Electron Injection from Copper Diimine Sensitizers into TiO₂: Structural Effects and Their Implications for Solar Energy Conversion Devices

Copper(I) diimine complexes have emerged as low cost replacements for ruthenium complexes as light sensitizers and electron donors, but their shorter metal-to-ligand-charge-transfer (MLCT) states lifetimes and lability of transient Cu(II) species impede their intended functions. Two carboxylated Cu(I) bis-2,9-diphenylphenanthroline (dpp) complexes [Cu(I)(dpp-O(CH₂CH₂O)₅)(dpp-(COOH)₂)]⁺ and [Cu(I)(dpp-O(CH₂CH₂O)₅)(dpp-(Φ-COOH)₂)]⁺ (Φ = tolyl) with different linker lengths were synthesized in which the MLCT-state solvent quenching pathways are effectively blocked, the lifetime of the singlet MLCT state is prolonged, and the transient Cu(II) ligands are stabilized. Aiming at understanding the mechanisms of structural influence to the interfacial charge transfer in the dye-sensitized solar cell mimics, electronic and geometric structures as well as dynamics for the MLCT state of these complexes and their hybrid with TiO₂ nanoparticles were investigated using optical transient spectroscopy, X-ray transient absorption spectroscopy, time-dependent density functional theory, and quantum dynamics simulations. The combined results show that these complexes exhibit strong absorption throughout the visible spectrum due to the severely flattened ground state, and a long-lived charge-separated Cu(II) has been achieved via ultrafast electron injection (<300 fs) from the ¹MLCT state into TiO₂ nanoparticles. The results also indicate that the TiO₂-phen distance in these systems does not have significant effect on the efficiency of the interfacial electron-transfer process. The mechanisms for electron transfer in these systems are discussed and used to develop new strategies in optimizing copper(I) diimine complexes in solar energy conversion devices.

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