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View Article Online
DOI: 10.1039/C7CC01678F

Journal Name

COMMUNICATION

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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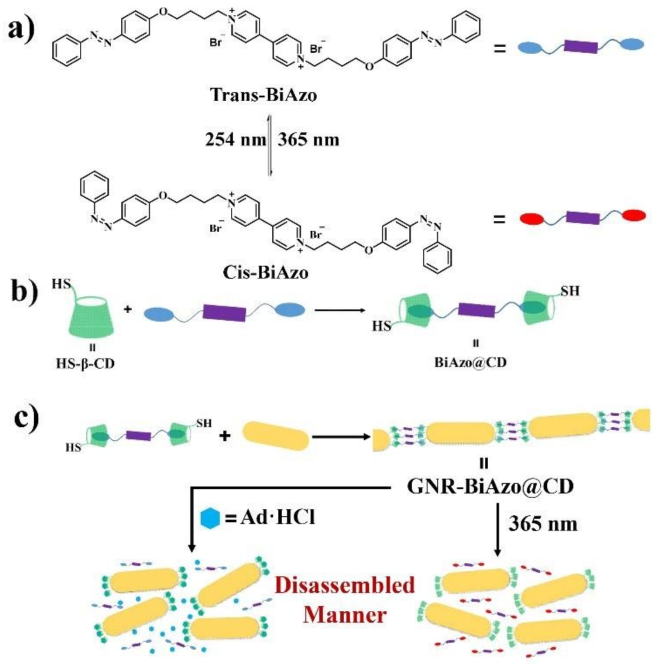
The host-guest interaction based on thiol-β-cyclodextrin and a symmetric compound containing two azobenzene units on ends has been utilized to form end-to-end assembly of gold nanorods. Both UV light irradiation and guest competition can be used to transform the GNRs alignments into disassembled manners.

Nanomaterials, such as nano-sensor, nano-catalyst and nano-semiconductor materials, have gained great attention in many fields. As one of the most widely studied nanomaterials, Gold nanorods (GNRs) have obtained unprecedented development in the past twenty years due to its anisotropy, controllable aspect ratio[1] and unique optical properties[2] in both visible and near-infrared regions. The optical properties of GNRs originate from surface plasmon resonance (SPR). Specially, the longitudinal surface plasmon band that can be tailored by diverse aspect ratios and different aggregating styles of GNRs ranges from 600 nm to 1600 nm[3]. The ends of the GNRs are found to be inclined to be exchanged with thiol-terminated compounds due to less CTAB protection there, which makes it possible to assemble GNRs in end-to-end arrangement[4]. A diversity of connecting methods can be employed to modify the ends of GNRs, such as metal-metal and π-π interactions[5], thiol-terminated antibody-antigen recognition[6], supramolecular host-guest interaction[7], electrostatic attraction[8] using porphyrins and phthalocyanines[9], hydrophobic interaction[10], hierarchical bottom-up assembly strategy creating nanoribbon-shaped GNRs nanocomposites[11]. GNRs possess potential applications in optical and electronic fields[12], biological hybrid nanomaterials[13], biological sensors[14], bioimaging[15] and drug delivery[16].

Supramolecular systems are increasingly utilized to assemble different types of molecules into unique architectures with particular structures and properties[17]. As one of the most important applied forces in supramolecular chemistry, the host-guest interaction can realize supramolecular assembly and disassembly[18] via diverse stimuli. So an emerging amount of researches which combine supramolecular chemistry with inorganic nanomaterials have given birth to hybrid materials with various intriguing characteristics or enhanced performances[19]. Cyclodextrin (CD) with favorable water solubility is usually utilized to construct water-soluble supramolecules because of the capability of forming complex with numerous guest molecules[20]. Usually selected as such a guest to be complexed by the cavity of CD, azobenzene[21] has photo-responsive character of switching between *trans*-configuration and *cis*-configuration upon irradiated with alternative light.



Scheme 1 Schematic illustration of (a) *trans-cis* isomerization of BiAzo, (b) formation of the 1:2 inclusion complex, BiAzo@CD, (c) functionalization of GNRs with BiAzo@CD to produce GNR-BiAzo@CD and transformation from end-to-end assembly to random style by 365nm UV light irradiation or adding Ad·HCl.

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†Electronic Supplementary Information (ESI) available: Detailed synthesis, Characterization data, UV/VIS absorption spectra, Transmission electron microscopic spectra. See DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C7CC01678F

Herein, we demonstrate the introduction of host-guest interaction based on the recognition of thiol-β-cyclodextrin (HS-β-CD) to azobenzene for directing linear assembly of GNRs. Especially, the resulting GNR alignments, which were covered with supramolecular complex consist of HS-β-CD and azobenzene-based soluble guest on their ends through strong covalent Au-S linkages, can be disturbed upon irradiated with 365 nm UV light under ultrasonic or added with competitive guest compound, adamantanamine hydrochloride (Ad·HCl). This novel approach provides control over GNRs end-to-end assembly, which may open up an emerging and effective way to obtain reversible hybrid nanomaterials.

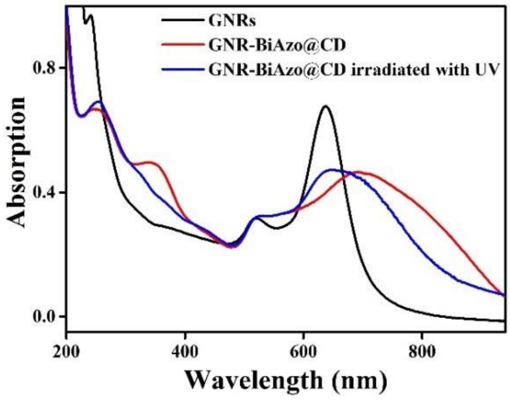

Fig. 1 UV-Vis absorption spectra of aqueous GNRs (black), GNR-BiAzo@CD (red) and GNR-BiAzo@CD irradiated with 365nm UV light (blue).

The GNRs with an aspect ratio of 3 (14 nm × 52 nm) were synthesized by a modification of seed-mediated method reported previously by Murphy[22] and El-Sayed[23]. As depicted in Scheme 1a, a symmetric compound, *trans*-BiAzo, containing two azobenzene units on both ends and one viologen unit capable of increasing molecular solubility was synthesized (see ESI). This compound was then mixed with 2 equivalents of HS-β-CD capable of binding with GNRs to yield a 1:2 inclusion compound BiAzo@CD through host-guest interaction between azobenzene and cyclodextrin. The UV-Vis absorption spectra of BiAzo and BiAzo@CD have also been studied (Fig. S2 and S3), finding that BiAzo showed two characteristic absorptions at 254 nm and 350 nm and could switch between *cis*- (Fig. S2b) and *trans*-configuration (Fig. S2a), and BiAzo@CD could generate (Fig. S3b) and dissociate (Fig. S3a) using 254 nm and 365 nm UV light, respectively. After 2 times of centrifugation to wash away excessive CTAB and unreacted chloroauric acid, the condensed GNRs solution was added dropwise into the mixture, and then bathed in 25 °C water for 4.5 h to give GNR-BiAzo@CD through strong covalent Au-S linkages as a result. As depicted in Scheme 1c, BiAzo@CD replaces CTAB to form S-Au bond on the ends of GNRs due to less CTAB protection there and performs as a soluble linker to allow for the end-to-end assembly of neighboring GNRs. The GNRs aggregates could turn into dispersive state when irradiated with 365 nm under ultrasonic wave as expected, which cannot happen only with UV light or ultrasonic. Meanwhile, when a solution of Ad·HCl was added into GNR-BiAzo@CD solution, the assembled GNRs could also turn into disordered state because of higher affinity (log K = 3.95) between Ad and CD, which has also been demonstrated by UV-Vis spectra (Fig. S4a) and TEM images (Fig. S4d).

The UV-Vis absorption spectra of GNRs and GNR-BiAzo@CD were studied and shown in Fig. 1. The GNRs exhibited two characteristic plasma absorption peaks at 520 nm and 640 nm corresponding to transverse and longitude surface plasmon resonance (LSPR), respectively. When BiAzo@CD modified GNRs (GNR-BiAzo@CD) were successfully prepared, the LSPR absorption band showed a red shift by 51 nm, which indicated the formation of end-to-end assembly of GNRs. When the GNRs alignment was irradiated with 365 nm UV light under ultrasonic, the absorption band of GNR-BiAzo@CD showed a blue shift by 46 nm, implying the disassembly of GNR alignment.

The end-to-end assembly and disassembly of GNR-BiAzo@CD have been characterized by TEM measurements (Fig. 2). GNRs were evenly dispersed in water without any aggregation (Fig. 2a). When GNRs were successfully modified with BiAzo@CD, they were found to form alignment in an "end-to-end" arrangement, as shown in the TEM images (Fig. 2b and 2C). Interestingly, upon irradiated with 365 nm under ultrasonic wave, the GNRs alignment turned into disassembled state due to the dissociation between cyclodextrin and *cis*-azobenzene, which could be found in Fig. 3d. All these TEM images are in conformity with UV-Vis absorption spectra shown in Fig. 1.

However, the resulted GNRs could not form back to end-to-end manner when irradiated with 254 nm UV light. The GNRs alignment was achieved due to the pre-organization of water-soluble linker and formation of S-Au bond to drag neighboring GNRs together. When the linker was break up, the affinity[24] (K_{eq} = 770) between CD and guest compound was not strong enough to turn GNRs into assemble state compared to covalent S-Au bond. To prove it, the GNRs modified with HS-β-CD (GNR-CD) were prepared. After it was added with *trans*-BiAzo aqueous solution, the UV-Vis spectra (Fig. S5a) didn't show obvious red shift, accompanied by even distribution in TEM image (Fig. S5d), which manifested the non-reassembly by 254nm UV light.

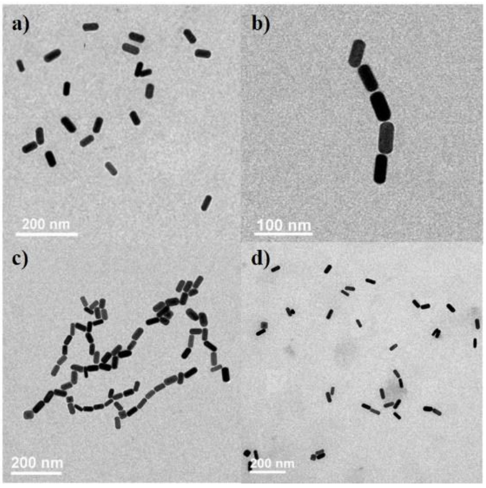

Fig. 2 TEM images of GNRs (a), GNR-BiAzo@CD (b and c) and GNR-BiAzo@CD irradiated with 365 nm UV light (d).

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The Raman spectrum of GNR-BiAzo@CD was compared with that of GNRs, which proved the existence of covalent S-Au bond on the surface of GNRs. As depicted in Fig. 3a, the Raman band of GNRs at 174 cm^{-1} was attributed to the Br-Au bond. And it was expected to find that the characteristic peaks at 116 cm^{-1} and 262 cm^{-1} attributed to Au-S-C bond and S-Au bond respectively were shown on the curve of GNR-BiAzo@CD. The changes of Raman spectra effectively proved the successful modification of GNRs with BiAzo@CD.

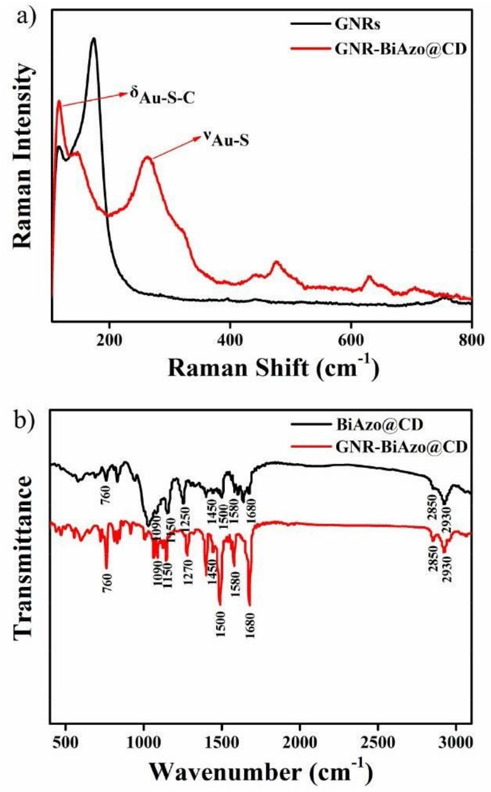

Fig. 3 (a) Normalized Raman spectra of CTAB-GNR (black) and GNR-BiAzo@CD (red). (b) FT-IR spectra of BiAzo@CD (black) and GNR-BiAzo@CD (red).

The FT-IR spectra (Fig. 3b) of BiAzo@CD and GNR-BiAzo@CD were also studied to reaffirm that GNRs was successfully modified with BiAzo@CD. The similar FT-IR signals at 2850 cm^{-1} and 2930 cm^{-1} attributed to CH_2 stretching vibration were observed in both spectra. The four signals at 1680 cm^{-1}, 1580 cm^{-1}, 1500 cm^{-1} and 1450 cm^{-1} were the characteristic peaks of skeleton deformation vibration of benzene ring. The band of symmetrical and asymmetrical stretching vibration of C-O-C was found at 1090 cm^{-1} and 1150 cm^{-1}, respectively. The signal at 760 cm^{-1} manifested the out-of-plane bending vibration of C-H in benzene ring. And the characteristic signals of the stretching vibration of C-S were shown at 1250 cm^{-1}. Thus, their FT-IR spectra also help to prove the successful attachment of BiAzo@CD onto GNRs.

In summary, we have constructed an end-to-end alignment of GNRs through a binary supramolecular system based on host-guest interaction and could use UV light to realize the transformation from assembly to disassembly of GNRs. The guest that possesses *trans*-azobenzene on both ends can be included in the hydrophobic cavity of HS-β-CD, forming a 1:2 inclusion compound performing as a water-soluble linker in arranging GNRs alignment. Moreover, when the GNRs alignment was irradiated by 365 nm UV light under ultrasonic, it would disassemble and form back to random style like CTAB-coated GNRs in water because *trans*-azobenzene underwent a conformational switching to *cis*-azobenzene and thus, the water-soluble linker plucked from cavity of CD. This work successfully developed a method to obtain hybrid GNR nanomaterials and effectively control their assembling/dissembling via both light stimuli and guest competition.

We acknowledge the financial support from Programme of Introducing Talents of Discipline to Universities (B16017), NSFC/China (21421004, 21476075 and 21272072) and the Fundamental Research Funds for the Central Universities.

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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

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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

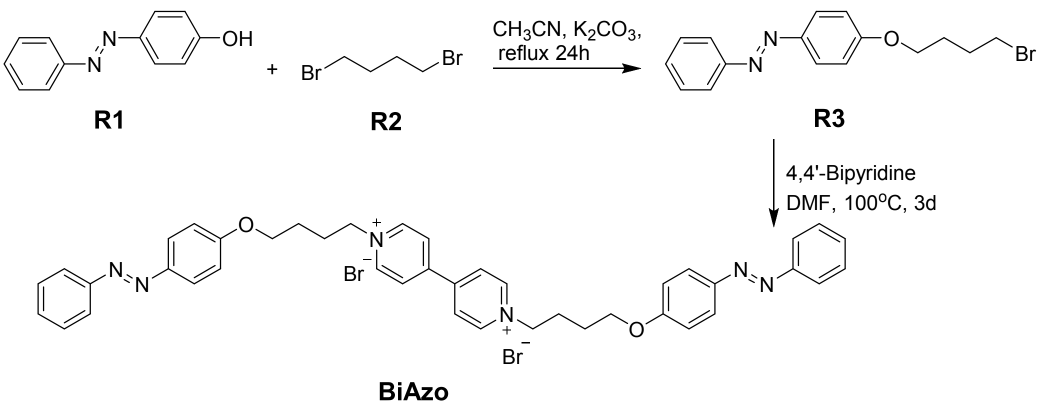

Fig S1. Schematic illustration of the synthesis of BiAzo.

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.

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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 ^{o}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 ^{o}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.

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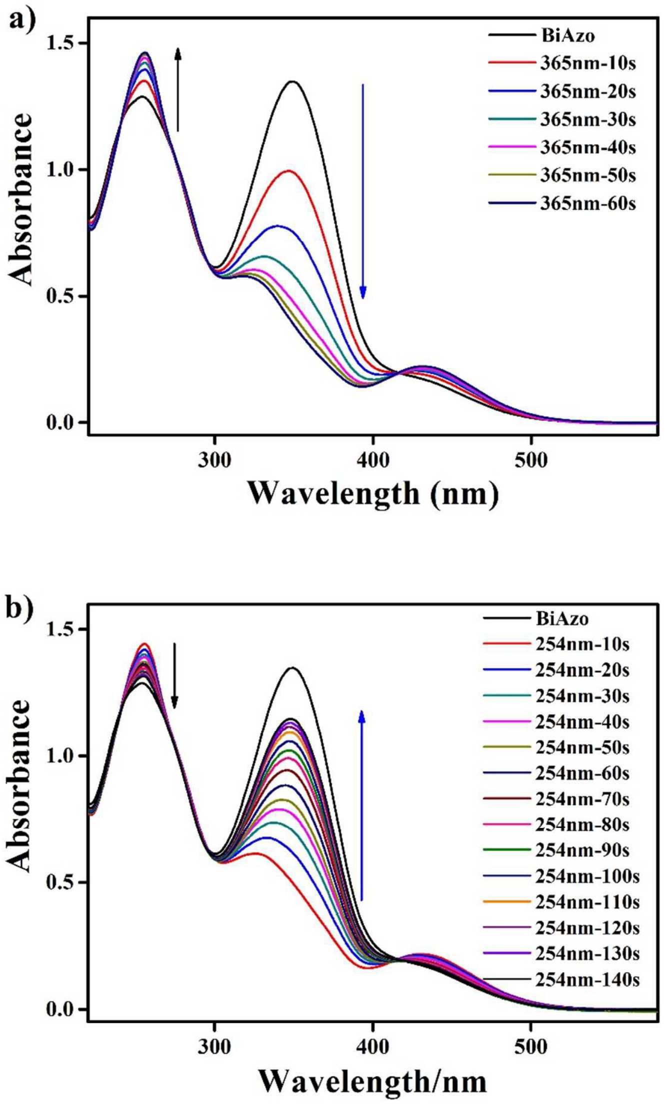

Fig. S2 UV-Vis absorption spectra of BiAzo in water (4×10^{-5} mol/L) irradiated with 365nm (a) and 254nm UV (b) light.

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).

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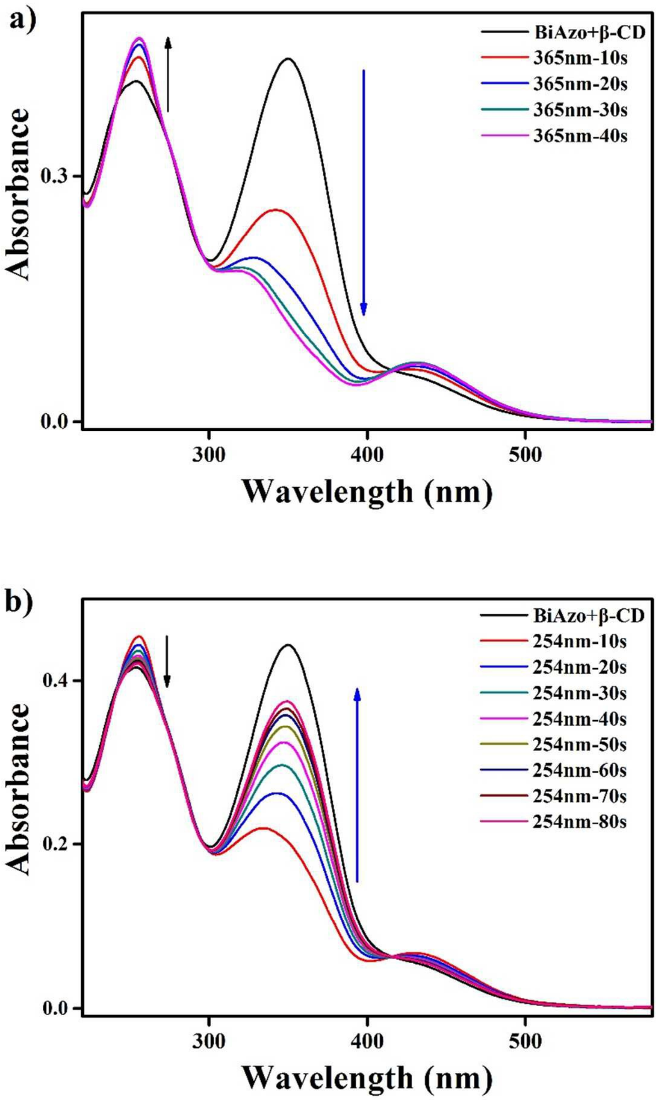

Fig. S3 UV-Vis adsorption spectra of BiAzo@CD in water (2×10^{-5} mol/L) irradiated with 365 nm (a) and 254 nm (b) UV light

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.

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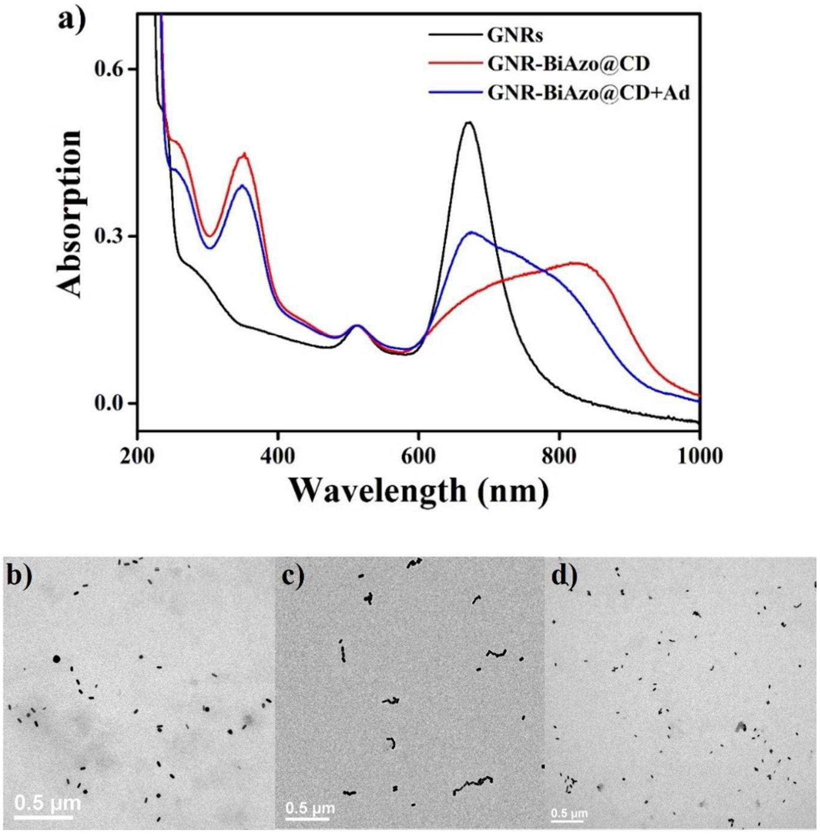

Fig. S4 UV-Vis absorption spectra (a) and TEM images (b, c, d) of aqueous GNRs (black), GNR-BiAzo@CD (red) and GNR-BiAzo@CD+Ad·HCl (blue).

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.

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DOI: 10.1039/C7CC01678F

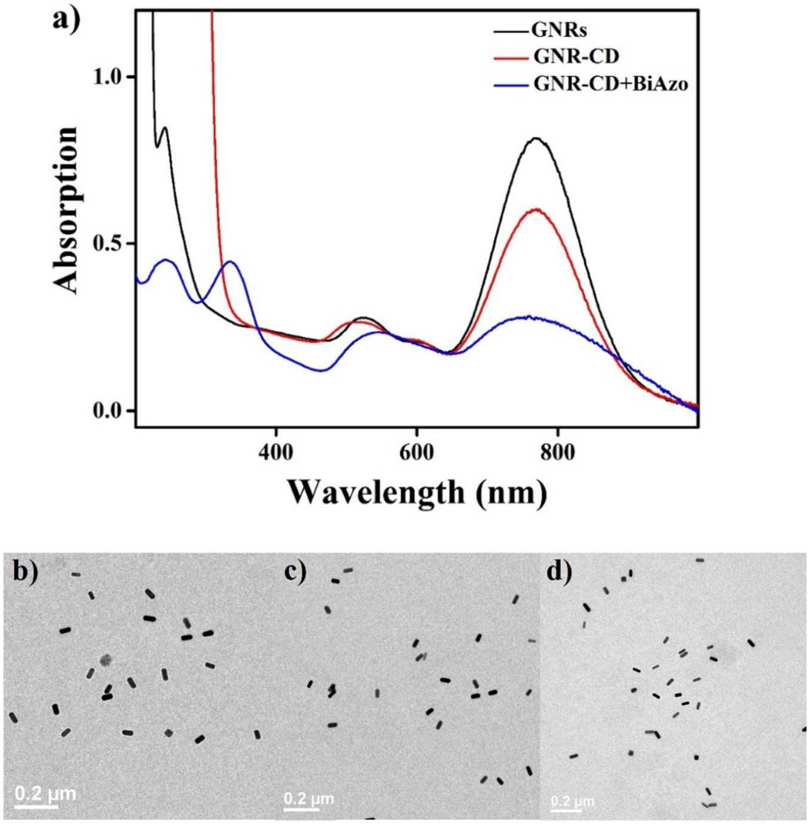

Fig. S5 UV-Vis absorption spectra (a) and TEM images (b, c, d) of aqueous GNRs (black), GNR-CD (red) and GNR-CD + BiAzo (blue).

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.
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