

Electronic Supplementary Information

Room temperature phosphorescence of 4-bromo-1,8-naphthalic anhydride derivatives based polyacrylamide copolymer with photo-stimulated responsiveness†

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Methods

Materials. All reagents were commercially available and used as supplied without further purification. Solvents were purified according to standard laboratory methods. The molecular structures were confirmed using ^1H NMR, ^{13}C NMR and high-resolution ESI mass spectroscopy.

General. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker AV-400 spectrometer. The electronic spray ionization (ESI) high-resolution mass spectra were tested on a Waters LCT Premier XE spectrometer. 2D ROESY NMR spectra were measured on a Bruker AV-500 spectrometer. The UV–Vis absorption spectra and fluorescence spectra were obtained on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1-cm quartz cell was used), respectively. ICD spectrum was measured

on a JASCO J-815 CD spectrophotometer (1-cm quartz cell used) at 25 °C. RTP spectra and lifetime were recorded on a Varian Cary Eclipse spectrophotometer (1-cm quartz cell was used). Phosphorescence mode; Excitation slit =20 nm; Emission slit = 20 nm; Delay time = 0.1 ms; Gate time = 2.0 ms; Excited light (350 nm); Excitation voltage = 800 V. The photoirradiation was carried on a UV lamp of 6 W in a 1 mm × 1 cm quartz cell. The distance between the lamp and the sample cell was 1 cm. Photostationary states were ensured by taking UV spectra at distinct intervals until no obvious changes in absorbance were observed. Aqueous GPC was performed on Series 200. Samples were using 0.05 mol NaNO₃/H₂O as mobile phase with 0.6 mL/min flow rate. Rheological property was measured using an MARS 3 rheometer at 15 °C.

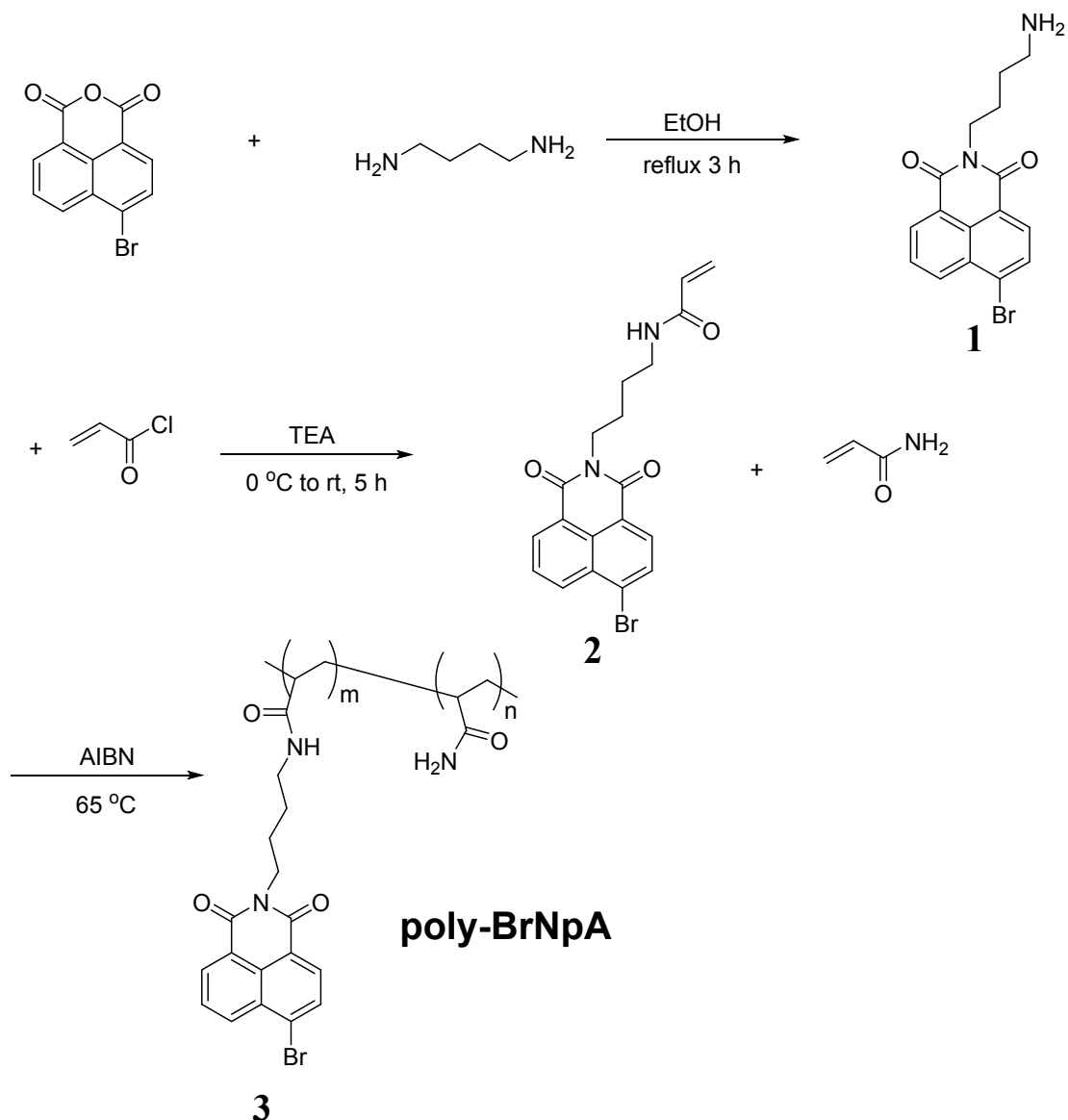


Figure S1. Preparation of poly-BrNpA.

Synthesis of 2-(4-aminobutyl)-6-bromo-1H-benzo [de]isoquinoline-1, 3(2H)-dione

(1). The compound **1** was synthesized according to literature procedure. ^[1] ¹H NMR (400 MHz, D₂O) δ 8.24 (d, J = 8.5 Hz, 1H), 8.19 (d, J = 7.4 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.64 (t, J = 7.9 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H), 3.06 (t, J = 6.9 Hz, 2H), 1.81-1.66 (m, 4H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 162.97, 162.92, 132.71, 131.67, 131.43, 131.05, 129.78, 129.25, 128.88, 128.25, 122.67,

121.89, 38.55, 24.71. HRMS (ESI) (m/z): [M+H]⁺ calcd for [C₁₆H₁₆BrN₂O₂]⁺, 347.0395; found, 347.0384.

Synthesis of N-(4-(6-bromo-1, 3-dioxo-1 H-benzo [de]isoquinolin-2(3H)-yl) butyl) acrylamide (2). The compound **1** (0.50 g, 1.44 mmol, 1 eq) and triethylamine (0.22 g, 2.16 mmol, 1.5 eq) were dissolved in dried dichloromethane and cooling with ice-water baths. Acryloyl chloride (0.16 g, 1.73 mmol, 1.2 eq) was added dropwise with a syringe under an argon atmosphere. After removing the ice-water baths, the mixture was stirred for 5 h at room temperature. The solution was concentrated and purified by column chromatography (petroleum ether/ ethyl acetate, 1/1, v/v) to afford a white solid **2** (0.41 g, 71 % yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.50 (d, J = 7.2 Hz, 1H), 8.47 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 7.9 Hz, 1H), 8.15 (d, J = 7.9 Hz, 1H), 8.09 (s, 1H), 7.94 (s, 1H), 6.18 (dd, J = 17.1, 10.1 Hz, 1H), 6.03 (dd, J = 17.1, 2.1 Hz, 1H), 5.54 (dd, J = 10.1, 2.1 Hz, 1H), 4.01 (t, J = 7.1 Hz, 2H), 3.15 (dd, J = 12.7, 6.6 Hz, 2H), 1.70 – 1.59 (m, 2H), 1.50 (dd, J = 14.9, 7.1 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 164.50, 162.89, 162.84, 132.59, 131.84, 131.58, 131.34, 130.96, 129.75, 129.13, 128.78, 128.24, 124.88, 122.70, 121.92, 38.40, 26.73, 25.21. HRMS (ESI) (m/z): [M+H]⁺ calcd for [C₁₉H₁₈BrN₂O₃]⁺, 401.0501; found, 401.0505.

Preparation of poly-BrNpA (3). The polymer was prepared by copolymerization of the compound **2** (0.050 g, 0.125 mmol, 1 eq) and acrylamide (0.443 g, 6.230 mmol, 50 eq) by a radical polymerization with 2,2'-azobis(2-methylpropionitrile) (AIBN) (0.0021 g, 0.0125 mmol, 0.1 eq) as radical initiator at 65 °C under an argon atmosphere in DMF for 12 h. The resulting mixture was added into methanol to

precipitate polymeric materials. Precipitation was repeatedly washed with methanol to give purified polymers. ^1H NMR (400 MHz, D_2O) δ 8.20-6.91 (m, broad, 5H, aromatic protons), 2.38-2.07 (broad, principal chain protons), 1.82-1.40 (broad, principal chain protons). GPC (H_2O): M_n (PDI) = 4.6 kDa (6.23).

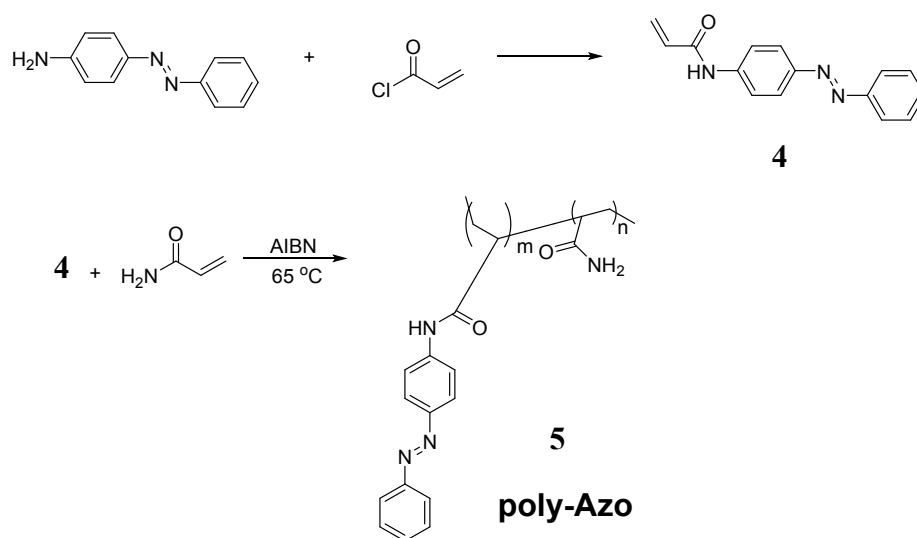


Figure S2. Preparation of poly-Azo.

Poly-Azo was synthesized conveniently according to our previous work. [2]

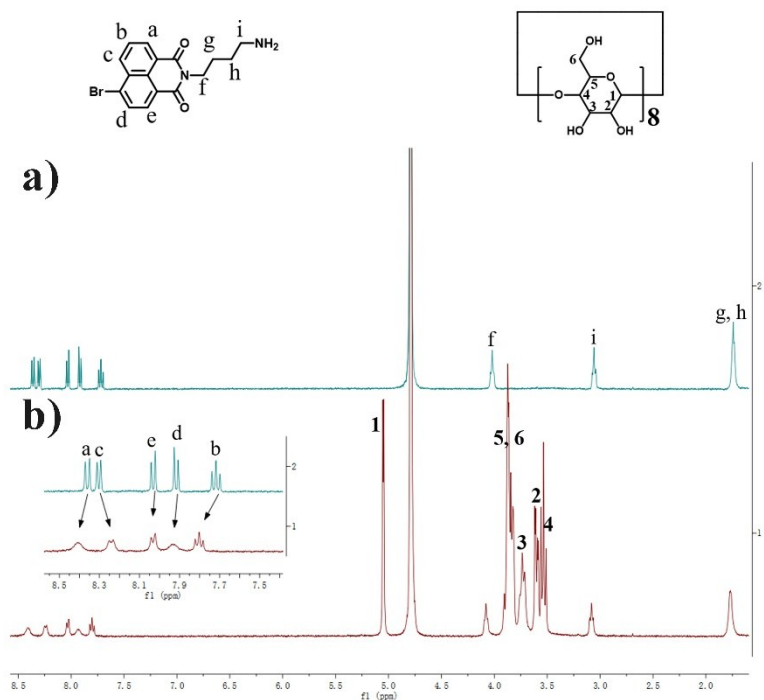


Figure S3. ^1H NMR spectrum of a) ANBrNpA and b) ANBrNpA@ γ -CD complex (1:1 molar ratio, 2.0 mM), D_2O , 25 $^\circ\text{C}$.

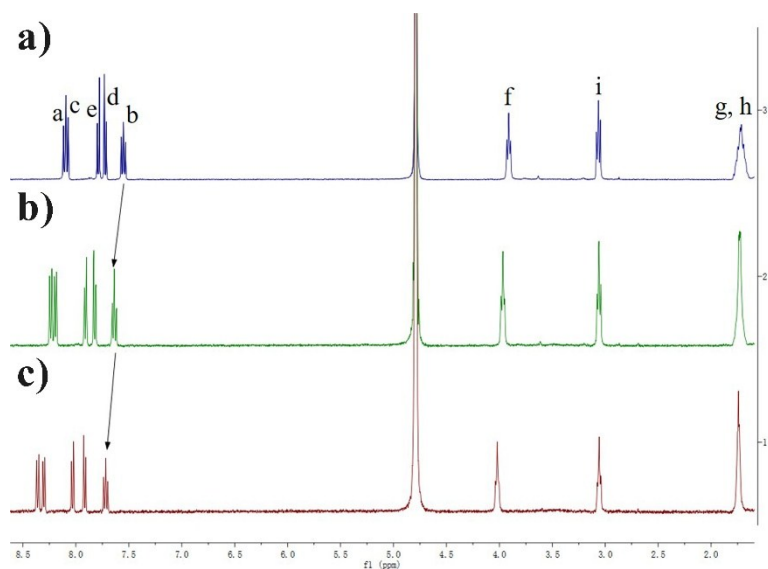


Figure S4. ^1H NMR spectrum of ANBrNp at different concentrations of a) 8.0 mM, b) 4.0 mM and c) 2.0 mM, D_2O , 25 $^\circ\text{C}$.

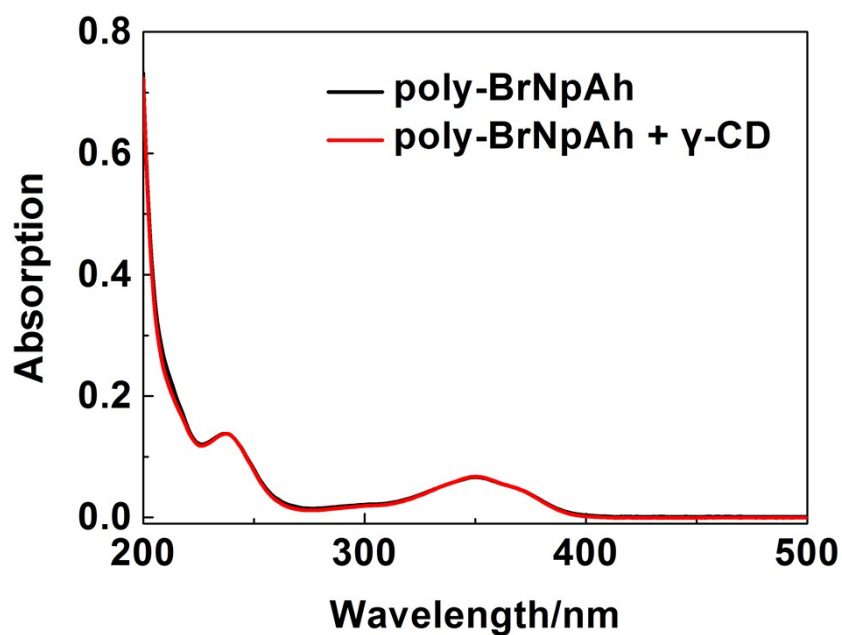


Figure S5. UV spectrum of poly-BrNpA aqueous solution ($[\text{poly-BrNpA}] = 1.0 \times 10^{-5} \text{ M}$) and UV spectrum of poly-BrNpA/ γ -CD aqueous solution ($[\text{poly-BrNpA}] = 1.0 \times 10^{-5} \text{ M}$, $[\gamma\text{-CD}] = 1.0 \times 10^{-5} \text{ M}$). The two spectra are very similar.

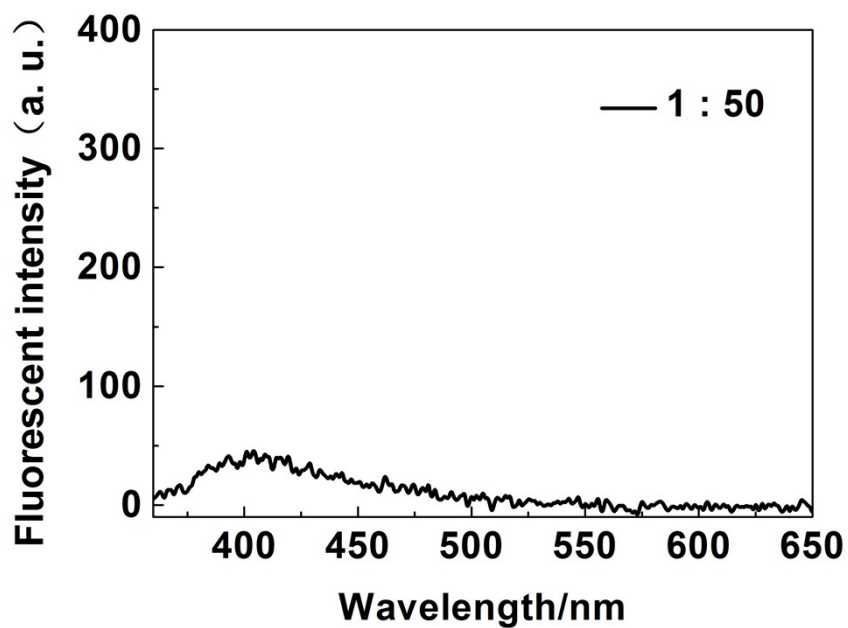


Figure S6. Fluorescence spectrum of binary poly-BrNpA/ γ -CD aqueous solution.

$[\text{poly-BrNpA}] = 5.0 \times 10^{-5} \text{ M}$, $[\gamma\text{-CD}] = 2.5 \times 10^{-3} \text{ M}$.

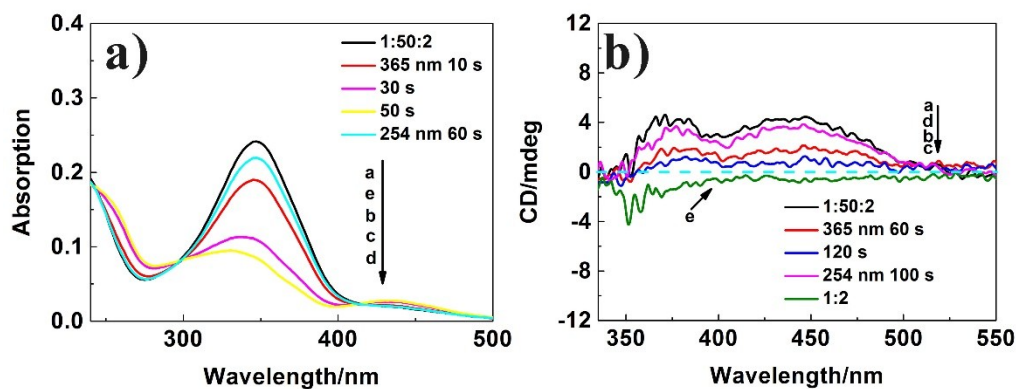


Figure S7. a) UV spectrum of ternary **poly-BrNpA/γ-CD/poly-Azo** aqueous solution.

($[\text{poly-BrNpA}] = 5.0 \times 10^{-6} \text{ M}$, $[\gamma\text{-CD}] = 2.5 \times 10^{-4} \text{ M}$, $[\text{poly-Azo}] = 1.0 \times 10^{-5} \text{ M}$).

After irradiation by 365 nm light for 10 s (b), 30 s (c), 50 s (d); then by 254 nm for 60

s (e). b) ICD spectrum of ternary **poly-BrNpA/γ-CD/poly-Azo** aqueous solution.

($[\text{poly-BrNpA}] = 5.0 \times 10^{-5} \text{ M}$, $[\gamma\text{-CD}] = 2.5 \times 10^{-3} \text{ M}$, $[\text{poly-Azo}] = 1.0 \times 10^{-4} \text{ M}$).

After irradiation by 365 nm light for 60 s (b), 120 s (c); then by 254 nm for 100 s (d).

The **poly-Azo** aqueous solution (curve e, $[\text{poly-Azo}] = 1.0 \times 10^{-4} \text{ M}$) showed no

obvious Cotton peak but only the systematic error of the measurement.

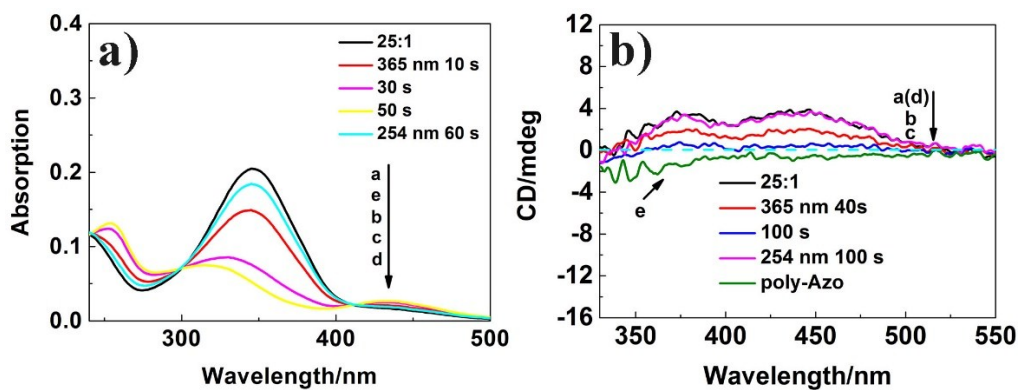


Figure S8. a) UV spectrum of binary γ -CD/**poly-Azo** aqueous solution. ($[\gamma\text{-CD}] = 2.5 \times 10^{-4}$ M, $[\text{poly-Azo}] = 1.0 \times 10^{-5}$ M). After irradiation by 365 nm light for 10 s (b), 30 s (c), 50 s (d); then by 254 nm for 60 s (e). d) ICD spectrum of binary γ -CD/**poly-Azo** aqueous solution. ($[\gamma\text{-CD}] = 2.5 \times 10^{-3}$ M, $[\text{poly-Azo}] = 1.0 \times 10^{-4}$ M). After irradiation by 365 nm light for 40 s (b), 100 s (c); then by 254 nm for 100 s (d). The **poly-Azo** aqueous solution (curve e, $[\text{poly-Azo}] = 1.0 \times 10^{-4}$ M) showed no obvious Cotton peak but only the systematic error of the measurement.

References

[S1] P. Guo, Q. Chen, T. Liu, L. Xu, Q. Yang, X. Qian, *ACS Med. Chem. Lett.*, 2013, **4**, 527-531.

[S2] H. Chen, X. Ma, S. Wu, H. Tian, *Angew. Chem. Int. Ed.*, 2014, **53**, 14149-14152.