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Quantum chemical study of spin crossover in Fe(II) complexes

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Ab initio calculations have been performed on $[\text{Fe}(\text{bpy})_3]^{2+}$ (bpy=bipyridine) and $[\text{Fe}(\text{tz})_6]^{2+}$ (tz=tetrazole) to establish the variation of the energy of the electronic states relevant to light-induced excited state spin trapping (LIESST) as function of the Fe–ligand distance. For the complex with bipyridine, the light-induced spin crossover takes place after excitation into the singlet metal-to-ligand (MLCT) band. We found that the corresponding electronic states have their energy minimum in the same region as the low-spin (LS) state and that the energy dependence of the triplet MLCT states is nearly identical to the 1MLCT states. The high-spin (HS) state is found to cross the MLCT band near the equilibrium geometry of the MLCT states. These findings give additional support to the hypothesis of a fast singlet-triplet interconversion in the MLCT manifold, followed by a 3MLCT–HS (5T₂) conversion accompanied by an elongation of the Fe–N distance.

On the other hand, the MLCT excitations have much higher energies in the tetrazole containing complex. LIESST is induced by excitation in a metal centered d–d transition. We discuss the deactivation path for this excited singlet state and find that this occurs either by overlap of the vibrational levels of the intermediate triplet or through an asymmetric Fe–L stretch, in which an intersystem crossing appears.