Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

End-to-end assembly and disassembly of gold nanorods based on photo-responsive host-guest interaction

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Experimental section

Materials

(E)-4-(phenyldiazenyl)phenol, 1,4-dibromobutane, 4,4'-bipyridine, potassium carbonate (K_2CO_3), chloroauric acid ($HAuCl_4 \cdot 3H_2O$), sodium borohydride ($NaBH_4$), ascorbic acid (AA), silver nitrate ($AgNO_3$), hexadecyl trimethyl ammonium bromide (CTAB) and all the solvents were commercial available and used without further purification. ^1H and ^{13}C NMR spectra were measured on a Brüker AV-400 spectrometer. The electrospray ionization (ESI) high-resolution mass spectra were tested on a HP 5958 mass spectrometer. The UV-Vis absorption spectra were obtained on a Varian Cary 100 UV-Vis spectrophotometer (1-cm quartz cell was used). Transmission electron microscopy (TEM) experiments were performed by using JEOL JEM-1400 equipment under an accelerating voltage of 100 kV. For the TEM observation, the samples in aqueous solution were dispersed on Cu grids pre-coated with thin carbon film (Cu-400 CN) and then completely dried for analysis. The FT-IR spectra were obtained on Nicolet 380 FT-IR spectrometer. The Raman spectra were carried out on InVia Reflex (Renishaw) spectrometer, the laser wavelength of which was 785nm.

Preparation of GNRs

GNRs were synthesized by seed-mediated method as described previously[1, 2]. In a typical experiment, an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (0.25ml, 0.01M) was added to a solution of CTAB (7.50ml, 0.10M) in a beaker. The solution was then mixed gently and turned into bright brown-yellow. An aqueous solution of ice-cold $NaBH_4$ (0.60ml, 0.01M) was added, followed by rapid and vigorous stir in 2min. Then the beaker was bathed in water at 28°C for 2h to form gold seed solution before preparation of GNRs. An aqueous solution of $AgNO_3$ (0.06ml, 0.01M) was added into the mixture of CTAB (9.50ml, 0.10M) and $HAuCl_4{\cdot}3H_2O$ (0.40ml, 0.01M) solution. Then AA (0.064ml, 0.10M) solution was added into it and then the mixture became colorless. 0.02ml of seed solution was added and mixed gently for 10s. At last, the mixture was incubating in water at 29°C for at least 3h.

General synthetic procedure

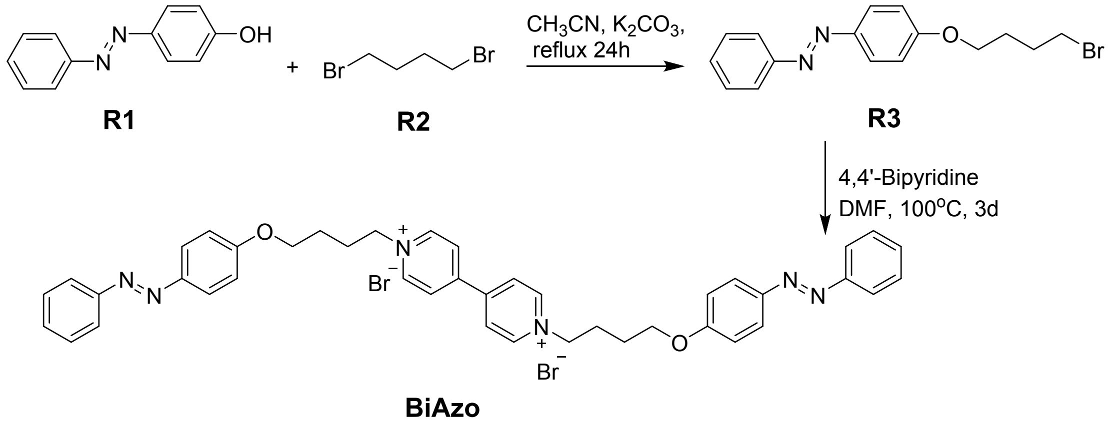


Fig S1. Schematic illustration of the synthesis of BiAzo.

Preparation of (E)-1-(4-(4-bromobutoxy)phenyl)-2-phenyldiazene (R3)

(E)-4-(phenyldiazenyl)phenol R1 (1.00g, 5.04mmol), 1,4-dibromobutane R2 (2.18g, 10.08mmol) and potassium carbonate (2.09g, 15.12mmol) were dissolved in 50 mL of acetonitrile. The resultant mixture was heated to reflux for 24h under nitrogen and then filtered in vacuum. The filtrate was distilled under vacuum to 2ml to afford an orange solid R3 (1.17g, 69.60%) which was collected by vacuum filtration and lavation with acetonitrile. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.9 Hz, 2H), 7.88 (d, J = 7.3 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 9.0 Hz, 2H), 4.09 (t, J = 6.0 Hz, 2H), 3.51 (t, J = 6.5 Hz, 2H), 2.16 – 2.05 (m, 2H), 2.05-1.94 (m, 2H) ppm.

Preparation of 1,1'-bis(4-(4-((E)-phenyldiazenyl)phenoxy)butyl)-[4,4'-bipyridine] -1,1'-diium bromide (BiAzo)

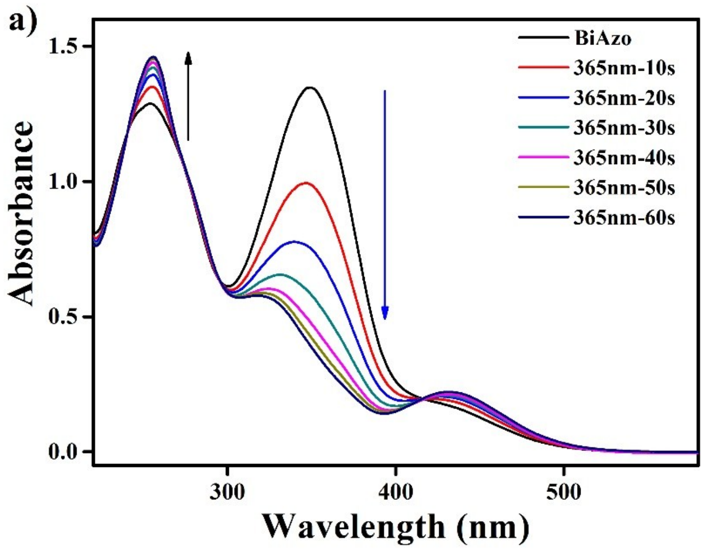
(E)-1-(4-(4-bromobutoxy)phenyl)-2-phenyldiazene R3 (0.80g, 2.40mmol) was dissolved in 25 mL of dimethylformamide (DMF). The mixture was heated to 100 °C and 4,4'-Bipyridine (0.094g, 0.60mmol) in 5 mL of DMF was then added dropwise. The resulting solution was stirred for 3d under nitrogen. The crude product was obtained by vacuum filtration and then purified by washing with 5 mL of DMF to yield an orange solid (0.14g, 28.30%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.44 (d, J = 6.4 Hz, 2H), 8.81 (d, J = 6.5 Hz, 2H), 7.90 (d, J = 8.9 Hz, 2H), 7.84 (dd, J = 7.2, 1.9 Hz, 2H), 7.57 (dt, J = 13.5, 7.1 Hz, 3H), 7.14 (d, J = 9.0 Hz, 2H), 4.79 (t, J = 7.4 Hz, 2H), 4.17 (t, J = 6.2 Hz, 2H), 2.24 – 2.15 (m, 2H), 1.85 (t, J = 7.4 Hz, 2H) ppm. m/z = 331.1669 $[(M - 2Br^-)/2]^+$.

Preparation of GNR-BiAzo@CD

GNR-BiAzo@CD was synthesized by mixing BiAzo@CD with freshly prepared GNRs. 10 mL of GNRs solution was first concentrated by double centrifugation to wash off superfluous CTAB and redistributed in 2 mL of deionized water. In a 100 mL round bottom flask, BiAzo (0.0066g, 0.008mmol) and HS-β-CD (0.018g, 0.016mmol) were mixed in 40 mL water and then sonicated for 30min to form inclusion complex, followed by adding the concentrated GNRs solution dropwise into it. The mixture was stirred in 25 °C oil bath over 4.5h under nitrogen and the resultant solution purified by double centrifugation at 9000 rpm to afford end-modified GNRs.

Disassembly of GNR-BiAzo@CD with Ad·HCl

After the end-modified GNRs were centrifuged twice, 2 mg of Ad·HCl was added into the solution and sonicated for 2 min.



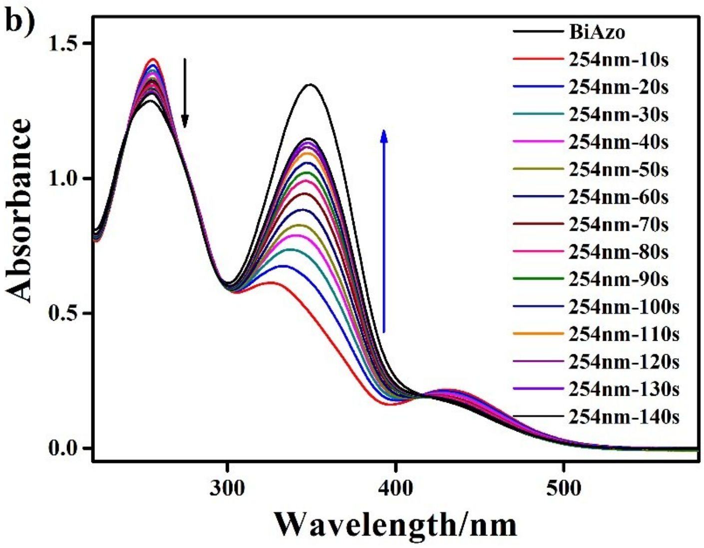


Fig. S2 UV-Vis absorption spectra of BiAzo in water (4×10^{-5} mol/L) irradiated with 365nm (a) and 254nm UV (b) light.

The UV spectrum of BiAzo was shown in Fig. S2. Owning to the *trans-cis* isomerization of BiAzo, the irradiation with 365nm light to the aqueous solution of BiAzo leads to a gradual decrease in the intensity of the maximal absorption peak at about 360nm and a gradual increase at 254 nm (Fig. S2a). The UV spectral changes can be shifted back by when irradiated with 254 nm light for 140 s (Fig. S2b).

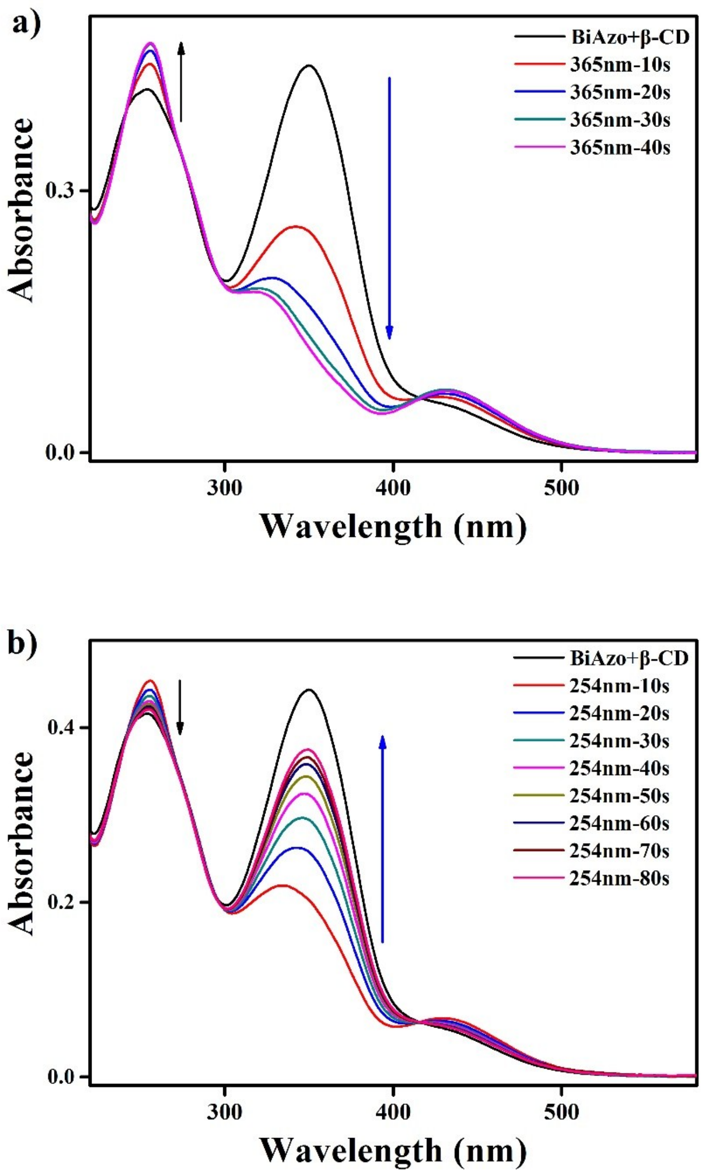
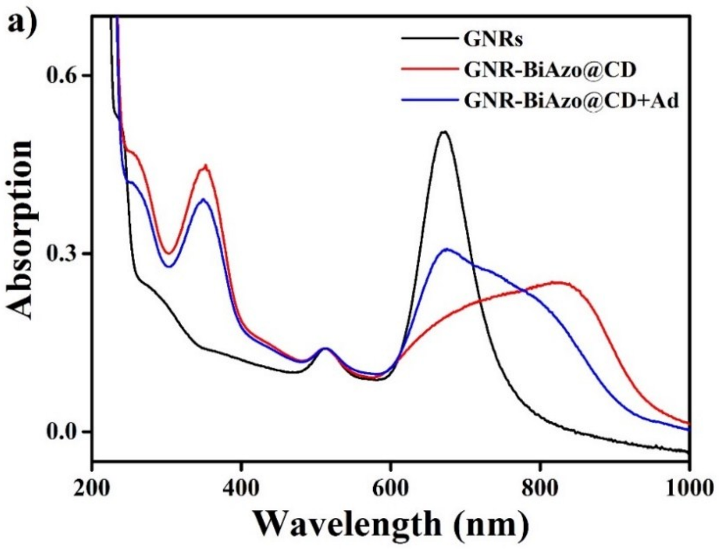


Fig. S3 UV-Vis adsorption spectra of BiAzo@CD in water (2×10^{-5} mol/L) irradiated with 365 nm (a) and 254 nm (b) UV light

The UV spectrum of BiAzo@CD was shown in Fig. S3. Owing to the *trans-cis* photoisomerization of azobenzene unit in BiAzo@CD, and its subsequent dethreading out of the β-CD cavity, the irradiation with 365 nm light resulted in a gradual decrease of the absorption 350 nm, but increase at 254 nm (Fig. S3a). And the spectral changes can be shifted back by irradiation with 254 nm light.



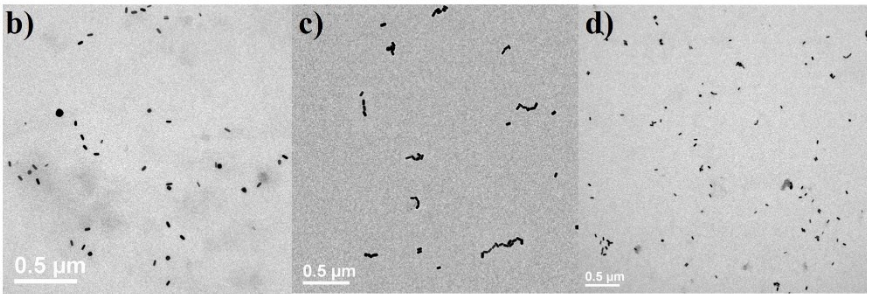


Fig. S4 UV-Vis absorption spectra (a) and TEM images (b, c, d) of aqueous GNRs (black), GNR-BiAzo@CD (red) and GNR-BiAzo@CD+Ad·HCl (blue).

In Fig. S4a, GNRs shows two characteristic absorption peaks at 672 nm and 514 nm. GNR-BiAzo@CD shows a red shift. Owing to the dethreading of azobenzene unit from cavity of CD by adding the competitive guest Ad·HCl, it shows a blue shift back. The TEM images in Fig. S4b-d correspond with their UV spectra.

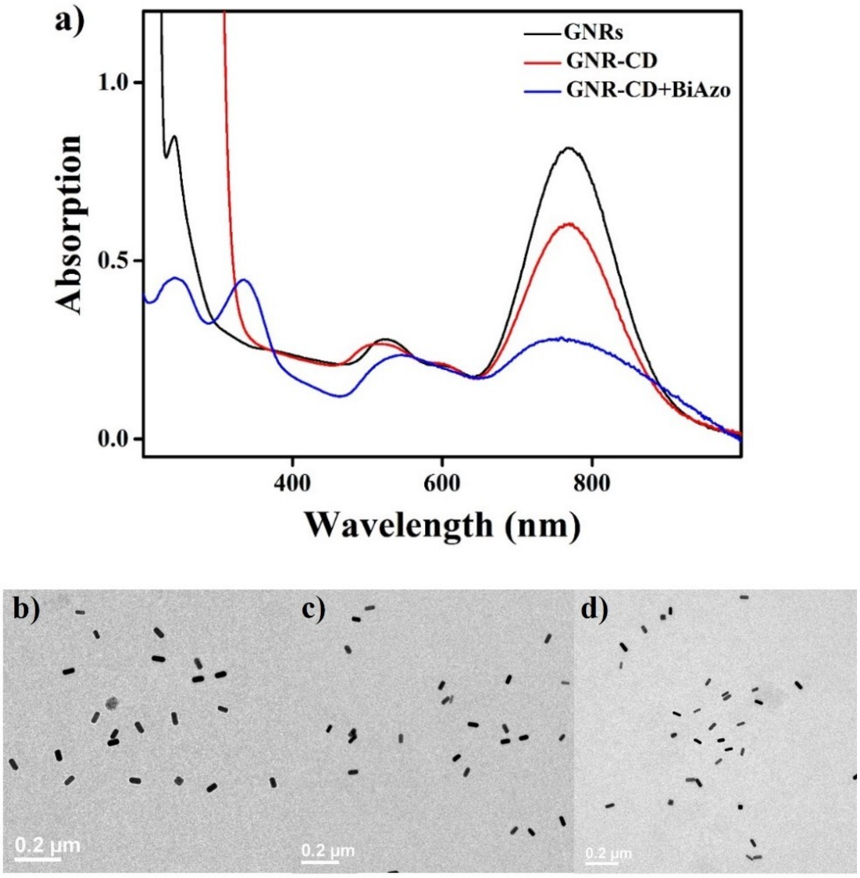


Fig. S5 UV-Vis absorption spectra (a) and TEM images (b, c, d) of aqueous GNRs (black), GNR-CD (red) and GNR-CD + BiAzo (blue).

In Fig. S5a, the CD-modified GNRs (GNR-CD) didn't exhibit any distinct shift compared with GNRs. After added with BiAzo into this system, the curve (GNR-CD + BiAzo) didn't show obvious change. The TEM images in Fig. S5b-d corresponded with UV spectra, in which GNRs distributed evenly in aqueous solution.

S1. T. K. Sau and C. J. Murphy, *Langmuir*, 2004, **20**, 6414.

S2. B. Nikoobakht and M. A. El-Sayed, *Chem. Mater*, 2003, **15**, 1957.