

2P030

Studying the substituent effect on ultrafast structural distortions in bis(diimine) Cu(I) complexes via nuclear wavepacket motion

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【Introduction】

The photophysical and photochemical properties of bis(diimine) copper(I) complexes have attracted a great deal of fundamental interest, because they exhibit a characteristic photoinduced structural change in the metal to ligand

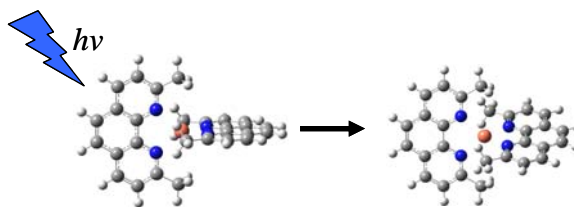


Fig.1 Flattening distortion in the MLCT excited state of $\text{Cu}(\text{dmphen})_2^+$

charge transfer (MLCT) excited state. Previously, we studied the ultrafast structural change of a prototype Cu(I) complex, $\text{Cu}(\text{dmphen})_2\text{PF}_6$ (dmphen is 2,9-dimethyl-1,10-phenanthroline), in solution by femtosecond time-resolved fluorescence and absorption spectroscopy^[1-2]. This Cu(I) complex has a D_{2d} structure in the ground state (Fig.1), where two ligands are attached perpendicularly to the central copper ion, whereas in the MLCT state, the dihedral angle between the two ligands gets smaller than 90 degrees (flattening distortion). It was found that the initial MLCT state (S_1) can stay undistorted for a short time, and then relaxes to the flattened structure in the S_1 state with a time constant of ~ 0.7 ps. For this class of Cu(I) complexes, it is known that steady-state emission in solution is observed only for complexes with bulky substituents introduced at the 2- and 9- positions of the phenanthroline ligands. This fact suggests that the steric hindrance between the two ligands can substantially affect photophysical properties of the complex.

To examine this substitution effect and the mechanism behind, we studied the excited-state dynamics and vibrational structure of the Cu(I) complexes having substituents of different bulkiness (Fig.2) by using ultrafast pump-probe spectroscopy.

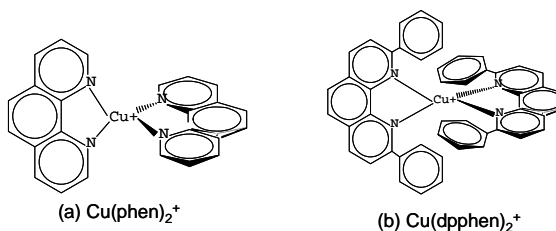


Fig.2 Molecular structure of Cu(I) complexes with different substituents.

【Experimental】

In the two-color pump-probe experiment with ~ 30 fs time resolution, we excited the molecule to the S_1 state by a 550-nm pulse (18 fs FWHM), and monitored the excited-state dynamics by a probe pulse

centered at 1000 nm (19 fs FWHM). Fresh CH₃CN solutions of Cu(phen)₂⁺ (phen is 1,10-phenanthroline) and Cu(dpphen)₂⁺ (dpphen is 2,9-diphenyl-1,10-phenanthroline) were prepared and circulated with a flow cell (0.2 mm thick).

【Results and discussion】

We carried out pump-probe experiments using a probe pulse centered at 1000 nm. Since this probe pulse has no spectral overlap with the S₁←S₀ absorption but is resonant with transitions of the excited state, we can selectively monitor the excited-state dynamics. As shown in Fig.3, both complexes clearly exhibit oscillation features due to coherent nuclear wavepacket motions in the S₁ state. It was found that the oscillation damps faster in Cu(phen)₂⁺ than in Cu(dpphen)₂⁺. This result implies that the structural change proceeds faster in Cu(phen)₂⁺, reflecting a smaller steric hindrance. Fig.4 shows Fourier transform power spectra of the oscillation component, representing the excited-state vibrational structure in the low-frequency region. On the basis of these experimental results, we discuss the substituent effect on the excited-state dynamics and vibrational structure of the bis(diimine) copper(I) complexes.

【References】

- [1] M. Iwamura, S. Takeuchi, and T. Tahara, *J. Am. Chem. Soc.* 129,5248(2007);
- [2] M. Iwamura, H. Watanabe, K. Ishii, S. Takeuchi, and T. Tahara, *J. Am. Chem. Soc.* 133,7728(2011).

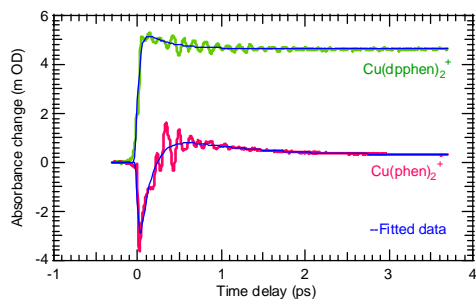


Fig.3 Time-resolved absorption signals obtained from Cu(phen)₂⁺ and Cu(dpphen)₂⁺ in acetonitrile.

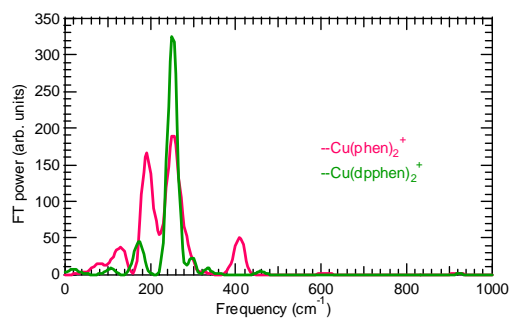


Fig.4 Fourier transform power spectra of the oscillatory components.