Electronic Supplementary Information

Valence Electronic Structure of Sublimated Fe₄ Single-Molecule Magnets: an Experimental and Theoretical Characterization

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Fe₄(pta)₆ isomers



Fig. S1 Top view of the three possible geometrical isomers of the $Fe_4(pta)_6$ cluster, where Iso1 is the most stable one. Fluorine atoms are in green, carbon atoms - in brown, oxygen atoms - in red, iron atoms - in gold.



Fig. S2 TDOS corresponding to the three isomers of the $Fe_4(pta)_6$ cluster.

Theoretical TDOS correction based on atomic photoionization cross-sections

The experimental intensity ratio of the peaks in region (ii), see main text, is not fully reproduced by theoretical TDOS, for both clusters. This could be due to the experimental photoionization cross section, which affects differently each element (H, C, O, F, Fe) and state (1s, 2s, 2p, 3d) in UPS spectra.¹ An attempt to correct the theoretical TDOS of $Fe_4(dpm)_6$ is reported in the left panel of Fig. S3. At 40.8 eV the cross section ratio of C(2p) : O(2p) : Fe(3d) is equal to 1 : 3.6 : 4.7. Therefore, in the experimental spectrum of $Fe_4(dpm)_6$ the weight of O 2p and Fe 3d PDOS becomes comparable to the C 2p PDOS, while the H 1s is quite negligible (C(2p) : H(1s) = 1 : 0.15). In the corrected c-TDOS, region (ii) is now more similar to the experimental one, supporting the assignation of the bands reported in the main text. However, now in the c-TDOS, the first band (i) and peak 9 seem unbalanced with respect the experimental corrispondents. As for the Fe₄(pta)₆ the correction works very well on the entire spectrum (right panel of Fig. S3). Indeed, the intensity ratio between the fluorine states (*) and the other bands now reflects exactly the one found in the

experimental spectrum. This is probably due to the relatively high photoionization cross section of the F 2p states (C(2p) : F(2p) = 1 : 4.5) together with the high number of fluorine atoms.



Fig. S3 Comparison between the UPS spectra and the total DOS, as calculated (TDOS) and corrected (c-TDOS) for the photoionization cross-sections at 40.8 eV, for both clusters $Fe_4(dpm)_6$ (left panel) and $Fe_4(pta)_6$ (right panel).

Fe₄-core bands



Fig. S4 Spin-resolved PDOS of the clusters' core, plotted with respect to the Fermi energy of each molecules. 3d-orbital contributions for the Fe^{c} and Fe^{p} (top graph) and oxygen 2p states in the different ligands (bottom graph).

Tuning the U parameter (DFT + U)

For the determination of the U parameter on the different atoms, our reference was the UPS spectra and the PDOS on the atoms calculated with the hybrid functional starting with $Fe_4(dpm)_6$. The U(Fe) = 4.1 eV is widely used for other iron-containing compounds.^{2,3} However, the exchange interaction J_1 is more antiferromagnetic than the experimental one (Table S1). Moreover, the TDOS (Fig. S5) does not reproduce well region (i), unlike the Fe PDOS which are very close in energy with respect to the Fermi level and in shape to the hybrid functional calculated one (Fig. S8). By applying a U on Fe equal to 9.8 eV, the magnetic interaction is similar to the experimental one. However, the Fe PDOS are more localized and occupied (unoccupied) states downshifted (upshifted) in energy, as a result of the high U value.

In order to reproduce better region (i), to which the oxygen states contribute significantly, and in agreement with several studies where an *U* is successfully applied on bridging atoms,^{4,5} we decided to tune the parameter on the O 2p states, keeping the U(Fe) equal to 4.1 eV. The more the U(O) value goes up, the better the agreement with experimental TDOS and the magnetic exchange constant is. The best agreement was achieved for U(O) = 3.0 eV, where

the two peaks in (i) region of the UPS spectrum are hinted and the exchange constant J_1 is reproduced for the experimental geometry of Fe₄(dpm)₆ as well as for the optimized one.

Applying U also on the C atoms (2p) did not bring significant changes. Therefore, it was not taken into consideration in further calculations.

As for $Fe_4(pta)_6$, the same *U* parameters on Fe and O led to a fair reproduction of region (i) while region (ii) was a little more problematic. There are states at about -3.5 eV with higher intensities which deteriorate the TDOS shape (see Fig. S6). At those energies there are the fluorine 2p states, which are also affected by the *U* applied on the Fe (Fig. S7). The tuning of the on-site parameter on the F 2p state results in achieving the right intensity ratio of the first band and a TDOS very close to the experimental UPS spectrum with best agreement for U(F) = 2.5 eV. The revPBE + *U* exchange constants are closer to the experimental ones than the PBE0 ones (Table S2).



Fig. S5 TDOS of the Fe₄(dpm)₆ cluster calculated with different U values.



Fig. S6 TDOS of the $Fe_4(pta)_6$ cluster calculated with different U values.



Fig. S7 F-PDOS calculated at different levels of theory.



Fig. S8 Fe-PDOS calculated at different levels of theory for Fe₄(dpm)₆ (top panel) Fe₄(pta)₆ (bottom panel).

Table S1 Results for the J_1 calculated by revPBE + U for different values of the U parameter on the X-ray and optimized structure of the Fe₄(dpm)₆ cluster.

	<i>U</i> (<i>Fe</i>), eV	<i>U</i> (<i>O</i>), eV	U(C), eV	J_1 , cm ⁻¹	$J_1, \operatorname{cm}^{-1}$
Fe4(dpm)6				(optimized)	(X-ray)
	9.8	-	-	17.66	-
	4.1	-	-	31.68	32.59
		0.5	-	28.86	-
		1.0	-	26.18	-
		1.5	-	23.62	-
		2.0	-	21.20	-
		2.5	-	18.89	-
		3.0	-	16.70	16.95
		3.5	-	14.63	14.79
		3.0	1.0	16.59	-
		3.0	3.0	16.37	-
		-	3.0	31.26	-
	PBE0 Experimental ⁶			13.83	14.43
				16.37(12)	

Table S2 Results for the J_1 calculated by revPBE + U for different values of the U parameter on the optimized structure of the Fe₄(pta)₆ cluster.

	$U(E_{\alpha}) = \Delta V$	U(0) = V	U(F), eV	$J_1, {\rm cm}^{-1}$
	U(re), ev	U(O), ev		(optimized)
	4.1	3.0	-	15.18
Fe ₄ (pta) ₆			1.0	15.20
			2.0	15.24
			2.5	15.28
			3.0	15.30
	PBE0			13.39
	Experimental ⁷			16.20(6)

	U(Fe), eV	U(O), eV	U(C), eV	Gap, eV
	9.8	-	-	3.06
		-	-	2.28
		0.5	-	2.30
		1.0	-	2.31
		1.5	-	2.33
		2.0	-	2.35
Fe ₄ (dpm) ₆	4.1	2.5	-	2.36
		3.0	-	2.38
		3.5	-	2.40
		3.0	1.0	2.39
		3.0	3.0	2.42
		-	3.0	2.31
		PBE0		3.75
		revPBE		0.99

Table S3 LUMO-HOMO gaps calculated upon variation of U for the Fe₄(dpm)₆ cluster.

Table S1 LUMO-HOMO gaps calculated upon variation of U for the Fe₄(pta)₆ cluster.

	U(Fe), eV	U(O), eV	U(F), eV	Gap, eV
Fe4(pta)6	9.8	-	-	2.83
	4.1	3.0	-	2.26
			1.0	2.26
			2.0	2.25
			2.5	2.24
			3.0	2.24
		PBE0		3.75
		revPBE		0.89
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Orbital Contribution to C and O PDOS for Fe₄(dpm)₆



Fig. S9 PDOS of the O (left) and C (right) for $Fe_4(dpm)_6$ cluster

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