Supporting Information

A Reversible Light-Operated Nanovalve on Mesoporous Silica Nanoparticles

Derrick Tarn,[†] Daniel P. Ferris, [†‡] Jonathan C. Barnes,[‡] Michael W. Ambrogio [‡] J. Fraser Stoddart[‡] and Jeffrey I. Zink[†]*

[†]Department of Chemistry and Biochemistry, California NanoSystems Institute, University of California, Los Angeles, California 90095, United States

[‡]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, United States

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Section A. Mesoporous Silica Nanoparticle Characterization

SI-1) *Transmission Electron Microscopy*

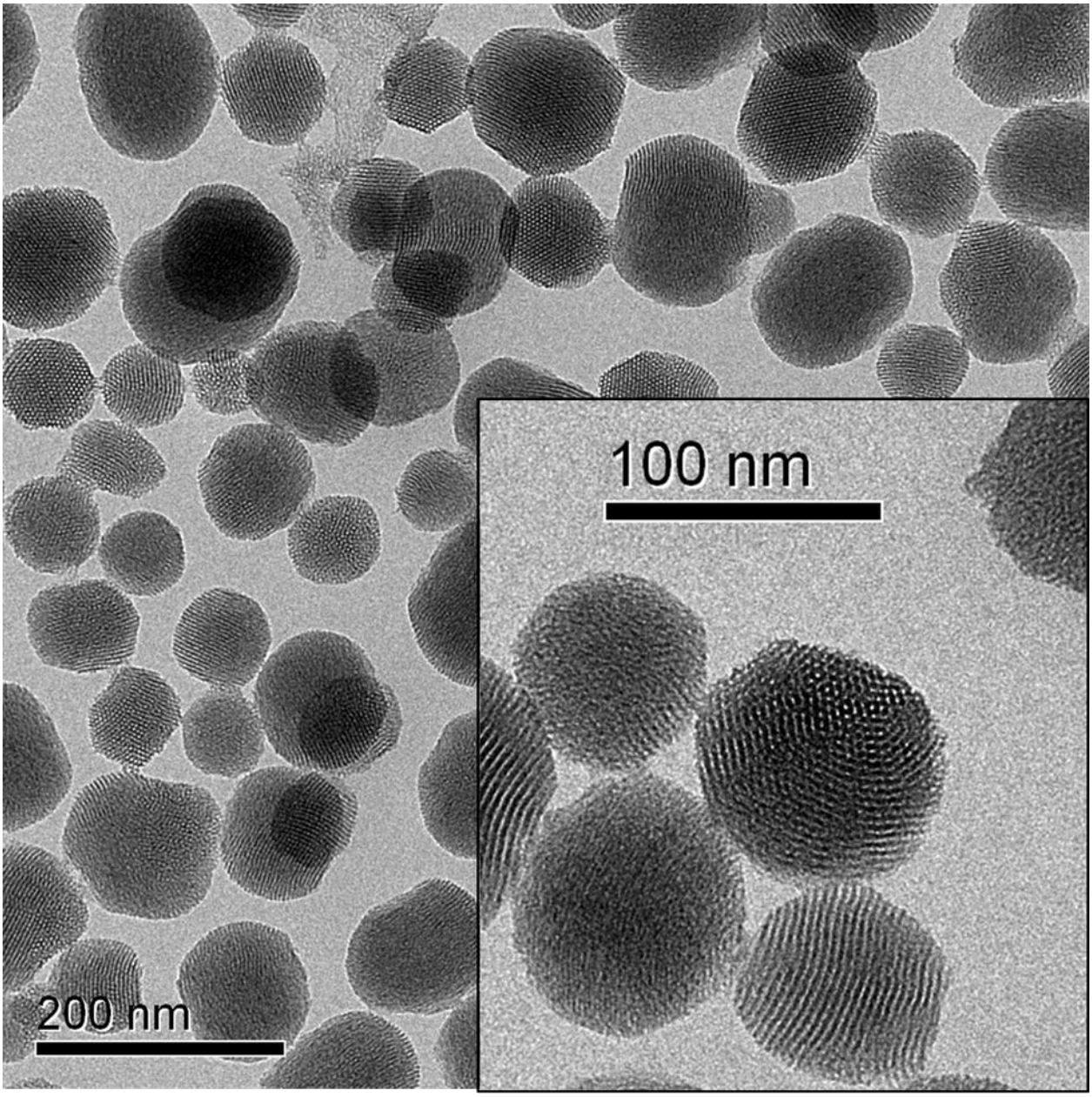

Fig. S1. TEM image of a typical batch of MCM-41 type nanoparticles showing the ordered, 2D hexagonal mesopore phase. In a typical batch, particles range from 80–120 nm in diameter, with an average pore size of 2.2 nm.

SI-2) ***Powder X-Ray Diffraction***

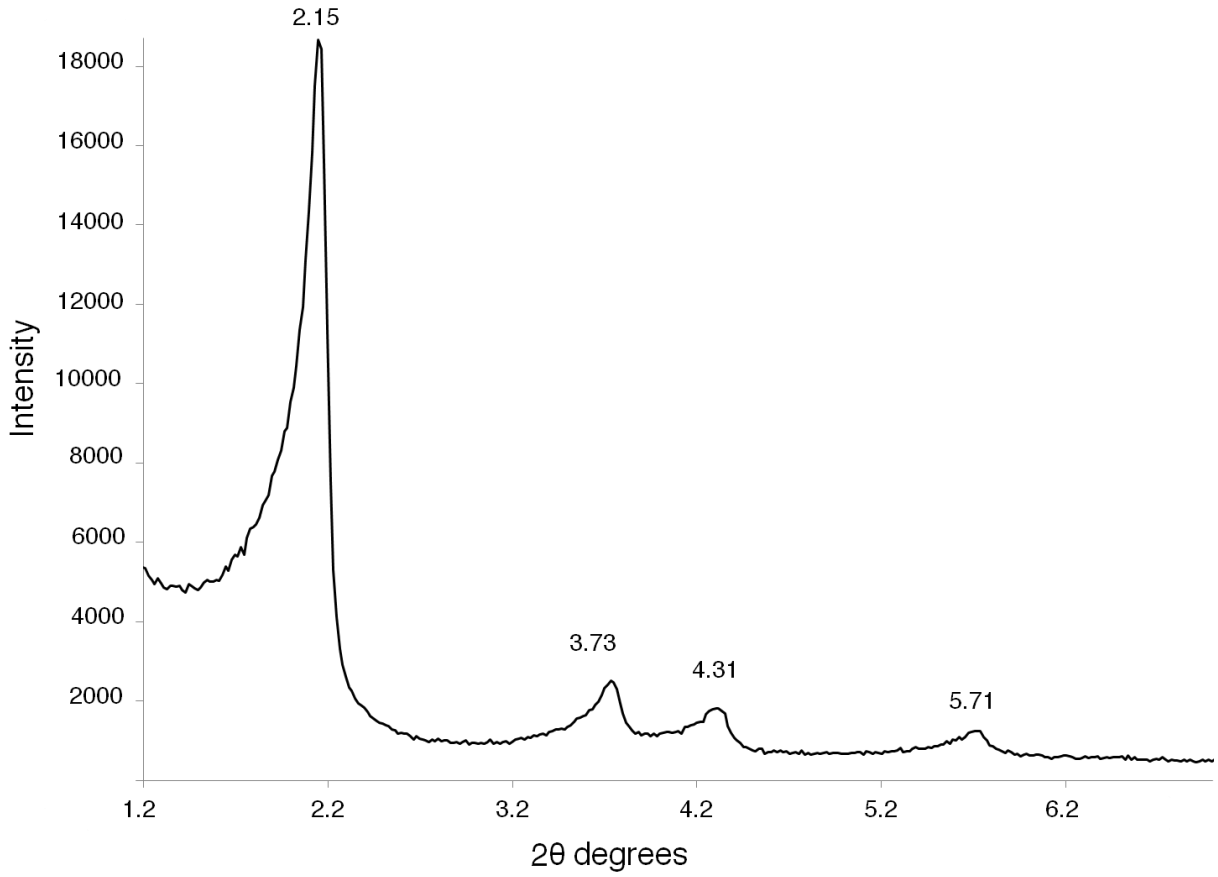

Fig. S2. Powder XRD of synthesized MCM-41 nanoparticles. The primary peak appears at 2.15, with a lattice spacing of 4 nm to give a calculated pore diameter of ~2 nm, in close agreement with TEM images of the synthesized nanoparticles.

SI-3) ***Fourier Transform Infrared Spectroscopy***

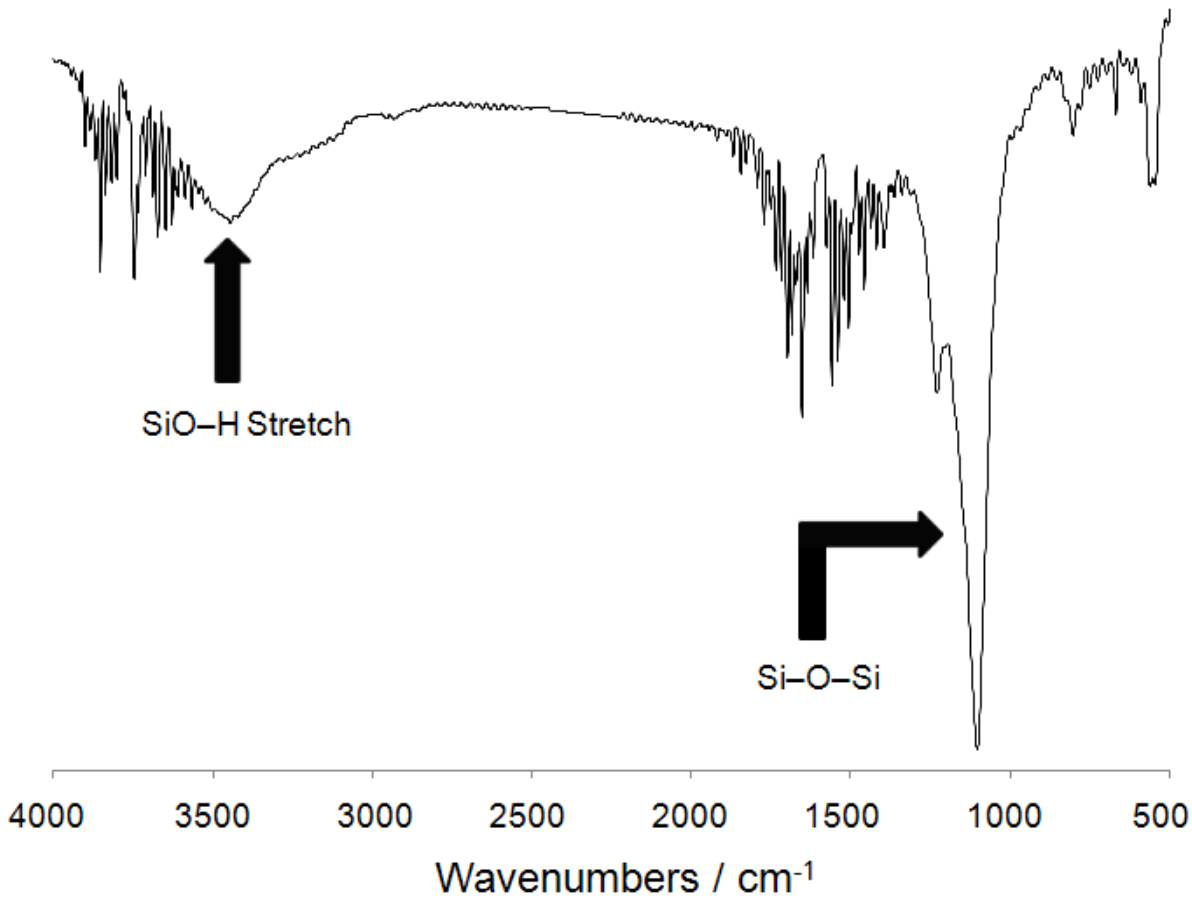

Fig. S3. FTIR spectrum of surfactant extracted MSN. The absence of C-H stretching bands at 3000 cm^{-1} indicates complete removal of the surfactant templating agent CTAB.

Section B. Thread Characterization

SI-4) *[1]H-NMR Spectrum of 1*

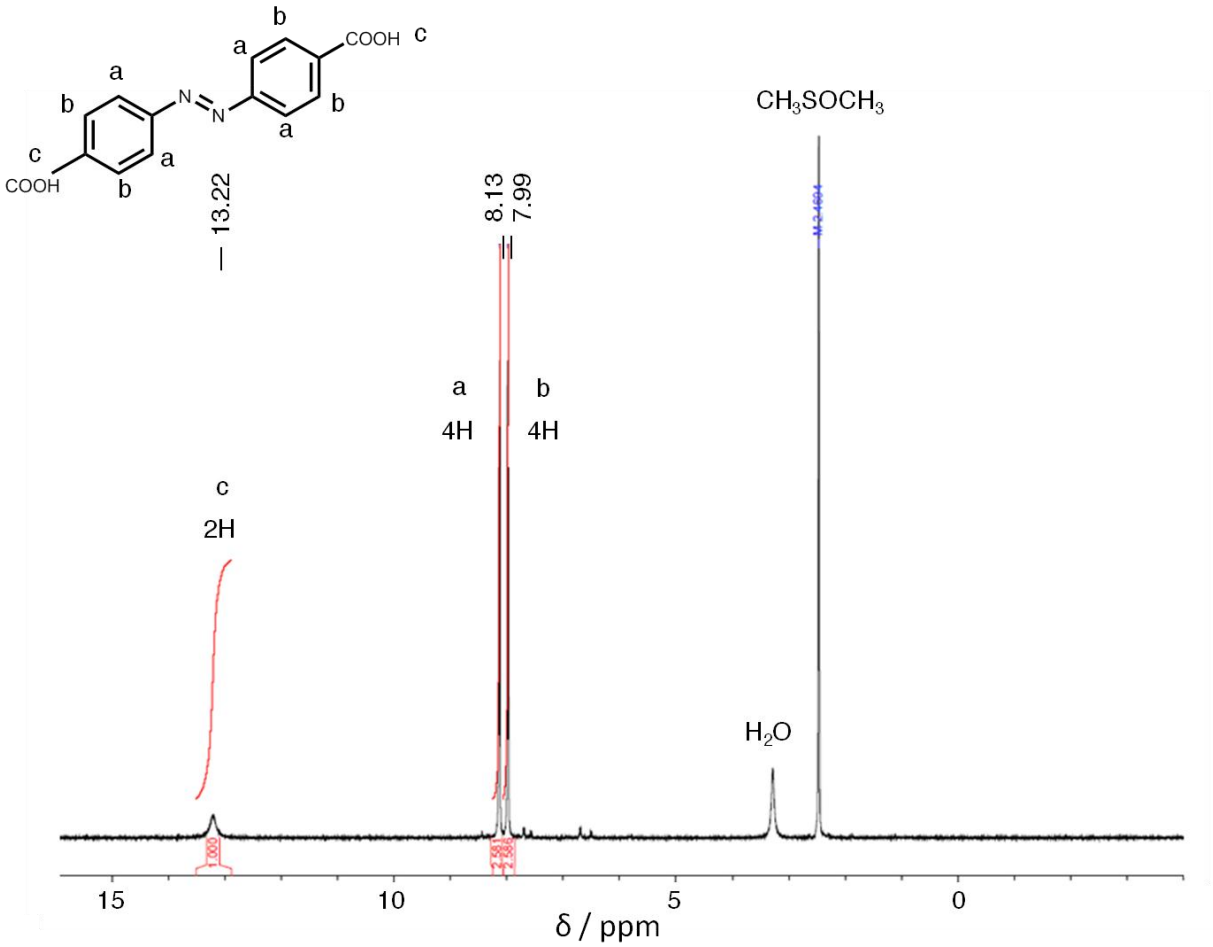

Fig. S4. ^{1}H-NMR spectrum of **1** in CD_3SOCD_3.

SI-5) ***[1]H-NMR Spectrum of 2***

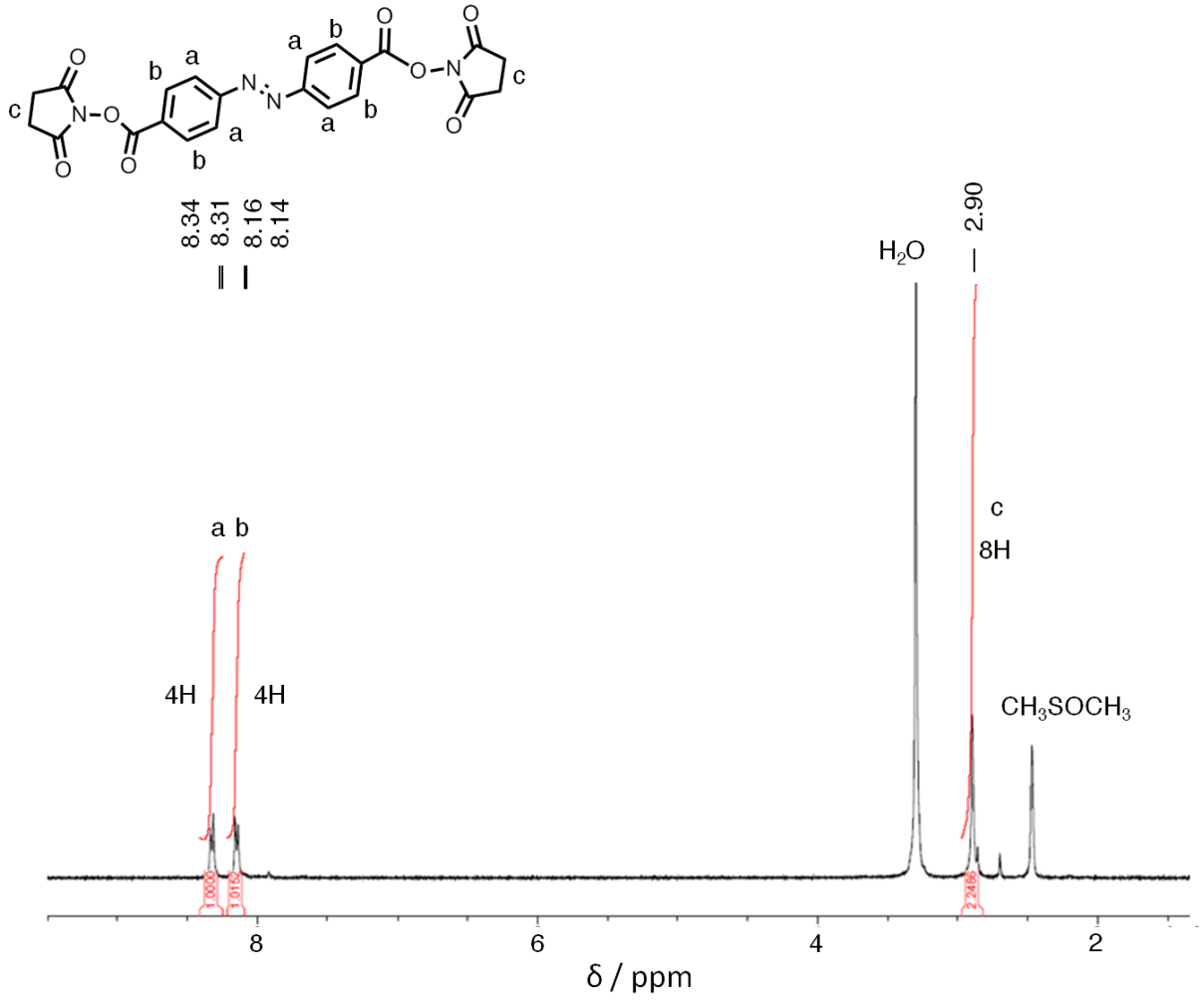

Fig. S5. ^{1}H-NMR spectrum of **2** in CD_3SOCD_3.

SI-6) ***[1]H-NMR Spectrum of 2b***

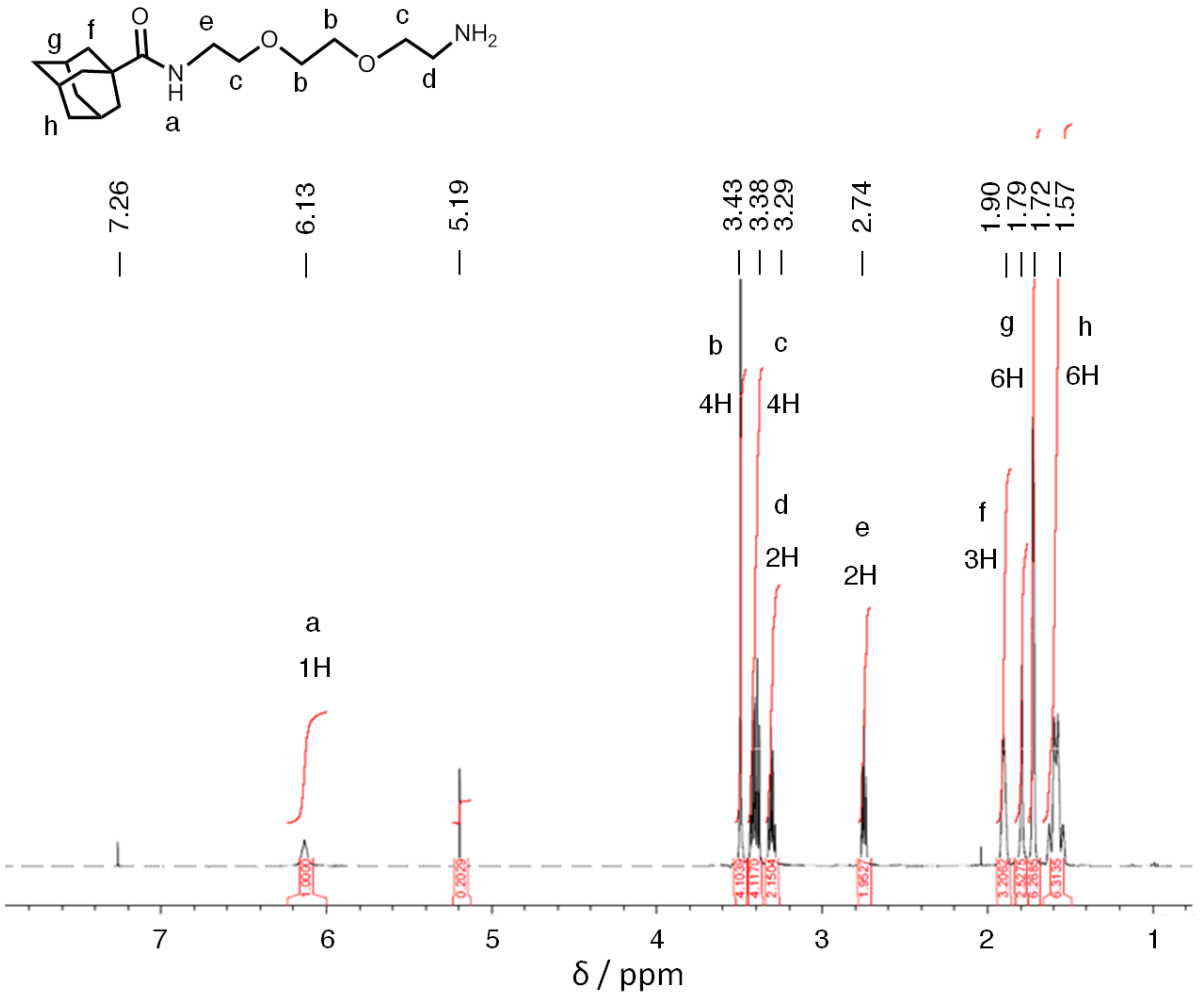

Fig. S6. ^{1}H-NMR spectrum of **2b** in $CDCl_3$.

SI-7a) ***[1]H-NMR Spectrum of 3a***

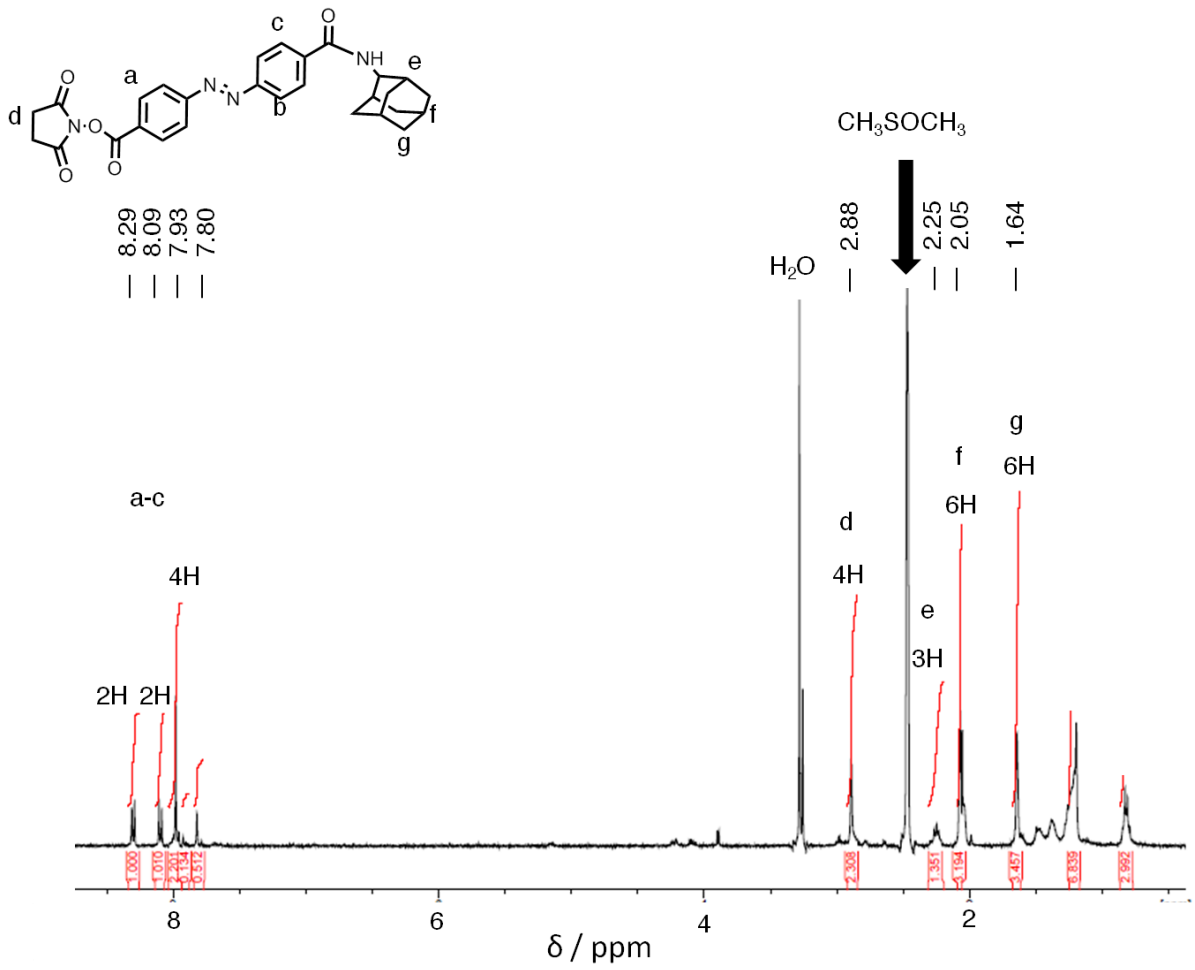

Fig. S7a. ^{1}H-NMR spectrum of **3a**CD_3SOCD_3.

SI-7b) ***ESI-TOF Mass Spectrum of 3a***

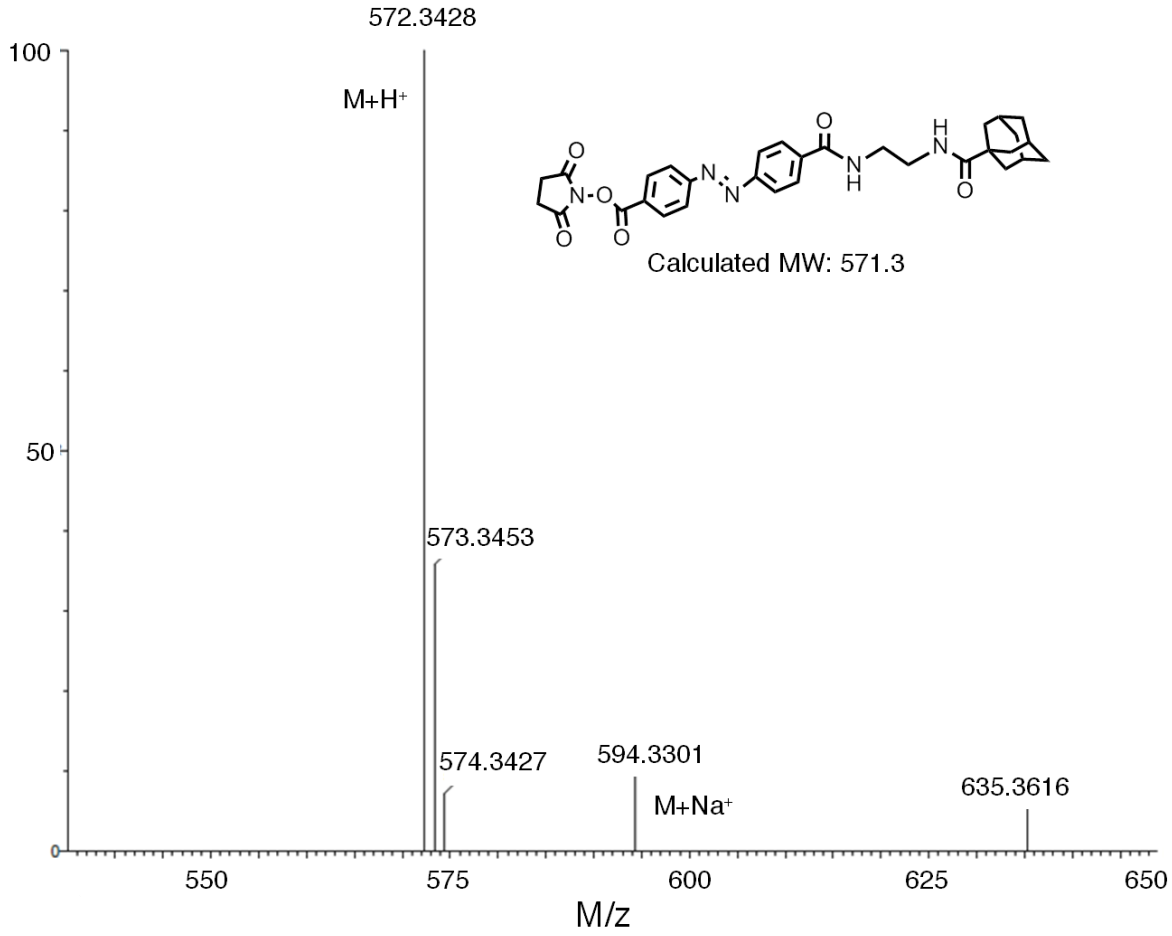

Fig. S7b. ESI-TOF mass spectrum of **3a**.

SI-8a) ***[1]H-NMR Spectrum of 3b***

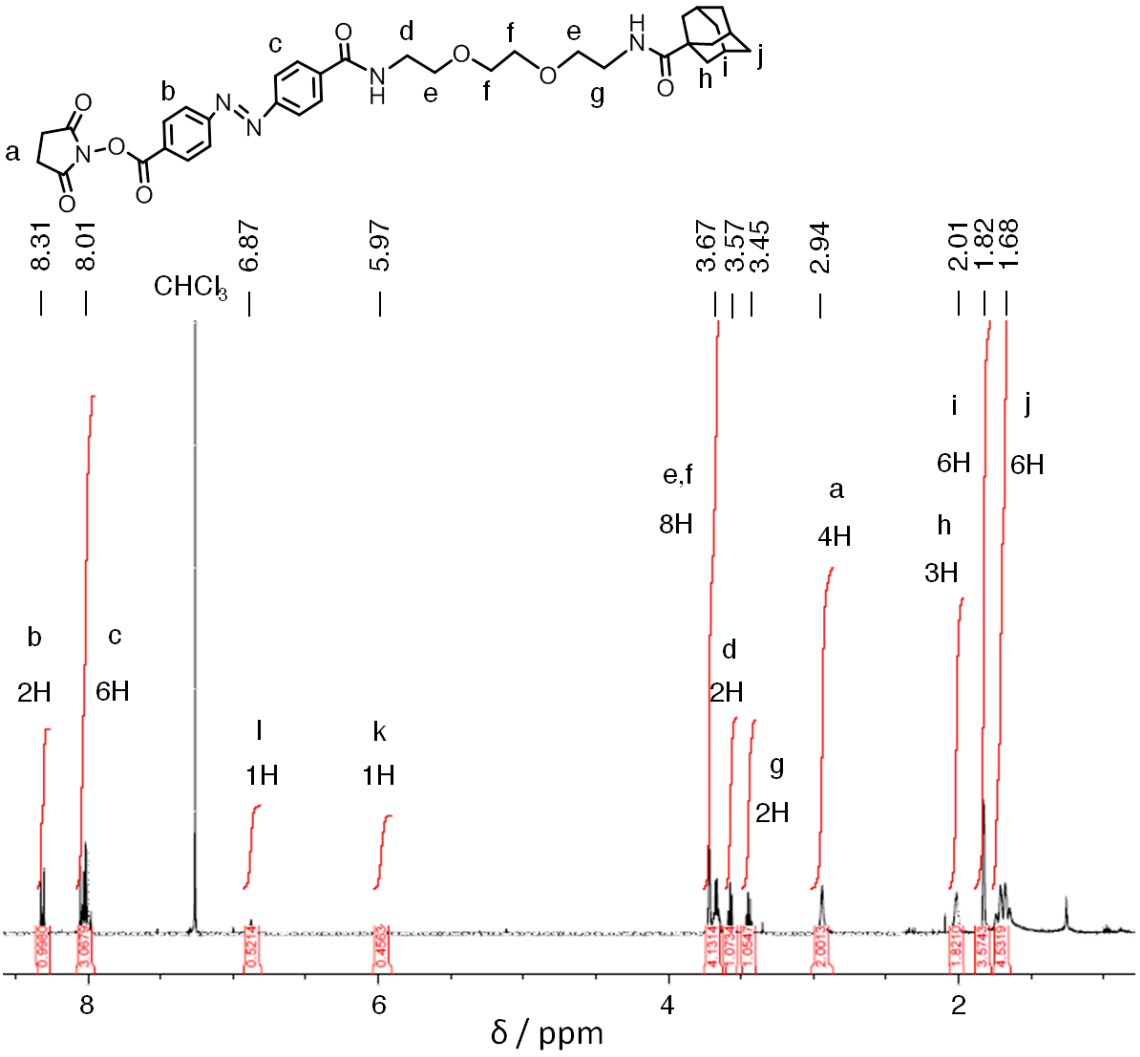

Fig. S8a. ^{1}H-NMR spectrum of **3b** in $CDCl_3$.

SI-8b) ***ESI-TOF Mass Spectrum of 3b***

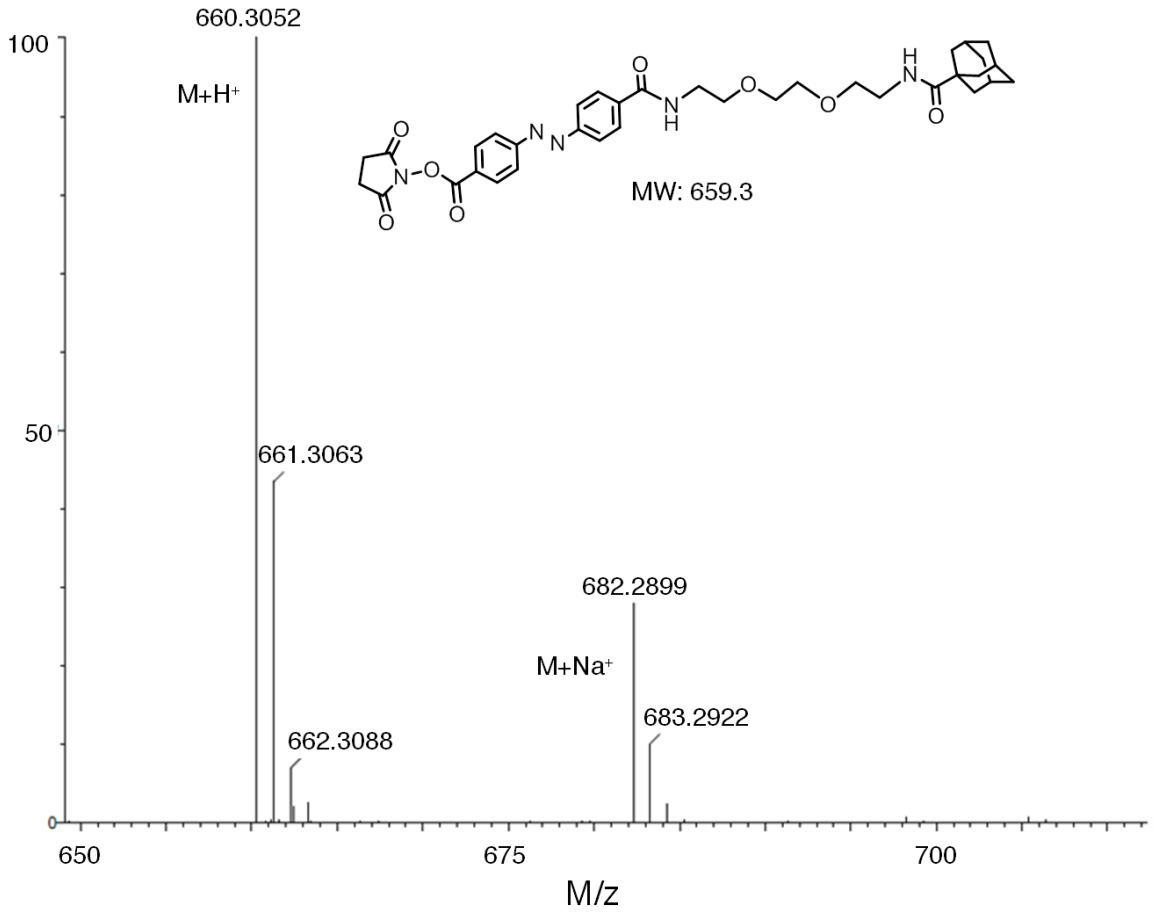

Fig. S8b. ESI-TOF mass spectrum of **3b**.

Section C. Thread-Modified Nanoparticle Characterization

SI-9) *UV-Vis Spectroscopic Analysis*

a) ***FRS1-MSN*** *– Surface Functionalization*

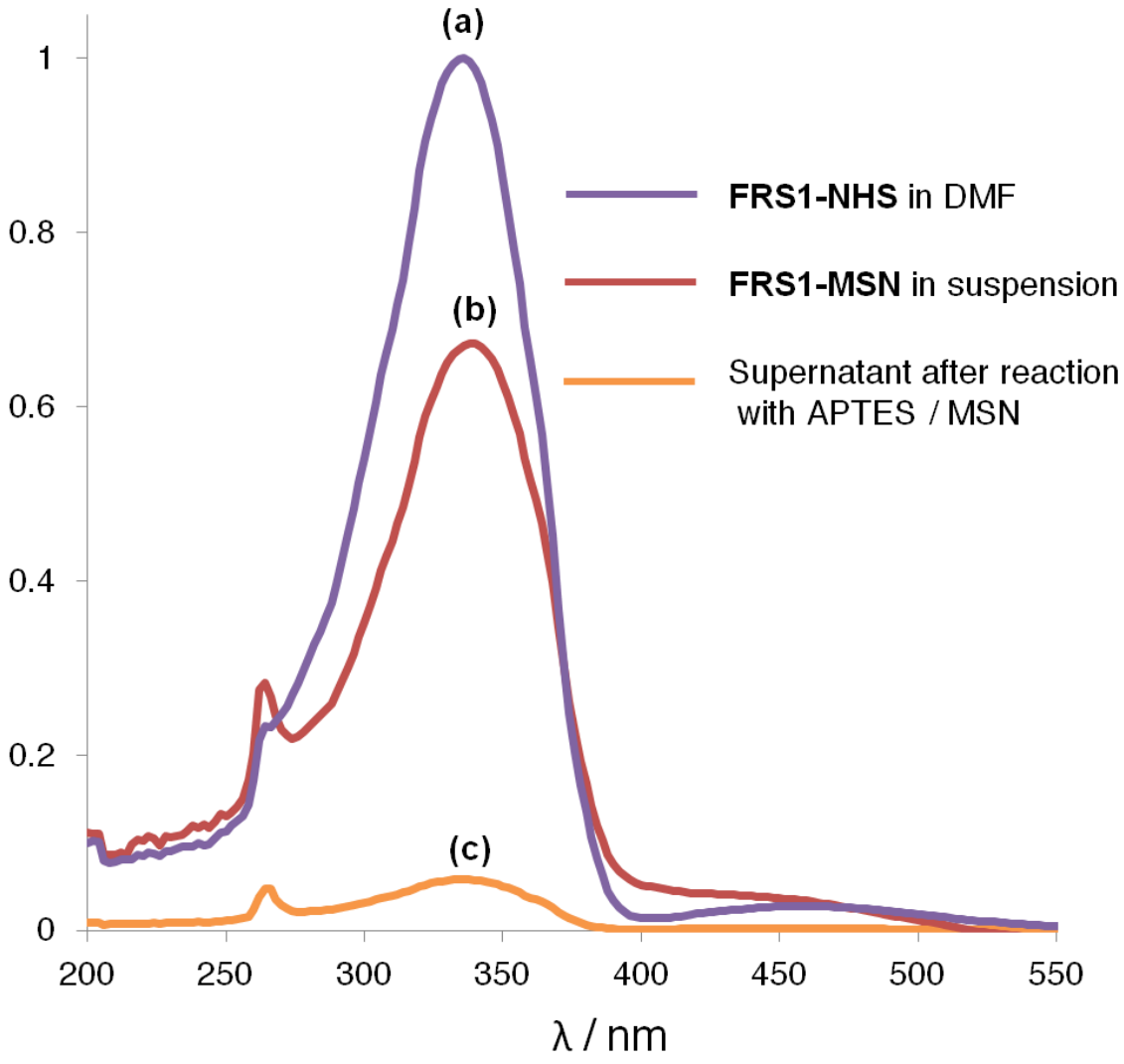

Fig. S9. UV-Vis absorption spectra proving successful reaction between Pseudorotaxane **FRS1-NHS** and APTES-modified MSN. Trace **(a)** shows the absorption of compound **FRS1-NHS** dissolved in DMF prior to reaction with APTES-modified MSN. After modification, an absorption spectrum of **FRS1-MSN** in suspension is shown in trace **(b)**. Finally, trace **(c)** shows the absorption of the supernatant solution after this attachment reaction has been completed, which indicates a successful reaction to attach the thread onto MSN. [All absorption spectra were normalized to trace **(a)]**.

SI-10) ***EXT2-MSN***

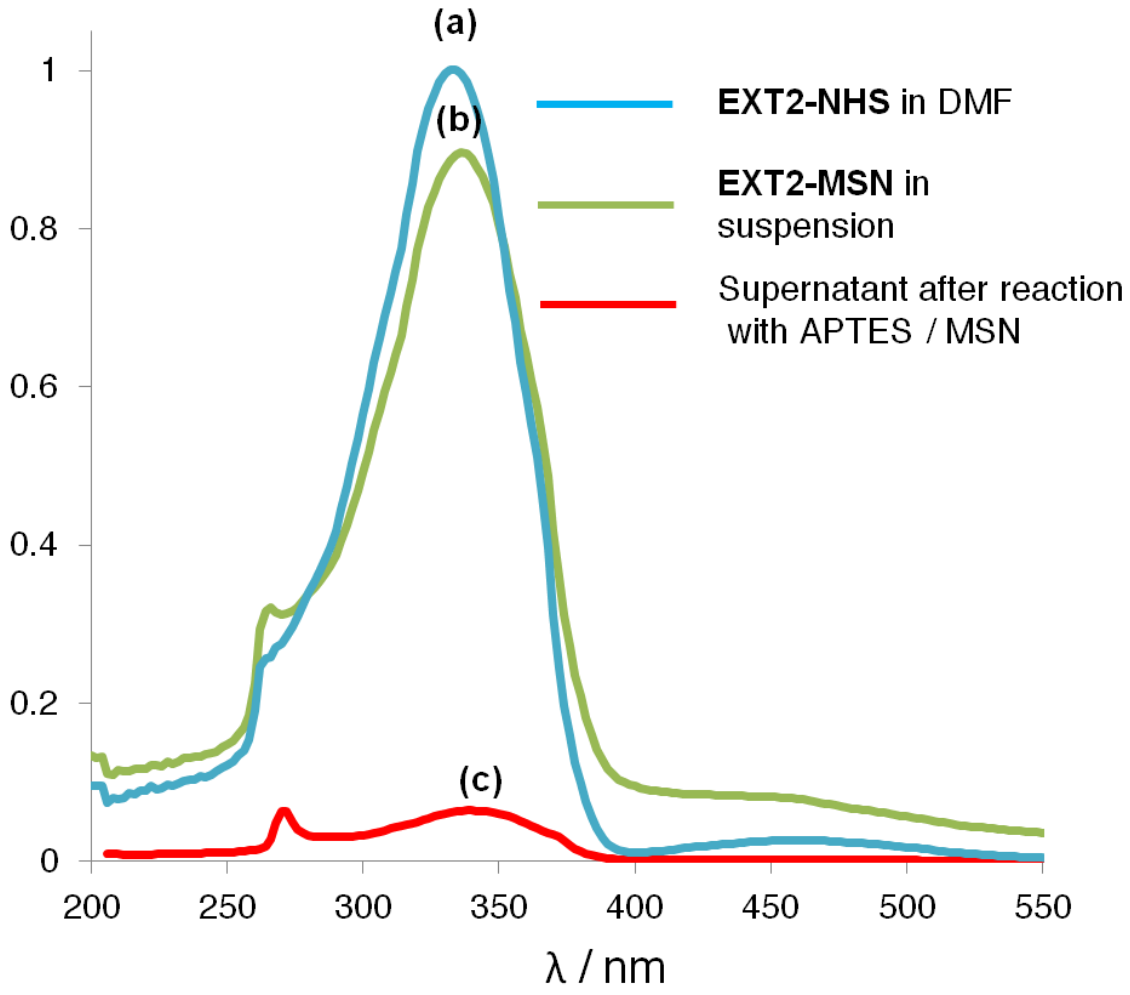

Fig. S10. UV-Vis absorption spectra proving successful reaction between **EXT2-NHS** and APTES-modified MSN. Trace **(a)** shows the absorbance of thread **EXT2-NHS** dissolved in DMF prior to reaction with APTES-modified MSN. Trace **(b)** shows the absorption of **EXT2-MSN** in suspension. Trace **(c)** shows the supernatant absorbance after the completed reaction, indicating that the thread has been successfully attached onto MSN. [All absorption spectra were normalized to trace **(a)**].

SI-11) ***FRS1-MSN*** *– Release of ARS*

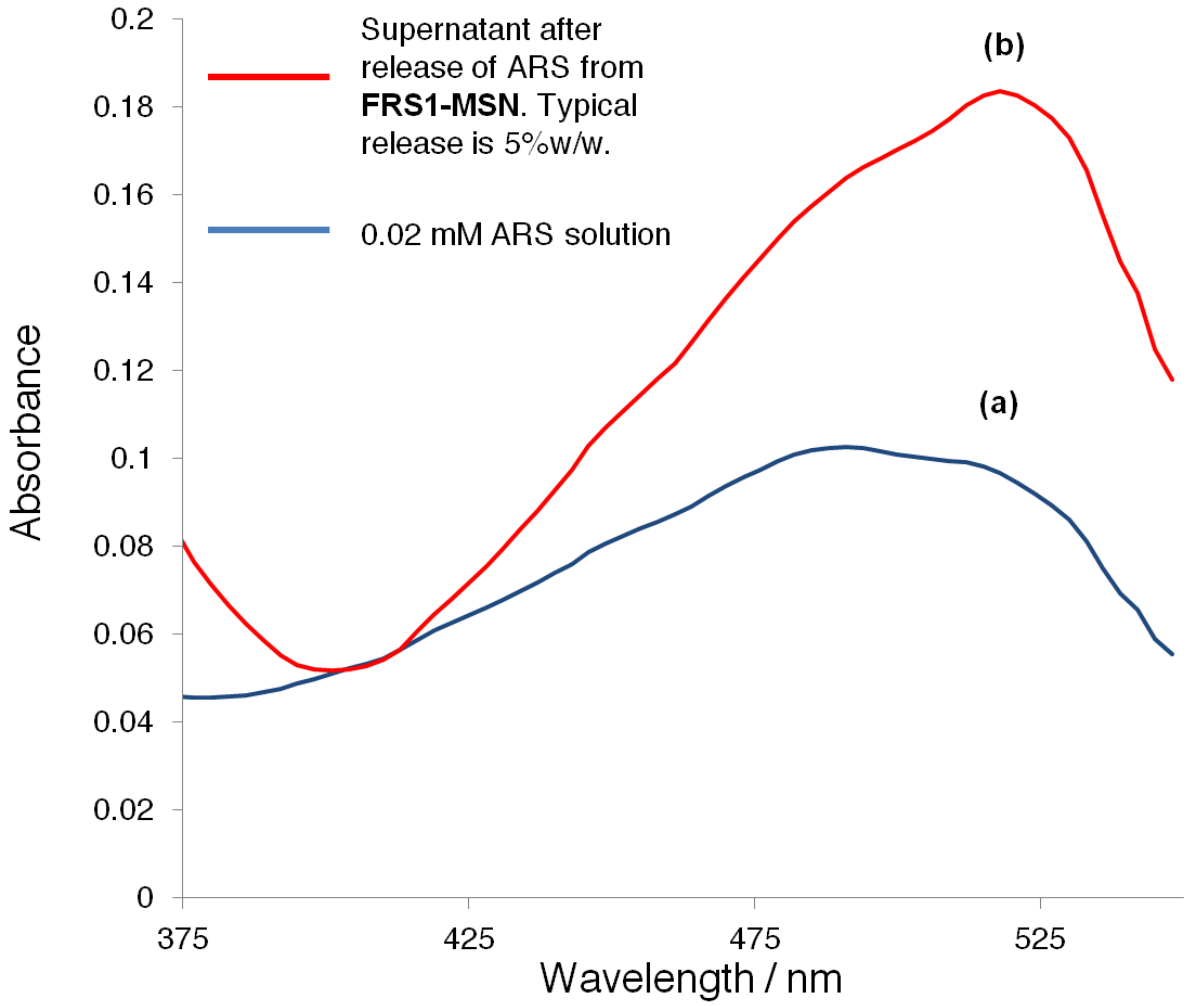

Fig. S11. UV-Vis absorption spectra of supernatant after release of ARS from **FRS1-MSN**. Trace **(a)** shows the absorbance of a 0.02 mM stock solution of ARS. Trace **(b)** shows the supernatant absorbance after a complete release from **FRS1-MSN**. Release weight percent was calculated from this trace to be 5% w/w.

Section D. Time-Resolved Spectroscopy

SI-12) *Experimental Setup for Time-Resolved Fluorescence Spectroscopy*

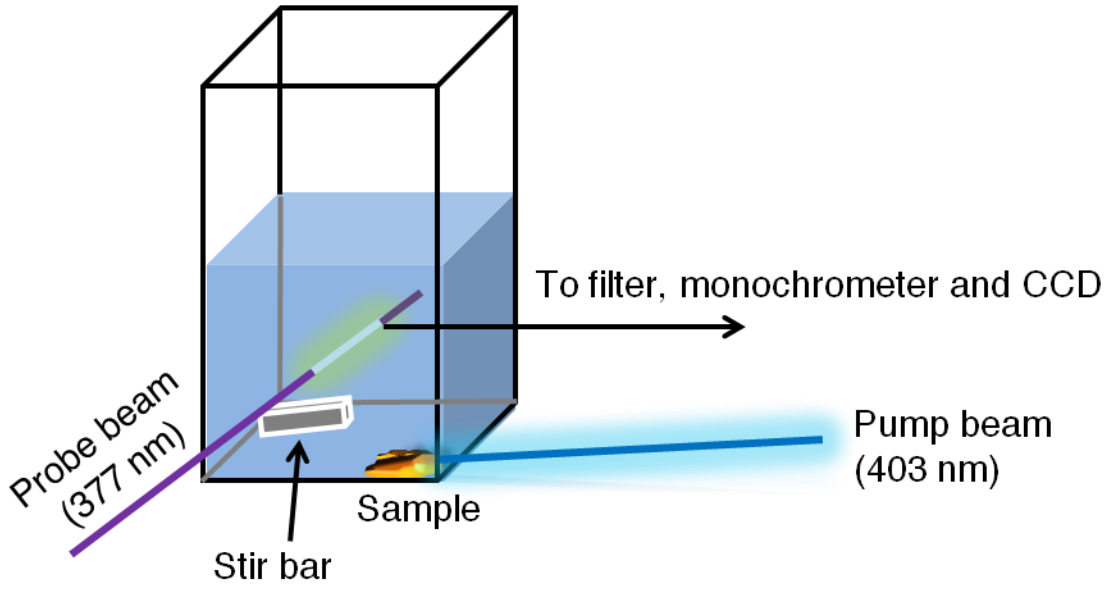

Fig. S12. Experimental setup for time-resolved fluorescence spectroscopy measurements. An excitation beam (377 nm, 1mW, 1 mm) is aimed at the solution supernatant, exciting any dye molecules present. The corresponding emission is passed through a cutoff filter, and a monochromator before being read on a CCD detector cooled to liquid nitrogen temperatures. Computer software integrates the intensities at a specified wavelength in real-time to generate a release profile. To initiate release, a pump beam (403 nm, 85 mW, 1 mm) is turned on and focused directly onto the sample to induce *trans*- to *cis*-azobenzene photoisomerization.

SI-13) ***Continuous Fluorescence Monitoring of FRS1-MSN and EXT2-MSN***

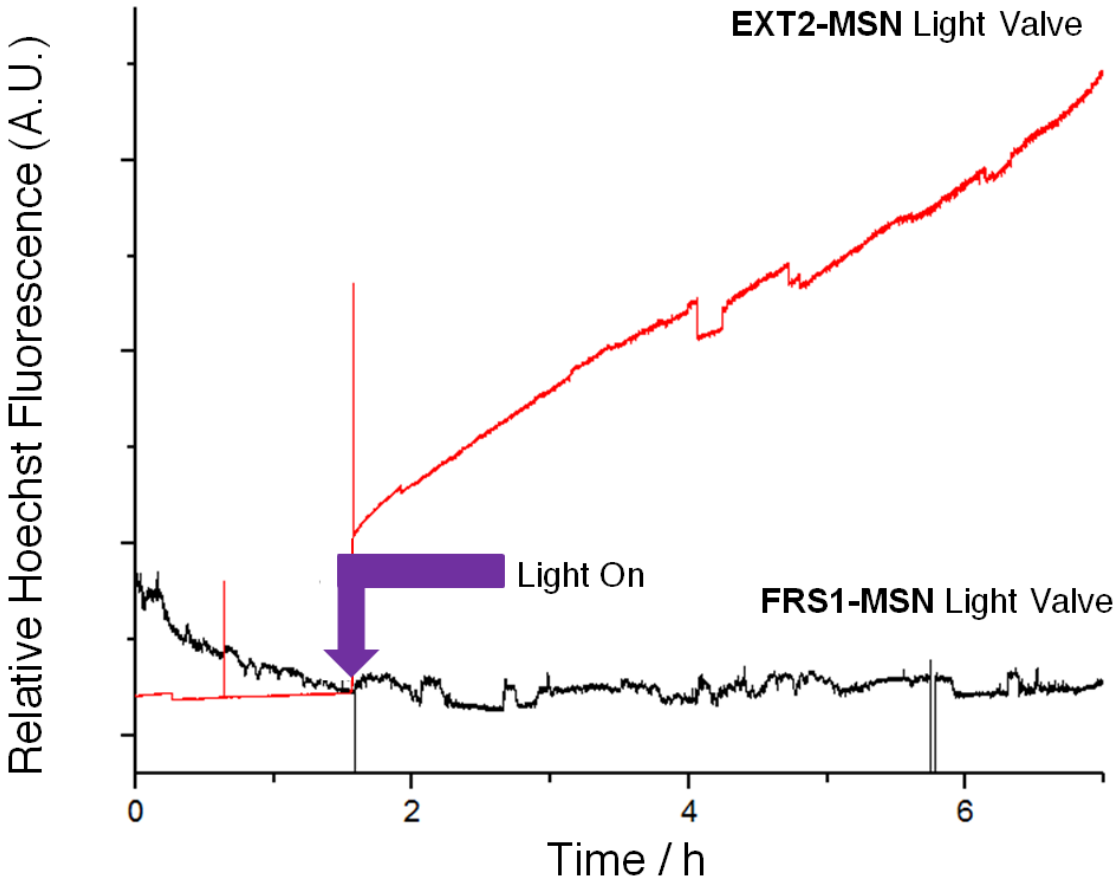

Fig. S13. Continuous fluorescence monitoring of **FRS1-MSN** loaded with Hoechst 33342 dye. No definite slope change is observed when the pump laser is turned on, indicating that this design cannot store and release larger cargo such as Hoechst, while **EXT2-MSN** shows a distinct fluorescence increase when irradiated.