Poster

Metallophilicity-assisted piezochromism in a Rh(I) complex: structural, energetic, electronic and spectroscopic investigations under pressure

Vishnu Vijayakumar-Syamala[1], Patryk Borowski[1], Lerato Bosman[2], Kinga Potempa[1], Damian Paliwoda[3], Piotr Łaski[1], Radosław Kamiński[1], Alice Brink[2], Katarzyna N. Jarzembska[1]

[1]Department of Chemistry, University of Warsaw, 02-089 Warsaw, Poland,[2]Department of Chemistry, University of the Free State, Nelson Mandela Drive, Bloemfontein, 9301, South Africa,[3]EuropeanSpallationSourceERICPartikelgatan2, 224 84 Lund, Sweden
v.vijayakumar-syamala@uw.edu.pl

Supramolecular architectures constructed via metallophilic interactions (M···M), especially using d^8 and d^{10} metallic centers, constitute an active topic of research due to the rich electronic properties offered by the metal centers and weak nature M···M. Furthermore, the latter can often be modified by external stimuli. In consequence, such materials may find applications e.g. in optoelectronics (1). Pressure as an external stimulus is known to be more promising than other stimuli, such as temperature, electric or magnetic fields, owing to the significant changes it can bring in the crystal packing and intermolecular interactions, resulting in interesting structure-properties correlations (2). The case studies involving Rh as the metal center in M···M and the associated photophysical properties are less explored to date, thus they became target of our study.

A nearly square-planar Rh(I) complex (***Rh4Br***), composed of a bidentate (N, O)- salicylidene p-bromoaniline and two carbonyl ligands, was chosen for initial phase our study (Figure1a). ***Rh4Br*** crystallizes in a monoclinic system (s.g. $P2_1/n$), in the form of yellow block-shaped crystals. High-pressure X-ray diffraction experiments were performed from 0.00(5) to 10.45(5) GPa, using a Membrane Diamond Anvil cell (MDAC) on the ID15b beamline at the European Synchrotron Radiation Facility (ESRF). Subsequent crystal packing analysis revealed the presence of dimeric units (D1) composed of Rh···Rh interactions (Figure1a), whose distance monotonically decreases from 3.4722(16) to 2.8718(17) Å with increasing pressure. D1 is also supported by two symmetry generated C-H···O hydrogen bonding interactions, which also shown a decrease in distance (2.27 to 1.97 Å) but a reduction in directionality (168.3° to 142.4°) under pressure. Energetic analysis using Crystal Explorer (Figure1b) showed that crystal packing is mainly governed by these D1, which experiences a reduction in total interaction energy from -87 to -114 kJ/mol, indicating its strengthening while increasing pressure.

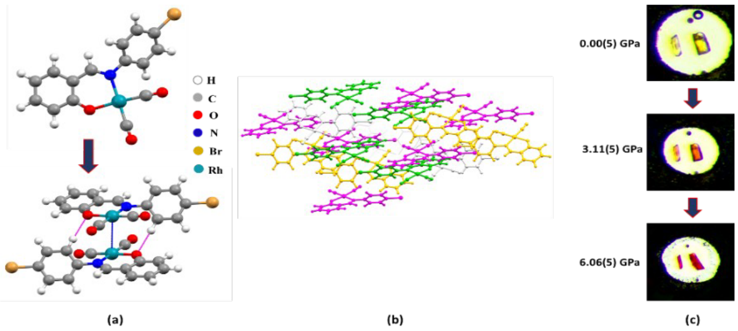

Figure 1. (a) Molecular structure of ***Rh4Br*** and dimeric unit composed of Rh···Rh metallophilic interaction (blue dotted lines) (b) molecular cluster generated around the central molecule in a radius of 3.8 Å for energetic analysis (c) Piezochromism of ***Rh4Br*** crystal under pressure.

Electronic characteristics of individual Rh···Rh and C-H···O interactions were explored via topological analysis, through local electronic and energetic properties found at the *BCPs*. Accordingly, evolution of r, $\nabla^2 r$, $|V|/G$ and delocalization index revealed strengthening of both these interactions under pressure, while Rh···Rh being relatively more affected, even showing a partial covalency above 1.50(5) GPa. ***Rh4Br*** crystals also exhibit reversible piezochromism (yellow to orange; Figure1c), where the emission maxima shift from 583 nm to 626 nm between 0.10(5) and 6.51(5) GPa. These reversible changes in emission properties can be correlated with the changes in metallophilic interaction and to the resulting changes in the emissive states and bandgap.

Therefore, this study reveals the potential use of metallophilic interactions as a guiding factor in tuning the photophysical properties of model Rh(I) complexes with near or square planar geometry in the solid-state.

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