

Electronic Supplementary Information (ESI)

for

**Smart mesoporous silica nanoparticles gated by pillararene-
modified gold nanoparticles for on-demand cargo release**

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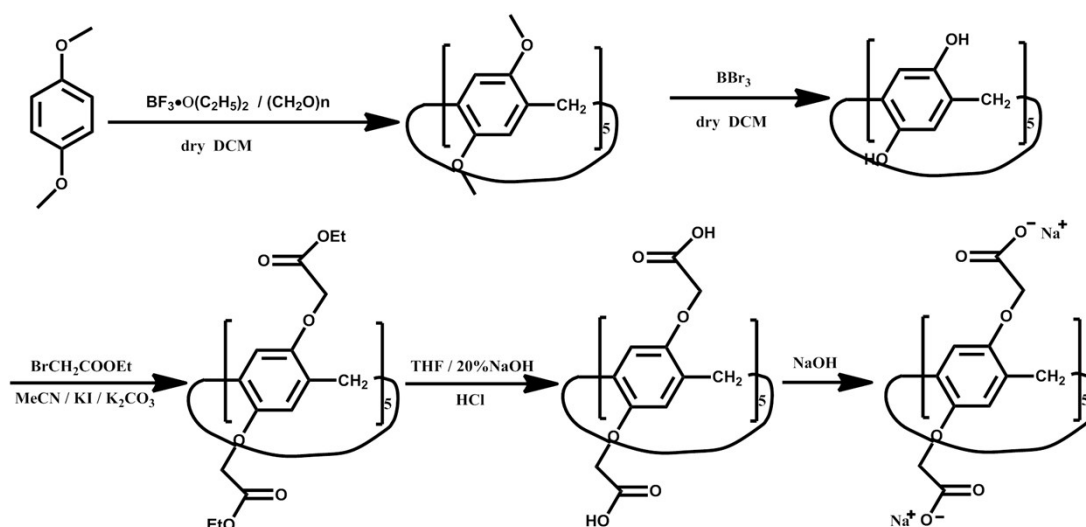
1. Materials and Methods

Unless otherwise noted, the reagents purchased from commercial sources and used directly as received. Deionized water, purifying by Experimental Water System (Lab-UV-20), was used in relevant experiments. ^1H NMR spectra were recorded on a Bruker AVANCE III 300 MHz NMR spectrometer at 25 °C. Scanning electron microscope (SEM) images were collected on a HITACHI SU8082 instrument. Transmission electron microscopy (TEM) images were collected on a Tecnai G2 S-Twin F20 instrument at an accelerating voltage of 200 kV. The low-angle powder X-ray diffraction (XRD) measurements were carried out using a PANalytical B.V. Empyrean powder diffractometer. Fourier transform infrared (FT-IR) spectra were recorded on a Vertex 80 V spectrometer. The controlled release experiments were recorded via UV-Vis spectroscopy on a Shimadzu UV-1800 spectrophotometer.

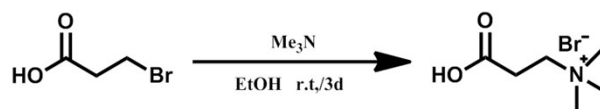
2. Preparation and Synthesis

2.1 Preparation of CP5, Q and MSN-Q

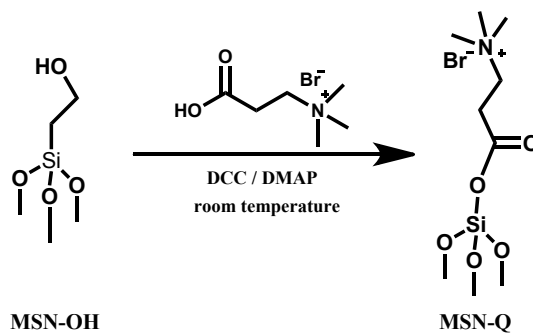
Carboxylatopillar[5]arenes (**CP5**)^{1,2}, quaternary ammonium salt (**Q**), and quaternary ammonium salt functionalized mesoporous silica nanoparticles (**MSN-Q**)³ were synthesized and characterized according to previously reported procedures.



Scheme S1 The synthetic route to CP5.



Scheme S2 The synthetic route to **Q**.



Scheme S3 The synthetic route to **MSN-Q**.

2.2 Preparation of CP5-AuNPs

CP5-AuNPs were synthesized by the reduction of HAuCl_4 in deionized water with NaBH_4 as a reducing agent and CP5 as a stabilizing ligand. HAuCl_4 ($0.0097 \text{ mmol}\cdot\text{L}^{-1}$, $931.5 \mu\text{L}$) was added to deionized ice water (15 mL), followed by the addition of an alkaline aqueous solution of CP5 ($4 \text{ mmol}\cdot\text{L}^{-1}$, $55.8 \mu\text{L}$, $[\text{CP5}]/[\text{HAuCl}_4] = 0.025$) and stirring to mix thoroughly. Then, NaBH_4 ($0.1 \text{ mol}\cdot\text{L}^{-1}$, $450 \mu\text{L}$) was freshly prepared with deionized ice water and added rapidly to the above reaction mixture. The solution immediately turned brownish red, CP5-modified AuNPs sol were thus obtained.⁴

3. Material Characterization

3.1 Ultraviolet-visible (UV-Vis) Spectroscopy of CP5-AuNPs.

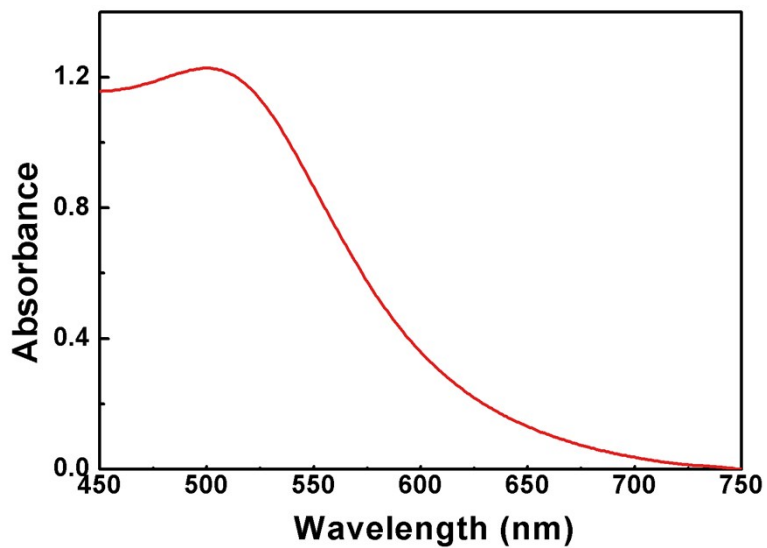


Fig. S1 UV-Vis spectra of CP5-AuNPs sol. ($\lambda=500$ nm, Abs.=1.2)

3.2 Particle size distribution of CP5-AuNPs.

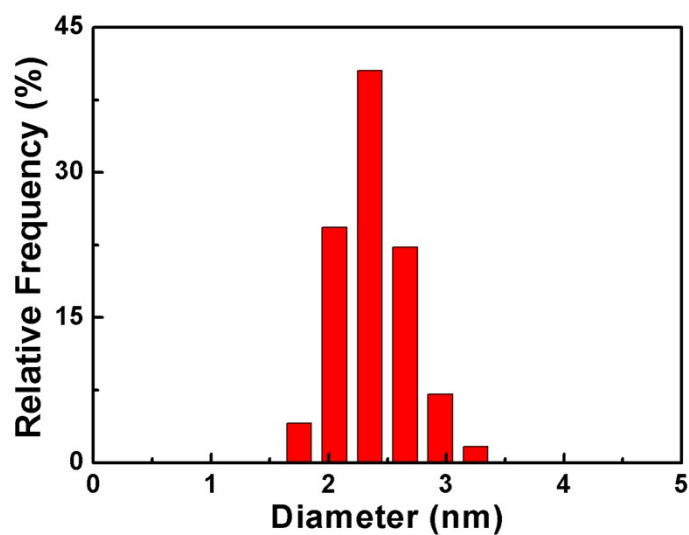


Fig. S2 The corresponding histograms of the AuNPs sizes based on 296 particles. The diameter is about 2.36 nm.

4. Cargo Loading and Controlled Release Experiments

4.1 RhB loading and CP5-AuNPs capping

RhB-loaded, AuNPs-capped MSNs were prepared as follows: MSN-Q materials (9 mg) were suspended in a $1.0 \text{ mmol}\cdot\text{L}^{-1}$ aqueous solution of RhB (15 mL), stirred for 9 h at room temperature under darkness. Then the upper layer of RhB solution was removed by centrifugation (1000 rpm, 15 min). The prepared CP5-AuNPs sol (15 mL) was added to the mixture and stirred for another 24 h. RhB-loaded, AuNPs-capped MSN-Q was separated by centrifugation (10000 rpm, 15 min), washed with deionized water (2 mL, 2 times), and dried under high vacuum oven overnight.

For comparison, RhB-loaded, uncapped MSNs materials were prepared under the same conditions as described above, except that 15 mL of CP5-AuNPs sol solution was replaced by 15 mL deionized water.

4.2 Controlled release experiments

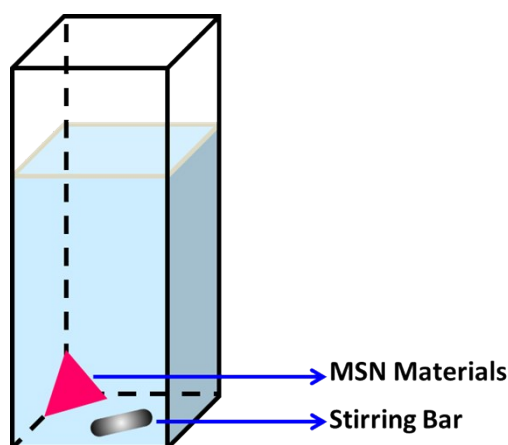


Fig. S3 Spectroscopic setup for controlled release experiments.

The RhB-loaded, AuNPs-capped MSN-Q nanomaterials (1 mg) were placed in the bottom corner of cuvette, and deionized water (3 mL) was added gently to avoid disturbing the nanomaterials. Activation of the nanovalves was accomplished by adding competitive binding agent (EDA, $8.8 \text{ mmol}\cdot\text{L}^{-1}$) and heating (at 25, 37, 45 and 60 °C, respectively). Control experiments were conducted without competitive binding agent at 25 °C. The maximum absorption wavelength of RhB is 553 nm. During this period time, UV-Vis absorption spectra of the solution in cuvette were collected at predetermined time to monitor the release amount of the

RhB molecules. These RhB-loaded, AuNPs-capped MSN-Q nanomaterials (1 mg) were triggered by excess EDA and stirred for 3 days to result in complete release ($\lambda = 553.00$ nm, $A = 0.718$), which was quantified by plotting the absorption calibration curve with standard cargo (RhB) solution of different concentrations (Fig. S1).

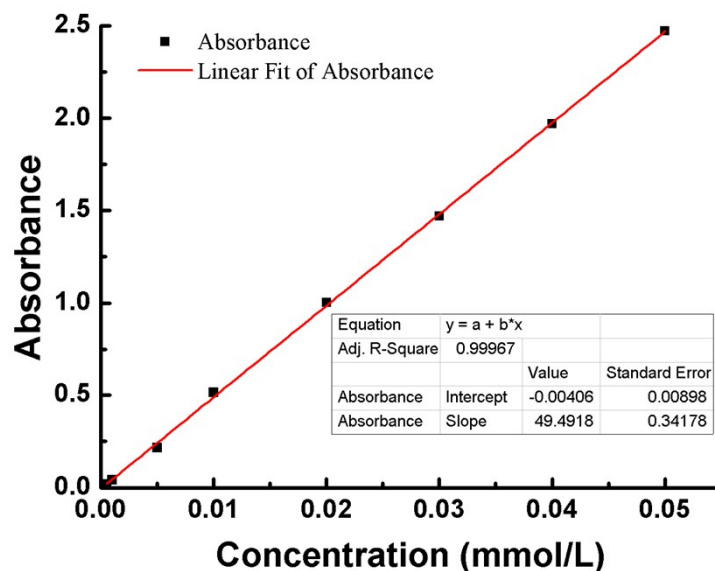


Fig. S4 UV-Vis spectra of RhB standard solution.

(The standard curve equation of RhB solution : $A = 49.4918 \cdot c - 0.0041$, $R^2 = 0.9997$)

According to the Beer's Law, it can be calculated that 45 μ mol (22 mg) of RhB molecules can be released for 1 g of nanomaterials.

The relative release percentage was calculated through the equation below:

$$\text{Relative release percentage (\%)} = M_t/M_\infty \times 100 \% = A_t/A_\infty \times 100 \%$$

Where the M_t is the amount of cargo (RhB) released from the materials at time t , M_∞ is the amount of cargo (RhB) released from the materials at time infinity. According to the Beer's Law, the amount of cargo (RhB) released from the materials (M_t , M_∞) was direct proportion to the UV-Vis absorbance (A_t , A_∞).

5. References

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