Controlled-Access Hollow Mechanized Silica

Nanocontainers

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Supporting Information

Nanoparticles XRD and TEM Studies.



Figure S1. Low-angle XRD patterns of hollow sphere mesoporous (solid-line) and conventional sphere mesoporous (dashed-line) silica nanoparticles. Inset: TEM images (A) and (B) are of hollow and conventional silica nanoparticles, respectively.



N₂ adsorption-desorption isotherms

Figure S2. N_2 adsorption-desorption isotherm of extracted hollow particles (A), linker-2 functionalized hollow particles (B), capped linker-2 functionalized hollow particles (C) and conventional particles (D). (The closed symbols represent the adsorption isotherm, and open symbols represent the desorption isotherm). Insert: BJH pore size distribution of the nanoparticles. The presence of macropores (65 nm—85 nm) can be seen in inset images of Figures (A), (B) and (C), this might be associated to the

inner, large core macropores. However, no macropores were detected in the inserted image in Figure (D).



Figure S3. ¹³C CP/MAS SSNMR spectra of pure hollow particles (a), and functionalized by different linkers: linker-3 (b), linker-1 (c) and linker-2 (d). All of the samples were dried under vacuum.



Figure S4. ²⁹Si CP/MAS SSNMR spectra of the pure hollow particles (a), and functionalized by different linkers: IPTMS (b), linker-3 (c), linker-2 (d), and linker-1 (e). All of the samples were dried under vacuum. It should be noted that new peaks emerged in spectra (b) — (e) (boxed-in T region) but was otherwise not detected in spectrum (a).



TGA Analysis

Figure S5. Thermogravimetric data for unfunctionalized hollow particles (a), linker-2 functionalized hollow particles (b), α -cyclodextrin capped linker-2 functionalized hollow particles without dye loaded (c), PI loaded, α -cyclodextrin capped linker-2 functionalized hollow particles (d).

Dynamic Light Scattering

	Particles Diameter (nm)	Standard Deviation (nm)
Run 1	276	106
Run 2	281	94
Run 3	277	98
Average	278	99

Table S1. Average Diameters of Extracted Hollow Nanoparticles from DLS Measurements.

Dynamic light scattering was performed on a Beckman Coulter N4 Plus particle sizer, with a 633 nm HeNe excitation source. The measurements were carried out in EtOH on extracted hollow nanoparticles prior to any surface functionalizations.

Luminescence Study



Figure S6. Controlled release profile of PI molecules from hollow particles with linker-2 without capping agents. a) No wash. b) Washed completely. After PI molecules were loaded in the absence of capping agents, these nanopaticles were washed. The release profile (b) showed no obvious release of PI from nanoparticles after acid was added. This demonstrates that the PI molecules that were loaded into both the nanopores and hollow cavity were washed away before testing.



Figure S7. The absorption spectra of PI molecules. A) 0.1 mM PI (pH=5) solution. B) Hollow SNV particles (in the solution above the hollow SNV nanoparticles). C) Conventional SNV particles (in the solution above the conventional SNV nanoparticles). Spectra 'a', 'b' and 'c' were taken before release, while spectra'd', 'e', 'f' were taken after acid-triggered release.



Figure S8. The absorption spectra of Hoechst 33342 molecules. A) 0.01 mM Hoechst 33342 (pH=5) solution. B) Hollow SNV particles (in the solution above the hollow SNV nanoparticles). C) Conventional SNV particles (in the solution above the conventional SNV nanoparticles). Spectra 'a', 'b' and 'c' were taken before release, while spectra'd', 'e', 'f' were taken after acid-triggered release.