# Supporting Information

# Nanovalve Activation by Surface-Attached Photoacids

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**General Methods**

All reagents such as tetraethyl orthosilicate, cetyl trimethylammonium bromide, sodium hydroxide, hydrogen chloride, α-cyclodextrin, triethylamine, 3-iodopropyltrimethoxysiliane, p-anisidine, propidium iodide, 6,8-Dihydroxy-1,3-pyrenedisulfonic acid disodium salt and 3-(triethoxysilyl)propyl isocyanate are commercially available and were used without further purification. Powder X-ray diffraction (XRD) measurements were carried out using a Panalytical X'Pert Pro powder diffractometer. The radiation source used was a copper (Kα1 and Kα2 = 1.5418 Å). FT-IR spectra were recorded on a Perkin-Elmer FT-IR Paragon 500 spectrometer. The transmission electron microscope (TEM) images of the silica nanoparticles were collected on JEM1200-EX (JEOL) instrument in the California NanoSystems Institute (CNSI). Microfilms for TEM imaging were made by putting a droplet of the particle suspension in methanol onto a 200-mesh copper TEM grid (Ted Pella, Inc., Redding, CA) and then dried at room temperature. The continuous monitoring of fluorescence release profiles were obtained using an Acton SpectraPro 2300i monochromator connected to a CCD was used for detection and CUBE 448, CUBE 375 and CUBE 408 (Coherent Inc., Santa Clara, CA, USA) diode lasers were used as the excitation source. UV-Vis spectra were collected on a Cary 5000 UV-Vis-NIP spectrophotometer.

**Characterization of the MSNs**

The MCM-41 nanoparticles where characterized using transmission electron microscope (TEM) images. The images showed particles around 100 nm with a pore diameter of about 2.5 nm as shown on Fig. S1.

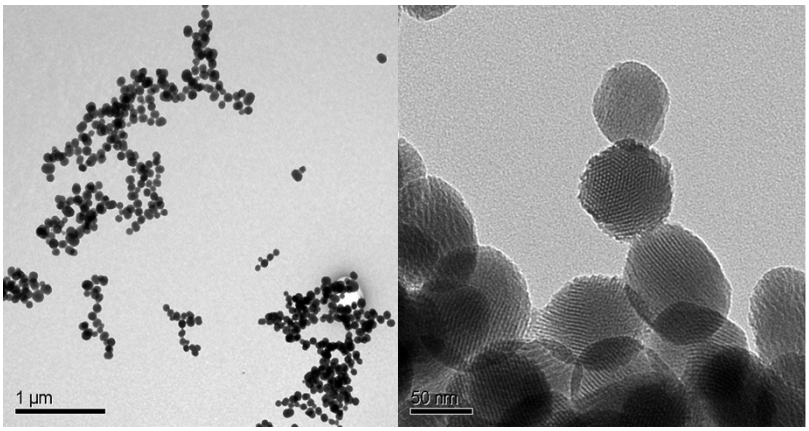


Fig. S1. TEM images of the surfactant extracted silica nanoparticles showing a hexagonal pore structure and a particles size of ~100 nm.

The UV-Vis spectrum of the stalk1-MSNs was taken. The absorbance peak matched that of the N-isopropyl-4-methoxyanaline, which has a very similar structure to the attached stalk1 as shown in Fig. S2.

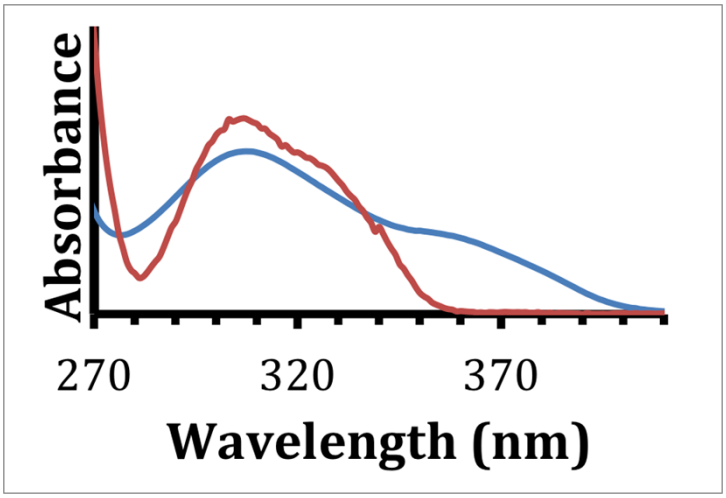


Fig. S2. The absorption spectra of a standard solution of N-isopropyl-4-methoxyaniline (blue, bottom) and of a solution of the stalk1-MSNs (red, top).

The fluorescence spectrum of DHDS-MSNs that was taken in a suspension matched that of the emission of DHDS in solution. This is evidence for the attachment of the DHDS to the silica nanoparticles.

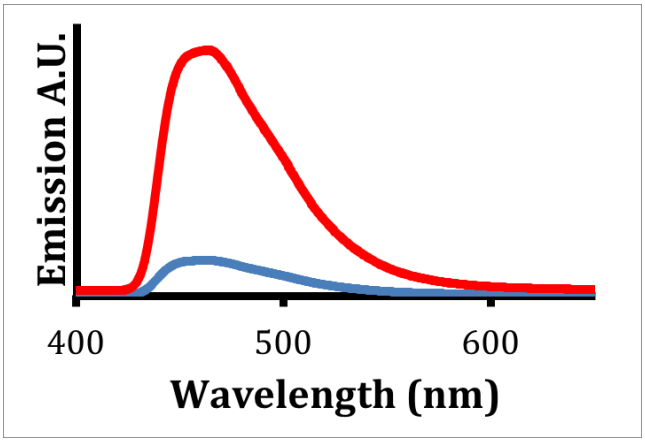


Fig. S3. Emission spectrum in DI water of DHDS-MSN (blue, bottom) and of the DHDS molecule in DI water (red, top).

As further evidence of the attachment of the photoacid to the MSNs, an IR spectrum of the modified particles was taken. It shows distinct stretches that correspond to the DHDS functionalization

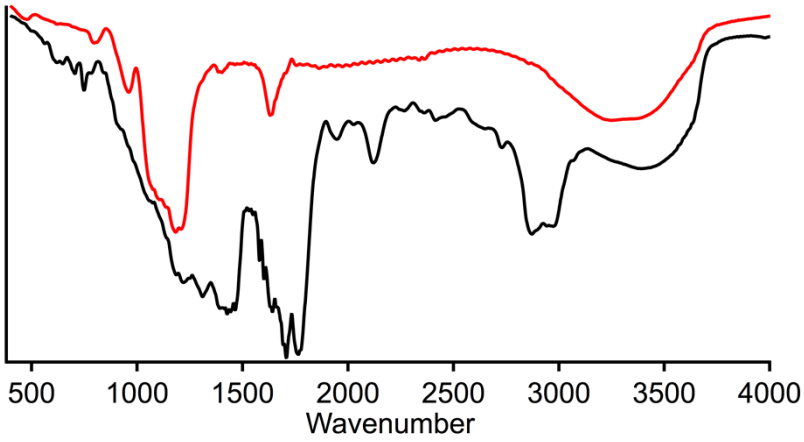


Fig. S4 IR spectrum of the DHDS-MSNs (bottom, black) and of the unfunctionalized surfactant extracted MSNs (top, red).

The synthetic scheme for the attachment of the alkoxysilanes to the DHDS molecule by reacting it with ICPES is shown in Fig. S5 below.

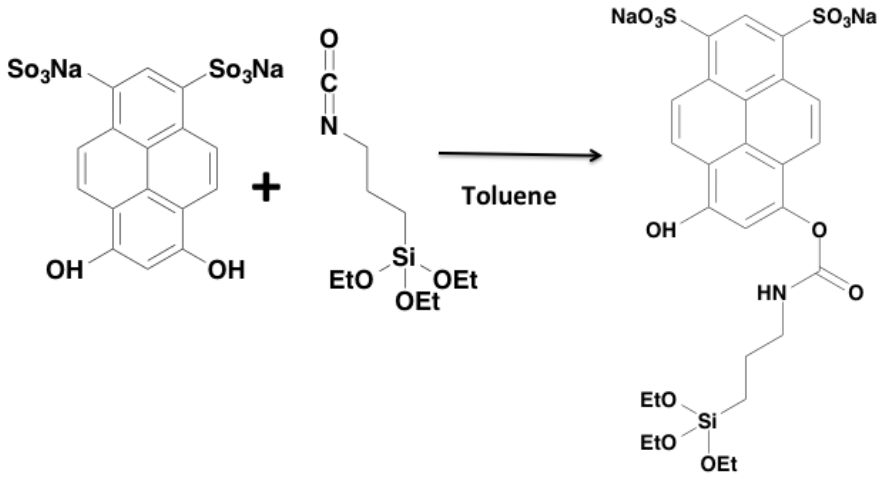


Fig. S5. DHDS Reaction with ICPES

The experimental set up used to obtain the cargo release profiles is shown in Fig. S6. A pump laser was used to activate the nanomachines. A probe laser was used to excite the fluorescent cargo dye. The fluorescence intensity from the dyes in solution was detected using a CCD connected to a monochromator. The fluorescence spectrum was taken every second and the integrated intensity in the wavelength region from 625 nm to 675 nm was plotted versus time.

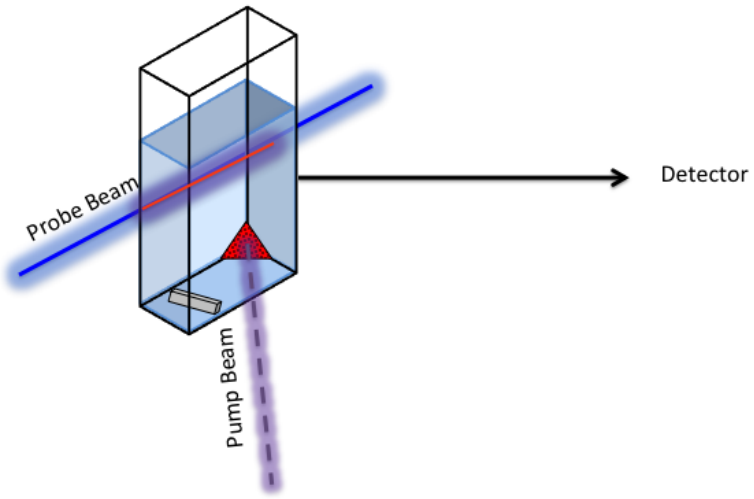


Fig. S6 Pictorial representation of the set up used for the continuous monitoring of the release of the dye. A one by two centimeter glass cuvette was used and the fluorescence was detected. The particle precipitate was placed in the back corner of the cuvette.

The absorption spectrum of the 6,8-Dihydroxy-1,3-pyrenedisulfonic acid disodium salt in ethanol solution is shown in Fig. S7. The 408 nm wavelength of the excitation pump laser is indicated by the arrow.

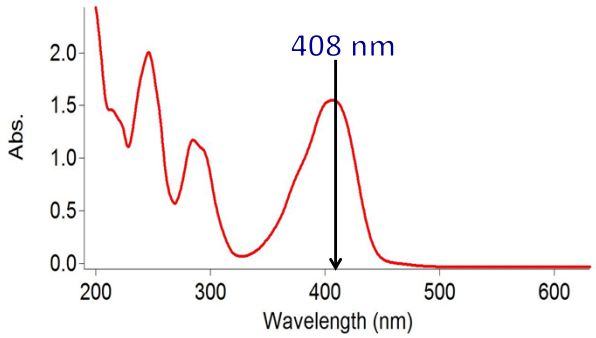


Fig. S7 UV-Vis spectra of DHDS in solution.

Fig. S8 shows the UV-vis absorption spectra of the photoacid in solution and of the DHDS-Stalk1-MSNs in solution.

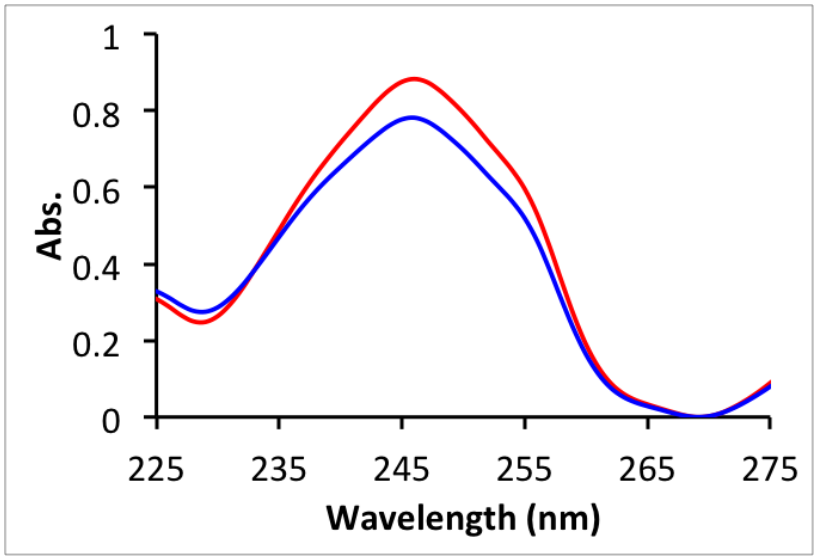


Fig. S8 UV-Vis spectra of DHDS in solution (bottom, blue) and DHDS-Stalk1-MSNS in solution (top, red).

Fig. S9 shows the eight hour release profile using 514 nm followed by 408 nm excitation.

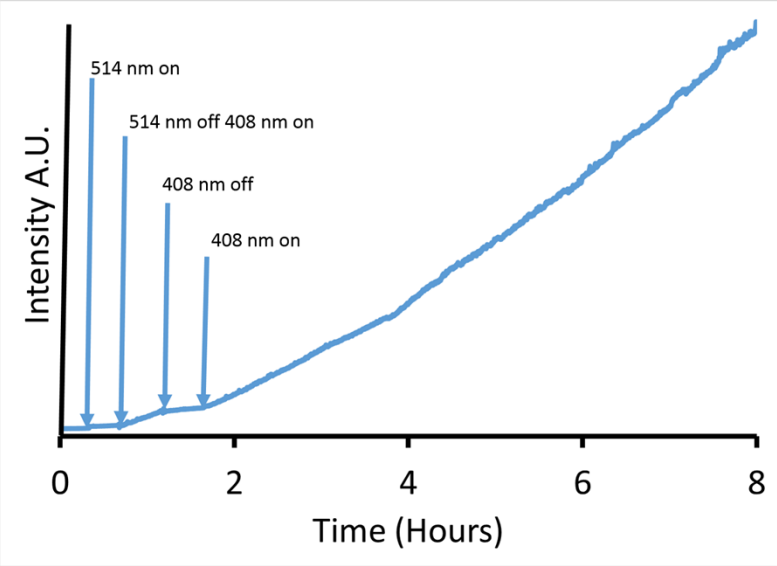


Fig. S9 Release profile over an 8 hour time period where 514 nm activation was used followed by 408 nm activation.