Poster

Nanosecond-lived excimer observation in a rhodium(I) crystalline complex via time-resolved Laue diffraction

P. Łaski[1], L. Bosman[2], J. Drapała[1,3], R. Kamiński[1], D. Szarejko[1], P. Borowski[1], A. Roodt[2], A. Brink[2], K. N. Jarzembska[1]

[1]Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, Warsaw, Poland, [2]Chemistry Department, University of the Free State, Nelson Mandela Drive, Bloemfontein, South Africa, [3]Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

katarzyna.jarzembska@uw.edu.pl

Detailed investigations of light and matter interactions are indispensable to understand mechanisms of many crucial (bio)chemical processes, the nature of excited-states and structural dynamics. Such knowledge can also be successfully applied to designing novel effective functional materials for applications in optoelectronics, solar-energy conversion systems, storage devices, various sensors etc. Since many of such materials are solid-state materials, crystals constitute convenient model systems as they can be relatively easily studied using crystallographic methods. In order to trace short-lived transient species advanced approaches have to be applied, such as laser-pump/X-ray-probe methods combined with serial crystallography, or Laue technique. To achieve the required fine time resolution, such experiments are realized at synchrotron beamlines or X-ray free-electron laser (XFEL) sources, where ultra-short X-ray pulses can be generated [1,2].

From a chemical perspective, coordination compounds containing transition metal centres with d^8–d^{10} electronic configurations are among the most interesting functional systems as far as spectroscopic properties are concerned. Such metal centres are prone to form intra- and/or intramolecular short metal-metal contacts, which usually influence the nature of the lowest laying emissive states. In this contribution a potential precatalyst of Monsanto reaction – a rhodium(I) coordination compound – was synthesized and its structure confirmed by single-crystal X-ray diffraction. The compound's molecules arrange into dimers in the crystal structure, held by metallophilic interactions and hydrogen-bond-like contacts (Fig. 1). Spectroscopic properties of both solid-state and solution samples were determined using UV-Vis absorption spectroscopy and time-resolved solid-state emission spectroscopy. It appeared that the examined system is fluorescent once excited with the near-UV light. Emission maximum is located around 560 nm, whereas the emission lifetime ranges from 1 to 2 ns at room temperature and at 100 K, respectively. A series of time-resolved Laue diffraction photocrystallographic experiments were conducted at the 14-ID-B BioCARS beamline at APS. The collected data were processed with our home-written LaueProc software, which was specifically adapted to handle TR Laue data acquired for small molecules. The resulting photodifference map is presented in Fig. 1. The refined excited-state model showed the excimer formation upon irradiation (Rh···Rh distance shortening from 3.379(4) to 3.19(1) Å at 100 K) and was convincingly attributed do the lowest-lying excited singlet state, S_1. The experimental findings were supported by quantum-mechanical computations and modelling, including TDDFT and QM/MM calculations for the S_0, S_1 and T_1 states.

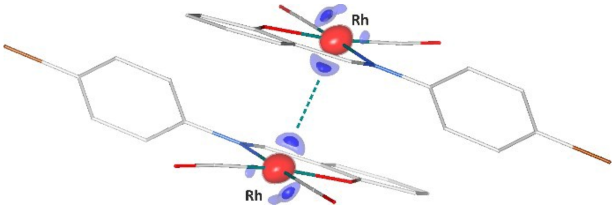

Figure 1. Photodifference map ('$F_{ON} - F_{OFF}$') calculated for the studied system showing atomic shifts in the S_1 excited state, superimposed onto the S_0 ground state geometry. Solid isosurfaces, ±0.50 $e \cdot Å^{-3}$; semi-transparent, ±0.41 $e \cdot Å^{-3}$; blue – positive; red – negative. The turquoise dashed line denotes the Rh···Rh interaction.

[1] Deresz, K. A., Łaski, P., Kamiński, R., Jarzembska, K. N. (2021). *Crystals*, **11**, 1345.

[2] Jarzembska, K. N., Kamiński, R. (2023), *Time Resolved Structural Studies in Molecular Materials*. In *Comprehensive Inorganic Chemistry III(Third Edition)*, Reedijk, J., Poeppelmeier, K. R., Eds. Elsevier: Oxford.

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