
Supporting Information

Polyurethane Derivatives for Highly Sensitive and Selective Fluorescent Detection of 2,4,6-Trinitrophenol (TNP)

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1. Experimental details

General

Materials obtained from commercial suppliers were used without further purification unless otherwise stated. All glassware, syringes, magnetic stirring bars, and needles were thoroughly dried in a convection oven. ^1H NMR spectra were recorded at 25 °C on a Varian 500 MHz spectrometer and were referenced internally to the residual proton resonance in DMSO- d_6 (δ 2.5 ppm). The molecular weights of the polymers were calculated from their ^1H NMR spectra. UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Photoluminescence spectra were collected on an Edinburgh FLS920 spectrophotometer.

Synthesis of PU Derivatives

PU1. A mixture of 2,5-dihydroxyterephthalic acid (2.62 mmol), polyethylene glycol mono-methyl ether ($M_w = 200 \text{ g mol}^{-1}$; 1.98 mmol), anhydrous THF (8 mL), hexamethylene diisocyanate (3.61 mmol) and DABCO (0.105 mmol) were added to dried two-neck round-bottom flask. The solution was heated at 75°C for 8 h under nitrogen atmosphere. After the clear solution became significantly viscous, product precipitated from excess diethyl ether. Then the product was dried under vacuum for 24 h to obtain the resulting **PU1** Yield: 84.6%. ^1H NMR (500 MHz, DMSO- d_6 , δ [ppm]): 12.41 (s, 2H), 7.01-7.95 (broad, 2H), 4.02 (s, 4H), 3.36-3.69 (broad, PEG protons), 3.23 (s, 6H; PEG terminal -OCH₃ protons), 2.63-2.98 (broad, 4H), 1.45 (broad, 4H), 1.29 (broad, 4H). FTIR: 3323 cm^{-1} (N-H), 2859 and 2941 cm^{-1} (-CH₂- asymmetric and symmetric stretch), 1704 (C=O), 1193 cm^{-1} (C-O-C stretch PEG). The molecular weight is 716 g mol^{-1} calculated from the ^1H NMR spectra.

PU2. The synthetic procedure for **PU2** was the same as **PU1**, except monomer hydroquinone (2.62 mmol) was used instead of 2,5-dihydroxyterephthalic acid. Yield: 83%. ^1H NMR (500 MHz, DMSO- d_6 , δ [ppm]): 7.04-7.21 (broad, 4H ;), 4.03 (s, 4H), 3.39-3.61 (broad, PEG protons), 3.23 (s, 6H; PEG terminal -OCH₃ protons), 2.98 (broad, 4H), 1.41 (broad, 4H), 1.26 (broad, 4H). FTIR: 3326 cm^{-1} (N-H), 2859 and 2942 cm^{-1} (-CH₂- asymmetric and symmetric stretching), 1705 cm^{-1} (C=O), 1193 cm^{-1} (C-O-C stretching PEG). The molecular weight is 1077 g mol^{-1} calculated from the ^1H NMR spectra.

PU3. The synthetic procedure of **PU3** was the same as **PU1**, except monomer 2, 7-dihydroxynaphthalene (2.62 mmol) was used instead of 2,5-dihydroxyterephthalic acid.

Yield: 80.5%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$, δ [ppm]): 7.04-7.95 (broad, 6H), 4.04 (broad, 4H), 3.45-3.62 (broad, PEG protons), 3.23 (s, 6H; PEG terminal $-\text{OCH}_3-$ protons), 3.01 (s, 4H), 1.43 (s, 4H), 1.31 (s, 4H). FTIR: 3322 cm^{-1} (N-H), 2858 and 2940 cm^{-1} ($-\text{CH}_2-$ asymmetric and symmetric stretching), 1704 cm^{-1} (C=O), 1191 cm^{-1} (C-O-C stretching PEG). The molecular weight is 3112 g mol^{-1} calculated from the ^1H NMR spectra.

Procedure for the sensing studies in the solution

Stock solutions of nitro-aromatic compounds, namely, picric acid (TNP), nitrobenzene (NB), 2,4-dinitrophenol (2,4-DNP) p-nitrophenol (NP), trinitrotoluene (TNT), 4-nitrotoluene (NT), 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) were prepared in acetonitrile-water mixture (1:1 v/v) at concentrations of $1 \times 10^{-3}\text{ M}$, respectively. The absorption and fluorescence measurements of PUs ($1 \times 10^{-5}\text{ M}$) were carried out by sequentially adding different nitro-aromatic compounds in a quartz cuvette ($3\text{ cm} \times 3\text{ cm}$). The absorption and fluorescence spectra of the resultant mixtures were then recorded after mixing thoroughly at room temperature.

Fluorescence quenching (%) measurement

The quenching percentage was calculated using the equation as follows:

$$\text{Fluorescence quenching \%} = (1 - I/I_0) \times 100\%$$

where I_0 is the initial fluorescence intensity in the absence of analyte, I is the fluorescence intensity in the presence of corresponding analyte.

Fluorescence quenching titration study

The Stern–Volmer relationship establishes the correlation of intensity changes with the quencher concentration $[Q]$ as follows:

$$I_0/I = 1 + K_{SV}[Q]$$

where I_0 and I are the intensity, in the absence and presence of TNP, respectively, K_{SV} is the Stern-Volmer quenching constant and $[Q]$ is the concentration of TNP.

Benesi–Hildebrand equation

$$1/(F_0 - F_i) = 1/\{K_a * (F_0 - F_{\text{Min}}) * [\text{PA}]\} + 1/(F_0 - F_{\text{Min}})$$

where, F_0 is the fluorescence intensity of sensor, F_i is the fluorescence intensity obtained with TNP at different concentration, F_{Min} is the fluorescence intensity obtained with excess amount of TNP.

Lifetime measurements

$$F(t) = \sum \alpha_i \exp(t / \tau_i)$$

Where, α_i is a pre-exponential factor representing the fractional contribution to the time resolved decay of the component with a lifetime τ_i .

Method for detection limit calculation

The detection limit (LOD) was then calculated using the equation $3\sigma/K$, where σ is the standard deviation (SD) for PUs solution intensity in the absence of TNP and K denotes the slope of the curve.

2. Structural characterization of PUs

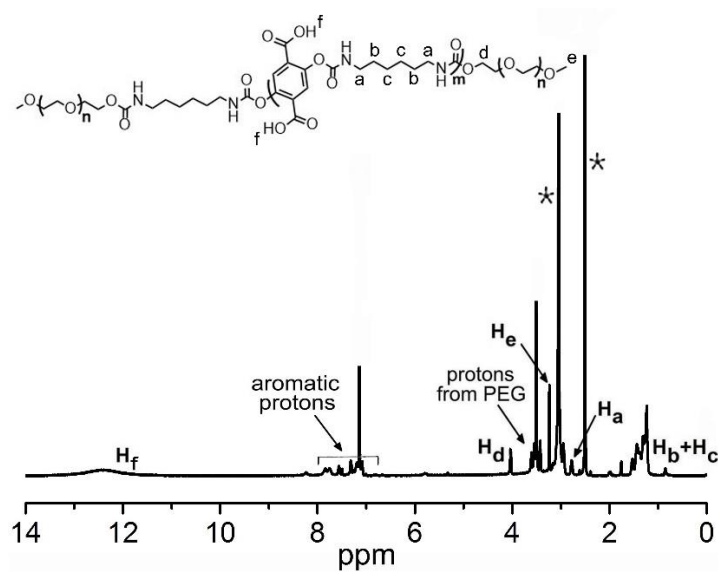


Fig. S1 ¹H NMR spectrum of **PU1** in DMSO-*d*₆ (* indicates peaks from the solvent and water)

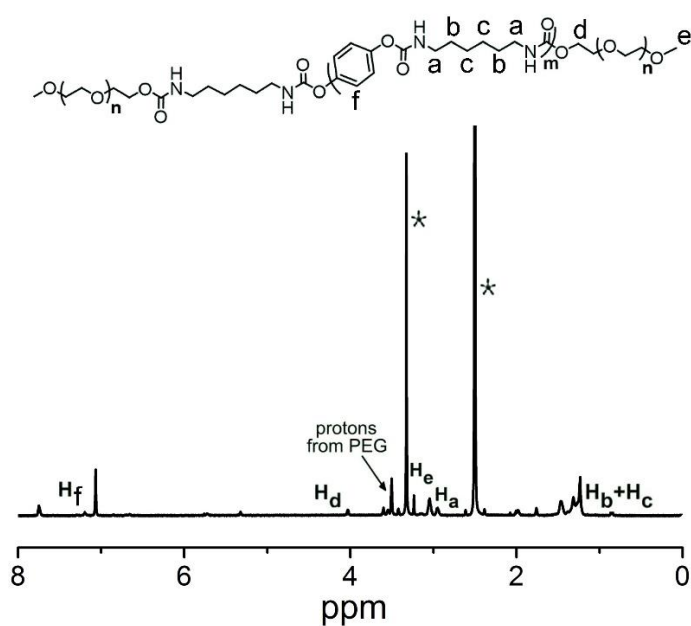


Fig. S2 ¹H NMR spectrum of **PU2** in DMSO-*d*₆ (* indicates peaks from the solvent and water)

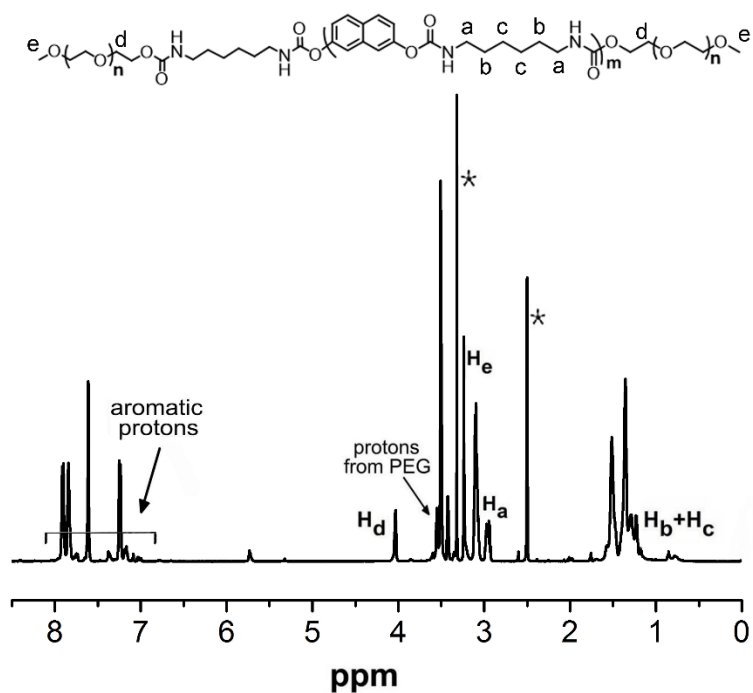


Fig. S3 ^1H NMR spectrum of **PU3** in $\text{DMSO-}d_6$ (* indicates peaks from the solvent and water).

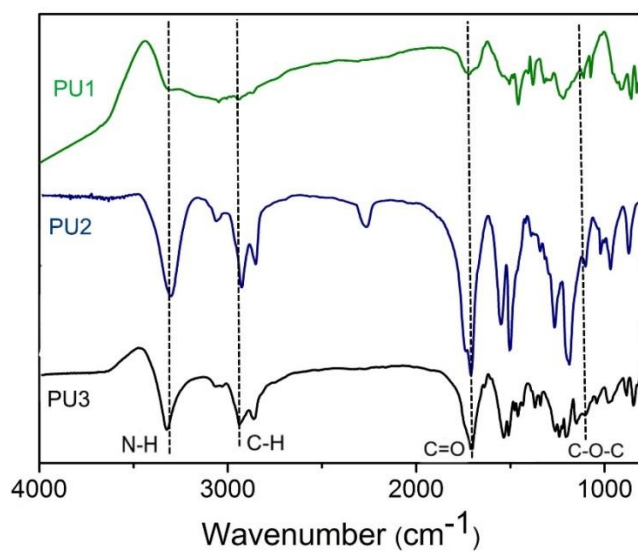


Fig. S4 FTIR spectra of **PU1**, **PU2** and **PU3**.

3. Photophysical properties and interactions of PUs with nitro-aromatic analytes

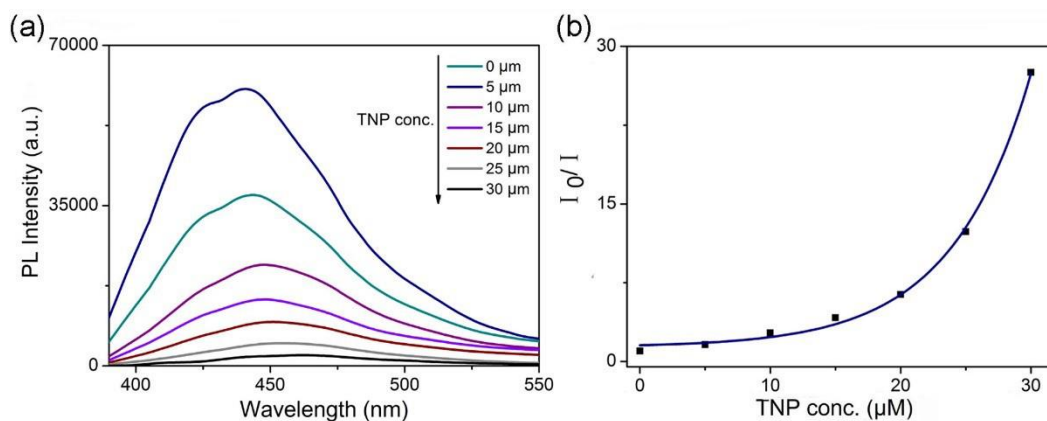


Fig. S5 (a) PL spectra of **PU2** (10 μM) in acetonitrile–water ($v/v = 1:1$) solution containing different amounts of TNP. (b) Corresponding Stern–Volmer plot of TNP.

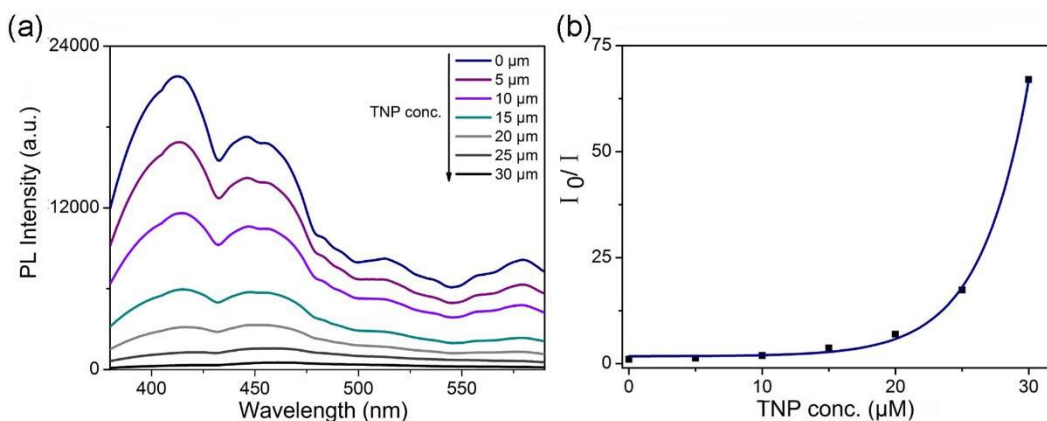


Fig. S6 (a) PL spectra of **PU3** (10 μM) in acetonitrile–water ($v/v = 1:1$) solution containing different amounts of TNP. (b) Corresponding Stern – Volmer plot of TNP.

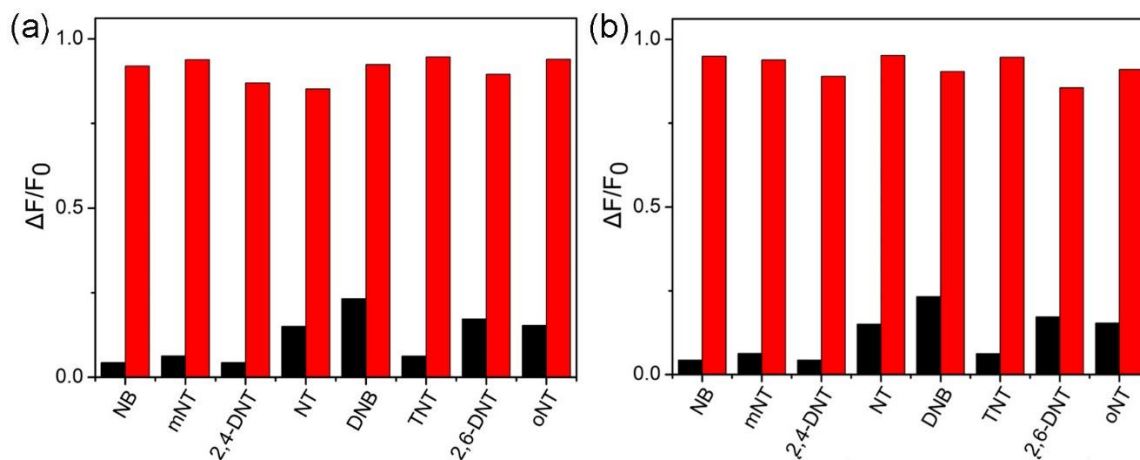


Fig. S7 (a) Quenching efficiency of **PU2** (10 μM) with analytes (30 μM) in acetonitrile–water ($v/v = 1:1$) solution before (black) and after (red) the addition of TNP (30 μM). (b) Quenching efficiency of **PU3** (10 μM) with analytes (30 μM) in acetonitrile–water ($v/v = 1:1$) solution before (black) and after (red) the addition of TNP (30 μM).

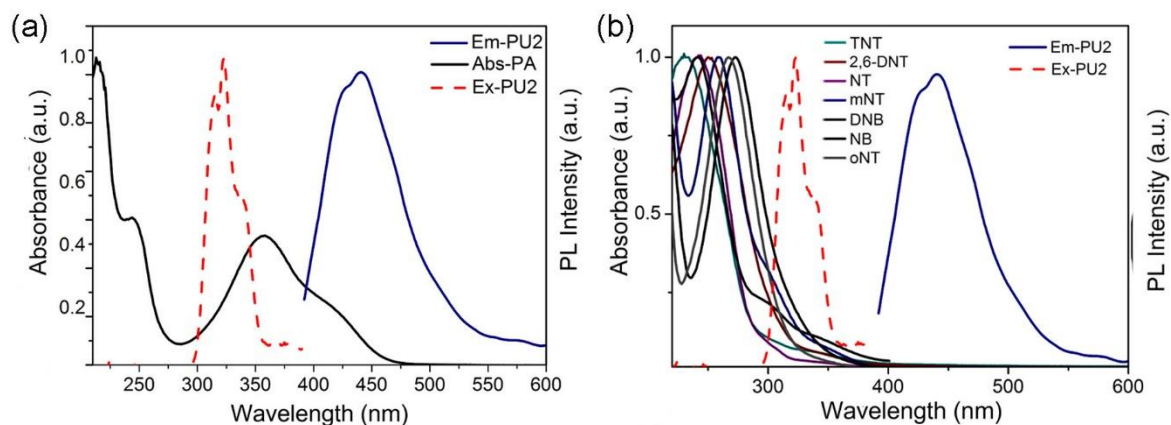


Fig. S8 (a) Normalized absorption spectrum of TNP and excitation/emission spectra of **PU2**. (b) Overlap between emission spectra of **PU2** and absorption spectra of various nitro-aromatics.

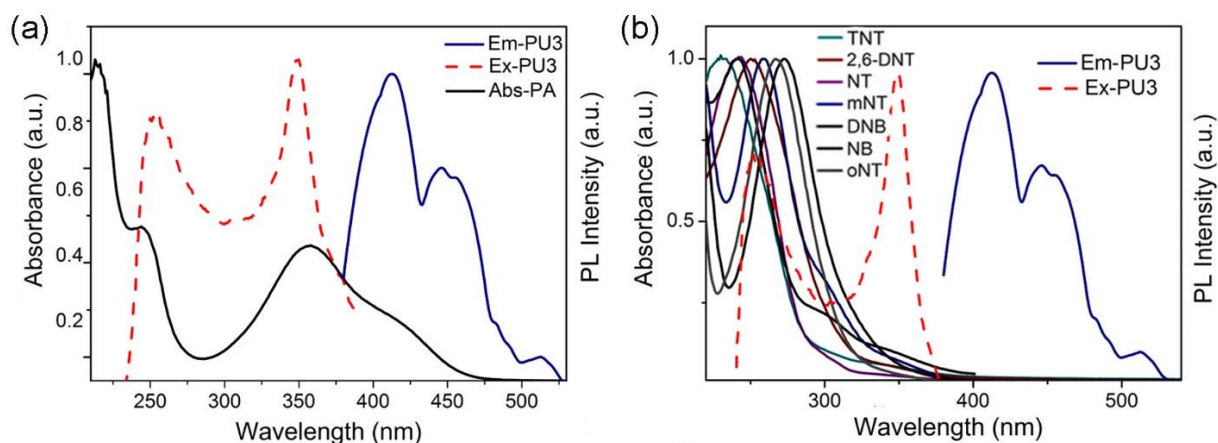


Fig. S9 (a) Normalized absorption spectrum of TNP and excitation/emission spectra of **PU3**. (b) Overlap between emission spectra of **PU3** and absorption spectra of various nitro-aromatics.

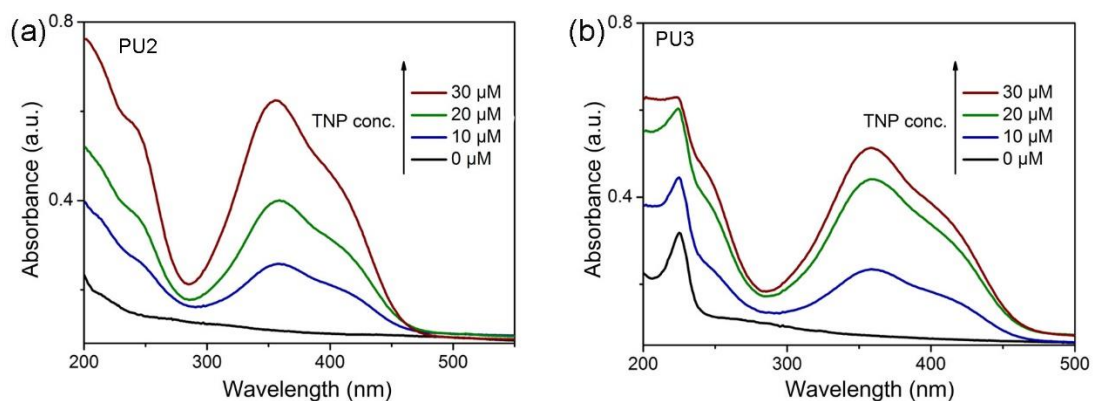


Fig. S10 UV-visible spectra of **PU2** (a) and **PU3** (b) (1×10^{-5} M) with increasing concentration of TNP.

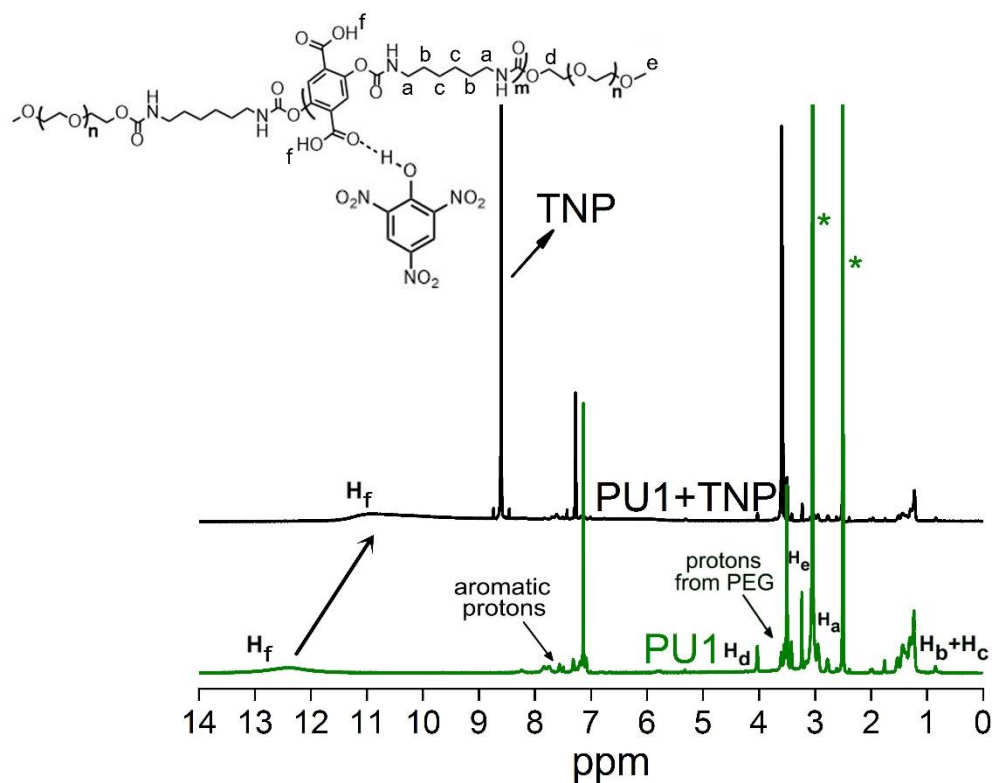


Fig. S11 ¹H NMR spectra of **PU1** before and after addition of 1 equivalent of TNP in DMSO-*d*₆.

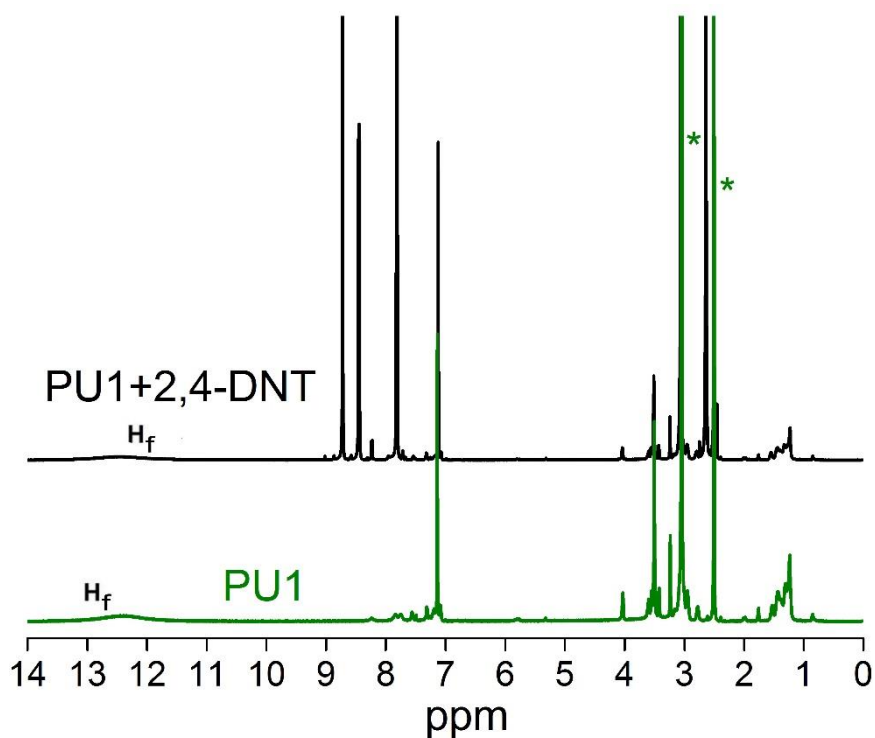


Fig. S12 ¹H NMR spectra of **PU1** before and after addition of 1 equivalent of 2,4-DNT in DMSO-*d*₆.

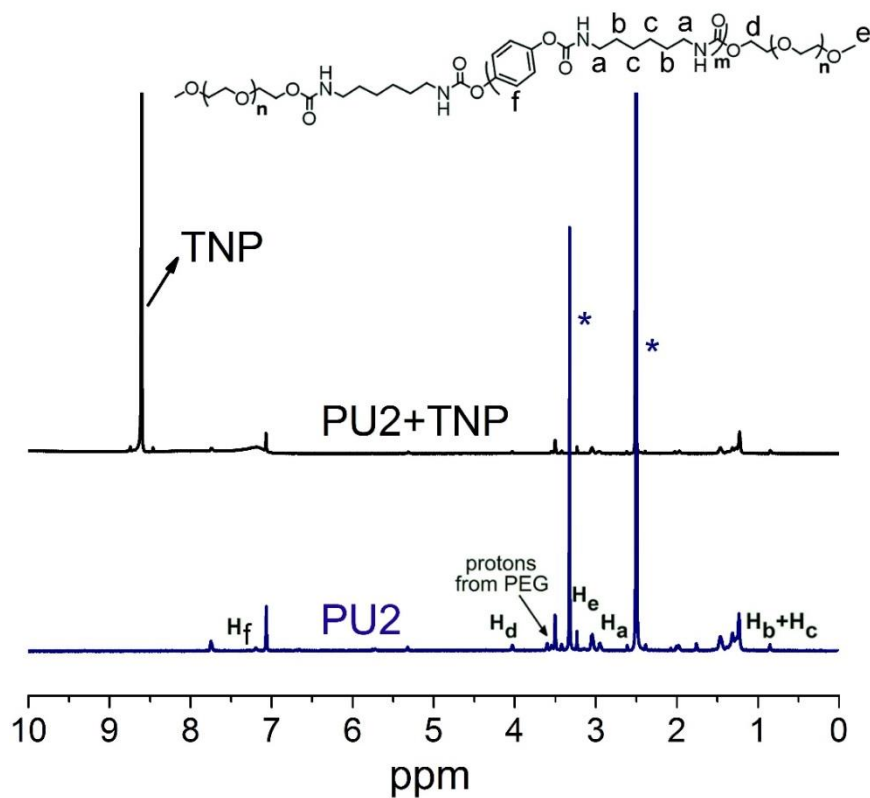


Fig. S13 ¹H NMR spectra of **PU2** before and after addition of 1 equivalent of 2,4-DNT in DMSO-*d*₆.

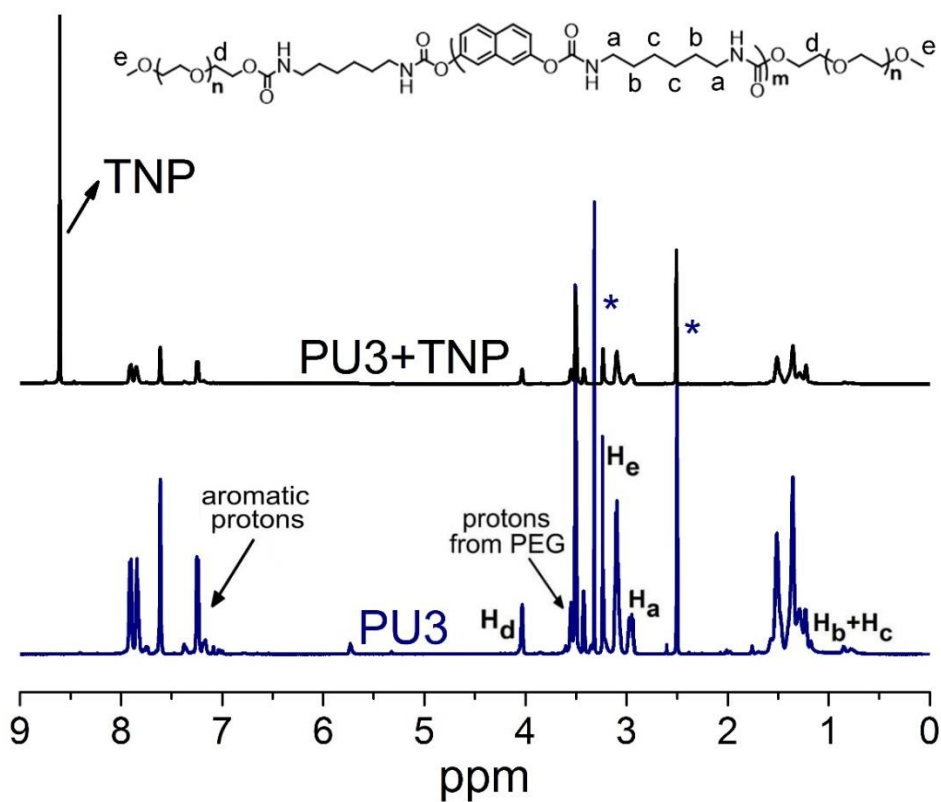


Fig. S14 ¹H NMR spectra of **PU3** before and after addition of 1 equivalent of 2,4-DNT in DMSO-*d*₆.

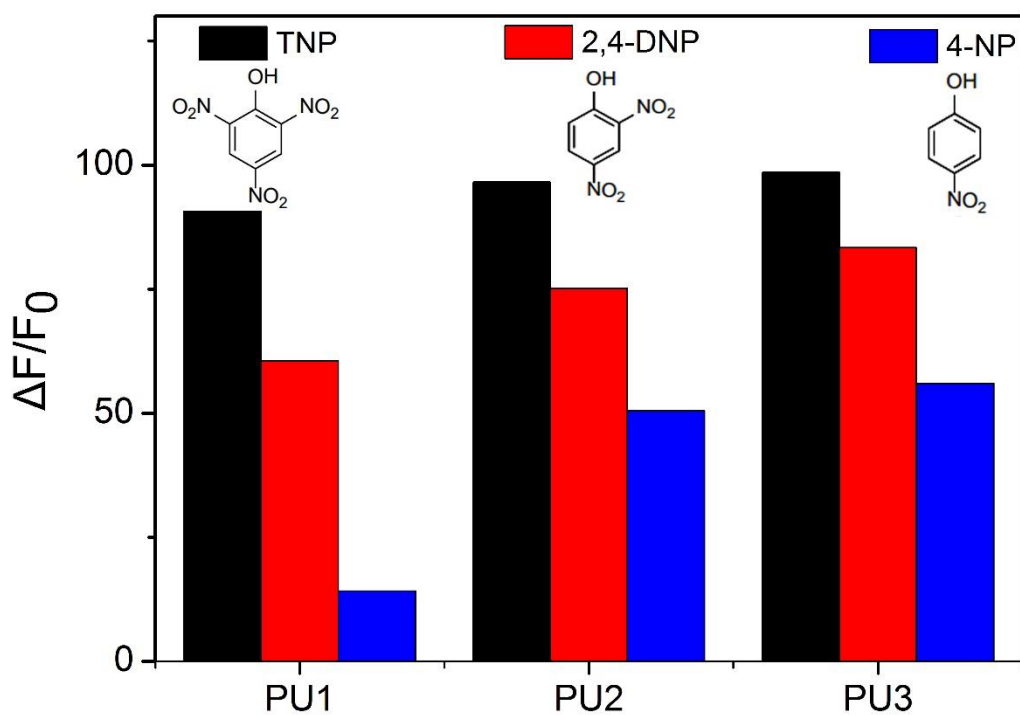


Fig. S15 Comparison of the fluorescence quenching of PUs caused by the addition of various nitrophenols (TNP, 2,4-DNP and 4-NP) (30 μM) in acetonitrile–water (v/v = 1:1) solution.

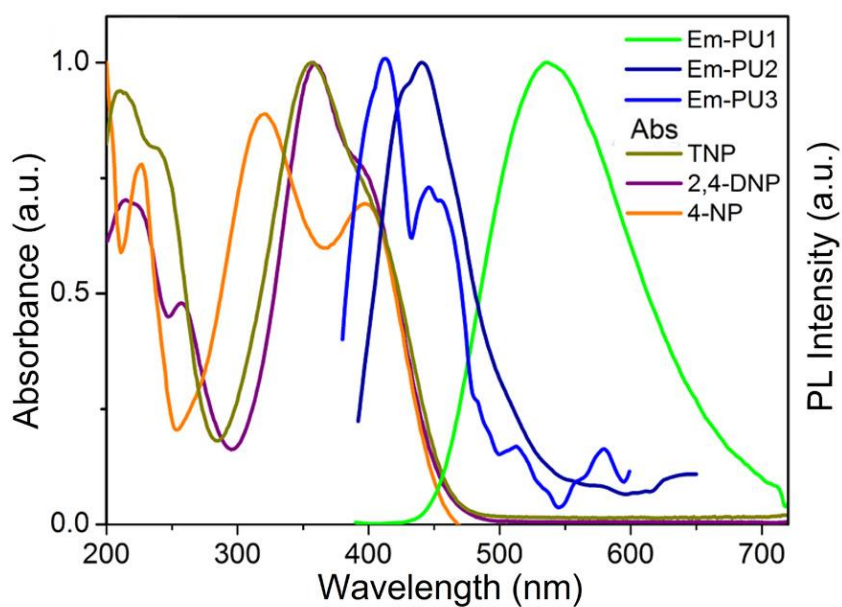


Fig. S16 Overlap between emission spectra of PUs and absorption spectra of various nitro-aromatics.

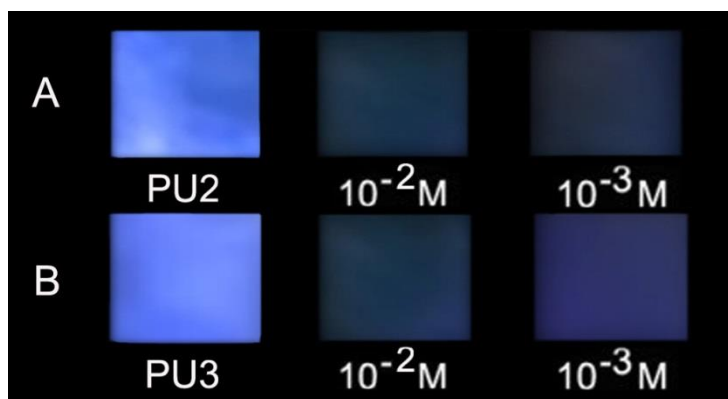


Fig. S17 (A) Luminescent photographs of **PU2**-coated filter paper with addition of different concentrations of TNP (10 μ L) water solutions. (B) Luminescent photographs of **PU3**-coated filter paper with addition of different concentrations of TNP (10 μ L) water solutions. All photographs were taken under 365 nm UV illumination.