

# Hollow mesoporous raspberry-like colloids with removable caps as photoresponsive nanocontainers

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# Materials and Methods

All starting materials and solvents were purchased from Sigma Aldrich and used as received unless stated otherwise. CB[8] was prepared as documented previously.<sup>1</sup>  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance QNP 400 MHz. ESI-MS was performed on a Fischer Thermo Scientific LTQ Velos Ion Trap Mass Spectrometer. UV-vis characterization was performed on a Varian Cary 4000 UV-vis spectrometer. Photoirradiation was carried out on a LZC-ORG photoreactor from Luzchem Research Inc. equipped with both UV and white T5 type lamps centered at  $\lambda = 350$  nm and  $\lambda = 420$  nm respectively. TEM imaging was performed on a FEI Philips Tecnai 20 TEM under an accelerating voltage of 80 kV. SEM imaging was conducted on a Hitachi S-5500 In-Lens FE SEM instrument. A drop of the particle suspension was placed onto a copper grid and left to dry under air. The average size was obtained by statistically sampling *ca.* 50 particles. The hydrodynamic diameter  $D_h$  and zeta potential of particles were determined using a Malvern Zetasizer NS90 instrument fitted with a He-Ne laser ( $\lambda = 663$  nm) at 25 °C.  $D_h$  was calculated according to the Stokes-Einstein equation. Zeta potential of the particles was estimated from the electrophoretic mobility according to the Helmholtz-Smoluchowski equation. DLS measurements were carried out in triplicate on three independent samples to give an average value.

## Experimental

### Preparation of viologen-functionalized $\text{Fe}_3\text{O}_4$ nanoparticles

For the preparation of native  $\text{Fe}_3\text{O}_4$  nanoparticles, iron(III) precursor ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.32 mol) and iron(II) precursor ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 0.16 mol) were dissolved in 3.5 L water, and 300 mL of ammonium hydroxide solution ( $\text{NH}_4\text{OH}$ , 8.6 M) was added at room temperature, resulting in the mixture turning black immediately. After 15 min, the nanoparticles were collected with a permanent neodymium magnet and the supernatant was discarded, yielding 30 g of  $\text{Fe}_3\text{O}_4$  nanoparticles.<sup>2</sup>

As shown in Figure S1, MV-functionalized silane was synthesized by adding 1-(2-hydroxyethyl)-

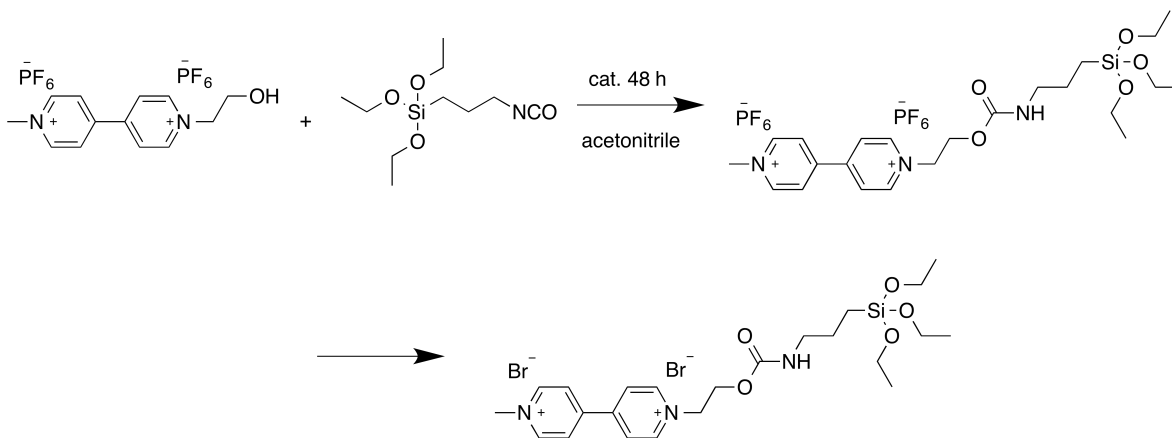


Figure S1: Synthesis of MV-functionalized silane.

1'-methyl-[4,4'-bipyridine]-1,1'-dium di(hexafluorophosphate) (0.5 g, 1.0 mmol) and excess 3-(triethoxysilyl) propyl isocyanate (3.1 g, 12.5 mmol) into 200 mL anhydrous acetonitrile together with 1 drop of dibutyltin dilaurate (TDL). The reaction mixture was stirred for 24 h at room temperature and the conversion was followed by infrared spectroscopy.<sup>3</sup> The solvent was evaporated under reduced pressure to approximately 10 ml. Four equivalent tetrabutylammonium bromide (4 mmol) was added and the yellowish precipitated was dried under reduced pressure to yield the title compound (81 %). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 9.41 (d, 2H), 9.35 (d, 2H), 8.87 (d, 2H), 8.82 (d, 2H), 7.38 (s, 1H), 4.99 (t, 2H), 4.50 (t, 2H), 4.45 (s, 3H), 3.70 (q, 6H), 3.15 (t, 2H), 1.56 (quin, 2H), 1.12 (t, 9H), 0.47 (t, 2H). HRMS:  $m/z$  calcd for  $[M-H]^+$  = 462.2413, found = 462.2406. FTIR:  $\tilde{\nu}$  = 1690 cm<sup>-1</sup> (–NH(CO)O–).

In order to functionalize the Fe<sub>3</sub>O<sub>4</sub> nanoparticles, the bare nanoparticles (5 g) were redispersed in ethanol (300 mL) and MV-functionalized silane (1 mmol) was added. The mixture was reacted at 60 °C for 1 h before being collected by a magnet. The final product was washed using ethanol and deionized water for several times. DLS measurement of the MV-Fe<sub>3</sub>O<sub>4</sub> nanoparticles showed a hydrodynamic diameter  $D_h$  of 15 nm and a polydispersity (PD) of 0.07. The collected MV-Fe<sub>3</sub>O<sub>4</sub> nanoparticles were dispersed in water with a concentration of 0.6 gL<sup>-1</sup>.

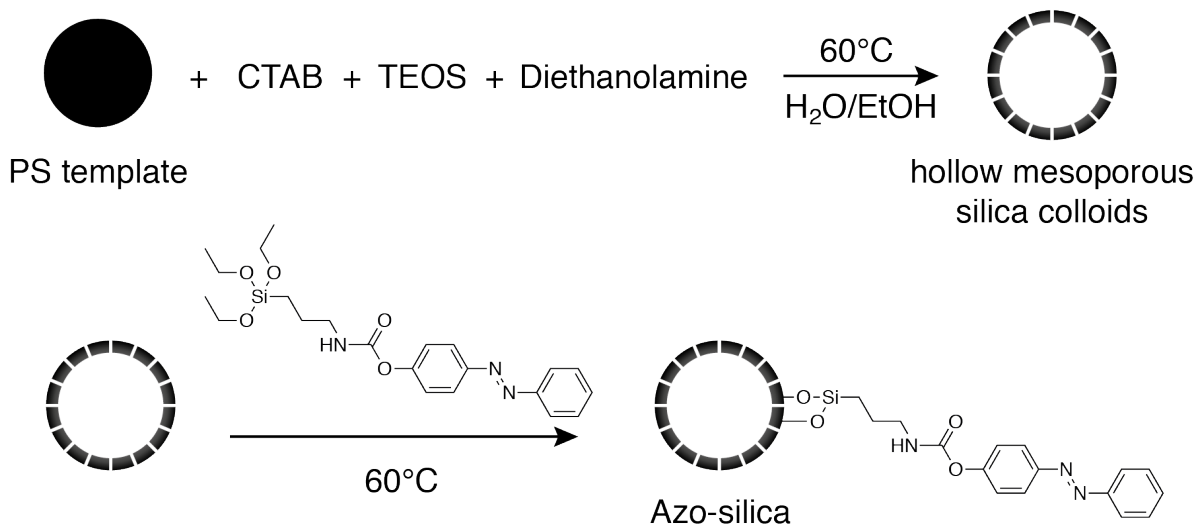


Figure S2: Preparation of Azo-silica colloids.

## Preparation of azobenzene-functionalized hollow mesoporous silica colloids

The monodispersed polystyrene (PS) particles were prepared by emulsifier-free emulsion polymerization, using  $\alpha$ ,  $\alpha'$ -azodiisobutyramidine dihydrochloride (AIBA) as the cationic initiator and poly(vinylpyrrolidone) (PVP) as the stabilizer. Styrene (10.0 g), PVP (1.5 g) and AIBA (0.26 g) were dissolved in water (100 mL) and deoxygenated by bubbling nitrogen gas for 1 h at room temperature. The reaction was carried out at 70 °C for 24 h under magnetic stirring. After centrifugation, the product was washed with water and ethanol for several times before being redispersed in 160 mL ethanol.<sup>4</sup>

For the preparation of hollow mesoporous silica colloids, diethanolamine (0.1 g) and hexadecyltrimethylammonium bromide (CTAB, 0.2 g, 0.55 mmol) were added to 30 mL water and stirred intensively for 1 h at 50 °C. Subsequently, tetraethyl orthosilicate (TEOS, 0.5 g, 2.4 mmol) and the PS colloidal solution (5 g) were injected into the above solution and the resulting mixture was stirred vigorously for another 2 h at 50 °C (Figure S2). The product was collected by centrifugation and washed with ethanol and water for several times to remove the residual reactants. Then the collected product was extracted for 3 h with sodium chloride (1 wt%) in methanol at room temperature to remove the template CTAB. The extraction was performed several times until no

CTAB can be detected by FTIR. In order to make sure the PS template was completely removed, the particles were stirred in tetrahydrofuran for 3 h and collected by centrifugation.<sup>5</sup>

For the synthesis of Azo-functionalized silane, 4-aminoazobenzene (98.5 mg, 0.5 mmol), 3-(triethoxysilyl) propyl isocyanate (12.4 mg, 0.05 mmol) were dissolved in anhydrous acetonitrile (1 mL). TDL was added and the mixture was stirred for 48 h at room temperature.<sup>3</sup>

In order to functionalize the hollow mesoporous silica spheres, the collected bare particles and the Azo-functionalized silane were dissolved in 30 mL ethanol. The mixture was stirred for 1 h at 60 °C. The final product was collected by centrifugation and washed with ethanol for several times before being resuspended in water at a concentration 0.3 gL<sup>-1</sup>.

## General method for the assembly of hybrid raspberry-like colloids

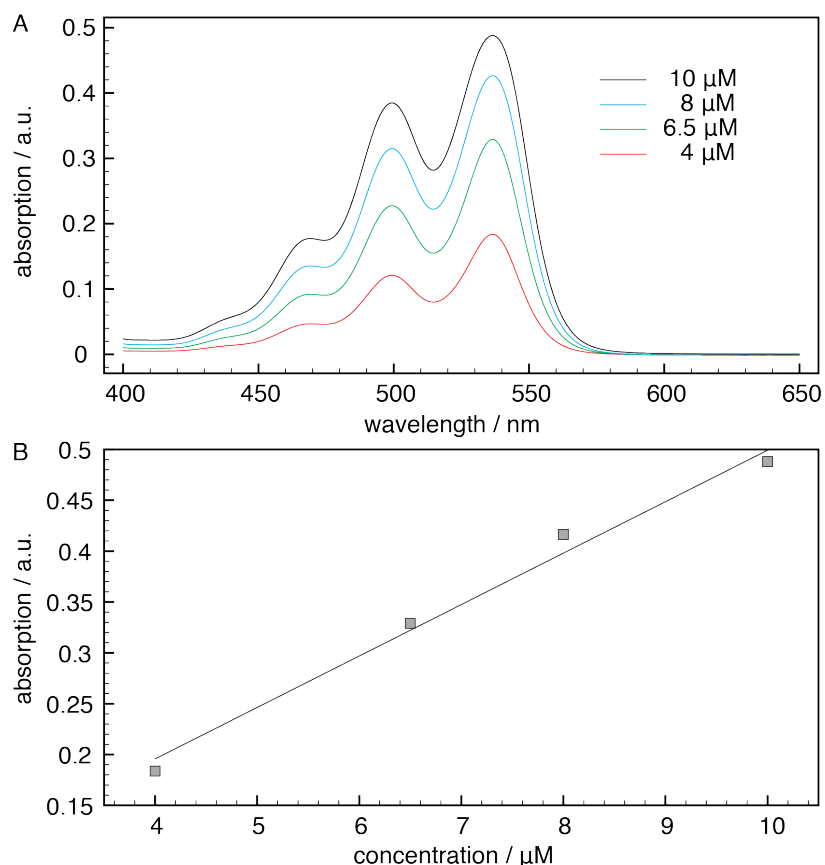


Figure S3: (A) Absorption spectra of PDI@CB[8] binary complex at different concentrations (B) Calibration curve for the absorption of PDI@CB[8] binary complex at 537 nm.

The binary complex between CB[8] and perylene bis(diimide) (PDI) can further accommodate

one MV or Azo group, resulting in the formation of a 1:1:1 heteroternary complex of (MV/PDI)⊂CB[8] or (Azo/PDI)⊂CB[8].<sup>6</sup> To determine the number of accessible MV groups in the nanoparticle solution, 10.0 mL solution of PDI⊂CB[8] (PDI:CB[8] = 1:1, 10 μM) and 5.0 mL suspension of MV-Fe<sub>3</sub>O<sub>4</sub> nanoparticles were mixed together and stirred for 30 min. The Fe<sub>3</sub>O<sub>4</sub> paramagnetic nanoparticles were removed by a magnet and the UV-vis spectrum of the filtrate was recorded. As the absorption intensity of PDI⊂CB[8] is determined by its concentration (see Figure S3), the concentration of the filtrate can be calculated. The concentration of MV derivatives in the nanoparticle solution was calculated to be 0.01 mM based on the concentration difference between the original PDI⊂CB[8] solution and the filtrate.<sup>7</sup> The density of MV groups on the surface of nanoparticles was calculated to be 9.16 molecules per nanoparticle or 0.06 molecules per square nanometer. The concentration of accessible Azo groups in the Azo-silica colloidal suspension was calculated as 0.01 mM by the same method.

For the assembly of hybrid raspberry colloids, CB[8] (1.7 mg, 1.0 μmol) was firstly added into 10.0 mL solution of MV-Fe<sub>3</sub>O<sub>4</sub> nanoparticles and the mixture was sonicated for 30 min. Subsequently the Azo-silica colloidal dispersion was titrated into the MV⊂CB[8]-Fe<sub>3</sub>O<sub>4</sub> nanoparticle solution and sonicated for 5 min.

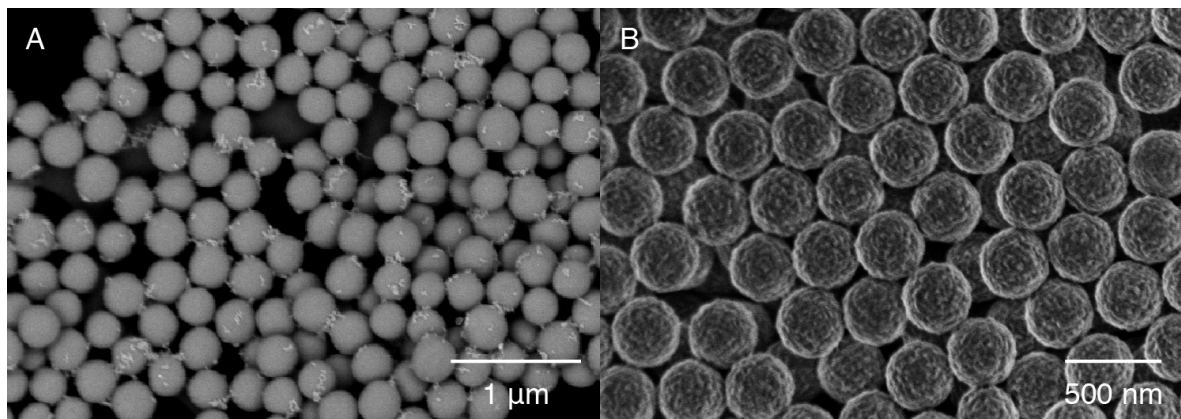


Figure S4: SEM images of (A) disassembled HMRCs and (B) reassembled HMRCs.

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