

Solvent induced amplification of the photoresponsive properties of α , ω -di-[4-cyanophenyl-4'-(6-hexyloxy)-azobenzene]-poly(N-isopropylacrylamide) in aqueous media.

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Supporting information

Materials and Methods. All chemicals were purchased from Wako chemicals Co. or TCI (Tokyo Chemical Industry) Co. and used as received, unless otherwise stated. *N*-isopropylacrylamide (NIPAM) was recrystallized from an acetone/hexanes (4:6, v/v) mixture. Azobisisobutyronitrile (AIBN) was recrystallized from methanol prior to use. Water was deionized using a Millipore Milli-Q system. α , ω -Di-[4-cyanophenyl-4'-(6-hexyloxy)azobenzene]-PNIPAM (Az₂-PNIPAM)¹, 2-(1-isobutyl)sulfanylthiocarbonyl-sulfanyl-2-methyl propionic acid^{2,3}, and 4-cyano-4'-(6-iodohexyloxy)azobenzene (I6Az)¹ were prepared as described previously. ¹H NMR spectra were recorded on a lambda-300 (JEOL) spectrometer. Dynamic light scattering (DLS) measurements were performed on a CGS-3 goniometer (ALV GmbH) equipped with an ALV/LSE-5003 multiple- τ digital correlator (ALV GmbH), a He-Ne laser ($\lambda = 633$ nm), and a C25P circulating water bath (Thermo Haake). Gel permeation chromatography (GPC) was performed with a Japan Spectroscopy Co., model DG-980-50 system equipped with a refractive index detector and three Shodex columns (K803 + K804 + K805) eluted with DMF at 40 °C. UV-visible absorption spectra were recorded on a JASCO, V-550 UV-visible spectrophotometer equipped with a JASCO, EHC-477T Temperature Controller.

Synthesis Methods

Ethyl 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionate (EIM). (see Scheme SI) Oxalyl chloride (6.0 ml, 75 mmol) was added while stirring to 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methyl propionic acid (2.0 g, 7.9 mmol) kept under nitrogen atmosphere at room temperature. At the end of addition, the mixture was heated to 40-50 °C for 2 h. The excess oxalyl chloride was removed in vacuo to yield 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methyl propionyl chloride. Excess ethanol was added dropwise to the product. The resulting solution was heated at 40-50 °C for 5 hr. At the end of reaction, the solution was cooled to room temperature and excess ethanol was removed under reduced pressure. The product was purified by column chromatography on silica gel using dichloromethane/hexane (3/1 v/v) as eluent. Yield: 2.2 g, 97 %. ¹H NMR (CDCl₃) ppm, δ 0.99 (d, 12H, -CH(CH₃)₂), 1.25 (t, 3H, -OCH₂CH₃), 1.65 (d, 12H, -SC(CH₃)₂C(=O)), 1.96 (septet, 1H, -CH(CH₃)₂), 3.19 (d, 4H, -SCH₂), 4.16 (q, 4H, -C(=O)OCH₂); UV (Chloroform): λ_{max} = 310 nm; ε = 13600 M⁻¹cm⁻¹.

Synthesis of α-2-(ethyl 2-methylpropionate)-ω-1-(isobutyl)sulfanylthiocarbonylsulfanyl-poly(*N*-isopropylacrylamide) (IBS-PNIPAM). A solution of the chain transfer agent (**EIM**, 74 mg, 0.26 mmol), the initiator (**AIBN**, 5 mg, 0.03 mmol), and the monomer (**NIPAM**, 2.5 g, 22 mmol) in 1,4-dioxane (10 ml) was placed in a round-bottom flask with rubber septa. The solution was deoxygenated by bubbling nitrogen for 30 min at room temperature. The reaction flask was placed in an oil bath preheated to 65 °C. The polymerization was allowed to proceed for 4 h under constant magnetic stirring. At the end of this polymerization, the solution was cooled to

room temperature. The polymer was isolated by precipitation in diethyl ether. It was purified further by two consecutive reprecipitations from THF into diethyl ether. Yield: 2.4 g, 93 %. ^1H NMR (CDCl_3) ppm, δ 1.00 (d, $-\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.11 (s, $-\text{NHCH}(\text{CH}_3)_2$), 1.27-2.30 (multiplets, polymer backbone protons), 3.17 (s, $-\text{SCH}_2$), 3.61 (s, $-\text{OCH}_2$), 3.99 (s, $-\text{NHCH}$), 6.20 (bs, $-\text{C}(=\text{O})\text{NH}$).

Synthesis of α -4-cyano-4'-(6-iodohexyloxy)azobenzene- ω -2-(ethyl 2-methylpropionate-poly(*N*-isopropylacrylamide) (Az-PNIPAM) (Scheme S2). *n*-Butylamine (0.17 g, 1.6 mmol) and tris(2-carboxyethyl) phosphine hydrochloride (TCEP, trace amount) were added to a solution of IBS-PNIPAM (2.3 g 0.23 mmol) in tetrahydrofuran (10 ml) The resulting solution was stirred for 1 h at room temperature under a nitrogen atmosphere. The product, α -(ethyl 2-methylpropionate- ω -mercapto-poly(*N*-isopropylacrylamide) (SH-PNIPAM) was recovered by precipitation in diethyl ether and purified by two consecutive reprecipitations from THF into diethyl ether. Yield: 2.1 g. ^1H NMR (CDCl_3) ppm, δ 1.17 (s, $-\text{NHCH}(\text{CH}_3)_2$), 1.30-2.20 (multiplets, polymer backbone protons), 3.96 (s, $-\text{NHCH}$), 6.20 (bs, $-\text{C}(=\text{O})\text{NH}$). The polymer SH-PNIPAM (1.0 g, 0.1 mmol SH) was dissolved in distilled DMF containing a trace amount of TCEP to prevent disulfide bond formation(10 ml). 4-Cyano-4'-(6-iodohexyloxy)azobenzene (I6Az) (0.067 g, 0.15 mmol, 1.5 equiv.) and sodium carbonate (1.1 g, 11 mmol) were added sequentially to the solution. The reaction mixture was stirred under nitrogen for 24 h at room temperature. The polymer was recovered by precipitation in diethyl ether and purified by two consecutive reprecipitations from THF into diethyl ether. Yield: 0.75 g, 69 %. ^1H NMR (CDCl_3) ppm, δ 1.13 (s, $-\text{NHCH}(\text{CH}_3)_2$), 1.30-2.35 (multiplets, polymer backbone protons), 3.96 (s, $-\text{NHCH}$), 6.40 (bs, $-\text{C}(=\text{O})\text{NH}$), 6.93 (d, Ar-**H**), 7.72 (m, Ar-**H**), 7.93 (m, Ar-**H**). UV-Vis (1,4-dioxane): $\lambda_{\text{max}} = 364$ nm.

Turbidity measurements. Solutions of a polymer (1.0 g/L) in water or in a water/1,4-dioxane mixture were placed in the sample compartment of the UV-Vis spectrometer and cooled to 5 °C. They were heated at a rate of 1 °C/min and the changes in transmittance at $\lambda = 650$ nm were measured as a function of temperature. The reported cloud point temperature corresponds to the temperature where the solution transmittance is 50 %. Cloud point temperatures were determined prior to irradiation and after UV irradiation at 366 nm or at >440 nm for 4 min (5 mW/cm²) at 5 °C with a Hg lamp (Ushio Optical Modulex, SX-UI501HQ).

Changes in absorption spectra of model azobenzene dye (4-(8-hydroxy-3,6-dioxaoctyl-1-oxy)-4'-cyanoazobenzene) as a function of the dioxane mole fraction in mixed water/dioxane solutions. 4-(8-Hydroxy-3,6-dioxaoctyl-1-oxy)-4'-cyanoazobenzene was prepared as reported previously⁴. Solutions for UV absorption spectra measurements were prepared by dissolving the model azobenzene dye (2.7×10^{-5} M) in water or dioxane. The solutions employed in the mixed-solvent experiments were prepared by mixing aliquots of each solution. Absorption spectra were measured prior to irradiation and after UV irradiation at $\lambda = 366$ nm or at $\lambda > 440$ nm for 4 min (5 mW/cm²) at 5 °C with a Hg lamp.

FIGURE CAPTIONS

- Figure S1** ^1H NMR spectrum of ethyl 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionate (EIM) (CDCl_3).
- Figure S2** ^1H NMR spectrum of α -4-cyano-4'-(6-iodohexyloxy)azobenzene- ω -2-(ethyl 2-methylpropionate-poly(*N*-isopropylacrylamide) (Az-PNIPAM) (CDCl_3)
- Figure S3** Changes of the wavenumber of maximum absorbance of the model azo dye as a function of solvent composition in water/1,4-dioxane mixtures.
- Figure S4** UV-Visible absorption spectra of solutions of the model dye in water (a), in a water/1,4-dioxane solution ($x_M = 0.06$) (b) and in 1,4-dioxane (c) before irradiation (black lines), after irradiation at $\lambda = 366$ nm (red lines) and after irradiation at $\lambda > 440$ nm (blue lines); dye concentration 2.7×10^{-5} mol/L; irradiation time: 4 min; irradiation temperature: 5 °C.
- Figure S5** Plots of the changes in the transmittance at 560 nm as a function of temperature for solutions of Az₂-PNIPAM (circles) and Az-PNIPAM (squares) in water before irradiation (a), after irradiation at $\lambda = 366$ nm (b) and after irradiation at $\lambda > 440$ nm (c); polymer concentration 1.0 g/L; irradiation time: 4 min; irradiation temperature: 5 °C.

SCHEME TITLES

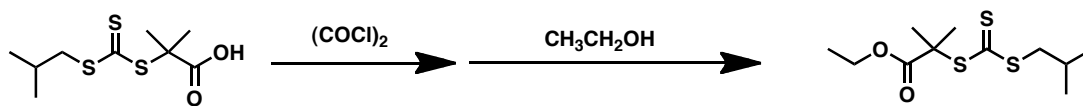
Scheme S1 Synthesis of ethyl 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionate (EIM).

Scheme S2 Synthesis of α -4-cyano-4'-(6-iodohexyloxy)azobenzene- ω -2-(ethyl 2-methylpropionate-poly(*N*-isopropylacrylamide) (Az-PNIPAM).

TABLES

Table S1 Molecular weight characteristics of the precursor polymers.

Table S2 Solution properties of aAz-PNIPAM and Az₂-PNIPAM samples in dilute aqueous solution from light scattering (N_{gg} , $M_{w,app}$, R_G , R_G/R_H , R_H and fluorescence probe measurements (C_{mic}))



Scheme S1.

EIM

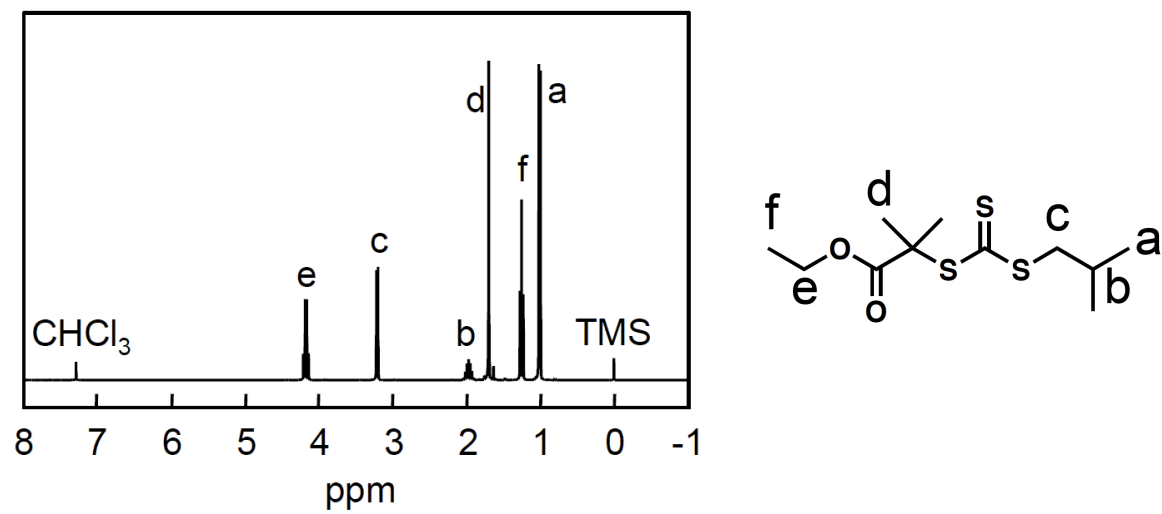


Figure S1.

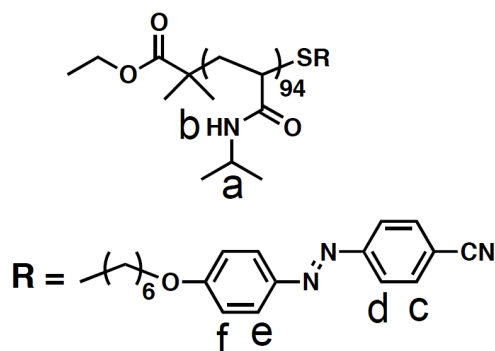
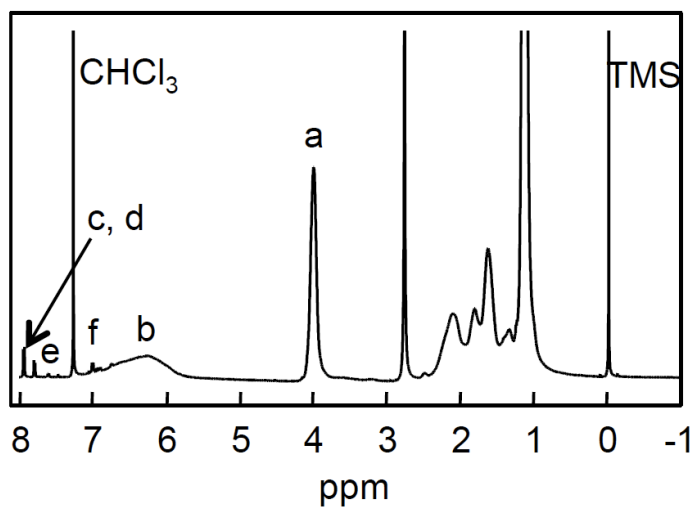


Figure S2.

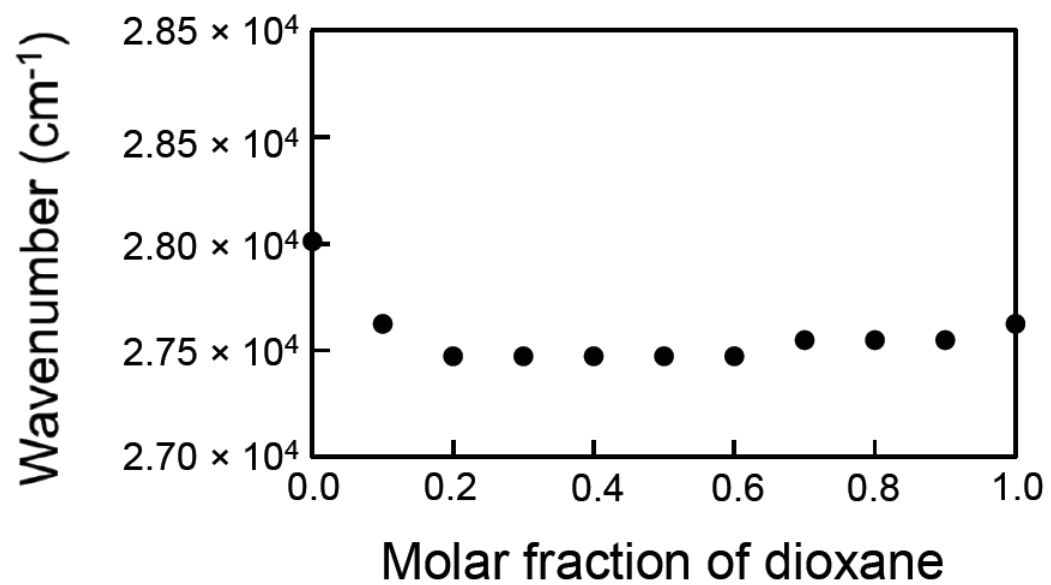


Figure S3.

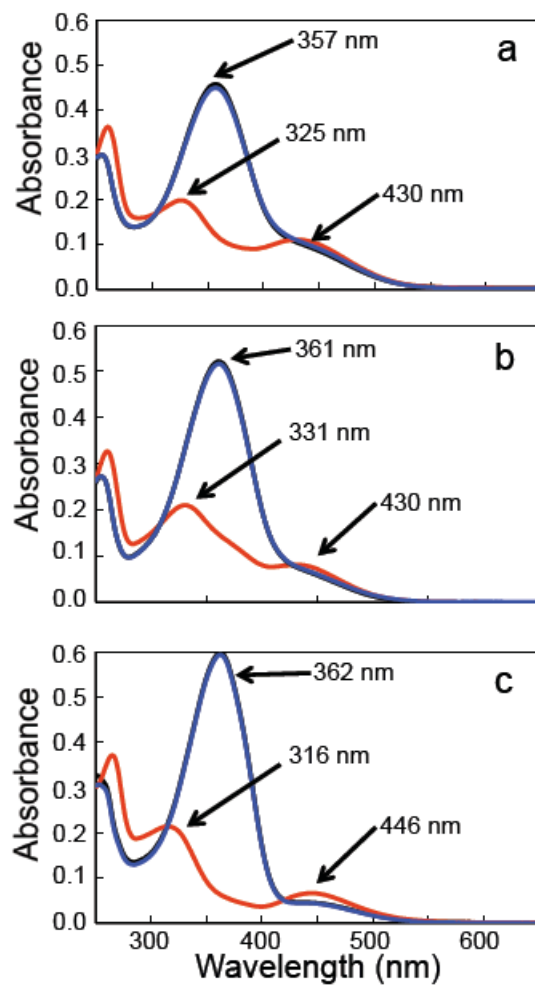


Figure S4.

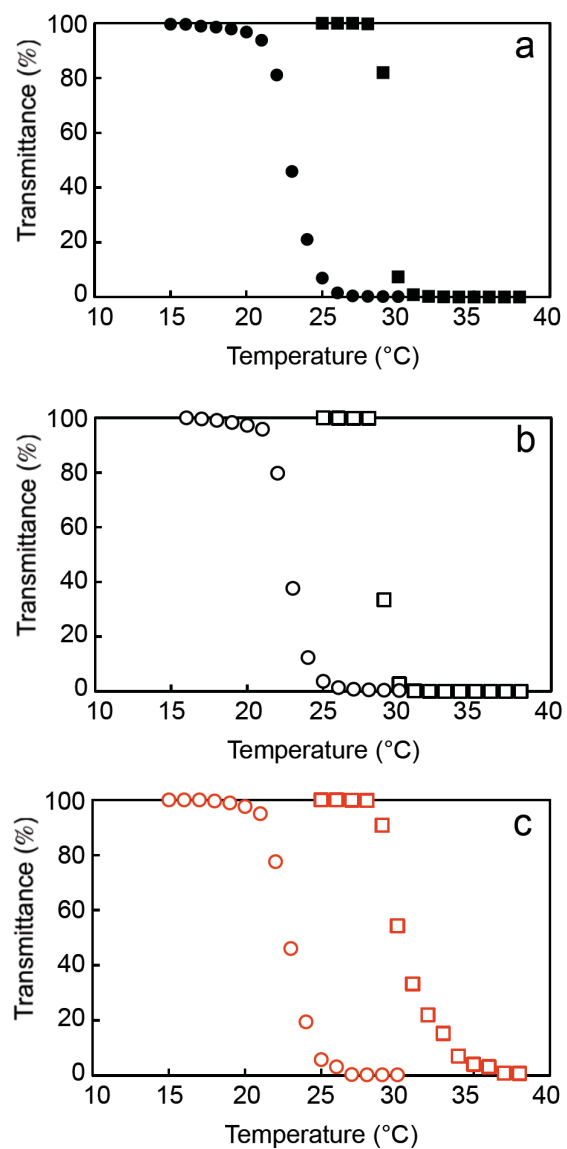


Figure S5.

Table S1.

| Sample | M_n (g/mol) | | | M_w/M_n (GPC) |
|-------------------------------|----------------------|-------|-------------------|-----------------|
| | UV-Vis ^{a)} | NMR | GPC ^{b)} | |
| IBS-PNIPAM | 10900 | - | 11900 | 1.07 |
| IBS₂-PNIPAM | 11800 | 11500 | 11500 | 1.08 |

a) $M_n = w/C_{CTA}$

b) GPC condition: Flow rate 1 ml/min, Solvent DMF, Temperature 40 °C

Table S2.

| Sample | C_{mic} (g/l) | $\frac{N_{\text{agg}}}{\text{SLS}}$ | $M_{w, \text{app}}$ (g/mol) | R_G (nm) | R_G/R_H | R_H (nm) |
|------------------------------|------------------------|-------------------------------------|-----------------------------|------------|-----------|------------|
| Az-PNIPAM | 0.55 | ~19 | 1.9×10^5 | 18.0 | 1.56 | 13.0 |
| Az₂-PNIPAM | 0.056 | ~29 | 2.9×10^5 | 17.5 | 1.60 | 8.0 |

At polymer concentration $c = 5$ g/l

Temperature $T = 8$ °C (Az-PNIPAM) and $T = 23$ °C (Az₂-PNIPAM)

References

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- (4) Altomare, A.; Ciardelli, F.; Gallot, B.; Mader, M.; Solaro, R.; Tirelli, N. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2957-2977