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Photoinduced charge transfer dynamics in coordination compounds

Coordination compounds are appealing targets for the development of light-harvesting devices. Currently Ru(II)-complexes are widely used but Cu(I)-compounds, in particular Cu(I)-phenanthrolines, are considered as promising alternative. In comparison Cu is more cost effective and environmentally friendly [1]. The metal-to-ligand-charge-transfer (MLCT) excited state of these Cu(I)-phenanthroline complexes is known to undergo structural reorganization, with the pseudotetrahedral D2d symmetry in the ground state changing to a flattened D2 symmetry in the MLCT state. This promotes ligation with solvent molecules, forming a so-called exciplex intermediate [2], dramatically shortening the lifetime of their excited state. Therefore, sterically active ligands could potentially be used to control the MLCT excited state properties of these compounds [3]. Using fs transient optical absorption spectroscopy, we have studied the ultra-fast kinetics, structural and electronic dynamics of new Cu(I)-phenanthroline complexes with varying degrees of steric hindrance in solution to identify structural origins of transient spectroscopic changes after their photoinduced MLCT excitation. We have demonstrated that for complexes with bulkier ligands a subpicosecond rising component is absent, which suggests that the Jahn–Teller distortion observed in other Cu(I)-phenanthroline complexes is effectively blocked by these functional groups. This implies that the pseudotetrahedral D2d symmetry is maintained and the solvent accessibility is reduced. These results together with our recent static X-ray emission spectroscopy experiments provide guidance for future X-ray structural studies in the ultrafast time regime, as well as for synthesis facilitating its applications in solar energy devices.

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