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Supporting Information:

Hidden ordered structure in the archetypical Fe(pyrazine)[Pt(CN)$_4$] spin-crossover porous coordination compound

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Table S1: Structural parameters used for depicting the structures (Fig. 1) and for the simulation of the expected powder diffraction patterns (Fig. 2) of Fe(pyrazine)[Pt(CN)$_4$] in low-spin state with the pyrazine rings in disordered, perpendicular and parallel configurations.

Configuration	Disordered	Perpendicular	Parallel
λ (Å)	1.54		
Crystal system	Tetragonal	Tetragonal	Orthorhombic
Space Group (No.)	P4/*mmm* (123)	P4/*mbm* (127)	P*mmm* (47)
a (Å)	7.1786	10.1520	7.1786
b (Å)	7.1786	10.1520	7.1786
c (Å)	6.7741	6.7741	6.7741
V (Å^3)	349.08	698.16	349.08
Pt: x	0.5	0.5	0.5
y	0.5	0.5	0.5
z	0.5	0.5	0.5
Fe: x	0	0	0
y	0	0.5	0
z	0.5	0.5	0.5
N(1): x	0	0	0
y	0	0.5	0
z	0.79800	0.79800	0.79800
N(2): x	0.19400	0.19400	0.19400
y	0.19400	0.5	0.19400
z	0.5	0.5	0.5
C(1): x	0.31200	0.31200	0.31200
y	0.31200	0.5	0.31200
z	0.5	0.5	0.5
C(2): x	0	0.08250	0
y	0.16500	0.58250	0.16500
z	0.89000	0.89000	0.89000
H / D: x	0	0.13745	0
y	0.27490	0.63745	0.27490
z	0.81780	0.81780	0.81780

Computational details

The DFT calculations were performed with the QuantumESPRESSO (QE) package[S1–S3] (v.6.4) within the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE)[S4] and long-range interactions described with the semiempirical approach proposed by Grimme (PBE+D2).[S5,S6] We employ the pseudopotentials from Garrity-Bennet-Rabe-Vanderbilt library (GBRV).[S7] The convergence threshold on forces is 0.0001 Ry/Bohr and the wavefunctions and charge density cutoffs are set to 100 Ry and 1000 Ry, respectively. These are carefully chosen to obtain converged phonon frequencies. To describe both the perpendicular and parallel orientation a supercell with lattice parameter $a''=\sqrt{2}a$ and $b''=\sqrt{2}b$ was used, with a, b and c the lattice parameters of the primitive cell. The PBE+D2 lattice parameters are $a''= b'' = 10.1$ Å and $c'' = 6.7$ Å. The Brioullin zone is sampled using 3×3×3 Monkhorst-Pack k-points grid.

The vibrational contributions to the enthalpy and entropy are computed using eqs. 2 and 3 of the main text. The phonon frequencies $\{\nu_i\}$ for perpendicular and parallel configuration in LS and HS are obtained by diagonalizing the dynamical matrix by employing the ph.x package implemented in Quantum Espresso. The harmonic interactomic force constants are computed using density functional perturbation theory.[S8,S9] The values of $\Delta \mathrm{E}_{vib}$ and $\Delta \mathrm{S}_{vib}$ that we present in the main text are obtained using the corresponding E_{vib} and S_{vib}. In the case of the disordered configuration, the average of E_{vib} and S_{vib} computed between the parallel and perpendicular configuration of the corresponding spin state, is taken.

We note that we obtain one negative frequency for the LS parallel case and for the HS perpendicular configuration, at -8.9 cm^{-1} and -27.8 cm^{-1}, respectively. Because the negative frequency is not counted in the summation of eqs. 2 and 3, one expects an underestimation of the vibrational entropy and enthalpy in these cases. Thus, in the two cases mentioned above we add one frequency in the low and one the intermediate energy range in two separate calculations and then compute the average. The corresponding values are indicated with an asterisk in Table 1. We add one frequency at 10 cm^{-1} (right after the three translational modes) and then one at 500 cm^{-1} (right before the internal modes associated with the pyrazine). We stress here that if we take the values of vibrational energy and entropy computed as they are, i.e. without adding any new frequency, the final results on the value of $T_{1/2}$ reported in the main article negligibly changes (by less that one 1 K).

To evaluate ΔE_{ad}, we use DFT within the Hubbard U-corrected density approach scheme, which has been recently proposed and tested by some of us.[S10] This method exploits the capabilities of the Hubbard U-correction method in DFT in improving the description of localized d electrons (more strongly affected by the self-interaction error in standard PBE) and at the same time removes the systematic bias toward high spin observed in Fe(II) complexes when the fully self-consistent PBE+U approach is used.[S11] In this work we adopt the linear-response approach proposed by Cococcioni et *al.*[S12] to compute the Hubbard parameter U for the iron site in the unit cell and we obtain 7.29 eV for HS and 8.87 eV for LS. The values of adiabatic energy differences reported in Table S2 and in the main paper are computed on the relaxed PBE+D2-geometries by employing the Hubbard U-density corrected approach that we name PBE[U], i.e. by taking the PBE+U total energy contribution and removing the Hubbard term as explained in detail in ref.[S10](we stress that no D2 term is used for this set of calculations).

Table S2: Adiabatic energy and vibrational energy and entropy for the three configurations (parallel, perpendicular and disordered) in HS and LS. *Average value between one frequencye added at low and one at high energy. The error is also reported. The label diso (*disordered*) referes to the average between parallel and perpendicular.

		Perpendicular	Parallel	Disordered (average)
HS	E_{ad} (kJ mol^{-1})	-890367.87373	-890364.31075	-890366.09224
	E_{vib} (kJ mol^{-1})	*339.02486 ±0.285385	338.61891	338.82188
	S_{vib} (J mol^{-1} K^{-1})	*285.41634 ±7.655215	286.28380	285.85007
LS	E_{ad} (kJ mol^{-1})	-890403.00375	-890402.46490	-890402.73433
	E_{vib} (kJ mol^{-1})	346.87958	*346.92117 ±0.285385	346.90038
	S_{vib} (J mol^{-1} K^{-1})	222.21025	*223.87080 ±7.655215	223.04053
difference between HS (diso) - LS (perp/para/diso)	ΔE_{ad} (kJ mol^{-1})	36.91151	36.37266	36.64209
	ΔE_{vib} (kJ mol^{-1})	-8.05770	-8.09929	-8.07850
	ΔS_{vib} (J mol^{-1} K^{-1})	63.63982	61.97927	62.80954

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