Enhanced Emission in a Specific Aggregation State of *trans*-Bis(iminomethylpyrrolato)platinum(II) Complex Bearing Vaulted Structure

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Phosphorescent metal complexes exhibiting aggregation-induced emission enhancement (AIEE) have emerged as an extraordinary breakthrough in the field of luminescent materials. As part of our program aimed at the development of phosphorescent materials which show strong emission in aggregation state induced by molecular design,[1] we synthesized a novel *trans*-bis(iminomethylpyrrolato)platinum(II) complex **1** bearing polymethylene bridge over the platinum atom. This complex was found to exhibit strong emission only in an aggregation state on glass surface which obtained from cold recrystallization condition, while it shows non-emission in solution, crystalline, and other aggregation states.

Complex **1** exhibits a unique AIEE phenomenon, in which only an aggregate recrystallized from low temperature on glass surface shows intense yellow emission (λ_{max} = 557 nm) with a high value of emission quantum yield (Φ_{298K}) at 0.33, while solution in 2-MeTHF and crystal from EtOH show no emission (Figure 1a). The non-emissive aggregates were obtained from warm recrystallization conditions such as room temperature (25℃) and oil bath (60℃). This phenomenon indicates that a kinetically semi-stable molecular aggregation form has strong emission. Additionally, the emissive aggregate can only be obtained on polar surface such as glass plate (SiO_2) while non-polar surfaces (polytetrafluoroethylene plate) result in non-emissive solids (Figure 1b). Moreover, complex **1** can also be applied to luminescence ON-OFF control, where the emissive state is changed to the non-emissive state by heat, grinding, and molecular vapor as external stimuli.

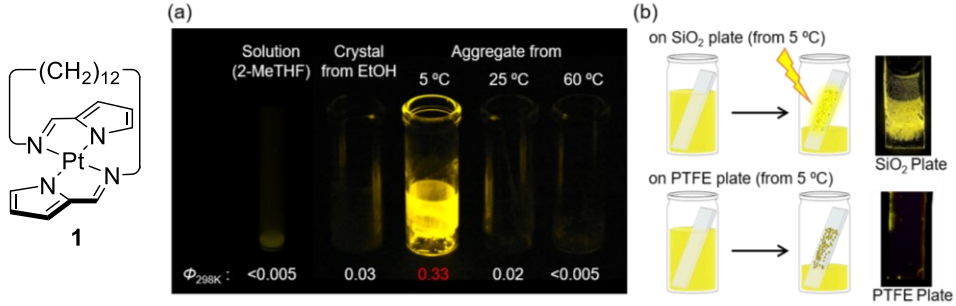

Figure 1. (a) Photographs of complex **1** in solution, crystalline and aggregate states under UV irradiation (λ_{ex} = 365 nm); (b) Schematic representation of recrystallization on different surfaces (SiO_2 and PTFE) from 5 ºC.

1) N. Komiya, M. Okada. T. Naota. *et al. J. Am. Chem. Soc.* **2011**, *133*, 6493−6496.