

# Supplementary Information

## List of Supplementary information

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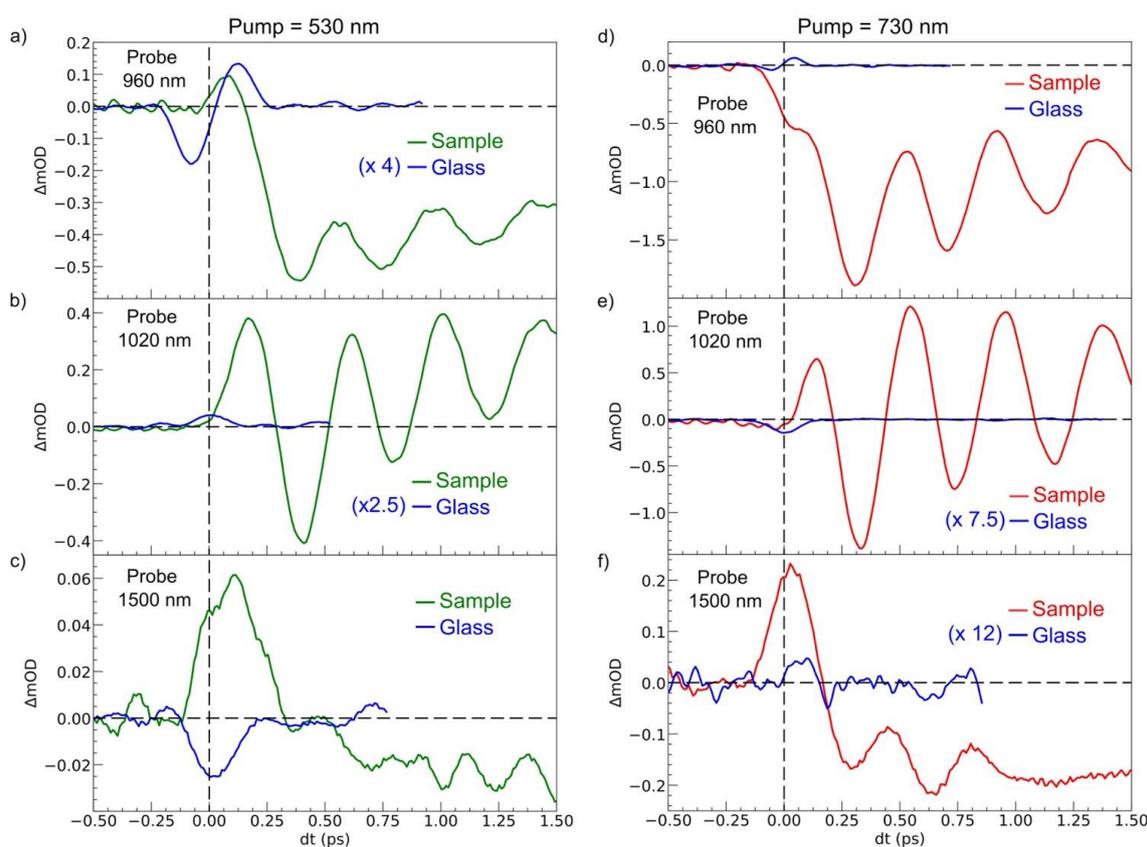
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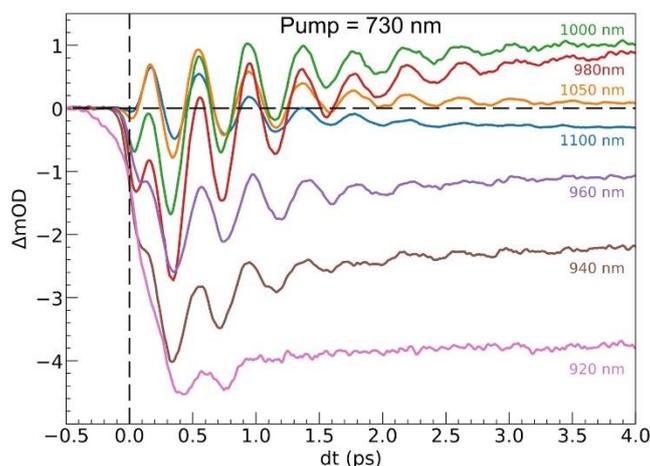
## 1 Optical pump-probe spectroscopy.

**1.1 Cross-phase modulation.** For each experiment on the sample deposited on the glass substrate, we checked possible cross-phase modulation (CPM) signal, by performing measurements with the same conditions (overlap, position, lasers power) on the glass substrate to find accurately the time zero (pum-probe overlap, Fig. S1). The amplitude of the CPM is negligible comparing to the real signal from the sample and we sometime had to increase the laser power by a factor  $\times 2.5$ -12 to observe weak CPM.



**Figure S1.** Timescan with and without the sample on the glass, showing weak cross-phase modulation. The laser power increase for detecting CPM on the glass is given in the figures.

**1.2 Time scan at different probing wavelengths.** We performed additional pump-probe measurements for pump wavelength set to 730 nm at different probing wavelengths. The data shown in Fig. S2 have in-phase oscillations, characteristic of the global shift of the d-d<sub>HS</sub> band with Fe-L change. Characteristic features of these time traces are similar to the ones presented in the manuscript (frequency of the mode,  $\tau_{\text{MLCT}}$ , ...). Time traces at 980 and 1000 nm show signatures of the intermediate state, but are also affected by the proximity of the isobestic point (970 nm, Figure 2(b)), which shifts in time during the vibrational cooling, as observed in other SCO crystals. The signal of these time traces therefore changes signs between 100-500 fs (hot HS state) and after 5 ps (vibrationally cool HS state). Below 940 nm oscillations are more difficult to observe.

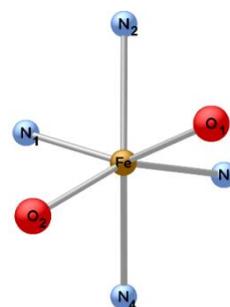


**Figure S2.** Time scans of relative milli-OD change at in the 920-1100 nm range revealing 80 (3) cm<sup>-1</sup> oscillations, upon d-d excitation at 730 nm.

## 2 DFT and TD-DFT calculation

### 2.1 Geometrical parameters

**Figure S3.** Schematic of bond lengths and angles outlines in tables S1-S2.



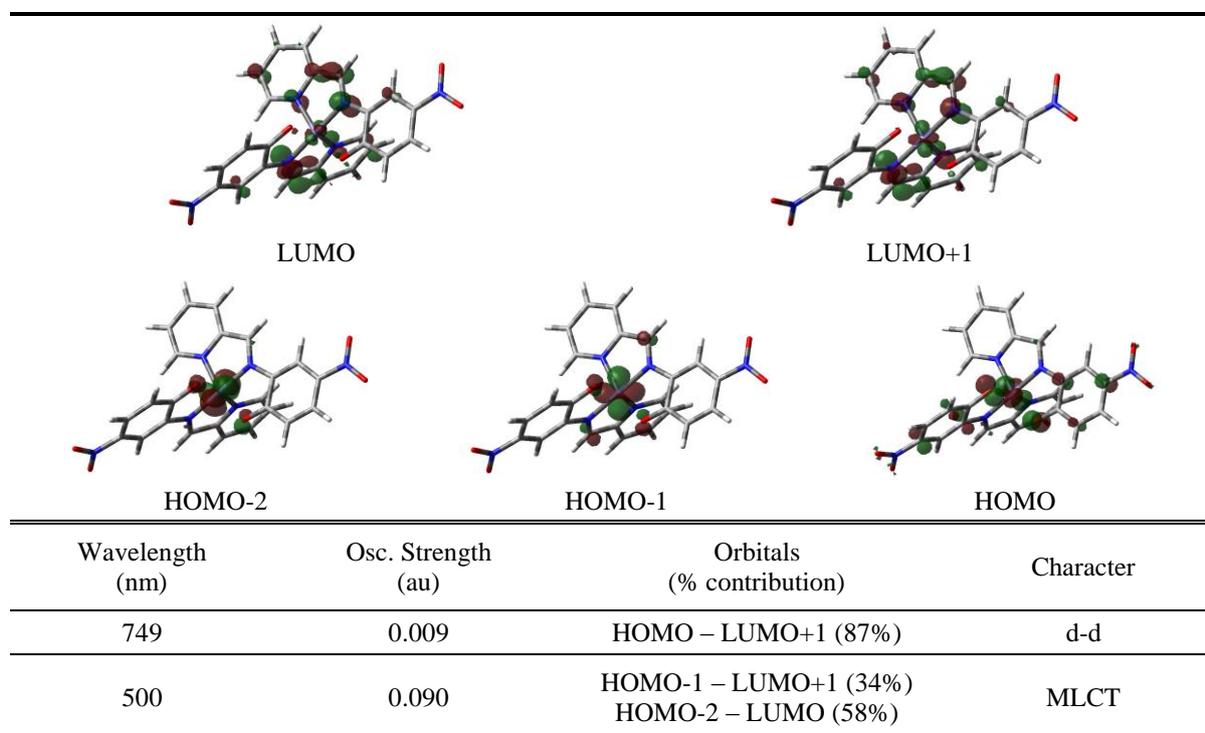
**Table S1.** Geometrical parameters of Fe-L core. Fe-L bond lengths (in Å) and angles (in °) are given.

Parameter	Singlet	Triplet	Quintet
Fe – N <sub>1</sub>	1.954	1.965	2.184
Fe – N <sub>2</sub>	1.883	1.905	2.091
Fe – N <sub>3</sub>	1.955	1.095	2.184
Fe – N <sub>4</sub>	1.883	1.905	2.091
Fe – O <sub>1</sub>	1.971	1.881	2.066
Fe – O <sub>2</sub>	1.971	1.881	2.066
∠ N <sub>1</sub> – Fe – N <sub>2</sub>	81.94	82.07	75.57
∠ N <sub>1</sub> – Fe – N <sub>3</sub>	90.93	88.41	90.30
∠ N <sub>1</sub> – Fe – N <sub>4</sub>	97.44	101.66	95.49
∠ N <sub>1</sub> – Fe – O <sub>1</sub>	165.82	166.59	152.82
∠ N <sub>1</sub> – Fe – O <sub>2</sub>	92.69	88.83	93.44
∠ N <sub>2</sub> – Fe – N <sub>3</sub>	97.44	101.66	95.49
∠ N <sub>2</sub> – Fe – N <sub>4</sub>	179.13	174.86	167.50
∠ N <sub>2</sub> – Fe – O <sub>1</sub>	83.99	85.27	77.28
∠ N <sub>2</sub> – Fe – O <sub>2</sub>	96.63	91.25	111.51

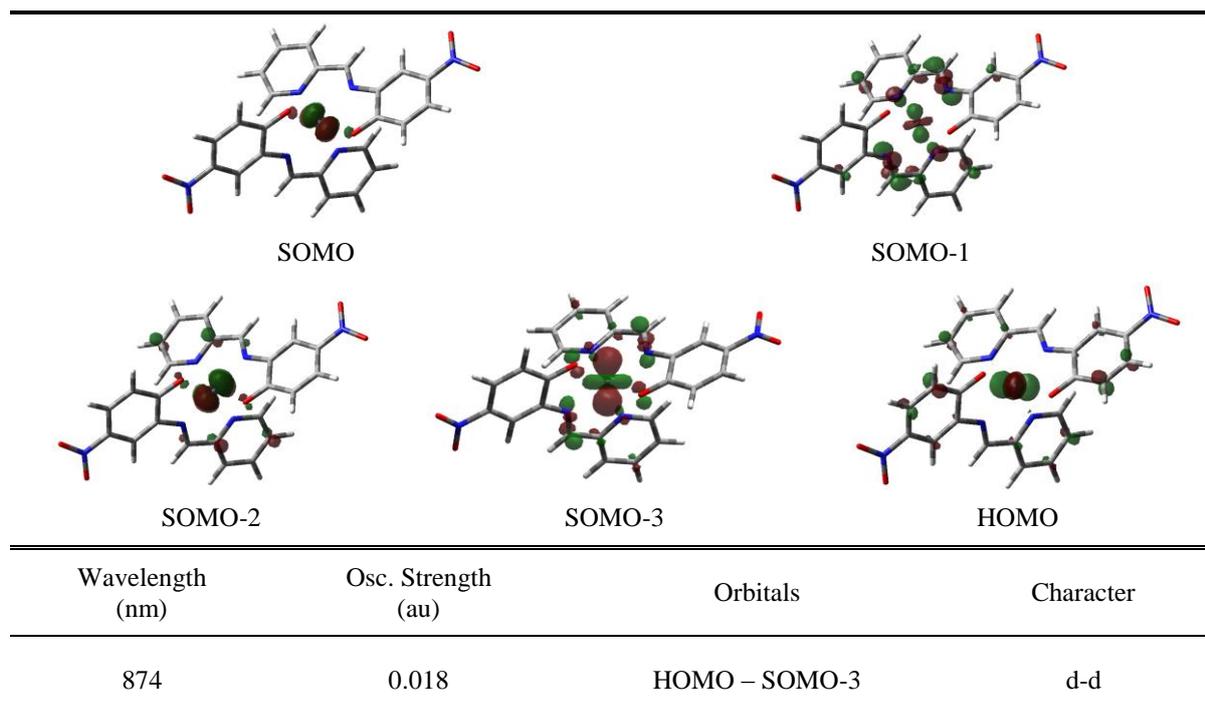
**Table S2.** Deviation of each spin species from a perfect octahedral environment (in terms of angles). Each Number represents the absolute value of the difference between the calculated angle and 90° or 180° where appropriate.

Parameter	$\Delta$ Singlet	$\Delta$ Triplet	$\Delta$ Quintet
$\angle N_1 - Fe - N_2$	8.06	7.93	14.43
$\angle N_1 - Fe - N_3$	0.93	1.59	0.3
$\angle N_1 - Fe - N_4$	7.44	11.66	5.49
$\angle N_1 - Fe - O_1$	14.18	13.41	27.18
$\angle N_1 - Fe - O_2$	2.69	1.17	3.44
$\angle N_2 - Fe - N_3$	7.44	11.66	5.49
$\angle N_2 - Fe - N_4$	0.87	5.14	12.5
$\angle N_2 - Fe - O_1$	6.01	4.73	12.72
$\angle N_2 - Fe - O_2$	6.63	1.25	21.51
MEAN	6.03	6.50	11.45

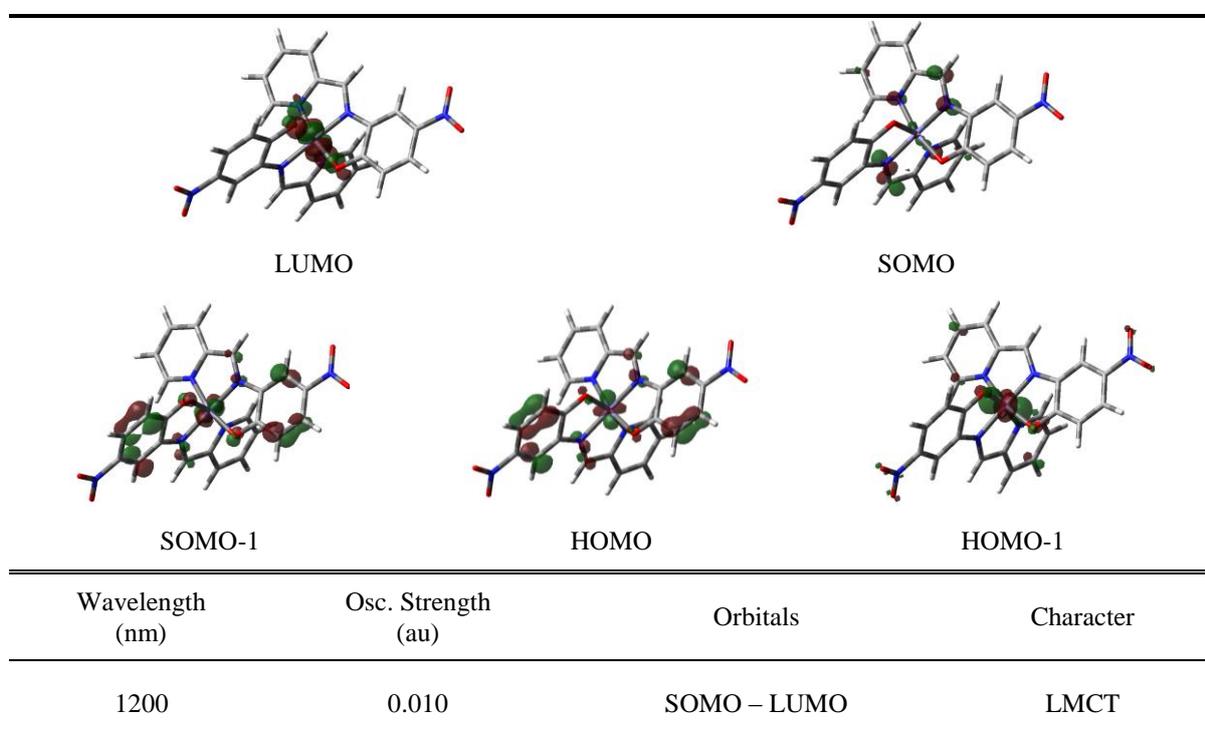
## 2.2 Frontier orbitals



**Figure S4.** Top: Frontier orbitals for the low-spin (singlet) species of  $Fe(pap-5NO_2)_2$ . Iso-contour value is 0.06. Bottom: MLCT and d-d transition information with the percentage contribution of significant transitions in the CI expansion, derived from the CI coefficients.



**Figure S5.** Top: Frontier orbitals for the high-spin (quintet) species of  $\text{Fe}(\text{pap-5NO}_2)_2$ . Iso-contour value is 0.06. Bottom: d-d transition information.



**Figure S6.** Top: Frontier orbitals for the intermediate-spin (triplet) species of  $\text{Fe}(\text{pap-5NO}_2)_2$ . Iso-contour value is 0.06. Bottom: LMCT transition information