

Heterometallic interaction emerges from resonant inelastic X-ray scattering in luminescent Tb–Pt molecules.

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The heterometallic complexes have been utilized in a variety of researches such as luminescence, catalysis, and magnetism. Luminescence has received particular interests from viewpoints of luminescence devices, bio-imaging, photosensitizers, etc. Moreover, heterometallic interaction is also an important issue in the luminescence event of heterometallic complexes, and great efforts have been devoted to the design of various intermetallic interactions. Although high-resolution X-ray diffraction can visualize the electron density of bonds,¹ theoretical calculation dominates the method to examine intermetallic interactions. We synthesized the heterometallic Ln–Pt complexes: $\text{NEt}_4\{\text{Pt}(\text{PhSAc})_4\}\text{Ln}[(\text{PhSAc})_4\text{Pt}]\cdot 2\text{DMF}$ ($\text{Ln} = \text{Gd}$ (**1**), Tb (**2**), Dy (**3**); $\text{PhSAc} = \text{benzothioacetate}$, $\text{NEt}_4 = \text{tetraethylammonium}$), in which both diamagnetic Pt(II) ions interact with the central Ln(III) ion. Pt- L_{III} resonant inelastic X-ray scattering (RIXS)² was used to experimentally to prove the unique role of the Ln–Pt interaction in the luminescence property of the Tb–Pt molecule. RIXS enabled to identify the distinguishing factors in the coordination environment and the existence of heterometallic interaction with implications to the observed luminescence.

The two-dimensional (2D) RIXS mapping which has a higher sensitivity to bonding interaction over XANES allowed us to observe the Pt–Ln interactions in **1**, **2** and **3** but not in $2\text{NBt}_4[\text{Pt}(\text{dmit})_2]$ (Fig. 1). The electronic structures revealed by the 2D RIXS mapping are different in the appearance with $2\text{NBt}_4[\text{Pt}(\text{dmit})_2]$ and **1-3**. **1-3** showed a clear shoulder peak along the direction of energy transfer (y axis) (Fig. 1). The difference arises from the difference in the coordination structure around Pt ions, where $2\text{NBt}_4[\text{Pt}(\text{dmit})_2]$ has a square planer structure and the complexes **1-3** have a square pyramidal structure. The details of the results

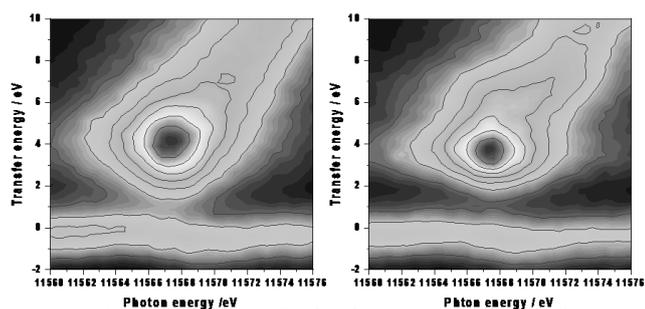


Fig. 1. 2D RIXS of (left) $2\text{NBt}_4[\text{Pt}(\text{dmit})_2]$ and (right) **2**.

of RIXS and luminescence will be presented in the talk. The RIXS confirmed the interaction between Ln and Pt ions, where the difference in the coordination environment of Pt complexes such as $2\text{NBt}_4[\text{Pt}(\text{dmit})_2]$ and $\text{NEt}_4\{\text{Pt}(\text{PhSAc})_4\}\text{Ln}[(\text{PhSAc})_4\text{Pt}]\cdot 2\text{DMF}$ was successfully visualized.

1) J. Overgaard, *et. al.*, *Appl. Crystal.*, 2020, **53**, 635. 2) J. Mizuki, *et. al.*, *ACS Catal.*, 2015, **5**, 1112.