Red-to-NIR Optical Tuning in Rhodium(I) Complexes

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Abstract

Piezochromic materials (PCMs) exhibiting large, reversible spectral modulation are highly desirable for applications in pressure sensing, anti-counterfeiting, optical switching, and smart photonics [1,2]. However, most molecular PCMs display relatively modest emission shifts (≈100–150 nm), and fully reversible visible to near infrared (NIR) transitions remain rare [3,4].

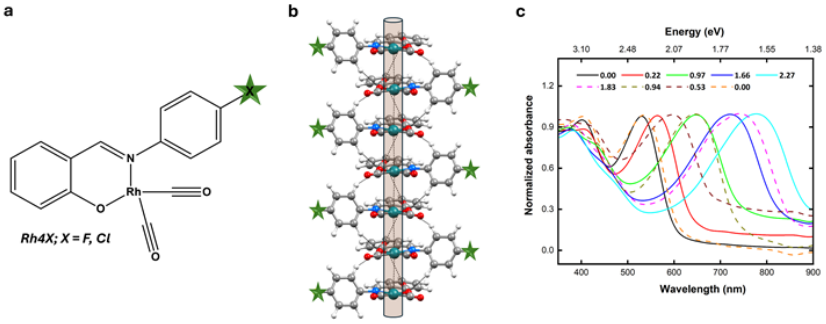

Fig. 1. (a) Molecular structure of **Rh4X** (X = F, Cl, Br), (b) 1D chains formed via Rh···Rh metallophilic interaction, highlighted within a cylindrical surface, and (c) reversible piezochromic shift (absorption spectra) seen in **Rh4F** from ambient pressure to 2.27(5) GPa.

In this contribution investigations on three square-planar rhodium(I) dicarbonyl Schiff-base complexes (**Rh4X**, X = F, Cl, Br; **Fig. 1a**) will be presented and discussed. The **Rh4Br** derivative was studied first both photocrystallographically and under high pressure since it formed best quality and most stable crystals out of the series [5,6]. This was due to a distinct crystal packing featuring with discrete Rh···Rh-stabilised dimer motifs in contrast to the **Rh4F** and **Rh4Cl** analogues forming isostructural crystals with metal···metal interactions stabilising the nearly linear 1-dimensional chains along the crystallographic *Z*-axis (**Fig. 1b**). As expected the spectroscopic properties of **Rh4Br** in a crystalline state are governed mainly by the metalophillic interactions which is supported by the observation of transient Rh···Rh excimer formation in a single crystal. Application of high pressure leads to strengthening of the metallophilic interaction and influences molecular orbitals contributing to the lowest-energy electronic transitions. Consequently, a reversible piezochromism (yellow-to-orange-to-red) under compression–decompression cycles with a bathochromic shift of ≈75 nm in emission maxima (up to 7 GPa) is observed. The piezochromic effect appeared to be much stronger in the case of the two other systems characterised by columnar architecture. High-pressure structural studies reveal anisotropic unit-cell compression dominated by contraction along the *Z*-axis, leading to significant strengthening of Rh···Rh interactions. Under moderate compression (< 5 GPa), both complexes display giant, continuous, and largely reversible bathochromic shifts spanning the visible to deep NIR region, reaching ≈245 nm in absorption and ≈388 nm in emission, with pressure sensitivities up to ≈106 nm GPa^{-1} (**Fig. 1c**). TD-DFT calculations reproduce the experimental observations and establish metallophilicity-assisted HOMO-LUMO gap narrowing as the origin of the giant piezochromism

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[1] X. Wang, N. Gan, M. Gu, K. Ling, C. Ma, H. Ma, W. Yao, Y. Zhang, H. Shi, Z. An, W. Huang, *Chin. Chem. Lett.* **2019**, *30*, 1935.

[2] X. Wu, H. Chen, Y. Luo, J. Yu, Y. Wang, K.L. Choy, Z. Li, *Nanomaterials* **2026**, *16*, 175.

[3] C. Li, C. Lv, M. Ouyang, Y. Zhang, *ChemPhysChem* **2023**, *24*, e202200922.

[4] A. Li, S. Xu, C. Bi, Y. Geng, H. Cui, W. Xu, *Mater. Chem. Front.* **2021**, *5*, 2588.

[5] P. Łaski, L. Bosman, J. Drapała, R. Kamiński, D. Szarejko, P. Borowski, A. Roodt, R. Henning, A. Brink, K.N. Jarzembska, *J. Phys. Chem. Lett.* **2024**, *15*, 10301.

[6] V. Vijayakumar-Syamala, P. Borowski, L. Bosman, K. Potempa, D. Paliwoda, K.P. Korona, P. Łaski, R. Kamiński, D.V. Kama, A. Roodt, A. Brink, K.N. Jarzembska, *J. Mater. Chem. C* **2025**, *13*, 15634.