

# Exciplex Formation of Copper (II) Octaethylporphyrin Revealed by Pulsed X-rays

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## Introduction, Methods, and Materials

The triplet excited structures of Cu(II) octaethylporphyrin (CuOEP) in toluene and in a 1:1 mixture of toluene and tetrahydrofuran (THF) (Fig. 1) were investigated by time-domain laser pulse pump, x-ray pulse probe x-ray absorption spectroscopy (pump-probe XAS) at room temperature by using x-rays from a third-generation synchrotron source with a 100-ps time resolution. Discussion

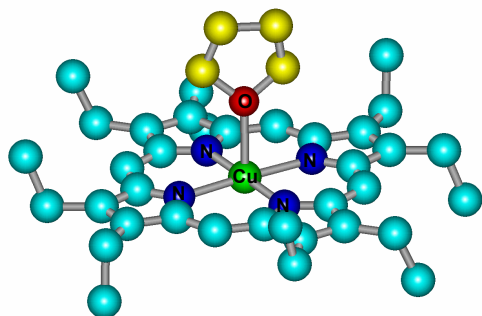


FIG. 1. Illustration of CuOEP-THF complex. H atoms are omitted for simplicity. The atoms are C unless otherwise labeled.

## Results and Discussion

The transient optical absorption measurements indicate a strong solvent dependency for the triplet excited-state lifetime as a result of the presence of oxygen-containing solvent molecules. While the ground-state CuOEP molecules remain square-planar in both solvents, the attenuation of a peak attributed to the  $1s \rightarrow 4p_z$  transition at the Cu K edge for the laser-excited CuOEP in the THF/toluene mixture revealed the penta-coordinated exciplex formation, which is responsible for shortening the triplet excited-state lifetime. Meanwhile, the average Cu-N distance in the triplet excited state is lengthened by 0.035 Å as the result of ligation with a THF solvent molecule, which agrees with a domed coordination structure for copper in the penta-coordinated exciplex (Fig. 2).

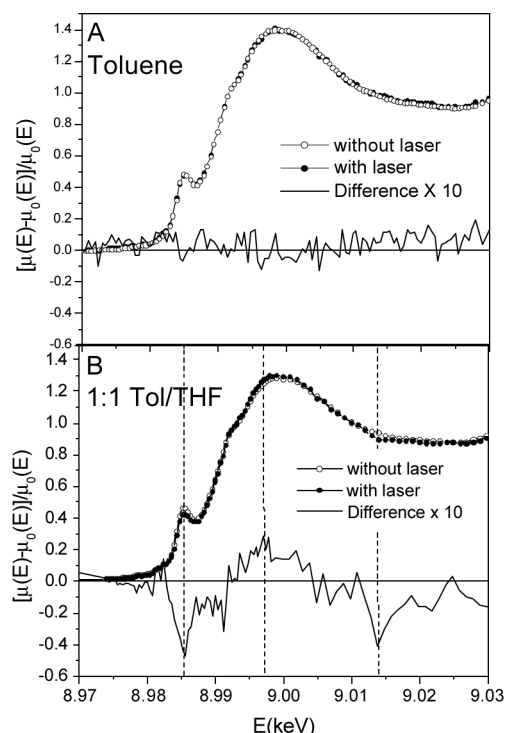


FIG. 2. XANES spectra of CuOEP with and without laser excitation.

## Acknowledgments

This work was supported by the Division of Chemical Sciences and Materials Science in the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES) under Contract No. W-31-109-ENG-38. The authors would like to thank the BESSRC beamline staff at the APS for their assistance. Use of the APS was supported by DOE BES under Contract No. W-31-109-ENG-38.