

## Electronic Supplementary Information, ESI

Water effect on the spin-transition behavior of Fe(II) 1,2,4-triazole 1D chains  
embedded in pores of MCM-41

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### Materials

All the chemicals were used as received without further purification.

Iron(II) tetrafluoroborate hexahydrate ( $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ , 97%, Aldrich).

1,2,4-4*H*-triazole(99%, Alfa Aesar).

Mesostructured silica (MCM-41 type, Aldrich).

Methanol, Ethanol (99.9 %, Merck).

Iron standard for AAS (1000 mg/L, Aldrich)

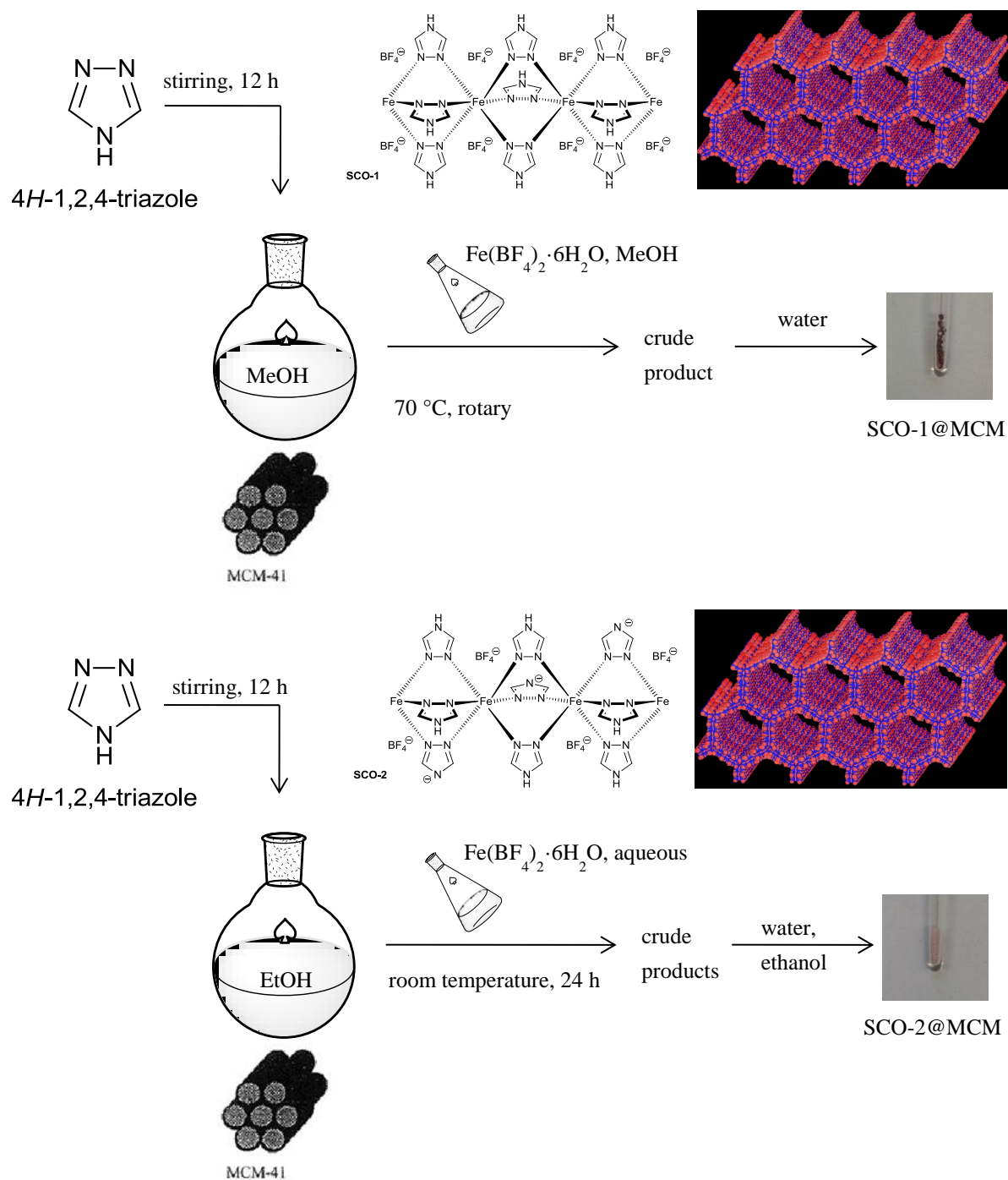
### Synthesis of SCO@MCM materials

**SCO-1@MCM** was prepared by follows: 1,2,4-4*H*-triazole (208 mg, 3.0 mmol) and MCM-41 (100 mg) were stirred in 100 mL of methanol for 12 h. A solution of 337.5 mg (1.0 mmol) of  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  in 60 mL of methanol was added to the slurry and the solvent was removed rapidly at 70 °C using a rotary evaporator. The formed product was collected and thoroughly washed with water 3 times and 10 mL each. The product was dried in an evacuated desiccator over silica gel. Yield ~253 mg of a red-pink powder (Fig. S1).

The **pure SCO-1** was synthesized according to ref. 1. Calcd for  $\text{C}_6\text{H}_9\text{N}_3\text{B}_2\text{F}_8\text{Fe} \cdot \text{H}_2\text{O}$  (454.67 g/mol): C 15.85; H 2.44; N 27.73, Fe 12.28. Found: C 16.26; H 2.64; 28.06.

**SCO-2@MCM** was prepared by follows: To a solution of 416 mg (6 mmol) of 1,2,4-4H-triazole in 2 mL ethanol, 100 mg of MCM-41 powder was added and the slurry was stirred for 12 h. The formed suspension was transferred to a solution of 675 (2 mmol) of  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  in 4 mL of water and the mixture was stirred for 24 h at room temperature. The solid product was filtered, washed with ethanol and water for 3 times (10 mL each), and dried in an evacuated desiccator over silica gel. Yield ~235 mg of a light-pink powder (Fig. S1).

The **pure SCO-2** was synthesized according to ref. 2. Calcd for  $\text{C}_6\text{H}_8\text{N}_9\text{BF}_4\text{Fe}$ : C 20.66; H 2.33; N 36.14. Found: C 20.33; H 2.27; N 35.46.

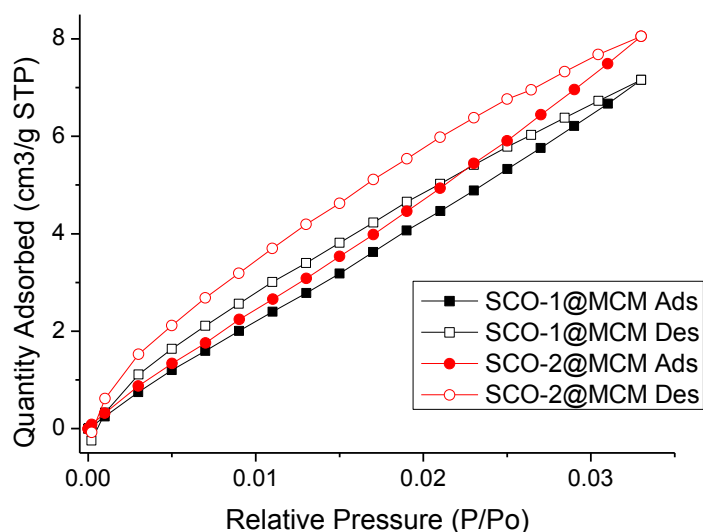


**Fig. S1** Schematic synthesis of SCO-1@MCM and SCO-2@MCM.

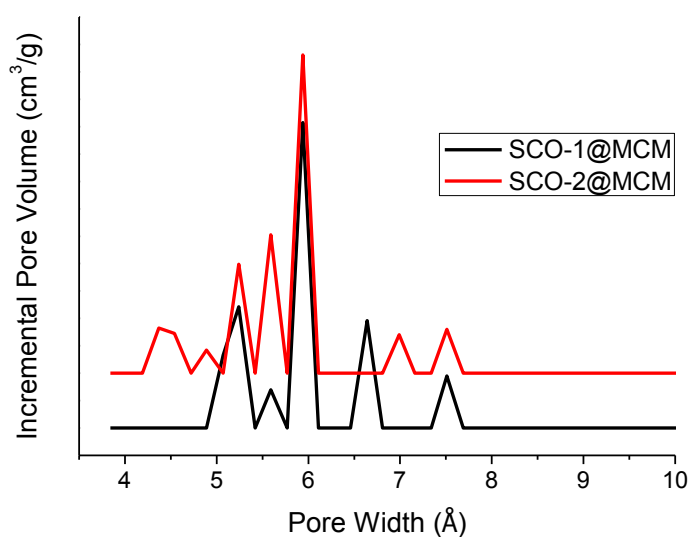
### Washing procedure:

Any SCO precipitate which formed on the outer MCM surface was removed by washing procedures. SCO-1@MCM was washed three times with water, because SCO-1 is very easy dissolved in water.

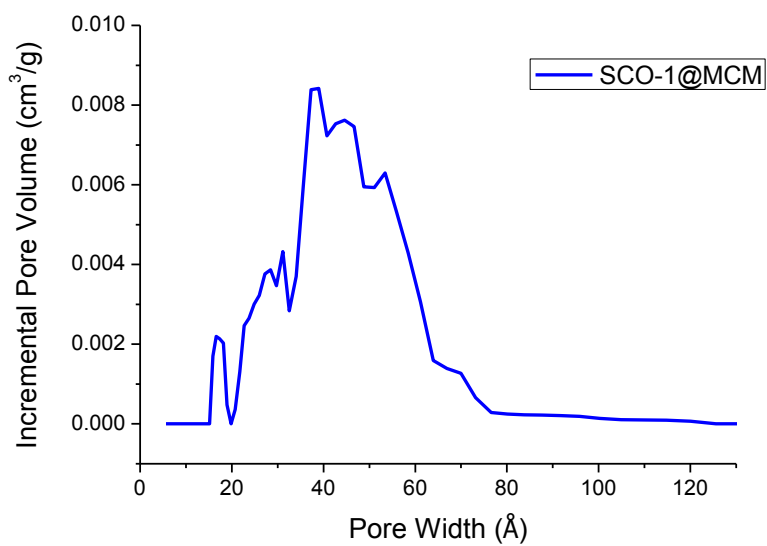
For SCO-2@MCM, the solid product was first placed in a beaker, stirred for 2 h with water and separated by centrifugation. This step was repeated 3 times. Then the solvent was changed to ethanol, stirred for 2 h again and centrifuged. The ethanol washing was repeated until no pink color appeared in the supernatant.



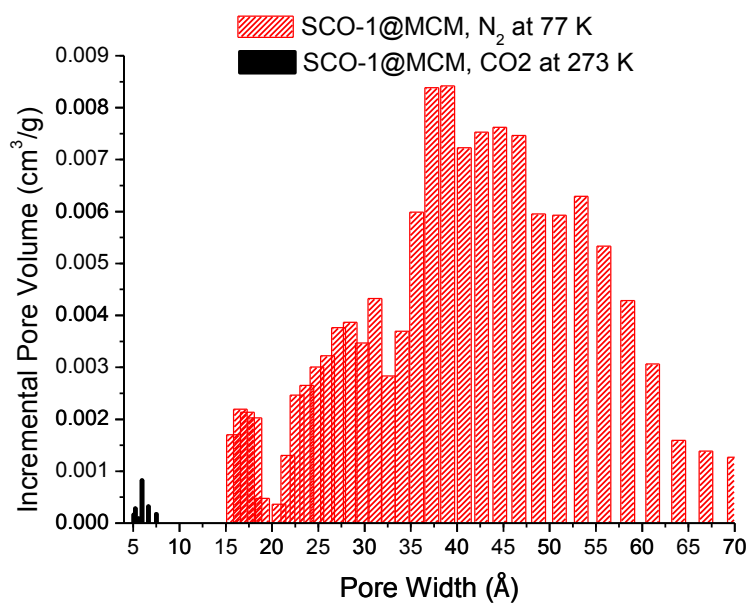
**Fig. S2** CO<sub>2</sub> sorption isotherms for SCO-1@MCM and SCO-2@MCM at 273 K.



**Fig. S3** NLDFT pore size distribution (PSD) curves of SCO@MCM from CO<sub>2</sub> adsorption (at 273 K) isotherms.



**Fig. S4** Pore size distribution of SCO-1@MCM from N<sub>2</sub> adsorption isotherm (at 77 K) analysis.



**Fig.S5** Pore size distribution of SCO-1@MCM from analysis of N<sub>2</sub> and CO<sub>2</sub> adsorption isotherm.

**Table S1** Summary of spin transition temperatures ( $T_c$  in Kelvin) with hysteresis (in K) between  $T_c^\uparrow$  and  $T_c^\downarrow$ .

Material	<sup>57</sup> Fe Mössbauer (Hysteresis)		Magnetic (Hysteresis)		Optical reflect. (Hysteresis)		Ref.
	$T_c^\uparrow$	$T_c^\downarrow$	$T_c^\uparrow$	$T_c^\downarrow$	$T_c^\uparrow$	$T_c^\downarrow$	
Free SCO-1	n.a. <sup>a</sup>	n.a. <sup>a</sup>	345 <sup>b</sup>	323 <sup>b</sup>	336 <sup>b</sup>	323 <sup>b</sup>	1
			(22)	(13)			
SCO-1@MCM	330	310	282 <sup>c</sup>	276 <sup>c</sup>	291 <sup>c</sup>	286 <sup>c</sup>	This work
			(6)	(5)			
SCO-1@MCM	330	310	389 <sup>d</sup>	340 <sup>d</sup>	394 <sup>d</sup>	345 <sup>d</sup>	This work
			(49)	(49)			
Free SCO-2	380	344	371 <sup>e</sup>	340 <sup>e</sup>	376 <sup>e</sup>	345 <sup>e</sup>	1, this work
			(20)	(31)	(31)		
SCO-2@MCM	380	344	385	345	373 <sup>f</sup>	343 <sup>f</sup>	This work
			(36)	(40)	(30)		
SCO-2@MCM	342	328	381	346	385	351	This work
			(14)	(35)	(34)		

<sup>a</sup> n.a.= not available. <sup>b</sup> Hydrated material, [Fe(Htrz)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. <sup>c</sup> Dehydrated material. <sup>d</sup> First heating and cooling cycle on hydrated material. <sup>e</sup> Second to fourth cycle on dehydrated material. <sup>f</sup> Optical reflectance measurements were recorded in this work on SCO-2 prepared as nanoparticles in the liquid state according to Ref. **Error!**

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## Instrumentation

**Powder X-ray diffractograms** were acquired at ambient temperature on a Bruker D2 Phaser using a flat low background sample holder and Cu-K $\alpha$  radiation ( $\lambda = 1.54182 \text{ \AA}$ ) at 30 kV covering 2-theta angles 5-70° over a time of 2 h.

**Nitrogen adsorption isotherms** were acquired on a Quantachrome Nova<sup>®</sup> at 77K, 2h degassing at a temperature of 120°C in vacuum prior to each measurement.

CO<sub>2</sub> sorption isotherms were measured using a Micromeritics ASAP 2020 automatic gas sorption analyzer at 0°C, 4 h degassing at a temperature of 120°C in vacuum prior to each measurement.

**Thermogravimetric analysis (TGA)** was measured on a Netzsch TG 209 F3 at 5°C/min heating rate using aluminum sample holders and nitrogen as carrier gas.

**FT-IR** measurements were carried out on a Bruker TENSOR 37 IR spectrometer at ambient temperature in the range of 4000 to 500 cm<sup>-1</sup> with an ATR unit (Platinum ATR-QL, Diamond).

**Scanning electron microscopy, SEM** images were obtained with an ESEM Quanta 400 FEG (University of Essen, Dipl.-Ing. S. Boukercha).

**Transmission electron microscopy, TEM** measurements were conducted with a FEI Tecnai G2 f20 with a FEG operated at 200 kVat the Ernst-Ruska centrum of Forschungszentrum Jülich. TEM samples were prepared as diluted suspensions in water and deposited on carbon coated copper grids.

**Atom absorption spectroscopy (AAS)** was conducted with a Perkin Elmer AAnalyst100

instrument (flame AAS, acetylene/air as firing gas, burner head length: 10 cm). The standard solution were prepared with concentrations of 1mg/L, 5mg/L and 10mg/L respectively.

Carefully about ~5 mg of each sample was weighed and completely dissolved in 2 mL of HNO<sub>3</sub> (65%) solution. These solutions were then diluted into 100 mL volumetric flasks ready for AAS analysis. Weight details are listed in in Table S2.

**Table S2** Weight and initial concentration of sample

Sample	Weight (mg)	Initial concentration (mg/L)
SCO-1@MCM	5.63	56.3
SCO-2@MCM	5.85	58.5

The direct AAS data is given in Table S3.

**Table S3** AAS analysis results (Fe)

Sample	c(Fe), mg/L	c(Fe)-c(HNO <sub>3</sub> ), mg/L
SCO-1@MCM	4.076	4.060
SCO-2@MCM	4.119	4.103
blind value of HNO <sub>3</sub>	0.0156	—

The calculated SCO content is given in Table S4.

SCO-1: C<sub>6</sub>H<sub>9</sub>N<sub>9</sub>B<sub>2</sub>F<sub>8</sub>Fe (without water, 436.65 g/mol), Fe: 12.79%.

SCO-2: C<sub>6</sub>H<sub>8</sub>N<sub>9</sub>BF<sub>4</sub>Fe (348.84 g/mol), Fe: 16.01%

**Table S4** SCO- and Fe-content based on the AAS analysis.

Sample	Fe content (wt%)	SCO content (wt%)
SCO-1@MCM	7.21	56.4
SCO-2@MCM	7.01	43.8

1. J. Kröber, J.-P. Audière, R. Claude, E. Codjovi, O. Kahn, J. G. Haasnoot, D. Grolière, C. Jay and A. Gonthier-Vassal, *Chem. Mater.*, 1994, **6**, 1404-1412.

2 (a) E. Coronado, J. R. Galán-Mascarós, M. Monrabal-Capilla, J. García-Martínez and P. Pardo-Ibáñez, *Adv. Mater.*, 2007, **19**, 1359-1361. (b) J. R. Galán-Mascarós, E. Coronado, A. Forment-Aliaga, M. Monrabal-Capilla, E. Pinilla-Cienfuegos and M. Ceolin, *Inorg. Chem.*, 2010, **49**, 5706–5714.