

Ultrafast photocrystallographic and spectroscopic studies of selected coinage-metal coordination compounds

P. Łaski¹, J. Drapała², R. Kamiński¹, K. Durka², K. N. Jarzemska¹

¹ Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland,

² Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

piotr.laski@gmail.com

Photoactive materials are among the most researched and engineered functional materials, due to the multiplicity of applications they find in research and industry. Investigating of the dynamics of short-lived excited states in crystal structures allows us to extract information on how such materials could be designed on the molecular level in order to obtain desired properties. Coordination compounds containing group XI transition-metal atoms, such as copper (I), silver(I), or gold(I), are excellent examples of compounds with interesting and diverse photoactive properties, and thus were chosen for this study.

Time-resolved photocrystallographic methods allow us to investigate structural changes occurring due to formation of short-lived laser-induced excited-state species in crystals. For the following study, several coinage-metal mononuclear and multinuclear coordination compounds were examined using time-resolved X-ray-pump / laser-probe Laue experiments, conducted at the 14-ID-B BioCARS APS synchrotron beamline. The studied complexes include the literature-reported Ag(PP)(PS) (PP = 1,2-bis(diphenylphosphino)ethane, PS = 2-(diphenylphospane)pyridine) and newly-synthesised Ag₂Cu₂(PS)₄ systems, both exhibiting bright luminescence in the solid state. The time-resolved data were processed with our home-made software and the photodifference maps were generated and analysed.

In order to comprehensively understand excitation-induced effects occurring in crystals, the abovementioned photocrystallographic measurements were supplemented with time-resolved luminescence spectroscopy experiments (355 nm excitation wavelength) and quantum computations yielding the nature of studied excited states and predicting the geometry changes (TDDFT and QM/MM methods) upon excitation. Results will be presented, and their accordance with photocrystallographic results assessed.

Keywords: photocrystallography, spectroscopy, coinage-metal complexes, time-resolved studies

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