

Influence of the guest organic molecules on the luminescence property for carboxy-appended platinum(II) complexes

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Metal complexes with Schiff-base ligands represented by salen-type tetradentate ligand have been extensively investigated because of their diverse functionalities depending on the metal ion species such as luminescence, catalyst, bioactivity. Above all, controlling the optical properties of the metal complexes by modification of the ligand has been getting attention for the development of molecular devices.¹

In this study, we focused on the luminescence property for Pt(II) complexes consisting of carboxy-appended salophen-type ligand. The carboxy substituents give selective dimerization and have anionic feature under basic conditions. Thus, we aimed to control the luminescence property by not only concentration and pH changes, but also by adding the guest organic molecules having carboxy acid substituents such as trimesic acid (BTC), isophthalic acid (Iso) and terephthalic acid (Tere) to control the molecular assembly.

Here, salophen-type Pt(II) complexes possessing two (= **Pt-1**) or three (= **Pt-2**) carboxy substituents were synthesized. We successfully obtained single crystal structure for **Pt-1**. **Pt-1** molecules were assembled through the hydrogen bond by carboxy groups, resulting in 1-D assembly (Fig. 1a). The 1-D assembly were dimerized by the π - π and Pt-Pt interactions, giving 2-D stacking structure. The 2-D assemblies were orthogonally arranged. **Pt-1** in DMSO solvent exhibited emission peak at 615 nm, however it was blue shifted with the peak at 585 nm in NaOH aqueous solution. This is due to the dissociation of the molecular assembly by electronic repulsion based on the negative charge at carboxy substituents in basic condition (Fig. 1b). Further, the emission spectra with the small organic molecules having carboxy acid substituents were slightly changed. Difference in the number and direction of the carboxy group influenced on the molecular assembly, resulted in the slight emission changes (about the assembly nature in solution is still under discussion).

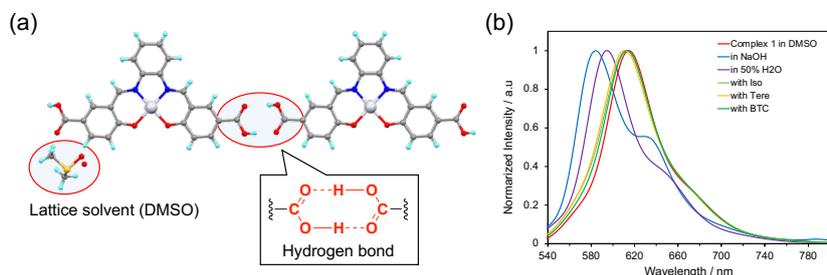


Fig. 1 (a) molecular assembly for **Pt-1** by hydrogen bond. (b) Luminescence properties for **Pt-1** (20 μ M) in DMSO (red), NaOH aq (Blue), 50 % H₂O (purple), with Iso (right green), Tere (orange), BTC (green).

1) J. Cheng, X. Ma, Y. Zhang, J. Liu, X. Zhou, H. Xiang, *Inorg. Chem.* **2014**, *53*, 3210-3219.