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Diamondoid Structure in a Metal-Organic Framework of Fe₄ Single-Molecule Magnets

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Abstract: A 3D Metal-Organic Framework comprising Single-Molecule Magnet (SMM) linkers was prepared in crystalline form using a tetrairon(III) complex functionalized with two divergent pyridyl groups, $[\text{Fe}_4(\text{pPy})_2(\text{dpm})_6]$ (**1**) (H_3pPy = 2-(hydroxymethyl)-2-(pyridin-4-yl)propane-1,3-diol, Hdpm = dipivaloylmethane). Reaction of **1** with silver(I) perchlorate afforded $\{[\text{Fe}_4(\text{pPy})_2(\text{dpm})_6]_2\text{Ag}\}(\text{ClO}_4)$ (**2**), which crystallizes in a cubic face-centred lattice and displays two diamondoid interlocked networks. In **2**, the SMMs act as linear ditopic synthons and silver(I) ions as tetrahedral nodes coordinated by four pyridyl nitrogen atoms. The magnetic properties of **1** ($S = 5$ and $D \sim -0.4 \text{ cm}^{-1}$ in the ground spin state) are largely preserved in **2**, which shows slow magnetic relaxation with anisotropy barriers $U_{\text{eff}}/k_{\text{B}} = 11.46(10) \text{ K}$ in zero field and $14.25(8) \text{ K}$ under a 1-kOe applied field. However, crystal symmetry triggers highly-noncollinear magnetic anisotropy contributions arranged at 109.47° from each other along the threefold axes of AgN_4 tetrahedra, unique scenario fully confirmed by a single-crystal investigation using Cantilever Torque Magnetometry. Magnetization curves down to 0.03 K demonstrated the occurrence of a wide hysteresis loop when the magnetic field was swept along one of the four Ag–N bonds. By symmetry, the crystalline compound can then be persistently magnetized parallel or antiparallel to the four main diagonals of the unit cell, although crystals have no overall second-order anisotropy.

Introduction

Single-Molecule Magnets (SMMs)^[1] have been widely investigated over the last two decades as nanoscale, chemically-tuneable entities displaying a directionally-bistable magnetic moment, a property that can find application in spin-dependent electronics and neighbouring fields.^[2,3] Currently SMMs display slow relaxation of the magnetization only well below liquid nitrogen temperature, but their performance can be for sure developed by exploiting exotic spin carriers^[4] or unusual coordination geometries.^[5] Another promising strategy consists in biasing the magnetic behaviour of SMMs by assembling them into extended coordination networks, so as to achieve enhanced magnetic remanence.^[6,7]

Our ongoing project focuses on the supramolecular chemistry of the tetrairon(III) complex $[\text{Fe}_4(\text{pPy})_2(\text{dpm})_6] \cdot 2\text{EtOH}$ (**1**·2EtOH), where H_3pPy = 2-(hydroxymethyl)-2-(pyridine-4-yl)propane-1,3-diol and Hdpm = dipivaloylmethane.^[7] As a member of the family of propeller-like Fe_4 SMMs,^[8,9] it comprises four high spin iron(III) ions ($s = 5/2$). The central metal (Fe^{c}) is antiferromagnetically coupled to the three peripheral ones (Fe^{p}), which are arranged at the vertices of an almost equilateral triangle, so as to give an $S = 5$ spin ground state. Complexes of this family feature an easy axis anisotropy along the normal to the metal plane, with $D \sim -0.4 \text{ cm}^{-1}$ and anisotropy barriers reaching up to 15–17 K. The presence of the two divergent 4-pyridyl

substituents on the tripodal ligands allows **1** to behave as a ditopic supramolecular synthon, as recently demonstrated by the assembly of 1D chains using ruthenium paddlewheel dimers as linkers.^[7]

The present work further shows the ability of this SMM to give extended supramolecular structures. In particular, by reaction of **1** with AgClO₄ we obtained the compound **{[Fe₄(pPy)₂(dpm)₆]₂Ag}(ClO₄)** (**2**), a three-dimensional Metal-Organic Framework (3D-MOF) crystallizing in a cubic space group. Its crystal structure consists of two interlocked **dia** networks, according to IUPAC nomenclature,^[10–12] with silver ions as the tetrahedral nodes coordinated by four pyridyl nitrogen atoms of Fe₄ complexes. Performing magnetic measurements and W-band Electron Paramagnetic Resonance (EPR) spectroscopy experiments we found that the Fe₄ units retain the same magnetic behaviour as in **1**·2EtOH. Single-crystal studies by Cantilever Torque Magnetometry (CTM) were then used to prove the highly noncollinear arrangement of anisotropy axes in the compound. Although crystals of **2** have by symmetry no second-order anisotropy, wide hysteresis loops were observed by microSQUID magnetometry when the magnetic field was applied along the main diagonal of the unit cell.

Results and Discussion

Synthesis and characterization

The reaction of **1**·2EtOH with AgClO₄ was investigated in different conditions exploiting tetrahydrofuran (THF) as appropriate solvent for both reactants. When the two reagents are dissolved in THF in a 2:1 molar ratio (**1**·2EtOH ca. 5 mM) no precipitate is formed. Crystal growth can be promoted by either liquid diffusion of dichloromethane (DCM), vapour diffusion of toluene or liquid diffusion of toluene. The best yield in the 3D-MOF is achieved by layering the reaction mixture in THF over an equal volume of DCM, so as to reach a final 1:1 (v/v) solvent ratio (*Method Ia*). Large red X-ray quality crystals of **2** (see below) were so obtained in a few days in reasonable yield (51.6%). Vapour diffusion of toluene into the THF reaction solution leads to **2** in mixture with a second, so far uncharacterized crystalline phase; pure **2** can be obtained using a slight understoichiometric amount of AgClO₄ in the reaction (*Method Ib*). Liquid diffusion of toluene also gives **2**, though as bad quality crystals and in poor yields. An alternative procedure to *Methods Ia* and *Ib* consists in separately dissolving AgClO₄ in THF (ca. 2.2 mM) and **1**·2EtOH in DCM (ca. 4.4 mM) and then allowing the former solution to slowly diffuse into an equal volume of the latter (*Method II*). This procedure gives crystals of superior quality to *Method Ia*, although in lower yield. By comparison, when the reaction was carried out directly in a THF:DCM 1:1 mixture with the

same concentration of the reactants, we observed immediate precipitation of an orange powder whose composition closely corresponds to the desired 3D-MOF.

The large cavities of this 3D-MOF (see below) can trap solvent molecules in addition to the perchlorate counterions. In order to check the ability of encapsulating THF or DCM, few crystals of **2** prepared using *Method Ia* were taken from the mother liquor, quickly dried at ambient pressure, weighed and then sonicated in deuterated benzene. Using ferrocene as internal standard, ^1H NMR spectra gave 2.6 molecules of DCM and 2.1 molecules of THF per formula unit, in agreement with the size of the lattice cavities (see below). Based on these data, solvent removal from the 3D framework should result in a 9.48% weight loss. The solvent content was then investigated by thermogravimetric analysis (TGA), which showed a continuous weight loss of 9.22% from room temperature to about 140 °C (Supporting Information, Figure S1a), in complete agreement with ^1H NMR results. The empty 3D-MOF structure was found stable up to 220 °C, before decomposition sets in in three exothermic steps (Supporting Information, Figure S1b). Also drying in vacuum at room temperature removes all lattice solvent molecules of **2**, but crystallinity and homogeneity remain unaffected as judged by visual inspection under an optical microscope and confirmed by several X-ray diffraction analyses on different batches of crystals, which are isomorphous with the solvated form (Supporting Information). X-ray diffraction studies and all magnetic characterizations were then carried out on vacuum-dried samples.

Comparison of the IR spectra of **1**·2EtOH^[7] and **2** shows significant similarities, with common bands arising from the dpm[−] and tripodal ligands, as well as from Fe–O bond stretching. The broad O–H stretching band at 3398 cm^{−1} in the spectrum of **1**·2EtOH, which contains hydrogen-bonded ethanol molecules, is of course absent in the infrared spectrum of **2**. The narrow C–O stretching band at 1105 cm^{−1} in **1** becomes more intense, broadens and moves to 1108 cm^{−1} in **2**, as expected from the additional, overlapping contribution of perchlorate stretching band (Supporting Information, Figure S2).

By comparison with the theoretical isotopic patterns, the two most intense peaks at $m/z = 1791.7$ and 1184.3 in the MALDI-ToF mass spectra of **2** can be unambiguously attributed to the fragments $[\text{Fe}_4(\text{pPy})_2(\text{dpm})_6 + \text{Ag}]^+$ and $[\text{Fe}_4(\text{pPy})_2(\text{dpm})_6 - \text{Fe}(\text{dpm})_3 + \text{Ag}]^+$ (Supporting Information, Figure S3), consistent with coordination of Ag⁺ ions by the nitrogen atoms of **1**.

X-ray structure determination

The structure of **2** in the solid state was investigated by single-crystal X-ray diffraction at 110 K. The compound crystallizes in the cubic space group $Fd\bar{3}c$ as well-formed red crystals with a remarkably large unit cell ($V = 87037(4) \text{ \AA}^3$). The unit cell contains 32 symmetry-equivalent Fe₄

units similar in structure to the tetrairon(III) complexes in **1**·2EtOH (Figure 1a).^[7] For instance the dihedral angle between the Fe₄ and Fe1(O1)₂Fe2 least square planes, a parameter of paramount importance for magnetic anisotropy,^[9] has the same value in **1**·2EtOH and **2** (68.7°). However, while in **1** crystallographic molecular symmetry is *C*₂, Fe₄ complexes in **2** develop on *D*₃-symmetry sites and have crystallographically-imposed threefold symmetry along the main diagonals of the cubic unit cell. The Fe₄ units thus adopt four different orientations in the structure, with threefold axes oriented at 109.47° from each other. Each Fe₄ unit coordinates two Ag⁺ ions in opposite (180°) directions through its 4-pyridyl nitrogen atoms. The Ag⁺ ions (16 per unit cell) lie on *T* symmetry sites and are coordinated by four 4-pyridyl groups each in a perfect tetrahedral geometry (Ag1–N1 = 2.258(7) Å, N1–Ag1–N1 = 109.47°) (Figure 1b, Supporting Information, Figure S4 for depiction of symmetry elements). This arrangement brings Fe1 at 9.60 Å from Ag1 and at 15.67 Å from equivalent atoms of neighbouring Fe₄ units, whereas the shortest intermolecular Fe···Fe distance in the structure is 12.94 Å.

Figure 1. a) Top and b) side views of the Fe₄ units in **2** highlighting the 180°-ditopic Fe₄ supramolecular linker with two Ag⁺ ions coordinated by the nitrogen atoms of the 4-pyridyl rings (Ag = big grey, Fe = big light grey, O = black, N = grey, C = light grey, H atoms and ClO₄[−] anions omitted for clarity, pyridyl rings appear in only one space orientation). Selected interatomic distances and interbond angles: Fe1···Fe2 = 3.1056(15) Å, Fe2···Fe2' = 5.3791(25) Å, Fe1–O1 = 1.977(4) Å, Fe2–O1 = 1.983(4) Å, Fe2–O2 = 1.972(4) and Fe2–O3 = 1.991(4) Å, Fe1–O1–Fe2 = 104.5(8)°.

Overall, the propeller-like Fe₄ units act as linear ditopic linkers between pairs of Ag⁺ ions, which function as tetrahedral nodes. The resulting 4-connected non-centrosymmetric diamondoid lattice (**dia**-net topology^[10–12]) is interlocked with a second lattice of the same type obtained by inversion (Figure 2 and Supporting Information, Figure S5). As a matter of notice, a CSD survey showed that very few coordination compounds crystallize in cubic space group *Fd*–3*c*,^[13–16] and none of them contains two interlocked **dia** networks as in **2**. As described in the Experimental Section, the structure exhibits three different types of disorder: *i*) the 4-pyridyl ring develops along a

crystallographic threefold axis and consequently is found disordered over three different positions; *ii*) a minority fraction [0.133(2)] of Fe₄ linkers is rotated by 60° around the Ag...Fe₄...Ag direction, with coinciding central ions (Fe1) but distinct peripheral metals (Fe2 and Fe2a), a feature already reported in the literature;^[17] *iii*) as found in few other isostructural Fe₄ derivatives,^[8] the two dpm[−] ligands bonded to the same iron(III) ion adopt two different coordination modes, propeller-like (*p*) and sandwich-like (*s*); the ratio *p*:*s* is close to 60:40 and a complex distribution of Fe₄ isomers is therefore expected. The arrangement of dpm[−] ligands in each unit will contribute to determine its local symmetry, besides influencing the symmetry of neighbouring units. It follows that the local symmetry of Fe₄ complexes is not necessarily threefold, in agreement with magnetic data (see below). The structure contains 12415 Å³ (14.3%) of accessible voids per unit cell, an empty volume sufficient to host the solvent content found by ¹H NMR and TGA experiments (see above) and the perchlorate anions, which were only partially located in the cavities (Supporting Information).

Figure 2. Perspective view of the unit cell of **2** with the two interlocked diamondoid networks, depicted in black and grey. Pyridyl rings appear in only one space orientation while dpm[−] ligands, H atoms and ClO₄[−] anions are omitted for clarity.

Direct current (DC) magnetic measurements and W-band EPR

The temperature dependence of the low field (1-10 kOe) molar magnetic susceptibility (χ_M) for a polycrystalline sample of **2** was measured between 1.9 and 300 K (data are here given per Fe₄ cluster). The $\chi_M T$ -vs-*T* curve, presented in Figure 3a, is typical for Fe₄ systems.^[8,9] Antiferromagnetic nearest-neighbour interactions lead to a room-temperature $\chi_M T$ value lower than expected for four uncoupled high spin iron(III) ions ($\chi_M T = 12.29$ emu K mol^{−1} vs. 17.51 emu K mol^{−1} for *g* = 2.00). Upon cooling, the $\chi_M T$ product first decreases, reaching a minimum (10.31 emu K mol^{−1}) at 120 K, and then increases again up to 13.93 emu K mol^{−1} at 12.5 K, in reasonable

agreement with the selective population of an $S = 5$ ground state (expected value $15.00 \text{ emu K mol}^{-1}$ with $g = 2.00$). Several factors may contribute to the final drop of $\chi_M T$ at the lowest T , including magnetic saturation, anisotropy effects or intermolecular interactions. In order to evaluate the magnetic exchange interactions among the four iron(III) centres, $\chi_M T$ -vs- T data were analysed using a Heisenberg *plus* Zeeman spin Hamiltonian, assuming three-fold molecular symmetry:

$$\hat{H}_0 = J (\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_4) + J' (\hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_4) + g\mu_B \hat{S} \cdot \mathbf{B} \quad (1)$$

In Eq. (1), $\mathbf{S}_1$ is the spin vector for Fe^c while $\mathbf{S}_2$, $\mathbf{S}_3$ and $\mathbf{S}_4$ are the spin vectors for the three Fe^p centres and J and J' are the nearest-neighbour (n.n.) and the next-nearest neighbour (n.n.n.) exchange coupling constants, respectively. $\mathbf{S}$ is used to indicate the total spin vector, μ_B is Bohr magneton and $\mathbf{B}$ is the external magnetic induction (when quoting quantitative magnetic data the CGSemu unit system is used and the applied field is given in Oe as $\mathbf{H}$). The best-fit values of J and J' so obtained are $16.41(6)$ and $0.035(36) \text{ cm}^{-1}$, respectively. The low temperature magnetic properties were better evaluated by measuring the field-dependent isothermal molar magnetization (M_M) at 1.9, 2.5 and 4.5 K. Data are plotted in the inset of Figure 3a as M_M -vs- H/T to highlight the nesting of isothermal curves typically associated with magnetic anisotropy. These data were fitted using an axial zero-field splitting (zfs) *plus* Zeeman Hamiltonian:

$$\hat{H}_{\text{zfs}} = D[\hat{S}_z^2 - S(S+1)/3] + g\mu_B \hat{S} \cdot \mathbf{B} \quad (2)$$

where $S = 5$ and S_z is the component of the total spin vector along the anisotropy axis (z), giving $D = -0.411(2) \text{ cm}^{-1}$. The exchange coupling constants and the D parameter are close to those found in **1**·2EtOH (Supporting Information, Table S1).^[7] The static magnetic behaviour of the Fe_4 units thus remains largely unaffected by their supramolecular organization.

Figure 3. a) Temperature dependence of the molar susceptibility (χ_M) multiplied by the temperature (T) for **2**; the inset shows the field dependence of the isothermal molar magnetization (M_M) at 1.9 (Δ), 2.5 (O) and 4.5 ($\square$) K; black lines are calculated data using the best fit parameters (see text). b) Arrhenius plots of $\ln(\tau)$ vs $1/T$ for compound **2** obtained from AC susceptibility measurements at zero and 1 kOe applied static field.

In order to obtain independent information on magnetic anisotropy, we also recorded W-band ($\nu \approx 94$ GHz) EPR spectra on microcrystalline powders of **2** at 40 K (Figure 4). The spectrum shows the typical features observed in several Fe₄ derivatives measured at this frequency.^[18–23] Of particular relevance for the determination of the axial zfs parameter D is the low-field transition, assigned to the $M_S = -4 \rightarrow M_S = -3$ resonance.^[18] For a quantitative estimation of the anisotropy parameters we undertook spectral simulations^[24] based on the following fourth-order spin Hamiltonian, which contains terms permitted by the crystallographic point-group symmetry of the Fe₄ units (D_3) but also allows for local deviation from axial symmetry:

$$\hat{H}_{EPR} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \hat{\mathbf{S}} + D \hat{S}_z^2 + E (\hat{S}_x^2 - \hat{S}_y^2) + B_4^0 \hat{O}_4^0 + B_4^3 \hat{O}_4^3 \quad (3)$$

Here, $\mathbf{g}$ is the Landé matrix, D and B_4^0 are the second- and fourth-order axial anisotropy parameters, respectively, E describes second-order transverse anisotropy, while B_4^3 accounts for transverse trigonal anisotropy.^[25] A reasonable reproduction of the spectrum could be obtained with the following parameter set: $S = 5$, $D = -0.409(3) \text{ cm}^{-1}$, $E = 0$, $B_4^0 = +3(1) \times 10^{-5} \text{ cm}^{-1}$, $B_4^3 = +1.0(2) \times 10^{-3} \text{ cm}^{-1}$, $g_{x,y} = 1.992(2)$, $g_z = 2.005(2)$.

It is to be noted that the position of the highest field perpendicular transitions could only be reproduced assuming $E = 0$ and including a nonzero transverse trigonal term. At the same time, the large variation of linewidth across the spectrum hints to broad distributions (i.e. strains) of the parameters around the given average values. Correct spectral simulation required including strains $\sigma(D) = 0.03 \text{ cm}^{-1}$, $\sigma(B_4^3) = 2.0 \times 10^{-3} \text{ cm}^{-1}$ and $\sigma(E) = 0.05 \text{ cm}^{-1}$. The latter should be exactly zero for an axial system, but local deviations from axial symmetry may be triggered by 4-pyridyl substituents and/or by p/s disorder (see above).

Figure 4. Experimental W-band ($\nu = 94.3247$ GHz) EPR spectrum of **2** measured at 40 K, together with its simulation using the best-fit parameters reported in the text.

Torque magnetometry

To gain further insight into the magnitude, sign and orientation of molecular anisotropies in **2**, we performed a single-crystal investigation by CTM. To this purpose, a face-indexed single crystal of **2** was mounted on a cantilever magnetometer and two rotations were carried out, hereafter referred to as **rot1** and **rot2** (Supporting Information for further details).^[26] In all cases the torque response was measured along the rotation axis, whereas the magnetic field was applied normal to it. To understand how the two rotations were performed, it is convenient to focus on the four noncollinear Fe₄ units linked to the same Ag⁺ ion (Figure 5), as all the other molecules in the unit cell are magnetically equivalent to them. The rotation axis for **rot1** was one of the main diagonals of the cubic unit cell, i.e. the [111] direction, which corresponds to a C₃ axis in the structure (Figure 5a). In **rot2** the rotation axis was one of the edges of the unit cell, i.e. the [001] direction, which is parallel to an S₄ axis (Figure 5b). The torque signal recorded at $T = 2$ K and variable field in **rot1** is presented in Figure 5a. The observation of *three* oscillations in the angular range from 0° to 180° provides direct evidence of the threefold magnetic symmetry around the rotation axis (the slightly different amplitude of the three oscillations in Figure 5a has to be attributed to small misalignments in the process of fixing the crystal on the cantilever). Since in **rot1** one Fe₄ unit (hereafter denoted as Fe₄-p) lies in the rotation plane, it is legitimate to expect that its in-plane anisotropy, described by the nonzero B_4^3 coefficient in Eq. (3), may contribute to the observed modulation. However, it has to be borne in mind that the effect is almost completely quenched by the strong intramolecular coupling, which causes second-order axial anisotropy to dominate over higher-order terms.^[26] The resulting deviations from cylindrical symmetry are then too small to account for the observed behaviour and the on-axis Fe₄ unit can be safely assumed to provide no contribution to the torque signal in this rotation. The three remaining Fe₄ units related by the C₃ axis (hereafter denoted as Fe₄-t) provide noncollinear anisotropic contributions which may indeed afford threefold modulation, as long as two requirements are fulfilled. First, the magnetic centres must be only weakly-coupled or magnetically independent. Second, their magnetic response must show deviations from the relationship $\mathbf{M}_i = \chi_i \cdot \mathbf{H}$, where χ_i is the individual T -dependent magnetic susceptibility tensor. Otherwise, the overall magnetic response would also be tensorial in nature and isotropic in a plane orthogonal to a threefold or fourfold axis. This requires working at sufficiently low temperatures and/or in large applied fields, as firmly established by previous reports.^[26–29]

Torque data recorded at $T = 2$ K and variable field in **rot2** (Figure 5b) feature only two oscillations from 0° to 180° (data at other temperatures and fields can be found in Supporting Information, **Figure S6**). In fact, pairs of Fe₄ units related by twofold rotation along the S₄ axis have

coincident projections of their easy axes in the rotation plane and the torque response arises from just two noncollinear contributions.

Figure 5. Left panels: Torque signal of **2** measured at $T = 2$ K and for different values of the applied field in a) **rot1** and b) **rot2**. The solid black curves provide the best fit to experimental data. Right panels: Polar plot of the absolute value of the torque at $T = 2$ K and $B = 2$ T (**rot1**) or $B = 1$ T (**rot2**) plotted on the molecular structure (dark grey: positive values, light grey: negative values).

For a quantitative treatment of the data, each Fe_4 unit was described using Eq. (2) and taking $g = 2.00$. The four local easy axes z were oriented at 109.47° from each other, in compliance with the T symmetry arrangement found in the structure. At nominally zero rotation angle the crystallographic components of the applied field vector were $[-0.408, -0.408, 0.816]$ in **rot1** and $[0.707, 0.707, 0]$ in **rot2**. To compensate for the limited accuracy of visual crystal alignment, allowance was first made for small misalignments in the direction of the rotation axis and for an offset in rotation angle. Using least-squares methods with D fixed to -0.41 cm^{-1} and refining a scale factor for each rotation, we found that the actual rotation axes deviate by 4.4° and 2.4° from the expected direction in **rot1** and **rot2**, respectively, whereas the offsets on rotation angles are zero within their estimated standard deviations (esds). The scale factors of the two rotations were also identical within their esds. The angular corrections were then held fixed and least squares fitting carried out on all recorded data (including those reported in Supporting Information, [Figure S6](#)) by refining the D parameter and an overall scale factor. The best fit was achieved with $D = -0.426(6) \text{ cm}^{-1}$ (black

lines in Figure 5), in remarkably good agreement with DC magnetic measurements and EPR spectra. For a more direct appreciation of the anisotropic magnetic response of **2**, in Figure 5 we present selected torque data in the form of a polar plot superimposed to molecular structure.

In addition, in Figure 6 we report free magnetic energy (F) surfaces computed for the ensemble of four noncollinear Fe_4 units linked to the same Ag^+ ion. At 2 K and 20 kOe (Figure 6a) F is minimum when the external field is applied along the unit cell axes ([001] and symmetry equivs.), which correspond to easy magnetic directions. Hard directions are found along [110] and symmetry equivs., whereas the main diagonals of the unit cell ([111] and symmetry equivs.) are intermediate magnetic axes for the crystal. As expected, when temperature is increased to 5 K and the applied field is lowered to 10 kOe (Figure 6b) F shows a vastly reduced angular dependence. The observed orientation of easy, intermediate and hard magnetic axes in Figure 6a can be easily grasped by modelling Fe_4 centres in **2** as purely Ising spins, *i.e.* with magnetic moment $\pm g\mu_B S$ along the easy axis. With this constrain, and choosing the spin configuration that minimizes Zeeman energy, the total magnetic moment (in units of $g\mu_B S$) for the ensemble of four noncollinear Fe_4 units equals $4/\sqrt{3} = 2.3094$ when the field is directed along [001], 2.0000 when the field is along [111] and $2\sqrt{2}/\sqrt{3} = 1.6330$ when it is along [110]. Compound **2** thus entails strongly anisotropic, high-spin units assembled into a highly symmetric cubic lattice with no second-order magnetic anisotropy. It was therefore of direct interest to probe magnetic relaxation rate, using both alternating current (AC) magnetic measurements and single-crystal microSQUID studies.

Figure 6. Free magnetic energy F for the ensemble of four noncollinear Fe_4 units in **2** as a function of applied field orientation, computed with $D = -0.42 \text{ cm}^{-1}$, $g = 2.000$ and a) $T = 2 \text{ K}$, $H = 20 \text{ kOe}$ or b) $T = 5 \text{ K}$, $H = 10 \text{ kOe}$. The distance of each point from the centre of each diagram is proportional to $F + F_0$, where F_0 is an offset used for a clearer representation. The angular dependence of F is also displayed using a colour scale (from blue to red). The F values in a) and b) span ca. 3.20 and 0.135 cm^{-1} , respectively.

Alternating current (AC) magnetic measurements

To investigate the magnetization dynamics, the same polycrystalline sample of **2** used for DC measurements was subject to AC susceptibility studies in zero static field. The analysis was performed as a function of both temperature (down to 1.8 K) and frequency of the oscillating field ($\nu = 10\text{--}10000$ Hz). Frequency dependent maxima were detected in the χ_M'' -vs- T plots, indicating that **2** behaves as a SMM like the pristine cluster **1**·2EtOH (Supporting Information, [Figure S7](#)). Quantitative data treatment was based on a generalised Debye model (Supporting Information), in order to extract the temperature-dependent relaxation time τ and the width of its distribution, α . Application of a static field $H = 1$ kOe was found most effective in slowing down relaxation by cutting quantum tunnelling (QT) pathways (Supporting Information, [Figures S8, S9 and S10](#)). The values of $\ln(\tau)$ obtained at both $H = 0$ and 1 kOe are plotted against $1/T$ in Figure 3b. In both cases, the linear trend indicates a thermally activated relaxation process in the explored temperature range, where the relaxation time obeys Arrhenius law $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$. A linear fit to the data gave $\tau_0 = 1.65(8) \times 10^{-7}$ s and $U_{\text{eff}}/k_B = 11.46(10)$ K in zero static field, and $\tau_0 = 3.21(11) \times 10^{-7}$ s, $U_{\text{eff}}/k_B = 14.25(8)$ K at 1 kOe. With only a slightly less negative D value, **2** has significantly lower effective relaxation barriers than **1**·2EtOH at both $H = 0$ and 1 kOe,^[7] hinting to more effective QT processes. These may result from the greater rhombic distortion evidenced by EPR spectra or from weak inter-SMM interactions.

MicroSQUID measurements

Using a microSQUID magnetometer, the magnetization of a single crystal of **2** was recorded with the external magnetic field applied along the [111] direction of the cubic cell. With this orientation, **B** is directed parallel to the easy axis of one fourth of the Fe_4 units ($\text{Fe}_4\text{-p}$) but lies at 109.47° from the easy axes of the remaining molecules in the crystal ($\text{Fe}_4\text{-t}$). Raw magnetization data are strongly affected by such pronounced noncollinearity and display a constant slope with no tendency to saturate up to the highest explored fields (1.2 T). To allow a direct comparison with other Fe_4 systems, a linear contribution was subtracted. Raw and corrected data recorded at 0.03 K and variable field sweep rates are available in Supporting Information, [Figures S11 and S12](#). The corrected data recorded at 0.035 T s^{-1} and different temperatures are presented in Figure 7a. Simple paramagnetic behaviour is detected above 1.0 K, while at lower temperatures a hysteresis loop opens, displaying increasing coercivity with decreasing temperature and increasing scan rate. The loop becomes temperature independent below 0.4 K, signalling that a purely QT regime is attained. To better characterize spin dynamics in the system, zero field relaxation was directly followed as a function of time (Supporting Information, [Figure S13](#)). As clearly outlined by the $\ln(\tau)$ -vs- $1/T$ plot

in Figure 7b, the Arrhenius law typical of thermally-activated relaxation is obeyed in the 0.75–1.1 K range, with $U_{\text{eff}}/k_B = 11.8(3)$ K and $\tau_0 = 4.9(1.7) \times 10^{-8}$ s, in good agreement with AC measurements. At lower temperature, however, the relaxation time approaches a temperature-independent value of ca. 20 s, a distinctive feature of spin relaxation via QT effects.

Figure 7. a) Field-dependence of the magnetization M_M/M_s at variable temperature with 0.035 T s^{-1} sweep rate for **2** after subtracting the contribution of the molecules transverse to the applied field (M_s is the saturation magnetization); b) $\ln(\tau)$ -vs- $1/T$ plot of the experimental data (grey circles and line), together with the best linear fit curve (black) using data in the 0.75–1.1 K; c) first derivative of the lower-branch of hysteresis loops taken at 0.03 K and variable field sweep rates (at the fastest field sweep rates curves are incomplete due to the occurrence of thermal avalanches, which reversed the entire magnetization in the timescale of milli-seconds); d) calculated distribution of internal fields in a model cubic crystal of **2**, after magnetic saturation along [111]: a positive value indicates that the internal field is parallel to the crystal magnetization.

The steps in the recorded field dependence of the magnetization indicate sudden accelerations of spin reversal, a phenomenon that is also the landmark of quantum spin dynamics.^[30] The step positions are best evaluated from the first derivative of the curve recorded at 0.03 K for representative (positive) values of the scan rate (Figure 7c). The peaks in dM/dB at $B = 0, \pm 0.45, \pm 0.90$ T can be readily explained starting from the Zeeman diagram for a Fe_4 system probed by a magnetic field directed along its easy axis.^[31] Magnetic moment reversal through transition from $M_S = \pm 5$ to $\mp 5, \mp 4, \mp 3$ etc. is expected to occur at integer multiples of $\pm |D|/(g\mu_B) = \pm 0.45$ T for $g = 2.00$ and $D = -0.42 \text{ cm}^{-1}$. Notice that spin-spin cross-relaxation, which gives rise to well-evident

pre-step features in **1**·2EtOH,^[7] is now hardly visible, consistent with the strongly reduced dipolar coupling between aligned Fe₄ molecules. The derivative peak associated to the third step is overlapped by a broader feature that extends from the second step up to the highest reached field. Because **1** has a relatively sharp step in this field region when the field is applied along its easy axis,^[7] it is reasonable to attribute the broad high field step to the non collinear Fe₄ units. To verify this we simulated the contribution of the two sets of Fe₄ units to the hysteresis loop using a quantum master matrix approach (Supporting Information, **Figure S14**). Though probed very close to their hard plane, the Fe₄-t complexes also show large departures from paramagnetic behaviour, with the first QT resonance considerably shifted upfield at 0.7–0.9 T due to the reduction of the field component along the easy axis.

Looking in greater detail at the zero-field step, we found that it exhibits a fine structure consisting in two sub-steps whose positions are scan-rate dependent (inset of Figure 7c). This behaviour suggests that Fe₄-p and Fe₄-t molecules may experience different magnetic bias due to internal fields originating from superexchange or dipolar interactions. The former imply overly long pathways through the 4-pyridyl substituents and the diamagnetic silver(I) ions, whereas dipolar fields can be significant even at long distances. We thus computed the distribution of dipolar fields in a model crystal comprising ca. 34000 molecules. All magnetic moments were directed along the local easy axes so as to have a positive component along [111]. In this configuration, the magnetic moment of Fe₄-p units is exactly parallel to [111], whereas Fe₄-t molecules have their magnetic moment at 70.53° from [111]. Such an arrangement reproduces the magnetic structure of the crystal after polarization in large **B** parallel to [111] and subsequent reduction of the field towards zero.

Crystal shape is important for this kind of calculations because demagnetizing fields are shape-dependent.^[32] Considering that the compound grows as approximately isodiametric crystals, we chose a cubic crystal bounded by the (100) face and its cubic equivalents. A spherical sample of comparable size gave very similar results but much narrower distributions because the demagnetizing field is uniform inside a general ellipsoid.^[33] As shown in Figure 7d, the dipolar field distributions for Fe₄-p and Fe₄-t molecules are peaked at 10.9 and –6.4 mT, respectively. The two types of molecules thus experience dipolar fields of comparable magnitude but opposite in sign, being parallel and antiparallel to the crystal magnetization, respectively. Since relaxation by QT at the “zero-field” resonance requires dipolar fields and **B** to cancel out exactly, the two sets of molecules respond in different ways during the field scan. As zero field is approached after application of negative fields (lower branch of hysteresis loop), Fe₄-t molecules reach the “zero-field” resonance at *negative* field values (i.e. before the external field goes to zero), whereas Fe₄-p molecules do so in *positive* fields due to the opposite bias they experience. The scenario is

complicated by the fact that, as molecules start to reverse their magnetic moment, the distribution of internal fields changes, a phenomenon known as “dipolar shuffling”.^[34] Most meaningful is thus the structure of the zero-field step measured at the fastest scan rate, which affords the smallest change in magnetization. The maxima in the derivative of the magnetization curve recorded at 0.280 T s^{-1} indeed mirror the calculated bimodal distribution of dipolar fields, suggesting that selective switching of the two sets of molecules is possible in different field ranges. The less pronounced magnetization changes arising from relaxation of $\text{Fe}_4\text{-t}$ molecules may seem surprising when one considers they account for 3/4 of the sample. However, the impact of magnetic moment reversal over crystal magnetization depends on the tilt angle and for $\text{Fe}_4\text{-t}$ molecules it is reduced by a factor $\cos(70.53^\circ) = 1/3$. At very slow scan rates (0.001 T s^{-1}), relaxation is significant even far from the maximum in the distribution of internal fields (inset of Figure 7c). The subsequent evolution of relaxation rate is then expected to be strongly influenced by dipolar shuffling effects, in a way which is beyond the scope of this paper.

Conclusion

The rational assembly of SMM units into complex supramolecular structures is a fertile strategy to modulate their magnetic response and combine new functionalities. In this paper, the use of tetrahedral silver(I) nodes and of pyridyl-functionalized tetrairon(III) SMMs (**1**) acting as 180° -ditopic supramolecular synthons was shown to afford a 3D-MOF (**2**) made of SMM units and mimicking diamond structure. Crystals have cubic symmetry and comprise four magnetically-distinct Fe_4 units developing along the threefold axes of AgN_4 tetrahedra (*i.e.* the main diagonals of the cubic cell). Similarly to the parent compound **1**, the tetrairon(III) building blocks in **2** maintain an $S = 5$ ground spin state and an easy-axis anisotropy with $D \sim -0.4 \text{ cm}^{-1}$, as revealed by DC magnetic measurements and EPR spectroscopy. However, the cubic symmetry generates a highly-noncollinear supramolecular magnetic structure that has no overall second-order magnetic anisotropy and was directly probed using CTM. Significantly, AC susceptometry and microSQUID magnetometry evidenced retention of slow magnetic relaxation, showing that Fe_4 units maintain a directionally-bistable magnetic moment along their local easy axes. Symmetry arguments then indicate that the crystalline compound has the potential of showing persistent magnetization along eight different directions, that is, parallel or antiparallel to the four main diagonals of the cubic unit cell.

Thanks to their recognized chemical and structural versatility,^[7–9,18,26,35] tetrairon(III) clusters represent a perfect benchmark in order to study the effect of supramolecular assembly over magnetic bistability in SMM materials. For instance, spin-phonon interactions and angular

momentum conservation are pivotal for magnetic moment reversal at the single molecule level.^[36] Differences in phonon spectrum between a rigid 3D framework and a molecular crystal held together by van der Waals forces may thus affect magnetic relaxation in a way that is worth investigating. Here, detecting true molecular responses requires suppressing dipolar interactions across the lattice by magnetic dilution. Previous work showed that such an operation is feasible without any metal scrambling by using tetragallium(III) complexes as diamagnetic analogues of Fe₄ SMMs.^[37]

Finally, although all structural and magnetic studies were carried out on desolvated samples, the large cavities in the 3D-MOF structure of **2** revealed to be able of captivating guest solvent molecules. The latter may provide a means for modulating magnetic properties, an appealing target for future studies.

Experimental Section

General procedures: Reagent grade AgClO₄, anhydrous DCM (VWR, max 10 ppm H₂O), anhydrous toluene (VWR, max 20 ppm H₂O) and anhydrous THF (VWR, max 30 ppm H₂O) were used as received. Elemental analyses were performed using a Carlo Erba EA1110 CHNS-O automatic analyser. Infrared spectra were recorded as KBr disks using a Jasco FTIR-4700LE spectrophotometer with a 2 cm⁻¹ resolution. MS-MALDI spectra (Supporting Information, Figure S3) were recorded using an Applied Biosystems/MDS SCIEX 4800 Plus MALDI ToF/ToF analyser equipped with a diode-pumped, solid-state Nd:YAG (355 nm) 200 Hz laser; samples were prepared dissolving the compound in THF and using 1,8,9-trihydroxyanthracene dissolved in CHCl₃ as matrix. ¹H NMR spectra at 400 MHz were recorded at room temperature using a Bruker FT-NMR Advance400 spectrometer with chemical shifts given in parts per million (ppm) versus external TMS. The chemical shifts reported were determined by reference to the solvent residual signal (7.16 ppm for [D₆]benzene). TGA analysis was performed with a Netzsch STA409EP Instrument in static air, using a Pt crucible, from room temperature up to 700 °C with a heating rate of 5 °C min⁻¹. **1·2EtOH**^[7] was synthesised as reported in the literature. Experimental details on the X-ray crystal structure determination, DC and AC magnetic measurements, W-band EPR spectroscopy, torque magnetometry and microSQUID measurements can be found in Supporting Information.

Synthesis of **[Fe₄(pPy)₂(dpm)₆]₂Ag}(ClO₄) (**2**)**

Method Ia. AgClO₄ (0.92 mL of a 0.00786 mol L⁻¹ solution in THF, 0.0721 mmol) was added to a solution of **1·2EtOH** (25.6 mg, 0.0144 mmol) in THF (2.0 mL). The resulting orange solution was stirred for 30 minutes and then carefully layered over DCM (3.0 mL) into a test tube and left

undisturbed until diffusion was complete (ca. 7 days). The red X-ray quality cubic crystals so formed were isolated by filtration, quickly washed with a DCM:THF 1:1 mixture (1 mL) and dried under vacuum for 30 minutes without affecting crystallinity (13.3 mg, 51.6%). Elemental analysis calcd (%) for $C_{168}H_{268}AgClFe_8N_4O_{40}$ (3574.08): C 56.46, H 7.56, N 1.57; found: C 56.36, H 7.81, N 1.72.

Method Ib. $AgClO_4$ (0.16 mL of a 0.0199 mol L⁻¹ solution in THF, 0.0033 mmol) was added to a solution of **1**·2EtOH (14.2 mg, 0.00799 mmol) in THF (2 mL). After stirring for 20 minutes, the orange solution was quickly filtered and then put in vapour diffusion with toluene (4.8 mL). After one month the red X-ray quality cubic crystals formed at the bottom of the test tube were isolated, washed with toluene (1 mL), *n*-hexane (2 × 5 mL) and dried in vacuum, without affecting the crystallinity (few mg's, yield n.d.). Elemental analysis calcd (%) for $C_{168}H_{268}AgClFe_8N_4O_{40}$ (3574.08): C 56.46, H 7.56, N 1.57; found: C 56.68, H 7.88, N 1.56.

Method II. A solution of $AgClO_4$ in THF (0.0199 mol L⁻¹, 0.22 mL, 0.0043 mmol) was diluted with THF to 2 mL, and then layered over a solution of **1**·2EtOH (15.2 mg, 0.00856 mmol) in DCM (2 mL). After one week, red X-ray quality cubic crystals formed on the walls of the test tube; they were isolated by filtration, quickly washed with a DCM:THF 1:1 mixture (1 mL) and dried in vacuum without affecting the crystallinity (few mg's, yield n.d.). Elemental analysis calcd (%) for $C_{168}H_{268}AgClFe_8N_4O_{40}$ (3574.08): C 56.46, H 7.56, N 1.57; found: C 56.35, H 7.63, N 1.67.

General spectroscopic characterization for **2** obtained with all Methods

IR (KBr): ν = 2964s and 2904w (CH₂, CH₃), 2865w (CH_{dpm}), 1592s, 1576s, 1564s, 1536s, 1506s (C=C, C=O, C=N), 1402s, 1385s, 1357s (CH), 1108br (ClO₄, C–O), 1075w (C–O), 561 (Fe–O) cm⁻¹. MALDI-ToF/ToF (with matrix): m/z (%) = 1791.72 (50) [$Fe_4(pPy)_2(dpm)_6Ag$]⁺ (calcd. for $C_{84}H_{134}AgFe_4N_2O_{18}$: 1791.61), 1184.27 (100) [$Fe_4(pPy)_2(dpm)_6Ag - Fe(dpm)_3$]⁺ (calcd. for $C_{51}H_{77}AgFe_3N_2O_{12}$: 1184.26), 422.16 (45) [$Fe(dpm)_2$]⁺ (calcd. for $C_{22}H_{38}FeO_4$: 422.21). MALDI-ToF/ToF (no matrix): m/z (%) = 1791.78 (75) [$Fe_4(pPy)_2(dpm)_6Ag$]⁺, 1721.83 (1) [$Fe_4(pPy)_2(dpm)_6 + K$]⁺ (calcd. for $C_{84}H_{134}Fe_4KN_2O_{18}$: 1721.67), 1705.85 (15) [$Fe_4(pPy)_2(dpm)_6 + Na$]⁺ (calcd. for $C_{84}H_{134}Fe_4N_2NaO_{18}$: 1705.69), 1499.68 (20) [$Fe_4(pPy)_2(dpm)_6 - dpm$]⁺ (calcd. for $C_{73}H_{115}Fe_4N_2O_{16}$: 1499.56), 1184.34 (40) [$Fe_4(pPy)_2(dpm)_6Ag - Fe(dpm)_3$]⁺, 422.20 (100) [$Fe(dpm)_2$]⁺.

Solvent content determination via ¹H NMR and TGA

Crystals of **2** were removed from the THF:DCM mother liquor, quickly dried on dry filter paper, checked under the microscope, weighed (5.30 mg) and then suspended in 0.5 mL of [D₆]benzene

into an NMR tube. The tube was then put into an ultrasound bath at room temperature for 5 minutes, during which the crystals crushed and the solution became orange. A standard solution of ferrocene in $[D_6]$ benzene ($0.0932 \text{ mol L}^{-1}$, $20.0 \text{ }\mu\text{L}$, 0.00186 mmol) was added and then ^1H NMR spectrum was registered (400 MHz, $[D_6]$ benzene, 298 K): $\delta = 4.27$ (DCM, 0.00347 mmol), 4.01 (ferrocene), 3.57 and 1.42 (THF, 0.00286 mmol) ppm. From the integrated areas of the peaks we estimated 2.6 molecules of DCM and 2.1 molecules of THF per formula unit of **2**.

Another batch of crystals of **2** was removed from the THF:DCM mother liquor, dried on dry filter paper, checked under the microscope, weighed (4.34 mg) and then pumped in vacuum (0.5 mmHg) for 8 h. The weight diminished to 4.08 mg (about 0.26 mg mass loss), but the crystals appeared unaltered under the microscope. They were then suspended in 0.5 mL of $[D_6]$ benzene into an NMR tube and sonicated at room temperature for 5 minutes. A standard solution of ferrocene in $[D_6]$ benzene ($0.0989 \text{ mol L}^{-1}$, $20.0 \text{ }\mu\text{L}$, 0.00198 mmol) was added and then ^1H NMR spectrum was registered (400 MHz, $[D_6]$ benzene, 298 K): $\delta 4.01$ (ferrocene), while peaks of DCM and THF were absent, showing that vacuum treatment removes all lattice solvent molecules.

A further batch of crystals of **2** was removed from the THF:DCM mother liquor, quickly dried on dry filter paper, checked under the microscope, weighed (12.24 mg) and then inserted into the Pt crucible of the TGA instrument. The analysis gave the following weight losses: 9.22 ($20\text{--}140 \text{ }^\circ\text{C}$), 7.36 ($220\text{--}250 \text{ }^\circ\text{C}$), 60.6 ($250\text{--}310 \text{ }^\circ\text{C}$), 6.40% ($310\text{--}370 \text{ }^\circ\text{C}$) (Supporting Information, Figure S1).

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Graphical Abstract

Tetrahedral Ag^+ nodes interlace together with Fe_4 Single-Molecule Magnets into an unprecedented diamondoid 3D Metal-Organic Framework which has cubic symmetry but retains magnetic bistability.

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