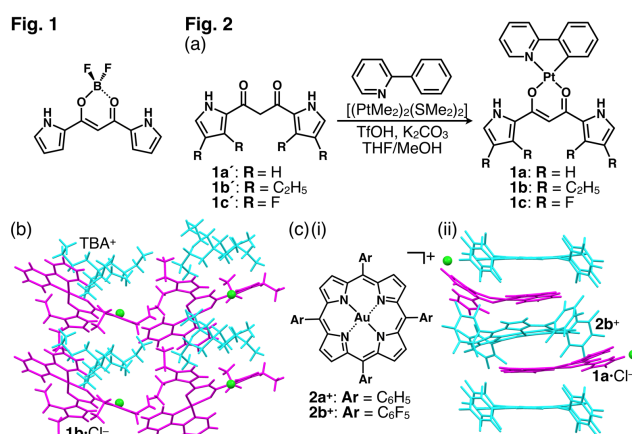


## Synthesis and Photophysical Properties of Dipyrrolyldiketone Pt<sup>II</sup> Complexes as Anion-Responsive $\pi$ -Electronic Systems Forming Ion-Pairing Assemblies

(College of Life Sciences, Ritsumeikan University) ○Atsuko Kuno, Hiromitsu Maeda

**Keywords:**  $\pi$ -electronic anion receptors; pyrrole derivatives; Pt<sup>II</sup> complexes; phosphorescence; ion-pairing assemblies

Well-controlled assemblies composed of appropriately designed charged  $\pi$ -electronic systems would provide functional materials. Dipyrrolyldiketone BF<sub>2</sub> complexes as anion-responsive  $\pi$ -electronic molecules (Fig. 1) are highly emissive and available as fluorescence sensors. Various dipyrrolyldiketone BF<sub>2</sub> complexes have been synthesized by the modifications at the pyrrole and boron units, and their anion complexes have provided ion-pairing assemblies in combination with various counteranions.<sup>1</sup> In this study, Pt<sup>II</sup> complexes were focused on as building units of assemblies based on their planar tetracoordinated geometries and modulating electronic properties.<sup>2</sup> Pt<sup>II</sup> complexes **1a–c**, synthesized under the appropriate conditions (Fig. 2a), displayed anion-binding behavior with the binding constants of 1,300, 520, and 10,000 M<sup>−1</sup>, respectively, for Cl<sup>−</sup> in CH<sub>2</sub>Cl<sub>2</sub>. In the solid state, the ion pair of **1b**·Cl<sup>−</sup> with a tetrabutylammonium (TBA) cation exhibited the formation of charge-by-charge assembly (Fig. 2b), while **1a**·Cl<sup>−</sup> and **1c**·Cl<sup>−</sup> showed the ion-pairing assemblies with porphyrin-Au<sup>III</sup> cations **2b**<sup>+</sup> and **2a**<sup>+</sup>,<sup>2</sup> respectively, forming the charge-by-charge assemblies (Fig. 2c). In addition, **1a** exhibited the emission at 520 nm with a quantum yield of 0.42 upon excitation at the absorption maximum (410 nm) in CH<sub>2</sub>Cl<sub>2</sub>. The large Stokes shift and emission lifetime (3.65  $\mu$ s) suggested the phosphorescent property. Furthermore, the component of the excited triplet state was observed in the transient absorption spectra.<sup>3</sup>



- 1) Recent reports: (a) Watanabe, Y.; Haketa, Y.; Nakamura, K.; Kaname, S.; Yasuda, N.; Maeda, H. *Chem. Eur. J.* **2020**, *26*, 6767; (b) Sugiura, S.; Maeda, H. *Org. Biomol. Chem.* **2020**, *18*, 4433.
- 2) (a) Haketa, Y.; Bando, Y.; Sasano, Y.; Tanaka, H.; Yasuda, N.; Hisaki, I.; Maeda, H. *iScience* **2019**, *14*, 241; (b) Tanaka, H.; Haketa, Y.; Yasuda, N.; Maeda, H. *Chem. Asian J.* **2019**, *14*, 2129.
- 3) Kuno, A.; Hirata, G.; Kobayashi, Y.; Yasuda, N.; Maeda, H. to be submitted.