

# ULTRAFAST ELECTRONIC RELAXATIONS IN DITHIOLENE COMPLEXES

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Transition-metal dithiolene complexes exhibit a variety of properties as a large second and third-order optical nonlinearity, optical limiting and conductivity when polymerized. In addition, several metal bis-dmit (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate) salts have been found to undergo superconducting transition.

For these reasons, they are the object of extensive studies for possible applications as different as dyes for laser and liquid crystal devices, light compensation filters for NIR radiation, but also electronic device applications (semiconductors for field-effect transistors, fabricating organic conductive films, etc).

The unique behaviour of this class of compounds originates from the highly delocalized nature of the frontier orbitals due to the conjugation of ligand  $\pi$  and metal  $d$  electrons, which gives them the possibility to easily change the oxidation state, as well as an enhanced polarizability. This is confirmed by investigation of the ultrafast third order nonlinearity of these systems whose instantaneous response points to a pure electronic origin, before any structural rearrangement.

Despite such a strong interest on their electronic properties, no studies have been carried out so far to investigate the first fs to ps time domain, where the early electronic dynamics occurs and most of the aforementioned properties originate. Here we present our first results on a series of square-planar  $d^8$  metal mixed-ligand dithiolene complexes investigated with fs time-resolved broadband transient absorption spectroscopy.

We studied the role played by the central atom, the ligands and the solvent. A common photocycle is found, where in a few ps the lowest long-lived triplet state is populated via an efficient intersystem crossing (ISC). Contrary to other metal-complexes these systems show a relatively slow ISC rate (typically  $10^{-11} \text{ s}^{-1}$ ) that increases accordingly to the spin-orbit coupling strength of the central metal. Along with the unexpected involvement of lower lying excited states, we found an unusually strong modulation of the electronic dynamics on the time scale of solvation response function. Possible models to rationalize this astonishing response to the solvent reorganization are discussed.