Supporting Information

Controllable Synthesis of Hollow Mesoporous Silica

Nanoparticles Templated Kinetic Self-Assembly of Gemini Surfactant

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1. Synthesis of mesoporous silica nanoparticles (MSNs)

General Methods. Materials obtained commercially were used without further purification. N,N,N',N'-tetramethylethylenediamine (TMEDA) (AR, SCRC), bromotetradecane (AR, Alatin), bromohexadecane (AR, Alatin), bromodecane (AR, Alatin), acetonitrile (AR, SCRC), chloroform (AR), acetone (AR, SCRC), sodium hydroxide (AR, SCRC), tetraethyl orthosilicate (TEOS, 99%, Alfar Aesar). NMR spectra were measured on a Bruker AV400 spectrometer. Field-emission scanning electron microscopy (FE-SEM) images were obtained on a FEI Sirion 200 instrument. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G220 instrument. X-Ray powder diffraction (XRD) patterns were recorded on X'Pert PRO X-ray diffractometer with Cu-K radiation with a wavelength of 0.1542 nm. The nitrogen adsorption experiments were performed at 77 K on a Micromeritics ASAP 2020 instrument. Samples were degassed at 573 K for 4 h prior to the measurements.
Synthesis of gemini surfactants $\text{C}_{14-2-14}$ and $\text{C}_{16-2-16}$

The TMEDA (0.1 mol) and 1-bromotetradecane or 1-Bromohexadecane (0.4 mol) were refluxed in MeCN for 2 days. After evaporation, the residue was re-crystallized from CHCl$_3$/acetone yielding the $\text{C}_{14-2-14}$ or $\text{C}_{16-2-16}$.

$\text{C}_{14-2-14}$: Yield, 80.1%. $^1\text{H NMR (CDCl}_3$, 400MHz): $\delta$, 0.88 (t, 6H, $J$=6.8Hz), 1.26-1.38(m, 44H), 1.82(s, 4H), 3.52(s, 12H), 3.71(t, 4H, $J$=8.0Hz), 4.77(s, 4H).

$\text{C}_{16-2-16}$: Yield, 69.6%. $^1\text{H NMR (CDCl}_3$, 400MHz): $\delta$, 0.88(t, 6H, $J$=7.2Hz), 1.26-1.37(m, 52H), 1.81(s, 4H), 3.49(s, 12H), 3.69(t, 4H, $J$=7.6Hz), 4.60(s, 4H).

Synthesis of gemini surfactants $\text{C}_{14-2-10}$

The TMEDA (0.1 mol) and 1-bromotetradecane (0.08 mol) reacted in MeCN (125 ml) at 40 °C for 3 days. After evaporation and crystallization from Et$_2$O, the corresponding pure $\text{C}_{14-2}$ was isolated in 42.0% yield. $\text{C}_{14-2}$ (0.1mol) and the 1-bromodecane (4 equiv.) were refluxed in EtOAc (125 ml) for 2 days, and purified by re-crystallization from CHCl$_3$/acetone yielding $\text{C}_{14-2-6}$ in 52.3%.

$\text{C}_{14-2-10}$: $^1\text{H NMR (CDCl}_3$, 400MHz): $\delta$, 0.88(t, 6H, $J$=7.2Hz), 1.26-1.38(m, 36H), 1.82(s, 4H), 3.52(s, 12H), 3.72(t, 4H, $J$=7.6Hz), 4.78(s, 4H).

Synthesis of mesoporous silica nanoparticles (MSNs) templated with $\text{C}_{14-2-14}$

To solution of $\text{C}_{14-2-14}$ (0.218g) in distilled water (240ml), sodium hydrate solution (2M, 1.75ml) were added at 80 °C and stirred. After a period of pre-assembly time ($t$ = 10, 30, 60 and 120 min), TEOS (2.5ml) was dropped slowly into the mixture solution and then kept stirring for 2h. The MSNs were obtained by filtration. Finally, the surfactant template ($\text{C}_{14-2-14}$) was removed by refluxing in a mixture of methanol and hydrochloric acid.

Synthesis of HMSNs templated with $\text{C}_{14-2-10}$

Following the similar procedure of MSNs templated with $\text{C}_{14-2-14}$, used the template of $\text{C}_{14-2-10}$, HMSNs were obtained.

Synthesis of HMSNs templated with $\text{C}_{16-2-16}$

Following the similar procedure of MSNs templated with $\text{C}_{14-2-14}$, used the template of $\text{C}_{16-2-16}$ with a longer pre-assembly time of $t$ = 180 min, HMSNs were obtained.
2. Characterization of MSNs templated with C_{14-2-14}

2.1 TEM images of MSNs templated with C_{14-2-14}

Fig. S1. TEM images of MSNs templated with C_{14-2-14} from different pre-assembly time of \( t = 10 \text{ min} \) (a), 30 min (b), 60 min (c) and 120 min (d).

2.2 SEM images of MSNs templated with C_{14-2-14}

Fig. S2. SEM images of MSNs templated with C_{14-2-14} from different pre-assembly time of \( t = 10 \text{ min} \) (a), 30 min (b), 60 min (c) and 120 min (d). The SEM image of broken HMSNs of \( t = 120 \text{ min} \) (e). Scale bar: 500 nm (a), 1 \( \mu \text{m} \) (b and c), 2\( \mu \text{m} \) (d) and 200 nm (e).
2.3 XRD spectra of MSNs templated with C$_{14-2-14}$

Fig. S3. XRD spectra of MSNs templated with C$_{14-2-14}$.

2.3 Nitrogen sorption isotherms and pore size distribution of MSNs templated with C$_{14-2-14}$

Fig. S4. Nitrogen adsorption isotherms (left) and Barett-Joyner-Halenda (BJH) pore size distribution (right) of HMSNs templated with C$_{14-2-14}$ from different pre-assembly time of $t = 10$ min (a), 30 min (b), 60 min (c) and 120 min (d).
3. Characterization of HMSNs templated with C\textsubscript{14-2-10}

3.1 SEM and TEM images of HMSNs templated with C\textsubscript{14-2-10}

Fig. S5. SEM (a) and TEM (b) images of HMSNs templated with C\textsubscript{14-2-10}. Scale bar: 500 nm (a), 50nm(b).

3.2 XRD spectrum of HMSNs templated with C\textsubscript{14-2-10}

Fig. S6. XRD spectrum of HMSNs templated with C\textsubscript{14-2-10}
3.3 Nitrogen sorption isotherms and pore size distribution of HMSNs templated with C_{14-2-10}

![Graph and figure description](image1)

Fig. S7. Nitrogen adsorption isotherm (a) and BJH pore size distribution (b) of HMSNs templated with C_{14-2-10}.

4. Characterization of HMSNs templated with C_{16-2-16}

4.1 SEM and TEM images of HMSNs templated with C_{16-2-16}

![SEM and TEM images](image2)

Fig. S8. SEM (a) and TEM (b) images of HMSNs templated with C_{16-2-16}. Scale bar: 500 nm (a), 100nm (b).
4.2 XRD spectrum of HMSNs templated with C\textsubscript{16-2-16}

![XRD spectrum of HMSNs templated with C\textsubscript{16-2-16}]

Fig. S9. XRD spectrum of HMSNs templated with C\textsubscript{16-2-16}

4.3 Nitrogen sorption isotherms and pore size distribution of HMSNs templated with C\textsubscript{16-2-16}

![Nitrogen adsorption isotherm (a) and BJH pore size distribution (b) of HMSNs templated with C\textsubscript{16-2-16}]

Fig. S10. Nitrogen adsorption isotherm (a) and BJH pore size distribution (b) of HMSNs templated with C\textsubscript{16-2-16}.

Reference