Electronic Supplementary Information (ESI)

for


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[**] This research was supported by the National Natural Science Foundation of China (21272093), the Research Fund for the Doctoral Program of Higher Education of China (20120061120117), and the Innovation Program of the State Key Laboratory of Supramolecular Structure and Materials.

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1. Materials and Methods

All reagents and starting materials were purchased from Aldrich and Aladdin, which were used as received. A series of phosphate buffers (PBS buffers) were prepared according to the Appendix XV of the Chinese Pharmacopeia (the Second Part, 2010 Edition). Unless otherwise stated, all reactions were performed under a nitrogen atmosphere and in dry solvents. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku SmartLab III powder diffractometer. The radiation source was copper ($K_\alpha = 1.39225$ Å). Scanning electron microscope (SEM) images were collected on a JEOL JSM 6700F instrument. Au coating of the nanoparticles used for imaging was carried out by sputtering for 2 min. Transmission electron microscopy (TEM) images were collected on a Hitachi H-800 instrument, where the accelerating voltage was 200 kV. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 300 MHz NMR spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 80V spectrometer. N$_2$ Adsorption and desorption isotherms (BET and BJH) were carried out using a Micromeritics Gemini instrument. Elemental analysis was done on a Vario micro cube (Elementar Analysensysteme) to test the content of C, H, N and S. The controlled release profiles were obtained via UV-vis spectroscopy on a Shimadzu UV-2550 spectrophotometer. Three-dimensional sizes of RhB cargo were calculated to be $9.7$ Å $\times$ $6.9$ Å $\times$ $2.3$ Å by molecular modeling.
2. Preparation and Synthesis

2.1 Synthesis of $\text{C}_1^{\text{S1}}$

\[
\text{BrCOOH} \quad + \quad \text{Me}_3\text{N} \quad \xrightarrow{\text{EtOH} \quad \text{r.t.} / 3 \text{ d}} \quad \text{Br} \quad \text{N} \quad \text{CH} \quad \text{COOH}
\]

Scheme S1. Synthesis of $\text{C}_1$

3-Bromopropionic acid (2.04 g, 13.3 mM) dissolved in ethanol (10 mL) was added into trimethylamine solution (42.86 mL, 120 mM) and the mixture was stirred for 3 days at room temperature. Excess trimethylamine was removed under reduced pressure, and then the residue was dried under vacuum overnight to give compound $\text{C}_1$ as a white solid (2.11 g, 75%). $^1\text{H} \text{NMR of } \text{C}_1 \text{ (300 MHz, D}_2\text{O, 25}^\circ\text{C) } \delta \text{ (ppm): } 3.66 \text{ (t, } J = 7.6 \text{ Hz, 2H), 3.16 \text{ (s, 9H), 2.91 \text{ (t, } J = 7.0 \text{ Hz, 2H).}$

2.2. Synthesis of $\text{C}_2$

2.2.1. Synthesis of $\text{C}_2$-$\text{s1}$

\[
\text{O} \quad \text{O} \quad \text{O} \quad + \quad \text{H}_2\text{N} \quad \text{NH}_2 \quad \xrightarrow{\text{r.t.} / 1 \text{ d}} \quad \text{O} \quad \text{N} \quad \text{CH} \quad \text{NH}_2
\]

Scheme S2. Synthetic route to $\text{C}_2$-$\text{s1}$

1,2-Diaminoethane (6.20 mL, 92 mM) was added into a 100 mL round-bottomed flask containing 1,4-dioxane (30 mL). Di-tert-butyldicarbonate (2.64 g, 12.08 mmol), pre-dissolved in 1,4-dioxane (30 mL), was added slowly to the above
reaction mixture under stirring at room temperature over a period of 2 h. After reacting for 24 h, the solution was filtered to remove the resulting white precipitate. Excess 1,2-diaminoethane and 1,4-dioxane was removed by flushing air. Addition of water (50 mL) led to the precipitation of bis(N,N′-t-butyloxycarbonyl)-1,2-diaminoethane, which was removed via filtration. Then, NaCl was added to make the aqueous solution saturated and then the resulting turbid solution was extracted with dichloromethane a few times. Anhydrous sodium sulfate was added to dry the organic layer followed by filtration. Then, the solvent was removed by rotary evaporation and the residue was dried under vacuum, to give a colorless oil **C2-s1** in 84% (1.63 g) yield. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C) $\delta$ (ppm): 4.89 (s, 1H), 3.19 (m, 2H), 2.82 (m, 2H), 1.53 (s, 2H), 1.46 (s, 9H).

### 2.2.2. Synthesis of **C2-s2**

![Scheme S3. Synthetic route to C2-s2](image)

**C2-s1** (1.60 g, 10 mM) was dispersed in MeCN (50 mL) and K$_2$CO$_3$ (5.31 g) was added. The mixture was stirred for 30 min at room temperature, then methyl iodide (2.2 mL) was added into the mixture, which was heated under reflux for 20 h. After cooling to room temperature, the mixture was filtered to remove K$_2$CO$_3$ and the filtrate was concentrated by rotary evaporation to give an oily crude product. Diethyl ether was added to the liquid, the product **C2-s2** was obtained as a colorless solid (2.67 g, 81 %) under ultrasonic conditions after filtration. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C) $\delta$ (ppm): 5.97 (s, 1H), 3.82 (m, 2H), 3.74 (m, 2H), 3.48 (s, 9H), 1.42 (s, 9H).
2.2.3. Synthesis of C2

\[ \text{C2-s2} \overset{\text{HCl / CHCl}_3}{\underset{\text{r.t. / 24 h}}{\longrightarrow}} \text{C2} \quad [86\%] \]

**Scheme S4.** Synthetic route to C2

C2-s2 (3.30 g, 10 mM) was dissolved in trichloromethane (50 mL), and the solution was cooled to 0 °C using an ice-salt bath. Hydrochloric acid (1 mL) was added to the solution which was stirred for 30 min under 0 °C, and further 24 h at room temperature. The solvent was removed by rotary evaporation after which diethyl ether was dropped into the oil liquid, then the light claybank solid was filtrated out from the solvent to give the final product (C2) after dryness (1.19 g, 86 %). 1H NMR of C2 (300 MHz, D2O, 25 °C) δ (ppm): 3.82 – 3.66 (m, 2H), 3.65 – 3.48 (m, 2H), 3.25 (s, 9H). 13C NMR of C2 (75 MHz, D2O, 25 °C) δ (ppm): 63.32, 55.73, 35.01.

2.3. Preparation of MSN-OH

Generally, CTAB (1.0 g), 2 M NaOH (aq, 3.5 mL), and H2O (240 mL) were mixed and heated at 80 °C for more than 30 min to activate the template. After the reaction mixture turned into a clear surfactant solution, TEOS (5.0 mL) were added dropwise. A white precipitation was formed during 15 minutes of vigorous stirring. The reaction temperature was maintained at 80 °C for another 2 h. The resulting precipitates were isolated by a hot filtration, washed with a mass of H2O and MeOH, and dried under vacuum overnight to get as-synthesized materials. In order to remove the template to generate porous materials, acid extraction on the as-synthesized materials (1.0 g) was performed in MeOH (100 mL) with concentrated HCl (1.0 mL) at 60 °C for 6 h. Finally, **MSN-OH** product was filtered.
and washed with H$_2$O and MeOH, and then dried under vacuum overnight. MSN-OH was characterized by SEM, TEM, XRD, FT-IR, BET and BJH.

2.4. Preparation of MSN-COOH

The same method was used for the preparation of carboxyl-modified MSN (MSN-COOH). Just after the reaction mixture turned into a clear surfactant solution, TEOS (5.0 mL) and ICPTES (0.6 mL) were added sequentially and rapidly via injection. The MSN-COOH product was filtered and washed with H$_2$O and MeOH, and then dried under vacuum overnight. MSN-COOH was characterized by SEM, TEM, XRD, FT-IR, BET and BJH.

2.5. Preparation of MSN-C1

C$_1$ (0.21 g, 1 mmol) was dispersed in anhydrous DMF (10 mL) with MSN-OH (0.1 g), followed by the addition of dicyclohexylcarbodiimide (DCC, 2 mmol, 0.41 g) and 4-dimethylaminopyridine (DMAP, 1 mmol, 0.12 g). The mixture was stirred for 2 d at room temperature. Subsequently the solvent was removed through reduced pressure distillation, and the product was collected by centrifugation followed by thoroughly washing with H$_2$O to give a white solid after drying under vacuum. MSN-C1 was characterized by SEM, TEM, XRD, FT-IR, BET and BJH.

2.6. Preparation of MSN-C2

C$_2$ (0.17 g, 1 mmol) was dispersed in anhydrous DMF (10 mL) followed by the addition of MSN-COOH (0.1 g), DCC (2 mmol, 0.41 g) and DMAP (1 mmol, 0.12 g). The reaction mixture was stirred for 2 d at room temperature. Then, the solvent was removed under reduced pressure, and the product was collected by centrifugation followed by washing with H$_2$O to give a slight yellowish powder after drying under vacuum. MSN-C2 was characterized by SEM, TEM, XRD, FT-IR, BET and BJH.

Sulfonatocalix[4]arene (SC[4]A) was synthesized according to a modified literature reported procedure. The synthesis route was displayed in Schemes S5, S6 and S7.


![Scheme S5](image)

**Scheme S5.** Synthetic route to t-BuC[4]A

P-tert-butylphenol (40.83 g, 0.27 mol) was suspended into HCHO (24.80 mL, 37 %) in a 1000 mL three-neck round-bottomed flask under mechanical stirring. NaOH (0.50 g) was added to the reaction for 1.5 h at 110 °C, then the target compound was obtained as a brown solid after cooling to room temperature. Diphenyl ether (400 mL) was dispersed into the reaction glass with magnetic stirring under an atmosphere of N\textsubscript{2} and heated to 260 °C for 2 h. The reaction mixture was cooled to room temperature then was put into a 1000 mL beaker followed by the addition of 600 mL ethyl acetate under stirring to result in a white solid precipitate. The crude product was filtered and washed with water to give the final white solid powder after drying in vacuo (19.8 g, 52%). Further purification was done by washing with ethyl acetate (40 mL × 3), deionized water (40 mL × 3) to remove any excess impurity. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, 25 °C) δ (ppm): 10.34 (s, 4H), 7.05 (s, 8H), 4.26 (d, J = 14.4 Hz, 4H), 3.50 (d, J = 13.8 Hz, 4H), 1.21 (s, 36H).
2.7.2. Synthesis of C[4]A

Scheme S6. Synthetic route to C[4]A

\[
\text{t-BuC[4]A} \xrightarrow{\text{AlCl}_3 / \text{PhMe} / \text{HCl}} \text{C[4]A} \quad [73\%]
\]

t-BuC[4]A (13.3 g), anhydrous aluminium trichloride (14.0 g), phenyl hydroxide (9.0 g), was suspended in anhydrous toluene (125 mL) in a 250 mL round bottom flask at room temperature under N\textsubscript{2} atmosphere for 1 h. The reaction mixture was dispersed to hydrochloric acid (250 mL, 0.2 mM) under stirring. The organic layer was collected and further washed with distilled water (100 mL × 4), which was subsequently dried over anhydrous sodium sulfate. After filtration, the solvent was removed by rotary evaporation to give a white solid product. The target molecule was obtained in 73% yield (6.34 g) after drying under vacuum. 'H NMR (300 MHz, CDCl\textsubscript{3}, 25 °C) δ (ppm): 10.19 (s, 4H), 7.05 (d, \(J = 7.6\) Hz, 8H), 6.72 (t, \(J = 7.5\) Hz, 4H), 4.24 (s, 4H), 3.55 (s, 4H).


Scheme S7. Synthetic route to SC[4]A

A solution of C[4]A (5 g) in concentrated sulfuric acid (50 mL) in a round bottom flask (100 mL) was heated to 80 °C under nitrogen atmosphere for 4 h. Saturated
Sodium chloride (100 mL) was added dropwise into the mixed solvent and subsequently the reaction was further continued to reflux for 5 minutes. After cooling to room temperature, the crude product was collected and recrystallized from distilled water and the product was obtained as a white solid powder (9.1 g, 87 %). $^1$H NMR (300 MHz, D$_2$O, 25 °C) δ (ppm): 7.61 (s, 8H), 4.06 (s, 8H).
3. **Cargo Loading and Controlled Release Experiments**


**MSN-C1/MSN-C2** (0.1 g) was suspended, respectively, in a 0.5 mM solution of RhB in aqueous (12 mL), sonicated and stirred for 12 h at room temperature. An excess of the SC[4]A was added to the mixture and stirred for another 2 days. The RhB-loaded, SC[4]A-capped MSNs were separated with centrifugation and washed with H₂O, the red products were dried under high vacuum oven overnight.

3.2. Controlled release experiments

The RhB-loaded, SC[4]A-capped MSNs (2 mg) were suspended in PBS solution then putted into dialysis bag, which was immersed into the cuvette that was stirred gently with 3 mL PBS solution. Activation of the nanovalves was accomplished by adding enzyme (0.3 mg/mL of final concentration) or competitive binding agent. During this period of time, UV-vis absorption spectra of the solution were recorded at predetermined times. The amount of released RhB was quantified by plotting the absorption curve with RhB solutions of different concentrations as a function of time.

3.3. Spectroscopic setup for controlled release experiments.

*Figure S1.* Spectroscopic setup for controlled release experiments.
3.4. The influence of pH on enzyme-responsive release

![Graph showing enzyme-responsive release over time at different pH values.]

Figure S2. The release profiles from RhB-loaded, SC[4]A-capped MSN-C1 by adding esterase under pH = 7.4 or 8

3.5 The influence of SC[4]A concentration in the release solution

Before we active RhB-loaded, SC[4]A-capped MSNs, a limited release can still be observed due to equilibrium thermodynamics in host-guest complexation. Therefore, a series of SC[4]A solutions were prepared in order to study the relationship between pre-release and the concentration of SC[4]A in MSN solution (Table S1, S2). The results show that the pre-release was lowered / suppressed significantly with increased concentration of SC[4]A in the MSN solution.

<table>
<thead>
<tr>
<th>$C_{SC[4]A}$ [mg/mL]</th>
<th>Release at 2h [%]</th>
<th>The release at 4h [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.32</td>
<td>10.70</td>
</tr>
<tr>
<td>2</td>
<td>4.89</td>
<td>9.41</td>
</tr>
<tr>
<td>4</td>
<td>4.53</td>
<td>8.80</td>
</tr>
<tr>
<td>8</td>
<td>3.92</td>
<td>7.79</td>
</tr>
<tr>
<td>16</td>
<td>3.41</td>
<td>6.86</td>
</tr>
<tr>
<td>32</td>
<td>2.84</td>
<td>5.78</td>
</tr>
</tbody>
</table>

Note: the relative release based on competitive binding method.


<table>
<thead>
<tr>
<th>$C_{SC[4]A}$ [mg/mL]</th>
<th>Release at 2h [%]</th>
<th>The release at 4h [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.49</td>
<td>6.41</td>
</tr>
<tr>
<td>2</td>
<td>3.93</td>
<td>5.54</td>
</tr>
<tr>
<td>4</td>
<td>3.71</td>
<td>5.15</td>
</tr>
<tr>
<td>8</td>
<td>3.23</td>
<td>4.76</td>
</tr>
<tr>
<td>16</td>
<td>2.57</td>
<td>3.84</td>
</tr>
<tr>
<td>32</td>
<td>2.05</td>
<td>3.01</td>
</tr>
</tbody>
</table>

Note: the relative release based on competitive binding method.
4. Material Characterization

4.1. Fourier transform infrared (FT-IR) spectroscopy

**Figure S3.** FT-IR spectra (from bottom to top) of MSN-OH (black), MSN-C1 (red), RbB-loaded, SC[4]A-capped MSN-C1 (blue).

**Figure S4.** FT-IR spectra (from bottom to top) of MSN-COOH (black), MSN-C2 (red), RbB-loaded, SC[4]A-capped MSN-C2 (blue).
FT-IR spectroscopy has been used to monitor the change of functionalities on the surface of MSNs. In Figure S3, an absorption band at 1659 cm$^{-1}$ was found corresponding to the C=O stretching mode, indicating that the molecule of C1 unit has been successfully modified on to mesoporous silica surface. After loading and capping, the peaks appeared from 1625 cm$^{-1}$ to 1446 cm$^{-1}$ represent the characteristic absorption of aromatic ring and peaks at 2934 cm$^{-1}$ and 2859 cm$^{-1}$ correspond to the stretching band of C-H. Beside, the peak at 3329 cm$^{-1}$ was sharper than before which is corresponding to the hydroxyl group of SC[4]A. Accordingly, Figure S4 shows another portion, in this part the enhanced bands at 2969 cm$^{-1}$ and the fresh pick at 2834 cm$^{-1}$ were observed from the stretching vibrations, which indicated that the number of C-H was aggrandized (red line). Compared the red curve with the black curve, the peak at 1657 cm$^{-1}$ was shifted to a low wavenumber (WN) of 1635 cm$^{-1}$, proving the existence of C2. As the blue curve of Figure S3, the feature absorption of aromatic ring was demonstrated in Figure S4.

4.2. Small-angle X-ray diffraction (XRD) patterns

The small-angle XRD can be used to verify the microcrystalline of these kinds of samples. As can be seen, the intermediate MCM-41 nanoparticles (MSN-OH and MSN-COOH) show clear standard Bragg peaks of (100), (110), (200) and faint peak of (210), reflecting a highly ordered 2D hexagonal array. Although intensities of the diffraction peaks appear to be a little less after the material was modified with choline derivatives, they still maintain characteristic reflections, which indicated an ordered 2D hexagonal structure. However, the diffraction peaks of MSNs were disappeared after loading with RhB and capped with SC[4]A, except that the (100) peak was still visible. Beyond that, the distance between adjacent
pores and pore diameter of these MSNs can be evaluated using small-angle XRD patterns.

According to the Bragg equation, \(2d\sin\theta = n\lambda\) (\(n = 1; \lambda = 1.392218\))

Interplanar spacing: \(d = n\lambda/2\sin\theta\)

100 interplanar spacing: \(d_{100} = \lambda/2\sin\theta\)

Pore distance: \(a = (2/1.732) d_{100} = 1.155\lambda/(2\sin\theta)\)

**Table S3.** Properties of the NPs calculated from XRD

<table>
<thead>
<tr>
<th>Samples</th>
<th>Interplanar Spacing [ nm ]</th>
<th>Pore Distance [ nm ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSN-OH</td>
<td>3.91</td>
<td>4.52</td>
</tr>
<tr>
<td>MSN-C1</td>
<td>3.90</td>
<td>4.50</td>
</tr>
<tr>
<td>MSN-COOH</td>
<td>3.91</td>
<td>4.25</td>
</tr>
<tr>
<td>MSN-C2</td>
<td>3.89</td>
<td>4.49</td>
</tr>
</tbody>
</table>

**Figure S5.** Small-anger XRD Patterns of MSN-COOH (black), MSN-C2 (red), RhB-loaded, SC[4]A-capped MSN-C2 (blue).
4.3. N₂ adsorption and desorption

*Figure S6.* BET of MSN-COOH, MSN-C2 and RhB-loaded, SC[4]A-capped MSN-C2
Figure S7. BJH of MSN-OH

Figure S8. BJH of MSN-C1
**Figure S9.** BJH of MSN-COOH

**Figure S10.** BJH of MSN-C2
Table S4. Properties of the MSNs by BET

<table>
<thead>
<tr>
<th>Samples</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt; [m&lt;sup&gt;2&lt;/sup&gt;/g]</th>
<th>V&lt;sub&gt;p&lt;/sub&gt; [mL/g]</th>
<th>D&lt;sub&gt;1&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; [nm]</th>
<th>D&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; [nm]</th>
<th>D&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSN-OH</td>
<td>1003</td>
<td>0.83</td>
<td>2.9</td>
<td>3.0</td>
<td>3.3</td>
</tr>
<tr>
<td>MSN-C1</td>
<td>565</td>
<td>0.45</td>
<td>2.8</td>
<td>2.5</td>
<td>3.2</td>
</tr>
<tr>
<td>RhB-loaded, SC[4]A-capped MSN-C1</td>
<td>327</td>
<td>0.36</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>MSN-COOH</td>
<td>777</td>
<td>0.53</td>
<td>2.5</td>
<td>2.6</td>
<td>2.7</td>
</tr>
<tr>
<td>MSN-C2</td>
<td>687</td>
<td>0.43</td>
<td>2.4</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>RhB-loaded, SC[4]A-capped MSN-C2</td>
<td>402</td>
<td>0.37</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Note: Three methods to obtain the particle diameters: <sup>a</sup> BJH method; <sup>b</sup> geometrical considerations of an infinite hexagonal array of cylindrical pores, expressed by averaged pore diameter (APD), APD = 1.213d<sub>100</sub>(ρV<sub>p</sub>/(1 + ρV<sub>p</sub>))<sup>1/2</sup> and <sup>c</sup> the model of simple cylindrical pores using the BET surface area, D<sub>p</sub> = 4V<sub>p</sub>/S<sub>BET</sub>.

4.4 Elemental analysis and surface coverage of functionalities

Table S5. The element contents of SC[4]A-capped MSN-C1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Element Content (Average)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C [%] H [%] N [%] S [%]</td>
</tr>
<tr>
<td>SC[4]A-Capped MSN-C1</td>
<td>20.08 3.03 1.23 5.33</td>
</tr>
</tbody>
</table>

The coverage rate of SC[4]A on the stalk components installed the outer surface of MSNs is calculated to be 48%.


<table>
<thead>
<tr>
<th>Samples</th>
<th>Element Content (Average)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C [%] H [%] N [%] S [%]</td>
</tr>
</tbody>
</table>

The coverage rate of SC[4]A on the stalk components installed the outer surface of MSNs is calculated to be 72%.
5. References


