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Photo-responsive reversible assembly of pillar[5]arenes stabilized gold nanoparticles

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Electronic Supplementary Information (10 pages)

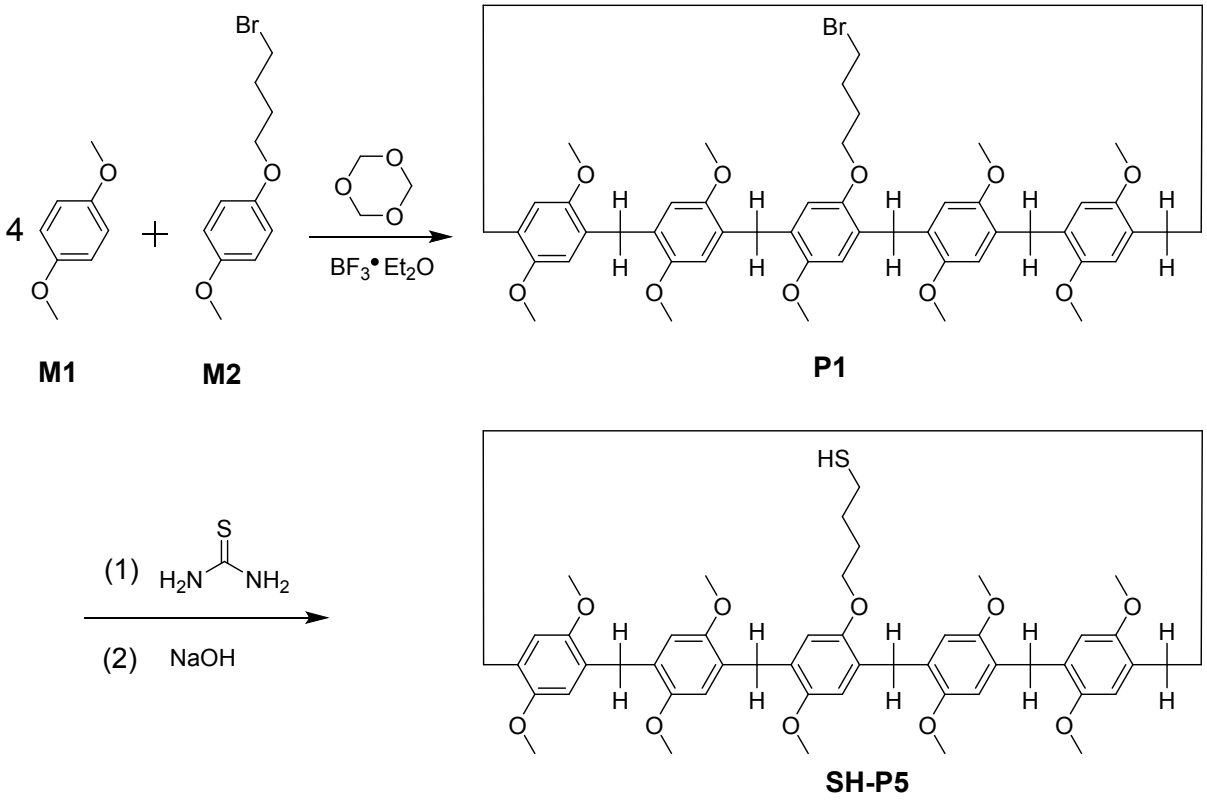
1. Materials and methods

1,4-dimethoxybenzene, 1,4-dibromo butane, 4-methoxyphenol, boron trifluoride etherate, triformol, thiourea, NaOH, anthrone, 1,10-dibromodecane, and trimethylamine solution were reagent grade and used as received. Solvents were either employed as purchased or dried according to procedures described in the literatures. ^{1}H NMR spectra were collected on a Varian Unity INOVA-400 spectrometer (Bruker) with internal standard TMS. ^{13}C NMR spectra were recorded on a Varian Unity INOVA-400 spectrometry at 100 MHz. Mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. HRMS were obtained on a Bruker 7-Tesla FT-ICRMS equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. UV−Vis spectroscopy was measured on a Shimadzu UV-2501 PC UV−Vis spectrometer. The spectral background absorption was subtracted by means of the UV−Vis spectrum of water. FT-IR spectra were taken with potassium bromide pellets on a TENSOR 27 spectrometer. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. The SEM samples were prepared on clean Si substrates. Each sample solution was deposited onto a Si substrate, placed in a refrigerator for 30 min, and freeze-dried in a freeze-drying machine at −20 °C under reduced pressure. Transmission electron microscopy (TEM) studies were obtained using a JEM-1200EX instrument with an accelerating voltage of 80 kV. Dynamic light scattering (DLS) measurements were performed on a goniometer ALV/CGS-3 using a UNIPHASE He-Ne laser operating at 632.8 nm. XRD data were obtained with a graphite monochromatic device and Cu Kα radiation (λ = 0.15406 nm) on the D8 Advance superspeed powder diffractometer (Bruker), operated in the θ:2θ mode primarily in the 20–85° (2θ) range and step-scan of 2θ = 0.04°, the tube voltage was 80 kV.

*2. Synthesis of **SH-P5** and guest molecule*

*2.1. Synthesis of compound **SH-P5***

Scheme S1. Synthetic route to ***SH-P5***



Compound **P1**:[S1] A solution of **M2** (2.59 g, 10.0 mmol), **M1** (11.1 g, 80.0 mmol) and triformol (5.45 g, 180 mmol) in $ClCH_2CH_2Cl$ (250 mL) was stirred at room temperature, 11.3 mL $BF_3{\cdot}Et_2O$ (12.8 g, 90 mmol) was added into the solution and kept stirring for about 20 minutes. Then the solvent was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2. The resultant solution was washed with H_2O. The organic phase was collected, dried over anhydrous Na_2SO_4 and concentrated to afford the crude product, which was isolated by flash column chromatography to give **P1** (3.50 g, 40%) as a white solid, mp 73.6−74.1 °C. The proton NMR spectrum of **P1** is shown in Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 6.76 (m, 9H), 6.71 (s, 1H), 3.82 (t, J = 8 Hz, 2H), 3.78 (d, J = 4 Hz, 10H), 3.66–3.64 (m, 27H), 3.24 (s, 4H), 1.84 (s, 2H), 1.78 (s, 2H).

Compound **SH-P5**: A solution of **P1** (0.87 g) and excess thiourea (0.2 g) was refluxed in DMF under nitrogen atmosphere for 8 hours. Then 1.00 g NaOH was added into the mixture and the mixture was refluxed for another 2 hours, The reaction mixture was evaporated to provide a crude product, which was purified by column chromatography (eluent: petroleum ether/ethyl acetate, 50:1) to afford **SH-P5** (0.73 g, 92%). Mp: 120.3–121.5 ℃. The ^{1}H NMR spectrum of **SH-P5** is shown in Fig. S2. ^{1}H NMR (400 MHz, $CDCl_3$, rt) δ (ppm): 6.86–6.66 (m, 10H), 4.44 (s, 2H), 3.87–3.82 (m, 27H), 3.80–3.77 (m, 10H), 3.75–3.67 (m, 2H), 2.75 (s, 2H), 1.82–1.78 (m, 2H). The ^{13}C NMR spectrum of **SH-P5** is shown in Fig. S3. ^{13}C NMR (100 MHz, $CDCl_3$, rt) δ (ppm): 150.86, 150.80, 150.71, 150.67, 149.91, 128.57, 128.28, 128.21, 128.13, 114.83, 114.40, 114.10, 114.01, 113.84, 113.77, 67.44, 55.96, 55.80, 55.76, 55.71, 33.24, 29.79, 29.73, 29.60, 29.36, 28.91, 28.36. LRESIMS is shown in Fig. S4: *m*/*z* 428.2 [**M** – H+ Cl]$^{2-}$. HRESIMS: *m*/*z* calcd for [**M** + Na]$^{+}$ $C_{48}H_{56}NaO_{10}S$, 847.3486, found 847.3486; error 0 ppm.

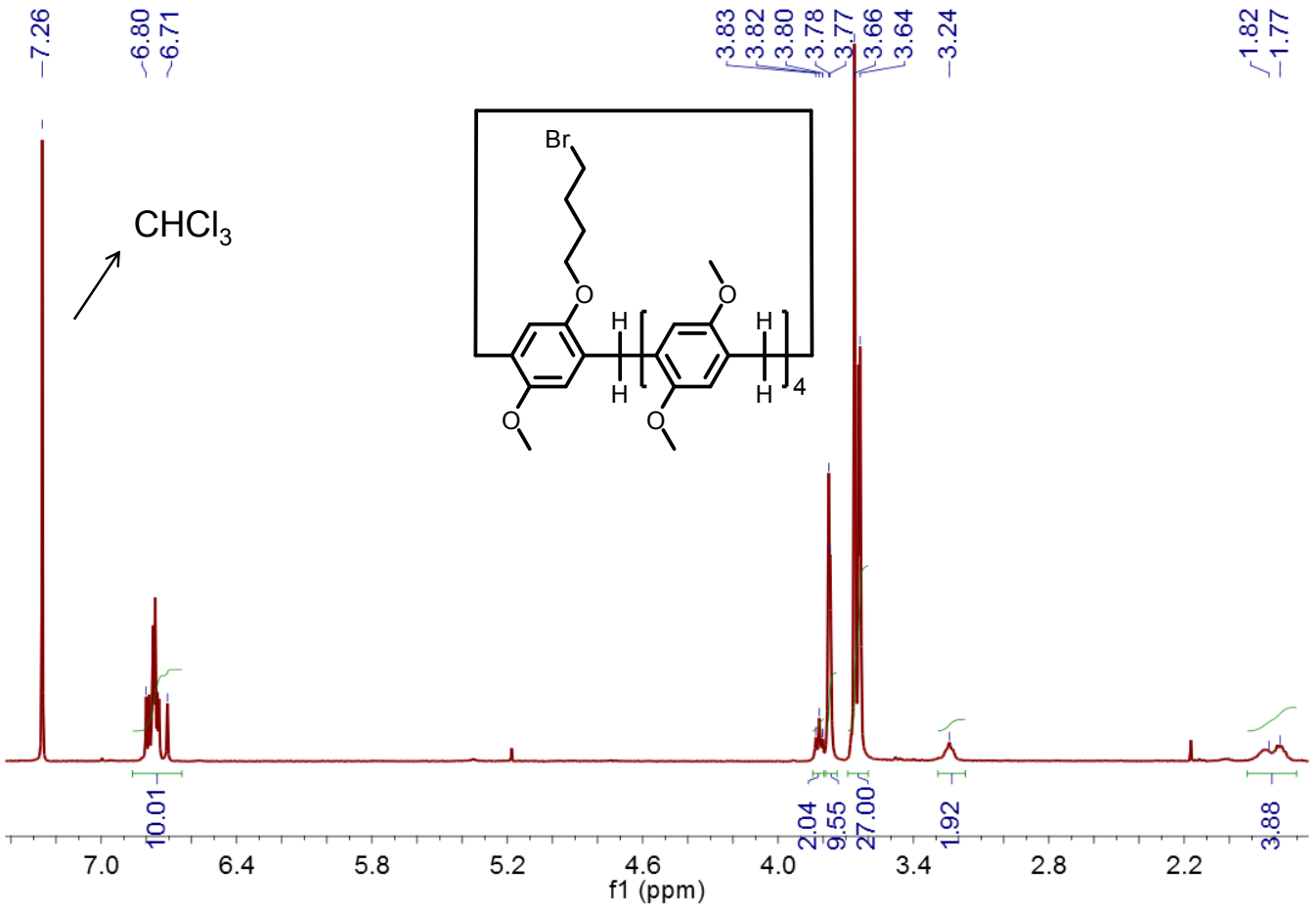


Fig. S1 ^{1}H NMR spectrum (400 Hz, $CDCl_3$, rt) of **P1**.

Fig. S2 ^{1}H NMR spectrum (400 Hz, $CDCl_3$, rt) of **SH-P5**.

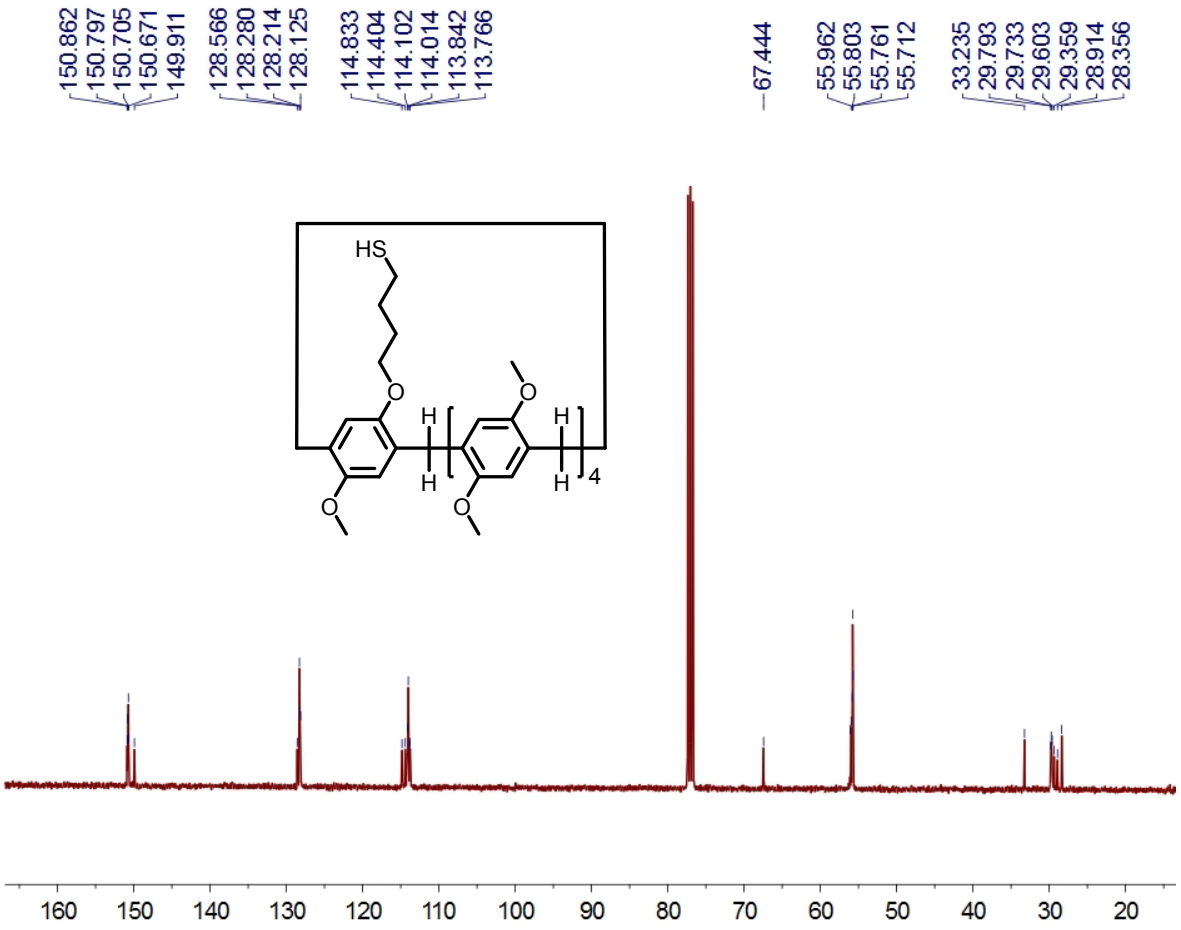


Fig. S3 ^{13}C NMR spectrum (100 Hz, $CDCl_3$, rt) of **SH-P5**.

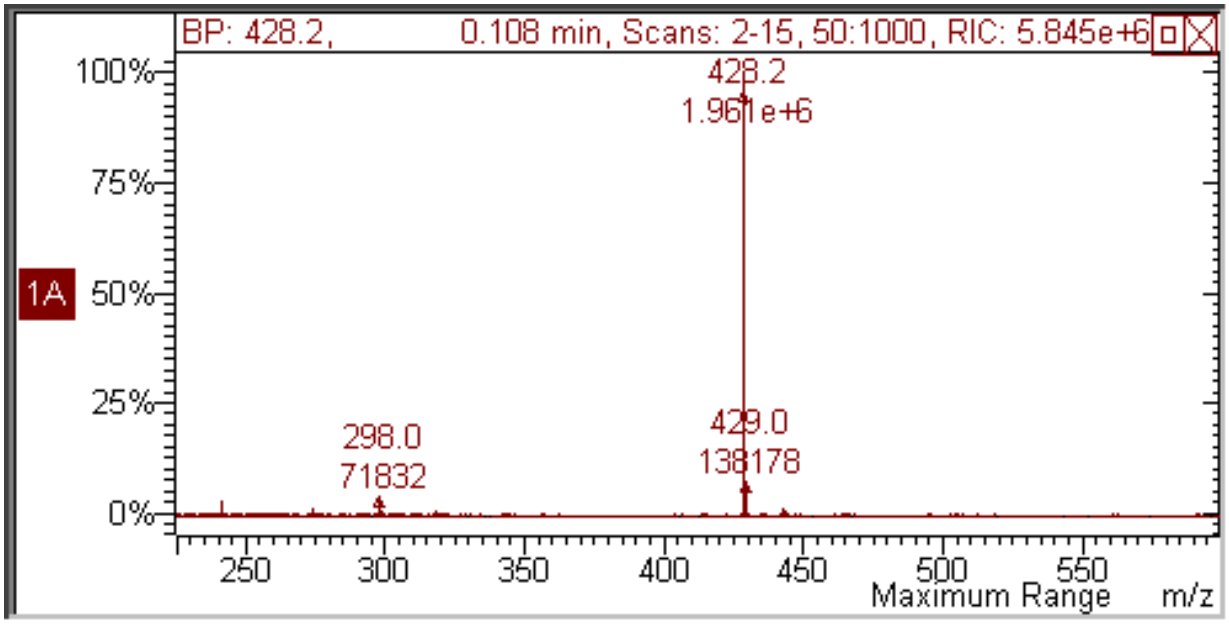
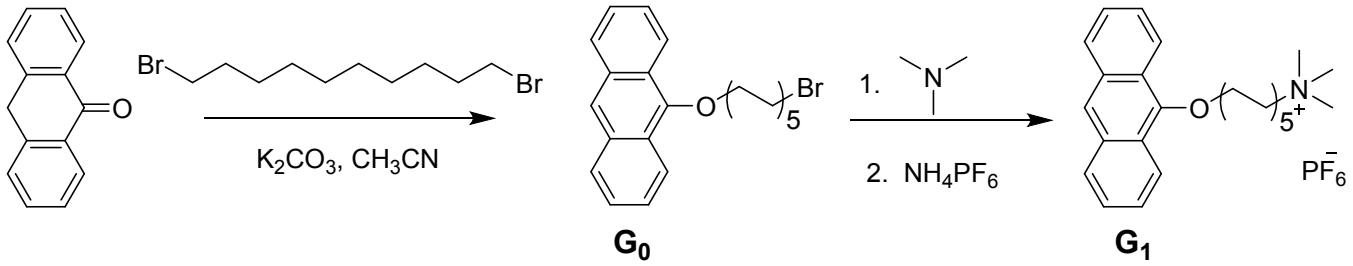


Fig. S4 Electrospray ionization mass spectrum of **SH-P5.** Assignment of the main peak: *m/z* 428.2 [**M** – H+ Cl]$^{2-}$ (100%).

2.2. Synthesis of compound ***G$_1$***



Anhydrous potassium carbonate (5.5 g, 40 mmol) was added to a solution of anthranone (3.9 g, 20 mmol) and 1,10-dibromodecane (30.0 g, 100 mmol) in dry acetonitrile (500 mL). The mixture was stirred at 80 °C for 24 hours under nitrogen atmosphere to obtain **G$_0$**. Then 0.43 g **G$_0$** and excess trimethylamine were refluxed in CH_3CH_2OH for 2 hours, the reaction mixture was poured in water and we added NH_4PF_6 to get **G$_1$** as a white solid (0.5 g, 94%). Mp: 163.2–165.8 ºC. The ^{1}H NMR spectrum of **G$_1$** is shown in Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$, rt) δ (ppm): 8.21 (s, 2H), 8.00 (s, 1H), 7.98 (s, 2H), 7.47-7.45 (m, 4H), 4.19 (t, J = 6 Hz, 2H), 3.55-3.53 (m, 2H), 3.43-3.39 (m, 10H), 2.05-2.03 (m, 2H), 1.70 (s, 14H). The ^{13}C NMR spectrum of **G1** is shown in Fig. S6. ^{13}C NMR (100 MHz, $CDCl_3$, rt) δ (ppm): 154.78, 129.90, 128.79, 126.53, 126.23, 124.46, 123.88, 76.97, 71.39, 66.82, 54.77, 28.95, 28.71, 27.80, 26.49, 23.59. LRESIMS is shown in Fig. S7: *m/z* 392.3 [**M** – PF_6]$^+$. HRESIMS: *m/z* calcd for [**M** – PF_6]$^+$ $C_{27}H_{38}NO$, 392.2948, found 392.2951; error 0.76 ppm.

Fig. S5 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of $\mathbf{G_1}$.

Fig. S6 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, rt) of $\mathbf{G_1}$.

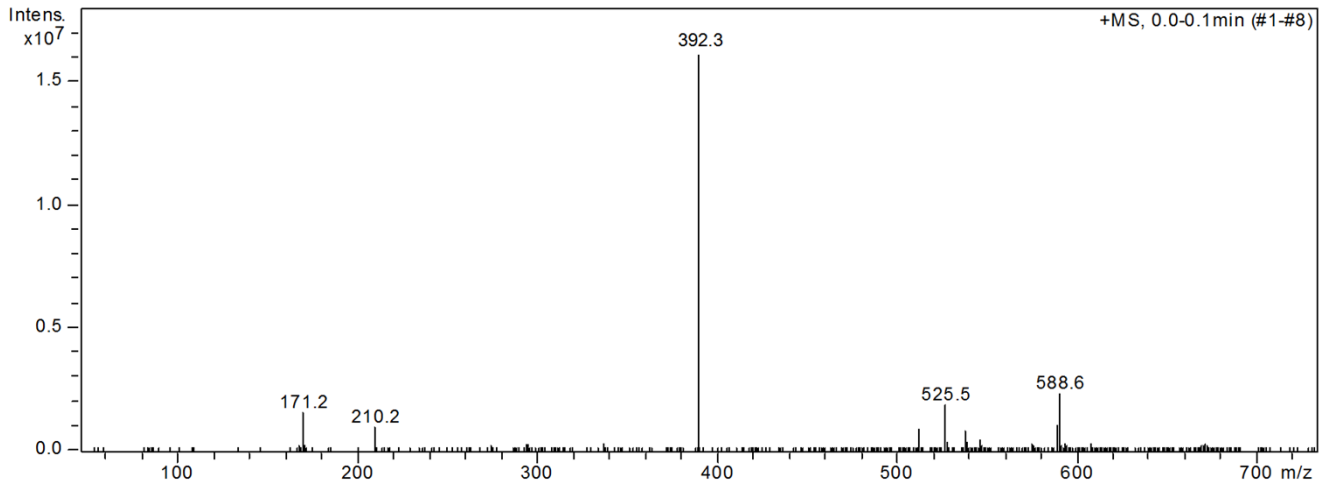


Fig. S7 Electrospray ionization mass spectrum of $\mathbf{G_1}$. Assignment of the main peak: *m*/*z* 392.3 $[\mathbf{M} - PF_6]^+$ (100%).

3. Synthesis and characterization of **SH-P5***-stabilized gold nanoparticles*

AuNPs were synthesized using methods reported previously.[S2] A 100 mg of $HAuCl_4$ was dissolved in 1 L of H_2O and heated to boiling under stirring. A 30 mL of sodium citrate (1 wt %) solution was then quickly injected. The reaction mixture was refluxed for 30 min. The **AuNPs** were then collected by centrifugation.

The surface modification of 5 nm **AuNPs** was performed using interfacial ligand-exchange method. Typically, 5 mg of **SH-P5** was first dissolved in 10 mL of toluene or chloroform which is immiscible with water. After adding this solution to an aqueous solution of 5 nm **AuNPs**, the mixture was sonicated for 2 h under room temperature. The formed emulsion was kept undisturbed overnight until the water phase became colorless. The oil phase containing **AuNPs** was then collected and dried under vacuum at 40 °C.

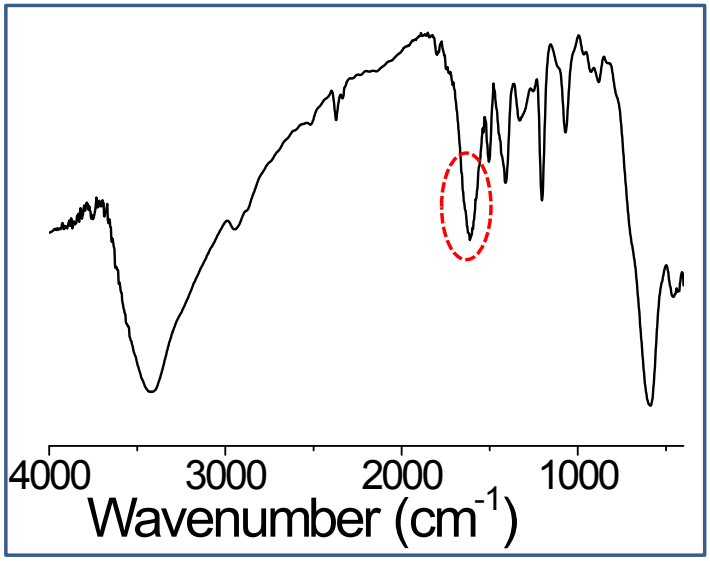


Figure S8. Fourier transform IR spectra of **SH-P5** stabilized **AuNPs**

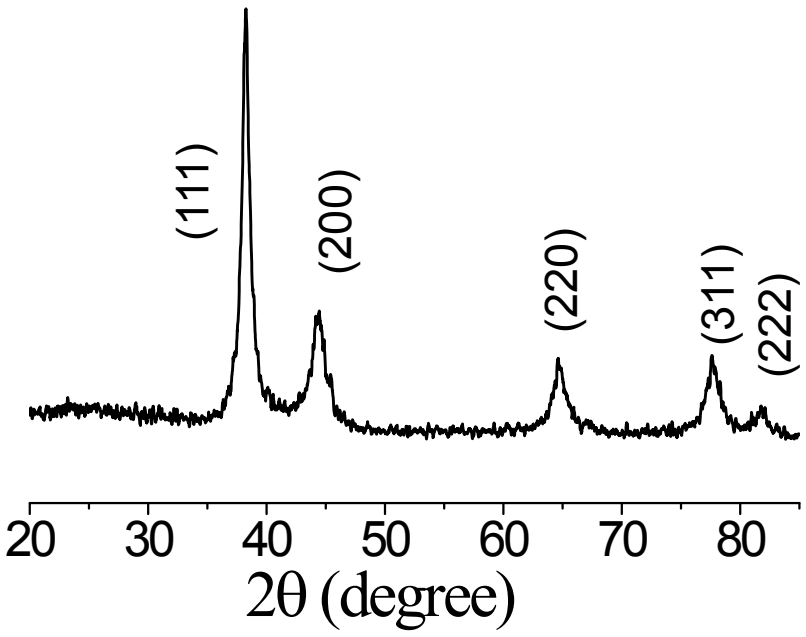


Fig. S9 XRD study of **SH-P5** stabilized **AuNPs**.

*4. Host-guest propoties of **DEP** and **G_1***

Due to **DEP** can easily dissolve in $CDCl_3$, so we firstlyinvestigate the host-guest interaction beiween **DEP** and **G_1**.

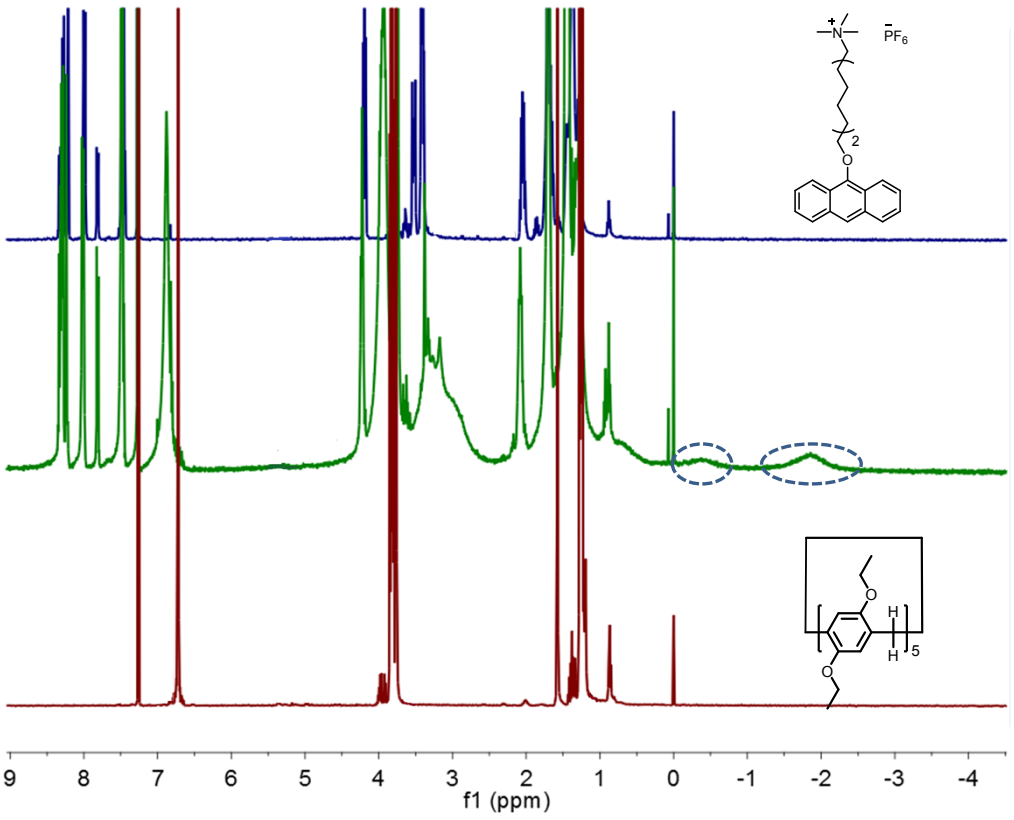


Fig. S10 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, rt) of **G_1**, **DEP⊃G_1**, and **DEP**.

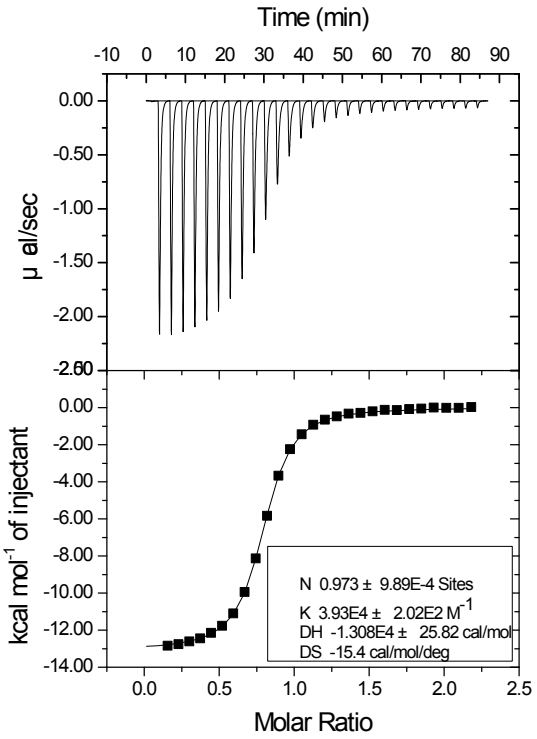
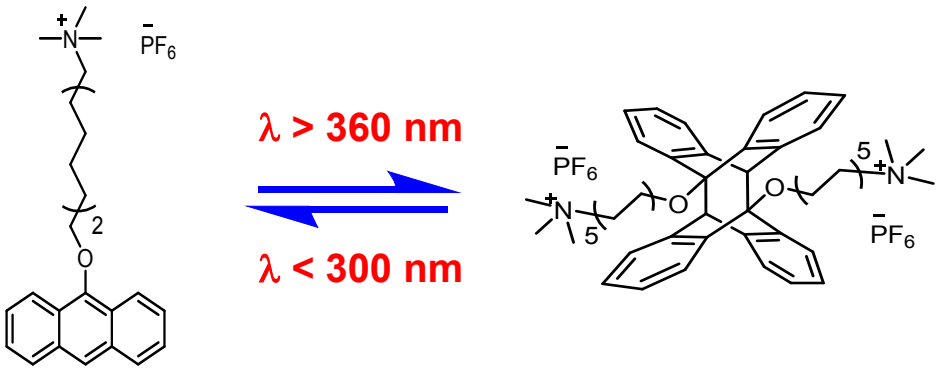


Fig. S11 ITC study of the host-guest property of **DEP⊃G$_1$.**

5. Photo-responsive transformation between ***G$_1$*** *and* ***G$_2$***



Scheme S2 *Photo-induced transformation between* ***G$_1$*** *and* ***G$_2$.***

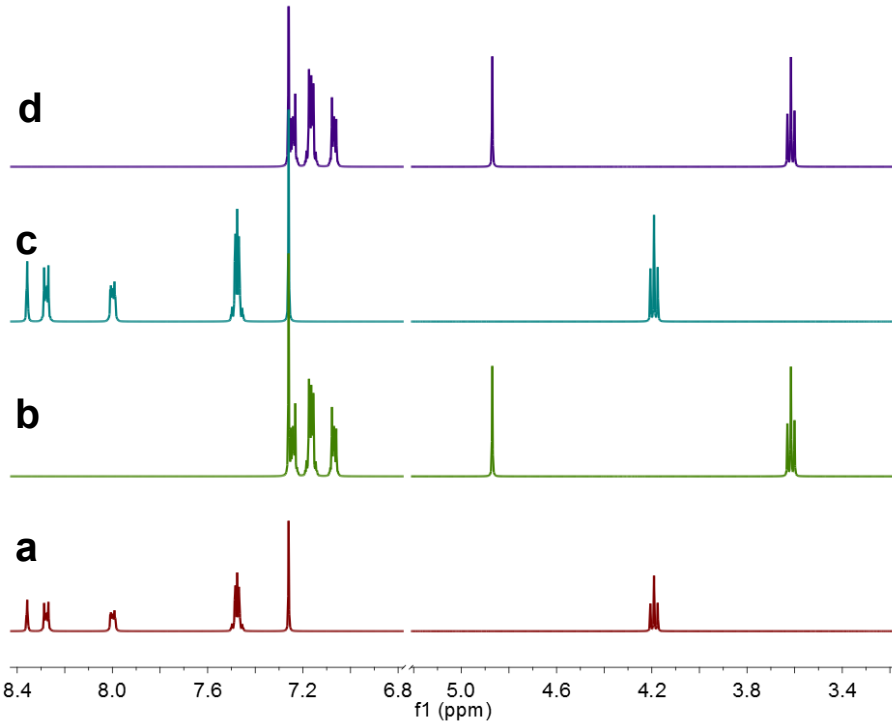


Fig. S12 Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 293 K): (a) $\mathbf{G_1}$; (b) irradiation of (a) for 12 h ($\lambda >$ 360 nm); (c) heating or irradiation ($\lambda <$ 300 nm) of (b) for 24 h; (d) irradiation of (c) for 12 h ($\lambda >$ 360 nm).

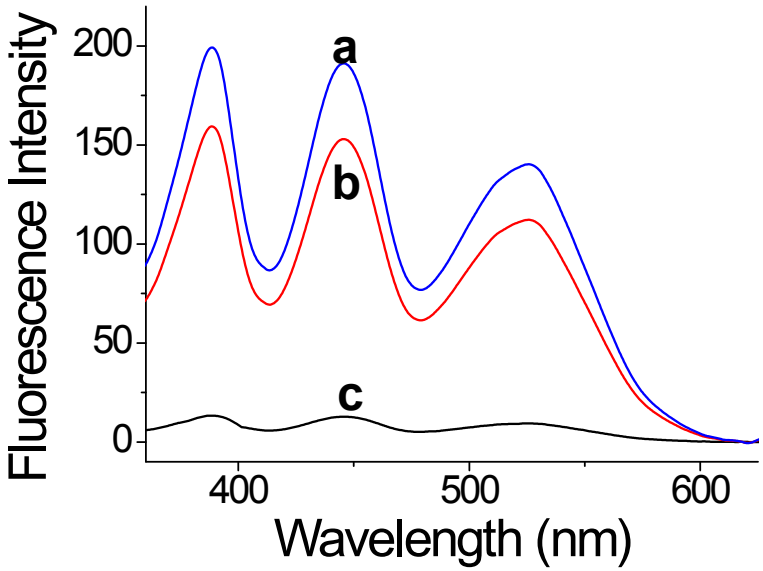


Fig. S13 Fluorescence spectra: (a) **G1**; (b) irradiation of (b) for 6 h at λ < 300 nm; (c) irradiation of (a) for 24 h at λ > 360 nm.

Fig. S14 The UV−Vis absorption of 2,6-dichloro-4-nitrophenol (black line) and after reduction o by excess $NaBH_4$ with **SH-P5** stabilized gold nanoparticles as catalyst (red line).

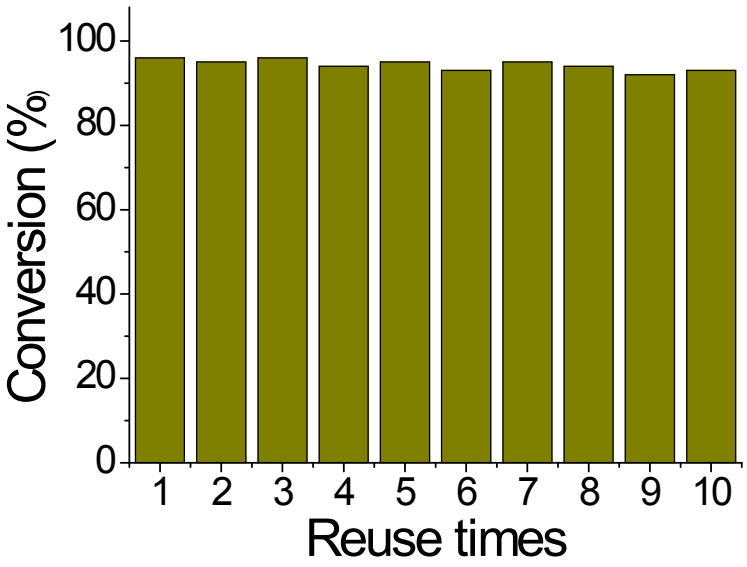


Fig. S15 Conversion of 2,6-dichloro-4-nitrophenol cataylst by **SH-P5** stabilized gold nanoparticles against reuse time.

Fig. S16 Calculated structural parameters of pillar[5]arene stabilized gold nanoparticle. $4\pi r_1^2 = n\pi r_2^2$, so n = 85. There is about 85 pillar[5]arene molecules on one gold nanoparticles. The diameter of pillar[5]arene was reported before.[S3]

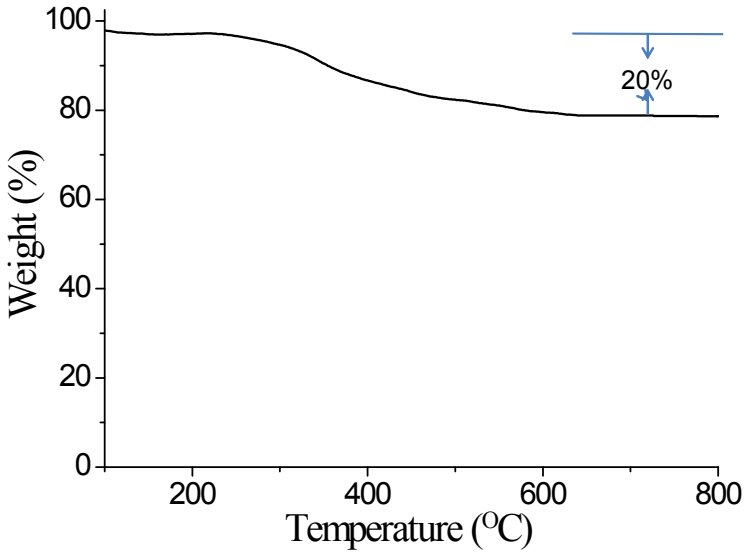


Fig. S17 TGA study of **SH-P5** stabilized gold nanoparticles.

6. References:

S1 J. Yang, Z. Li, Y. Zhou ang G. Yu, *Polym. Chem.* 2014, ***5***, 6645.

S2 M. N. Martin, J. I. Basham, P. Chando and S. K. Eah, *Langmuir* 2010, **26**, 7410.

S3 C. Han, F. Ma, Z. Zhang, B. Xia, Y. Yu and F. Huang, *Org. Lett.* 2010, **12**, 4360.