Electronic Supplementary Information (ESI) for Polymer Chemistry.

Water-soluble sunlight erasable ink based on [4 + 4] cycloaddition of 9-substituted anthracene

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Scheme S1 Synthetic route towards 4-(4-(anthracen-9-yl)-1H-1,2,3-triazol-1-yl) benzoic acid.

1.1. Synthesis of 4-azidobenzoic acid (1).

In a 100 mL flask, 4-aminobenzoic acid (1.38 g, 10 mmol, 1 eq), 11 mL dist. H₂O and 11 mL conc. HCl was added in turn and stirred for a few minutes, then the suspension was cooled to 0 °C. NaNO₂ (0.80 g, 11.6 mmol, 1.16 eq) was dissolved in 8 mL dist. H₂O, the solution was cooled to 0°C and subsequently added dropwise to the reaction mixture. Subsequently, the mixture was stirred for 20 min in an ice bath. NaN₃ (0.74 g, 11.4 mmol, 1.14 eq) was dissolved in 8 mL dist. H₂O and also cooled to 0°C. The solution was added dropwise to the cooled reaction mixture, which was then stirred for another hour. The white precipitate was filtered off, subsequently washed with ice-cooled dist. H₂O, and dried under vacuum to yield **4-azidobenzoic acid** (**1**, 1.5 g, yield 91 %). The ¹H NMR spectrum (400 MHz, CDCl₃) was shown in Fig. S1.



Fig. S1 (a) ¹H NMR and (b) ¹³C NMR spectra of 4-azidobenzoic acid (1) in DMSO-*d*6.

1.2. Synthesis of 9-ethynylanthracene (2).

In a 250 mL flame-dried Schlenk flask equipped with a stirring bar, 9-bromoanthracene (2.045 g, 8 mmol, 1 eq), CuI (178 mg, 0.93 mmol, 0.11 eq), Pd(PPh₃)₂Cl₂ (563 mg, 0.8 mmol, 0.1 eq), and ethynyltrimethylsilane (3 mL, 21.2 mmol, 2.7 eq) were dissolved in piperidine (6 mL) and dry TEA (64 mL). The reaction mixture was stirred at 110°C overnight and subsequently 100 mL sat. NH₄Cl solution was added. The aqueous phase was extracted with 50 mL hexane three times. The combined organic phases were dried over Na₂SO₄ and concentrated under vacuum. The crude product was purified by

column chromatography on silica gel running with petroleum ether to give the product as yellow crystal ((Anthracen-9-ylethynyl)trimethylsilane, 1.6 g, yield 73%). The ¹H NMR spectrum (400 MHz, CDCl₃) was shown in Fig. S2.



Fig. S2 (a) ¹H NMR and (b) ¹³C NMR spectra of anthracen-9-ylethynyl)trimethylsilane in CDCl₃.

(Anthracen-9-ylethynyl)trimethylsilane (423 mg, 1.54 mmol, 1 eq) and K₂CO₃ (1.50 g, 10.8 mmol, 7 eq) were dissolved in a mixture of 40 mL MeOH/THF (1/1 v/v) and stirred overnight at ambient temperature. Dist. water (20 mL) was subsequently added and the mixture was extracted with Et₂O (40 mL). The organic phase was washed with dist. water (20 mL \times 2), dried over MgSO₄ and concentrated in vacuum. The crude

product was purified by column chromatography on silica gel running with petroleum ether to give product as yellow oil (**9-ethynylanthracene (2)**). This compound quickly polymerized at ambient temperature to become dark polymer solid and thus was used immediately upon isolation. The ¹H NMR spectrum (400 MHz, CDCl₃) was shown in Fig. S3.



Fig. S3 (a) ¹H NMR and (b) ¹³C NMR spectra of 9-ethynylanthracene (2) in CDCl₃.

1.3. Synthesis of 4-(4-(anthracen-9-yl)-1H-1,2,3-triazol-1-yl)benzoic acid (3).

In a 50 mL flame-dried Schlenk tube 4-azidobenzoic acid (1, 300 mg, 1.84 mmol), 9ethynylanthracene (2, all) and PMDETA (460 μ L, 386 mg, 2.23 mmol) were mixed in 8 mL dry toluene/DMF (1/1 v/v), and the tube was purged with N₂ for 30 min. CuBr (335 mg, 2.33 mmol) was added under N₂ atmosphere and the content was stirred overnight at ambient temperature. The reaction mixture was diluted with 30 mL DCM and subsequently extracted with 30 mL sat. NH₄Cl solution three times. The organic layer was dried with Na₂SO₄ and concentrated under vacuum. The raw product was filtered through a short column of silica gel (methanol) to yield **4-(4-(anthracen9-yl)-1H-1,2,3-triazol-1-yl)benzoic acid** (**3**, 369 mg, yield 66 %). The ¹H NMR and ¹³C NMR spectra were shown in Fig. S4. ¹³C NMR (101 MHz, DMSO-*d6*) δ 166.45, 143.69, 139.72, 131.12, 130.83, 130.57, 128.48, 128.32, 126.51, 125.76, 125.51, 124.41, 124.07, 119.95. ESI-MS: m/z calculated for C₂₃H₁₅N₃O₂ [M+H]⁺ 366.1237, found 366.1243.



Fig. S4 (a) ¹H NMR and (b) ¹³C NMR spectra of 4-(4-(anthracen-9-yl)-1H-1,2,3triazol-1-yl) benzoic acid (3). The solvents of ¹H NMR and ¹³C NMR were CD₃OD and s6

DMSO-d6, respectively.



Fig. S5 GPC profiles of PEG before and after the termination of anthracene.



Fig. S6 MALDI-TOF MS of An-PEG (a,c) and PEG (b,d).



Fig. S7 FT-IR spectra of 4-(4-(anthracen-9-yl)-1H-1,2,3-triazol-1-yl) benzoic acid (An-COOH), mPEG, and An-PEG.

The characteristic absorption band at 1724 cm⁻¹ could be ascribed to the C=O stretching vibration of ester bond in An-PEG, which did not appear in An-COOH and mPEG. The characteristic absorption bands at 1608, 1518, 772, and 742 cm⁻¹ could be ascribed to the aromatic ring of anthracene in An-PEG.



Fig. S8 ¹H NMR spectra of 4-(4-(anthracen-9-yl)-1H-1,2,3-triazol-1-yl)benzoic acid (3) before and after photoirradiation with 365 nm light for 20 min. The solvent is DMSO- d_6 .



Fig. S9 Normalized fluorescence intensity as a function of the concentration of An-PEG aqueous solution.

The anthracene moieties in An-PEG were fluorescent. However, the anthracene moieties were hydrophobic and had poor solubility in aqueous solution, so the fluorescence was weak. When An-PEGs formed micelles, anthracene could be solubilized in the micelle core and the fluorescence could be enhanced. Therefore, the critical micelle concentration (CMC) of An-PEG in water could be determined by the change of fluorescence with concentration.



Fig. S10 ¹H NMR spectrum of An-PEG in D₂O. The concentration was 5 mM.



Fig. S11 (a) Fluorescence emission spectra of An-PEG in water and DMSO. $\lambda_{ex,water} =$ 449 nm. $\lambda_{ex,DMSO} =$ 437 nm. (b) Changes of relative PL intensity of An-PEG after photoirradiation with 365 nm light for different times in water or DMSO. The concentration of An-PEG solutions was fixed as 1.5 mM.



Fig. S12 UV-vis spectra of An-PEG in water (a) and DMSO (b) heating at 90 °C for different times. Black line: An-PEG, red line: An-PEG dimer.



Fig. S13 UV-vis spectra of An-PEG in DMSO heating at 150 °C for different times. Black line: An-PEG, red line: An-PEG dimer.