Supporting Information

Functioning of Nanovalves on Polymer Coated Mesoporous Silica Nanoparticles

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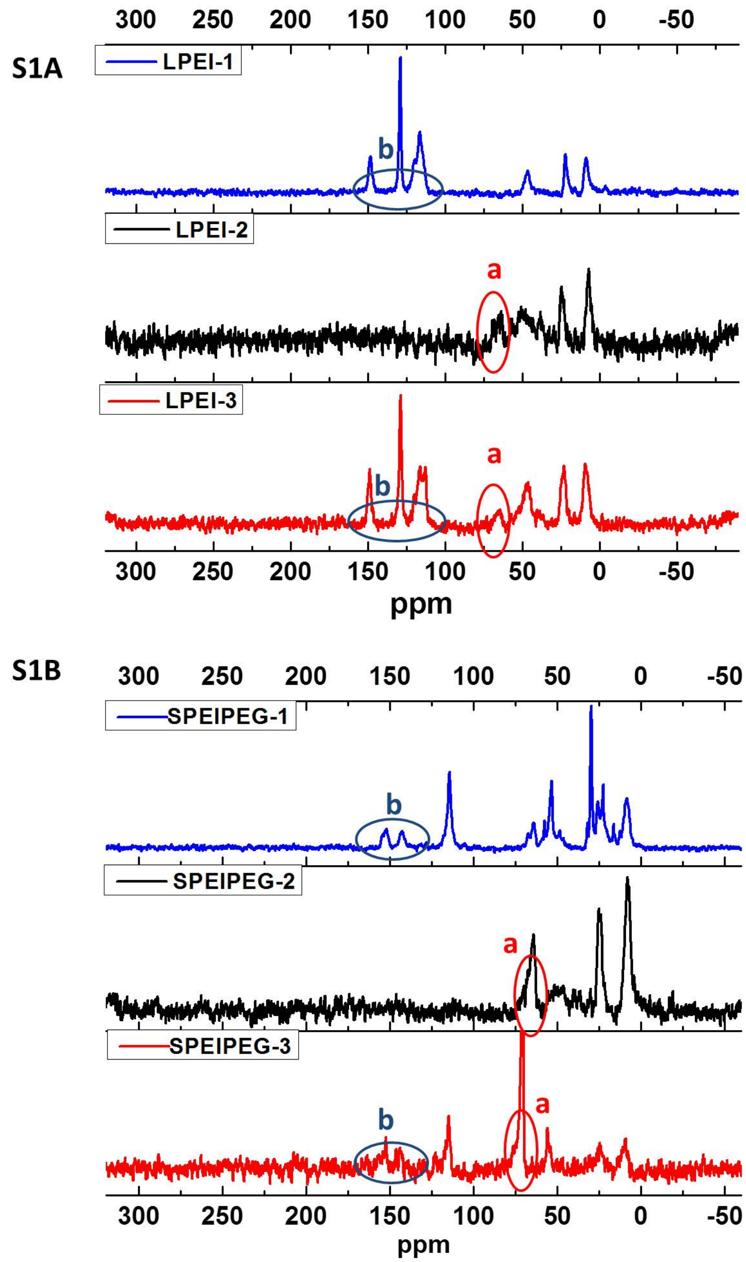

Figure S1. ^{13}C CPMAS solid state NMR spectra for LPEI group (S1A) and SPEIPEG group (S1B). Range **a** marks the characteristic peaks for substituted alkanes on the polymer coatings and range **b** represents the major aromatic carbons on the nanovalve stalks. The spectra confirm that both the nanovalve modifications and polymer coatings are successfully performed for LPEI-3 and SPEIPEG-3. [1]

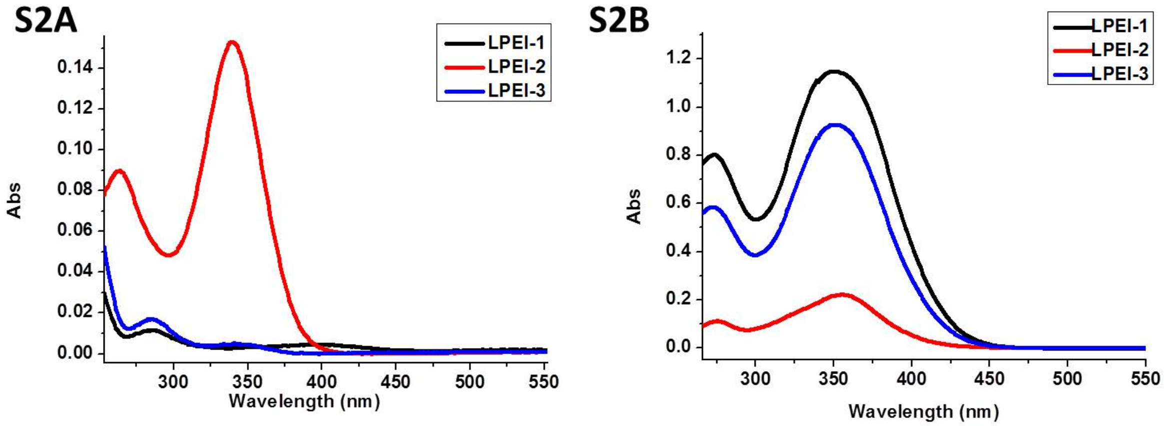

Figure S2. Supernatant absorption spectra of LPEI group before (S2A) and after cargo release(S2B). The nanovalves on LPEI-1 and LPEI-3 were able to trap the cargo in the mesopores under neutral pH and release them after acidification.

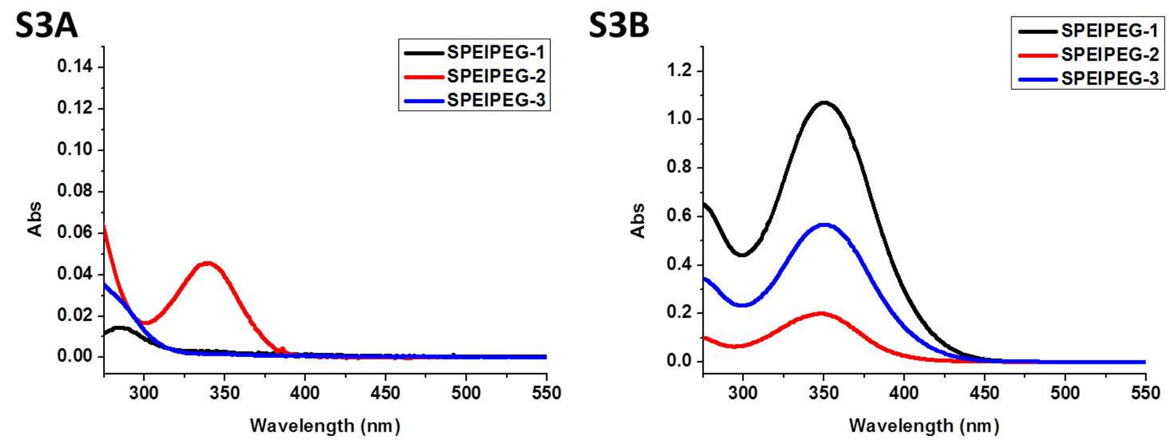

Figure S3. Supernatant absorption spectra of SPEIPEG group before (S3A) and after cargo release(S3B). The nanovalves on SPEIPEG-1 and SPEIPEG-3 were able to trap the cargo in the mesopores under neutral pH and release them after acidification.

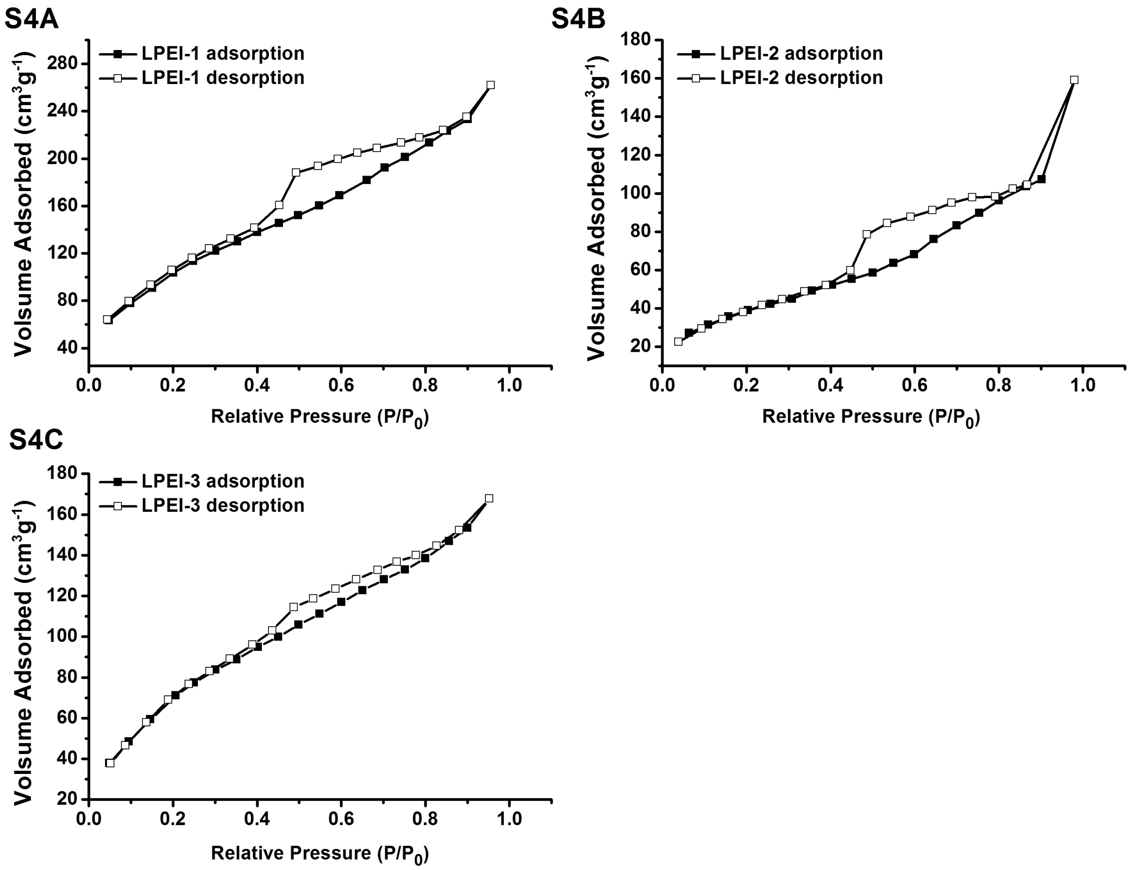

Figure S4. N_2 adsorption-desorption isotherms of LPEI samples exhibiting the type IV isotherms for ordered mesoporous structures. The surface areas calculated by BET model are 418 m^2/g for LPEI-1, 149 m^2/g for LPEI-2 and 305 m^2/g for LPEI-3.

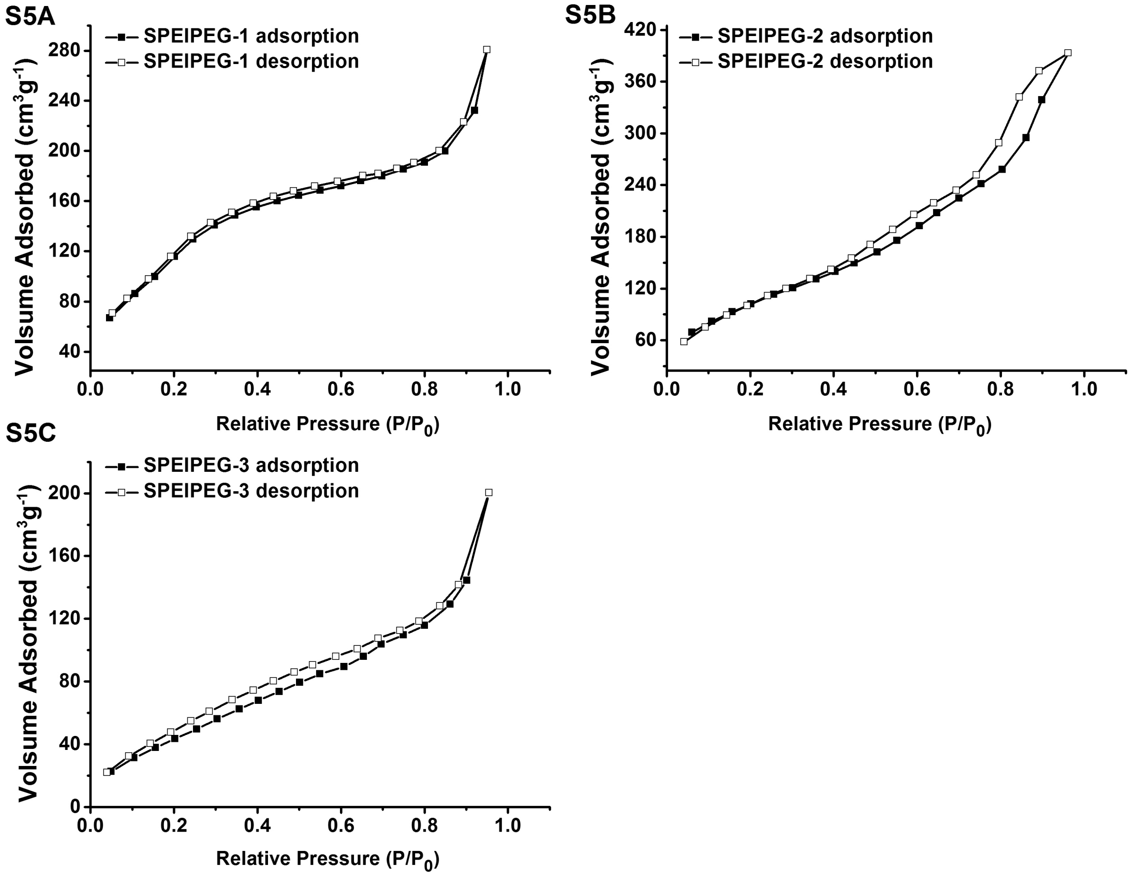

Figure S5. N_2 adsorption-desorption isotherms of SPEIPEG groups exhibiting the type IV isotherms for ordered mesoporous structures. The surface areas based on BET model are: 492 m^2/g for SPEIPEG-1, 397 m^2/g for SPEIPEG-2 and 189 m^2/g for SPEIPEG-3.

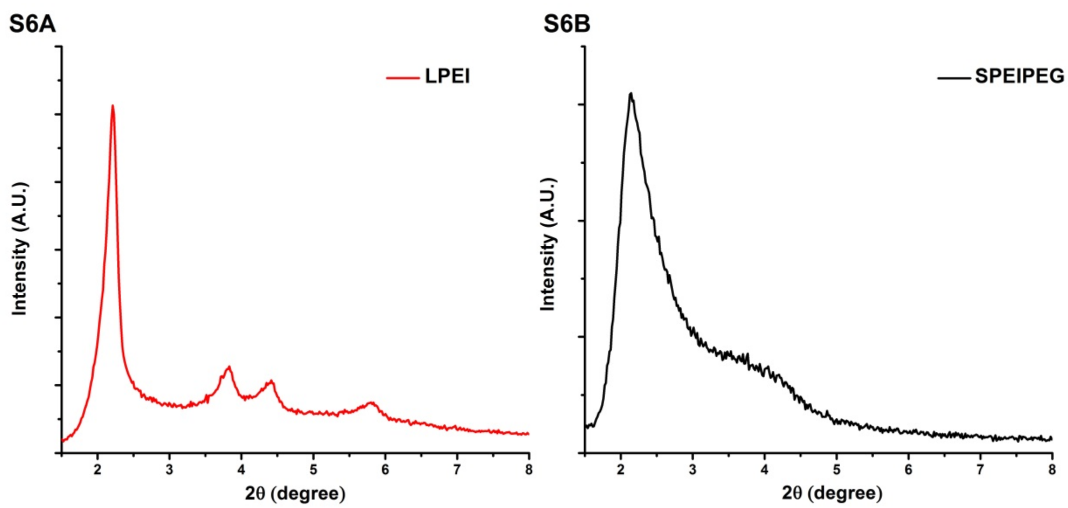

Figure S6. The XRD spectra of LPEI (left) and SPEIPEG (right) particles. The interplanar spacing *d*(100) is 4.0 nm for LPEI and 4.1 nm for SPEIPEG. The SPEIPEG particles have used two templating agents that broaden the d-space distributions.

Estimation of the Polymer Coverage on the MSNs

In this part, we calculated the total surface area of silica nanoparticles and that of the polymer molecules coated on the particles. In comparing the two areas, we try to estimate the polymer coverage on the surface of MSNs.

The surface areas of polymer molecules were calculated using software ChemBio3D. Assuming all the molecules are flat, the surface area of an 1800 Da PEI molecule is about 9.97 nm^2 and that of a 5000 Da PEG molecule is about 10.19 nm^2.

The LPEI-3

For LPEI-3, polymer weight percentage: 31.2-14.8 = 16.4

For 100 mg of MSN, there is about 16.4 mg of PEI polymer on the silica surface. The weight for the silica nanoparticles is: 100-31.2 = 68.8 mg

Assume the silica density is 2.65 g/cm^3, the particle radius is 60 nm.

Number of silica particles in 68.8 mg MSN:

$$N_{MSN} = \frac{68.8mg}{\frac{2.65g}{cm^3}} \times \frac{1}{\frac{4}{3}\,\pi(60\;nm)^3} = 2.87 \times 10^{13}$$

Total surface area of 68.8 mg MSN:

$$S_{MSN-total} = S_0 \times N_{MSN} = 4\pi \times (60nm)^2 \times 2.87 \times 10^{13} = 1.30 \times 10^{18}\,nm^2$$

For a PEI molecule of weight 1800 Da, if we assume it is a flat molecule, the length is roughly 61.68 Å and the width is 16.17 Å. Then the area of every molecule would be 61.68 × 16.17 ≈ 9.97 nm^2

Total area of 16.4 mg PEI polymer molecules:

$$S_{polymer-total} = \frac{9.97\;nm^2 \times 16.4\;mg \times 6.02 \times 10^{23}}{1800\;g} = 5.47 \times 10^{19}\,nm^2$$

Since $S_{polymer-total} \gg S_{MSN-total}$, this indicates that the PEI polymer has a full coverage on the particle surface.

The SPEIPEG-3

Due to the lack of information about the exact weights of PEI and PEG components, an exact calculation similar to that of the LPEI group cannot be conducted. Nevertheless, we can estimate the polymer coverage if it is all composed of PEI or if it is all made of PEG, and the actual coverage should fall between the these two extremes.

In 100mg of SPEIPEG-3, the polymer part weight is: 31.3-23.1=8.2 mg

The silica nanoparticle weight is: 100-31.3=68.7 mg

Number of silica particles in 68.7 mg of small particle (30 nm radius):

$$N_{MSN} = \frac{68.7mg}{\frac{2.65g}{cm^3}} \times \frac{1}{\frac{4}{3}\,\pi(30\;nm)^3} = 2.29 \times 10^{14}$$

Total surface area of silica nanoparticles:

$$S_{MSN-total} = S_0 \times N_{MSN} = 4\pi \times (30nm)^2 \times 2.29\times10^{14} = 2.59\times10^{18}\,nm^2$$

If the polymer is mainly composed of PEI, then the total area of 8.2 mg PEI polymer molecules:

$$S_{PEI-total} = \frac{9.97\,nm^2 \times 8.2\,mg \times 6.02 \times 10^{23}}{1800\,g} = 2.73 \times 10^{19}\,nm^2$$

Since $S_{PEI-total} \gg S_{MSN-total}$, the MSNs are fully covered by the polymer, if it is mainly PEI.

If the polymer is mainly composed of PEG, then the total area of 8.2 mg PEG polymer molecules:

Assuming that PEG is a flat molecule, then the surface area of one molecule would be : 405.5 Å × 2.513 Å ≈ 10.19 nm^2 .

$$S_{PEG-total} = \frac{10.19\,nm^2 \times 8.2\,mg \times 6.02 \times 10^{23}}{5000\,g} = 1.01 \times 10^{19}\,nm^2$$

Since $S_{PEG-total} \gg S_{MSN-total}$, the small MSNs are fully covered by the polymer, if it is mainly PEG.

The calculation results suggested that the PEI-PEG co-polymer has a good coverage on the surface of SPEIPEG-3, regardless of the actually composition between the PEI part and the PEG part.

References

[1] L. Du, S. Liao, H. A. Khatib, J. F. Stoddart, J. I. Zink, *Journal of the American Chemical Society* **2009**, *131*, 15136-15142.