

Excited State Dynamics in Dinuclear $\{\text{Cu}_2(\mu\text{-I})_2\}$ Complexes Bearing Ar-BIAN Ligands

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Dynamics of the excited state of three complexes **C1**, **C2** and **C3** in dichloromethane have been probed by Transient Absorption Spectroscopy in the femtosecond time domain at different excitation wavelengths. The three complexes, regardless to the substitution pattern of corresponding free ligands (Figure I), revealed almost identical photophysical behaviour. In all case the excited complexes from an initially $^1(\text{M}+\text{X})\text{LCT}$ state either relax to the ground state or undergo fast Intersystem Crossing to $^3(\text{M}+\text{X})\text{LCT}$ within ~ 1 ps. In these dimeric systems the radiationless relaxation from $^3(\text{M}+\text{X})\text{LCT}$ occurs within the very fast time constant of ~ 25 ps. This unusual fast spin forbidden deactivation can be explained by Energy Gap Law through nested Potential Energy Surfaces of T_1 and S_0 .

When samples were excited at higher energies (440 nm) some photodegradation with ligand dissociation was observed. Despite of similar photophysical behaviour the extent of photodegradation is significantly reduced by introduction of NO_2 group in acenaphthene moiety of the free ligands. This functionalization made us possible to study the deactivation dynamics of the excited states in halide-bridged dimeric Cu(I) complexes bearing Ar-BIAN ligands.

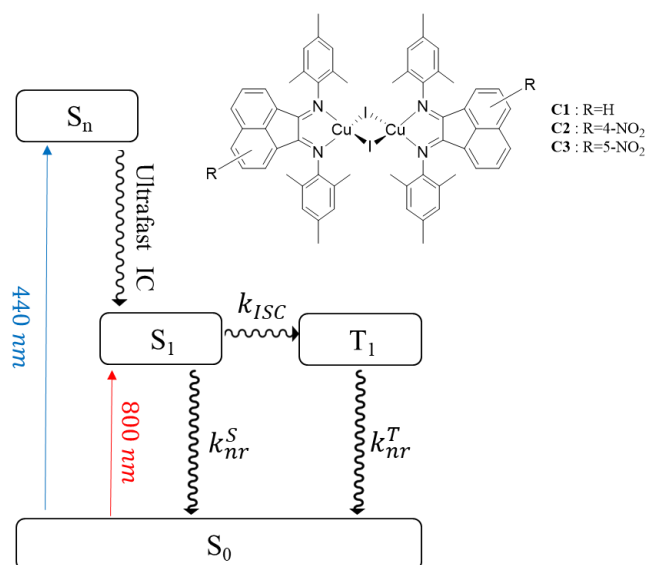


Figure I. Kinetic compartment modelling and chemical structure of the studied complexes.