Electronic Supplementary Information (ESI)

Solvent-triggered relaxative spin state switching of [Fe(HB(pz)₃)₂] in closed nano-confinement of NH₂-MIL-101(Al)†

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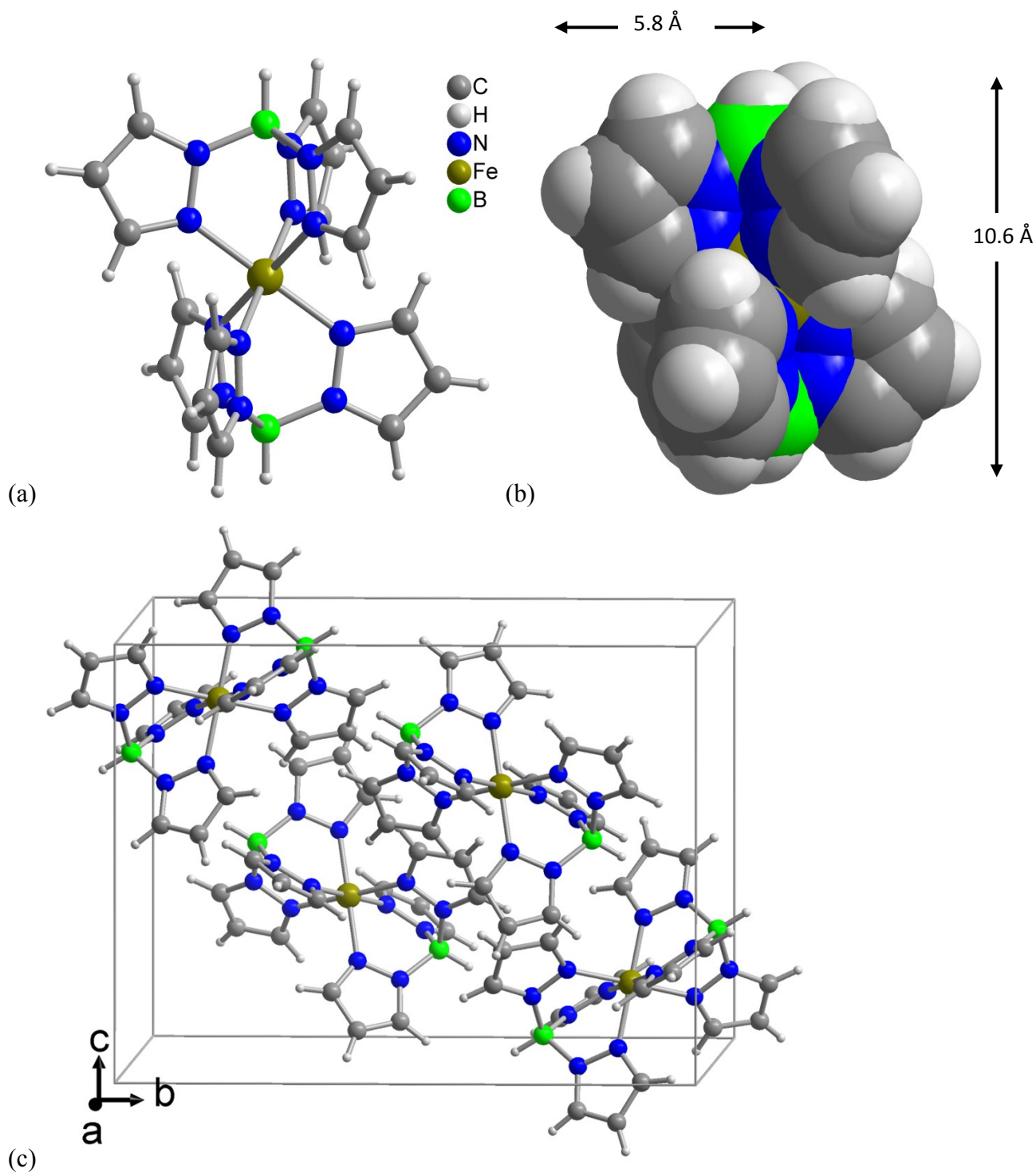
Molecular structure of [Fe(HB(pz)₃)₂]

(a)

(b)

(c)

Fig. S1 Single-crystal X-ray structure of [Fe(HB(pz)₃)₂] (Refcode HPZBFE03);[1] (a) ball-and-stick presentation, (b) space-filling presentation of single molecule, (c) unit-cell packing.

Estimation of the molecular volume of [Fe(HB(pz)₃)₂]: the shape of the molecule is approximated by a cylinder with a height of 10.6 Å and a radius of 5.8 Å (Fig. S1b). The height is estimated as the H(B)···(B)H distance of 8.16 Å and twice of the van-der-Waals radius of a hydrogen atom 1.2 Å, which add up to ~10.6 Å.

The radius is estimated from the H(4-C)··· B distance of 4.60 Å with the vdW radius of the hydrogen atom, 1.2 Å, added to give 5.8 Å. The volume of the model cylinder is $\pi r^2 h$ = $3.14 \times (5.8)^2 \times 10.6$ Å^3 = 357 Å^3.

On the other hand the volume of space associated with a single molecule, as derived from one of the reported single-crystal XRD structures of [Fe(HB(pz)$_3$)$_2$] with unit cell volume of 2157.85(78) Å^3 and Z = 4, is 2158 / 4 = 540 Å^3.

The ratio of the two values, 357 / 540 = 0.66 is in effect the estimated packing coefficent and it is within the range of 0.65-0.77 characteristic for the majority of molecular crystals,[2] which corroborates the molecular volume estimation by using the simple cylinder model.

Scanning electronmicroscopy

Scanning electron microscopy (SEM) images (Fig. S2) show the morphology of NH$_2$-MIL-101(Al) with irregular particles, which is in a good agreement with the reported literature.[3] The morphology of S@M composites is similar to the bulk NH$_2$-MIL-101(Al). This supports the assumption that the iron containing species should be located inside the pores of NH$_2$-MIL-101(Al).
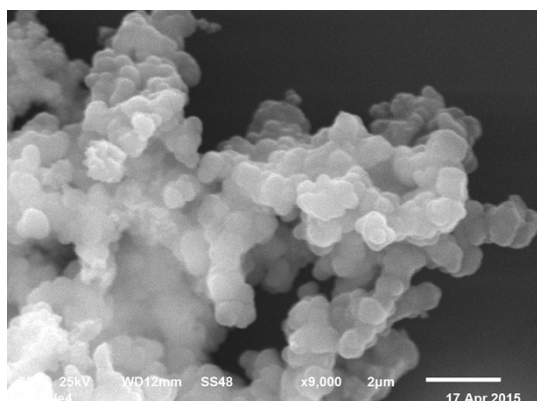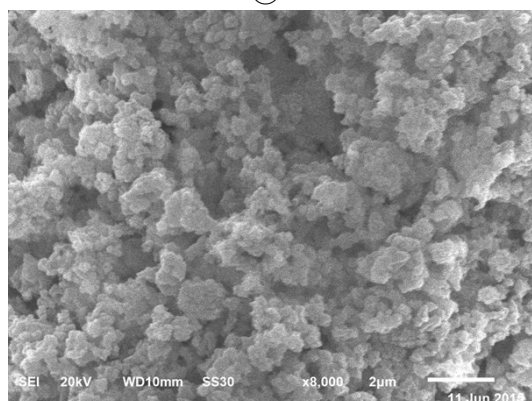

NH$_2$-MIL-101(Al)
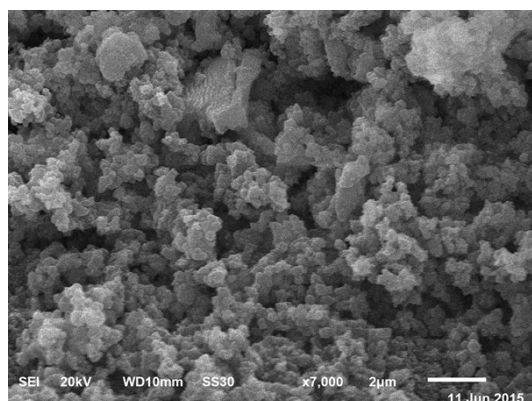
S@M-1
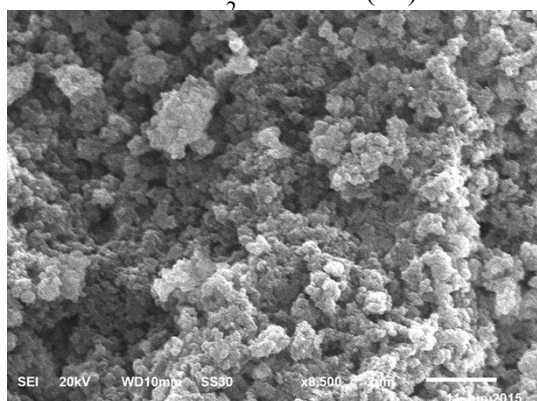
S@M-2

S@M-3

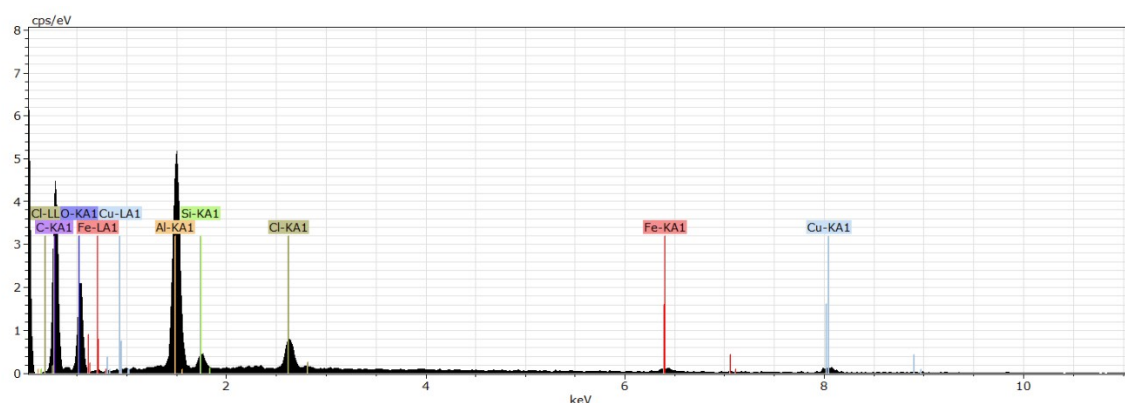**Fig. S2a** SEM images of S@M materials in comparison to the bulk NH$_2$-MIL-101(Al).

Fig. S2b Energy-dispersive X-ray spectrum of S@M-1 with peak assignment. Determination of the Al : Fe ratio was based on the Al-KA1 and the Fe-KA1 peaks (KA = Kα)

Temperature stability of S@M samples and thermogravimetric analysis of [Fe(HB(pz)$_3$)$_2$]

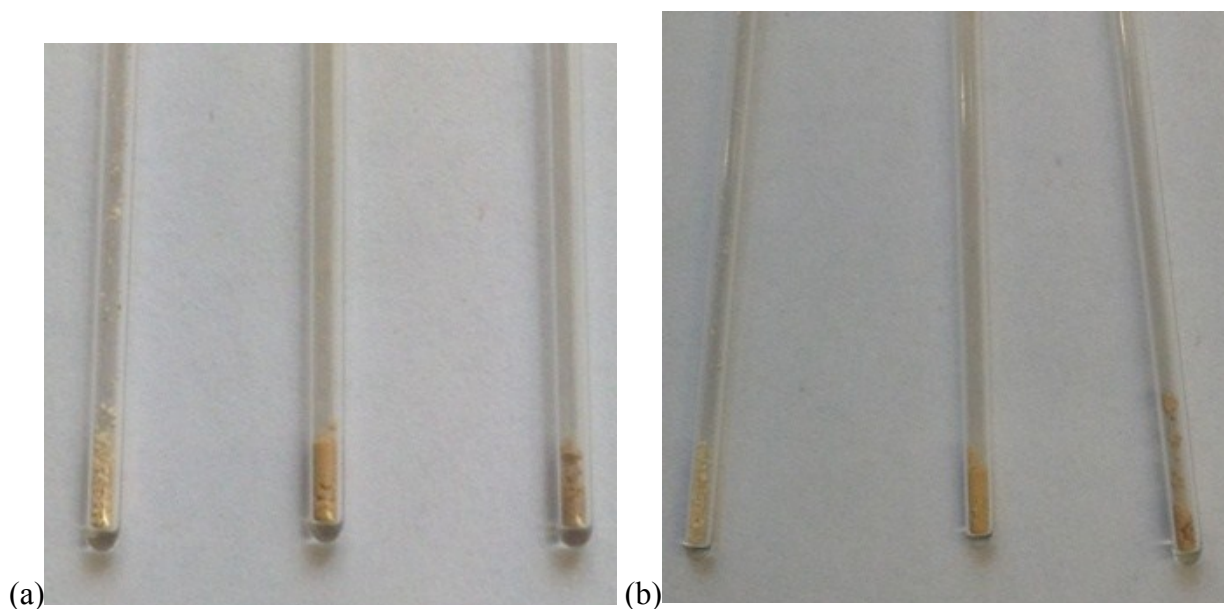(a)   (b)

Fig. S3 Photographs of the S@M sample at 25 °C (a) and after heating to 230 °C (503 K) (b). The order from left to right is S@M-1, S@M-2 and S@M-3 for each photograph.

The photographs in Fig. S3b were taken after heating in a melting point determination device to 230 °C, with a heating rate of 10 °C/ min. After heating, all samples kept the same color, and the SCO still can be triggered by the addition of solvent; in this case, methanol was used.
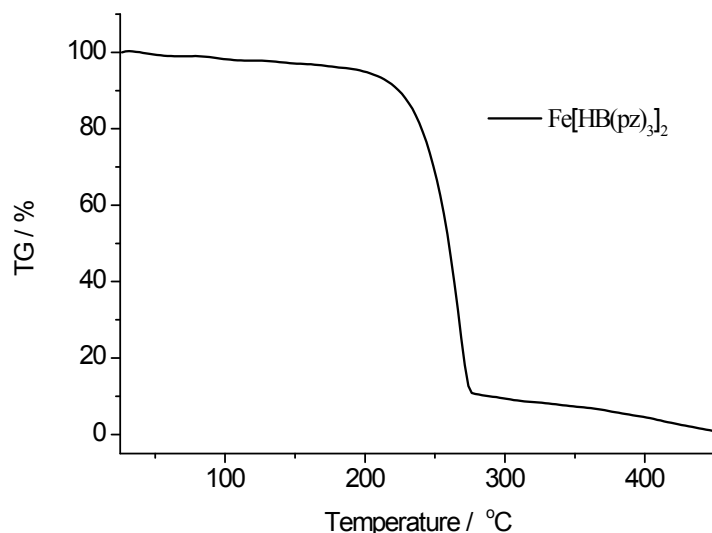
Fig. S4 TG curve for [Fe(HB(pz)$_3$)$_2$], which shows sublimation of the complex above 220 °C under nitrogen gas and ambient pressure.

Temperature dependent magnetism of [Fe(HB(pz)$_3$)$_2$] and the S@M materials

Introductory note. μ is magnetic moment per one Fe^{2+} ion given in Bohr magnetons (μ_B). For spin only value magnetic moment can be calculated as $\mu = g\sqrt{S(S+1)}\,\mu_B$, or experimentally from the $\mu = \sqrt{8\chi_{mol}T}$ relation. For 4 unpaired electrons, and for spin only magnetic moment, $\chi_{mol}T$ ought to be 3 emu K Oe^{-1}mol^{-1}. In low spin state, LS, S = 0, i.e. μ = 0 and complex should be diamagnetic. In practice it is not so because of a number of factors. Among them the existing positive temperature independent paramagnetism of Fe(II) and the presence of species with non-zero spin, as $^5T_{2g}$ level (HS) is populated in some degree even at low temperatures, and because of Fe^{3+} admixtures.

In high spin state with 4 unpaired electrons S = 2 and μ = 4.9 μ_B (it is assumed that g = 2, where g is the Lande factor). In the real world values are usually larger, because spin-orbit interaction contributes to some extent. For Fe(II) L = 2 and S = 2, and maximal magnetic moment can be about 5.48 μ_B. In the literature some authors claim that acceptable value for $\chi_{mol}T$ product, for Fe(II) complexes, is up to 3.92 emu K mol^{-1} Oe^{-1}, i.e. μ=5.6 μ_B.[4]

Literature data regarding [Fe(HB(pz)₃)₂] complex.
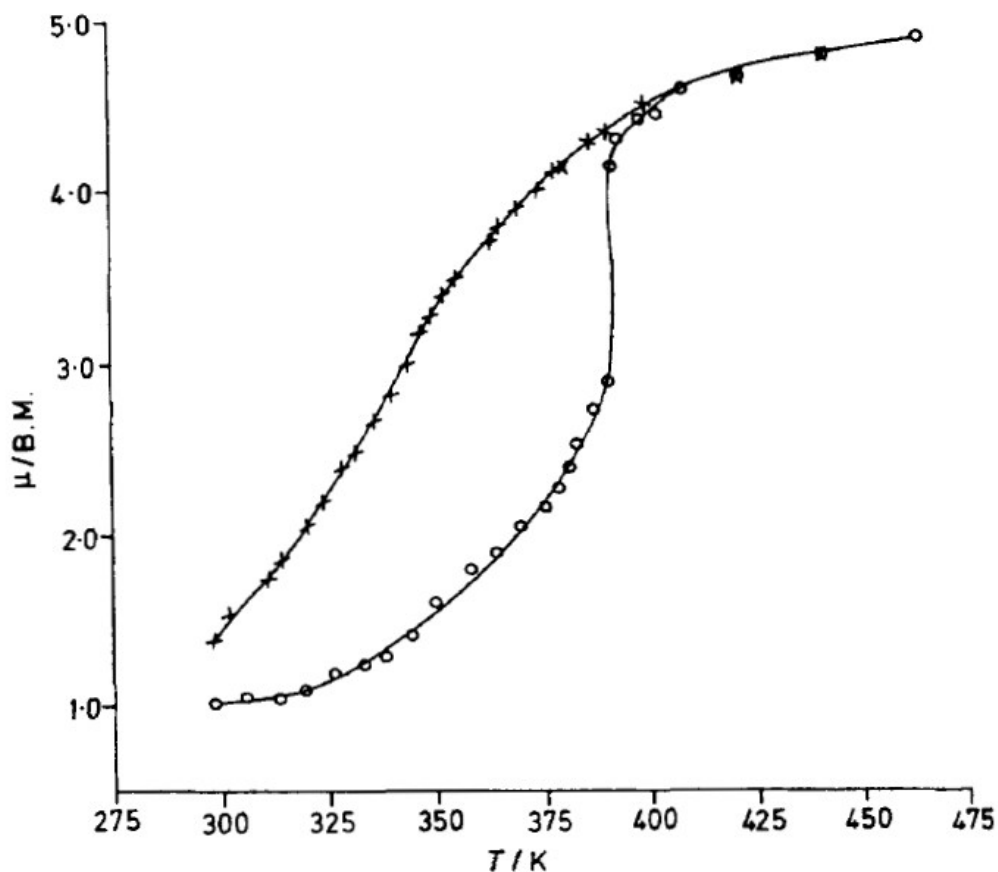
Fig. S5 Temperature dependence of the effective magnetic moment of crystalline [Fe(HB(pz)$_3$)$_2$] (open sphere for heating and cross for cooling). Figure taken from ref. 5.
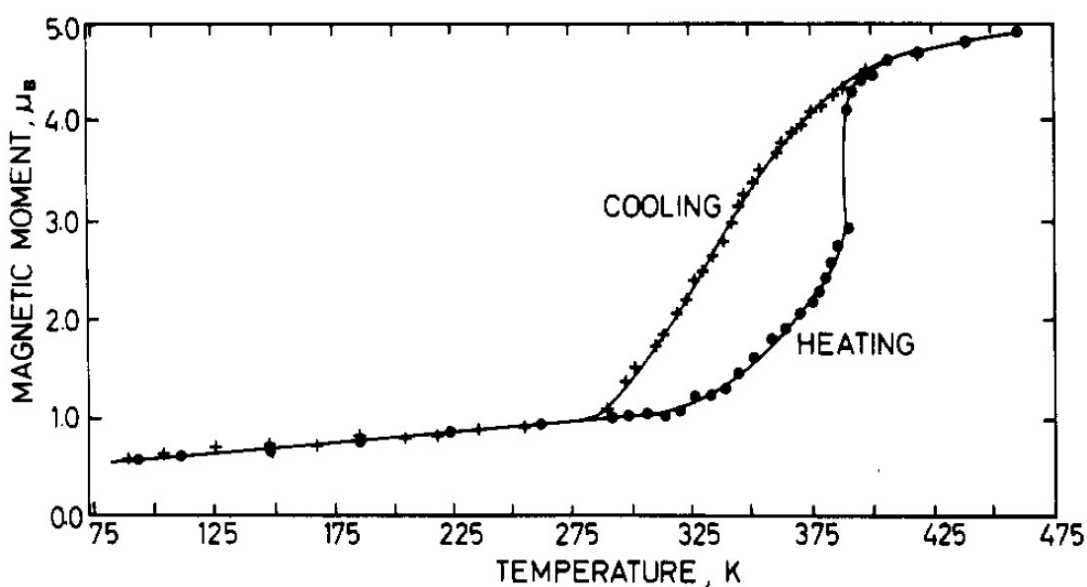

Fig. S6 Temperature dependence of the magnetic moment for [Fe(HB(pz)$_3$)$_2$] during heating and cooling. The figure is taken from ref.6

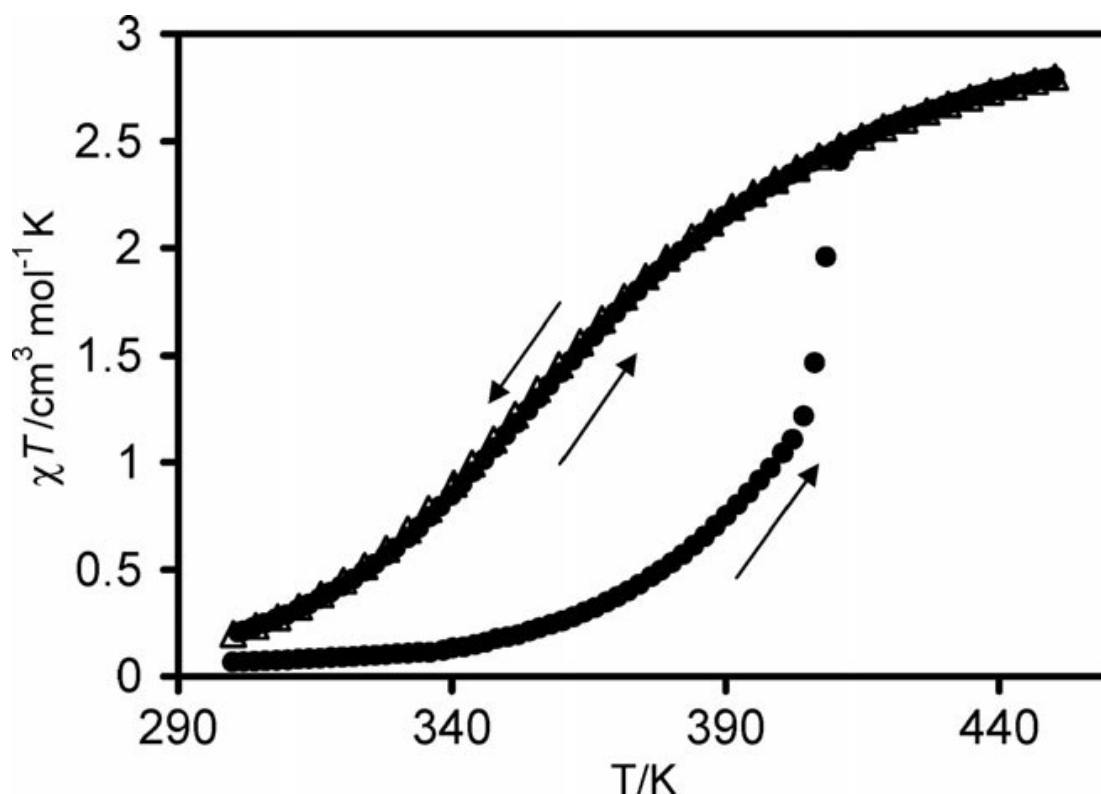**Fig. S7** The temperature dependence of the $\chi_M T$ product of [Fe(HB(pz)$_3$)$_2$] upon two successive thermal cycles (first cycle: closed circles, second cycle: open triangles). The figure is taken from ref. 1.

Experimental data on S@M composites. The molar susceptibilities were calculated as given below. Assuming that all the iron in the sample is incorporated in the form of [Fe(HB(pz)$_3$)$_2$], the relative content of the latter is calculated using the iron content determined by the AAS analytics. The content of actual content of the iron complex and the matrix in a sample with a weight m is m*x and m*(1-x), where x is the calculated content of the iron complex. The calculated weights allow to apply the diamagnetic corrections. In the case of the matrix it was determined experimentally for a non loaded sample to be $\chi_{dia=}$ -1.1·10^{-9}*T – 2.2·10^{-7} emu g^{-1} Oe^{-1}, while for the [Fe(HB(pz)$_3$)$_2$] the value of -3.55 10^{-4} emu g^{-1} Oe^{-1} estimated from the Pascal constants were used. The corrected absolute values of the susceptibilities, emu Oe^{-1}, are related to molar quantities, ν = m*x/M$_{FeL2}$, (M$_{FeL2}$ = 481.9), thus giving the molar values, from which, subsequently the magnetic moment per one Fe-ion in Bohr magnetons is calculated using the μ=2.828($\chi_{mol} \times$T)$^{0.5}$.

The spin-only value for one moles of iron ions is 4.9 Bohr magnetons, μ_B, but experimentally this value might be up to 5.6.
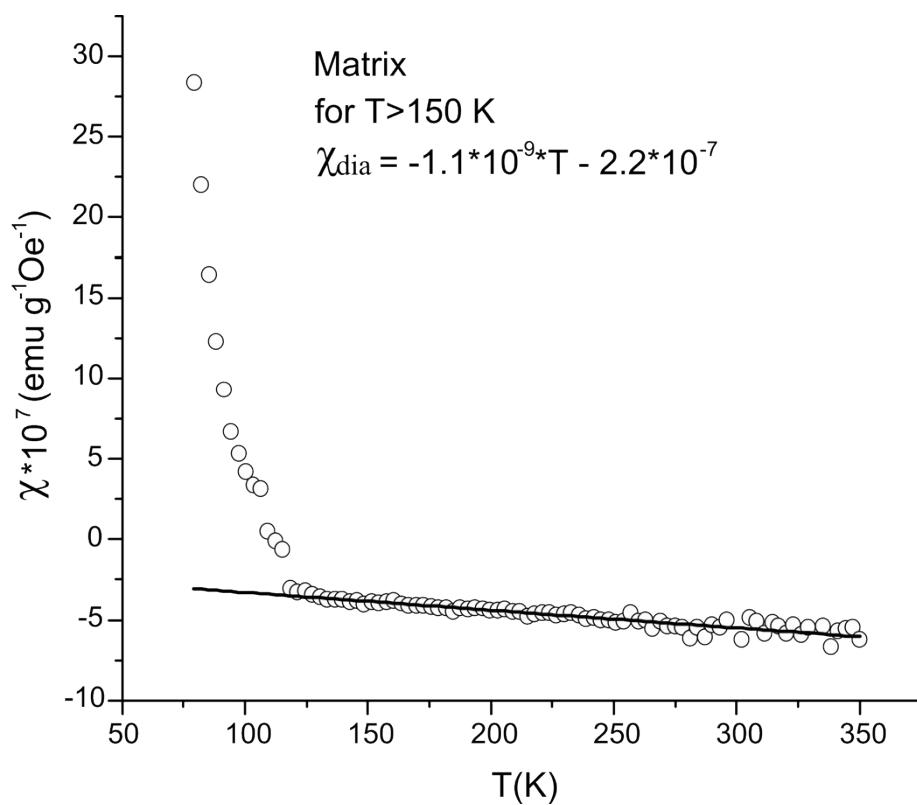
Fig S8 Temperature-variable magnetic curve for NH_2-MIL-101(Al) reference sample.
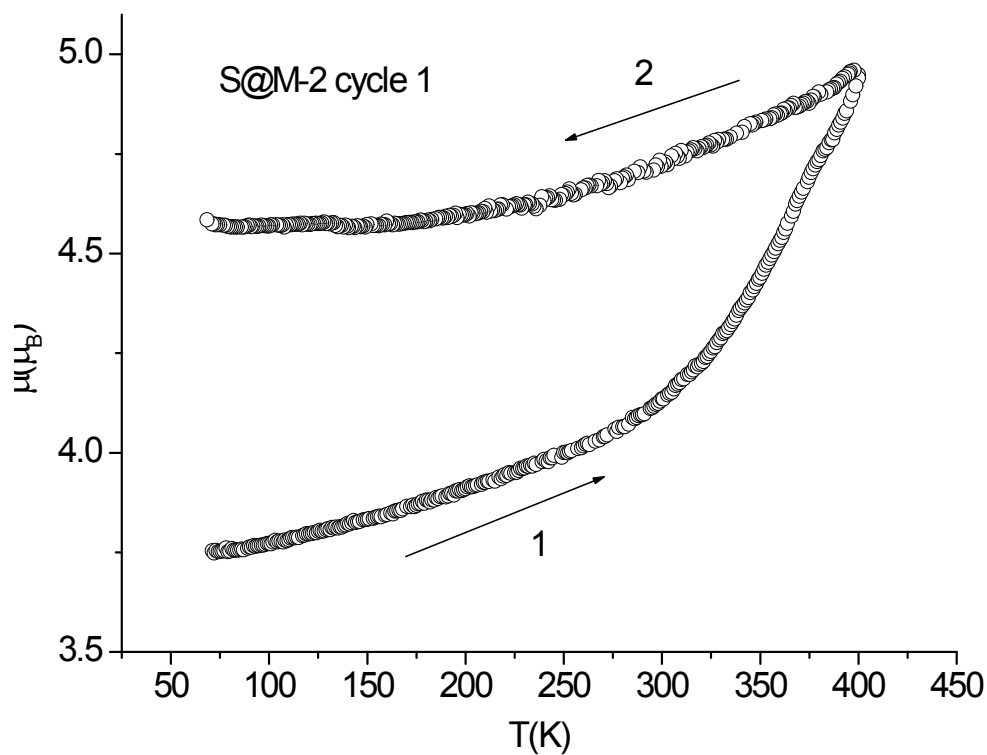
Fig S9 Temperature dependence of the magnetic moment for S@M-2 (first cycle).
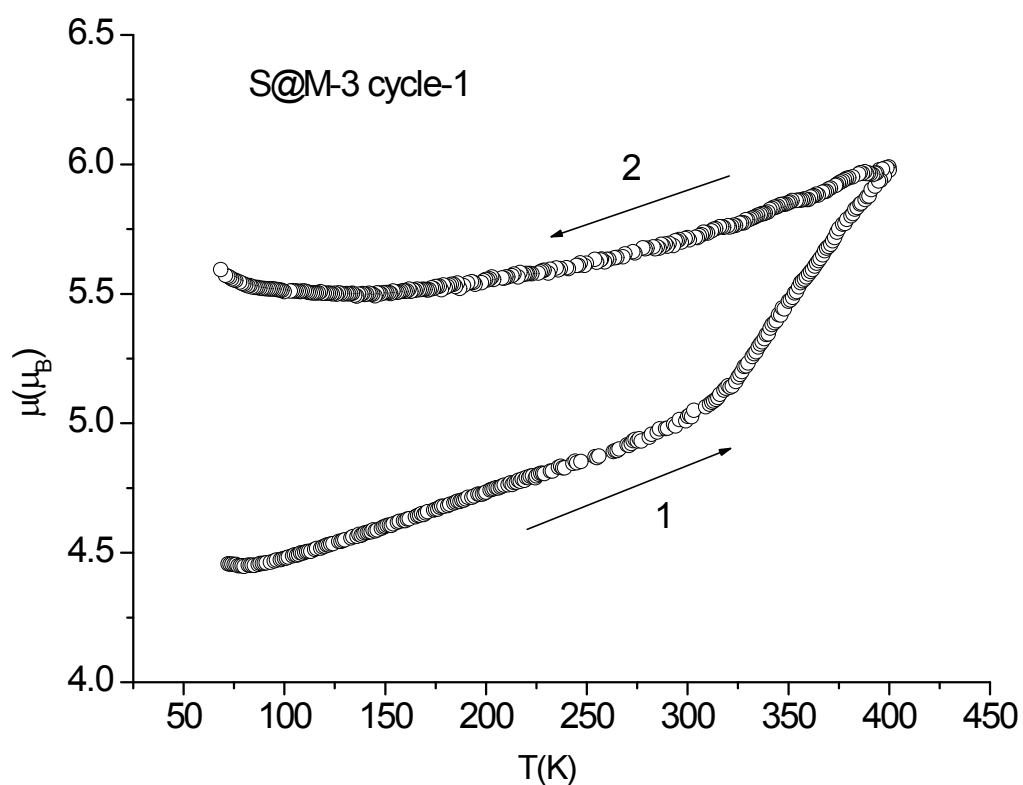
Fig S10 Temperature dependence of the magnetic moment for S@M-3 (first cycle).
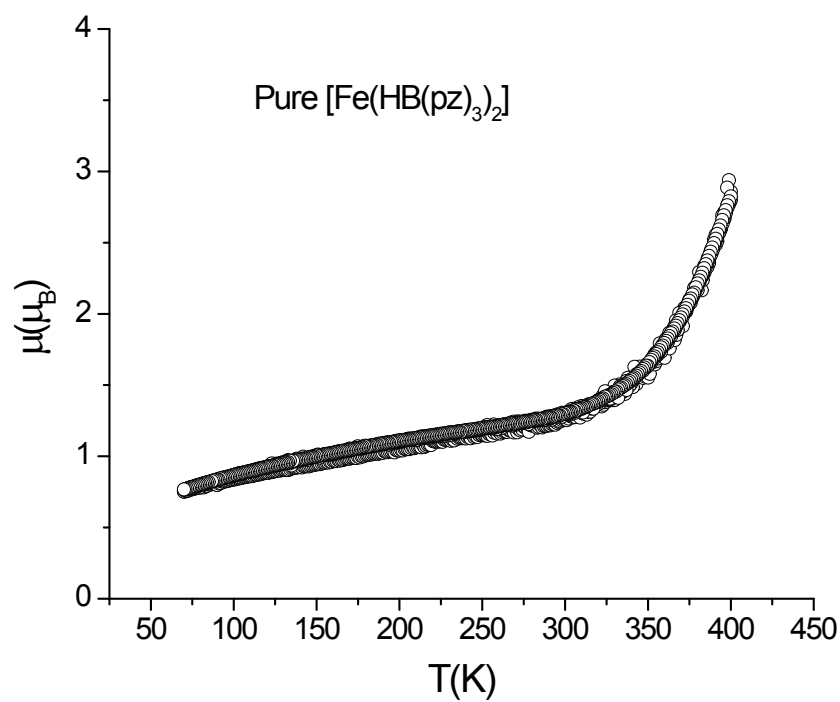
Fig S11 Temperature dependence of the magnetic moment for $[Fe(HB(pz)_3)_2]$ (first cycle).

Temperature dependent diffuse reflectance spectrum of the S@M-3 material
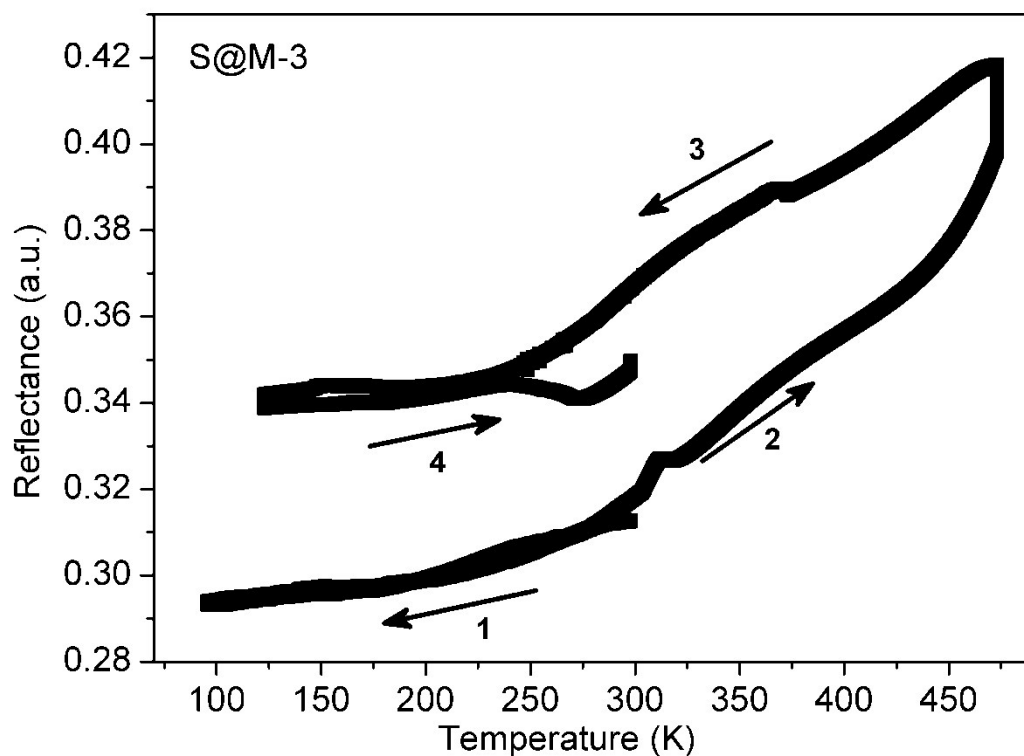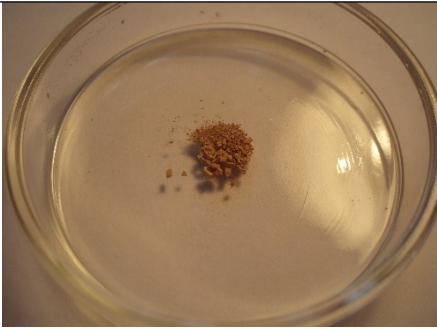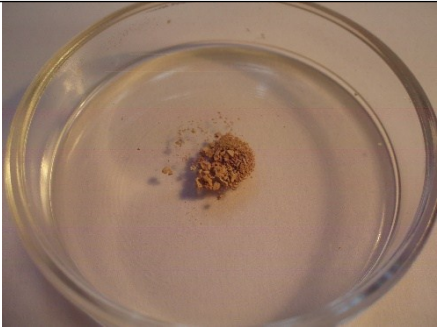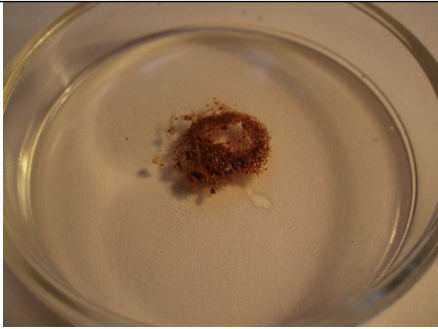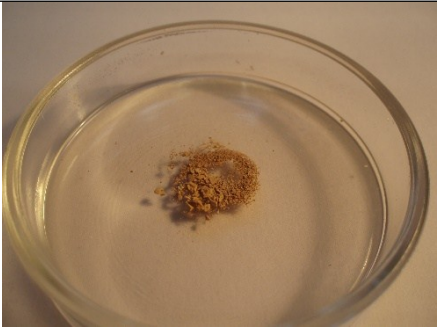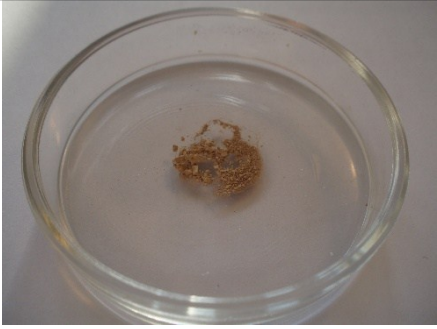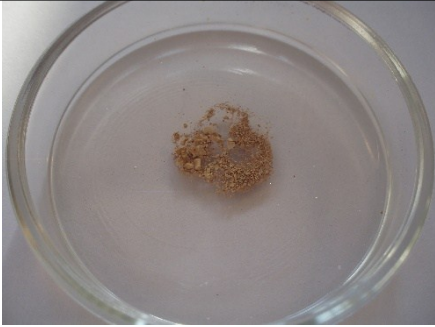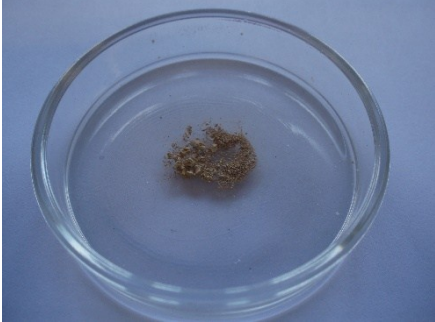

Fig. S12 Thermal dependence of the diffuse reflectance recorded on S@M-3 sample.
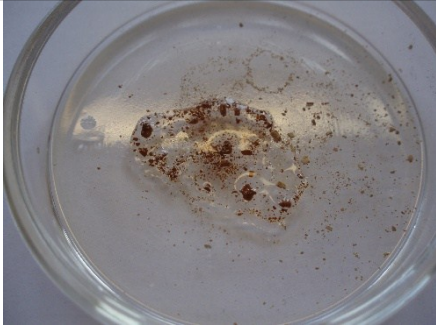
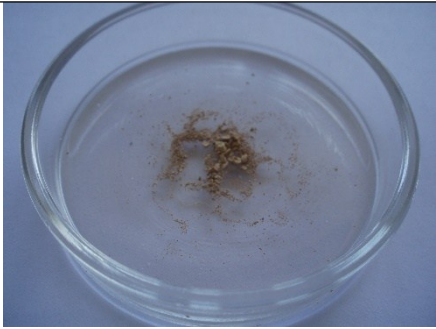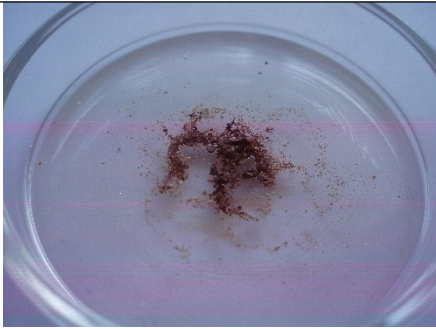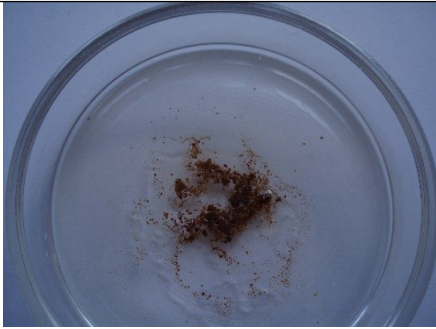**Table S1** Photographs of bulk $[Fe(HB(pz)_3)_2]@NH_2\text{-MIL-101(Al)}$ as sample S@M-2 with different solvents added for colour comparison.
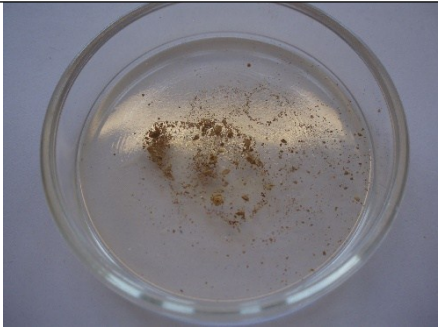
(The sample was dried after each new addition, either at 70 °C or at 120 °C, depending on the solvent's boiling point, under membrane pump vacuum (~ 10 Torr). The order in the following Table corresponds to the chronological order of solvent addition experiments.)
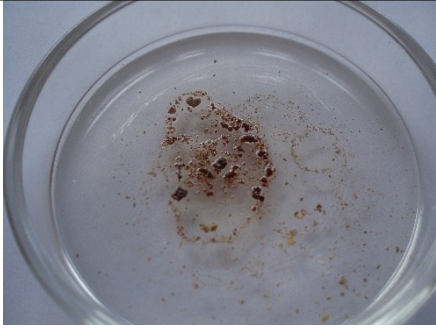
Solvent	before solvent addition	after solvent addition
CCl_4		

CHCl$_3$		
CH$_2$Cl$_2$		
CH$_3$CN		
THF		
MeOH		

i-PrOH		
n-BuOH		
n-pentane		
n-hexane		
n-heptane		

cyclohexane		
toluene		
H$_2$O		
mesitylene		
DMF		

ethylacetate		

1 L. Salmon, G. Molnár, S. Cobo, P. Oulié, M. Etienne, T. Mahfoud, P. Demont, A. Eguchi, H. Watanabe, K. Tanaka and A. Bousseksou, *New J. Chem.*, 2009, **33**, 1283–1289.

2 A. I. Kitaigorodskii, Molecular Crystals and Molecules, Academic Press, New York, 1973.

3 B. Seoane, C. Téllez, J. Coronas and C. Staudt, *Sep. Purif. Technol.*, 2013, **111**, 72–81.

4 A. S. Tolla, A. Banerjee, S. Stjepanovic, J. Li, W. W. Brennessel, R. Loloee and F. A. Chavez, *Eur. J. Inorg. Chem.*, 2013, 2115–2121.

5 B. Hutchinson, L. Daniels, E. Henderson, P. Neill, G. J. Long and L. W. Becker, *J. Chem. Soc., Chem. Commun.*, 1979, 1003-1004.

6 F. Grandjean, G. J. Long, B. B. Hutchinson, L. Ohlhausen, P. Neill and J. D. Holcomb, *Inorg. Chem.*, 1989, **28**, 4406-4414.