Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Photocontrolled reversible supramolecular assemblies of diblock azo-copolymer based on β-cyclodextrin/Azo host-guest inclusion complexation

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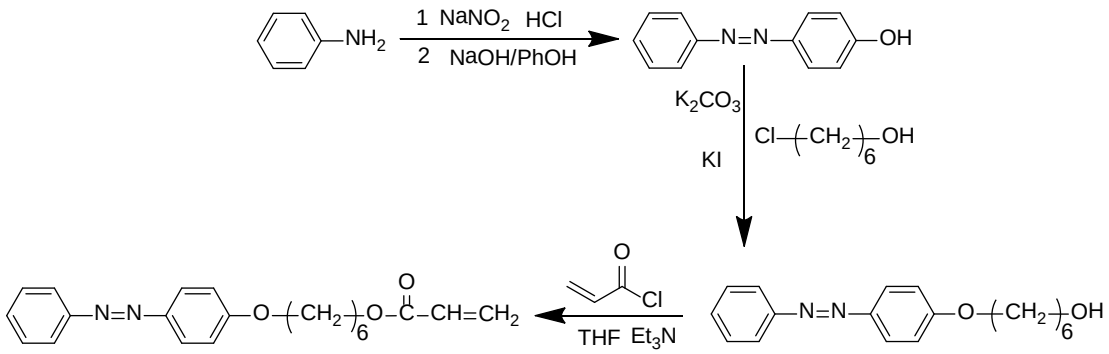
Scheme S1. The synthetic route of 6-(4-(phenyldiazenyl) phenoxy) hexyl acrylate monomer



Synthesis of 4-(phenyldiazenyl) phenol

4-(Phenyldiazenyl) phenol was synthesized according to the literature[1]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.94 (d, J = 8.4 Hz, 2H), 7.52-7.43 (m, 3H), 7.89-7.86 (m, 4H).

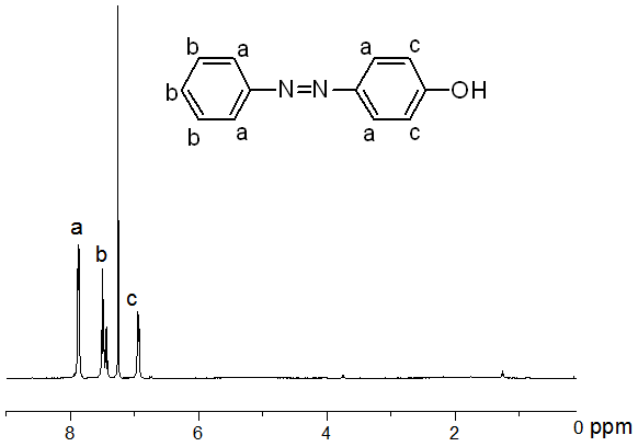


Fig. S1. ^{1}H NMR spectrum of 4-(phenyldiazenyl) phenol.

Synthesis of 6-(4-(phenyldiazenyl) phenoxy) hexan-1-ol

The 6-(4-(phenyldiazenyl) phenoxy) hexan-1-ol was prepared using the similar procedures according to the literature[2]. Typically, 4-(phenyldiazenyl) phenol (9.9 g, 50 mmol), 6-chloro-1-hexanol (10.2 g, 75 mmol), potassium carbonate (10.35 g, 75 mmol) and a trace amount of potassium iodide were dissolved in 200 mL DMF. The mixture solution was refluxed for 12 h and washed with a large amount of water. The product was extracted with chloroform, dried with anhydrous $MgSO_4$. After the solvent was removed by evaporation, the crude product

was purified by recrystallization from ethanol to obtain the purified product (8.95 g, 30 mmol) in 60% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26(s, 1H), 1.54-1.44(m, 4H), 1.63(m, 2H), 1.84(m, 2H), 3.67 (q, 2H), 4.05 (t, 2H), 7.00(d, 2H), 7.52-7.43(m, 3H), 7.92-7.86(m, 4H).

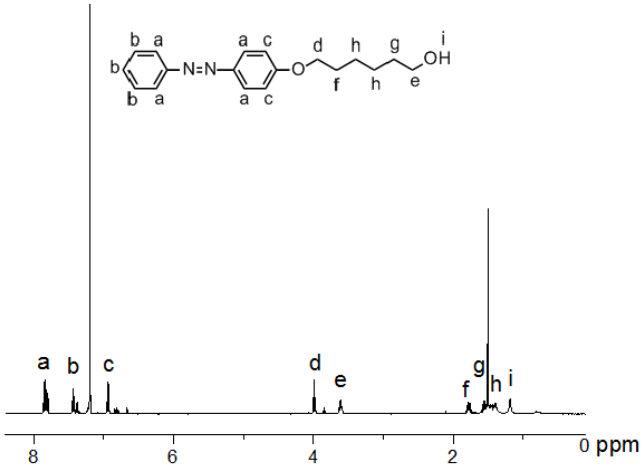


Fig. S2. ^{1}H NMR spectra of 6-(4-(phenyldiazenyl) phenoxy) hexan-1-ol

Synthesis of 6-(4-(phenyldiazenyl) phenoxy) hexyl acrylate

6-(4-(phenyldiazenyl) phenoxy) hexan-1-ol (5.96 g, 20 mmol) and triethylamine (3.04 g, 30 mmol) were dissolved in 80 mL anhydrous tetrahydrofuran. Then, acryloyl chloride (2.72 g, 30 mmol) in 10 mL anhydrous tetrahydrofuran was added dropwise to the mixed solution at 0 °C. The mixture was stirred overnight at room temperature. 200 mL deionized water was added, and the product was extracted with chloroform. After washed with deionized water three times, the product was dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (chloroform) to obtain the purified product (3.8 g, 10.8 mmol) in 54% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.55-1.45(m, 4H), 1.73(m, 2H), 1.84(m, 2H), 4.05(t, 2H), 4.18(t, 2H), 5.82(d, 1H), 6.12(dd, 1H), 6.40(d, 1H), 7.00(d, 2H), 7.52-7.43(m, 3H), 7.93-7.86(m, 4H).

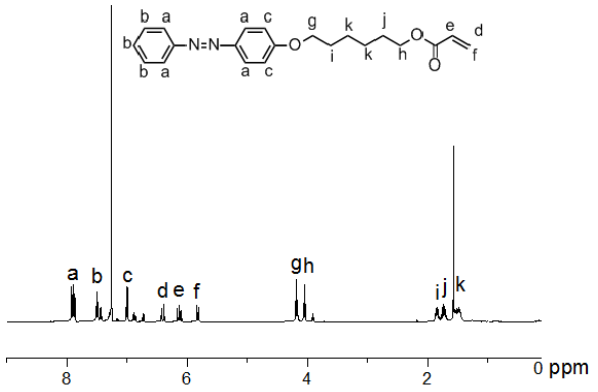


Fig. S3. ^{1}H NMR spectra of 6-(4-(phenyldiazenyl) phenoxy) hexyl acrylate.

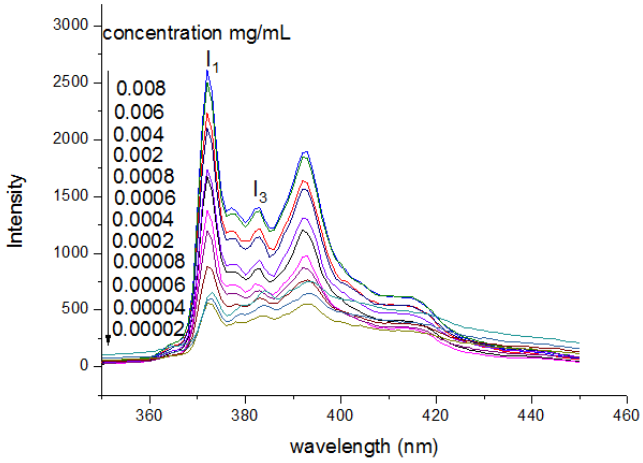


Fig. S4. The excitation spectra of pyrene in $PAzo_{10}$-*b*-PS_{70}/*β*-CD aqueous solution with different polymer concentration.

Table S1. The DLS results of $PAzo_{10}$-*b*-PS_{70} with *β*-CD micelles with different ratio of *β*-CD/azobenzene

Molar ratio (cyclodextrin : Azo group)	D_h [nm]	PDI ($\mu_2/<\Gamma>^2$)
0.5 : 1	262 nm	0.199
1 : 1	241 nm	0.121
2 : 1	250 nm	0.131
5 : 1	244 nm	0.170

References

1. B. Kiskan, F. Dogan, Y. Y. Durmaz and Y. Yagci, *Designed Monomers and Polymers*, 2008, **11**, 473-482.

2. H. Yu, T. Kobayashi and G.-H. Hu, *Polymer*, 2011, **52**, 1554-1561.