X-ray single-crystal diffraction study of the light-induced metastable HS state of the [Fe(mepy)₃tren](PF₆)₂ compound.

Experiments were performed both on neat [Fe(mepy)₃tren](PF₆)₂ and on the diluted system [FeₓZn₁₋ₓ(mepy)₃tren](PF₆)₂ (x=0.37). Icing was sometimes problematic but for each system we were able to collect good datasets as a function of the laser power. From these dataset, structural model could be found at each laser power. The evaluation of the power dependence using a mean-field approach allowed extrapolation of the light-induced structure to a HS fraction of 100%. The extrapolated structural parameters are in very good agreement with those of the analogous zinc compound as well as with the related system having a lifetime of several hours at 10 K. The mean-field model parameters for the cooperative effects extracted from the dynamic photo-crystallographic study agrees with those independently collected from the thermodynamic treatment of the thermal spin transition. This protocol was successfully applied to the neat compounds and to the diluted one, and both experiment allowed with the corresponding reference structures also allowed an accurate determination of the molecular structure of the short-lived HS state.

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Mean field model

During the irradiation, a competition between photo-excitation and relaxation processes takes place and the evolution of the HS fraction (γ_{HS}) is governed by the following differential equation:

$$\frac{dg_{HS}}{dt} = k_{ex}g_{LS} - k_{HL}g_{HS} = -\frac{dg_{LS}}{dt}$$

where k_{ex} is the photo-excitation rate constant and k_{HL} the HS-LS relaxation rate constant.

A laser power dependent steady-state value of the HS fraction, noted γ_{HS}^{ss}, is obtained under irradiation:

$$g_{HS}^{ss} = \frac{k_{ex}}{k_{ex} + k_{HL}} = \frac{1}{1 + k_{HL}/k_{ex}} = \frac{1}{1 + k_{HL}/cP}$$

For neat crystals

Cooperatives effects are present and $k_{HL} = k^0 e^{ag_{LS}} = k^0 e^{a(1-g_{HS})}$ where α is the self-acceleration factor and k^0 is the rate constant at $g_{LS} = 0$
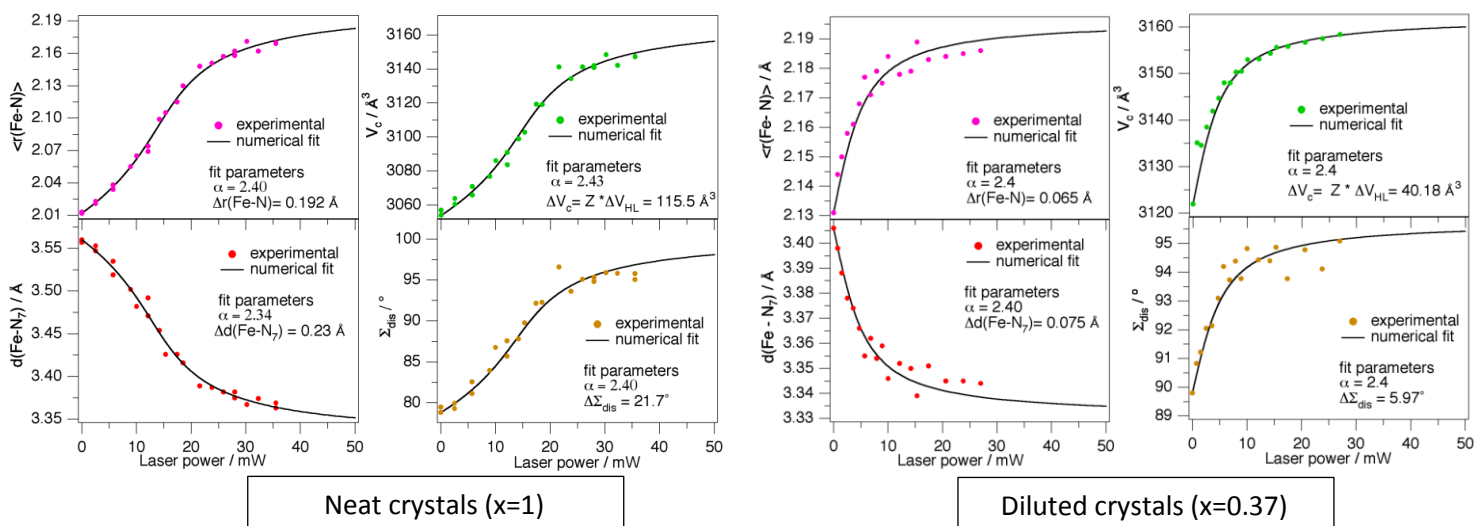
$$g_{HS}^{ss} = \frac{1}{1 + k^0 e^{a(1-g_{HS}^{ss})}/cP}$$

For diluted crystals

Cooperative effects cannot be fully neglected and equation (6) can be modified with a reduced value for the acceleration factor fixed at αₓ = xα.

$$g_{HS}^{ss} = \frac{1}{1 + k^0 e^{xa(1-g_{HS}^{ss})}/cP}$$

Neat crystals (x=1)

Diluted crystals (x=0.37)

Variation of the different structural parameters as a function of nominal laser power for

$[Fe_xZn_{(1-x)}n(6\text{-}mepy)_3tren](PF_6)_2$ at 10 K and the numerical fit (——) using a mean-field model.

The structural parameters obtained from the fits are reported in the table below

	Neat crystal	Mixed crystal[b]	Zn-reference[c]	Long-lived ref [d]
α	2.4(3)	2.4	-	-
x	1	0.37(3)	0	-
ΔV_{HL} / $\text{Å}^{3\,a}$	29(2)	26.8(2)	30.7(1)	24.3(1)
$<\Delta r(\text{Fe-N})>$ / Å	**0.192(6)**	**0.173(3)**	**0.190(1)**	**0.192(1)**
$\Delta d(\text{Fe-N}_7)$ / Å	**0.233(6)**	**0.200(4)**	**0.231(4)**	**0.317(4)**
$\Delta\Sigma_{dis}$ / °	21.7(4)	15.9(3)	15.69(3)	25.55(4)

[a] *The volume change calculated for one Fe atom.*

[b] *All the values are extrapolated to one Fe by taking into account the value of x. x was calculated from the average M-N (M= Zn or Fe) bond lengths at 10 K without irradiation*

[c] *It is the difference in the structure of $[Zn(6\text{-}mepy)_3tren](PF_6)_2$ and $[Fe(6\text{-}mepy)_3tren](PF_6)_2$ at 10 K.*

[d] *For $[Fe(6\text{-}mepy)_3tren](PF_6)_2 \bullet C_7H_8 \bullet CH_3CN$ from Antoine Tissot, doctoral thesis, University Paris XI, France, 2011*