Electronic Supplementary Material (ESI) for Dalton Transactions

Light-Induced Excited Spin State Trapping effect on $[Fe(mepy)_3tren](PF_6)_2$ solvated crystals.

Antoine Tissot,*[a,b] Eric Rivière,[a] Régis Guillot,[a] Loic Toupet,[c] Eric Collet,[c] Marie-Laure Boillot*[a]

[a] *Université Paris Sud, ICMMO-ECI, UMR CNRS 8182, Université Paris-Sud, 91405 Orsay, France. marie-laure.boillot@u-psud.fr*

[b] *Université de Genève, Département de Chimie Physique, 30 Quai E. Ansermet 1211 Genève 4, Switzerland. antoine.tissot@unige.ch*

[c] *Institut de Physique de Rennes, UMR 6251, Université Rennes 1-CNRS, Rennes, France*

Supporting information.

Table S1: Analysis of the short-ring interactions (inter-ring distances < 6 Å and β < 60.0º). Distances are given in Å.

The rings are defined as follow:
5-Membered Ring (1) Fe(1) - N(1) - C(22) - C(21) - N(7) (noted Cg(1)).
5-Membered Ring (2) Fe(1) - N(2) - C(15) - C(14) - N(5) (noted Cg(2)).
5-Membered Ring (3) Fe(1) - N(3) - C(8) - C(7) - N(6) (noted Cg(3)).
6-Membered Ring (4) N(1) - C(22) - C(23) - C(24) - C(25) - C(26) (noted Cg(4)).
6-Membered Ring (5) N(2) - C(15) - C(16) - C(17) - C(18) - C(19) (noted Cg(5)).
6-Membered Ring (6) N(3) - C(8) - C(9) - C(10) - C(11) - C(12) (noted Cg(6)).
6-Membered Ring (7) C(102) - C(103) - C(104) - C(105) - C(106) - C(107) (noted Cg(7)).

	293 K	100 K	10 K (light off)	10 K (660 nm)
Cg(4) [1] -> Cg(4)	4.127(2)	4.0333(7)	4.2379(19)	3.9955(17)
Cg(5) [1] -> Cg(7)	4.305(7)	4.2474(9)	4.266(2)	4.2682(18)
Cg(6) [1] -> Cg(6)	3.830(2)	3.7543(8)	3.898(2)	3.7649(16)
Cg(7) [2] -> Cg(5)	4.305(7)	4.2473(9)	4.266(2)	4.2684(18)
Cg(1) [1] -> Cg(6)	4.506(2)	4.4290(7)	4.1289(19)	4.4340(16)
Cg(2) [1] -> Cg(4)	4.417(2)	4.4189(7)	4.113(2)	4.4519(17)
Cg(3) [1] -> Cg(5)	4.168(2)	4.1131(7)	3.916(2)	4.1310(16)

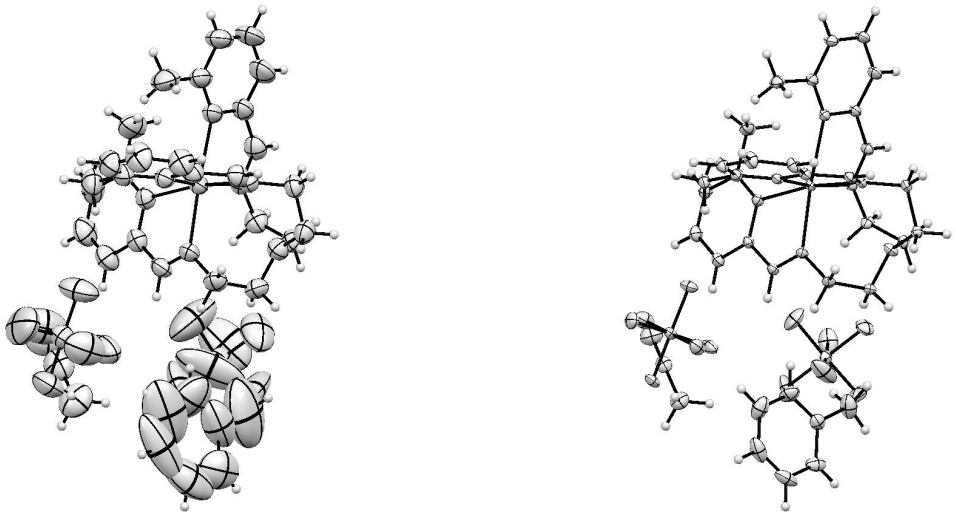
Interactions Cg(6) [1] -> Cg(6) and Cg(4) [1] -> Cg(4) are noted in the text interaction A and B, respectively.

Table S2: Analysis of X-H…Cg (Pi-ring) interactions (H..Cg < 3.0 Å and γ < 30.0º). Distances are given in Å.

	293 K	100 K	10 K (light off)	10 K (660 nm)
C(2) -H(2B) [1] -> Cg(3)	2.91	2.88	2.61	2.90
C(4) -H(4A) [1] -> Cg(7)	2.96	2.81	2.97	2.74
C(4) -H(4B) [1] -> Cg(1)	2.76	2.79	2.55	2.82
C(6) -H(6B) [1] -> Cg(2)	2.79	2.74	2.51	2.75
C(13) -H(13C) [1] -> Cg(1)	2.84	2.87	-	2.54 (H13A)
C(20) -H(20C) [1] -> Cg(6)	2.85	2.75	-	-
C(20) -H(20C) [1] -> Cg(3)	-	2.93	-	-
C(27) -H(27C) [1] -> Cg(2)	-	2.76	-	2.48

Table S3: Analysis of the intermolecular contacts (distance between Atom1 and Atom2 < sum of Van der Waals Radii - 0.1 Å). Atom1 is always located in the x, y, z position. Distances are given in Å.

Number	Atom1	Atom2	Position Atom2	293 K	100 K	10 K (light off)	10 K (660 nm)
1	C24	H10C	-1/2+x, 1/2-y, -1/2+z	-	-	2.513	2.496
2	C25	H10C	-1/2+x, 1/2-y, -1/2+z	2.789	-	2.788	2.688
3	C104	H14	1/2-x, -1/2+y, 1/2-z	-	-	2.748	-
4	F1	H105	1-x, -y, -z	-	2.56	2.511	2.548
5	F2	H3B	1/2+x, 1/2-y, -1/2+z	-	-	-	2.551
6	F2	H5A	1/2+x, 1/2-y, -1/2+z	-	-	2.503	-
7	F2	H10C	x, y, z	-	-	2.554	2.441
8	F5	H13C	x, y, z	2.559	2.469	2.567	-
9	F6	H10C	x, y, z	-	2.539	2.348	2.424
10	F6	H21	x, y, z	2.482	2.427	2.431	2.421
11	F7	H5B	1/2-x, 1/2+y, 1/2-z	2.476	2.439	2.458	2.424
12	F7	H27B	-x, 1-y, -z	-	2.444	-	-
13	F8	H7	1/2-x, 1/2+y, 1/2-z	-	2.566	-	2.556
14	F8	H11	1/2+x, 1/2-y, 1/2+z	-	2.471	2.414	2.439
15	F9	H10B	x, y, z	-	-	2.366	-
16	F10	H10D	x, y, z	-	2.528	-	-
17	F10	H17	1+x, y, z	2.358	2.359	2.307	2.365
18	F11	H25	-x, 1-y, -z	2.534	2.458	2.456	2.428
19	F12	H1B	x, y, z	2.541	2.53	-	2.513
20	F12	H3A	x, y, z	-	-	2.534	-
21	F12	H11	1/2+x, 1/2-y, 1/2+z	-	2.553	2.544	2.531
22	F8	C7	1/2-x, 1/2+y, 1/2-z	-	2.961	2.999	2.915
23	F11	C21	x,y,z	-	-	-	3.027



(a) (b)

Figure S1. Ortep view of the $[Fe(mepy)_3tren](PF_6)_2.C_7H_8.C_2H_3N$ HS structure at 293 K (a) and 100 K (b).

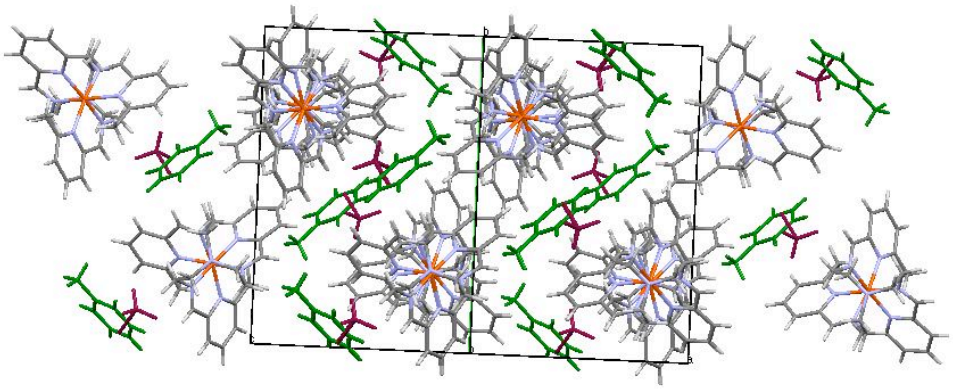


Figure S2. View of the 10 K packing showing the cations alignement (along ***a***+***c*** axis) with respect to the toluene (green) and acetonitrile (violet) molecules. The PF_6^- anions are omitted for clarity.

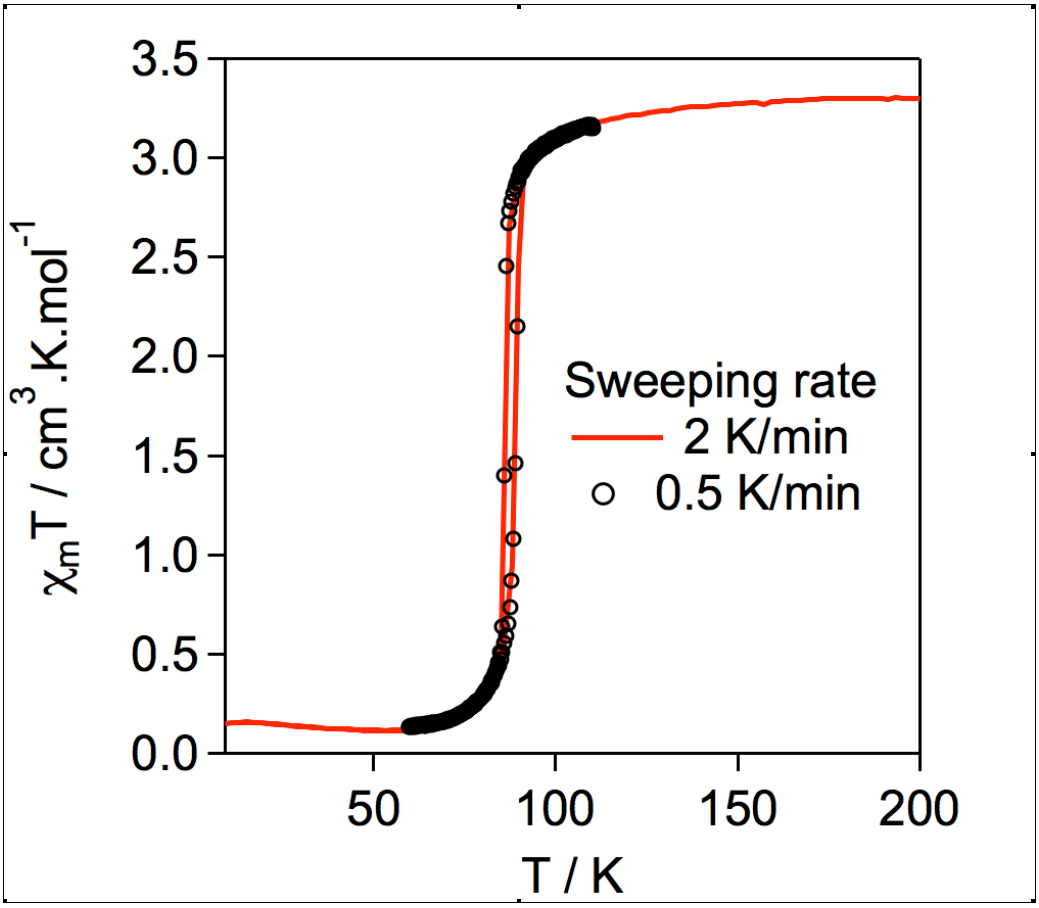


Figure S3. Evolution of the product of the magnetic susceptibility by the temperature $\chi_M T$ vs. temperature T registered at 2 K/min between 10 and 200 K and at 0.5 K/min between 60 and 110 K on $[Fe(mepy)_3tren](PF_6)_2.C_7H_8.C_2H_3N$ single crystals.

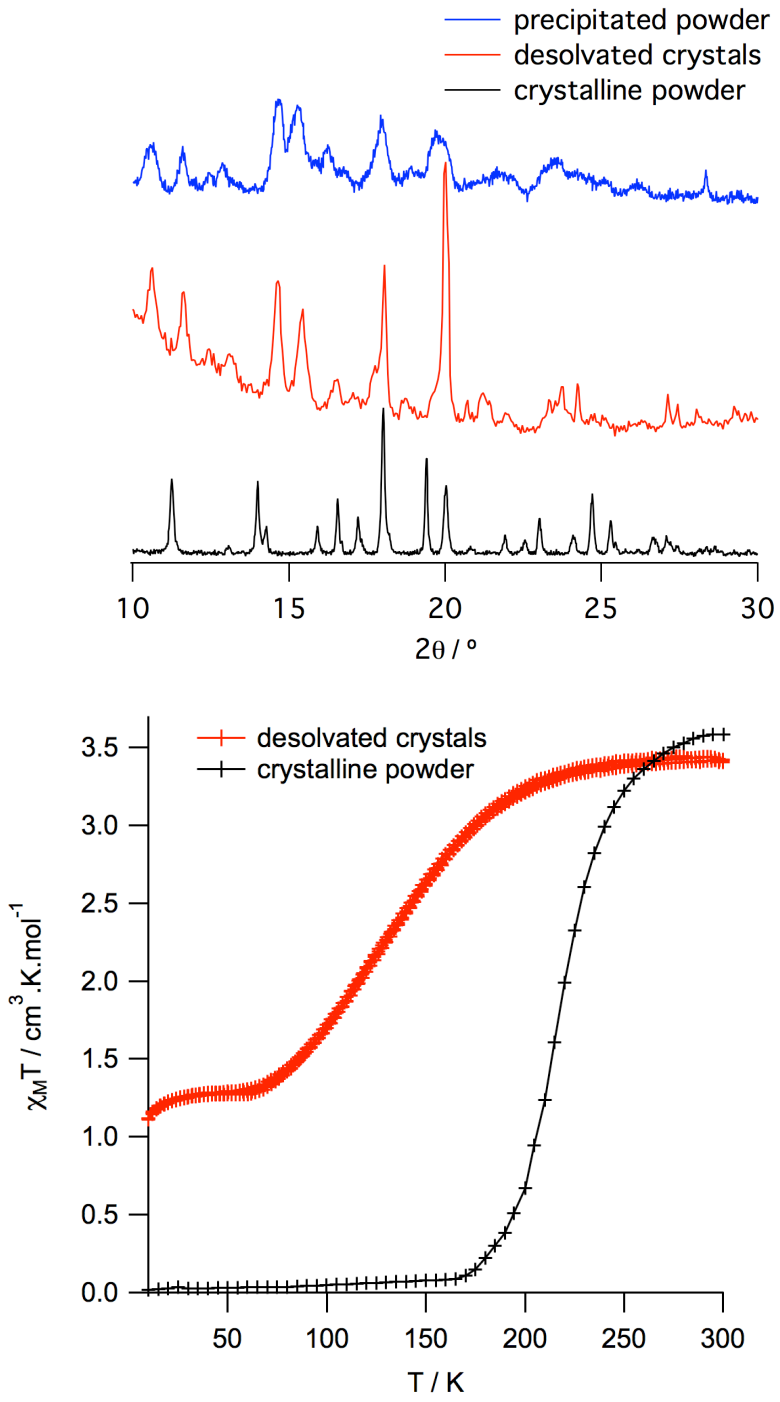


Figure S4. Powder X-Ray diffraction pattern of $[Fe(mepy)_3tren](PF_6)_2$ synthesized as described in [1], $[Fe(mepy)_3tren](PF_6)_2.C_7H_8.C_2H_3N$ desolvated by thermal treatment at 140 ºC and $[Fe(mepy)_3tren](PF_6)_2$ precipitated as described in ref [2] (up) and magnetization measurement performed on the desolvated crystals and on a crystalline powder synthesized as described in [1].

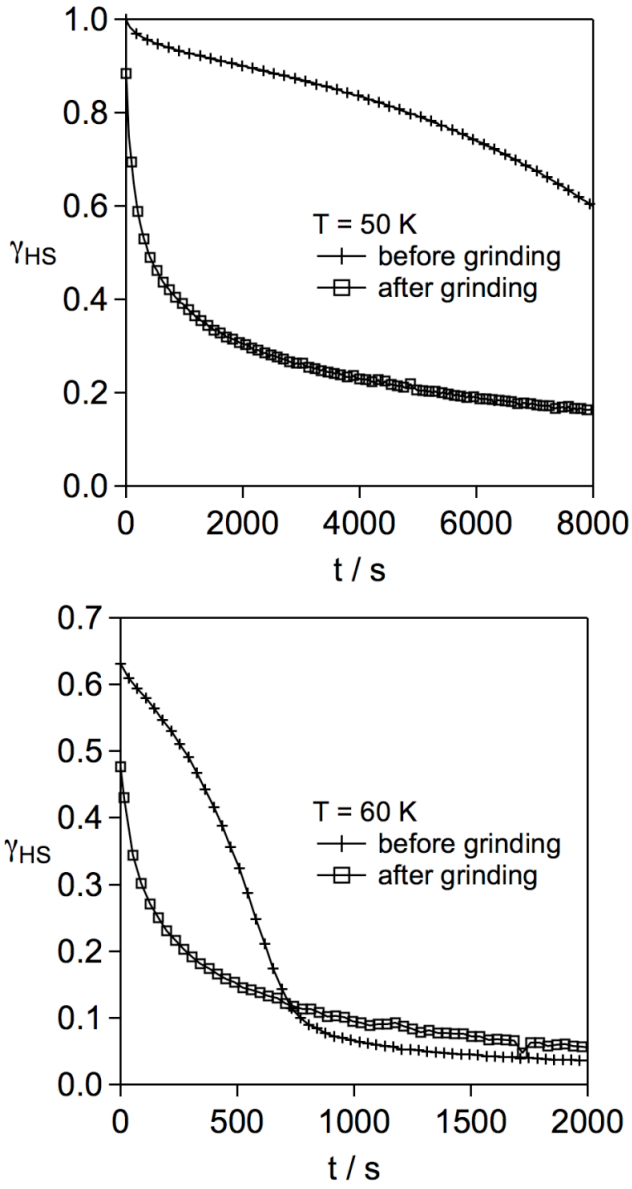


Figure S5. HS-LS relaxation curves registered on $[Fe(mepy)_3tren](PF_6)_2.C_7H_8.C_2H_3N$ crystals at 50 and 60 K before (+) and after (□) grinding.

[1] M. A. Hoselton, L. J. Wilson, R. S. Drago, *J. Am. Chem. Soc.* **1975**, *97*, 1722.

[2] A. Tissot, J.-F. Bardeau, E. Rivière, F. Brisset, M.-L. Boillot, *Dalton Trans.*, **2010**, *39*, 7806.