Supplementary Information

Pressure tunable electronic bi-stability in Fe (II) Hoffmann-like 2D coordination polymer [Fe(Fpz)_2Pt(CN)_4]: comprehensive experimental and theoretical study.

Ruixin Li, † Georgiy Levchenko*, †, §, Francisco Javier Valverde-Muñoz†, Ana Belén Gaspar*, †, ‡, Victor V. Ivashko, † Quanjun Li, † Bingbing Liu, † Mengyun Yuan, † Hennagii Fylymonov, § Jose Antonio Real*, ‡

*State Key Laboratory of Superhard Materials, International Centre of Future Science, Jilin University, Changchun 130012, China
†Institut de Ciència Molecular/Departament de Química Inorgànica, Universitat de València, E-46980 València, Spain
§Donetsk Institute of Physics and Engineering named after A. A. Galkin, Kyiv 03028, Ukraine
‡Department of Correlation Optics, Chernivtsi National University, Chernivtsi 58012, Ukraine

Corresponding Authors

Georgiy Levchenko: Email: g-levch@ukr.net
Ana Belén Gaspar: Email: ana.b.gaspar@uv.es
Jose Antonio Real: Email: jose.a.real@uv.es
Figure S1. Deconvolution of the optical absorption spectra of [Fe(Fpz)$_2$Pt(CN)$_4$] at pressure increase.

The measured spectrum consists of two bands: one at central wavelength of 415 nm (red color) and a second at 450 nm (green color). With pressure increase the first band decreases and the second one increases (see Figure S1 at P = 2.01 GPa). At higher pressure the first band vanishes, the second increases and appears a third band (blue color) with a central wavelength of 493 nm (see P = 3.78 GPa). Based on the previous analyzes of optical absorption spectra in Hoffman-like complexes we assign the first band to the metal–ligand charget transfers (MLCT) in the HS state, and the second and third bands to the $^1A_{1g} \rightarrow ^1T_{2g}$ and $^1A_{1g} \rightarrow ^1T_{1g}$ transitions, respectively, belonging to low spin state. So, at ambient pressure we see that the compound under studying is in the HS state. The observed small amount of LS state (the band centered at $\lambda = 450$ nm) is caused by the difficulties to receive ambient pressure in anvil pressure cells, because even a very small moving of the anvils increases the pressure. Under pressure increase the decrease of the HS state and increase the LS state is observed. The received $\gamma_{HS}$-P diagram is presented in Figure 5.
Figure S2. Raman spectra measured at room temperature for [Fe(Fpz)₂Pt(CN)₄]: a) at pressure increase; b) at pressure decrease. The band with the wavenumber of 1333 cm⁻¹ belongs to anvils.

Figure S3. The dependence of Raman shifts with pressure for F-pyrazine bands of the [Fe(Fpz)₂Pt(CN)₄] complex. In the region of intermediate pressures (~ 1 – 2 GPa), two bands are observed, which indicates the presence of a mixture of the two phases, HS and LS. These points are marked with asterisks in the figure. For each pressure, two bands are observed, one at the top and the other at the bottom of the figure.
Figure S4. The evolution of the vibrational modes M-CN upon decreasing pressure in [Fe(Fpz)\textsubscript{2}Pt(CN)\textsubscript{4}]: a) C-N stretching vibration (left) and b) in-plane bending vibration (right).

Figure S5. XRD spectra for [Fe(Fpz)\textsubscript{2}Pt(CN)\textsubscript{4}] measured at room temperature: a) at pressure increase; b) at pressure decrease.
Table S1: Pressure dependence of the unit cell parameters for [Fe(Fpz)$_2$Pt(CN)$_4$] in the increasing and decreasing pressure modes.

**Pressure increase:**

| P (GPa) | a (Å)   | b (Å)   | c (Å)   | Volume (Å$^3$) |
|---------|---------|---------|---------|---------------|
| 0       | 7.4478  | 7.123   | 15.134  | 802.86901     |
| 0.19    | 7.414   | 7.1132  | 14.9828 | 790.15189     |
| 0.25    | 7.4136  | 7.0885  | 14.926  | 784.38074     |
| 0.36    | 7.3805  | 7.074   | 14.815  | 773.48602     |
| 0.44    | 7.3524  | 7.0553  | 14.7479 | 765.02354     |
| 0.58    | 7.3309  | 7.0456  | 14.673  | 757.86912     |
| 1.04    | 7.2614  | 7.006   | 14.4149 | 733.33454     |
| 1.26    | 7.2017  | 6.9538  | 14.33   | 717.63471     |
| 1.43    | 7.1526  | 6.9272  | 14.327  | 709.86685     |
| 1.68    | 7.11    | 6.8862  | 14.247  | 697.54568     |
| 2.04    | 7.0768  | 6.8657  | 14.171  | 688.52895     |
| 2.29    | 7.0691  | 6.8644  | 14.172  | 687.69812     |
| 2.64    | 7.04914 | 6.85578 | 14.12244| 682.47699     |
| 2.78    | 7.0455  | 6.8569  | 14.101  | 681.22338     |
| 2.89    | 7.0556  | 6.8641  | 14.044  | 680.15575     |

**Pressure decrease:**

| P (GPa) | a (Å)   | b (Å)   | c (Å)   | Volume (Å$^3$) |
|---------|---------|---------|---------|---------------|
| 0       | 7.4331  | 7.1185  | 15.11   | 799.50824     |
| 0.19    | 7.3943  | 7.094   | 14.875  | 780.27055     |
| 0.33    | 7.3924  | 7.0804  | 14.856  | 777.58008     |
| 1.04    | 7.2651  | 7.0216  | 14.389  | 734.02065     |
| 1.24    | 7.1512  | 6.9355  | 14.191  | 703.83312     |
| 1.37    | 7.12684 | 6.92205 | 14.11602| 696.377       |
| 1.51 | 7.12074 | 6.92079 | 14.09429 | 694.583 |
| 1.65 | 7.10819 | 6.91456 | 14.05405 | 690.757 |
| 1.76 | 7.0978  | 6.9038  | 14.03    | 687.4951|
| 1.9  | 7.092   | 6.9005  | 14.03    | 686.60496|
| 1.95 | 7.0773  | 6.8805  | 14.015   | 682.46551|
| 2.04 | 7.0584  | 6.8657  | 13.993   | 678.11276|
| 2.17 | 7.0639  | 6.8589  | 14.059   | 681.16676|
| 2.34 | 7.0508  | 6.8515  | 14.042   | 678.34873|
| 2.62 | 7.0473  | 6.8565  | 14.063   | 679.52151|
The third-order Birch–Murnaghan equation:

\[ P(V) = \frac{3B_0}{2} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left[ 1 + \frac{3}{4}(B'_0 - 4) \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \]  

where \( P \) is the pressure, \( V_0 \) is the reference volume, \( V \) is the deformed volume, \( B_0 \) is the bulk modulus, and \( B'_0 \) is the derivative of the bulk modulus with respect to pressure.

Figure S6. Pressure dependence of the bulk modulus (a) before (left side) and (b) after (right side) the spin transition.

Figure S7. A fitting of the TIST curves under pressure using the equation:

\[ T_i = \frac{\Delta H_{HL}(T) + (\Delta_{elast} - \Gamma) + P \cdot \Delta V_{HL}}{\Delta S_{HL}} \]
Table S2: Thermodynamic parameters of TIST under pressure obtained using the elastic model.

| P (Gpa) | $T_{1/2}^\downarrow$ (K) | $T_{1/2}^\uparrow$ (K) | $T_{1/2}$ (K) | $\Delta T_{1/2}$ (K) | $\Delta H$ (K) | $\Gamma$ (K) | $\Delta_{\text{elast}}$ (K) | $\Delta_{\text{elast}} - \Gamma$ (K) | $\Gamma/(\Delta H + \Delta_{\text{elast}} - \Gamma + P \Delta V_{\text{HL}})$ |
|---------|-----------------|-----------------|-------------|-----------------|-------------|-------------|-----------------|-----------------|-----------------------------------|
| 0       | 149.04          | 164.5           | 156.77      | 15.46           | 1317.7      | 469.31      | 505.41          | 36.10           | 0.347                             |
| 0.1     | 169.97          | 185.97          | 177.97      | 16              | 1317.7      | 523.46      | 589.65          | 66.18           | 0.343                             |
| 0.3     | 207.93          | 221             | 214.46      | 13.07           | 1317.7      | 572.80      | 685.92          | 113.12          | 0.308                             |
| 0.45    | 234.95          | 245.62          | 240.28      | 10.67           | 1317.7      | 613.72      | 722.02          | 108.30          | 0.297                             |
| 0.55    | 241.86          | 250.75          | 246.31      | 8.89            | 1317.7      | 616.13      | 631.77          | 15.64           | 0.291                             |
| 0.59    | 245.62          | 254.5           | 250.06      | 8.88            | 1317.7      | 619.73      | 607.70          | -12.03          | 0.289                             |
| 0.68    | 272.84          | 276             | 274.42      | 3.16            | 1317.7      | 619.73      | 697.95          | 78.22           | 0.262                             |
| 0.7     | 275.14          | 278.18          | 276.66      | 2.3             | 1317.7      | 625.75      | 685.92          | 60.2            | 0.262                             |
| 0.73    | 280.17          | 273.17          | 276.6       | 7               | 1317.7      | 630.45      | 500.5           | -130            | 0.281                             |
| 0.85    | 267.22          | 272.23          | 269.725     | 5.01            | 1317.7      | 631.77      | 427.19          | -204.57         | 0.272                             |
**Figure S8.** Pressure dependence of the ratio of the interaction parameter between molecules to the splitting energy $\Gamma/(\Delta H + \Delta_{\text{elast}} - \Gamma + P\Delta V_{\text{HL}})$. This ratio determines the width of the hysteresis in all theoretical approximations and, as can be seen from its behavior and the experimental change in the width of the hysteresis (Figure 3), it qualitatively reflects the experimental behavior of the hysteresis width, when the change of entropy at ST is a constant value.
The Monte Carlo model

Theoretical study was conducted in framework of microscopic Ising-like model with the help of Monte Carlo technique based on the Heatbath algorithm. Given model considers intermolecular interaction in the nearest neighbor’s approach according to the following Hamiltonian:

\[ H = -J \sum_{<i,j>} s_i s_j - h \sum_i s_i \#(S3) \# \]

where \( s_i \) is the fictitious spin for each site \((i = 1, 2, \ldots, N)\) which takes two values ±1 and corresponds to HS and LS states, respectively. The first term in the Hamiltonian describes the intermolecular interactions through a parameter which accounts the ferromagnetic coupling \((J > 0)\) between neighboring spins \(i\) and \(j\). \(<i,j>\) – sum over all nearest-neighboring spins (sites). The second term characterizes the occurrence of intramolecular processes and describes the action of the crystal field together with the influence of temperature and external pressure on the spin-crossover site:

\[ h = -\frac{1}{2} \left( \Delta - k_B T\ln \left( g \right) + P\Delta V \right) \#(S4) \]

where \( \Delta \) is the energy gap between HS and LS states; \(T\) is the absolute temperature (in Kelvin degree); \( k_B \) is the Boltzmann constant; \( g = g_{HS}/g_{LS} \) is degeneracy ratio of spin crossover states; \( p \) is the external pressure, \( \Delta V_{HL} \) is the molecular volume change during transition between the states. The second term of the ligand field (2) is the heat energy \( k_B T \) and it account is justified by the internal entropy effects. Since the applied pressure simultaneously changes the molecular volume, the pressure action in given model is considered by the product \(-P\Delta V_{HL}\).

Simulation technique was conducted on a two-dimensional square lattice with periodical boundary conditions and the size of \( N = L \times L = 70 \times 70 \) \((L – the side length)\) which is enough to eliminate the size effect. The system was initialized with all spins down at a low temperature. Then we increase the temperature and put the system in contact with heat bath at every considered temperature \( T \). When the temperature increases, the spins randomly flip. The transition probability of each spin according to Heatbath algorithm is defined as:

\[ P(s_i \rightarrow -s_i) = \min \left\{ 1, \frac{1}{\exp \left( \frac{\Delta H\{s_i\}}{k_B T} \right) + 1} \right\} \#(S5) \]

here \( \Delta H\{s_i\} \) is the energy difference when a spin changes between spin states.

For modeling we used 5000 Monte Carlo steps per Kelvin degree. Besides, the first 1000 of which were discarded to eliminate the effect of the Monte Carlo steps length and to balance the system before averaging its parameters. One Monte Carlo step is considered completed when all molecules are swept. In given approach we took \( k_B = 1 \) and \( g = 150 \) for reasons of obtaining entropy close to the generally accepted value.

The resulted system magnetization was calculated as average on Monte Carlo steps \((N_{MC})\).
\[ m = \frac{\langle s \rangle}{N_{MC}} \] where
\[ \langle s \rangle = \frac{1}{N} \sum_s s_i \]

The relation between this magnetization and system’s order parameter is the following:
\[ n_{HS} = \frac{m + 1}{2} \]

The fitting of the phase diagrams using the equation:
\[ P(\gamma_{HS}) = \frac{T \left[ N_A k_b \left( \frac{1 - \gamma_{HS}}{\gamma_{HS}} \right) + \Delta S_{HL} - \Delta H_{HL}(T) - \Delta_{elast} + 2 \cdot \gamma_{HS} \cdot \Gamma \right]}{\Delta V_{HL}} \]

Figure S9. The fitting of the phase diagrams using the equation:

a) The diagram obtained by the measuring the optical absorption of the FepzPt complex;
b) The diagram obtained using the measuring of the FepzPt complex Raman scattering.

In the case of gradual spin transition with hysteresis it is not possible to fit the all curve \( \gamma_{HS}(P) \). It possible to fit the curve at only at \( \gamma_{HS} = 1/2 \) and at \( P_{1/2} \). This fitting allows receiving the change of enthalpy \( \Delta H_{HL} \) and interaction parameter \( \Gamma \) at PIST.