Synthesis of a poly(N-isopropylacrylamide) charm bracelet decorated with a photomobile α-cyclodextrin charm

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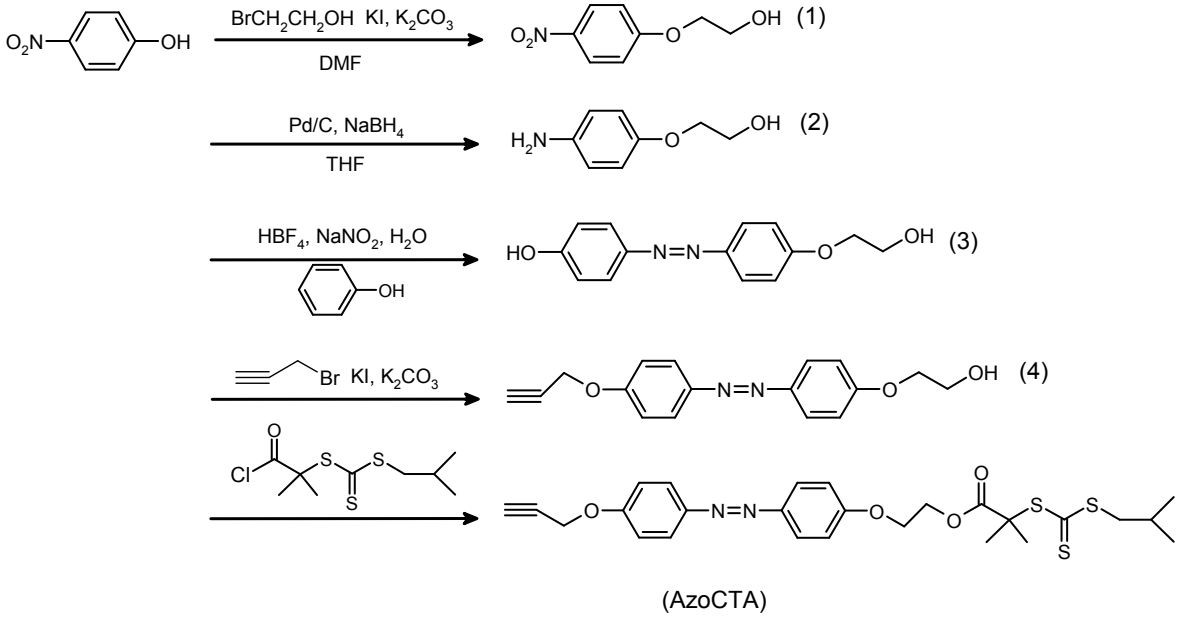
1. Experimental procedure for the synthesis of the chain transfer agent AzoCTA prepared according to the reaction sequence described in scheme S1.

Scheme S1. Synthesis of azobenzene-containing chain transfer agent (AzoCTA)



1. Synthesis of 2-(p-nitrophenoxy)ethanol (1)

A mixture of *p*-nitrophenol (6.2 g, 44 mmol), 2-bromoethanol (6.0 g, 50 mmol), and potassium carbonate (9.0 g, 66 mmol) in dry DMF (20 mL) was stirred at 80 °C for 16 hrs. The resulting mixture was diluted with 50 mL of water and extracted with $CHCl_3$ (3×30 mL). The organic phase was washed with 1 M HCl aqueous solution and water, then dried over anhydrous magnesium sulfate and filtered. The solvent was removed from the filtrate under reduced pressure. The residue was purified by flash silica chromatography using hexane/ethyl acetate (20:80) as eluent. Yield: 5.6 g, 70 %. ^{1}H NMR ($CDCl_3$) ppm, δ 2.05 (bs, 1H, -CH_2O*H*), 4.03 (t, 2H, -C*H*$_2$OH), 4.19 (t, 2H, -C*H*$_2$OAr), 7.00 (d, 2H, Ar-*H*), 8.20 (d, 2H, Ar-*H*).

2. Synthesis of 2-(p-aminophenoxy)ethanol (2)

Sodium borohydride (1.8 g, 48 mmol) was added to a mixture of *1* (3.0 g, 16 mmol) and 10 % palladium on carbon (0.5 g) in methanol (30 mL). The mixture was stirred in an ice-water bath for 5 hrs. After that, the solid was removed by filtration and the solvent was removed by rotary-evaporation. The product was obtained by trituration of the residue with THF. Yield 2.9 g, 100%. ^{1}H NMR (DMSO-d_6) ppm, δ 3.64 (t, 2H, -C***H***$_2$OH), 3.82 (t, 2H, -C***H***$_2$OAr), 4.50 (bs, 2H, Ar-N***H***2), 6.51 (d, 2H, Ar-***H***), 6.64 (d, 2H, Ar-***H***).

3. Synthesis of 4-hydroxyl-(4'-(2-hydroxyethoxy)azobenzene (3)

An aqueous potassium nitrite (1.6 g, 19 mmol) solution (20 mL) was added dropwise to a mixture of *2* (2.9 g, 19 mmol) and a 42 wt% tetrafluoroboric acid aqueous solution (7.0 g, 38 mmol) kept at 5 °C in an ice-water bath. At the end of the addition, the reaction mixture was stirred for 30 min. A solution of phenol (2.1 g, 23 mmol) and potassium hydroxide (KOH, 2.3 g, 40 mmol) in water (50 mL) was added slowly, followed by the addition of an aqueous KOH solution to bring the reaction mixture pH to 8. The resulting mixture was stirred for 1 hr in an ice-water bath. After that, a 1.0 M HCl solution was added slowly to adjust the solution pH to 5. The reaction mixture was allowed to stir for another 1 hr. The resulting precipitate was collected with a Buchner funnel, washed with hot water to yield a yellow solid. Yield 4.0 g, 82%. ^{1}H NMR

(DMSO-d_6) ppm, δ 3.75 (t, 2H -C***H***$_2$OH), 4.08 (t, 2H, ArOC***H***$_2$), 4.94 (t, 1H, -CH$_2$O***H***), 6.91 (d, 2H, Ar-***H***), 7.09 (d, 2H, Ar-***H***), 7.74-7.80 (dd, 4H, Ar-***H***), 10.19 (s, 1H, Ar-O***H***).

4. Synthesis of 4-propargyloxy-4'-(2-hydroxyethoxy)azobenzene (4)

A solution of the yellow solid *3* (2.58 g, 10 mmol), propargyl bromide (1.8 g, 15 mmol), potassium carbonate (4.1 g, 30 mmol) in dry DMF (20 mL) was stirred at 80 °C under a N_2 atmosphere overnight. The insoluble salts were removed by filtration. The product was recovered by precipitation in aqueous HCl solution and purified by recrystallization from ethyl acetate. Yield: 2.0 g, 66 %. ^{1}H NMR (DMSO-d_6) ppm, δ 3.76 (t, 4H, -C***H***2-OH), 4.09 (t, 4H, Ar-O-C***H***2), 4.91 (t, 2H, -CH2-O***H***), 7.15(d, 4H, Ar-***H***), 7.82 (d, 4H, Ar-***H***). UV/Vis (methanol): λ_{max}= 310 nm; ε_{310} = 26,800 M^{-1}·cm^{-1}.

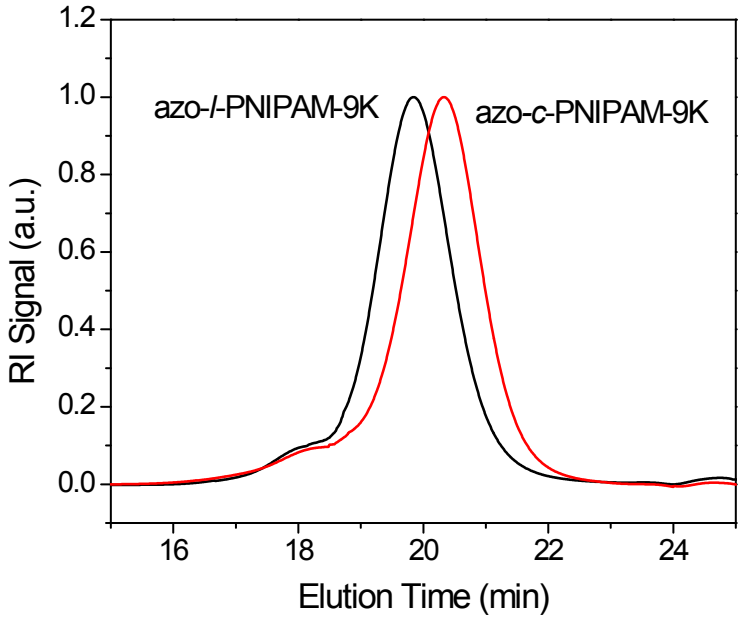


Figure S1. GPC traces of linear and cyclic azo-PNIPAM-9K in DMF at 40 °C.

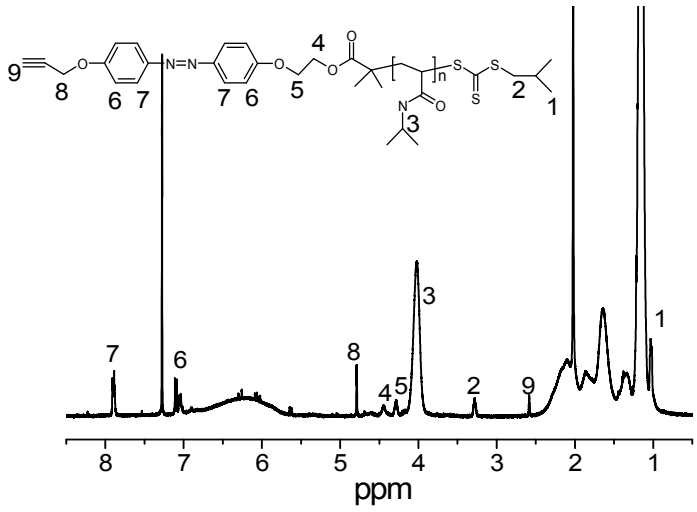


Figure S2. ^{1}H NMR spectrum of azo-*l*-PNIPAM-Tr in $CDCl_3$.

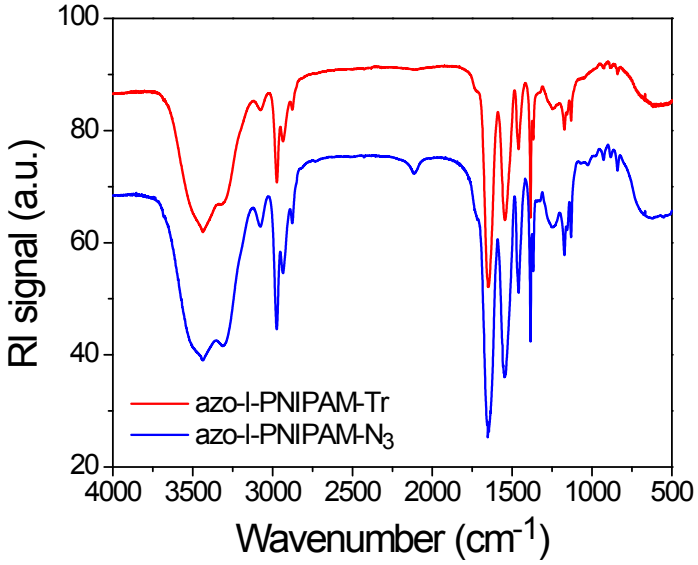


Figure S3. FT-IR spectra of azo-*l*-PNIPAM-Tr and azo-*l*-PNIPAM-N_3.

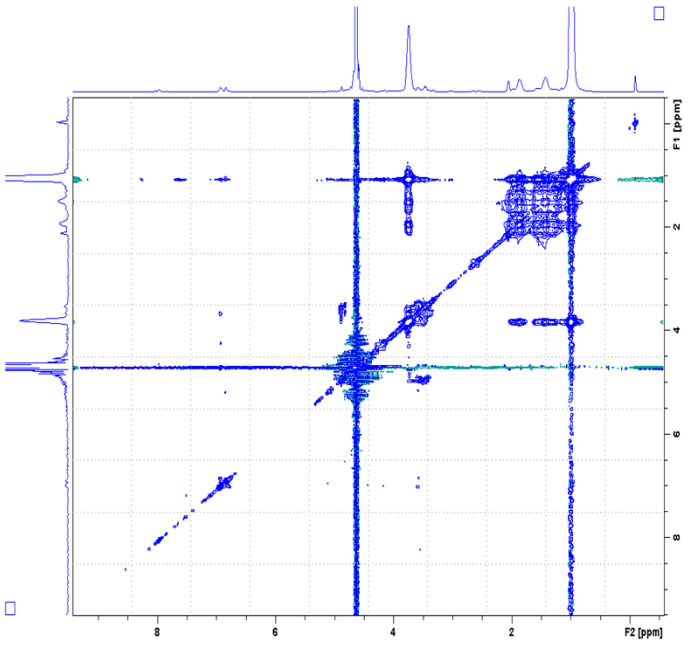
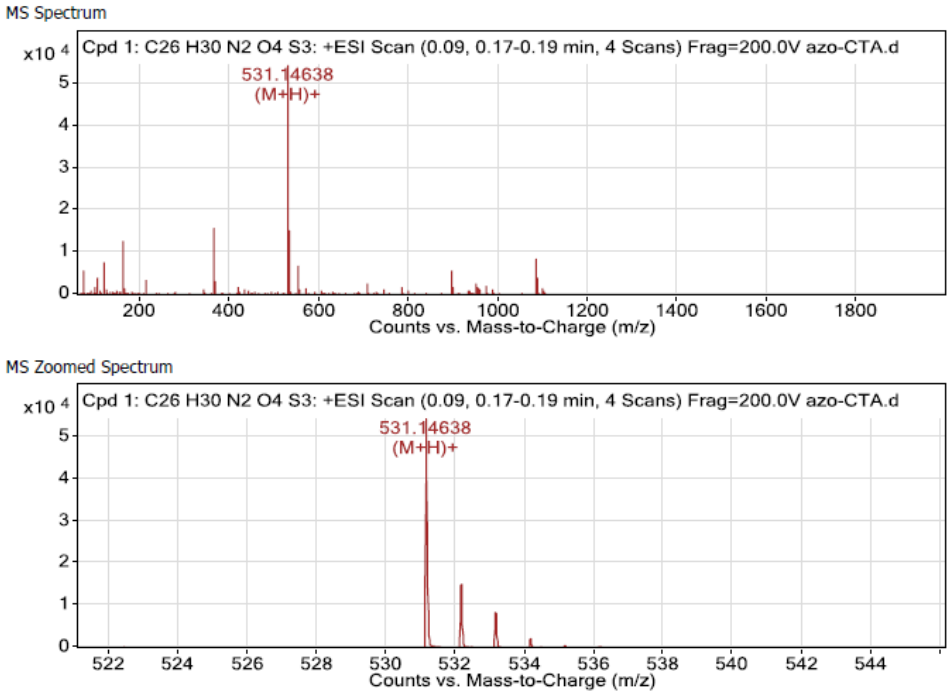


Figure S4. 2D NOESY spectrum of azo-*c*-PNIPAM-αCD after irradiation with UV 365 nm for 10 min in D_2O at 25 °C.



MS Spectrum Peak List

Ion	Formula	Abund	Observed m/z	Calc m/z	Diff (ppm)
(M+H)+	C26H30N2O4S3	54356.14	531.14638	531.14405	-4.4

Fig S5 High resolution mass spectrum of Azo-CTA.

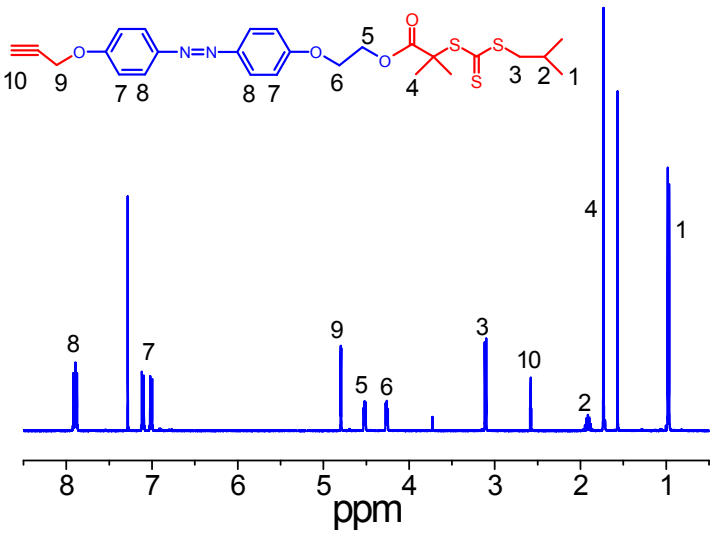


Figure S6: ^{1}H NMR spectrum of AzoCTA (solvent: $CDCl_3$).

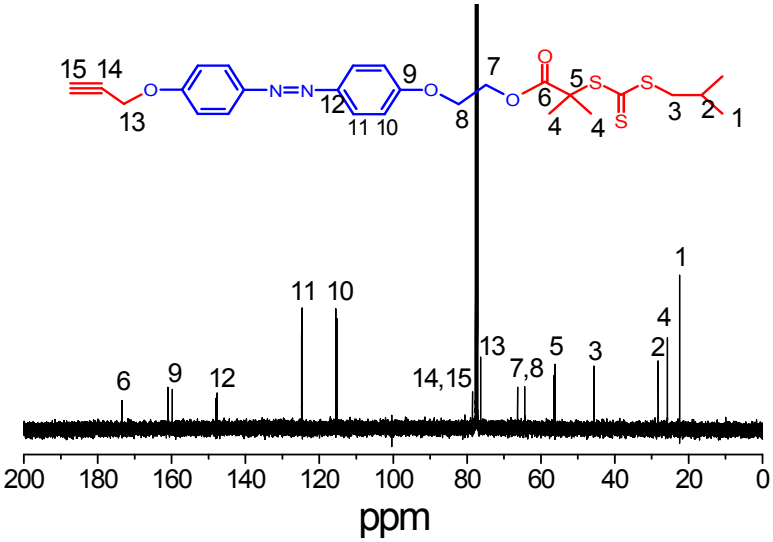


Fig. S7: ^{13}C NMR spectrum of azo-CTA (solvent :$CDCl_3$).