

**Vacuum-evaporable spin–crossover complexes:
Physicochemical properties in the crystalline bulk
and in thin films deposited from the gas phase**

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Table S1: Variable temperature crystallographic studies of 6·0.5 toluene at 293 K, 200 K and 110 K

Empirical formula	$C_{29.50}H_{31.50}B_2FeN_{10}$	$C_{29.50}H_{31.50}B_2FeN_{10}$	$C_{29.50}H_{31.50}B_2FeN_{10}$
Formula weight	603.62	603.62	603.62
Crystal size	0.3 x 0.2 x 0.2 mm ³	0.3 x 0.2 x 0.2 mm ³	0.3 x 0.2 x 0.2 mm ³
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
Temperature	293 K	200 K	110 K
a, Å	11.5171(6)	11.4773(5)	11.4442(5)
b, Å	12.3371(7)	12.3580(5)	12.4056(5)
c, Å	12.7977(7)	12.6893(5)	12.5831(6)
α , deg	79.224(4)	78.624(3)	77.935(3)
β , deg	69.756(4)	69.827(3)	69.600(3)
γ , deg	63.512(4)	62.909(3)	62.577(3)
V, Å ³	1525.82(14)	1502.30(11)	1483.73(11)
Z	2	2	2
D _{calc.} , Mg/m ³	1.314	1.334	1.35
Parameters	354	390	390
Absorption coefficient, mm ⁻¹	0.532	0.540	0.547
F000	629	629	629
2-Theta range	2.13-27.00	1.71-27.00	1.73-27.00
Reflections collected	12773	14320	12804
Independent reflections	6472	6482	6345
R(int)	0.0305	0.0415	0.0372
Observed reflections (I>2 σ (I))	4581	5284	5283
R1 (I>2 σ (I))	0.0489	0.0422	0.0390
wR2 all data	0.1336	0.1037	0.0962
Goof	1.004	1.043	1.027
Selected Bond length (Å):			
Fe-N(1)	2.206(2)	2.1986(17)	2.1971(16)
Fe-N(2)	2.183(2)	2.1790(17)	2.1808(17)
Fe-N(3)	2.170(2)	2.1716(17)	2.1693(16)
Fe-N(4)	2.206(2)	2.1998(18)	2.1963(17)
Fe-N(5)	2.222(2)	2.2210(17)	2.2200(16)
Fe-N(6)	2.201(2)	2.1952(17)	2.1945(16)

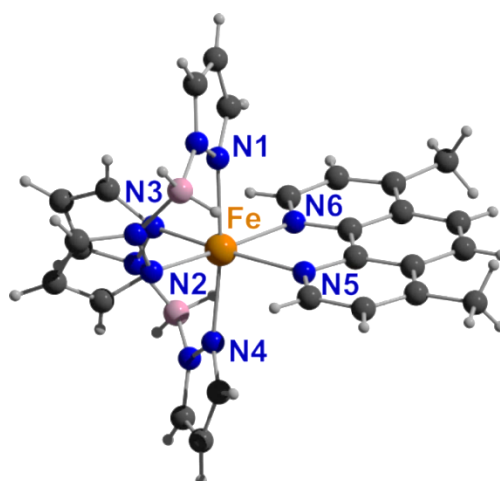


Figure S1. A molecule of 6·0.5 C_7H_8 at 293 K. Color code: C (black), H (grey), B (pink), N (blue), Fe (orange).

S2. XRPD of bulk material

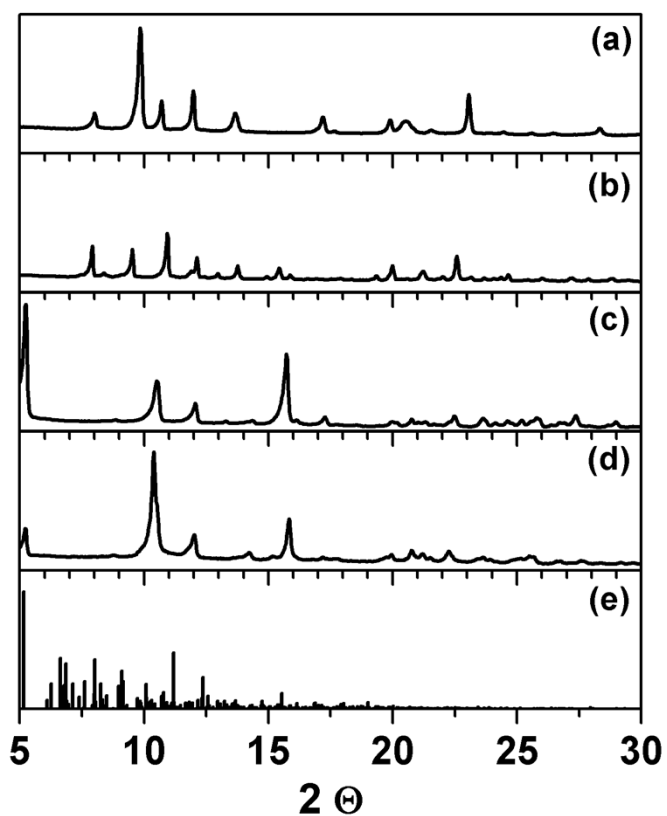


Figure S2. Experimental XRPD pattern of the compounds **3** (a), **4** (b), **5** (c) and **6** (d) as well as calculated pattern of $6 \cdot 0.5 C_7H_8$ (e).

S3. Physical vapour deposition on glass substrate

Compound	T / °C	p / mbar	t / min	film (300K/80K)
3	178	9×10^{-3}	12	
4	180	5×10^{-4}	7	
5	176	5×10^{-4}	15	
6	178	8×10^{-2}	10	

Figure S3. Pressure, temperature and time of thermal deposition and photographs of the resulting films on glass substrate of **3-6**.

S4. Infrared-spectra of bulk versus film

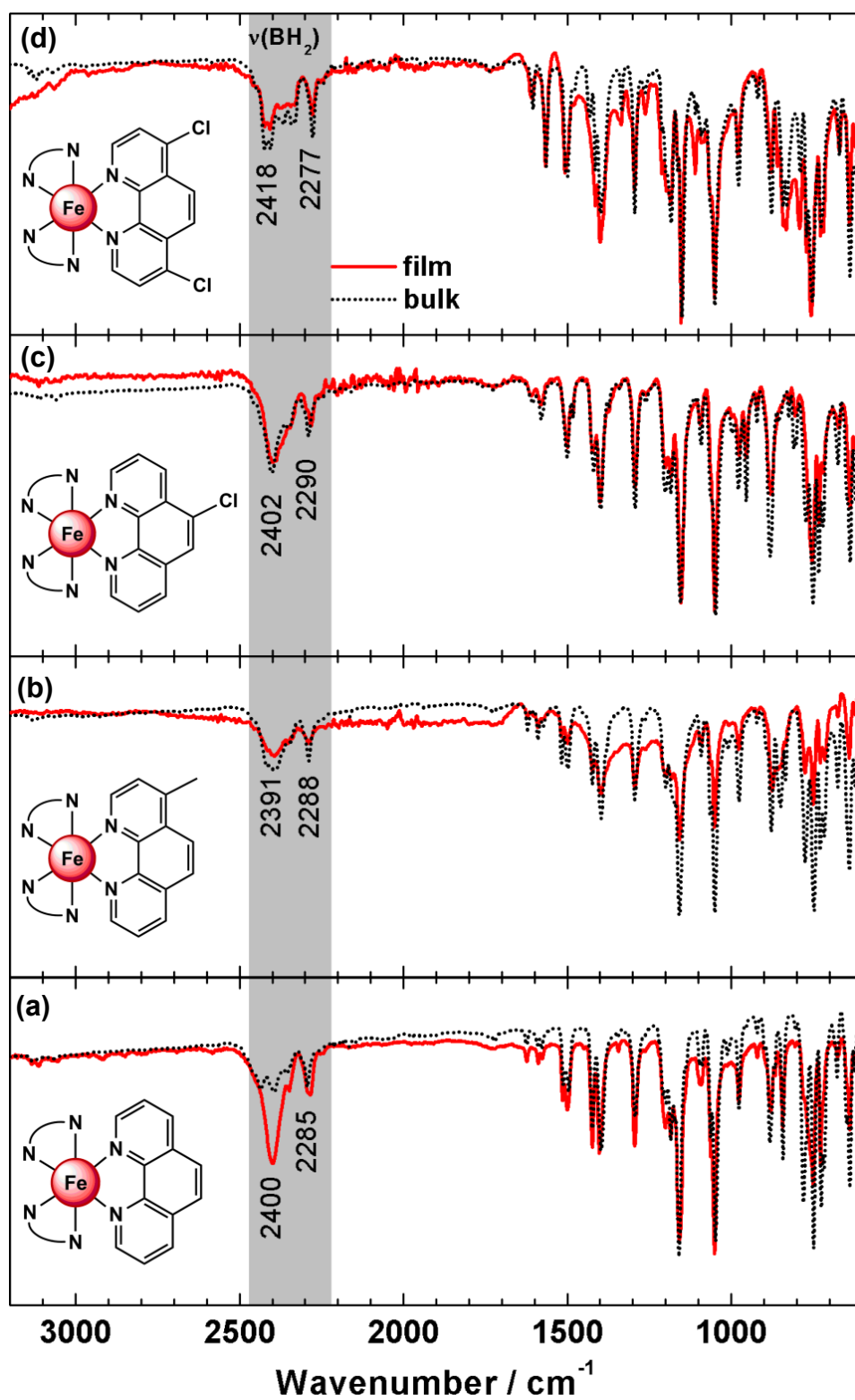


Figure S4. Infrared-spectra of 2 (a), 3 (b), 4 (c) and 5 (d) in bulk material (black dotted lines) and vacuum deposited material (red lines) at 300K.

S5. Uv/vis of 2 in polysterene

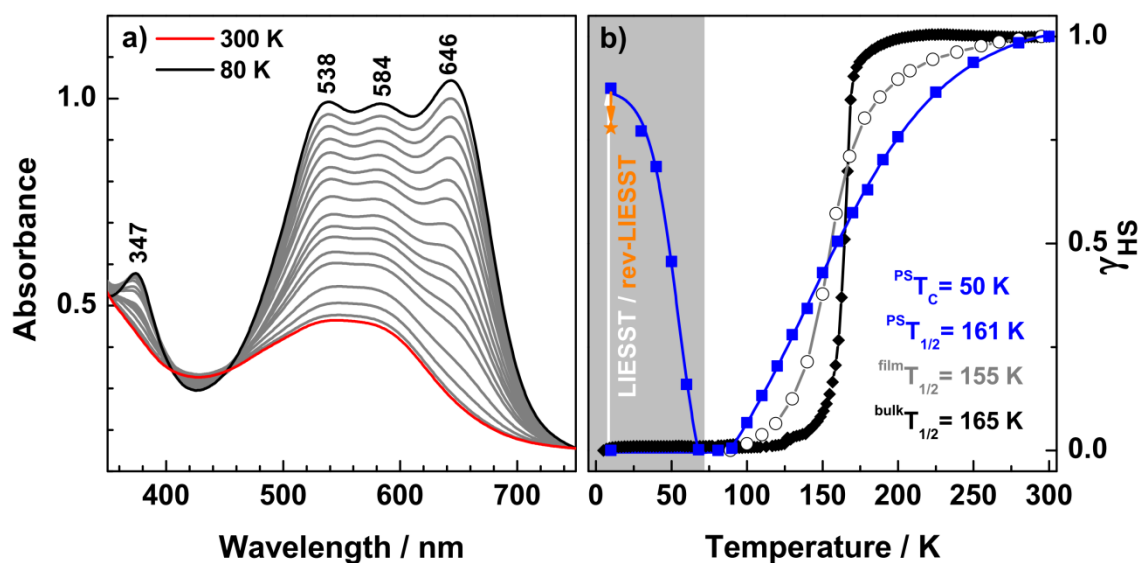


Figure S5.1. Temperature dependent UV/Vis absorption spectra of **2** embedded in polystyrene of 2% of weight (a). Amount of high-spin fraction γ_{HS} of **2** in polystyrene (blue dots), thin film on quartz disc (grey dots) and microcrystalline material (black dots)

The SCO-complex in polymer matrix was fabricated by dissolving polystyrene (Sigma Aldrich, average M_w 230,000) and the complex each in dry dichloromethane. A solution with 2 % of weight of **2** was injected in an O-ring and the solvent was removed by storage overnight.

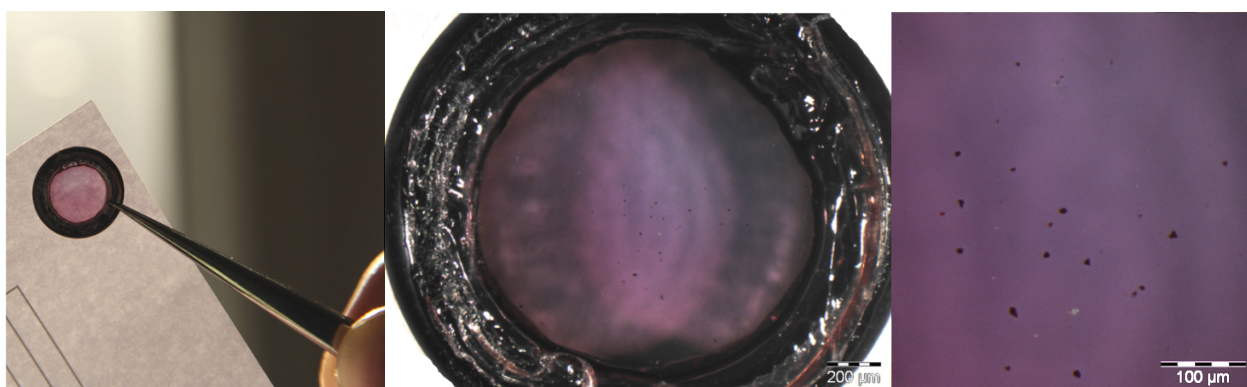


Figure S5.2. SCO-compound **2** embedded in polystyrene.

S6. XA-spectra of 6

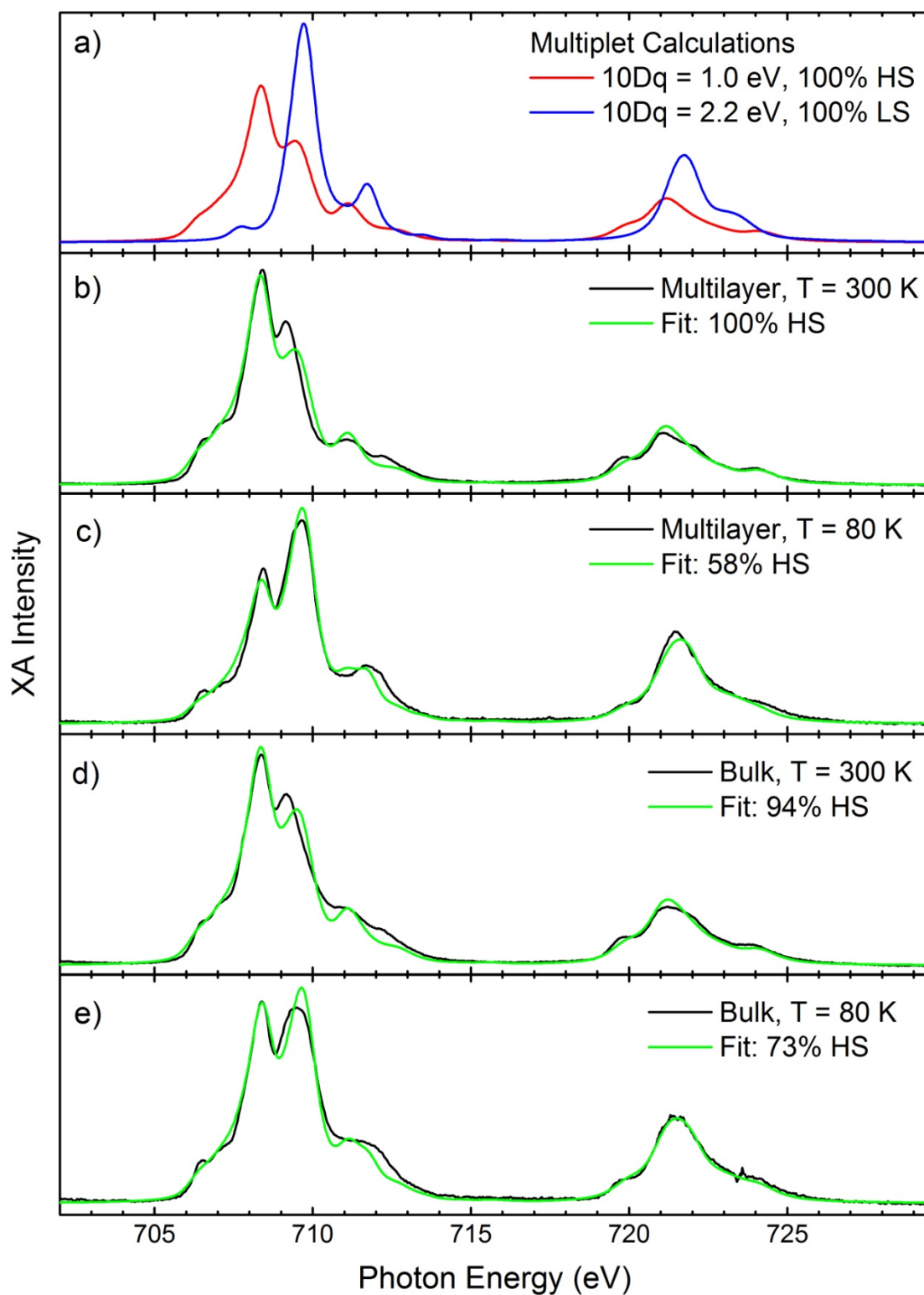


Figure S6.1. Calculated Fe L_{2,3} XA spectra (a) for a crystal field splitting parameter 10Dq of 1.0 and 2.2 eV. Fit of a linear combination of the calculated spectra to the temperature dependent Fe L_{2,3} XA spectra of 4 ML of 6 on HOPG (b and c) and the bulk powder sample pressed into indium foil (d and e).

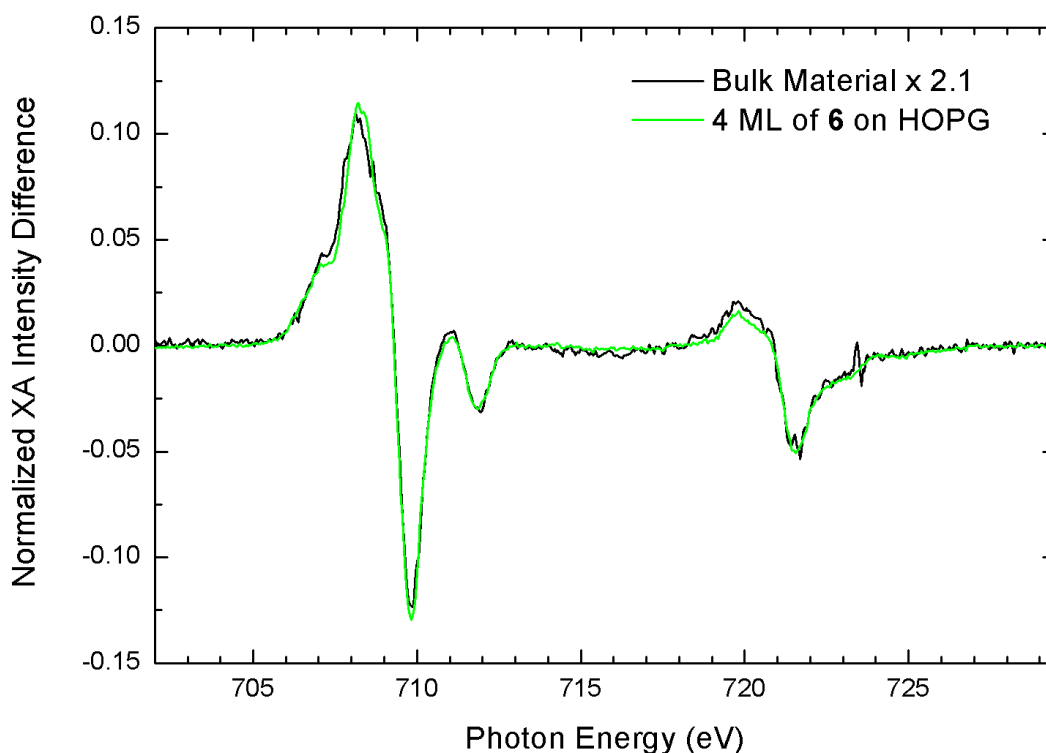


Figure S6.2. Fe $L_{2,3}$ XA difference spectra between the room-temperature and the 80 K measurement after normalization to the integrated XA intensity of 4 ML of **6** on HOPG and bulk powder sample pressed into indium foil (2.1 x enlarged).

Multiplet simulations without charge transfer were carried out in O_h symmetry with the multiplet program of Cowan and the CTM4XAS program¹ version 5.5. The spectra were calculated using the same parameters² as obtained for a thin film of **1**, i.e. a Slater reduction factor of $\kappa = 0.8$ and crystal field splitting parameters $10Dq$ of 1.0 and 2.2 eV for the HS and LS spectrum, respectively (Figure S5.1a). The HS fraction for each experimental XA spectrum was obtained by fitting a linear combination of the two calculated spectra (Figure S5.1b-e).

The relative amount of molecules that undergo SCO in the multilayer compared to the bulk material was determined independently from the XA difference spectra between the room-temperature and the 80 K measurement after normalization to the integrated XA intensity (Figure S5.2). Through this normalization the XA spectra become independent of the amount of molecules probed in the experiment and can be directly compared to each other. In the multilayer sample the amount of molecules that undergo SCO is higher by a factor of 2.1 compared to the bulk measurement.

[1] Stavitski, E.; de Groot, F. M., *Micron* 2010, **41**, 687 – 694.

[2] Warner, B.; Oberg, J. C.; Gill, T. G.; El Hallak, F.; Hirjibehedin, C. F.; Serri, M.; Heutz, S.; Arrio, M.-A.; Sainctavit, P.; Mannini, M.; Poneti, G.; Sessoli, R.; Rosa, P, *The Journal of Physical Chemistry Letters* 2013, **4**, 1546.