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Electronic Supplementary Information

Analyte-Responsive Hollow Mesoporous Silica Nanoparticles with Nanovalves Exhibiting Inverse Functionality and an AND Logic Response

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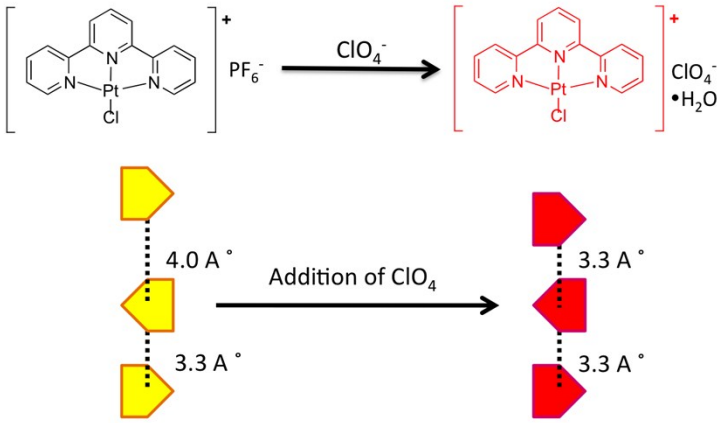

Fig. S1 **1**·PF_6 converting to **1**·ClO_4·H_2O.

All reagents including tetraethyl orthosilicate, dodecyltrimethylammonium bromide (DTAB), sodium hydroxide, hydrogen chloride, sodium bicarbonate, N-phenylaminomethyltriethoxysilane (PhAMTES), sodium 1- allyloxy-2-hydroxypropane sulfonate, aerosol MA-80-1, α-cyclodextrin, triethylamine, ammonium persulfate, divinyl benzene, styrene, are commercially available and were used without further purification. The structure of hollow mesoporous silica nanoparticles was confirmed by powder X-ray diffraction (XRD) experiments in Bragg-Brentano geometry (θ-2θ) on a Philips X'Pert Powder Diffractometer operated at 40 kV, 40 mA using CuKα radiation (λ=1.54 Å). To confirm the presence of the hollow core, shell thickness, and confirmation that 1•PF_6 crystalized inside the hollow core, transmission electron microscopy (TEM) was done. The particles were dispersed in ethanol and then deposited and dried on a carbon Cu grid. Images were recorded on a JEM1200-EX (JEOL) electron microscope operating at 50 kV. Infrared (FTIR) measurements were acquired on a Jasco Model 420 spectrometer to confirm the attachment of PhAMTES. For monitoring the emission of **1**•PF_6, the samples were illuminated using the 514 nm line of a Coherent I306C argon ion laser (40 mW). The photoluminescence spectra of the samples were collected using an Acton 2300i monochromator and

a Princeton Instruments CCD. A 550 nm cut-off filter was placed in front of the CCD to block stray laser light.

Synthesis of Polystyrene Beads

Polystyrene beads were made using a previously published procedure.[1] In a reaction vessel, 0.171 g of sodium bicarbonate was added to 138 mL of water under nitrogen. The water solution was then deoxygenated by bubbling nitrogen through the solution for 40 minutes. Afterwards, 2.5 g of Aerosol MA-80-1 was dissolved in 10 mL of water and then added to the solution. The solution was brought to 50 °C and 2.33 g of divinyl benzene and 60 mL of styrene was slowly added. Sodium 1- allyloxy-2-hydroxypropane sulfonate was dissolved in 10 mL of water and was immediately injected into the solution 5 minutes after the addition of divinyl benzene and styrene. The temperature was then brought to 70 °C at which point a solution of 0.75 g of ammonium persulfate in 5 mL of water was injected. The reaction continued for 4 hours. The particles were washed through dialysis for 3 days changing the water twice a day. They were then centrifuged with water twice and then with methanol two more times. They were then left to dry under vacuum. The size of the particles was confirmed by taking a TEM image of the particles (Fig. S2).

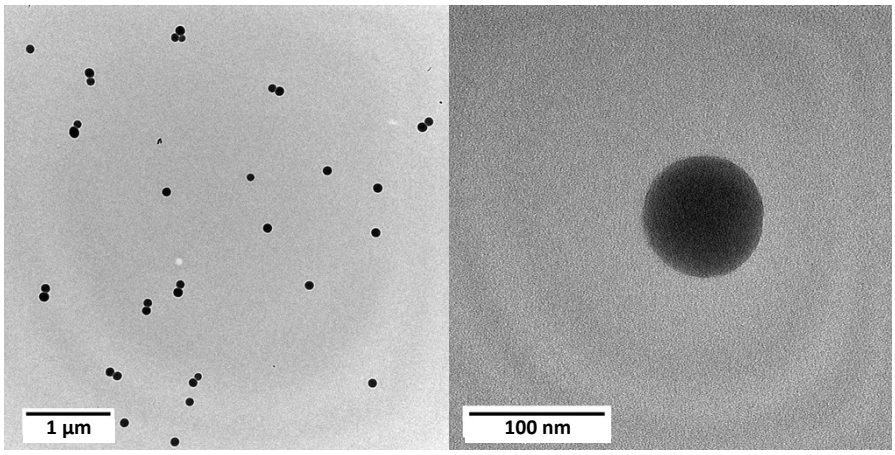

Fig. S2 TEM images of the polystyrene beads.

Synthesis of Hollow Mesoporous Silica Nanoparticles

Hollow mesoporous silica nanoparticles were synthesized by adding 0.5 g of DTAB and 0.25 g of the polystyrene beads into 20 mL of water. The solution was sonicated for 20 minutes and then allowed to rest for 30 minutes to allow any large aggregates of the polystyrene beads to settle. The solution was then carefully poured into 100 mL of water and 450 µL of 2 M NaOH was added. After

30 minutes, 500 μL of TEOS was added and the reaction was left at room temperature for 24 hours. The particles were washed thoroughly with water and methanol and then calcined at 500 °C to remove the surfactant and the polystyrene beads. XRD was used to confirm the pore size and TEM images were taken to confirm the presence of the hollow cavity (Fig. S3)

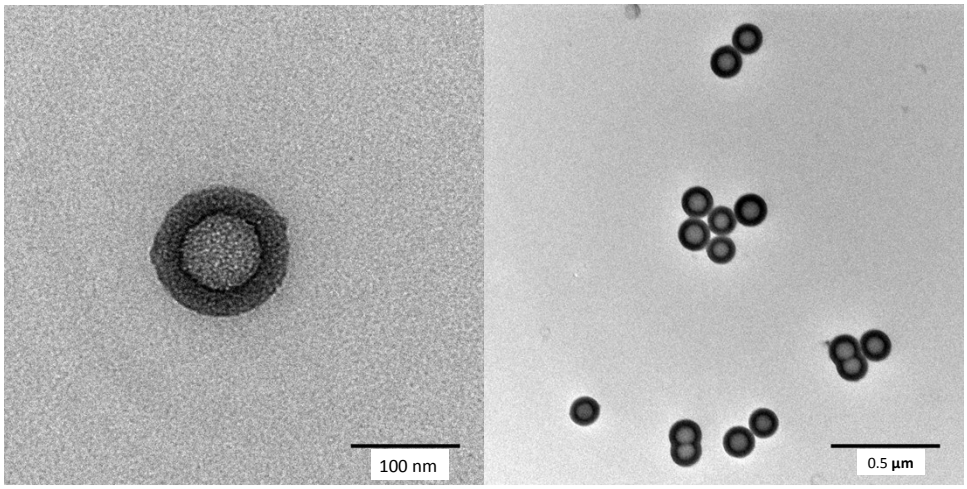

Fig. S3 TEM images of template free hollow nanoparticles

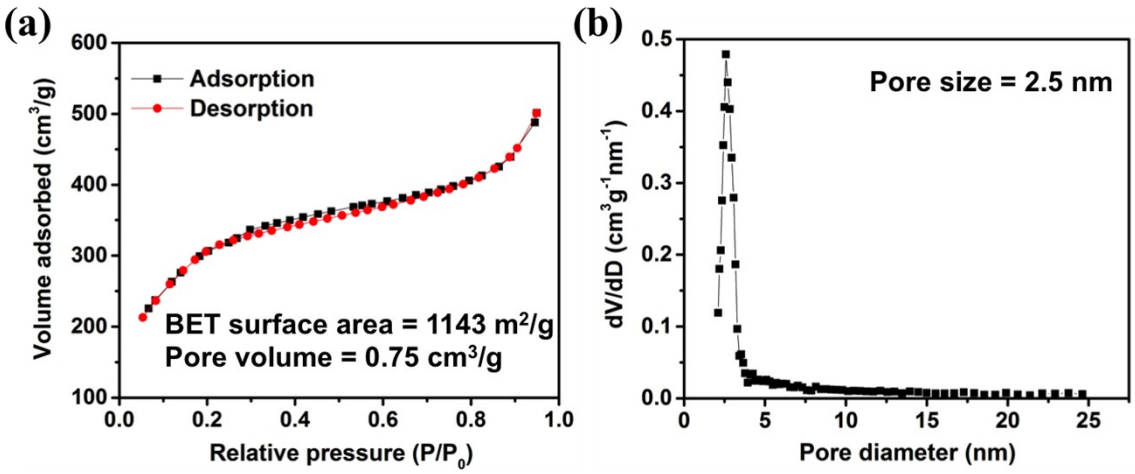

Fig. S4 (a) Nitrogen adsorption/desorption isotherms of hollow mesoporous silica nanoparticles. The BET surface area and pore volume are 1143 m^2/g, and 0.75 cm^3/g, respectively. (b) Pore size distribution of hollow mesoporous silica nanoparticles. The pore size is 2.5 nm.

Surface Modification of the Hollow Mesoporous Silica Nanoparticles

50 mg of the hollow mesoporous silica nanoparticles and 50 μL of PhAMTES were placed in 3 mL of toluene and the reaction was left overnight stirring at room temperature. The particles were then washed with methanol and then with water and then dried in a vacuum. An IR spectrum of the particles was taken to confirm the presence of PhAMTES (Fig. S5)

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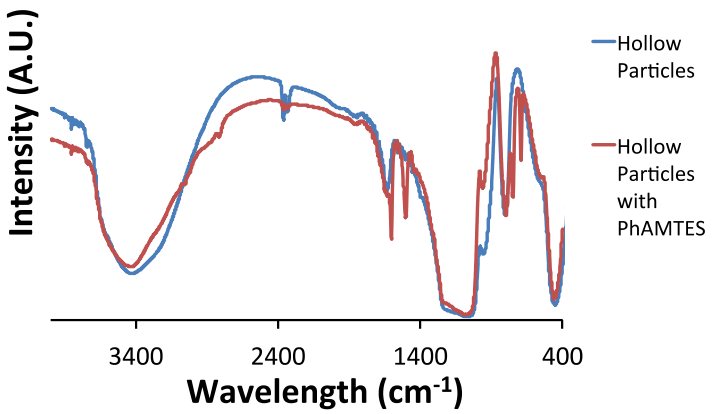

Fig. S5 IR spectra of hollow particles and hollow particles after PhAMTES modification. The band at 2900 cm^{-1} is assigned to C-H streches and that at 1475 cm^{-1} is from aromatic C=C streches.

Crystalizing 1•PF_6 Inside the Hollow Core

A highly concentrated solution of **1**•PF_6 was made by taking 10 mg of the crystal and dissolving it in 300 μL of dimethyl sulfoxide. 20 mg of the particles were added to the solution and it was left stirring for 24 hours. The solution was then allowed to slowly evaporate until the particles were dry.

Blocking the Pore Openings with α-Cyclodextrin

The particles were washed twice with dimethyl sulfoxide and then twice with water to remove any **1**•PF_6 from the surface of the hollow particles. The particles were then left in 1.5 mL of water and 50 mg of α-cyclodextrin was added. The particles were then left stirring overnight.

Controlled Activation of the System

The operation of the system was monitored using fluorescence spectroscopy. 10 mg of the particles were placed in an NMR tube. Enough water was added to just wet the particles and the NMR tube was placed in front of a

CCD. The emission of **1**•PF_6 was measured as a function of time at 1-second intervals by using a 514 nm excitation beam (40 mW). The activation profile of the system was obtained by plotting luminescence intensities of **1**•PF_6 at the emission maximum (670 nm) as a function of time. 40 μL of a 30 mM solution of $NaClO_4$ was added to the sample followed by addition of 40 μL of an acid solution to bring the pH to 3 in order to activate the system.

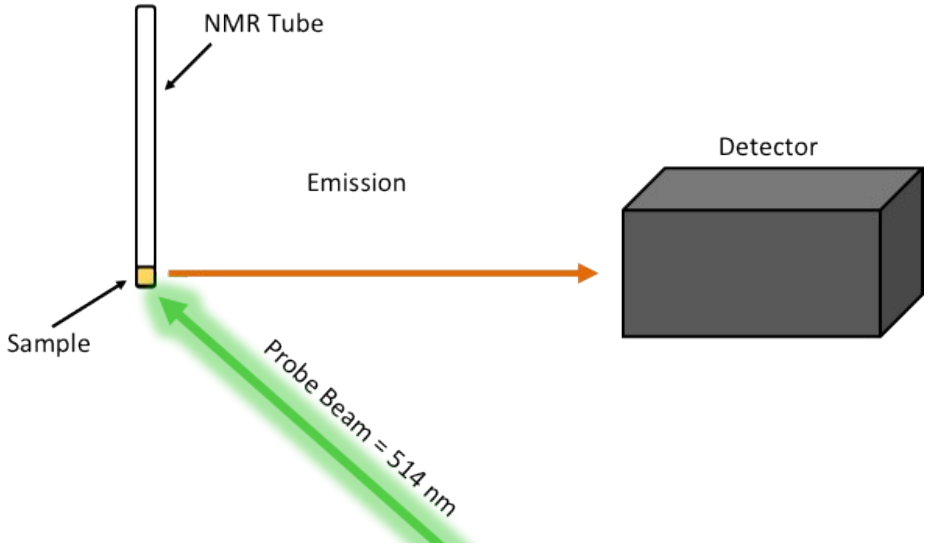

Fig. S6 Experimental set up for sequential fluorescence spectra measurements.

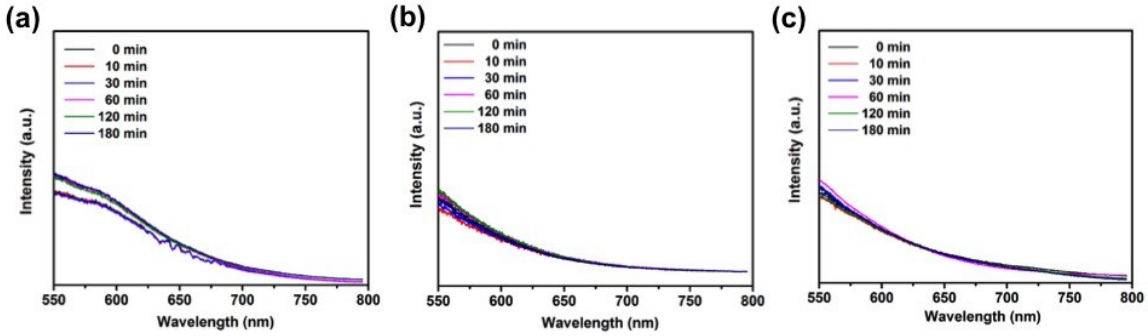

Fig. S7 Luminescence spectra of the **1**•PF_6 crystal-loaded hollow mesoporous nanoparticles with aniline stalks as a function of time (a) without the addition, (b) after the addition of ClO_4^-, and (c) after the addition of HCl when αCD is not used as a cap.

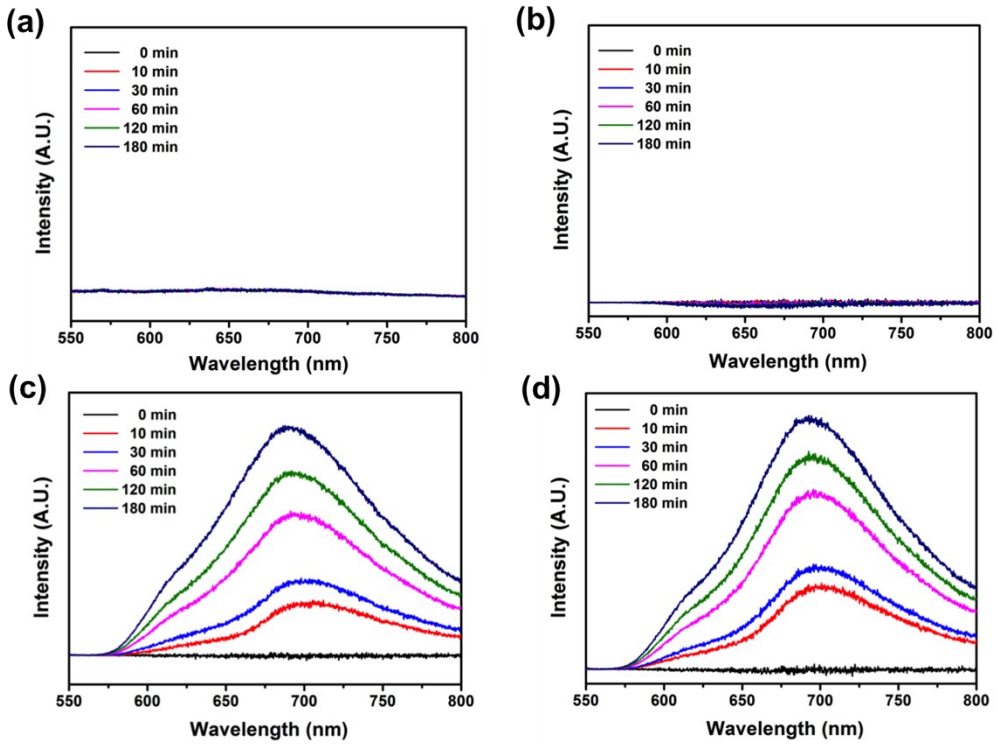

Fig. S8 Luminescence spectra of the **1**•PF_6 crystal-loaded hollow mesoporous nanoparticles without aniline stalks as a function of time (a) without the addition, (b) after the addition of the HCl, (c) after the addition of ClO_4^-, and (d) after the addition of HCl and perchlorate.

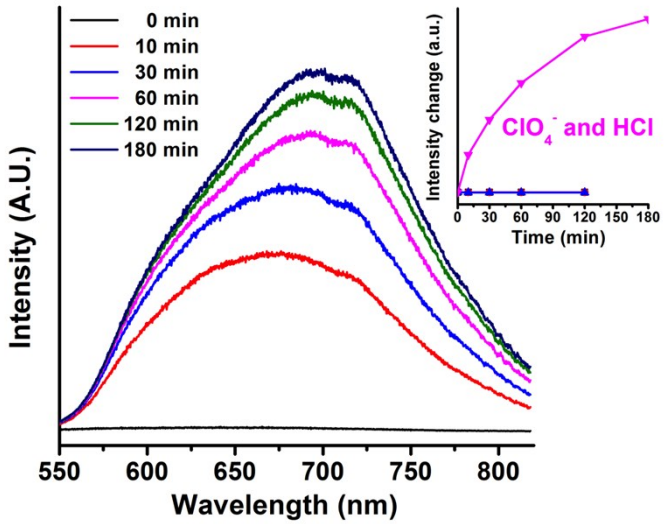

Fig. S9 Luminescence spectra of nanoparticles gated by the PhAMTES stalk and αCD as a function of time after the addition of acid and perchlorate.

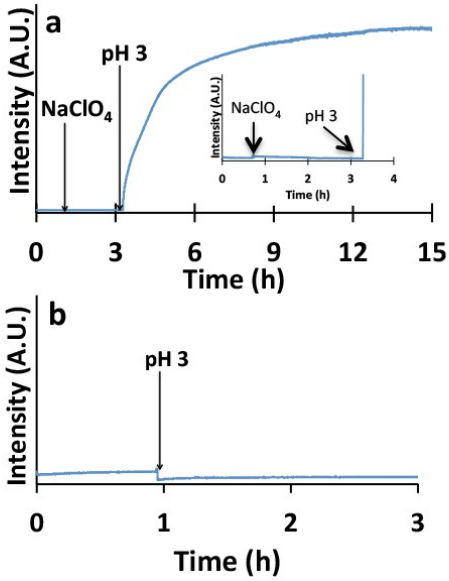

Fig. S10 (a) Emission intensity at 690 nm as a function of time. At ~45 minutes $NaClO_4^-$ was added and after 2.5 hours the system was brought to a pH of 3. Inset shows close up of $NaClO_4^-$ addition and pH lowering. (b) Emission intensity at 690 nm as a function of time. At ~55 minutes the system was brought to a pH of 3 and no change in the intensity was observed.

References

1. C. E. Reese, C. D. Guerrero, J. M. Weissman, K. Lee and S. A. Asher, *J. Colloid Interface Sci.*, 2000, **232**, 76-80.