Supporting Information for

Photochromic organic cage encapsulated Au nanoparticles: light-regulated cavity for catalytic reduction of 4-nitrophenol

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1. Measurements

Reagent grade tris(2-aminoethyl)amine (tren) and CH₃OH were purchased from commercial sources and used without further purification. The synthesis of compound 1,2-Bis(5-formyl-2-methylthiophen-3-yl)perfluorocyclopentene (DEA-CHO) according to previous methods with slight adjustment.¹ The Fourier transform infrared (FT-IR) spectra were recorded on a NICOLET 6700 FT-IR spectrometer. The liquid Chromatograph Mass Spectrometer (LC-MS) analysis was conducted on a MALDI SYNAPT MS instrument. NMR spectra were recorded on AVANCE III (400 MHz) instrument at 298 K using standard Varian or Bruker software, and chemical shifts were reported in parts per milion (ppm) downfield from tetramethylsilane. Element analyses were conducted on an Elementar Corporation vario Micro cube analyzer. Photoirradiation was carried out at room temperature using a 200 W mercury-xenon lamp (Moritex MUV-202) and a visible lamp (> 500 nm, 60 W, TZ-1006) as the light source. UV-vis absorbance spectra were carried out by using oTU-1950 UV-vis spectrophotometer with a quartz cell at room temperature. Scanning Electron Microscopy (SEM) images were obtained on a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) images were obtained on a JEOL model JEM-2100plus transmission electron microscope. The samples were dispersed in alcohol by sonication, then dropped onto carbon reinforced copper grids (200 mesh) and dried in air for at least 12 h to make sure that the samples were monodisperse, homogeneous and well defined. The X-ray photoelectron spectra (XPS) were carried out by multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI), from which we can analyze the composition of elements. The calculation method to optimize the configuration of Au@DPC is MM2 molecular mechanics of minimum energy in Chem 3D. The relevant parameters are as follows:

Entry	Au@o-DPC	Au@c-DPC	
Stretch	40.0141	14.8045	
Bend	524.8851	179.6908	
Stretch-Bend	etch-Bend -4.7085		
Torsion	82.3436	49.7802	
Non-1,4 VDW -216.6810		-180.9535	
1,4 VDW 79.7722		54.3198	
Dipole/Dipole	le/Dipole 92.4896 92.8453		
Total Energy	598.1152 kcal/mol	209.6121 kcal/mol	

Table S1 MM2 molecular mechanics parameters of Au@o-DPC and Au@c-DP



Fig. S1 Synthesis of diarylethene-based photochromic cage (DPC).

2. Synthesis of Diarylethene-based photochromic cage (DPC)

DEA-CHO (0.212 g, 0.5 mmol) was dissolved in 150 mL dry CH₃OH in a 3-neck 500 mL round-bottom flask equipped with a magnetic stirrer. A solution of tren (0.05 mL, 0.33 mmol) in dry CH₃OH (30 mL) was added dropwise (2 - 3 drops/min) to the constant stirred solution of DEA by a dropping funnel under N2 atmosphere at room temperature. After approximately 3-4 hours, all tren solution was added, and the yellow solution was allowed to stir at room temperature under N₂ atmosphere for another 16 h. Then excess NaBH₄ (0.12 g, 0.003 mol) was added in batches within 3-4 hours. At this stage, the solution was stirred at room temperature for 2 h and heated to 66 °C followed by refluxing for another 20 hours in order to ensure the reduction was completed. Next, after filtering, the solvent was removed under reduced pressure, and the residue was treated with distilled water (30 mL). The product was extracted with $CHCl_3$ (30 × 3 mL). The organic layer was further washed with saturated brine solution (30×5 mL) and then it was dried over anhydrous Mg₂SO₄ and evaporated to obtain a yellow brown semisolid. The product was purified by column chromatography on silica gel (eluent: ethyl acetate and petroleum ether =1:1) to afford **DPC** (5.6 g, 60 %). FT-IR (KBr, cm⁻¹): 2920, 2850, 1564, 1439, 1334, 1269, 1107, 1047, 982. UV-vis (CH₃OH) λ_{max} : 522 nm. ¹H NMR (400 MHz, CDCl₃, d ppm): 1.58 (s, 24H), 1.83 (s, 6H), 1.91 (s, 18H), 4.78 (s, 12H), and 6.97 (s, 6H). MS⁺ (ESI): 1469.34 m/z. Anal. calcd (%) for C₆₃H₆₆F₁₈N₈S₆: C, 51.49; H, 4.49; N, 7.63; F, 23.29; S, 13.08; found: C, 51.44; H, 4.31; N, 7.73; F,23.42; S, 13.01.

3. Synthesis of Au@o-DPC and Au@c-DPC

Two 25 mL round bottom flasks equipped with a stirrer were prepared for this reaction. As the chemical structure of **DPC** was greatly affected by light, the round bottom flask was covered with a layer of tin foil. Then, the **DPC** (11 mg, 0.0075 mmol) was dissolved in 6 mL MeOH under ambient conditions, respectively. One of the flasks was irradiated with 254 nm ultraviolet light for a period of time to make the **DPC** a closed loop structure. Then a MeOH solution (4 mL) containing HAuCl₄·3H₂O (7.645 mg, 0.0225 mmol) was added dropwise to the two flasks under vigorous stirring respectively. After the mixture was stirred at room temperature for 2 h, a MeOH solution (2 mL) of NaBH₄ (2.72 mg, 0.09 mmol) was added dropwise in 10 minutes. After stirring for another 2 h at room temperature, the precipitate was collected by centrifugation and thoroughly washed with MeOH (3 × 10 mL) to remove any impurity. Finally the two samples of Au@*o*-**DPC** and Au@*c*-**DPC** were further dried in a vacuum drying oven at 50 °C for 12 h, yield 80%.

4. General experimental procedures for catalytic reduction of 4-nitrophenol (4-NP)

The reduction of 4-NP by NaBH₄ in the presence of Au@**DPC** was carried out to evaluate the catalytic activity of the Au@**DPC** catalysts. Typically, 0.5 mg of Au@**DPC** nanoparticles was dispersed in 0.5 mL water with ultrasound scattered evenly. Amounts of 2.5 mL of deionized water, 30 μ L of p-nitrophenol (10 mM) and 300 μ L of fresh NaBH₄ (10 mM) solutions were mixed together in a quartz cuvette to form a transparent bright yellow solution under stirring. And the 20 μ L of the prepared Au@**DPC** catalyst (0.06 mg) was added to the quartz cuvette to achieve the total volume for 2.9 mL. The color of the solution changed gradually from bright yellow to transparent as the reaction proceeded. The UV-vis absorbance change in the spectral range of 250 nm to 550 nm was measured to monitor the progress of the reaction at a time interval of 30 s. The rate constants of the reduction process were determined through measuring the change in absorbance at 400 nm as a function of time.



Fig. S2 Infrared spectra of DEA-CHO and DPC.



Fig. S3 Reversible changes of absorbance at 656 nm of **DPC** during alternating irradiation with UV and visible light irradiation.



Fig. S4 ESI(+)-MS spectrum of Au@**DPC** recorded in CH₃OH. Inset shows the experimental (red line) and simulated (black line) isotope patterns.



Fig. S5 Schematic diagram of reduction of Au(III) to Au(0) by NaBH₄.



Fig. S6 XPS survey spectrum of Au@o-DPC.



Fig. S7 XPS survey spectrum of Au@c-DPC.

No.	Name of catalyst	k (s ⁻¹)	Au size (nm)	Refs.
1	3Au Vis	0.041	3.72	This work
2	3Au UV	0.017	3.26	This work
3	Au NPs–GO	0.016	0.235	[2]
4	Au NPs	0.0094	/	[3]
5	K10_B@Au	0.098	/	[3]
6	Au(0)@TpPa-1	0.0054	5 ± 3	[4]
7	Neutral crosslinked PS/AuNP	0.025	3~8	[5]
8	Polyquinoline/AuNPs	0.003	130	[6]
9	Cellulose fiber/AuNPs	0.0054	21	[7]
10	Au@[C ₄ C ₁₆ Im]Br	0.0018	/	[8]
11	AuDSNs	0.0065	2.6 ± 0.4	[9]
12	CMC-PVA hydrogel/Au@MWCNTs	0.0049	10 ~ 35	[10]
13	PDA-g-C ₃ N ₄ /Au	0.0514	26.1	[11]
14	AuNP-5	0.0263	2.0 ± 1.0	[12]
15	AuNPs/TOBCNs	0.0067	4.30 ± 0.97	[13]
16	AuNPs@vesicle	0.0026	10.2	[14]

 Table S2 Comparison of apparent rate constants for 4-NP reduction with different Au nanocatalysts.

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