Poster Presentation

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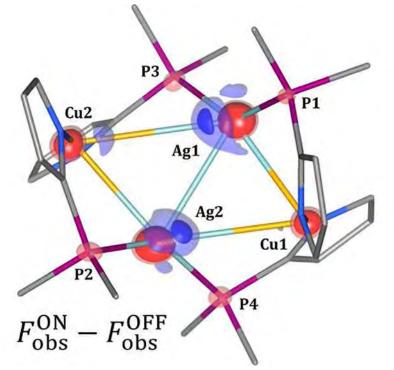
Direct observation of the excited state structure of a Ag(I)-Cu(I) complex

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Heterodentate coordination complexes have been extensively studied because of their rich electronic and luminescent properties, which are of importance in the design of molecular devices. The short metal-metal contacts found in such complexes determine the nature of the lowest lying emissive states, and must be explored in order to understand their physical properties. Recent advances in time-resolved (TR) synchrotron techniques supported by specific data collection strategies and data processing procedures [1] allow for elucidation of molecular excited state geometries in the solid state. The approach has been so far successfully applied to several high-quality Laue-data sets collected at the 14-ID BioCars beamline at the Advanced Photon Source.[2] In this contribution we present synchrotron TR experiment results obtained for a new solvent-free crystal form of a model complex containing Ag(I) and Cu(I) (Ag2Cu2L4, L = 2-diphenylphosphino-3-methylindole).[3] This system exhibits red solid-state luminescence with a lifetime of about 1 µs. This is one of the shortest-lived excited states we have studied so far with the Laue technique. The relatively short lifetime goes along with significant structural changes observed upon irradiation, such as, the Ag...Ag distance shortening of about 0.2 Å in the excited state. The results clearly show strengthening of the Ag...Ag interactions suggesting a bond formation upon excitation. The photocrystallographic findings are supported by spectroscopic measurements and quantum computations. The results confirm the triplet nature of the emissive state originating mainly from a ligand-to-metal charge transfer. Research funded by the NSF (CHE1213223). BioCARS Sector 14 is supported by NIH, National Center for Research Resources (RR007707). APS is funded by the U.S. DOE, Office of Basic Energy Sciences (W-31-109-ENG-38). KNJ is supported by the Polish Ministry of Science and Higher Education through the "Mobility Plus" program.

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