A strong steric hindrance effect on ground state, excited state, and charge separated state properties of a CuI-diimine complex captured by X-ray transient absorption spectroscopy - DTU Orbit (20/10/2019)

Photophysical and structural properties of a CuI diimine complex with very strong steric hindrance, \([\text{CuI(dppS)}_2]^+\) (dppS = 2,9-diphenyl-1,10-phenanthroline disulfonic acid disodium salt), are investigated by optical and X-ray transient absorption (OTA and XTA) spectroscopy. The bulky phenylsulfonic acid groups at 2,9 positions of phenanthroline ligands force the ground state and the metal-to-ligand charge-transfer (MLCT) excited state to adopt a flattened pseudo-tetrahedral coordination geometry in which the solvent access to the copper center is completely blocked. We analyzed the MLCT state dynamics and structures as well as those of the charge separated state resulting from the interfacial electron injection from the MLCT state to TiO2 nanoparticles (NPs). The OTA results show the absence of the sub-picosecond component previously assigned as the time constant for flattening, while the two observed time constants are assigned to a relatively slow intersystem crossing (ISC) rate (∼13.8 ps) and a decay rate (100 ns) of the \([\text{CuI(dppS)}_2]^+\) MLCT state in water. These results correlate well with the XTA studies that resolved a flattened tetrahedral Cu(i) coordination geometry in the ground state. Probing the 3MLCT state structure with XTA establishes that the 3MLCT state has the same oxidation state as the copper center in \([\text{CuI(dppS)}_2]^2+\) and the Cu-N distance is reduced by 0.06 Å compared to that of the ground state, accompanied by a rotation of phenyl rings located at 2,9 positions of phenanthroline. The structural dynamics of the photoinduced charge transfer process in the \([\text{CuI(dppS)}_2]^+\)/TiO2 hybrid is also investigated, which suggests a more restricted environment for the complex upon binding to TiO2 NPs. Moreover, the Cu-N bond length of the oxidized state of \([\text{CuI(dppS)}_2]^2+\) after electron injection to TiO2 NPs shortens by 0.05 Å compared to that in the ground state. The interpretation of these observed structural changes associated with excited and charge separated states will be discussed. These results not only set an example for applying XTA in capturing the intermediate structure of metal complex/semiconductor NP hybrids but also provide guidance for designing efficient CuI diimine complexes with optimized structures for application in solar-to-electricity conversion. This journal is