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Strong Field Iron(II) Complex Converted by Light into a Long-Lived High-Spin State**

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Octahedral coordination compounds of transition metal ions with a d^4 to d^7 electronic configuration can be classified according to the ligand-field strength (LFS) into three groups: 1) low-spin (LS) state (strong LFS); 2) high-spin (HS) state (weak LFS), and 3) thermal spin crossover between HS ↔ LS (intermediate LFS), for example in the case of iron(II) complexes with a HS($^5T_{2g}$) ↔ LS($^1A_{1g}$) transition.[1]

More than ten years ago, the surprising observation was made that thermally switchable Fe^{II} spin-crossover complexes can also be optically switched from the LS to the HS state (LIESST = light-induced excited spin-state trapping“[2, 1a]) and from the HS to the LS state (reverse LIESST[1a]).

Usually, LS Fe^{II} complexes decay after photoexcitation within nanoseconds from the metastable HS state back to the LS state.[3] Herein, we report on an entirely unexpected observation: Complex molecules of [Fe(tpy)$_2$]$^{2+}$ (tpy = 2,2′:6′,2′′-terpyridine) embedded at a 2% concentration in the host matrix of the corresponding manganese compound [Fe$_{0.02}$Mn$_{0.98}$(tpy)$_2$](ClO$_4$)$_2$ (**1**) exhibit LS behaviour at room temperature, yet may be converted by light to the HS state with an effectively infinite lifetime (low-temperature tunneling lifetime $t^0_{HL} > 10^5$ s) at 10 K (LIESST effect).

The compounds **1** and [Fe(tpy)$_2$](ClO$_4$)$_2$ (**2**) were prepared by literature methods.[4a, 5] The Mössbauer spectra[4b] of **1** (Figure 1) and **2** exhibit LS behavior at ambient and lower temperatures ($^1A_{1g}$, ground state). The spectra of **1** at 300, 170, and 10 K each exhibits a quadrupole doublet of isomer shift values ($\delta = 0.13$, 0.20, 0.22 mm s^{-1}) and quadrupole splitting values ($\Delta E_Q = 0.98$, 0.95, 0.98 mm s^{-1}), respectively. These values are typical for LS Fe^{II}.[6]

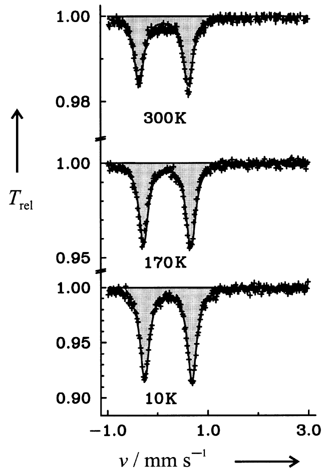

Figure 1. Mössbauer spectra of **1** at 300, 170, and 10 K. The spectra indicate only one quadrupole doublet, which is typical for Fe^{II} in the LS state.

Figure 2 shows the Mössbauer spectrum of **1** recorded after 30 min irradiation with green light at 10 and 80 K. At 10 K the spectrum now contains two quadrupole doublets: one ($\delta = 0.22$ mm s^{-1}, $\Delta E_Q = 0.97$ mm s^{-1}) originates from the original LS ground state; the other ($\delta = 0.95$ mm s^{-1}, $\Delta E_Q = 2.08$ mm s^{-1}) is indicative of Fe^{II} in the HS state (LIESST).[6] Presuming the Lamb–Mössbauer factors for the LS and HS states are equal, the fraction of [^{57}Fe(tpy)$_2$]$^{2+}$ complex molecules converted by light to the long-lived LIESST state is 66%, as estimated from the area fraction of the HS doublet. The spectrum recorded at 80 K (Figure 2) shows only the quadrupole doublet ($\delta = 0.21$ mm s^{-1}, $\Delta E_Q = 0.94$ mm s^{-1}) of the original LS ground state. This observation—which shows that the light-induced metastable HS state has relaxed back to the LS state—was fully reproducible. No light-induced spin-state conversion was observed for compound **2**, the pure iron compound.

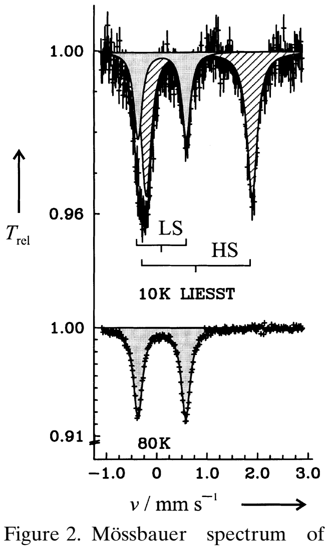

Figure 2. Mössbauer spectrum of compound **1** after irradiation with green light at 10 K. Comparison with Figure 1 shows that the major fraction has been converted to the HS state. After heating to 80 K, the Mössbauer spectrum indicated only the LS state remained.

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Compounds **1** and **2** contain aromatic ligands with energetically low lying π^* orbitals, which favour the appearance of metal-to-ligand charge-transfer (MLCT) transitions. The population of the metastable HS states of Fe^{II} occurs essentially through MLCT transitions (as recognized by the intense color of the LS complexes), which cover the weaker d–d transitions. Excitation at 514 nm excites primarily the $^1A_1 \rightarrow ^1MLCT$ transition (Figure 3).

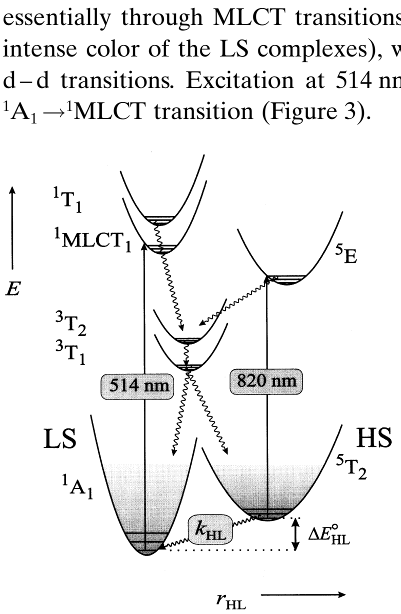

Figure 3. Mechanism of the "light-induced excited spin-state trapping" (LIESST) and reverse LIESST.

The relaxation kinetics of the decaying LIESST state was examined experimentally by Hauser[3] and described with an nonadiabatic multiphonon relaxation model based on an earlier theory proposed by Buhks et al.[7] One of the essential features of the model is that t^0_{HL} (namely, the low temperature tunneling relaxation rate $k^0_{HL} = (t^0_{HL})^{-1}$) of the LIESST state is strongly correlated with the energy difference ΔE^0_{HL} between the lowest vibronic levels of the HS and LS states involved (inverse energy-gap law; Figure 3). The energy gap ΔE^0_{HL} increases with increasing LFS. Since ΔE^0_{HL} is not experimentally accessible, Hauser[3] instead presented the logarithm of k^0_{HL} versus the transition temperature $T_{1/2}$ (the temperature at which 50 % of the Fe^{II} centers are in the HS state during the thermal spin transition) for a series of spin-crossover compounds (Figure 4).

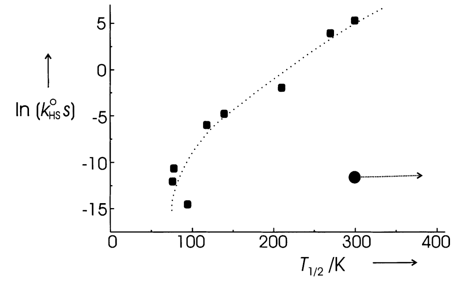

Figure 4. Experimental low-temperature tunneling rates $\ln k^0_{HL}$ plotted against $T_{1/2}$ for some Fe^{II} spin-crossover complexes[3] (square). The dashed line indicates the trend of the inverse energy-gap law. Complex **1** deviates unexpectedly from this law (circle; with $T_{1/2} \gg 300$ K). The data are from reference [3] ($T_{1/2}$ values in K): $[Fe/Zn(ptz)_6](BF_4)_2$ (95), $[Fe/Mn(pic)_3]Cl_2 \cdot EtOH$ (76), $[Fe/Zn(pic)_3]Cl_2 \cdot EtOH$ (78), $[Fe/Mn(pic)_3]Cl_2 \cdot MeOH$ (118), $[Fe/Zn(pic)_3]Cl_2 \cdot MeOH$ (140), $[Fe/Zn(mepy)_3(tren)](PF_6)_2$ (210), $[Fe(mepy)_2(py)(tren)]^{2+}$ in PMMA (270). ptz = 1-*n*-propyltetrazole, pic = α-picoline, mepy = 2-methylpyridine, tren = tris(2-aminoethyl)amine.

The idea behind this approximation is that $T_{1/2}$, given by the Boltzmann population of the HS manifold, is essentially proportional to ΔE^0_{HL}. Hauser[3] therefore collected data of highly diluted compounds and complexes of similar type (with six nitrogen donor atoms around the metal), such that the vibrational partition functions are similar. From the dependence of $T_{1/2}$ on t^0_{HL}, short t^0_{HL} are expected for strong-field complexes of Fe^{II} with LS behaviour at room temperature, that is, $T_{1/2}$ is well above room temperature. For example, t^0_{HL} is on the order of microseconds for tris(bipyridine) iron(II) complexes[3] (15 μs for $[Fe/Zn(bipy)_3](PF_6)_2$ at 10 K) and of nanoseconds for tris(phenanthroline) iron(II) complexes[8] (<6 ns for $[Fe/Zn(phen)_3](PF_6)_2$ at 10 K). Experimentally, we found a lifetime for the metastable HS state of complex **1** of the order of several days at ≤ 20 K. The observed lifetime of the LIESST state in **1** is more than eight orders of magnitude larger than expected on the basis of the inverse energy-gap law. We therefore name this new phenomenon the strong-field LIESST effect (SF-LIESST).

In conclusion, we have found that metal-diluted LS Fe^{II} complexes also show a LIESST effect; so far the LIESST effect has appeared to be restricted to thermal spin-crossover complexes of Fe^{II} with a $T_{1/2}$ below about 200 K. These results introduce a new class of optically switchable Fe^{II} complexes with possible device applications. While we are not yet able to explain the unexpectedly long lifetime of the optically induced LIESST state in an Fe^{II} complex, which is in the LS state at room temperature, low temperature X-ray diffraction and EXAFS studies before and after irradiation are underway to explore this aspect further.

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