

Supporting Information

Organo-soluble Photoresponsive Azo Thiol Monolayer-protected Gold Nanorods

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1. Materials and Instruments.

All chemicals and solvents were purchased from commercial supplies and used without further purification. Deionized water was used in the preparation of gold nanorods. H₂AuCl₄ is a 30 wt % in diluted HCl solution. Cetyltrimethylammonium bromide (CTAB), NaBH₄, AgNO₃, and ascorbic acid were used. ¹H and ¹³C NMR spectra were recorded in CDCl₃ or d-acetone. Chemical shifts are in δ units (ppm) with the residual solvent peak as the internal standard. The coupling constant (J) is reported (s, singlet; d, doublet; t, triplet; and m, multiplet). Column chromatography was carried out on silica gel (60-200 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh F₂₅₄ glass plates. Spots were rendered visible by exposing the plate to UV light. Infrared FT-IR spectra were recorded with a KBr plates. UV-vis spectra were measured by a Perkin Elmer Lambda 19 Spectrometer. Elemental analysis was performed by Robertson Microlet Inc. Raman spectra were measured on a Jobin Yvon HR 800 Raman Spectrometer with inverted microscope (Olympus IX71). Sample for Raman spectra was deposited on a glass slide and left to dry then was used in the measurement. The wavelength of the laser used was 785nm. TEM images were taken on a Hitachi H-7600 transmission electron microscope. The UV irradiation was carried out by 4 μ W/cm² UV lamp with 365 nm peak wavelength.

2. Synthesis of azo thiol surfactant 1.

The azo thiol **1** was synthesized starting from 4-aminophenol **2** which was reacted with sodium nitrite in aqueous HCl to give diazonium salt followed by coupling with phenol to obtain azo intermediate **3**. The azo intermediate was treated with 1-bromohexadecane in the presence of K₂CO₃ to get **4**. The phenol intermediate **4** was reacted with 11-thioacetoxyl-1-bromoundecane **7** which was synthesized starting from 11-bromoundecan-1-ol to get the intermediate **8**. The intermediate **8** was de-protected in the presence of tetrabutylammonium cyanide (TBACN) to get azo thiol **1** (Fig. S1). The structure of azo thiol **1** was well identified by ¹H NMR, ¹³C NMR, FT-IR, and elemental analysis.

Data for 4,4'-dihydroxyazobenzene **3**

¹H NMR (d-acetone): δ 2.88 (br, 2H), 6.98 (m, 4H), 7.78 (m, 4H); ¹³C NMR (d-acetone): 116.38, 125.00, 146.95, 160.42.

Data for 4-(4-hexadecyloxy-phenylazo)-phenol **4**

¹H NMR (CDCl₃): δ 0.88 (t, 3H), 1.26 (m, 26H), 1.81 (m, 2H), 4.03 (t, 2H J = 6.6 Hz), 6.94 (m, 4H), 7.85 (m, 4H); ¹³C NMR (CDCl₃): 14.32, 23.30, 26.70, 28.65, 29.03, 29.42, 29.80, 30.04, 30.19, 30.26, 30.58, 32.26, 32.60, 68.95, 115.55, 116.52, 124.88, 125.20, 147.12, 147.61, 160.86, 162.11.

Data for thioacetic acid *S*-(11-(4-(4-hydroxy-undecyl)-phenyazo)-phenoxy) ester **6**

^1H NMR (CDCl_3): δ 1.27 (m, 14H), 1.56 (m, 4H), 2.32 (s, 3H), 2.86 (t, 2H, $J = 7.2$ Hz), 3.63 (t, 2H, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3): δ 28.78, 29.07, 29.15, 29.39, 29.42, 29.46, 29.16, 29.39, 29.42, 29.46, 29.47, 29.52, 29.54, 29.55, 29.57, 30.63, 32.77, 62.98, 196.20.

Data for 11-thioacetoxyl-1-bromoundecane **7**

^1H NMR (CDCl_3): δ 1.26 (m, 16H), 1.84 (m, 2H), 2.31 (s, 3H), 2.85 (t, 2H, $J = 6.99$ Hz), 3.40 (t, 2H, $J = 5.99$ Hz).

Data for thioacetic acid *S*-(11-[4-(4-hexadecyloxy-phenyazo)-phenoxy]-undecyl) ester **8**

^1H NMR (CDCl_3): δ 0.88 (t, 3H), 1.26 (m, 42H), 1.78 (m, 4H), 2.32 (s, 3H), 2.86 (t, 2H, $J = 7.1$ Hz), 4.03 (t, 4H, $J = 6.4$ Hz), 6.96 (d, 4H, $J = 9.0$ Hz), 7.83 (d, 4H, $J = 8.8$ Hz); ^{13}C NMR (CDCl_3): 14.19, 22.76, 26.10, 28.89, 29.18, 29.23, 29.31, 29.44, 29.47, 29.52, 29.58, 29.65, 29.68, 29.78, 30.87, 32.01, 68.40, 114.74, 124.37, 147.04, 161.25.

Data for the target thiol **1**

Yellow solid; ^1H NMR (CDCl_3): δ 0.88 (t, 3H), 1.30 (m, 42H), 1.78 (m, 4H), 2.51 (t, 2H, $J = 7.1$ Hz), 4.03 (t, 4H, $J = 6.4$ Hz), 6.97 (m, 4H), 7.85 (m, 4H); ^{13}C NMR (CDCl_3): δ 14.12, 22.70, 24.65, 26.03, 28.38, 29.07, 29.23, 29.37, 29.49, 29.6; IR (KBr) ν_{max} (cm^{-1}): 2917.21, 2848.60, 1604.11, 1463.74, 1253.00, 1151.63, 1107.21, 1019.79, 843.89, 823.02, 750.00, 603.49, 555.52; Anal. calcd for $\text{C}_{39}\text{H}_{64}\text{N}_2\text{O}_2\text{S}$: C, 74.95; H, 10.32; N, 4.48; S, 5.13. Found: C, 74.74; H, 10.58; N, 4.42; S, 5.09.

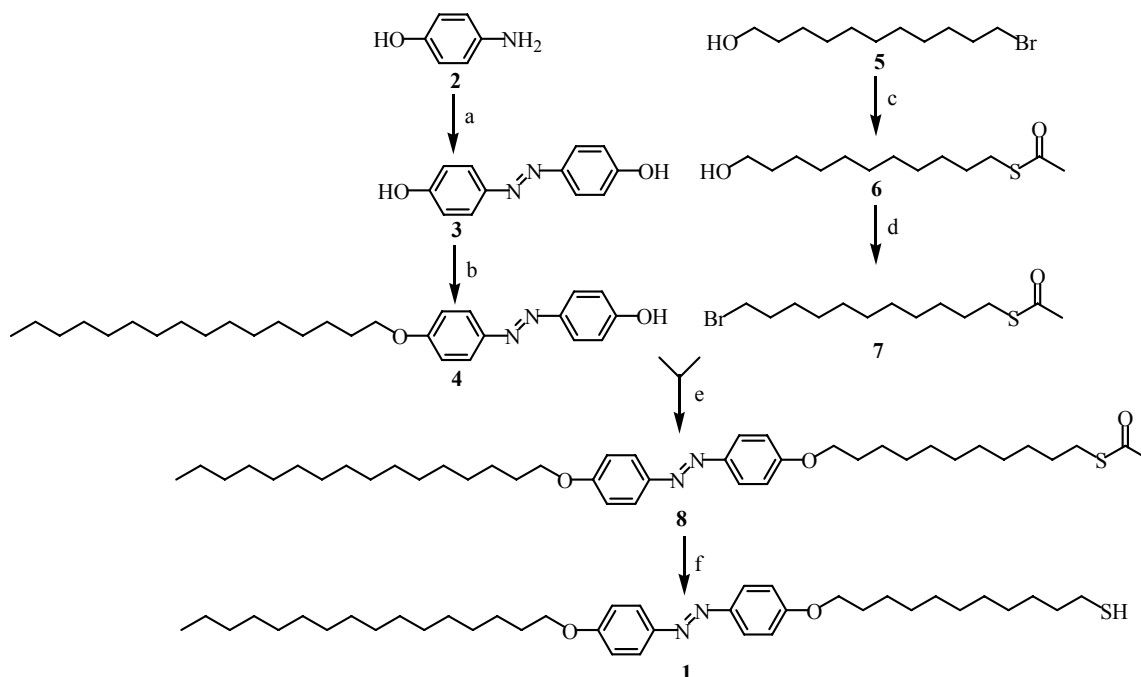


Figure S1 Synthesis of azo thiol surfactant **1**. a: (1) NaNO_2 , aq. HCl (2) Phenol; b: $n\text{-C}_{16}\text{H}_{33}\text{Br}$, K_2CO_3 , KI , Acetone; c: CH_3COSH , CH_3OH , Et_3N ; d: CBr_4 , PPh_3 , CH_2Cl_2 ; e: K_2CO_3 , KI , Acetone; f: Tetrabutylammonium cyanide, CH_3OH , CHCl_3 .

3. Synthesis of organo-soluble gold nanorods.

a. Preparation of Au seed solution.

The gold seed solution was prepared in a tube according to the reference 6 and was used within 2 h after its preparation. The concentration of CTAB in the seed solution is 0.1 M. The solution color is bright brown.

b. Synthesis of CTAB-capped gold nanorods.

4.75 mL of 0.1 M CTAB solution in water was added to a tube, then 0.20 mL of 0.01 M solution of HAuCl_4 and 0.03 mL of 0.01 M AgNO_3 were added in this order and mixed by inversion. Then 0.03 mL of 0.1 M of ascorbic acid solution was added and the resulting mixture at this stage became colorless. 0.01 mL of the seed solution was added to the above mixture tube, and the tube was slowly mixed for 10 s and left to sit still in the water bath at 25-30 °C for 3 h. The final solution turned purple within minutes after the tube was set undisturbed. The resulting solution of gold nanorods was centrifuged to remove the excessive CTAB and other soluble components. The gold nanorods capped with CTAB were re-dispersed in water.

c. Surface modification of gold nanorods.

Photoresponsive azo thiol surfactant **1** was used in the exchange reaction on the surface of the CTAB stabilized gold nanorods. The exchange procedure is as follows. The above CTAB-capped gold nanorods solution (2 mL) was added dropwise to a flask that contains 100 mg of **1** in 50 mL of dry THF with stirring under the protection of nitrogen. The color of the reaction mixture is purple. The reaction mixture was continued to stir at room temperature for 4 d. The mixture was evaporated to dryness under reduced pressure. Methylene chloride was added to dissolve the nanorods followed by centrifuging twice to remove excess azo thiol **1** and CTAB (at 12,000 rpm, 16 min). The resulting sample was redispersed in organic solvent such as methylene chloride and chloroform, and is very stable. The same procedure was repeated with the CTAB gold nanorods without thiol treatment as a controlled experiment, where it resulted in sample aggregation.

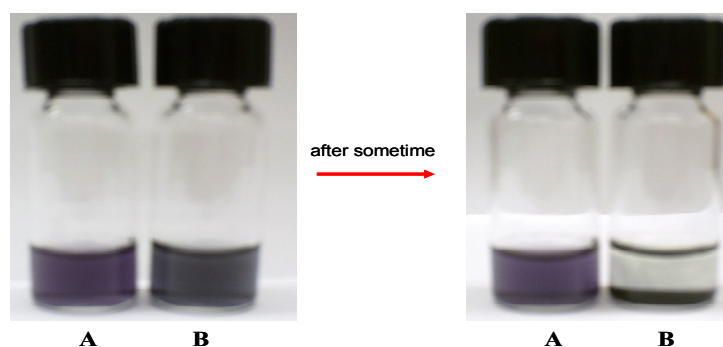


Figure S2 Photographs of photoresponsive azo hybrid nanorods (A) and CTAB-capped gold nanorods (B).

4. IR spectra of the photoresponsive azo hybrid gold nanorods.

The photoresponsive azo hybrid gold nanorods showed a similar IR absorption with the free azo thiol surfactant **1** (Fig. S3). When the hybrid gold nanorods sample was centrifuged and washed 4 times but not irradiated by UV, the top layer did not show any IR peak; and the absorption intensity of the peaks from the hybrid gold nanorods did not drop much. When irradiating the samples by UV, some azo thiol surfactants were released into the solution. However, after irradiating the sample two times, IR was taken again for the top layer. There was no free azo surfactant in the top layer.

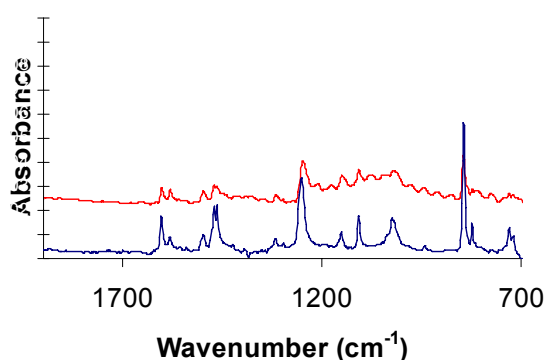


Figure S3 IR spectra. Red: the azo hybrid nanorod sample was irradiated twice and centrifuged for 4 times; blue: the free azo surfactant **1**.

5. Photoresponsive spectra.

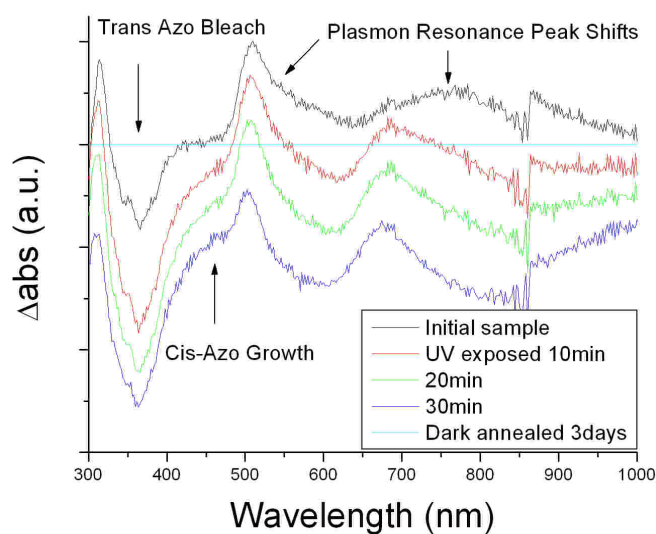


Figure S4 Differential comparison of absorption data to highlight spectral changes. Spectra referenced to dark annealed sample (0 Δ abs). *trans* Azo bleaching apparent in all samples, *cis* azo growth is evident in the shoulder of the shifted Plasmon peak. Blue shift of both longitudinal and transverse Plasmon modes is evident.

6. Control experiment.

There was no dramatic change to be observed in setting the irradiated azo hybrid gold nanorod in dark for 30 min after UV irradiation (Fig. S5).

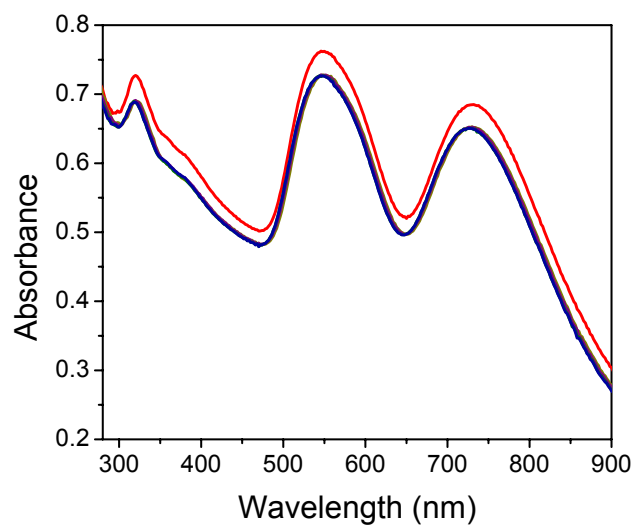


Figure S5 UV-vis-NIR spectra of photoresponsive hybrid gold nanorods in CHCl_3 with and without irradiation (Red: before UV-irradiation; blue: after UV-radiation for 40 min; green: dark for 10min without UV irradiation; blue: dark for another 20 min without UV irradiation).