

Supplementary Materials

New Silver(I) Coordination Polymer with Fe₄ Single-Molecule Magnets as Long Spacer

Experimental Section (cont.)

Synthesis of 2-(4-bromophenyl)acetaldehyde (3)

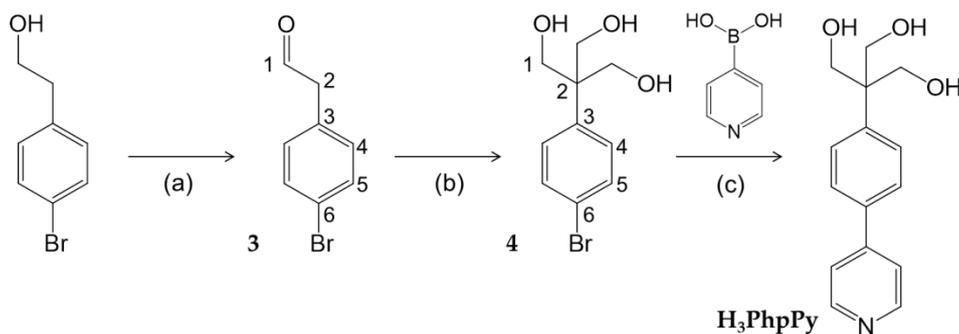
2-(4-bromophenyl)ethanol (0.50 g, 2.49 mmol) was dissolved in a Schlenk tube in CH₂Cl₂ (7 mL, anhydrous over molecular sieves) under Ar atmosphere and the resulting solution was cooled with an ice bath. After 10 minutes TICA (0.50 g, 2.15 mmol) was added, and after further 20 minutes TEMPO (0.30 mL of a 0.070 mol L⁻¹ solution in CH₂Cl₂, 0.021 mmol) was also added dropwise. The orange suspension obtained was stirred for 15 minutes and then filtered over celite, washing with CH₂Cl₂ (2 × 5 mL). The clear orange filtrate was transferred in a separating funnel and washed with aqueous Na₂CO₃ (0.5 g in 2 mL H₂O), becoming almost colorless. The aqueous phase was extracted with CH₂Cl₂ (1 mL). The organic phases were unified and washed with aqueous HCl 5% *w/w* (5 mL), then filtered and dried over MgSO₄. The solvent was removed under reduced pressure yielding the title compound as white crystalline solid (0.47 g, 95%). TLC (PE:Et₂O 1:1) r.f. = 0.3. GC-MS: r.t. = 11.97, *m/z* = 198-200 [M]⁺. ¹H NMR (400 MHz, 298 K, CDCl₃): δ 3.66 (d, *J* = 2.12 Hz, 2H, H₂), 7.09 (m, 2H, H₄), 7.49 (m, 2H, H₅), 9.73 (t, *J* = 2.12 Hz, 1H, H₁) (see Scheme S1 for atom numbering).

Synthesis of 2-(4-bromophenyl)-2-(hydroxymethyl)propane-1,3-diol (4)

3 (0.50 g, 2.51 mmol), paraformaldehyde (0.50 g, 16.7 mmol), Ca(OH)₂ (0.25 g, 3.37 mmol) and Al(O*i*Pr)₃ (0.05 g, 0.24 mmol, 10%) were suspended in THF (2.9 mL, anhydrous over molecular sieves) under Ar atmosphere. The obtained reaction mixture was left under stirring at 65 °C for 5 days, then cooled to room temperature, filtered on Gooch G3 and Celite and washed with CH₂Cl₂ (5 × 1 mL), yielding a yellow solution. The solvent was removed under reduced pressure and the crude yellow oil was purified via column chromatography (h = 14.0 cm, Ø = 2.0 cm) with silica and PE:AcOEt:CH₂Cl₂ (35.0:12.5:2.5, 50.0 mL), PE:AcOEt:CH₂Cl₂ (22.5:25.0:2.5, 50.0 mL), PE:AcOEt:CH₂Cl₂ (17.5:30.0:2.5, 50.0 mL), PE:AcOEt:CH₂Cl₂ (15:80:5, 200 mL), AcOEt:CH₂Cl₂ (95:5, 100 mL) as eluent. The fractions containing the desired product were collected and the solvent removed under reduced pressure, yielding a yellow oil (0.28 g, 42%). TLC (PE:AcOEt 1:4) r.f. = 0.12. GC-MS: not performed due to the high affinity of the triol unit to the stationary phase of the column. ¹H NMR (400 MHz, 298 K, CDCl₃): δ 3.00 (br, 3H, OH), 3.97 (s, 6H, H₂), 7.24 (m, 2H, H₄), 7.48 (m, 2H, H₅) (see Scheme S1 for atom numbering).

Attempted Synthesis of H₃PhpPy from 4

4 (0.203 g, 0.777 mmol), pyridin-4-ylboronic acid (0.086 g, 0.70 mmol) and anhydrous Na₂CO₃ (0.083 g, 0.78 mmol) were introduced in a Schlenk tube under Ar atmosphere. Then Pd(PPh₃)₄ (0.045 g, 0.039 mmol) was added together with the DMF:H₂O solvent mixture (6+2 mL, 3:1). The dark yellow solution was kept under stirring at 110 °C for 24 h, and then it was cooled to room temperature and open to air to decompose any unreacted catalyst. The reaction mixture was extracted with CH₂Cl₂ (2 × 5 mL), and the organic layer was checked by TLC (both PE:AcOEt 1:4 and AcOEt:EtOH 9:1) revealing the presence of different spots, neither of them corresponding to the desired product, as also confirmed by ¹H NMR analysis. Several attempts modifying reaction temperature or time did not yield any improvement.



Scheme S1. (a) TICA, TEMPO, CH_2Cl_2 , 0 °C, 15 min; (b) paraformaldehyde, $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{O}i\text{Pr})_3$, THF, 65 °C, 5 days; (c) Na_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, DMF:H₂O 3:1, 110 °C, 24 h; atom numbering as used for NMR assignment.

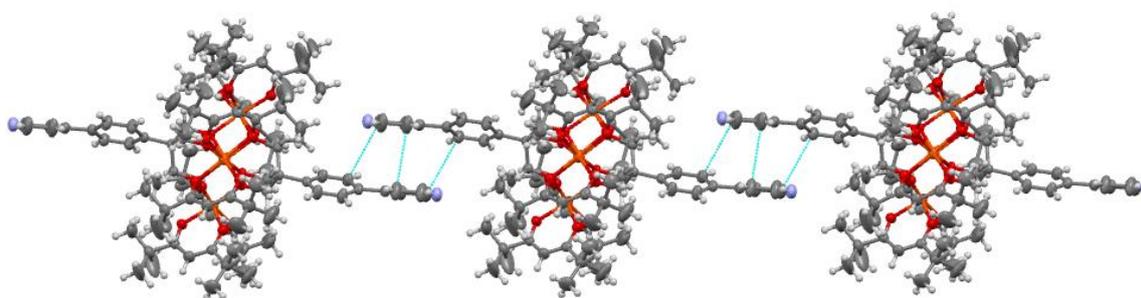


Figure S1. Crystal packing in Fe_4 with ellipsoids at 20% probability and highlighted weak $\pi\cdots\pi$ stacking interactions in light blue; color code: Fe = orange, O = red, N = blue, C = grey, H = white.

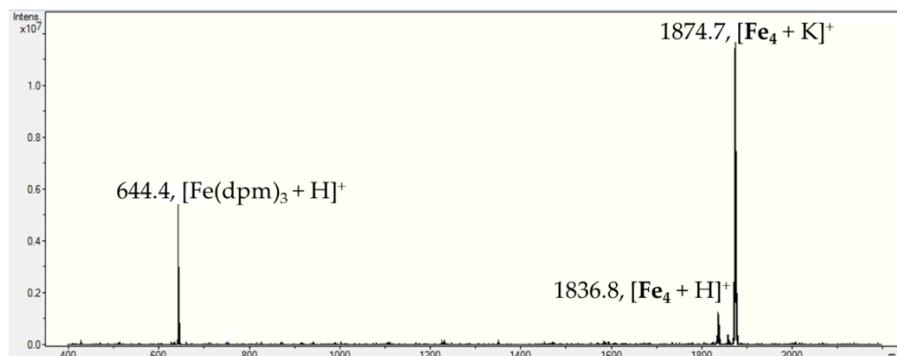


Figure S2. ESI-MS spectrum in THF/ CH_3CN of the reaction mixture for the synthesis of Fe_4 after 5 h of stirring in EtOH at room temperature.

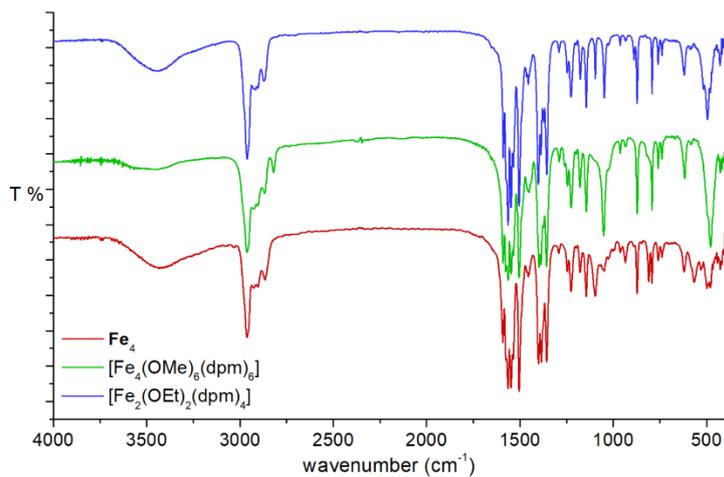


Figure S3. Comparison among the infrared spectra of $[\text{Fe}_2(\text{OEt})_2(\text{dpm})_4]$, $[\text{Fe}_4(\text{OMe})_6(\text{dpm})_6]$ and Fe_4 as KBr disks.

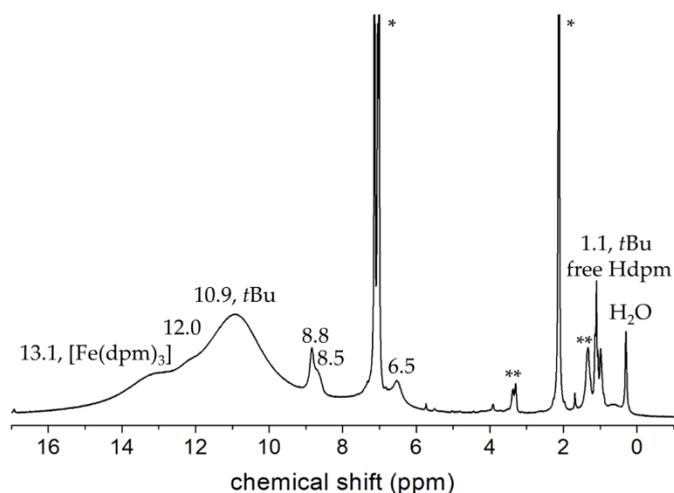


Figure S4. ^1H NMR spectrum of Fe_4 in toluene- d_8 at room temperature; * indicates toluene residual signals, while ** denotes EtOH.

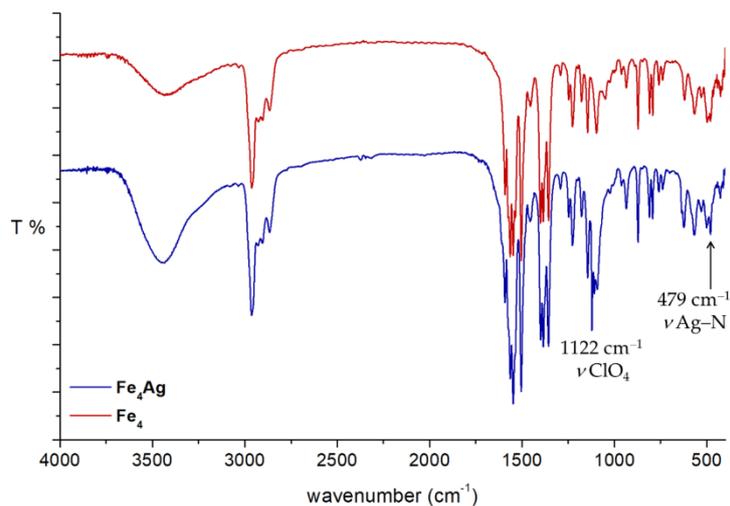


Figure S5. Comparison among the infrared spectra of Fe_4 and Fe_4Ag as KBr disks.

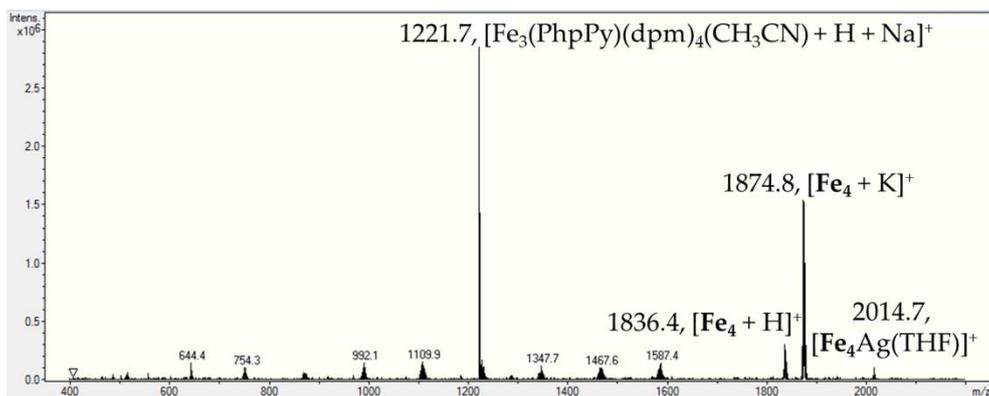


Figure S6. ESI-MS spectrum in THF/CH₃CN of Fe₄Ag.

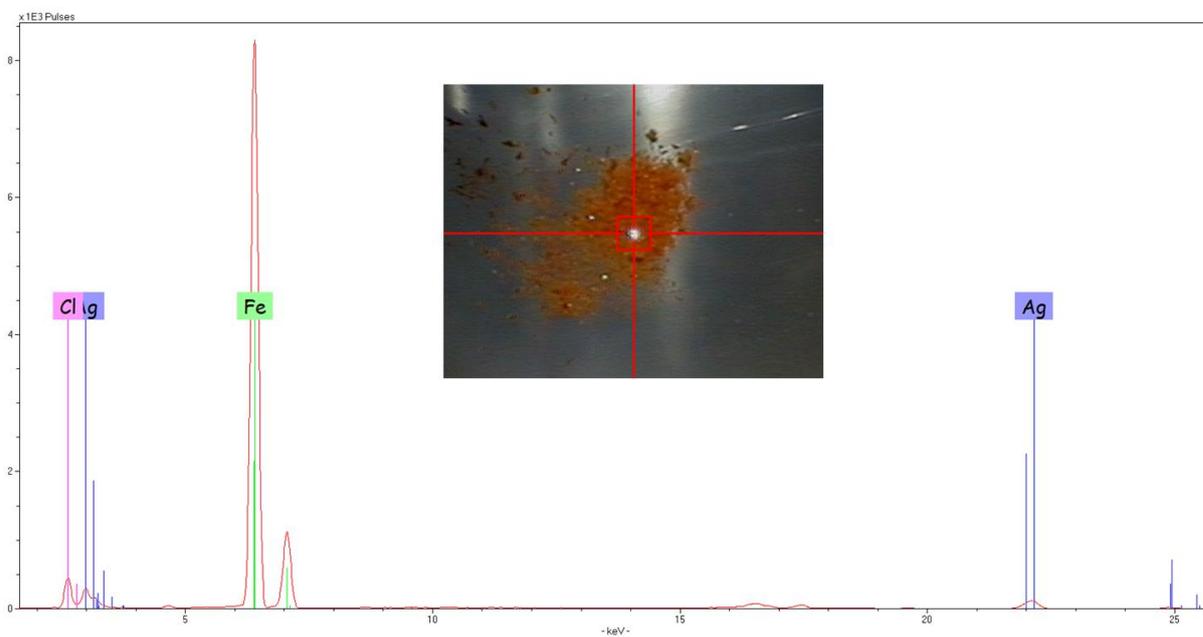


Figure S7. X-ray fluorescence (XRF) spectrum of Fe₄Ag with a view of the orange microcrystals.

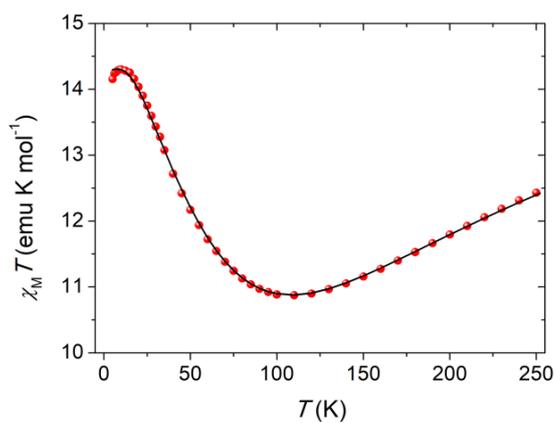


Figure S8. Temperature dependence of $\chi_M T$ for Fe₄; solid curve is calculated using the best-fit parameters reported in the text.

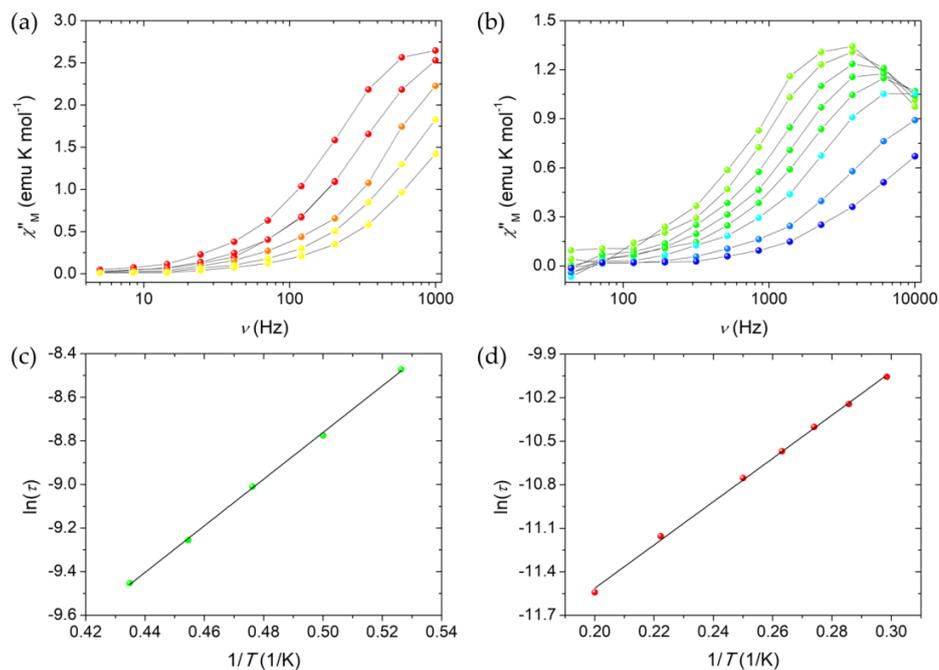


Figure S9. Imaginary component of the ac susceptibility, χ''_M , of Fe_4 measured at (a) zero applied static field in the 1.9(red)–2.3(yellow) K temperature range and in the 10–1000 Hz frequency range, and (b) 1 kOe applied static field in the 3.2(green)–5.0(blue) K temperature range and in the 40–10000 Hz frequency range; grey lines are a guide for the eye. Arrhenius plots for Fe_4 both at (c) zero and (d) 1-kOe applied static field; black lines are given by fitting data with the Arrhenius law.