

*Supporting Information*

# Influence of Synthesis Conditions on Properties of Ethane-Bridged Periodic Mesoporous Organosilica Materials as Revealed by Spin-Probe EPR

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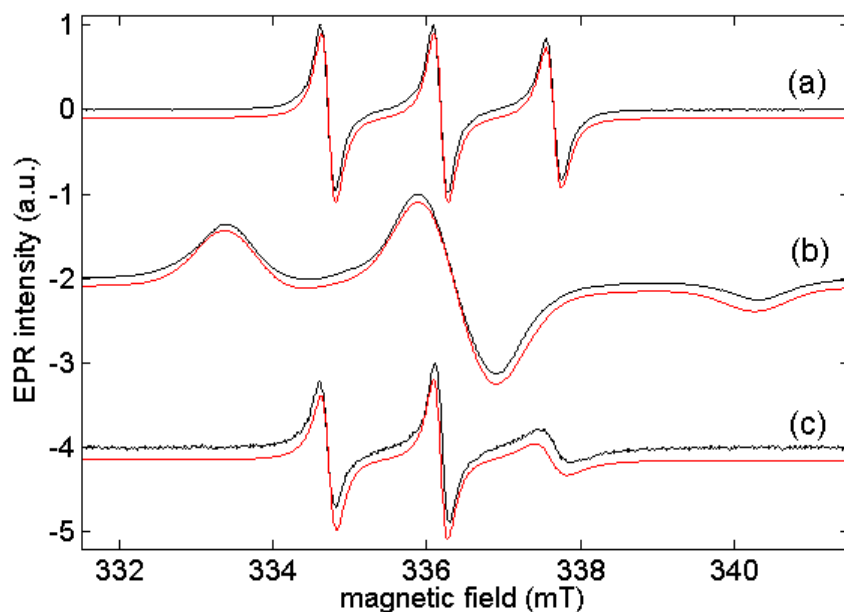
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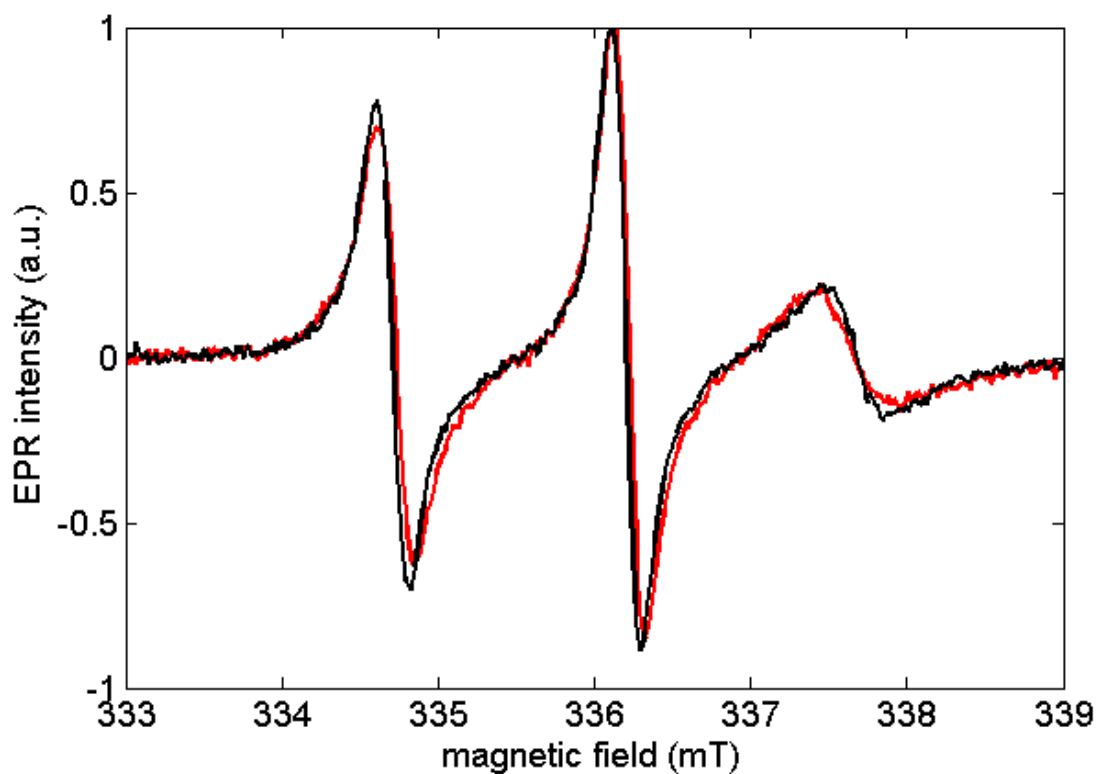
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S1. Simulations of spectra in Figure 1.



**Figure S1.** Experimental (black) and simulated (red) X-band EPR spectra of 5-DSA in H<sub>2</sub>O:EtOH (70:1) recorded at room temperature (a), 5-DSA in CH<sub>2</sub>Cl<sub>2</sub> with a drop of toluene recorded at 50 K (b), and of a 5-DSA:C<sub>16</sub>TMACl:H<sub>2</sub>O:EtOH mixture (1.12x10<sup>-3</sup>:0.12:231:3.3) recorded at room temperature (c). The simulations were performed assuming  $g_x=2.0086$ ,  $g_y=2.0068$ ,  $g_z=2.0028$ ,  $A_x=13.8$  MHz,  $A_y=13.8$  MHz, and  $A_z=96.0$  MHz, and (a)  $\tau_C = 0.1$  ns, (b) the solid state, (c)  $\tau_C=1.2$  ns.

## S2. Effect of addition of NaOH to mixture



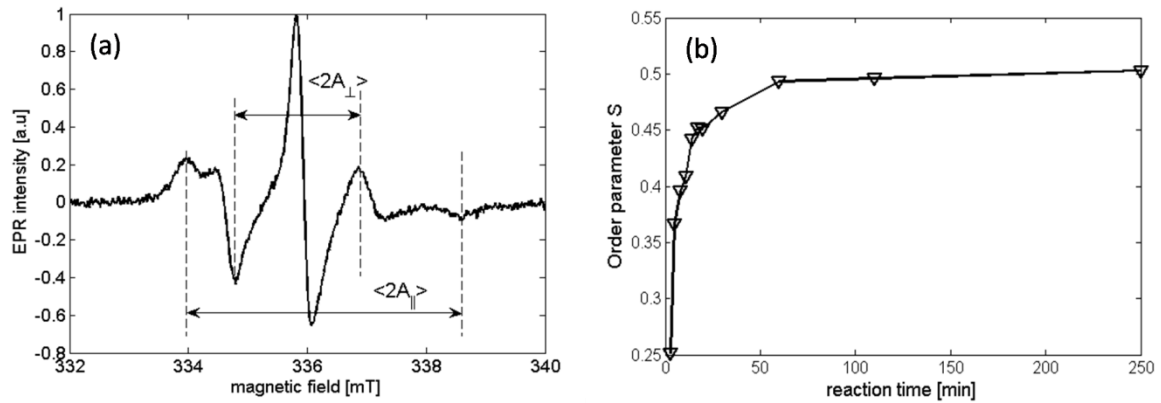
**Figure S2.** Comparison of room-temperature CW-EPR spectra of a 5-DSA:C<sub>16</sub>TMACl:H<sub>2</sub>O mixture ( $1.12 \times 10^{-3}$ :0.12:231) (black) and a 5-DSA:C<sub>16</sub>TMACl:NaOH:H<sub>2</sub>O:EtOH mixture ( $1.12 \times 10^{-3}$ :0.12:1.0:231:3.3) (red). We notice a broadening of the lines in the red spectrum typical for a slowing down of the spin-label motion.

### S3. Evaluation of EPR spectra during PMOs synthesis

While the EPR spectra of the label in the solvent could still be satisfactorily simulated using a simple isotropic motion model, this is no longer the case for the spectra recorded during the PMO synthesis (Figure 2, main text). In fact, as also described for the MCM-41 case<sup>1</sup>, the motion needs to be described using a model assuming microscopic order and macroscopic disorder (MOMD)<sup>1</sup>. However, it has been often reported that EPR experiments at different microwave frequencies are needed in order to be able to determine the motional parameters of the spin probes correctly.<sup>3</sup> Nevertheless, EPR experiments performed at a single microwave frequency can be used to evaluate in a qualitative manner the motional behaviour. It has been shown that the order parameter  $S$  of the spin probe motion can be directly derived from the spectrum<sup>4</sup> in the following way:

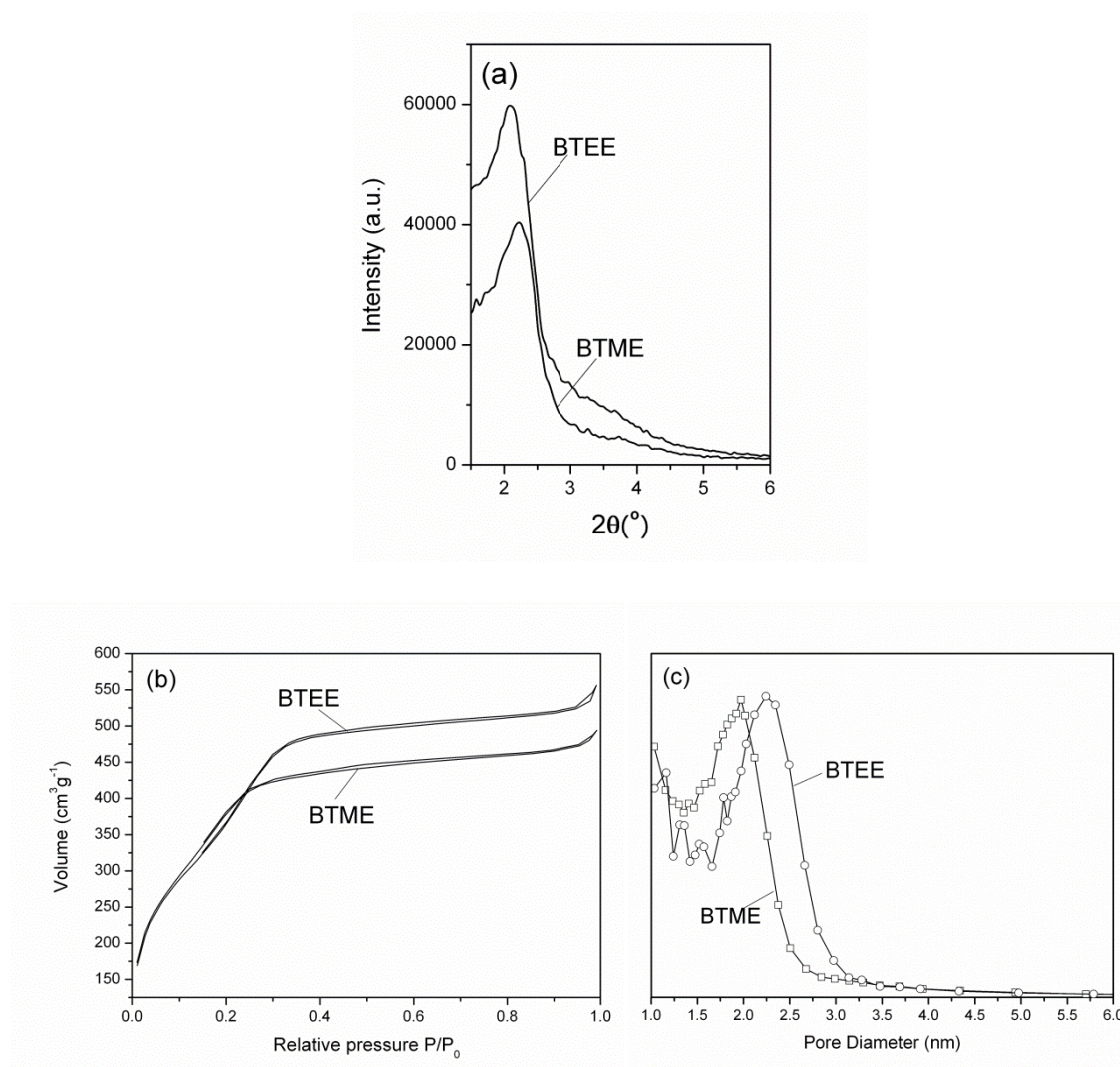
$$S = 1.66 \frac{\langle A_{||} \rangle - [\langle A_{\perp} \rangle + C]}{\langle A_{||} \rangle + 2[\langle A_{\perp} \rangle + C]} \quad (1)$$

With  $C = 4.06 - 0.053(\langle A_{||} \rangle - \langle A_{\perp} \rangle)$  and  $\langle A_{||} \rangle$  and  $\langle A_{\perp} \rangle$  (in MHz) defined in Figure S3.



**Figure S3.** (a) Definition of the parameters  $\langle A_{||} \rangle$  and  $\langle A_{\perp} \rangle$ , and (b) the temporal evolution of the order parameter  $S$  calculated from the experimental spectra using equation (1).

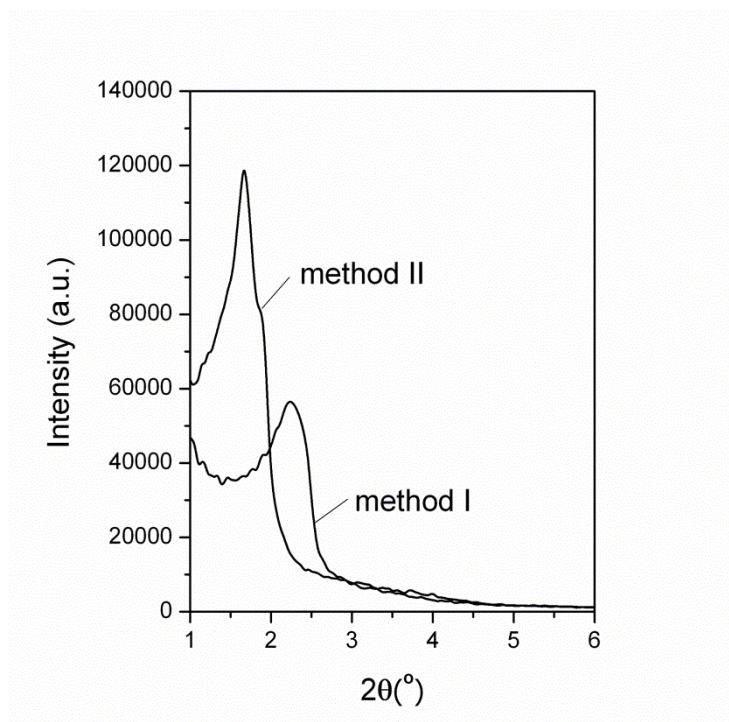
#### S4. N<sub>2</sub> sorption experiments of ethane-bridged PMOs with BTME or BTEE precursors



**Figure S4.** (a) Comparison between the XRD patterns of the as-synthesized ethane-bridged PMO materials synthesized with BTME or BTEE, (b) N<sub>2</sub>-sorption isotherms of the template-free PMO materials synthesized with BTME and BTEE, and (c) the corresponding pore-diameter distribution.

The peak positions in the small-angle XRD of the ethane-bridged PMO materials synthesized with BTME and BTEE are detected around  $2\theta=2.20^{\circ}$  and  $2\theta=2.08^{\circ}$ , respectively. The small shift of the main diffraction peak towards lower  $2\theta$  suggests an enlargement of the pore size. This is in agreement with the N<sub>2</sub>-sorption experiments, which show clearly a larger pore size when BTEE is used instead of BTME.

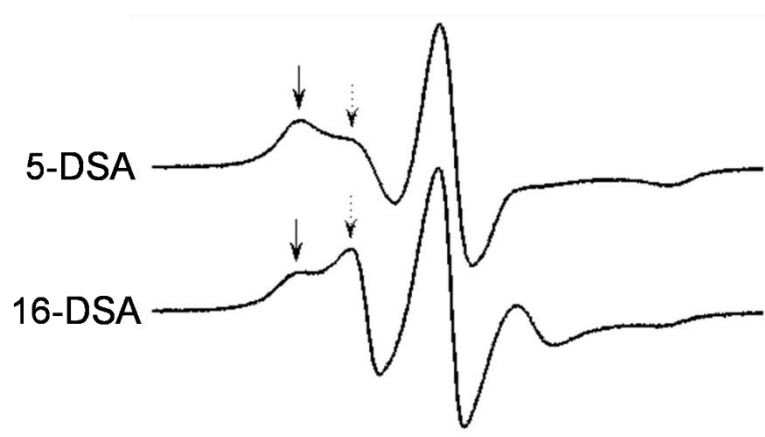
S5. XRD patterns of ethane-bridged PMOs synthesized with method I and method II



**Figure S5.** The XRD patterns of the as-synthesized ethane-bridged PMO materials synthesized with method I and method II, respectively.

The XRD patterns confirm the data obtained using low temperature N<sub>2</sub>-adsorption–desorption isotherms (Figure 4, main text).

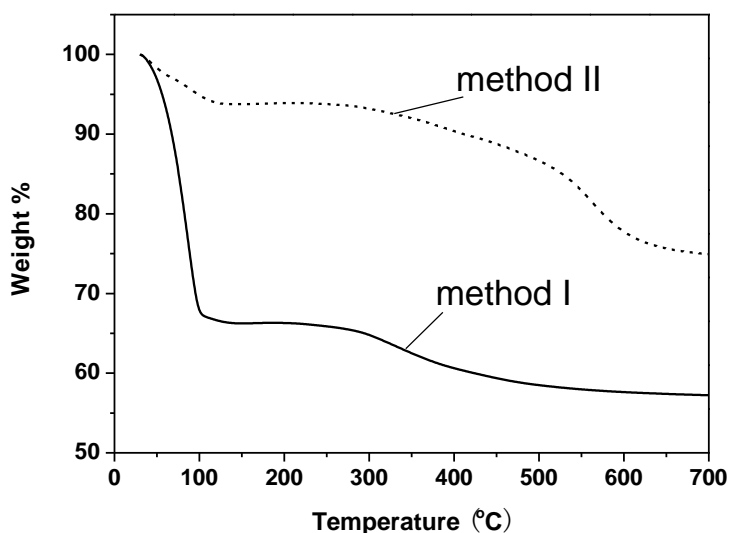
## S6. Motional behaviour of spin labels adsorbed to PMOs



**Figure S6.** Room-temperature EPR spectra of 5-DSA and 16-DSA spin probes adsorbed on ethane-bridged PMOs synthesized using method II. The spectra are shown such that they reflect the real relative intensity of the spectra. The solid arrow marks the slow-motion part and the dashed arrow marks the fast motion part.

From the EPR spectra of 5-DSA and 16-DSA adsorbed on PMO(method II), it can be observed that the signal intensity of the two spin labels are approximately the same, which means that the same amount of 5-DSA and 16-DSA has been adsorbed onto the PMO materials, respectively. However, we can also notice that the intensity of slow-motion part of 5-DSA is going up and the intensity of the fast motion part of 5-DSA is going down, compared with 16-DSA, which means that 5-DSA adsorbed on PMO(method II) have a lower mobility than that of 16-DSA. The different motional behaviour of 5-DSA and 16-DSA can be explained by the different location of the nitroxyl group within the molecule.

## S6. TGA results for ethane-bridged PMOs



**Figure S7.** Thermogravimetric analysis of the template-free PMO materials synthesized using methods I and II

A thermogravimetric analysis was performed under air flow for the template-free PMO materials synthesized using method I and II. The observed weight loss below 130 °C was due to the thermodesorption of physisorbed water or ethanol, and the weight loss between 300-700 °C was assigned to the decomposition of the ethane moieties within the framework. No obvious weight loss due to the surfactant was observed, indicating a negligible amount of residual surfactants exist after solvent extraction. However, it could be noted that the weight loss (below 130 °C) of PMOs synthesized with method I (~33%) was much higher than that of the PMOs synthesized with method II (~7%). It means that the PMO(method I) materials contain much more surface water than those of PMOs(method II), which is in agreement with the FT-IR spectra.



#### ■ References to this suppl. information

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Ref. 4: Vartuli, J. C.; Schmitt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Beck, J. S.; Schlenker, J. L.; Olson, D. H.; Shepard, E. W. Effect of Surfactant Silica Molar Ratios on the Formation of Mesoporous Molecular-Sieves-Inorganic Mimicry of Surfactant Liquid-Crystal Phases and Mechanistic Implications. *Chem. Mater.* **1994**, *6*, 2317-2326.