclooctadiene).

Rh(I) catalyst is prepared referring to the procedure reported by de Bruin and coworkers as follows.¹ L-proline (0.245 g, 2 mmol) and NaOH (0.08 g, 2 mmol) was dissolved in anhydrous methanol CH₃OH (20 mL) under stirring at room temperature for 45 min. The solution was added into the yellow suspension solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (0.493 g, 1 mmol) in 10 mL methanol. Then the mixture was stirred at room temperature reaction for 60 min to obtain clear yellow solution. The solvent was removed and then the solid was redissolved in anhydrous CH₂Cl₂. After filtering and removing the solvent of the filtrate under reduced pressure, 0.35 g yellow solid catalyst of (L-prolinate)Rh^I(1,5-cyclooctadiene) was obtained in 52% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.61-3.50 (s, 4H, CH=CH), 3.95 (m, 1H, COOCH), 3.5 (s, 1H, NH), 3.05 (m, 2H, NHCH₂), 2.60 (m, 2H, CH=CHCH₂), 2.42 (m, 2H, CH=CHCH₂), 2.22 (m, 2H, COOCHCH₂), 2.02 (m, 1H, NHCH₂CH₂), 1.99 (m, 2H, CH=CHCH₂), 1.75 (m, 2H, CH=CHCH₂), 1.67 (m, 1H, NHCH₂CH₂).

2. Synthesis of N,N'-ditosylhydrazine (DTHZ).

The *p*-toluenesulfonylhydrazide (65.1 g, 349.7 mmol), tosyl chloride (100.0 g, 524.5 mmol) and CH₂Cl₂ (250 mL) were added into a 1000 mL three-neck round bottom flask, then the reaction system was cooled down to below 3 °C. After adding the mixed solution of pyridine (41.5 g, 524.5 mmol) in CH₂Cl₂ (80 mL) dropwise under mechanical agitation (700 rpm), a transparent yellow solution was obtained. Then quickly some white precipitation appeared and the mixture was stirred at a rate of 1000 rpm reaction for 3 h. After adding ethanol (200 mL) and continuing reaction with stirring for 0.5 h, the suspension solution was transferred into a 1500 mL large beaker, with adding a mixed solvent of distilled water (200 mL) and ethanol (200 mL) and stirring for 10 min, the resulting mixed solution was filtered to obtain the solid crude product. The crude product was refluxed for 3 h in 900 mL methanol, then the suspension mixture was filtered and the filter residue was successively washed with CH₃OH (300 mL) and H₂O (300 mL). The resulting solid was dried at 50 °C under vacuum overnight, and then 97.12 g dry product N,N'-ditosylhydrazine (DTHZ) was obtained in 82% yield. ¹H NMR (400 MHz, DMSO) δ (ppm): 9.58 (s, 2H, NH), 7.65 (d, 4H, Ar-H), 7.38 (d, 4H, Ar-H), 2.40 (s, 6H, CH₃).

3. Synthesis of other diazo ester monomers *Mm*TPE (*m* = 2-5, 8, 10, 12).

The other diazo ester monomers *Mm*TPE (*m* = 2-5, 8, 10, 12) were synthesized according to the similar procedures as described for preparing the representative M6TPE.

Diazo ester monomer with two-carbon alkyl spacer M2TPE. Yield 67%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.11 (m, 15H, Ar-H), 6.94 (d, 2H, Ar-H), 6.63 (d, 2H, Ar-H), 4.76 (s, 1H, OOCCHN₂), 4.50 (t, 2H, Ar-OCH₂), 4.16 (t, 2H, CH₂OOCCHN₂).

Diazo ester monomer with three-carbon alkyl spacer M3TPE. Yield 85%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.08 (m, 15H, Ar-H), 6.92 (d, 2H, Ar-H), 6.64 (d, 2H, Ar-H), 4.74 (s, 1H, OOCCHN₂), 4.33 (t, 2H, Ar-OCH₂), 3.96 (t, 2H, CH₂OOCCHN₂), 2.09 (m, 2H, CH₂). FTIR (cm⁻¹): 2933, 2859, 2112, 1731, 1692, 1603, 1504, 1026, 697, 566.

Diazo ester monomer with four-carbon alkyl spacer M4TPE. Yield 77%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.10 (m, 15H, Ar-H), 6.93 (d, 2H, Ar-H), 6.62 (d, 2H, Ar-H), 4.74 (s, 1H, OOCCHN₂), 4.20 (t, 2H, ArOCH₂), 3.90 (t, 2H, CH₂OOCCHN₂), 1.80 (m, 4H, CH₂). FTIR (cm⁻¹): 2936, 2858, 2110, 1735, 1693, 1603, 1505, 1025, 698, 567.

Diazo ester monomer with five-carbon alkyl spacer M5TPE. Yield 87%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.08 (m, 15H, Ar-H), 6.89 (d, 2H, Ar-H), 6.62 (d, 2H, Ar-H), 4.73 (s, 1H, OOCCHN₂), 4.17 (t, 2H, Ar-OCH₂), 3.87 (t, 2H, CH₂OOCCHN₂), 1.73 (m, 4H, ArOCH₂CH₂, CH₂CH₂OOCCHN₂), 1.60 (m, 2H, CH₂). FTIR (cm⁻¹): 3025, 2953, 2108, 1695, 1603, 1504, 1241, 1170, 1050, 701, 694, 616, 566.

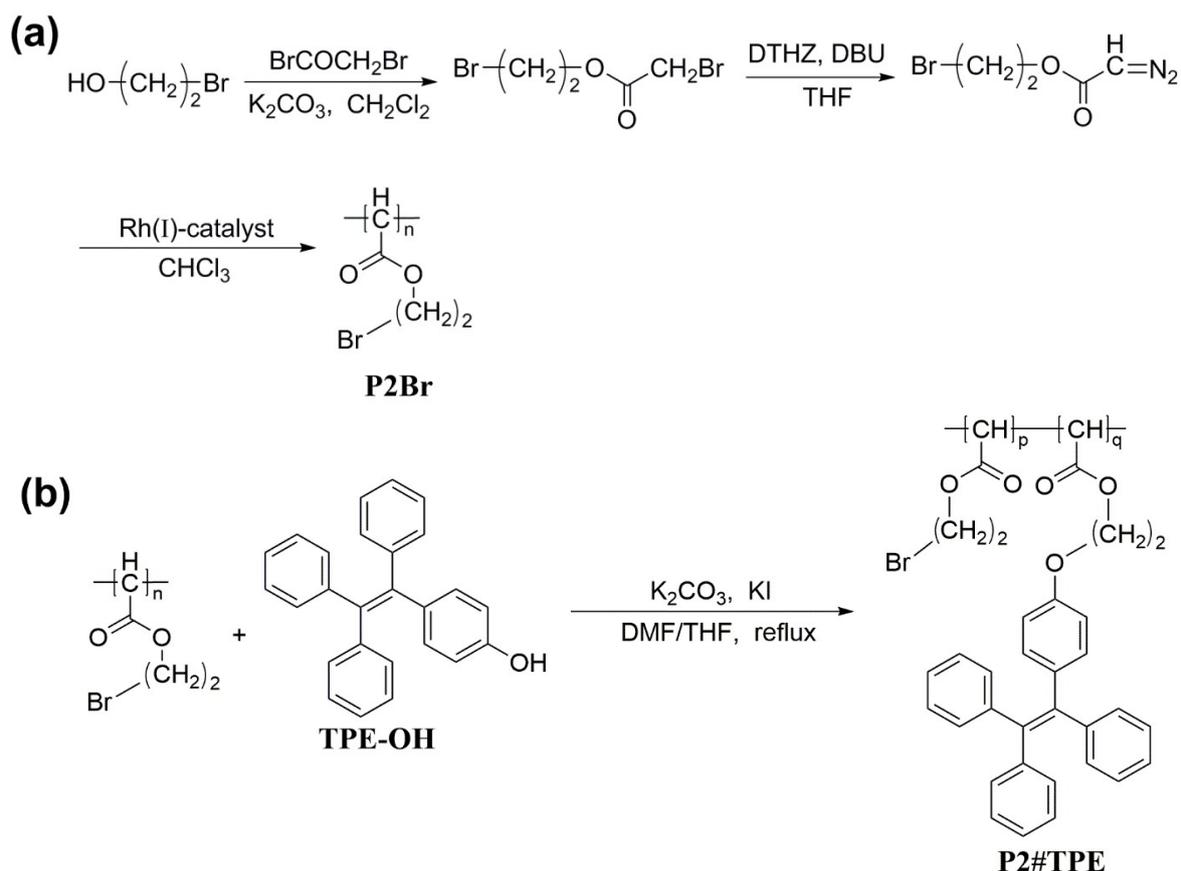
Diazo ester monomer with eight-carbon alkyl spacer M8TPE. Yield 82%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.07 (m, 15H, Ar-H), 6.91 (d, 2H, Ar-H), 6.62 (d, 2H, Ar-H), 4.72 (s, 1H, OOCCHN₂), 4.17 (t, 2H, Ar-OCH₂), 3.89 (t, 2H, CH₂OOCCHN₂), 1.73 (m, 4H, ArOCH₂CH₂, CH₂CH₂OOCCHN₂), 1.37 (m, 8H, CH₂). FTIR (cm⁻¹): 2919, 2852, 2110, 1696, 1600, 1508, 1237, 1175, 1034, 965, 801, 739, 693, 609, 563.

Diazo ester monomer with ten-carbon alkyl spacer M10TPE. Yield 80%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.07 (m, 15H, Ar-H), 6.92 (d, 2H, Ar-H), 6.63 (d, 2H, Ar-H), 4.72 (s, 1H, OOCCHN₂), 4.17 (t, 2H, Ar-OCH₂), 3.86 (t, 2H, CH₂OOCCHN₂), 1.71 (m, 4H, ArOCH₂CH₂, CH₂CH₂OOCCHN₂), 1.36 (m, 12H, CH₂). FTIR (cm⁻¹): 2926, 2852, 2110, 1696, 1600, 1504, 1396, 1351, 1237, 1175, 1028, 744, 693, 609, 569.

Diazo ester monomer with twelve-carbon alkyl spacer M12TPE. Yield 83%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.07 (m, 15H, Ar-H), 6.91 (d, 2H, Ar-H), 6.63 (d, 2H, Ar-H), 4.71 (s, 1H, OOCCHN₂), 4.17 (t, 2H, Ar-OCH₂), 3.87 (t, 2H, CH₂OOCCHN₂), 1.69 (m, 4H,

ArOCH₂CH₂, CH₂CH₂OOCCHN₂), 1.37 (m, 16H, CH₂). FTIR (cm⁻¹): 2914, 2852, 2110, 1679, 1605, 1504, 1402, 1356, 1237, 1175, 1028, 739, 699, 614, 569.

4. Synthesis of C1 polymer with two-carbon alkyl spacer via an indirect route.



Scheme S1. Synthesis of C1 polymer with two-carbon alkyl spacer through an indirect route: a) precursor polymer P2Br, and b) P2#TPE via etherification polymer grafting reaction.

Due to the high steric hindrance for C1 polymerization of TPE side groups attached through very short spacers, the direct carbene polymerization from the TPE-based diazo ester monomer was hardly possible. So the target polymer with two-carbon alkyl spacer P2#TPE was prepared by a two-step indirect route as shown in Scheme S1, which included the synthesis of precursor polymer P2Br through Rh-catalyzed carbene polymerization, and then the preparation of TPE side-chain polymer P2#TPE via a Williamson etherification polymer grafting reaction between P2Br and TPE-OH, as reported for the preparation of π -conjugated

polythiophene liquid crystalline polymers functionalized with side-chain triphenylene discotic mesogens.²

Precursor polymer P2Br.

To a mixture of 2-bromoethanol (6.2 g, 50 mmol) and anhydrous potassium carbonate (34.5 g, 250 mmol) in dichloromethane (150 mL), bromoacetyl bromide (30 g, 150 mmol) was slowly added at 0 °C under a dry N₂ atmosphere. The reaction solution was stirred for 1.5 h at room temperature with TLC checks to trace the reaction process. After adding saturated sodium bicarbonate aqueous solution (100 mL) to quench the reaction, and then the organic layer was washed with saturated brine. With evaporating the solvent of the combined organic phase a liquid crude product was obtained, upon further purification through silica gel column chromatography with dichloromethane as the eluent, then 11.4 g transparent colorless liquid 2-bromoethyl bromoacetate was obtained in 93% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.48 (t, 2H, CH₂OOC), 3.88 (s, 2H, OOCCH₂Br), 3.53 (t, 2H, BrCH₂).

To a solution of 2-bromoethyl bromoacetate (3.70 g, 15 mmol) in THF (20 mL), N,N'-ditosylhydrazine (DTHZ, 10 g, 30 mmol) in THF (100 mL) was added and then the mixture solution was cooled down to 0 °C. After slowly adding 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 67.5 mL, 45 mmol) under a dry N₂ atmosphere, and then the reaction mixture was stirred for 10 min at room temperature. Then upon quenching the reaction by adding saturated sodium bicarbonate aqueous solution (150 mL), the product mixture was extracted with dichloromethane, after removing the solvent and further purifying through silica gel column chromatography with petroleum ether as the eluent, the resulting product was dried at 50 °C vacuum oven overnight to harvest 2.4 g transparent yellow-green liquid 2-bromoethyl diazoacetate in yield 85%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.75 (s, 1H, OOCCHN₂), 4.66 (t, 2H, CH₂OOC), 3.65 (t, 2H, BrCH₂).

To a clear yellow solution of Rh(I)-catalyst (0.065 g, 0.2 mmol) in anhydrous chloroform (8.5 mL) 2-bromoethyl diazoacetate (1.92 g, 10 mmol) was added under a dry N₂ atmosphere. After reaction for 24 h with stirring at room temperature, the reaction solution was slowly added dropwise to a mixed 200 mL solvents of dichloromethane and methanol (CH₂Cl₂:CH₃OH = 1:2, v/v), then stirred overnight. The resulting precipitation was collected and dried at 70 °C under vacuum for 10 h, and 1.1 g yellow-green solid P2Br of poly(2'-bromoethyl 2-ylideneacetate) was obtained (yield 69%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.44 (s, 2H, CH₂OOC), 3.56 (s, 2H, BrCH₂), 3.26 (s, 1H, OOCCH). M_n = 24800, PDI = 1.58.

C1 polymer with two-carbon alkyl spacer P2#TPE.

The mixture solution of TPE-OH (0.70 g, 2 mmol), potassium iodide (catalytic quantity), potassium carbonate (0.552 g, 4 mmol) in dimethylformamide (78 mL) was heated at 70 °C for 1.2 h under a dry N₂ atmosphere, and then the precursor polymer P2Br (0.19 g, 1.0 mmol) in THF (30 mL) was added. The reaction solution was refluxed in a 135 °C oil bath for 3 days and then cooled down. The solvents THF and DMF were removed and the residual solid was washed repeatedly with distilled water until the complete elimination of water-soluble impurities. Then the solid was redissolved in minimum dichloromethane and added dropwise into 60 mL mixed solvents of methanol and dichloromethane (CH₃OH:CH₂Cl₂ = 1:1, v/v). After stirring the suspension for 4 h, the precipitation was harvested by centrifugation. Then dried at 60 °C vacuum oven for 15 h to obtain 0.1 g pale yellow solid product (yield 65%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.96 (s, 17H, Ar-H), 6.47 (s, 2H, Ar-H), 3.82 (br, 5H, CH₂OOCCH, Ar-OCH₂, OOCCH). FTIR (cm⁻¹): 2959, 2919, 1730, 1147, 1056, 1011, 796, 659, 569. FTIR (cm⁻¹): 2959, 2919, 1730, 1147, 1056, 1011, 796, 659, 569.

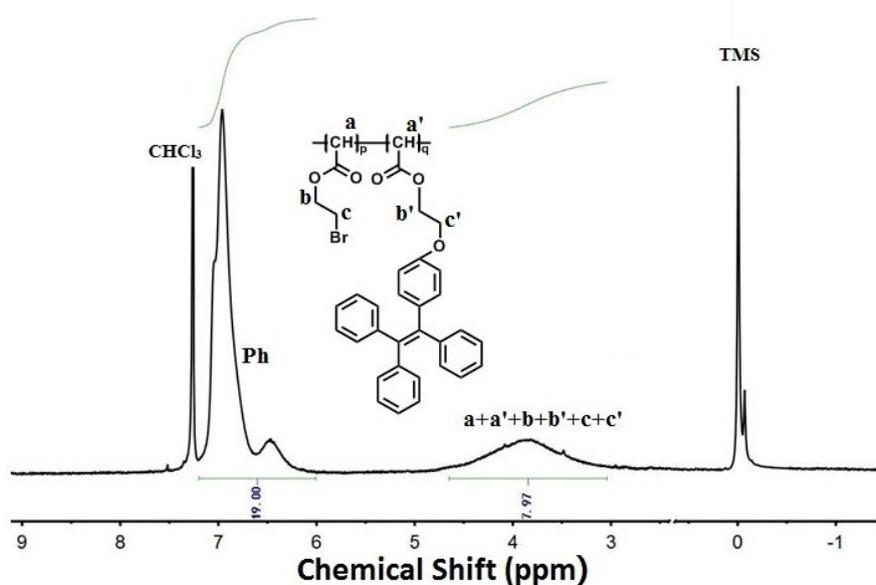


Fig. S1. ¹H NMR spectrum of P2#TPE in CDCl₃.

Figure S1 shows the ¹H NMR spectrum of P2#TPE and the corresponding hydrogen signal assignments. It is convenient to estimate the grafting rate of TPE side groups from the the integral area ratio, that is: when the integral area of aromatic ring hydrogens (Ph) is assumed to be 19.0, the sum hydrogens of all the fatty hydrocarbon in the side-chain and backbone (a+a'+b+b'+c+c') is measured to be 7.97, then (a' + b' + c') = (5/19)×19.0 = 5.0, so (a + b + c) = 7.97-5.0 = 2.97, therefore, the grafting rate of TPE through macromolecular etherification reaction was calculated to be 5.0/7.97 = 62.7%, with 2.97/7.97 = 37.3% unreacted bromoethyl side groups left.

5. Characterization results of other homologous TPE-based side-chain C1 polymers.

Polymer with three-carbon alkyl spacer P3#TPE. Yield 15%. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.00 (s, 15H, Ar-H), 6.77 (s, 2H, Ar-H), 6.47 (s, 2H, Ar-H), 4.05 (s, 2H, Ar-OCH₂), 3.73 (s, 2H, CH₂OOCCH), 3.24 (s, 1H, OOCCH), 1.87 (s, 2H, CH₂). FTIR (cm^{-1}): 2946, 2847, 1710, 1637, 1603, 1504, 1469, 1247, 1161, 1013, 801, 694, 609, 551.

Polymer with four-carbon alkyl spacer P4TPE. Yield 67%. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.04 (s, 15H, Ar-H), 6.78 (s, 2H, Ar-H), 6.41 (s, 2H, Ar-H), 3.99 (s, 2H, Ar-OCH₂), 3.66 (s, 2H, CH₂OOCCH), 3.19 (s, 1H, OOCCH), 1.52 (s, 4H, ArOCH₂CH₂, CH₂CH₂OOCCH). FTIR (cm^{-1}): 2926, 2874, 1730, 1600, 1509, 1441, 1237, 1169, 1028, 751, 699, 609, 575.

Polymer with five-carbon alkyl spacer P5TPE. Yield 74%. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 6.93 (s, 15H, Ar-H), 6.77 (s, 2H, Ar-H), 6.39 (s, 2H, Ar-H), 3.94 (s, 2H, Ar-OCH₂), 3.61 (s, 2H, CH₂OOCCH), 3.17 (s, 1H, OOCCH), 1.63 (d, 4H, ArOCH₂CH₂, CH₂CH₂OOCCH), 1.37 (s, 2H, CH₂). FTIR (cm^{-1}): 2940, 2867, 1704, 1639, 1596, 1504, 1241, 1163, 1020, 845, 801, 701, 544.

Polymer with eight-carbon alkyl spacer P8TPE. Yield 65%. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.03 (s, 15H, Ar-H), 6.87 (s, 2H, Ar-H), 6.52 (s, 2H, Ar-H), 3.97 (s, 2H, Ar-OCH₂), 3.79 (s, 2H, CH₂OOCCH), 1.60 (d, 4H, ArOCH₂CH₂, CH₂CH₂OOCCH), 1.33 (s, 8H, CH₂). FTIR (cm^{-1}): 2919, 2852, 1730, 1600, 1504, 1237, 1175, 1028, 744, 699, 614, 569.

Polymer with ten-carbon alkyl spacer P10TPE. Yield 69%. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.06 (s, 15H, Ar-H), 6.86 (s, 2H, Ar-H), 6.52 (s, 2H, Ar-H), 3.98 (s, 2H, Ar-OCH₂), 3.75 (s, 2H, CH₂OOCCH), 1.62 (d, 4H, ArOCH₂CH₂, CH₂CH₂OOCCH), 1.31 (s, 12H, CH₂). FTIR (cm^{-1}): 2926, 2852, 1730, 1600, 1504, 1441, 1237, 1169, 1028, 751, 693, 614, 569.

Polymer with twelve-carbon alkyl spacer P12TPE. Yield 72%. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.03 (s, 15H, Ar-H), 6.84 (s, 2H, Ar-H), 6.51 (s, 2H, Ar-H), 4.00 (s, 2H, Ar-OCH₂), 3.78 (s, 2H, CH₂OOCCH), 1.63 (d, 4H, ArOCH₂CH₂, CH₂CH₂OOCCH), 1.24 (s, 16H, CH₂). FTIR (cm^{-1}): 2924, 2852, 1730, 1600, 1504, 1441, 1237, 1169, 1026, 750, 693, 614, 569.

6. Representative NMR spectra of polymer P6TPE.

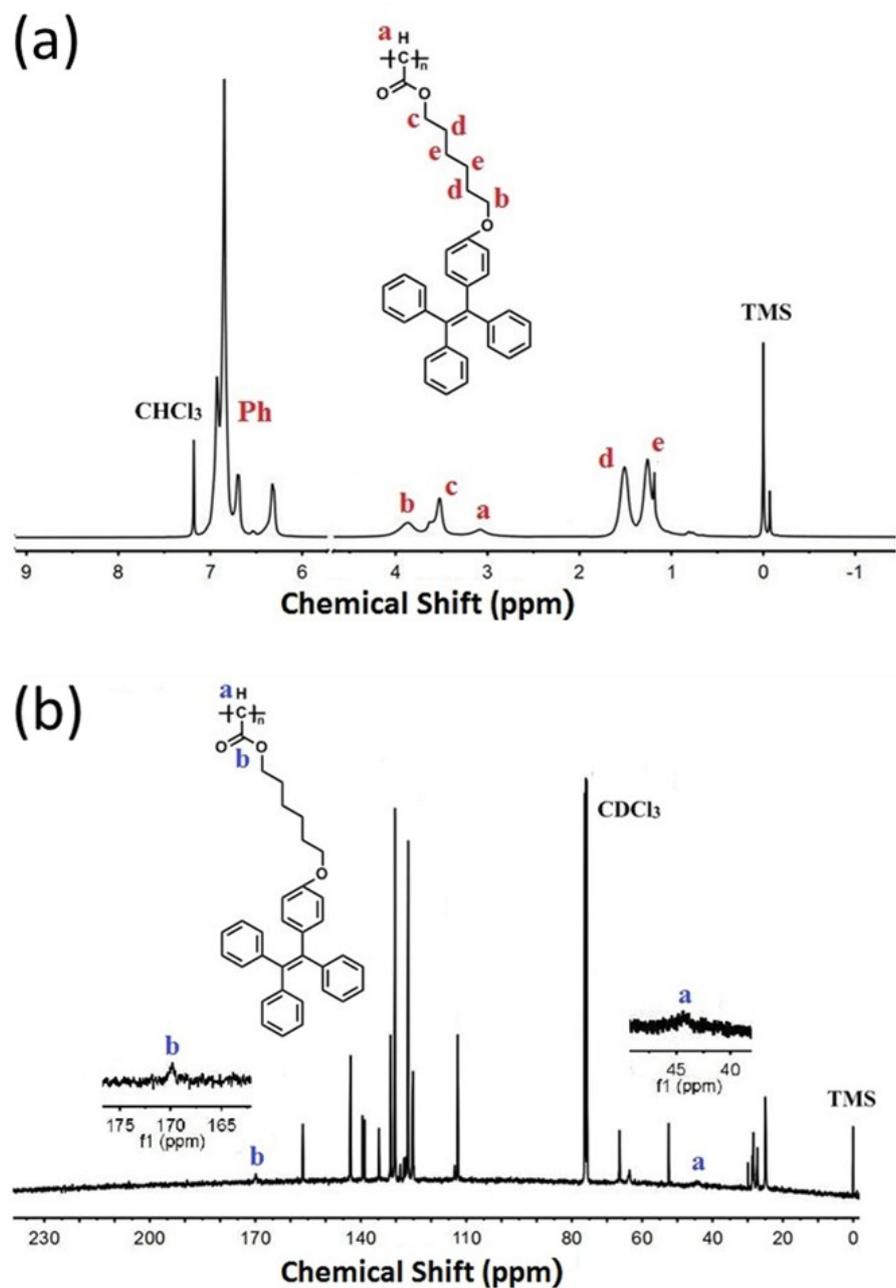


Fig. S2. Representative NMR spectra of a typical TPE side-chain C1 polymer P6TPE in CDCl₃. a) ¹H NMR spectrum (400 MHz); b) ¹³C NMR spectrum (100 MHz).

7. DSC curves of polymers P*m*TPE (*m* = 2#, 3#, 4, 5, 6, 8, 10, 12).

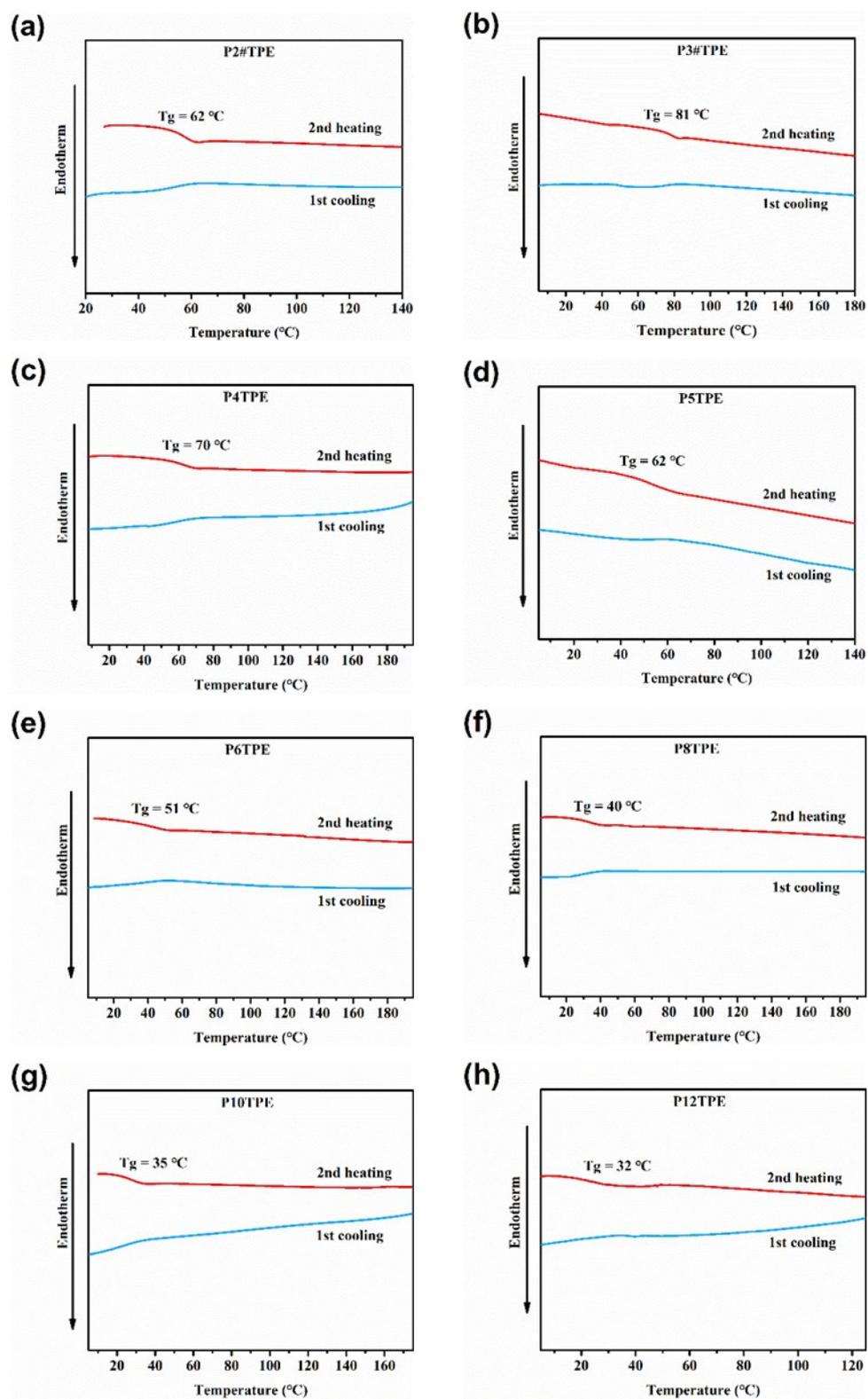


Fig. S3. DSC curves of the series TPE side-chain C1 polymers, the scanning rate was 10 °C min⁻¹.

8. DLS measurements for representative C1 polymer P4TPE aggregate in solution.

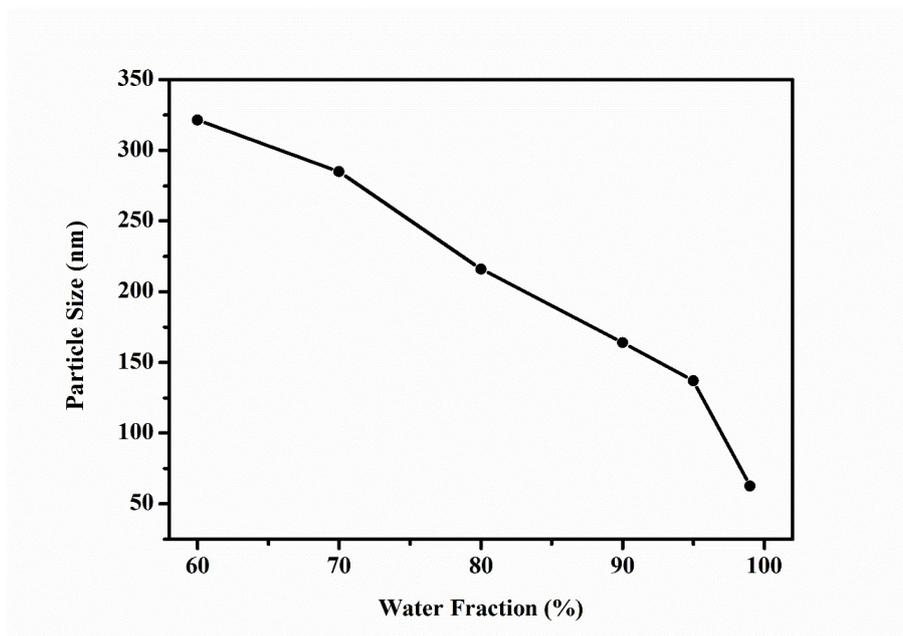


Fig. S4. Aggregate nanoparticle sizes changed with water fraction from 60% to 99% of a representative C1 polymer P4TPE in THF/H₂O mixture solution as measured by dynamic light scattering (DLS).

9. Photophysical properties of other C1 polymers P*m*TPE (*m* = 2#, 6, 8, 10, 12).

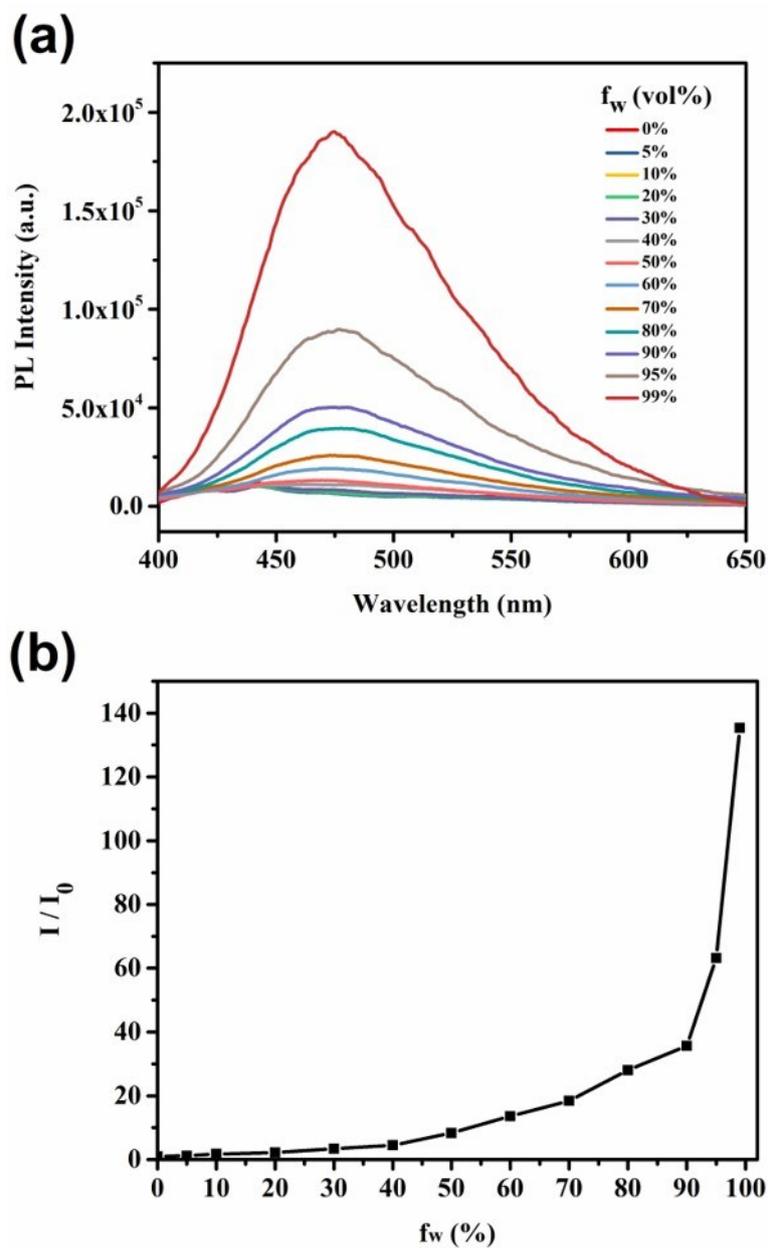


Fig. S5. a) Fluorescence spectra of polymer P2#TPE in THF/H₂O mixtures with increased H₂O volume percentage ($\lambda_{\text{ex}} = 330 \text{ nm}$, [P2#TPE] = 40 $\mu\text{g mL}^{-1}$); b) Plots of emission intensity ratio I/I_0 at the peak of 474 nm for P2#TPE versus water percentage in the solution.

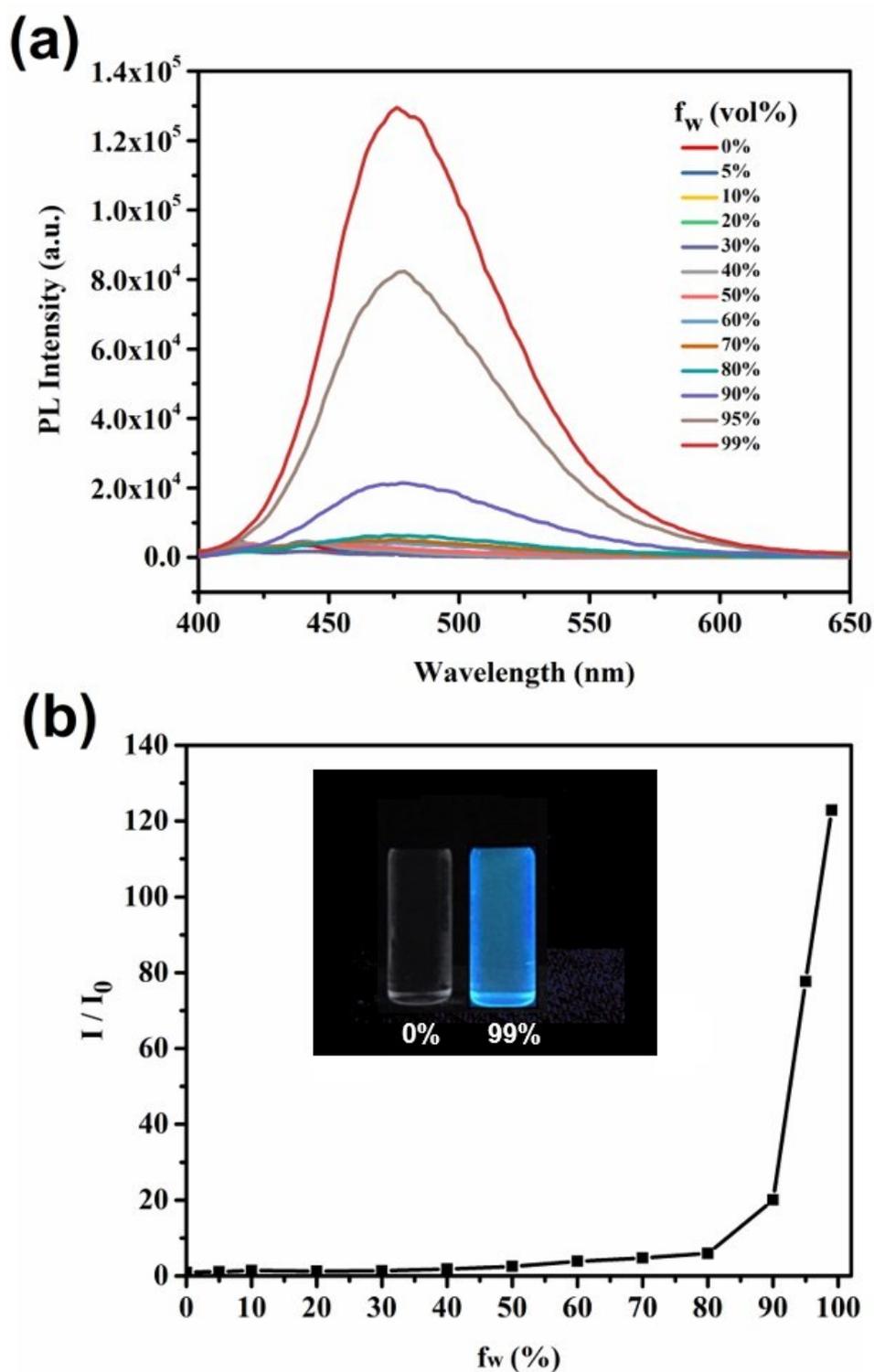


Fig. S6. a) Fluorescence spectra of polymer P6TPE in THF/H₂O mixtures with increased H₂O volume percentage ($\lambda_{\text{ex}} = 330 \text{ nm}$, $[\text{P6TPE}] = 40 \mu\text{g mL}^{-1}$); b) Plots of emission intensity ratio I/I_0 at the peak of 476 nm for P6TPE versus water percentage in the solution; Inset: comparative photographs of P6TPE in THF and THF/H₂O (1/99, v/v) mixture solution under UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$) illumination.

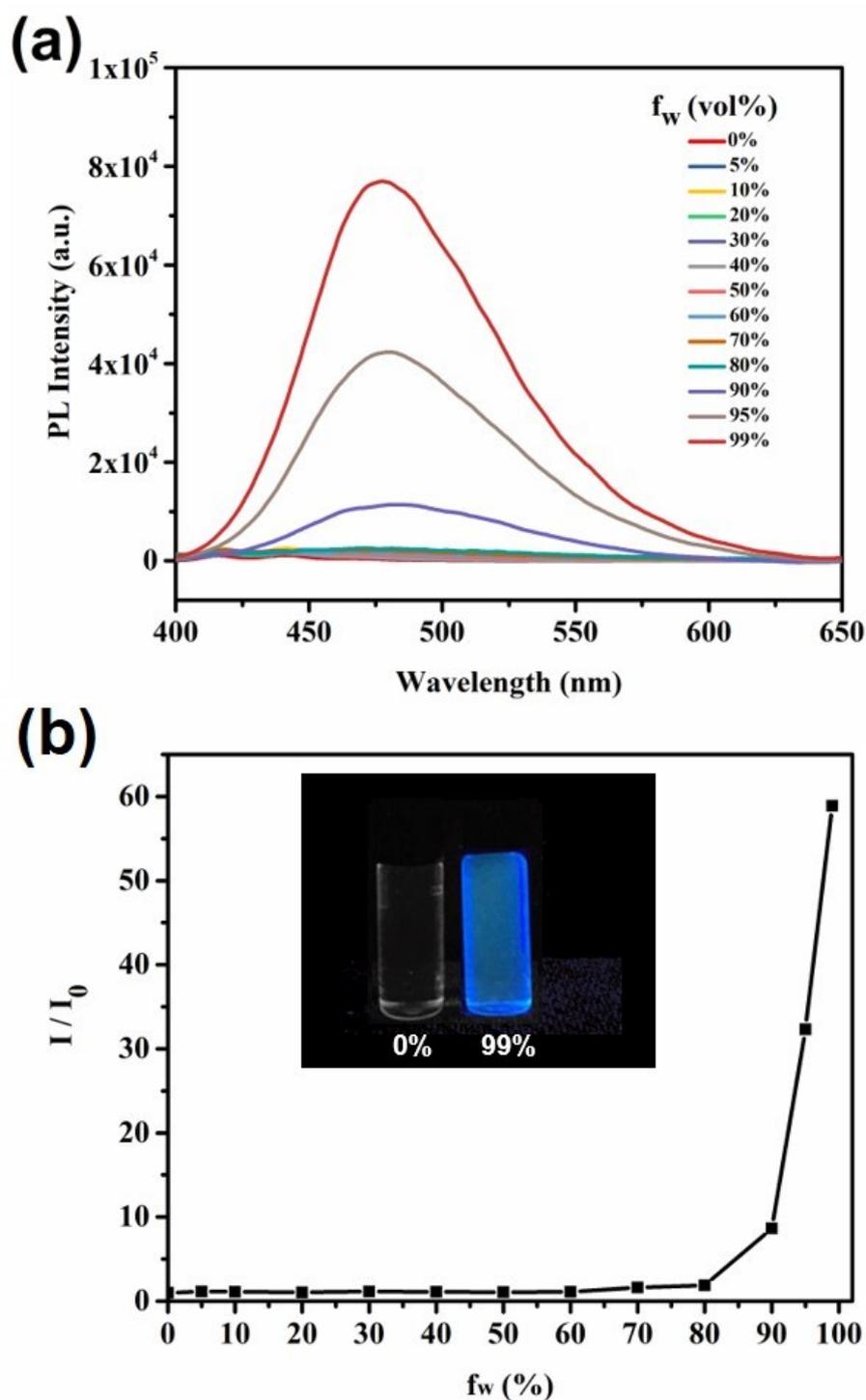


Fig. S7. a) Fluorescence spectra of polymer P8TPE in THF/H₂O mixtures with increased H₂O volume percentage ($\lambda_{\text{ex}} = 330 \text{ nm}$, $[\text{P8TPE}] = 40 \mu\text{g mL}^{-1}$); b) Plots of emission intensity ratio I/I_0 at the peak of 478 nm for P8TPE versus water percentage in the solution; Inset: comparative photographs of P8TPE in THF and THF/H₂O (1/99, v/v) mixture solution under UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$) illumination.

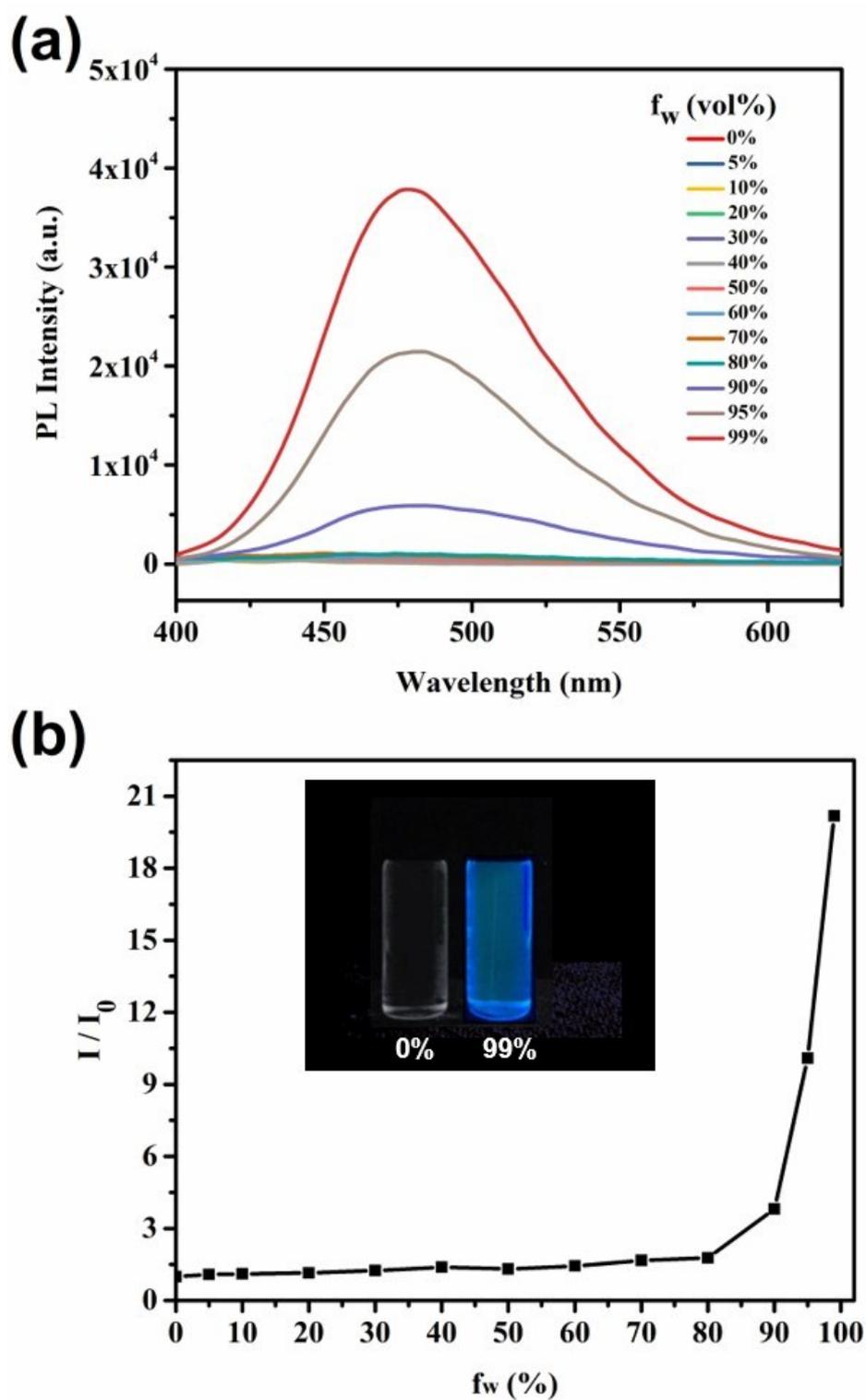


Fig. S8. a) Fluorescence spectra of polymer P10TPE in THF/H₂O mixtures with increased H₂O volume percentage ($\lambda_{\text{ex}} = 330 \text{ nm}$, $[\text{P10TPE}] = 40 \mu\text{g mL}^{-1}$); b) Plots of emission intensity ratio I/I_0 at the peak of 478 nm for P10TPE versus water percentage in the solution; Inset: comparative photographs of P10TPE in THF and THF/H₂O (1/99, v/v) mixture solution under UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$) illumination.

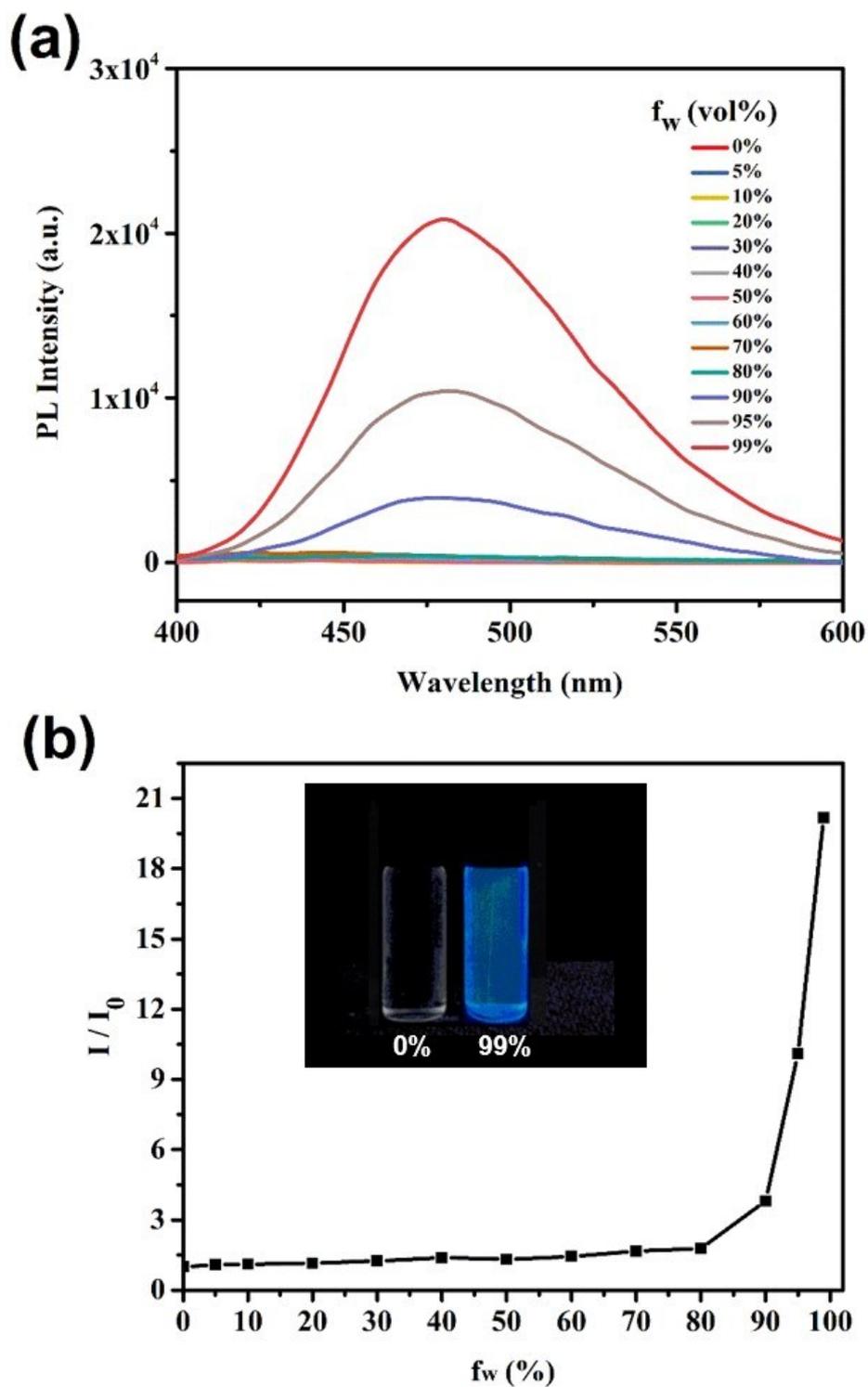


Fig. S9. a) Fluorescence spectra of polymer P12TPE in THF/H₂O mixtures with increased H₂O volume percentage ($\lambda_{\text{ex}} = 330 \text{ nm}$, $[\text{P12TPE}] = 40 \mu\text{g mL}^{-1}$); b) Plots of emission intensity ratio I/I_0 at the peak of 480 nm for P12TPE versus water percentage in the solution; Inset: comparative photographs of P12TPE in THF and THF/H₂O (1/99, v/v) mixture solution under UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$) illumination.

10. Fluorescence emission intensity comparison of polymers $PmTPE$ in their solution aggregate states and solid films, and an example for the measurement of absolute quantum yields by the integrating sphere method

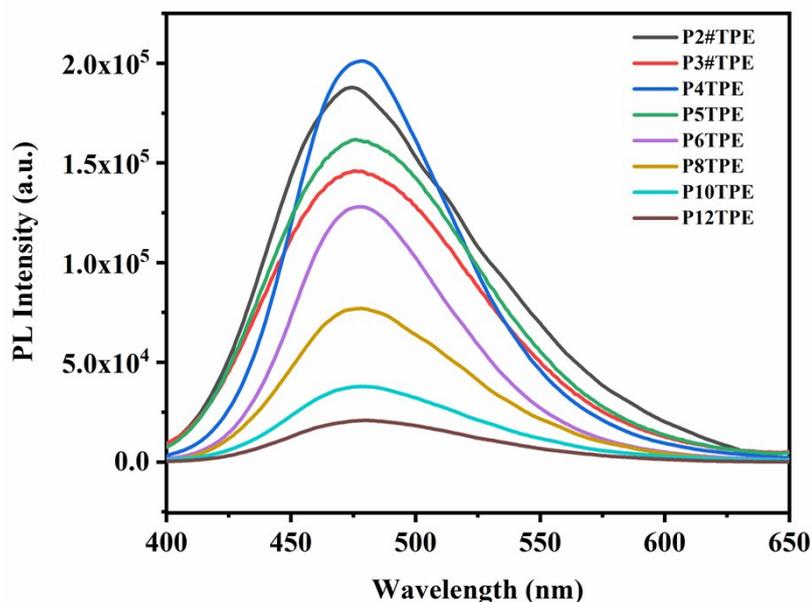


Fig. S10. Fluorescence emission intensity comparison of polymers $PmTPE$ ($m = 2\#, 3\#, 4, 5, 6, 8, 10, 12$) in their aggregate states in the THF/H₂O (1/99, v/v) mixture solutions with the same concentration of 40 $\mu\text{g mL}^{-1}$.

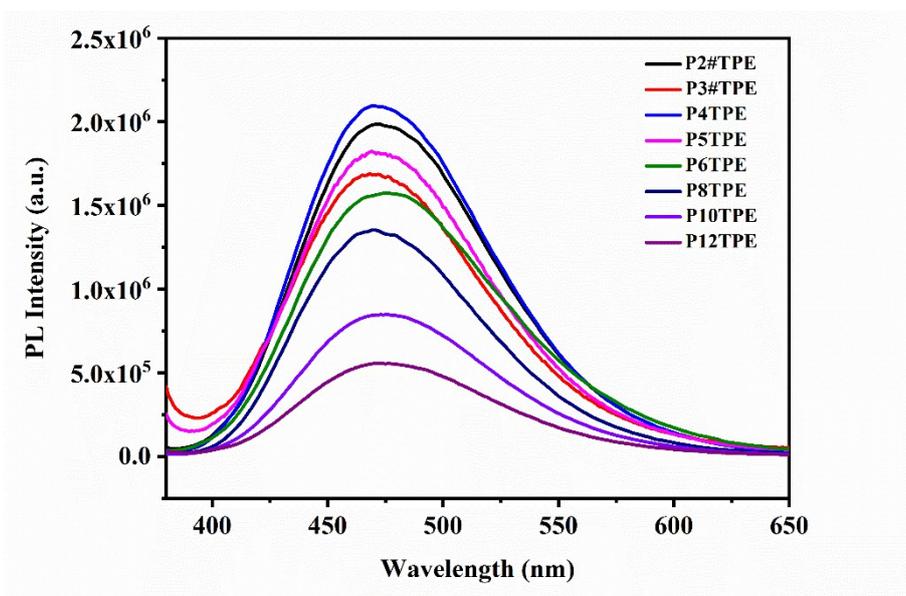


Fig. S11. Fluorescence emission intensity comparison of polymer films dip-coated from the THF solution at a concentration of 6 mg mL^{-1} of $PmTPE$ ($m=2\#, 3\#, 4, 5, 6, 8, 10, 12$).

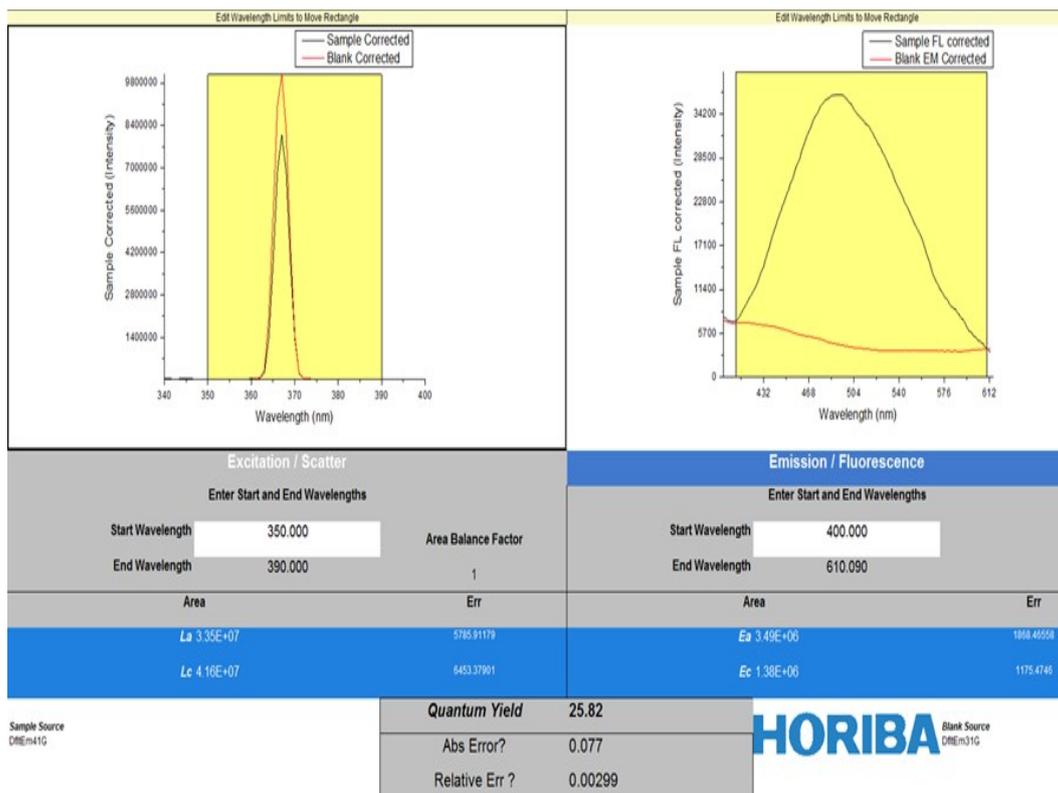


Fig. S12. An example to show the measurement signals by integrating sphere for the as-prepared P4TPE polymer film sample (black line) and the blank (red) in the excitation and emission areas. The measurements of absolute fluorescence quantum yields refer to the detailed and instructive protocol reported by Resch-Genger and coworkers.³

11. The Stern-Volmer plots of P4TPE thin film to variant concentration of TNT.

The Stern-Volmer plots of the P4TPE thin film quenched by different concentration TNT solutions are sketched as below with referring to the literature method.^{4,5}

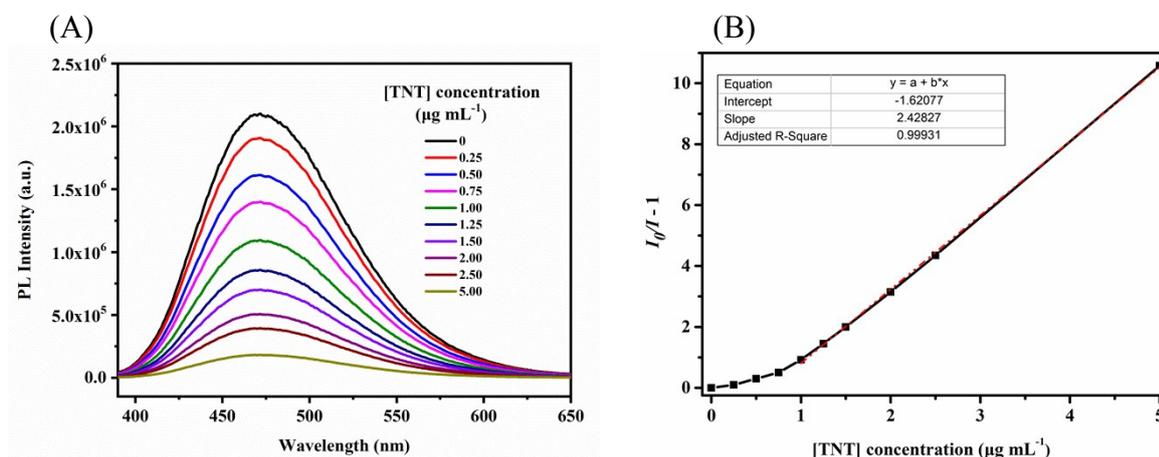


Fig. S13. (A) The fluorescence spectra of the P4TPE thin film after dripped with different concentration TNT solutions. (B) The Stern-Volmer plots of the P4TPE thin film quenched by variant concentration TNT solutions.

Equation:

$$I_0/I = K_{SV} \times [\text{TNT}] + 1$$

$$\text{Intercept} = -1.62077$$

$$\text{Slope} = 2.42827$$

$$\text{Adjusted R-Square} = 0.99931$$

$$K_{SV} = 2.428 (\mu\text{g/mL})^{-1}$$

$$\left(\frac{1 \times 10^{-6} \text{ g}}{227 \frac{\text{g}}{\text{mol}}} \right)^{-1}$$

$$= 2.428 \times 1 \times 10^{-3} \text{ L}$$

$$= 5.5116 \times 10^5 \text{ M}^{-1}$$

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