

ELECTRONIC SUPPLEMENTARY INFORMATION

for

Deposition of intact tetrairon(III) Single Molecule Magnet monolayers on gold: an STM, XPS, and ToF-SIMS investigation

by

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Synthesis

11-(Acetylthio)-2,2-bis(hydroxymethyl)undecan-1-ol (H_3L) and $[Fe_4(OMe)_6(dp\text{m-}d_{18})_6]$ were synthesised following literature procedures [1,2]. Methanol, diethyl ether and 1,2-dimethoxyethane (DME) were carefully dried by treatment with $Mg(OMe)_2$, benzophenone ketyl and CaH_2 , respectively, and distilled under nitrogen prior to use. Sodium methoxide solution was prepared just before use by careful addition of Na metal to anhydrous methanol. 1H and ^{13}C NMR spectra were recorded at 302 K with a Bruker FT-DPX200 spectrometer. Chemical shifts are reported in ppm relative to Me_4Si and the coupling constant values J are expressed in Hz.

2-(Hydroxymethyl)-2-(9-mercaptononyl)propane-1,3-diol (H_3L').

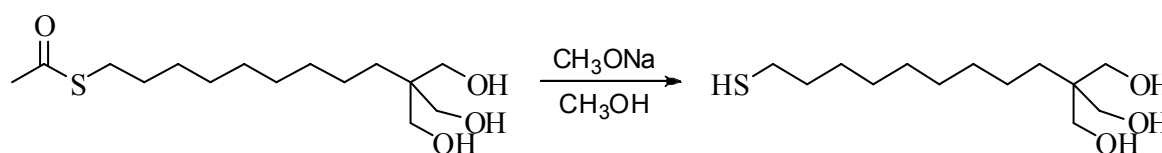


Figure S1

11-(acetylthio)-2,2-bis(hydroxymethyl)undecan-1-ol (0.201 g, 0.656 mmol) was dissolved in 5.5 mL of anhydrous methanol and the colourless solution was degassed with N_2 for 30 min. with stirring. Sodium methoxide (3.068 M in methanol, 0.220 mL, 0.675 mmol) was added dropwise and the yellow mixture was stirred at room temperature for 4 hours under N_2 flow. Excess sodium methoxide was quenched with 5 M HCl until acidic pH, 10 mL of water were added and the reaction extracted with DCM (4 x 30 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuum. The crude product was purified with column chromatography on silica gel (DCM:methanol 14:1 v/v) to yield 2-(hydroxymethyl)-2-(9-mercaptononyl)propane-1,3-diol (0.119 g, 69%) as a whitish solid.

δ_H (200 MHz; $CDCl_3$; Me_4Si) 3.74 (6H, s, 3 x CH_2OH), 2.52 (2H, dt, J 7.6 and 7.2, CH_2SH), 2.43 (3H, br s, 3 x OH), 1.68-1.53 (2H, m, CH_2CH_2SH), 1.32 (1H, t, J 7.6, SH), 1.40-1.19 (14H, m, 7 x CH_2); δ_C (50,3 MHz, $CDCl_3$; Me_4Si) 67.52 (CH_2OH), 42.78 (C^{IV}), 33.78 (CH_2CH_2SH), 30.51 (CH_2), 29.40 (CH_2), 29.36 (2 x CH_2), 28.98 (CH_2), 28.29 (CH_2), 24.59 (CH_2SH), 22.98 (CH_2).

$[Fe_4(L)_2(dp\text{m-}d_{18})_6]$ ($Fe_4C_9S\text{Ac-d}$). To a stirred solution of $[Fe_4(OMe)_6(dp\text{m-}d_{18})_6]$ (0.120 g, 0.0741 mmol) in anhydrous diethyl ether (45 mL), H_3L (0.061 g, 0.20 mmol) was added. The reaction mixture was stirred until complete dissolution of the ligand. Slow evaporation of the solvent afforded a microcrystalline residue that was extensively washed with

methanol until pale yellow washings and dried in vacuum. The solid was dissolved in the minimum volume of anhydrous DME and the solution was left undisturbed until complete evaporation of the solvent. The large yellow-orange crystals so obtained were washed with a methanol:DME (5:1 v/v) mixture and then with pure methanol, and finally dried under vacuum (0.109 g, 72%).

Monolayers of H_3L and H_3L'

Monolayers of H_3L and H_3L' were prepared by soaking flame-annealed Au(111) substrates in a DCM solution of H_3L (0.5 mg/mL, 40 h) or of H_3L' (0.3 mg/mL, 45 h), followed by extensive washing with pure solvent and drying in a nitrogen flow.

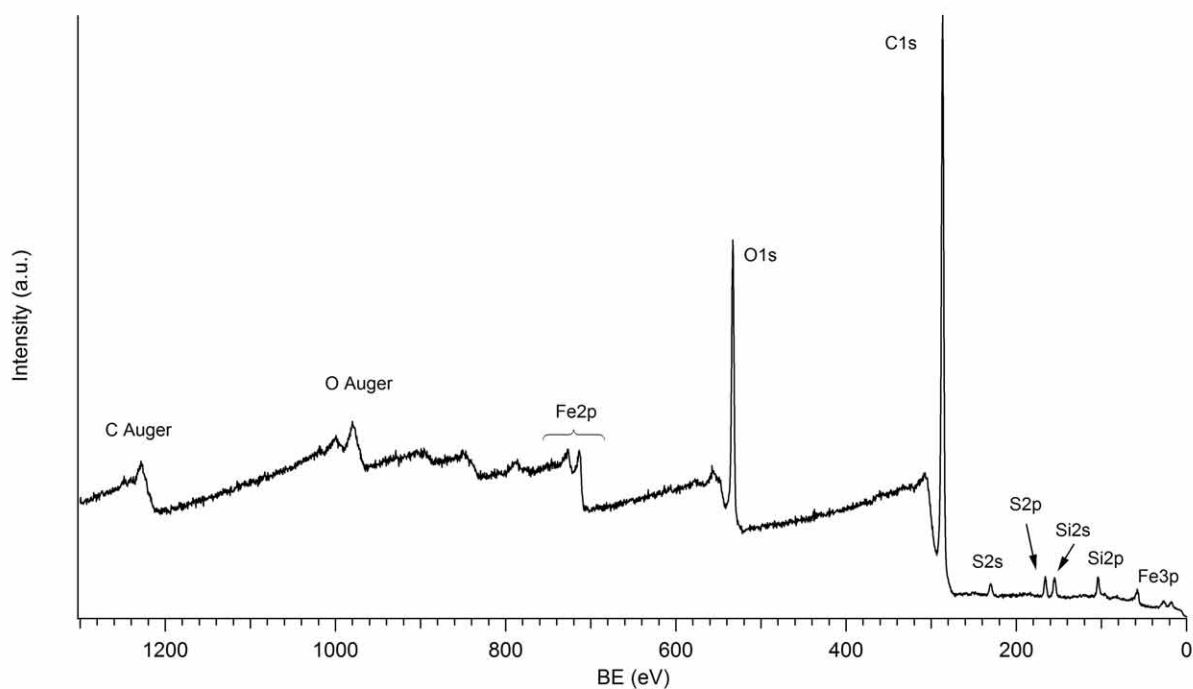


Figure S2. XPS survey spectrum of a drop cast sample of Fe_4C_9SAc . Si peaks have been attributed to a contamination with silicon grease.

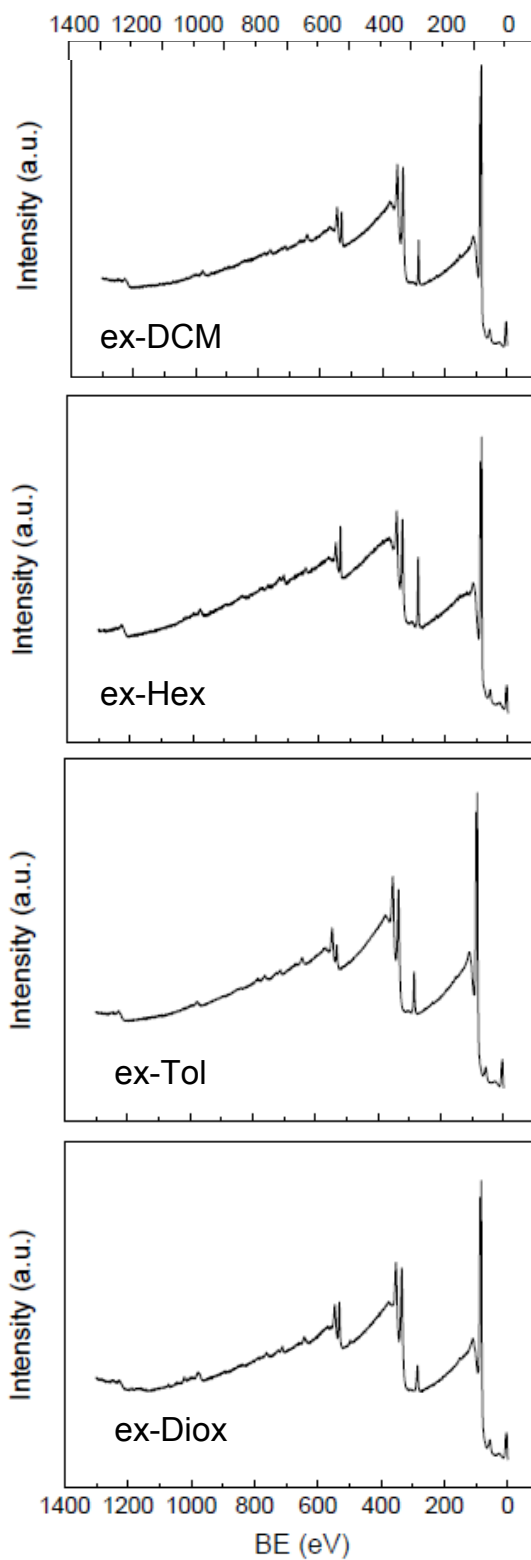


Figure S3. XPS survey spectra of **Fe₄C₉SAc** adsorbates on Au(111) from the four investigated solvents.

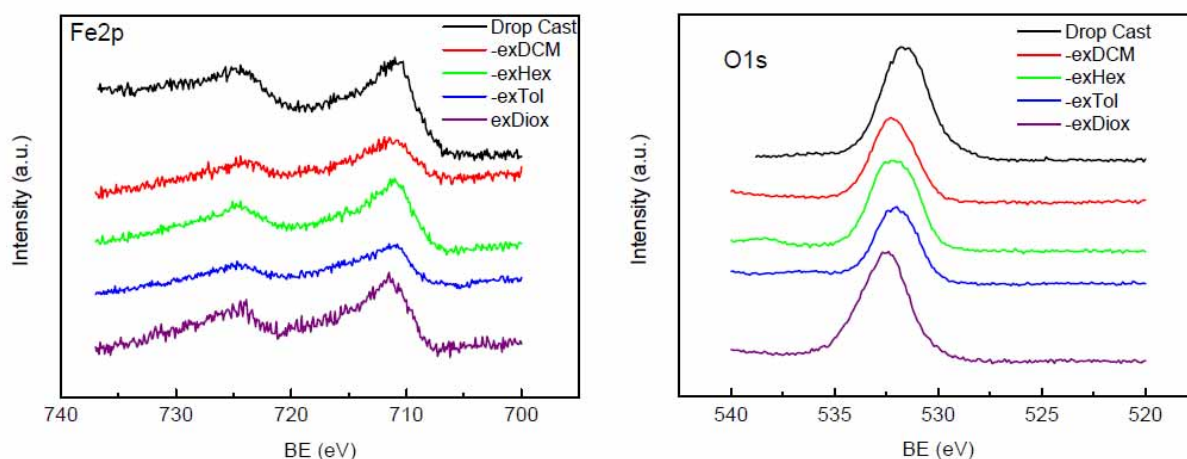


Figure S4. Detailed XPS spectra of Fe_{2p} and O_{1s} peaks recorded on Fe₄C₉Sac drop cast sample and on Au(111) adsorbates prepared from the four investigated solvents.

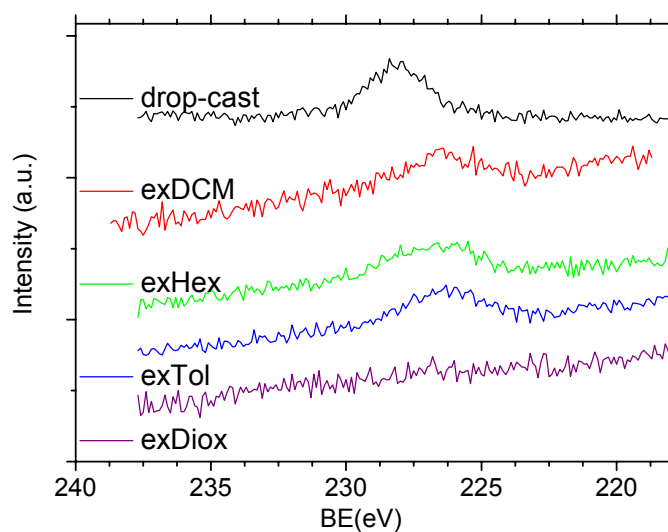


Figure S5. Detailed XPS spectra of the S_{2s} peaks recorded on Fe₄C₉Sac drop cast sample and on Au(111) adsorbates prepared from the four investigated solvents.

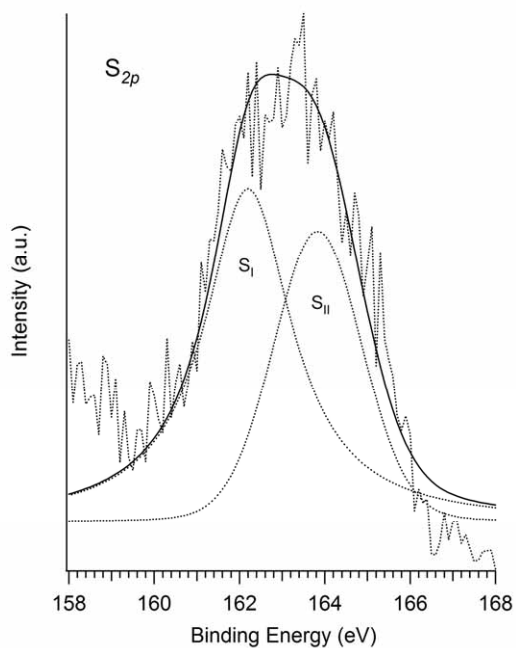


Figure S6. S_{2p} fitting components for the **Fe₄C₉SAc –exHex** monolayer sample. The two components at 162.1 eV (S_I) and 163.6 eV (S_{II}) are likely related to the surface bound and unbound sulfur atoms of the SMM molecules, respectively. The quality of the fitting is very poor, due to the low signal-to-noise ratio.

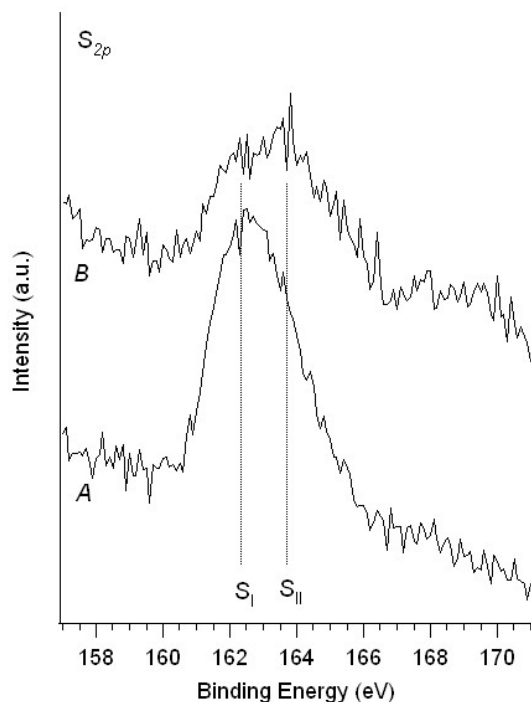


Figure S7. Comparison between the S_{2p} photopeak observed in a monolayer of the pure H₃L ligand (A) and in the **Fe₄C₉SAc-exHex** sample (B). The presence of a broad signal at ca. 168 eV in B may be associated to some sulphur oxidation.

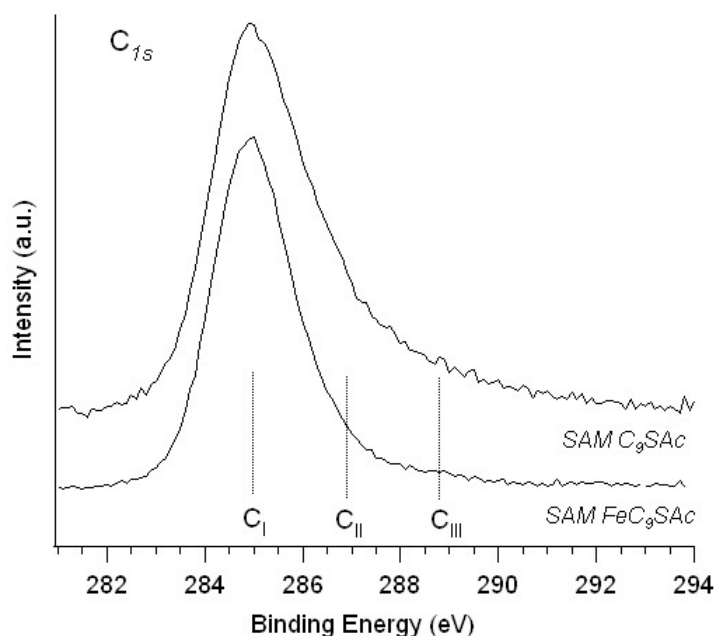


Figure S8. Comparison between the C_{1s} photopeak observed in a monolayer of the pure H₃L ligand and in the **Fe₄C₉SAc-exDCM** sample.

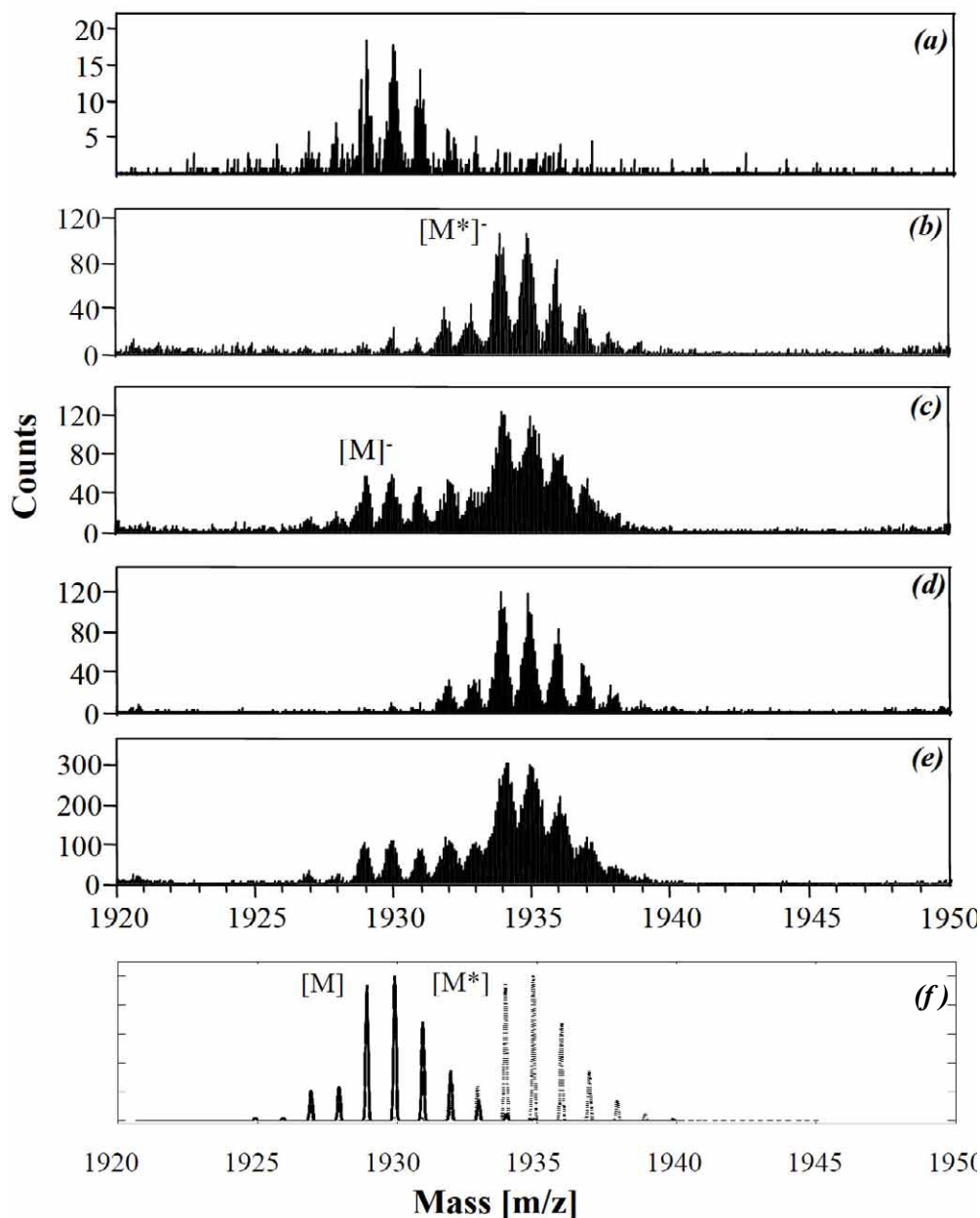


Figure S9. Negative ToF-SIMS spectra of the molecular peak area of $\text{Fe}_4\text{C}_9\text{SAC}$ drop cast sample (a), and of $-\text{exDCM}$ (b), $-\text{exHex}$ (c), $-\text{exTol}$ (d), and $-\text{exDiox}$ (e) SAMs on Au. Panel (f) shows the theoretical isotopic distributions for the molecular peak, $[\text{M}]^-$, and its oxidized form, $[\text{M}^*]^-$, corresponding to $[\text{Fe}_4(\text{LL}^*)(\text{dpm})_6]^-$, where L^* is an oxidized tripodal ligand containing a terminal sulphonate group.

Stability experiments in solution by ^2H NMR

The stability of isotopically-enriched $\text{Fe}_4\text{C}_9\text{SAc}$ in four different solvents (anhydrous DCM, 1,4-dioxane, toluene and *n*-hexane, purchased from Sigma-Aldrich) was tested using ^2H -NMR. Previous studies [1-3] demonstrated that ^2H nuclei in Fe_4 complexes isotopically-enriched on *dpm*⁻ *t*-butyls are sensitive magnetic probes to monitor structural changes in the tetrairon(III) core, as well as to investigate assembly and disassembly processes in solution. For this purpose, the deuterated precursor $[\text{Fe}_4(\text{OMe})_6(\text{dpm-}d_{18})_6]$ was reacted with excess H_3L ligand, as described above, to yield the cluster $[\text{Fe}_4(\text{L})_2(\text{dpm-}d_{18})_6]$ ($\text{Fe}_4\text{C}_9\text{SAc-d}$).

Solutions were prepared directly in 5-mm NMR test tubes using weighed single crystals of $\text{Fe}_4\text{C}_9\text{SAc-d}$ in order to avoid possible contaminations. The spectra were recorded immediately after dissolution, and checked after 20, 27 and 50 hours, so as to cover (and exceed) the timeframe needed for monolayer formation (20 h). ^2H NMR experiments were performed on a Bruker FT-DPX200 spectrometer operating at 30.72 MHz and 302 K; deuteron chemical shifts are referred to acetone- d_6 , as external standard ($\delta = 2.16$ ppm).

The ^2H -NMR spectra recorded immediately after dissolution are dominated by the broad peak around 10 ppm (Figure S10 (a)), that accounts for the 108 deuterium atoms of the *dpm*⁻ ligands, while the narrow signals are due to naturally-occurring deuterium traces in the solvents. After 20 and 27 hours (Figure S10 (b) and (c)), the spectra are still substantially the same, except for the appearance of a very weak signal from free $\text{Hdpm-}d_{18}$ at around 1 ppm in all solvents investigated except toluene. Its integrated area accounts for less than 2% of the total *t*Bu signal and remains approximately constant all over the timeframe explored. After 50 hours (Figure S10 (d)), DCM and 1,4-dioxane solutions show a barely visible peak around 13 ppm, which accounts for less than 2% of the total *t*Bu signal and is typical of magnetically uncoupled $\text{Fe}(\text{dpm})$ complexes. In conclusion $\text{Fe}_4\text{C}_9\text{SAc-d}$ is stable in all the four solvents used for deposition of monolayers and no significant decomposition processes are detected well beyond the timeframe required for monolayer formation.

[1] A. L. Barra, F. Bianchi, A. Caneschi, A. Cornia, D. Gatteschi, L. Gorini, L. Gregoli, M. Maffini, F. Parenti, R. Sessoli, L. Sorace and A. M. Talarico, *Eur. J. Inorg. Chem.* **2007**, 4145.

[2] S. Accorsi, A. L. Barra, A. Caneschi, G. Chastanet, A. Cornia, A. C. Fabretti, D. Gatteschi, C. Mortalò, E. Olivieri, F. Parenti, P. Rosa, R. Sessoli, L. Sorace, W. Wernsdorfer and L. Zoppi, *J. Am. Chem. Soc.* **2006**, *128*, 4742.

[3] C. Danieli, A. Cornia, C. Cecchelli, R. Sessoli, A. L. Barra, G. Ponterini and B. Zanfognini, *Polyhedron* **2009**, 2, 2029.

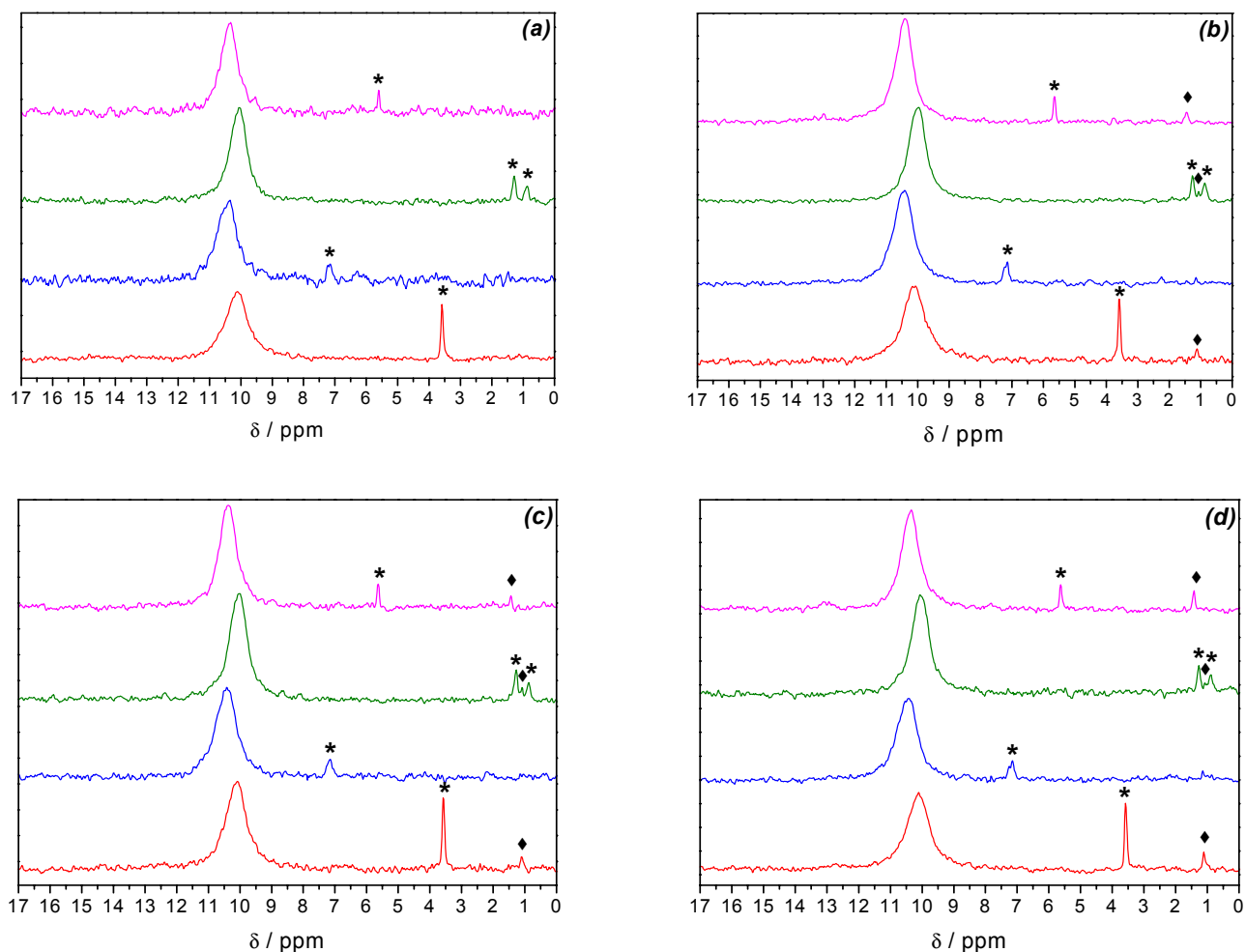


Figure S10. ^2H -NMR spectra of $\text{Fe}_4\text{C}_9\text{SAc-d}$ in the four investigated solvents. Color code: red = 1,4-dioxane (1.3 mM), blue = toluene (1.4 mM), green = *n*-hexane (1.3 mM), magenta = DCM (1.3 mM). Deuterium solvents peaks are marked with *, while traces of free Hdpm-d_{18} are marked with ♦; (a) immediately after dissolution; (b) after 20 hours; (c) after 27 hours; (d) after 50 hours.