

## Electronic Supplementary Information (ESI)

*for the article untitled "Spray-dried mesoporous silica microspheres with adjustable textures and pore surfaces homogenously covered by accessible thiol functions"*

**Table SA.** Morphological properties from SEM.

**Table SB.** Textural properties from XRD.

**Table SC.** S/Si and N/Si ratios.

**Table SD.**  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts and assignments.

**Fig. SA.** Solid state NMR  $^1\text{H}$ - $^1\text{H}$  BaBa experiments.

**Fig. SB.** XRD diagrams obtained when varying  $h$  from 5 to 10 (samples **D** to **I**).

**Fig. SC.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  solid state NMR spectra of the as-synthesised thiol-functionalised mesoporous microspheres.

**Fig. SD.** SEM and X-ray cartography analysis of  $\text{Ag}^+$  containing sample **E-SE** +  $\text{Ag}^+$ .

**Fig. SE.**  $^{14}\text{N}$  solid state NMR spectra.

**Table SA:** morphological properties from SEM.

Sample	Shape	$D_{AV}^a / \mu\text{m}$	$\sigma^a / \mu\text{m}$	$D_{GM}^b / \mu\text{m}$	$S_G^b / \mu\text{m}$	Elongation
A	aggl	2.51	1.31	1.76 ± 0.17	0.58 ± 0.09	1.037
B	slightly agglom.	2.19	1.42	1.45 ± 0.04	0.19 ± 0.03	1.032
C	slightly agglom.	2.49	1.35	1.51 ± 0.20	0.77 ± 0.13	1.054
D	slightly agglom.	2.17	0.95	1.61 ± 0.10	0.51 ± 0.06	1.039
E	spheres	2.23	1.53	1.21 ± 0.08	0.60 ± 0.05	1.035
F	spheres	2.03	1.3	1.14 ± 0.06	0.59 ± 0.04	1.044
G	spheres <sup>c</sup>	1.87	1.14	0.89 ± 0.14	0.80 ± 0.13	1.03
H	spheres <sup>c</sup>	1.92	2.07	1.00 ± 0.08	0.64 ± 0.07	1.053
I	spheres <sup>c</sup>	2.18	1.53	1.00 ± 0.09	0.70 ± 0.07	1.037
J	gel	-	-	-	-	-
K	slightly agglom.	2.1	1.51	1.06 ± 0.11	0.59 ± 0.09	1.058

a: average diameters  $D_{AV}$  and standard deviations  $\sigma$  obtained from the experimental size distribution.

b: values obtained by modelling the experimental size distribution (Fig. 2). The uncertainties given come from the fitting procedure.

c: particles solidified in the course of fragmentation like in Fig. 2c are also observed for these samples.

**Table SB:** textural properties from XRD.

Sample	$d_{Broad}^a / \text{\AA}$	$d_{100}^b / \text{\AA}$	$a_{HEX}^c / \text{\AA}$	% Broad <sup>d</sup>	% SP <sup>e</sup>	FWHM (100) peak
<b>A</b>	35.4	33.5	39.1	49.0	8.7	0.225
<b>B</b>	37.0	35.0	40.8	54.3	6.1	0.206
<b>C</b>	36.0	34.2	40.2	58.4	7.5	0.248
<b>D</b>	36.4	34.4	40.2	54.0	7.6	0.229
<b>E</b>	37.5	35.1	40.8	49.6	6.3	0.226
<b>F</b>	38.2	35.7	41.5	47.8	7.5	0.239
<b>G</b>	38.0	35.5	41.5	48.7	6.4	0.241
<b>H</b>	37.8	35.6	41.6	50.4	6.1	0.254
<b>I</b>	38.0	35.5	41.6	50.7	6.4	0.264
<b>J</b>	35.8	34.3	40.0	67.8	3.8	0.172
<b>K</b>	35.2	34.7	40.4	87.8	3.4	0.258

a: characteristic distances relative to the broad “scattering” peak at low  $2\theta$  used for modelling.

b: characteristic distances relative to the thin “diffraction” peak at low  $2\theta$  used for modelling.  
It corresponds to the inter-reticular distance of (100) planes.

c: average values of  $a_{HEX}$  obtained from (100), (110) and (200) diffraction peaks.

d: percentage of the area of the broad “scattering” peak at low  $2\theta$  used for modelling.

e: percentage area of the (110), (200) and (210) diffraction peaks of the  $p6mm$  phase.

**Table SC:** S/Si and N/Si ratios.

Sample	$f(\text{S/Si init.})$	S/Si elem. <sup>a</sup>	S/Si ( <sup>1</sup> H) <sup>b</sup>	S/Si ( <sup>29</sup> Si) <sup>b</sup>	S/Si( <sup>13</sup> C) <sup>b</sup>	N/Si init.	N/Si elem. <sup>a</sup>
<b>A</b>	0.102		0.064			0.160	
<b>B</b>	0.103		0.078			0.160	
<b>C</b>	0.104		0.074			0.160	
<b>D</b>	0.103	0.099	0.084	0.088		0.160	0.175
<b>E</b>	0.102	0.113	0.085	0.099	0.089	0.159	0.152
<b>F</b>	0.100	0.083	0.064			0.160	0.167
<b>G</b>	0.104	0.103	0.080			0.159	0.169
<b>H</b>	0.104	0.102	0.081			0.160	0.162
<b>I</b>	0.104	0.100	0.093			0.159	0.159
<b>J</b>	0.200	0.190	0.142	0.206		0.160	0.169
<b>K</b>	0.195	0.170		0.167		0.160	0.184

a: from elemental analysis.

b: from <sup>1</sup>H, <sup>29</sup>Si or <sup>13</sup>C solid state NMR.

**Table SD:**  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts and assignments.

$\text{CTA}^+$  is numbered from the head group (C'1) to the tail (C1 to C16).

Chemical group	$\delta(^1\text{H}) / \text{ppm}$	$\delta(^{13}\text{C}) / \text{ppm}$
<i>CTA<sup>+</sup></i>		
C1	3.7 - 3.8	67 - 68
C'1	3.4 - 3.5	54.1
C2	1.4 - 1.5	23 - 24
C3	1.3 - 1.4	26 - 27
C4 to C13	1.4 - 1.5	30.4 - 30.6
C14	1.4 - 1.5	32.7
C15	1.4 - 1.5	23.3 - 23.4
C16	0.9 - 1.0	14.6 - 14.8
<i>Si-(CH<sub>2</sub>)<sub>3</sub>-SH</i>		
Si-CH <sub>2</sub> -	0.8 - 1.0	12.5 - 12.9
C-CH <sub>2</sub> -C	1.7 - 1.9	27 - 28
CH <sub>2</sub> -S	2.6 - 2.8	27 - 28
C-SH	1.3 - 1.5	-
<i>Si-OEt</i>		
Si-O-CH <sub>2</sub>	3.8 - 4.0	60.4
C-CH <sub>3</sub>	1.3 - 1.5	18.6
<i>Si-O<sup>i</sup>Pr</i>		
Si-O-CH	4.3 - 4.5	66.2
C-CH <sub>3</sub>	1.4 - 1.5	25 - 26
<i>Hydroxy</i>		
Si-OH ... H <sub>2</sub> O	~6	-

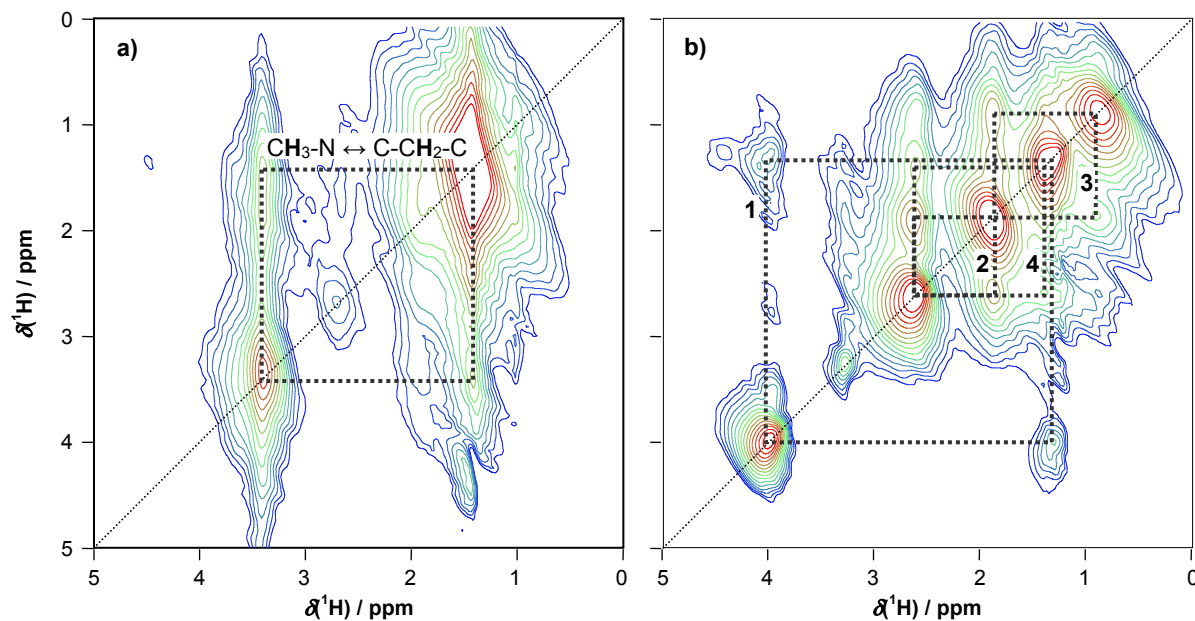
**Fig. SA:** Solid state NMR  $^1\text{H}$ - $^1\text{H}$  BaBa experiments.

The original DQ-SQ spectra have been sheared in order to present the 2D correlations as symmetrical SQ-SQ spectra (the double-quantum vertical dimension is replaced by a “pseudo-single quantum” dimension). In addition, the spectra are zoomed to the 0-5 ppm interval that contains most of the peaks (except the wide peaks of the OH groups).

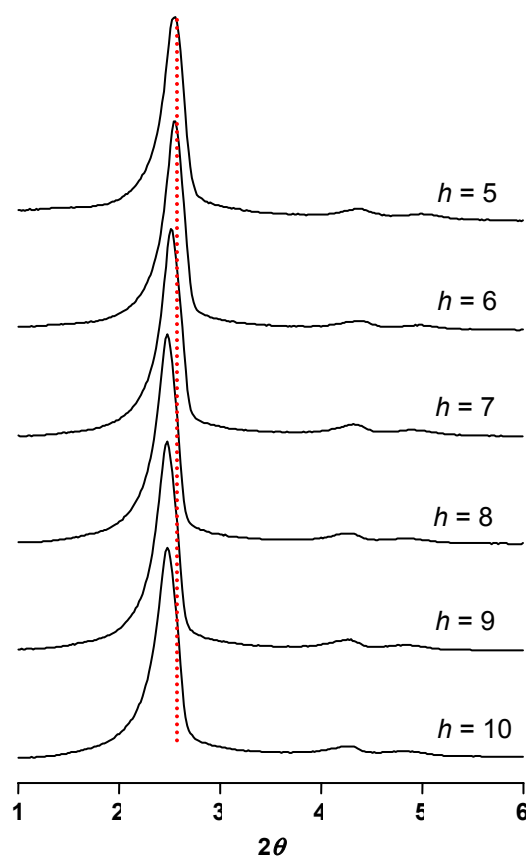
a) Sample E.

b) Sample E-TT-SE. The numbered correlations are:

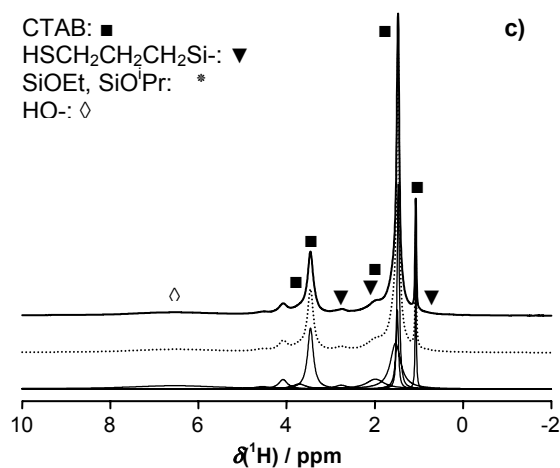
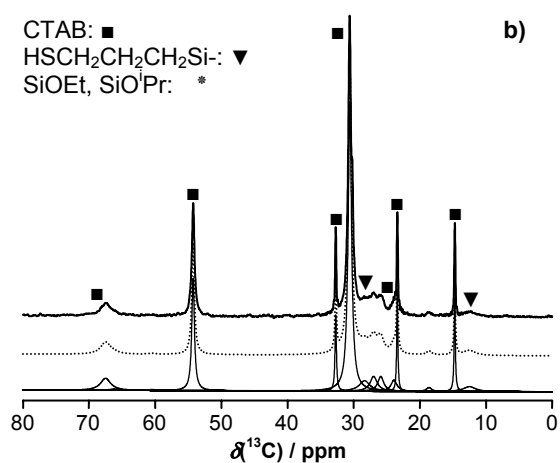
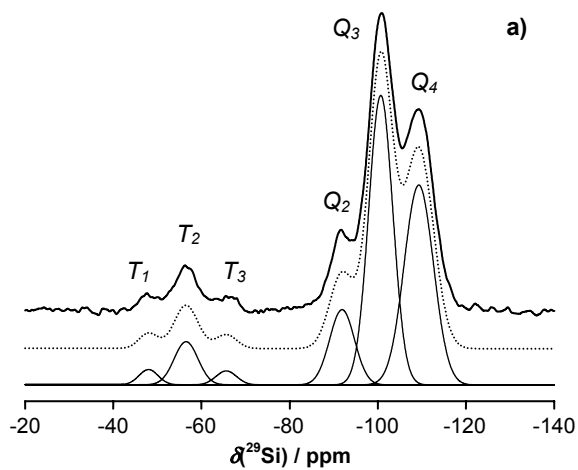
- 1)  $\text{SiOCH}_2\text{CH}_3 \leftrightarrow \text{SiOCH}_2\text{CH}_3$  ;
- 2)  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH} \leftrightarrow \text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH}$  ;
- 3)  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH} \leftrightarrow \text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH}$  ;
- 4)  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH} \leftrightarrow \text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH}$  ;



**Fig. SB:** XRD diagrams obtained when varying  $h$  from 5 to 10 (samples **D** to **I**).

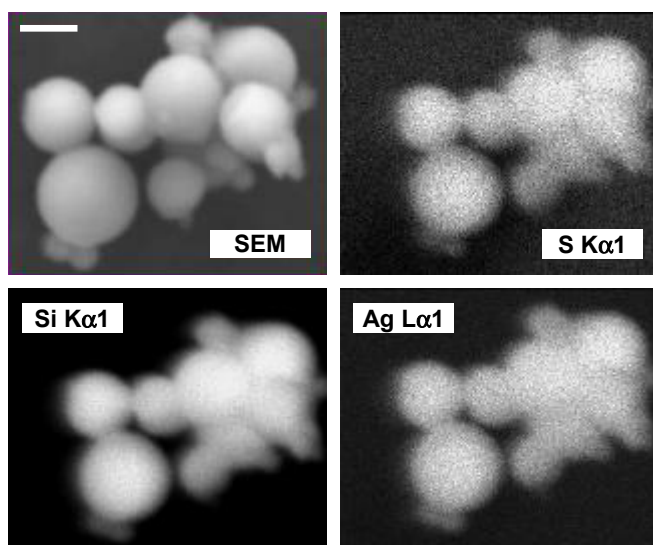


**Fig. S3.** Solid state NMR single pulse spectra of the as-synthesised thiol-functionalised mesoporous microspheres (here sample **E**) with their modelling and assignment. (a)  $^{29}\text{Si}$  (3058 scans). (b)  $^{13}\text{C}$  (9546 scans). (c)  $^1\text{H}$  (16 scans).





**Fig. SD.** SEM and X-ray cartography analysis of  $\text{Ag}^+$  containing sample **E-SE +  $\text{Ag}^+$** . The scale bar represents 2  $\mu\text{m}$ .



**Fig. SE.**  $^{14}\text{N}$  solid state NMR spectra of: (a) crude crystalline CTAB, (b) treated sample **E-NH3- $\gamma$** , (c) as-synthesised sample **E**. Acquisition conditions were the same for the three samples except the number of scans. We used 4096, 136980 and 163840 scans in 12a, 12b and 12c respectively. The vertical scales have been normalised in order to account for these differences. For spectra 12b and 12c, the scales are magnified by a factor 10.

