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 (H₃L) and [Fe₄(OMe)₆(dpm-d₁₈)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 CaH₂, 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 ¹³C NMR spectra were recorded at 302 K with a Bruker FT-DPX200 spectrometer. Chemical shifts are reported in ppm relative to Me₄Si and the coupling constant values J are expressed in Hz.

2-(Hydroxymethyl)-2-(9-mercaptononyl)propane-1,3-diol (H₃L').

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\text{CH}_3\text{ONa} \quad \text{CH}_3\text{OH}
\]

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 N₂ 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 N₂ 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 MgSO₄, 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-mercaptollynyl)propane-1,3-diol (0.119 g, 69%) as a whitish solid.

δH (200 MHz; CDCl₃; Me₄Si) 3.74 (6H, s, 3 x CH₂OH), 2.52 (2H, dt, J 7.6 and 7.2, CH₂SH), 2.43 (3H, br s, 3 x OH), 1.68-1.53 (2H, m, CH₂CH₂SH), 1.32 (1H, t, J 7.6, SH), 1.40-1.19 (14H, m, 7 x CH₂); δC (50.3 MHz, CDCl₃; Me₄Si) 67.52 (CH₂OH), 42.78 (CIV), 33.78 (CH₂CH₂SH), 30.51 (CH₂), 29.40 (CH₂), 29.36 (2 x CH₂), 28.98 (CH₂), 28.29 (CH₂), 24.59 (CH₂SH), 22.98 (CH₂).

[Fe₄(L₂)(dpm-d₁₈)] (Fe₄C₉SAC-d). To a stirred solution of [Fe₄(OMe)₆(dpm-d₁₈)₆] (0.120 g, 0.0741 mmol) in anhydrous diethyl ether (45 mL), H₃L (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 $\text{Fe}_4\text{C}_9\text{SAc}$ adsorbates on Au(111) from the four investigated solvents.
Figure S4. Detailed XPS spectra of Fe\textsubscript{2p} and O\textsubscript{1s} peaks recorded on Fe\textsubscript{4}C\textsubscript{9}SAc drop cast sample and on Au(111) adsorbates prepared from the four investigated solvents.

Figure S5. Detailed XPS spectra of the S\textsubscript{2s} peaks recorded on Fe\textsubscript{4}C\textsubscript{9}SAc drop cast sample and on Au(111) adsorbates prepared from the four investigated solvents.
Figure S6. $S_{2p}$ fitting components for the $\text{Fe}_4\text{C}_9\text{SAc-exHex}$ 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 $H_3L$ ligand (A) and in the $Fe_4C_9SAC$-$ex$-$Hex$ 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 $H_3L$ ligand and in the $Fe_4C_9SAC$-$ex$-$DCM$ sample.
Figure S9. Negative ToF-SIMS spectra of the molecular peak area of Fe₄C₉SAc drop cast sample (a), and of -exDCM (b), -exHex (c), -exTol (d), and -exDiox (e) SAMs on Au. Panel (f) shows the theoretical isotopic distributions for the molecular peak, [M]⁻, and its oxidized form, [M*]⁻, corresponding to [Fe₄(LL*)₆(dpdm)₈]⁻, where L* is an oxidized tripodal ligand containing a terminal sulphonate group.
Stability experiments in solution by $^2$H 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 $^2$H-NMR. Previous studies [1-3] demonstrated that $^2$H nuclei in Fe$_4$ complexes isotopically-enriched on $\text{dpm}^\text{t}$-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 $\text{H}_3\text{L}$ 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). $^2$H 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 $^2$H-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 $\text{dpm}^\text{t}$ 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 $\text{tBu}$ 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 $\text{tBu}$ signal and is typical of magnetically uncoupled 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.

Figure S10. $^2$H-NMR spectra of Fe$_4$C$_9$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.