Electronic Supplementary Information for

Ultrahigh Sensitivity and Extremely Low Limit of Detection of Picric Acid with Ionic-Liquid Modified Poly(diphenylacetylene)

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Experimental Section

Caution! *Highly explosive nitro-explosives such as PA and TNT must be handled with extreme caution, and the amount used should be carefully controlled to prevent accidents.*

Materials. 1-bromo-4-(trimethylsilyl)benzene, trimethylsilylacetylene, 4-iodobenzyl alcohol, 1-methylimidazole and lithium bis((trifluoromethyl)-sulfonyl)azanide were purchased from Bidepharm. Nitro-explosives including 4-nitrophenol (NP), 2,4-dinitrophenol (2,4-DNP)2,4-dinitrotoluene (2,4-DNT), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT), 4-nitroaniline (NA), nitrobenzene (NB), 1,3-dinitrobenzene (DNB) and all other reagents and chemicals were obtained without purification from Macklin, Aladdin, TCI, J&K Scientific, etc. All solvents such as THF and DMF used in the experiments are of spectroscopic grade.

Characterizations. The samples were characterized by nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR), gel permeation chromatograph (GPC), fluorescence spectrophotometer, UV-vis spectrophotometer. NMR spectra were recorded on a Bruker 400 MHz instrument in CDCl$_3$ by using tetramethylsilane (TMS) as an internal reference. The number-averaged molecular weight (M_w) and polydispersity index (PDI) were obtained using a PL-GPC 220 chromatograph (Polymer Laboratories, Ltd., Santa Clara/United States) equipped with an HP 1100 pump from Agilent Technologies (Shanghai, China) and differential refractive index (dRI) detectors. Photoluminescence spectra and fluorescence decay curves were collected from a FS1000 transient fluorescence spectrometer (Edinburgh Instruments) with an excitation source of xenon lamp. UV-Vis absorption spectra were recorded on UV-vis spectrophotometer of Cary 100. Inductively coupled plasma mass spectrometry (ICP-MS) was employed to determine the elemental weight fractions in the polymer, utilizing the PerkinElmer NexION 300X instrument model. The Photos were recorded by a Cannon EOS 90D. Cyclic voltammetry studies were carried out at a scan rate of 50 mV s^{-1} in an inert atmosphere using an electrochemical workstation consisted of a three-electrode system viz. reference electrode (Ag/AgNO$_3$), working electrode (glassy carbon), and counter electrode (Pt wire). A 0.1 M solution of tetra *n*-butyl ammonium hexafluorophosphate (TBAPF$_6$) in CH$_3$CN or CH$_2$Cl$_2$ was used as a supporting electrolyte and ferrocene as an internal reference. The polymer thermal analysis was tested using a Netzsch TG 209 F3 Tarsus instrument with a ramp rate of 10 °C/min. The DSC curves were measured with a TA DSC250 instrument at a ramp rate of 10 °C/min. And the AFM images were taken by Bruker Dimension Icon.

Synthesis of trimethyl(4-((trimethylsilyl)ethynyl)phenyl)silane. Pd(PPh$_3$)$_2$Cl$_2$ (21.0 mg, 0.03 mmol), CuI (11.4 mg, 0.06 mmol) and PPh$_3$ (15.7 mg, 0.06 mmol) were charged into a Schlenk tube with a stirring bar. Trimethylsilylacetylene (0.5 mL, 3.6 mmol), (4-bromophenyl)trimethylsilane (0.56 mL, 3 mmol), THF (super dry, 3.0 mL) and Et$_3$N (3.0 mL) were added by syringe respectively. The reaction mixture was heated at 70 °C for 12 h with stirring, and then was concentrated via reduced pressure. The residue was purified by chromatography with PE as the eluent, giving the product as yellow oil in 0.59 g (80%).

Synthesis of (4-ethynylphenyl)trimethylsilane. Trimethyl(4-((trimethylsilyl)-ethynyl) phenyl)silane (0.62 g, 2.5 mmol), K$_2$CO$_3$ (1.38 g, 10 mmol) and MeOH (10 mL) were charged into a 50 mL of round-bottomed flask. The mixture was stirring at room temperature for 5 h, and then was concentrated via reduced pressure directly. The residue was purified by chromatography with PE as the eluent, giving the product as

yellow oil (0.31 g, 71%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.47 (s, 4H), 3.08 (s, 1H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 143.0, 136.7, 134.4, 132.5, 120.5, 90.0, 0.

Synthesis of 1-(*p*-trimethylsilyl)phenyl-2-(*p*-hydroxyethyl)phenylacetylene. First, a 500 mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar, followed by flushing with nitrogen. Second, 2-(4-iodophenyl)ethanol (12.4 g, 50.0 mmol), PdCl$_2$(Ph$_3$P)$_2$ (0.0964 g, 0.138 mmol), Ph$_3$P (0.157 g, 0.598 mmol), and CuI (0.149 g, 0.780 mmol) were added into the flask. Third, triethylamine (150 mL) was added into the flask, followed by the addition of p-trimethylsilylphenylacetylene (11.2 g, 64.2 mmol) in triethylamine (50 mL) at room temperature. The reaction mixture was stirred at reflux temperature for 24 h and then allowed to cool to room temperature. After the evaporation of triethylamine, the crude product was dissolved in ether (300 mL), and the insoluble salt was filtered off. The solution was washed three times using 1.0 M HCl aq., and ether was evaporated. This product was purified by silica-gel column chromatography (eluent: EtOAc:PE = 1:4) and then recrystallized three times from hexane to give white crystals to afford 1-(*p*-trimethylsilyl)phenyl-2-(*p*-hydroxyethyl)phenylacetylene (10.2 g, 69 % yield).

Synthesis of 1-(*p*-trimethylsilyl)phenyl-2-(*p*-bromoethyl)phenylacetylene. To a solution of 1-(*p*-trimethylsilyl)phenyl-2-(*p*-hydroxyethyl)phenylacetylene (4.4 g, 15 mmol) in anhydrous Et$_2$O (100 mL) were added carbon tetrabromide (6.1 g, 18 mmol) and triphenylphosphine (4.7 g, 18 mmol). The reactants was mixed at ambient temperature for 12 h, filtered, and the filtrate was concentrated under reduced pressure. Purification on silica gel with PE/EtOAc = 8:2 as eluent led to the desired compound and then recrystallized three times from methanol to give white needle-shaped crystals (4.5 g, 84 % yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.49 (d, 4H), 7.21 (d, 2H), 3.57 (t, 2H), 3.18 (t, 2H), 1.55 (s, 1H), 0.27 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 143.2, 140.3, 134.4, 133.1, 131.9, 129.9, 124.7, 123.2, 90.9, 90.7, 40.4, 33.7, 0.

Polymerization. Polymerization was carried out in a glass tube equipped with a three-way stopcock under dry nitrogen. Unless otherwise specified, the reaction was carried out at 60 °C for 1 h under the following conditions: [monomer] = 0.125 M, [TaCl$_5$] = 12.5 mM, and [*n*-Bu$_4$Sn] = 25 mM. A detailed procedure of polymerization is as follows: The monomer solution was prepared in a glass tube. Another glass tube was charged with TaCl$_5$, *n*-Bu$_4$Sn, and 1,2-dichloroethane; this catalyst solution was aged at 80 °C for 10 min, and then monomer solution was added to it. Polymerization was run at 60 °C for 1 h, which was quenched with a small amount of methanol. The resulting polymer **P1** was isolated by precipitation into a large excess of methanol, and its yield was determined gravimetrically. Due to the high molecular weight, the corresponding peaks of the polymers could not be detected by NMR spectroscopic method.

Substitution of 1-methylimidazole. The reaction was carried out at 70 °C using an excess of 1-methylimidazole. A detailed procedure is as follows: **P1** (ca. 0.50 g) was put into a flask. A mixture of 1-methylimidazole (7.0 mL) and CH$_3$CN (43 mL) was poured into the flask, and the flask was heated at 70 °C. After 72 h, the resulting polymer **P2** was isolated by precipitating the mixed solution into a large excess of EtOAc.

Exchange of counter anion. The reaction was carried out at rt. using an excess of (CF$_3$SO$_2$)$_2$NLi. A detailed procedure is as follows: **P2** (ca. 0.30 g) was put into a flask. A mixture of (CF$_3$SO$_2$)$_2$NLi (10.0 g) and

MeOH (50 mL) was poured into the flask at room temperature. After stirring for 72 h, the resulting polymer P3 was isolated by precipitating the mixed solution into a large excess of H_2O.

Stern-Volmer Plot and Detection Limit Calculations. To study the quenching efficiency, a Stern−Volmer (SV) plot was obtained as I_0/I vs [Q], where I_0 is the initial emission intensity of P3 and I indicates the emission intensity after adding quencher molecule [Q] i.e. PA. The slope of the curve represents Stern-Volmer constant (K_{SV}). To determine the limit of detection (LOD), different P3 solutions (100 μM) each containing variable concentrations of PA were subjected to fluorescence measurement by exciting at 440 nm. A curve was plotted between the change in emission intensity and concentration of PA. LOD value was then calculated using the known equation:

LOD = 3 σ/s

Where, σ denotes standard deviation of emission intensity of P3 in the presence of PA and s represents the slope of the curve.

Theoretical Calculation. All the compounds were fully optimized with the density functional theory (DFT) method by using B3LYP density functional and 6-31G(d) basis setS3. London-dispersion effects were also taken into consideration using Grimme's DFT-D3 correction, to further describe long range interactionsS4.

(S3) (a) Hariharan, P. C.; Pople, J. A. Accuracy of AH Nequilibrium Geometries by Single Determinant Molecular Orbital Theory. *Mol. Phys.* 27,209-214(1974). (b) Petersson, G. A. Bennett, A.; Tensfeldt, T. G.; Laham, Al, M. A., Shirley, W. A.; Mantzaris, J. A Complete Basis Set Model Chemistry. I. the Total Energies of Closed-Shell Atoms and Hydrides of the First-Row Elements. *J. Chem. Phys.* 89, 2193-2218(1988).

(S4) (a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* 132, 154104 (2010). (b) S. Grimme, S. Ehrlich, L. Goerigk, Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput, Chem.* 32, 1456-1465(2011).

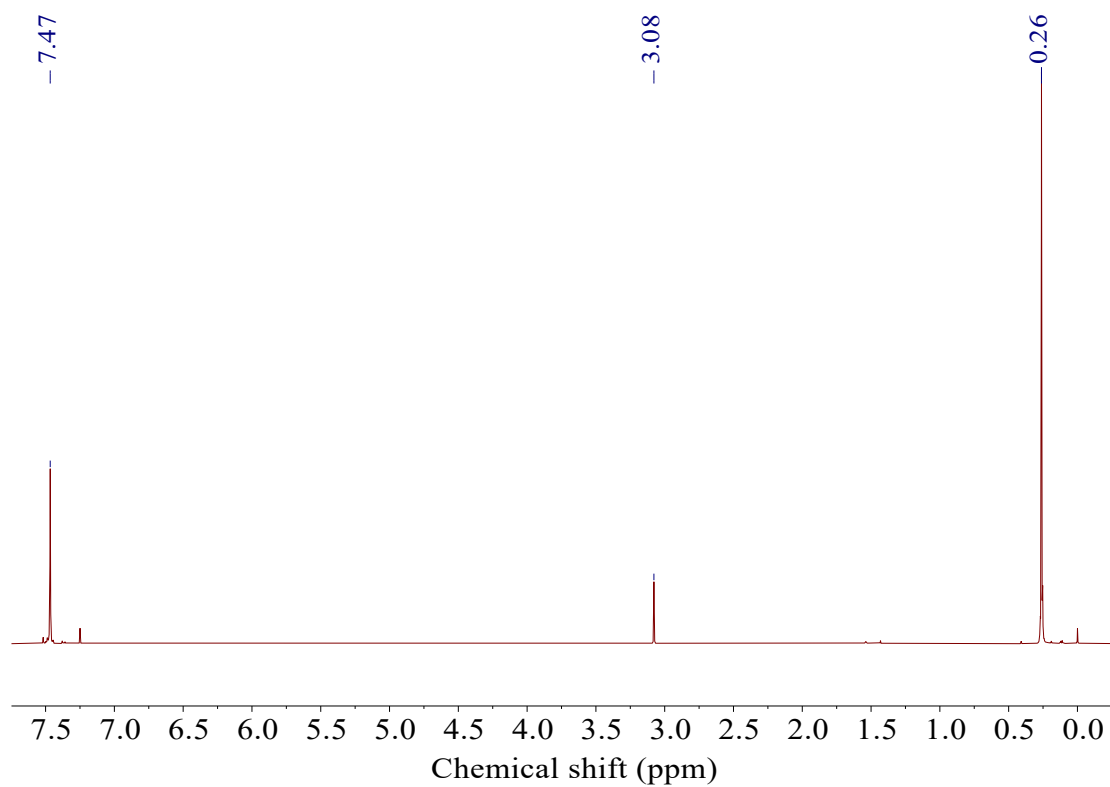**Scheme S1.** Synthetic route to the monomer and P1.

Pd(PPh₃)₂Cl₂ , CuI,
PPh3 , Et₃N

THF , 70 ºC

K₂CO₃
MeOH

Pd(PPh₃)₂Cl₂ , CuI,
PPh3 , Et₃N

CBr₄ , PPh₃
Et₂O

monomer

Polymerization

P1
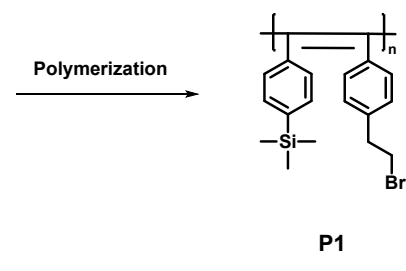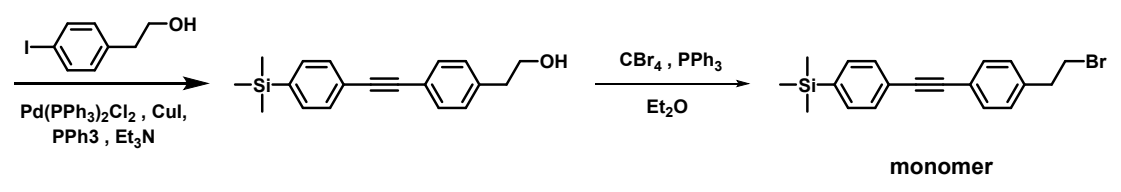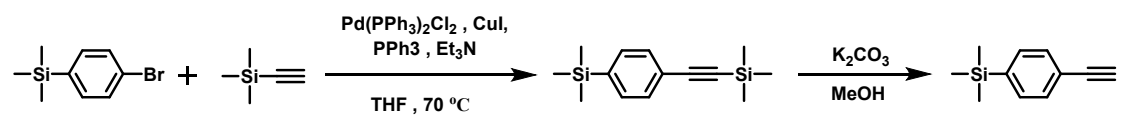
Figure S1. ^1H NMR spectra of (4-ethynylphenyl)trimethylsilane dissolved in CDCl$_3$, 400 Hz.
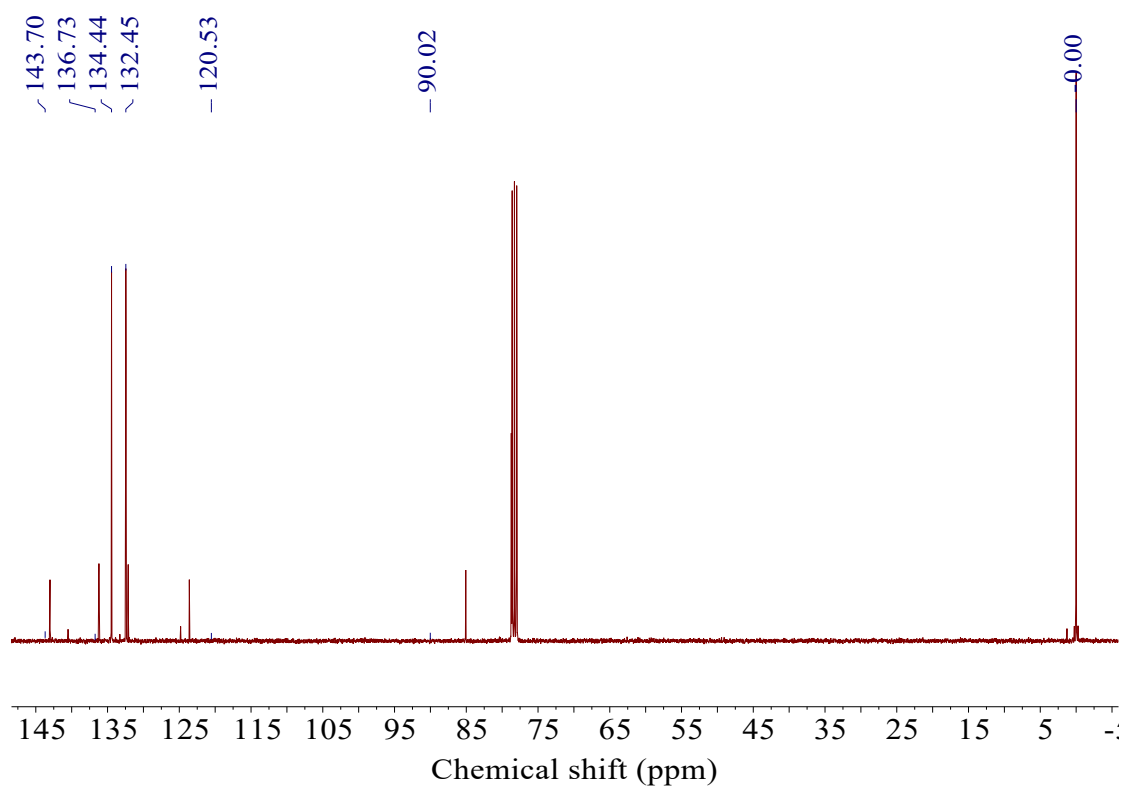

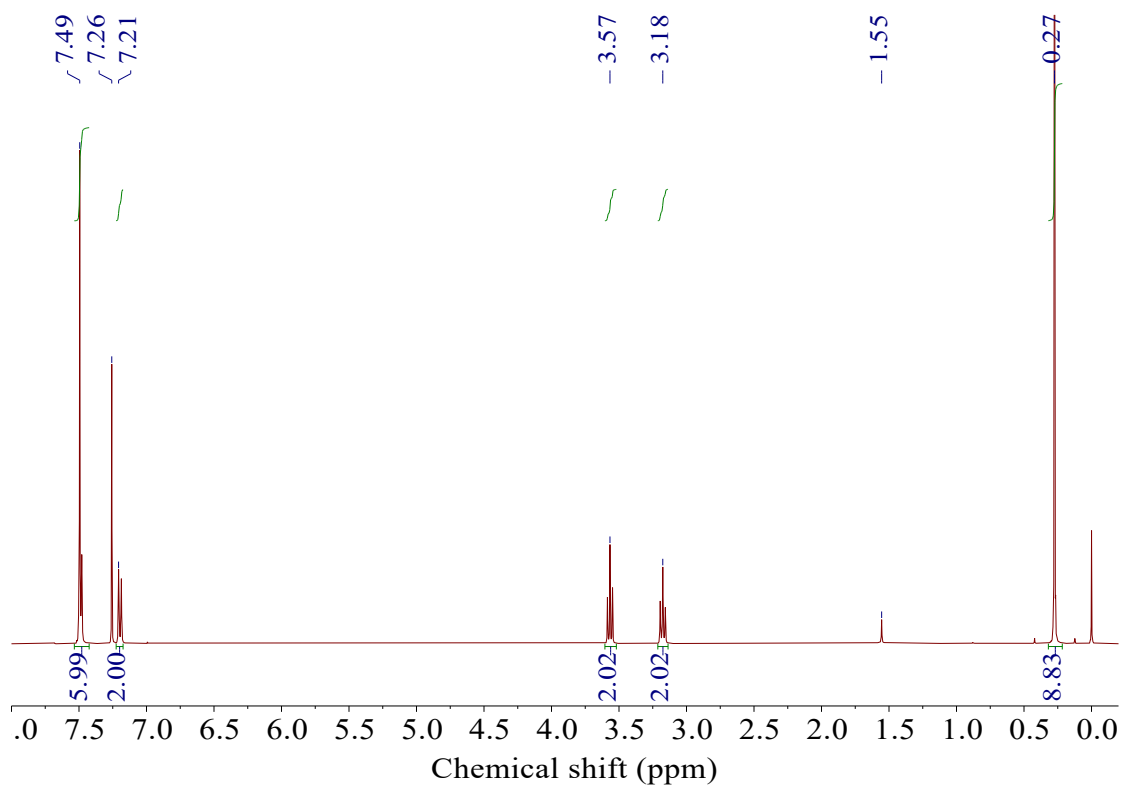**Figure S2**. ^{13}C NMR spectra of (4-ethynylphenyl)trimethylsilane dissolved in CDCl$_3$, 400 Hz.

Figure S3. ¹H NMR spectra of 1-(*p*-trimethylsilyl)phenyl-2-(*p*-bromoethyl)phenylacetylene dissolved in CDCl₃, 400 Hz.
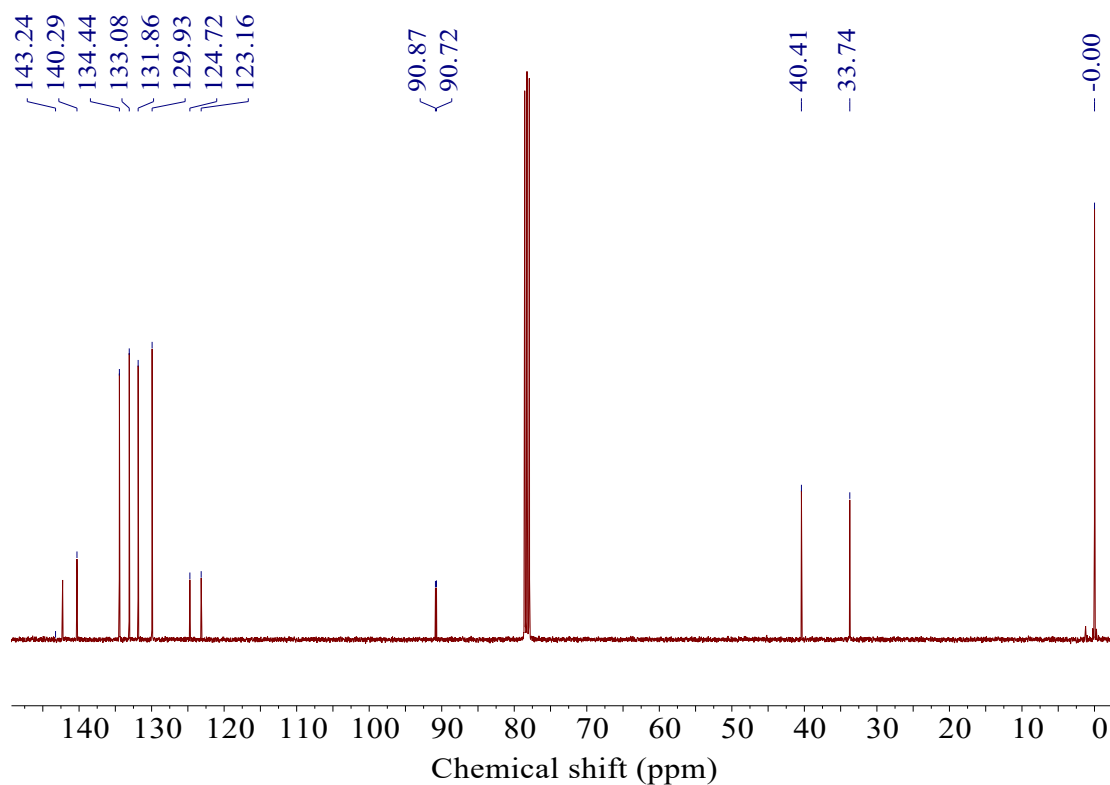

Figure S4. ¹³C NMR spectra of 1-(*p*-trimethylsilyl)phenyl-2-(*p*-bromoethyl)-phenylacetylene dissolved in CDCl₃, 400 Hz.

Table S1. Solubility of the resulted polymers[a].

Polymer	Hexane	Toluene	CHCl$_3$	DCM	THF	ACE	ACN	DMSO	DMF	MeOH
P1	-	+	+	+	+	-	-	-	-	-
P2	-	-	-	-	-	-	+	+	+	+
P3	-	-	-	-	-	+	+	+	+	+

[a] +, soluble; ±, partially soluble; –, insoluble.

Table S2. The results of the ICP-MS measurements.

Entry	Sample weight (mg)	Fixed volume (mL)	Analyte element	Element concentration (µg/kg)	Element content (%)
1	48.0	25	Si	24497104.8	2.45
2	48.0	25	Si	24530672.5	2.45
3	48.0	25	S	78482153.5	7.85
4	48.0	25	S	78579779.4	7.86
5	54.0	25	Br	480769.9	0.05
6	54.0	25	Br	479248.6	0.05
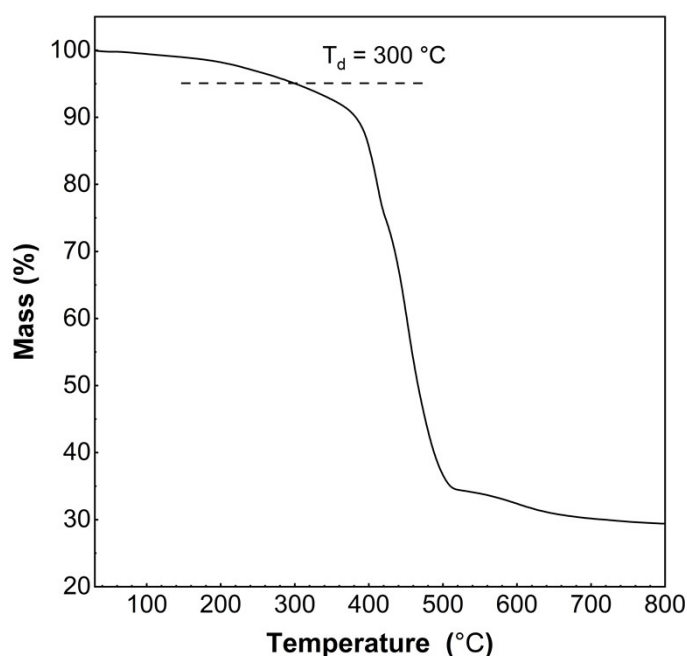
Figure S5. TGA thermograms of P3. T_d (decomposition temperature) represents the temperature of 5% weights loss.
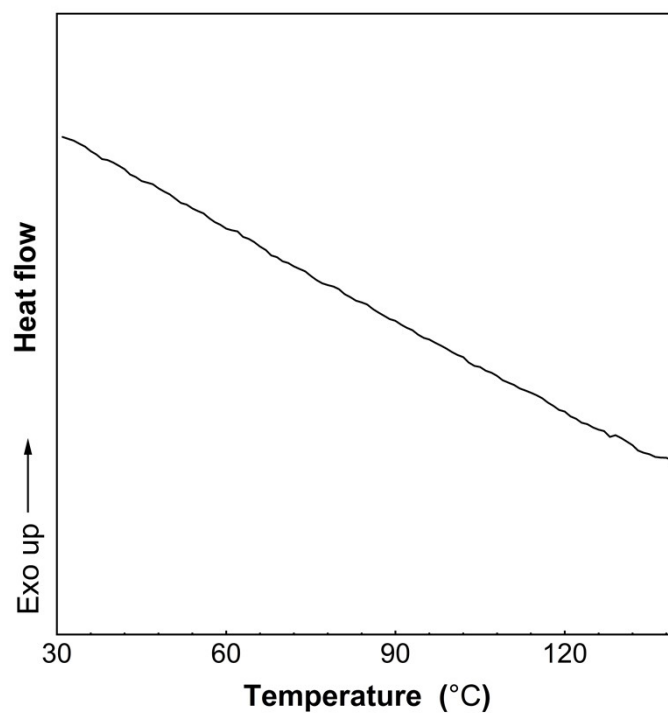
Figure S6. DSC curve of P**3**.
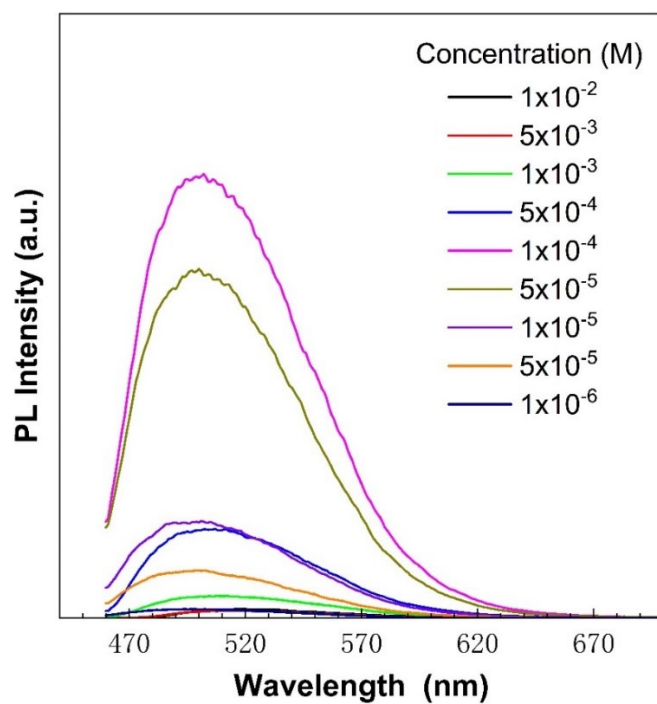
Figure S7. Photoluminescence (PL) spectra of P**3** in DMF with different concentrations, concentration of P**3** (c) = 10^{-5} M, excitation wavelength (λ_{ex}) = 440 nm.
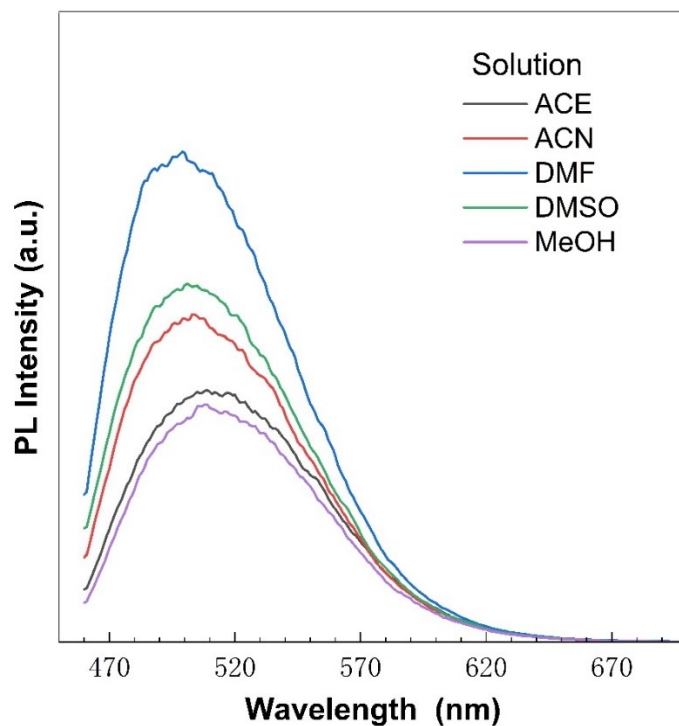
Figure S8. PL spectra of **P3** in different solvents, c $= 10^{-4}$ M, $\lambda_{ex} = 440$ nm.
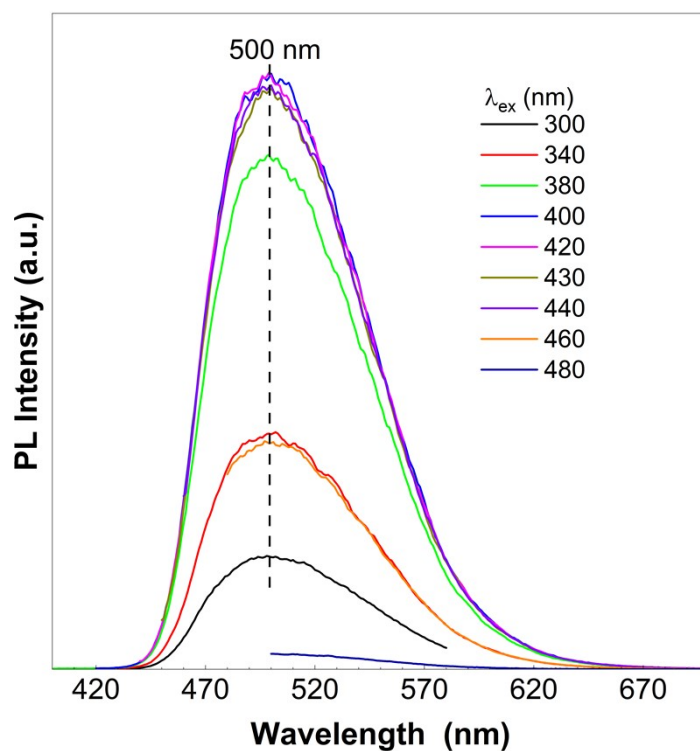
Figure S9. PL spectra of **P3** in DMF (c $= 10^{-4}$ M) excited at different wavelengths.
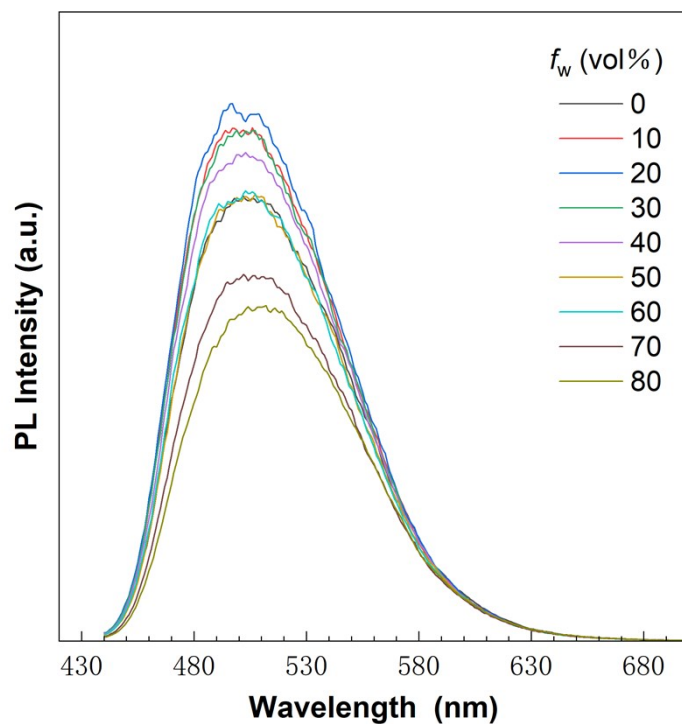
Figure S10. PL spectra of P**3** in DMF/water mixtures with different water fractions (f_w). f_w = volume fraction of water in water/DMF mixtures. Concentration (c) = 10^{-5} M, λ_{ex} = 440 nm.
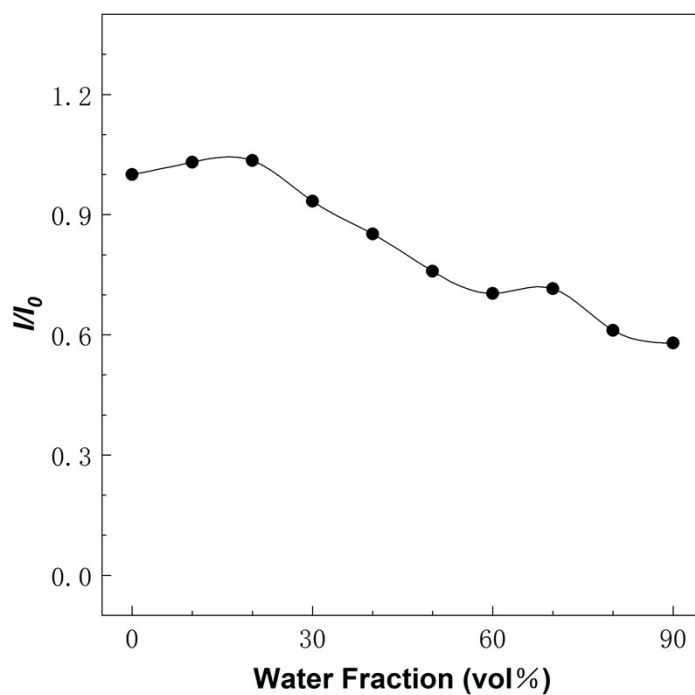
Figure S11. Plots of relative PL intensity (I/I_0) versus f_w. c = 10^{-5} M, λ_{ex} = 440 nm, I_0 = intensity at f_w = 0%, where f_w = volume fraction of water in water/DMF mixtures.
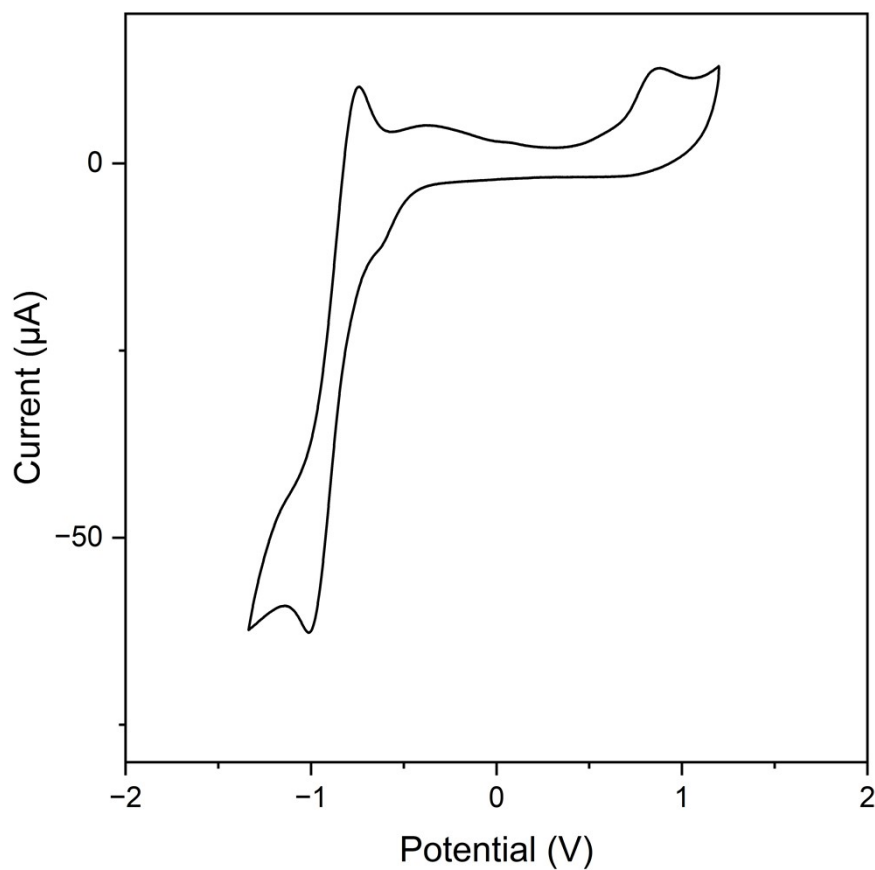
Figure S12. Cyclic voltammogram (CV) of **P3** film obtained on glassy carbon electrode with a scan rate of 50 mV s^{-1}. The detailed calculations are summarized as follows: The HOMO energy level was estimated based on the following equation:

E_{HOMO} (eV) $= - (E_{red\text{-}onset} + 4.8) = - (E_{pc\text{-}onset} - E_{Fc} + 4.8)$

$E_{Fc} = 0.23$ eV

The LUMO level was calculated based on the optical band gap obtained from absorption onset.

$E_{HOMO} = - (4.8 + E_{pc\text{-}onset} - E_{Fc}) = - (4.8 - 0.558 - 023) = -5.12$ eV

$(E_g\,^{optical} = 2.69$ eV)

$E_{LUMO} = E_{HOMO} + E_g\,^{optical} = -5.12 + 2.69 = -2.43$ eV
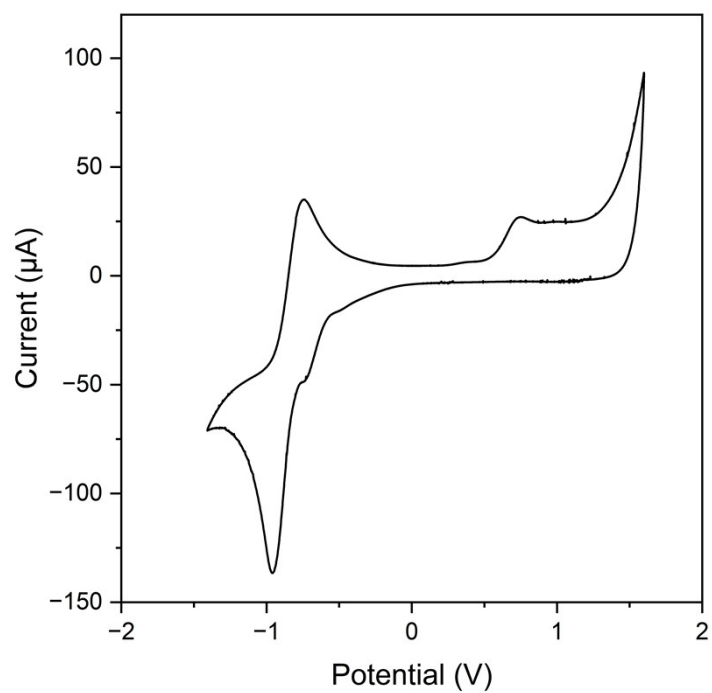
Figure S13. Cyclic voltammogram of **P1** film obtained on glassy carbon electrode, scan rate: 50 mV s^{-1}.
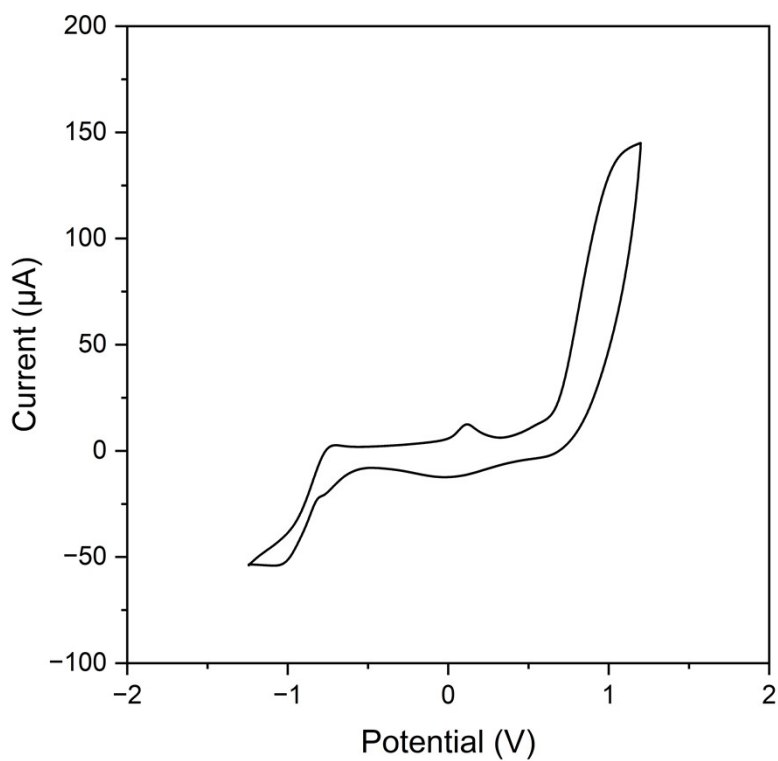
Figure S14. Cyclic voltammogram of **P2** film obtained on glassy carbon electrode, scan rate: 50 mV s^{-1}.
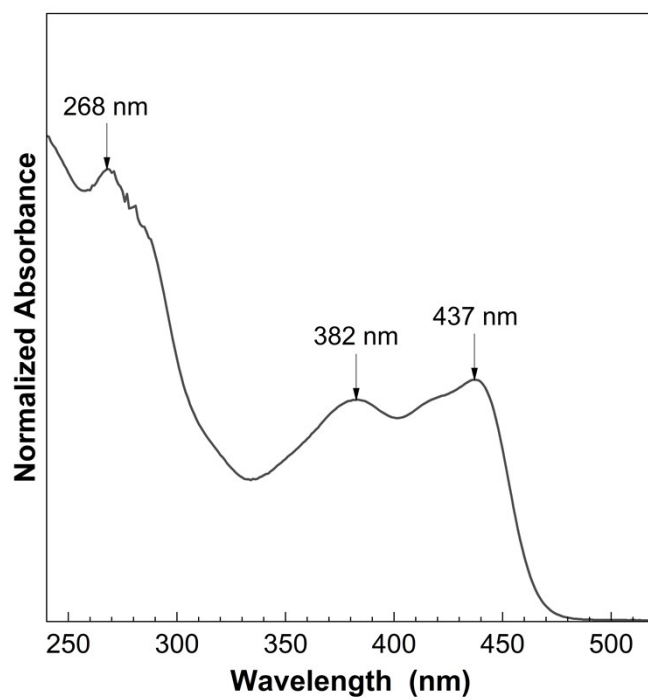
Figure S15. The normalized absorption spectra of P**1** in THF (c = 10^{-4} M).
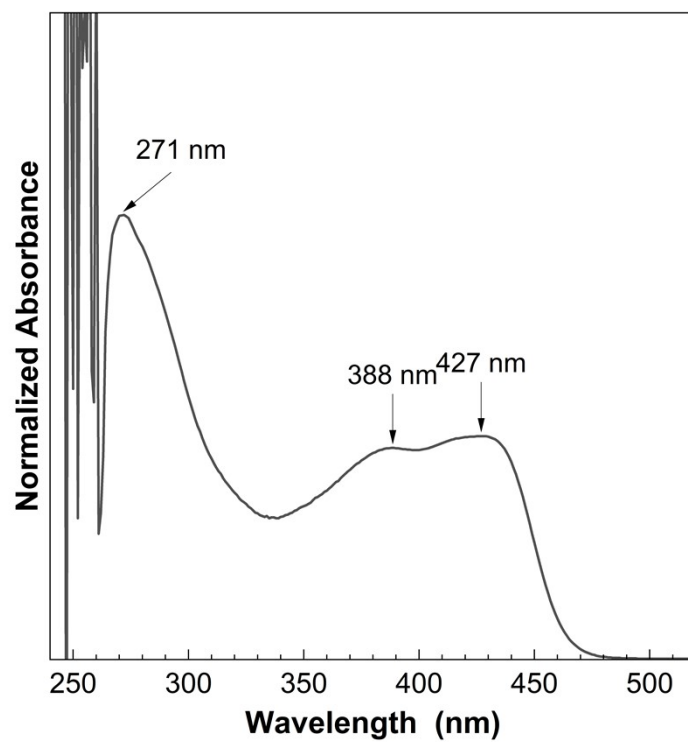
Figure S16. The normalized absorption spectrum of P**2** in DMF (c = 10^{-4} M).
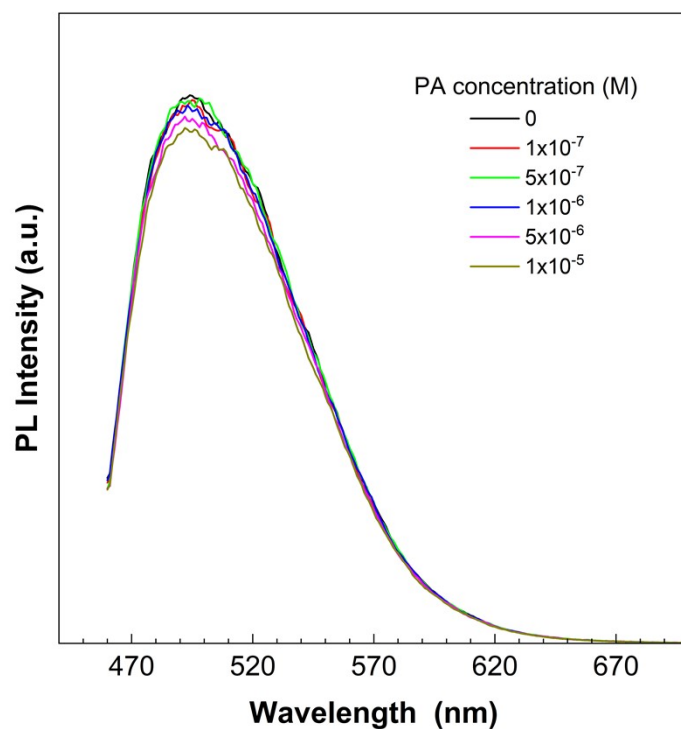
Figure S17. Fluorescence response of **P1** (c = 10^-4 M) to the addition of different amounts of picric acid (PA) into THF solution, λ_{ex} = 440 nm.
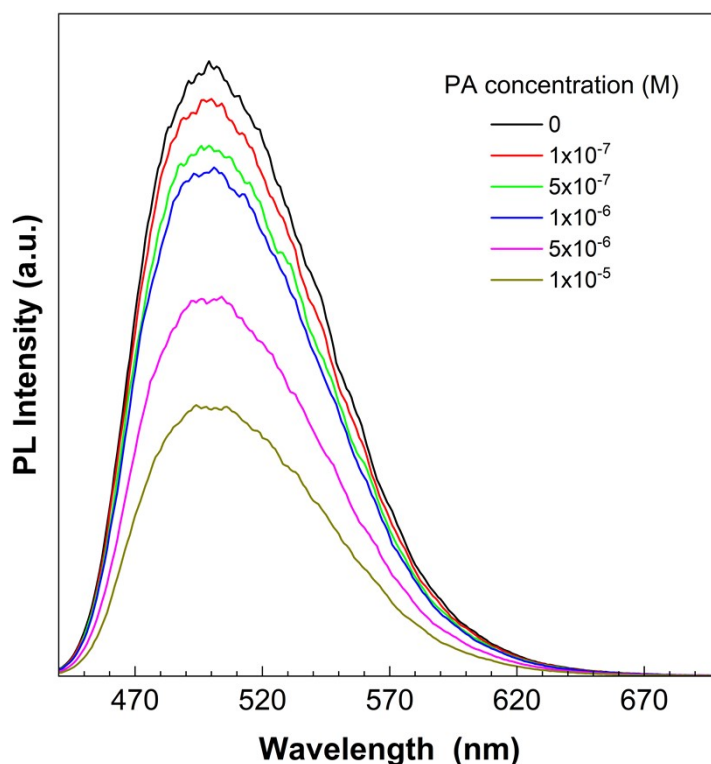
Figure S18. Fluorescence response of **P2** (c = 10^-4 M) to the addition of different amounts of picric acid (PA) into DMF solution, λ_{ex} = 420 nm.
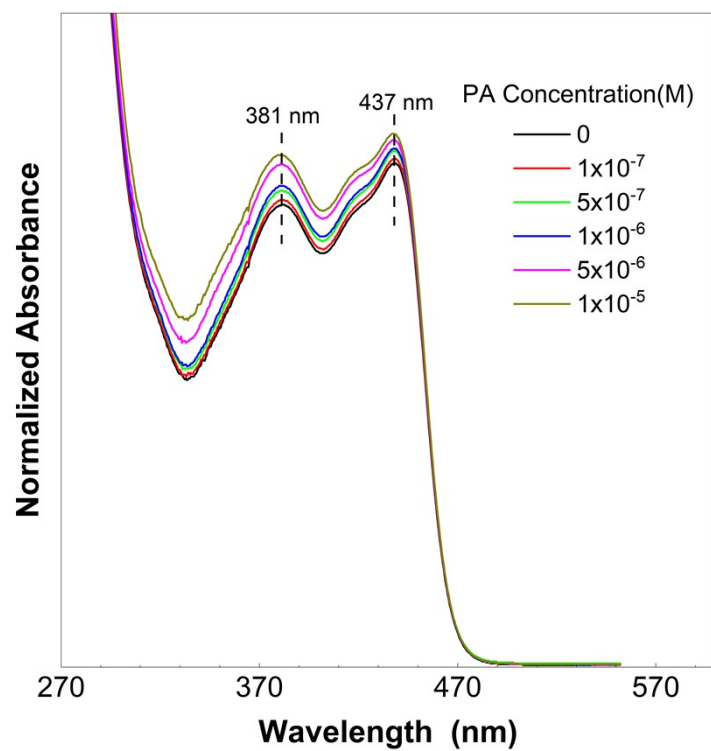
Figure S19. UV/vis absorption spectra of **P1** (10^{-4} M) upon additions of PA in THF solution.
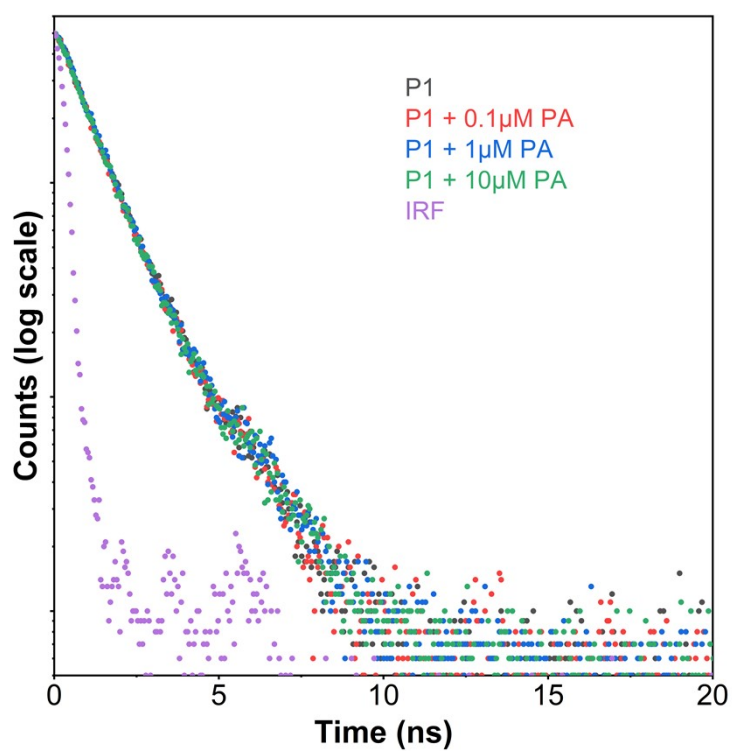
Figure S20. Time-resolved decay curves of **P1** (10^{-4} M) in absence and presence of different concentrations of PA.
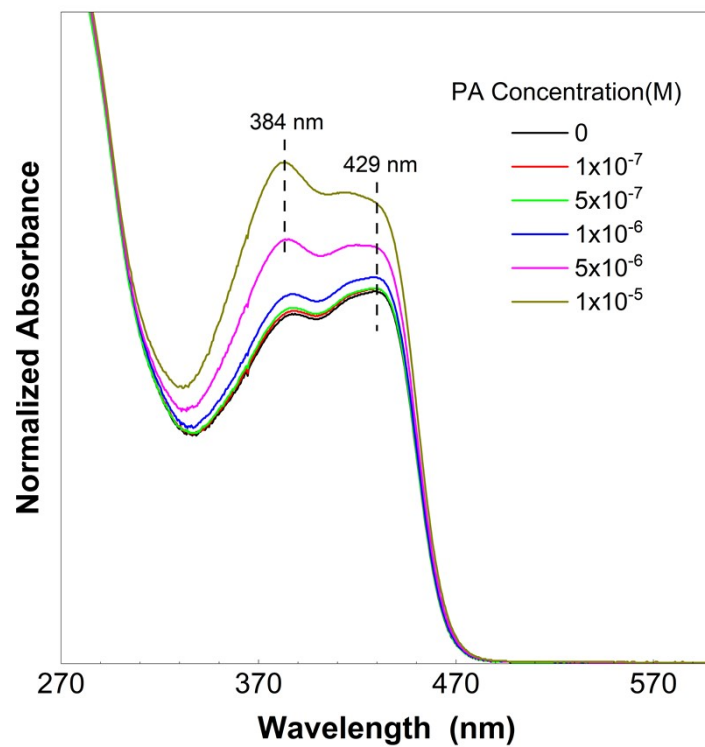
Figure S21. UV/vis absorption spectra of **P2** (10^{-4} M) upon additions of PA in DMF solution.
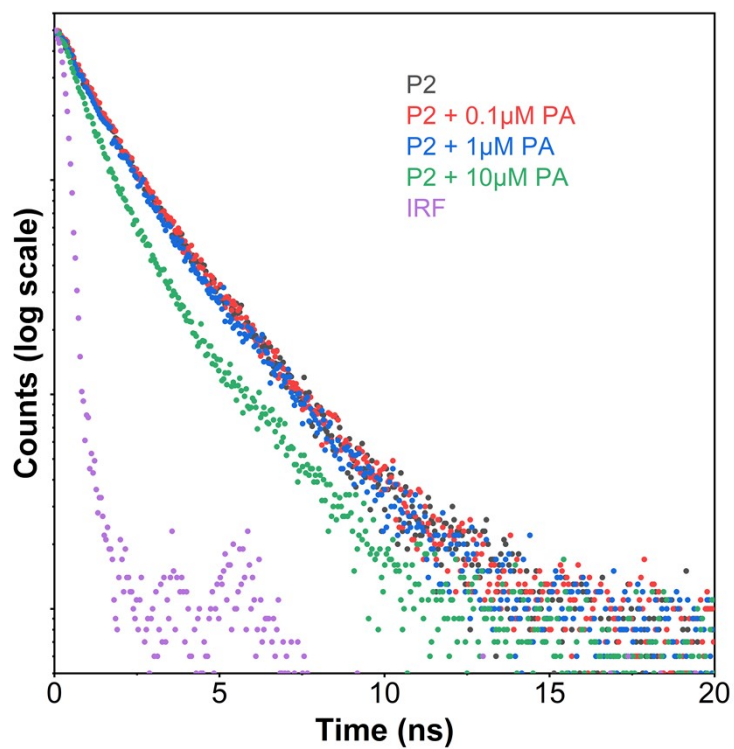

Figure S22. Time-resolved decay curves of **P2** (10^{-4} M) in absence and presence of different concentrations of PA.
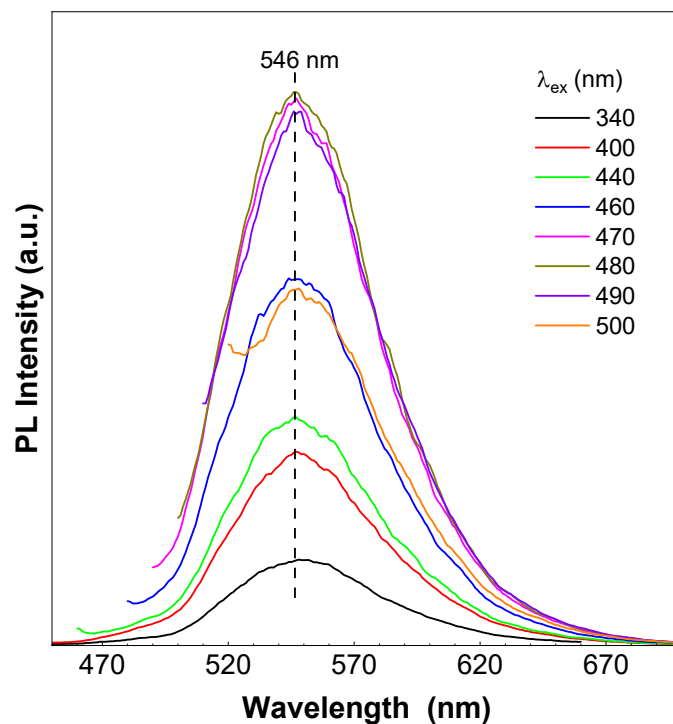
Figure S23. PL spectra of **P3** solid film recorded at different excitation wavelengths.

Film formation: Films coated on glass substrates were prepared by the spin-coating process. Polymer films were spin-coated from acetonitrile solutions onto a glass plate (microscope slide, 20*20*1 mm) and spun at 2000 rpm by using a Chemat KW-4A spin-Coater. To prepare thick films, 5-10 mg of **P3** in 1 mL of solvent were used.
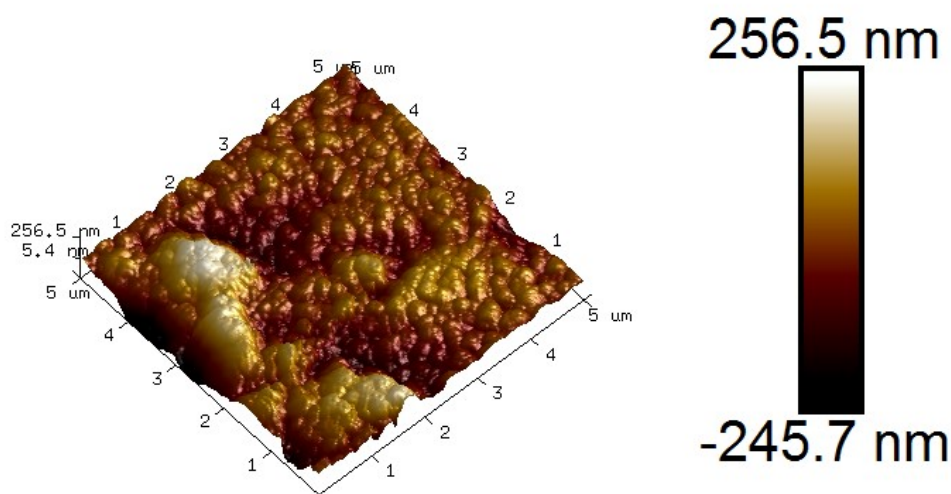

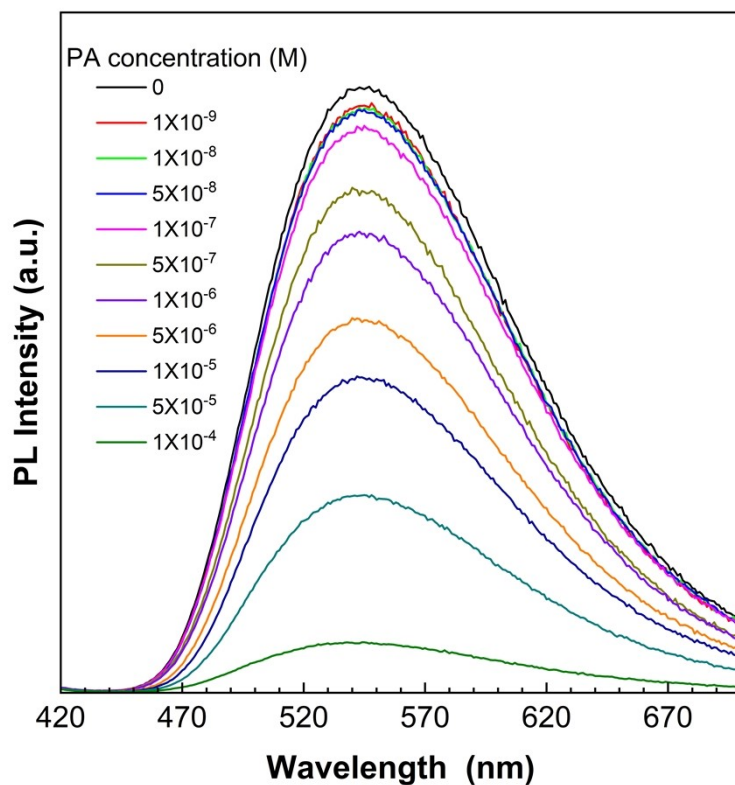**Figure S24.** A typical AFM image of **P3** film obtained by spin-coating.

Figure S25. PL response of P**3** solid film after immersed into PA water solutions with different concentrations, λ_{ex} = 400 nm.
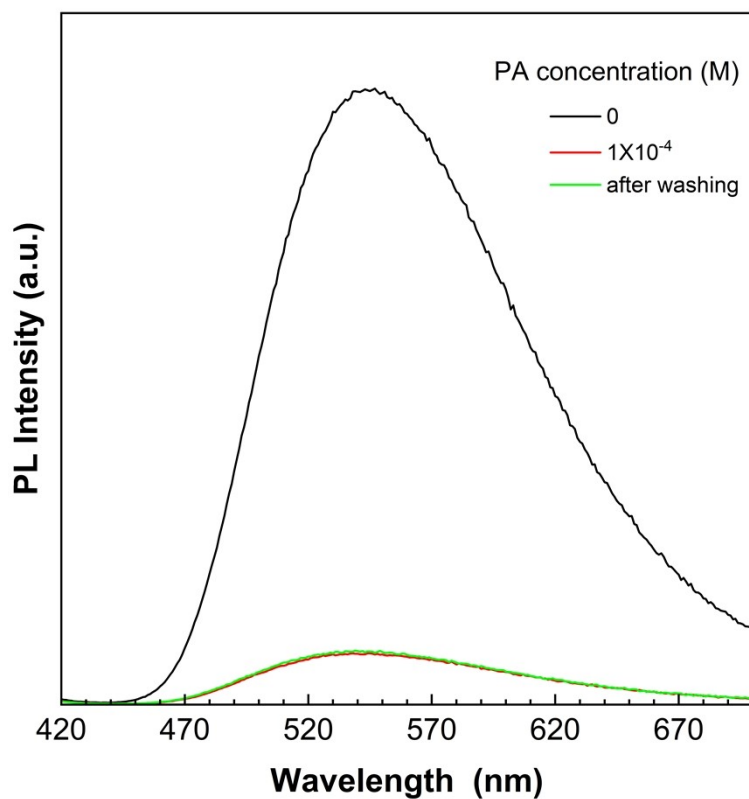

Figure S26. PL spectra of P**3** solid film after immersed in pure water for 30 s and PA water solution for 30 s (10^{-4} M), and then washed with water, λ_{ex} = 400 nm.