Supplementary Information for

Photo-Reversible Supramolecular Hyperbranched Polymer Based on
Host-Guest Interactions

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1. Materials

Tosyl chloride (TsCl) (99%, Shanghai Sinopharm Chemical Reagent Co. Ltd.), sodium azide (NaN₃) (99%, Aldrich), tripropargylamine (98%, Aldrich), copper(I) bromide (CuBr) (98%, Aldrich), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) (98%, Alfa Aesar), nitrosobenzene (97%, Aldrich), p-aminotoluene (99%, Aldrich), N-bromosuccinimide (NBS) (99%, Shanghai Sinopharm Chemical Reagent Co. Ltd.), benzoyl peroxide (BPO) (99%, Shanghai Sinopharm Chemical Reagent Co. Ltd.), 4,4′-bipyridine (98%, Alfa Aesar), sodium hydroxide (NaOH) (99%, Shanghai Sinopharm Chemical Reagent Co. Ltd.), hydrochloric acid (HCl) (37%, Shanghai Sinopharm Chemical Reagent Co. Ltd.), were used as received. β-Cyclodextrin (β-CD) (Shanghai Sinopharm Chemical Reagent Co. Ltd.) was dried for 48 h in a vacuum oven before use. Dimethyl-formamide (DMF), and carbon tetrachloride (CCl₄) from Shanghai Sinopharm Chemical Reagent Co. Ltd., were treated with calcium hydride and distilled before use. Acetic acid, acetone, ethyl acetate, petroleum ether, diethyl ether, ethanol from Shanghai Sinopharm Chemical Reagent Co., Ltd, and distilled water were used as received.

2. Characterization methods

¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury plus 400 NMR spectrometer (400 MHz) with dimethyl sulfoxide-d₆ (DMSO-d₆), CDCl₃ and D₂O as solvents. The 2D ¹H NMR ROESY spectra were recorded on a Bruker-Avance III NMR spectrometer (400 MHz) with dimethyl-formamide-d₇ (DMF-d₇)/D₂O (1/1, v/v) as solvents. Q-TOF-MS measurements were performed on a Waters-ACQUITY™ UPLC & Q-TOF-MS Premier with deionized water as the solvent. Viscosity studies were performed by using a Ubbelohde viscometer at 25 °C in DMF/H₂O (1/1, v/v). Dynamic light scattering measurements were carried out in an Autosizer 4700 Dynamic/Static Light Scattering Instrument. The light source was a He-Ne laser operating at 632 nm.
(Malvern). The dust was eliminated by filtering the sample solutions with a pore size of 0.45 \(\mu m\). The sample solutions were placed in the cell for at least 10 min prior to the measurement to allow for thermal equilibration. The morphology of supramolecular polymers was visualized using a VEECO-BioScope atomic force microscopy (AFM) with a dimension 3100 model and a Nanoscope IIIa controller. The UV-Vis measurements were performed on a Thermo Electron-EV300 UV-Vis spectrophotometer. The fluorescence emission spectra were recorded on a PTI-QM/TM/IM steady-state & time-resolved fluorescence spectrofluorometer.

UV irradiation at 365 \(nm\) for 10 min of the Diazo/\(\beta\)-CD\(_3\) (1/1, molar ratio) solution caused the isomerization of the azobenzene group from the \textit{trans} form to the \textit{cis} form. After visible light irradiation at 450 \(nm\) for 45 min, the \textit{cis}-Diazo transformed to \textit{trans}-Diazo reversibly. The UV absorption, fluorescence intensity and supramolecular polymer morphology could be switched for periodic variation by UV/visible light irradiation alternatively.

3. Synthesis details of \(\beta\)-cyclodextrin trimer (\(\beta\)-CD\(_3\))

![Scheme S1. Synthesis route of \(\beta\)-CD trimer](image)
Synthesis of mono-(6-O-(p-tolylsulfonyle))-β-cyclodextrin (β-CD-OTs)

According to the literature procedure,\(^1\) dry β-cyclodextrin (50.0 g, 44.0 mmol) was dissolved in 500 mL of 0.4 M aqueous sodium hydroxide and cooled down to 0 °C. Subsequently, p-toluenesulfonyl chloride (35.0 g, 184 mmol) was added in small portions under vigorous stirring over 10 min to the solution. The resulting suspension was stirred for 30 min below 5 °C, and then filtered quickly. The filtrate was neutralized to pH 8.5 with hydrochloric acid and stirred for another 1 h. The resultant precipitate was filtered off, washed three times with water and dried at 60 °C for 48 h. Yield: 20.0 g (15.5 mmol, 35%).

\(^1\)H NMR (DMSO-\(d_6\), 400 MHz) (Fig. S1): \(\delta\)\(\text{H} \, (\text{ppm}) = 2.41 \, (s, \text{Ph-CH}_3, 3\text{H}), 3.16-3.75 \, (\text{m}, \text{H-2,3,4,5,6, 42H}), 4.11-4.55 \, (\text{m}, \text{OH-6, 6H}), 4.72-4.90 \, (\text{m}, \text{H-1, 7H}), 5.25-6.25 \, (\text{br, OH-2,3, 14H}), 7.40 \, (\text{d, } J = 8.6 \text{ Hz, H-Ph-CH}_3, 2\text{H}), 7.75 \, (\text{d, } J = 7.8 \text{ Hz, H-Ph-SO}_3, 2\text{H}).

\(^13\)C NMR (DMSO-\(d_6\), 400 MHz): \(\delta\)\(\text{C} \, (\text{ppm}) = 21.90, 60.57, 72.70, 73.07, 73.37, 73.73, 82.15, 102.59, 128.25, 130.57, 133.28, 145.52.

Synthesis of mono-(6-azido-6-desoxy)-β-cyclodextrin (β-CD-N\(_3\))

According to Ref. 2, mono-(6-O-(p-tolylsulfonyle))-β-cyclodextrin (10.0 g, 7.76 mmol) was suspended in 100 mL of water and heated to 80 °C. Subsequently, sodium azide (2.53 g, 38.5 mmol) was added to the suspension, and stirred for 12 h until the reaction mixture became transparent. The solution was precipitated in 800 mL of acetone and the white solid was filtered, and then dissolved in 50 mL of water and precipitated in 400 mL of acetone again. The collected white powder was then dried in vacuum oven at 60 °C for 48 h yielding 8.19 g (7.06 mmol, 91.1%).

\(^1\)H NMR (DMSO-\(d_6\), 400 MHz) (Fig. S1): \(\delta\)\(\text{H} \, (\text{ppm}) = 3.12-3.42 \, (\text{m}, \text{H-2,4, 14H}),\)
3.49-3.82 (m, H-3,5,6, 28H), 4.40-4.58 (m, OH-6, 6H), 4.75-4.92 (m, H-1, 7H), 5.52-5.92 (m, OH-2,3, 14H). $^{13}$C NMR (DMSO-$d_6$, 400 MHz): $\delta_c$ (ppm) = 51.73, 60.57, 70.85, 72.68, 73.03, 73.71, 82.16, 83.62, 102.58.

**Synthesis of $\beta$-cyclodextrin trimer via click chemistry ($\beta$-CD$_3$)**

The reaction between tripropargylamine (0.187 g, 1.43 mmol) and $\beta$-CD-N$_3$ (5.5 g, 4.74 mmol) was conducted with 60 mL anhydrous $N,N$-dimethyl-formamide (DMF) by adding catalyst CuBr (0.618 g, 4.31 mmol) and PMDETA (0.747 g, 4.31 mmol). Under the protection of nitrogen, the reaction was carried out at 70 °C with vigorous stirring for 48 h. The resulting solution was diluted with 200 mL of DMF and passed through neutral alumina to remove the copper catalyst. Then the solution was concentrated to 50 mL and recrystallized in acetone twice to obtain the white solid. The crude product was dissolved in 30 mL deionized water, enclosed in dialysis membrane (MWCO 2.0 kDa), and then purified by dialyzing in deionized water for 48 h to remove the excess $\beta$-CD. After removal of the water by freeze drying, a white powder was obtained (2.0 g, yield: 40%).

$^1$H NMR (D$_2$O, 400 MHz) (Fig. S1): $\delta_H$ (ppm) = 2.74 (d, $J = 11.13$ Hz, H-$6'$-triazole, 3H), 3.02 (d, $J = 11$ Hz, H-$6'$-triazole, 3H), 3.20-4.00 (m, H-2,3,4,5,6, 120H), 4.08 (t, $J = 9.5$ Hz, N-CH$_2$-triazole, 3H), 4.50 (t, $J = 11.2$ Hz, N-CH$_2$-triazole, 3H), 4.90 (m, H-1, 21H), 7.85 (s, H-triazole, 3H). UPLC & Q-TOF-MS of $\beta$-CD$_3$ (Fig. S2): calculated for [M + H]$^{2+}$: 1806.09, found m/z: 1806.1184 [M + H]$^{2+}$. 

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Fig. S1. $^1$H NMR spectra of $\beta$-CD-OTs (a), $\beta$-CD-N$_3$ (b) in DMSO-$d_6$, and $\beta$-CD$_3$ (c) in D$_2$O.
4. Synthesis details of azobenzene dimer (Diazo)

\[
\text{N}^+ \text{N}^+ + \text{NH}_2 \xrightarrow{\text{AcOH}, \text{N}_2, \text{r.t., 24 h}} \text{N}^+ \text{N}^+ \xrightarrow{\text{BPO, NBS, CCl}_4, \text{N}_2, \text{reflux for 24 h}} \text{N}^+ \text{N}^+ \cdot \text{Br}^{-}
\]

Scheme S2. Synthesis route of azobenzene dimer.

Synthesis of 4-methyl azobenzene (Azo-Me)

According to Ref. 3, nitrosobenzene (3.00 g, 27.8 mmol) and p-aminotoluene (3.00 g, 27.8 mmol) were dissolved in 50 mL acetic acid. The resulting solution was stirred for 24 h at room temperature under an atmosphere of nitrogen. After evaporation of acetic acid under reduced pressure, the resulting solid was recrystallized from ethanol-water, followed by purification with silica gel column chromatography (petroleum ether-ethyl acetate). Yield: 5.1 g (85%).
$^1$H NMR (CDCl$_3$, 400 MHz) (Fig. S3): $\delta_H$ (ppm) = 2.44 (s, Ph-CH$_3$, 3H), 7.29-7.35 (m, N=N-Ph-CH$_3$, H of Ph close to CH$_3$, 2H), 7.435-7.545 (m, Ph-N=N, H of Ph away from N=N, 3H), 7.815-7.865 (m, Ph-N=N, H of Ph close to N=N, 2H), 7.88-7.935 (m, N=N-Ph-CH$_3$, H of Ph close to N=N, 2H).

**Synthesis of 4-bromomethyl azobenzene (Azo-Br)$^3$**

A mixture of Azo-Me (3.00 g, 15.3 mmol), NBS (2.72 g, 15.3 mmol), BPO (0.148 g, 0.57 mmol) and CCl$_4$ (60 mL) was refluxed for 24 h under an atmosphere of nitrogen. The resulting solution was filtered while hot, and the filtrate was concentrated under reduced pressure. The final crude product was purified by silica gel column chromatography (petroleum ether-ethyl acetate) to yield a brown powder (3.8 g, 90.5%).

$^1$H NMR (CDCl$_3$, 400 MHz) (Fig. S3): $\delta_H$ (ppm) = 4.56 (s, Ph-CH$_2$Br, 2H), 7.47-7.57 (m, Ph-N=N, H of Ph away from N=N and N=N-Ph-CH$_2$Br, H of Ph close to CH$_2$Br, 5H), 7.88-7.94 (m, Ph-N=N and N=N-Ph-CH$_2$Br, H of Ph close to N=N, 4H).

**Synthesis of azobenzene dimer (Diazo)$^3$**

A solution of Azo-Br (2.00 g, 7.27 mmol) and 4,4'-dipyridine (0.475 g, 3 mmol) in 35 mL DMF was allowed to react at 100 °C for 24 h. After being cooled to room temperature, the precipitate was filtered and washed with ethyl ether for three times, collected and dried at 60 °C in vacuum to yield an orange powder (1.8 g, 75%).

$^1$H NMR (DMSO-d$_6$, 400 MHz) (Fig. S3): $\delta_H$ (ppm) = 6.07 (s, BPy-CH$_2$-azobenzene, 4H), 7.55-7.65, 7.77-8.00 (m, m, H-azobenzene, 18H), 8.83 (d, J = 7 Hz, H of BPy away from N$^+$, 4H), 9.58 (d, J = 7 Hz, H of BPy close to N$^+$, 4H). UPLC & Q-TOF-MS of Diazo (minus two Br anions) (Fig. S4): calculated for [M + H]$^+$: 547.51, found m/z: 547.2577 [M + H]$^+$. 

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Fig. S3. $^1$H NMR spectra of 4-methyl-azobenzene (a), 4-bromomethyl-azobenzene (b) in CDCl$_3$, and Diazo (c) in DMSO-$d_6$. 
5. 2D ROESY spectrum for cis-Diazo/β-CD₃ (1/1) solution after UV irradiation

![2D ROESY spectrum](image)

Fig. S5. Partial 2D ROESY ¹H NMR spectrum of a 1/1 mixture of cis-Diazo guest and β-CD₃ host in DMF-δ/D₂O (1/1, v/v) at 15 mM at 30 °C. Asterisks indicate the signals of DMF-δ and D₂O.
6. Determination of association constant for trans- and cis-Azo with β-CD by UV-Vis method

As shown in Fig. S6 and Fig. S7, the association constant between trans-Azo-Br or cis-Azo-Br and β-CD in DMF/H₂O (1/1, v/v) solution was determined by following the UV absorptions at 327 nm and 428 nm, respectively. The concentration of trans-Azo-Br or cis-Azo-Br was kept at 2 × 10⁻⁵ M. Upon addition of excess β-CD, the absorption of trans-Azo-Br or cis-Azo-Br increased remarkably. With an assumption of a 1:1 stoichiometry, the inclusion complexation of β-CD (H) with trans-Azo-Br or cis-Azo-Br (G) is expressed by the following equations, respectively:

\[
H + G \leftrightarrow H \cdot G
\]

We employed the usual double reciprocal plot according to the modified Hidebrand-Benesi equation:

\[
\frac{1}{\Delta A} = \frac{1}{k_n \Delta \varepsilon [G]} + \frac{1}{\Delta \varepsilon [H]}
\]

Where H, G, \(K_a\) represents guest (trans-Azo-Br or cis-Azo-Br), host (β-CD), association constant respectively. \(\Delta A\) denotes the absorbance difference before and after host molecules are added. \(\Delta \varepsilon\), which denotes the difference of the molar extinction coefficient between the host and host-guest complex at the same wavelength, are \(4.87 \times 10^2\) M⁻¹cm⁻¹ for trans-Azo-Br/β-CD system and \(4.14 \times 10^3\) M⁻¹cm⁻¹ for cis-Azo-Br/β-CD system, respectively. The association constant \(K_a\) is calculated by the equation:

\[
K_a = \frac{b}{k} = 5.36 \times 10^3\ \text{M}^{-1} \text{ (for trans-Azo-Br/β-CD system)};
\]

\[
K_a = \frac{b}{k} = 3.15 \times 10^2\ \text{M}^{-1} \text{ (for cis-Azo-Br/β-CD system)}.
\]

Where \(k\) is the slope value of line plot, and \(b\) is the intercept of the line plot.
Fig. S6. The UV absorption of trans-Azo-Br upon stepwise addition excess β-CD. The concentration of trans-Azo-Br was $2 \times 10^{-5}$ M.

Fig. S7. The UV absorption of cis-Azo-Br upon stepwise addition excess β-CD. The concentration of cis-Azo-Br was $2 \times 10^{-5}$ M.
7. AFM images of photo-responsive SHPs after evaporation

*Fig. S8.* Larger-scale AFM amplitude images of photo-responsive SHP before UV irradiation.

*Fig. S9.* AFM images of photo-responsive SHPs (a) before and (b) after UV irradiation.
8. Liquid-phase AFM images of photo-responsive SHPs in solution

Fig. S10. Liquid-phase AFM images of SHPs in DMF/H₂O (1/1, v/v).
9. UV-Vis and fluorescence emission spectra of SHPs solution

Fig. S11. (a) UV-Vis spectra and (c) fluorescence emission spectra ($\lambda_{\text{ex}} = 360$ nm) of $\beta$-CD$_3$/Diazo (1/1, mol/mol) and Diazo in DMF/H$_2$O (1/1, v/v) before UV irradiation, after UV irradiation and after Vis irradiation. (b) Changes of maximum absorbance at around 323 nm and (d) changes of maximum emission intensity at around 440 nm upon alternating irradiation with UV and Vis light. The concentration of Diazo was kept at $2.5 \times 10^{-3}$ M.

10. References

