Concentration dependence of absorption and emission spectra of Pt(II) and Au(I) complexes oligomers in aqueous solutions

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Metallophilic oligomers of gold and platinum complexes have been attracted because their emission colors widely vary depending on the degree of oligomerization. The assignments of the absorption and emission bands of oligomers of $[Pt(CN)_4^{2-}]_n$, one of the most primal metallophilic oligomers, were made by Schindler and other workers based on the concentration dependence of the band intensity in aqueous solutions.[1] However, the effects of ionic strength were not considered in their works though the equilibrium constants for oligomer formation of charged species may depend strongly on the ionic strength in the solutions. In this work, the concentration dependence of emission and absorption spectra for $[Pt(CN)_4]^{2-}$ and $[Au(CN)_2]^-$ in aqueous solutions were re-investigated with controlled ionic strength to determine the photophysical properties of the oligomeric species.

An absorption band at 300 nm for $K_2[Pt(CN)_4]$ solutions was assigned to dimer because its intensity is proportional to the square of the analytical concentration under a controlled ionic strength (Figure 1a and b), though assigned to trimer in the previous work.[1] Emission bands at 350 nm and 407 nm were assigned to fluorescence from S_1 dimer and trimer, respectively, based on the concentration dependence of the populations of the emitting species (Figure 1c and d). These assignments also differ from those for uncontrolled ionic strength.[1]

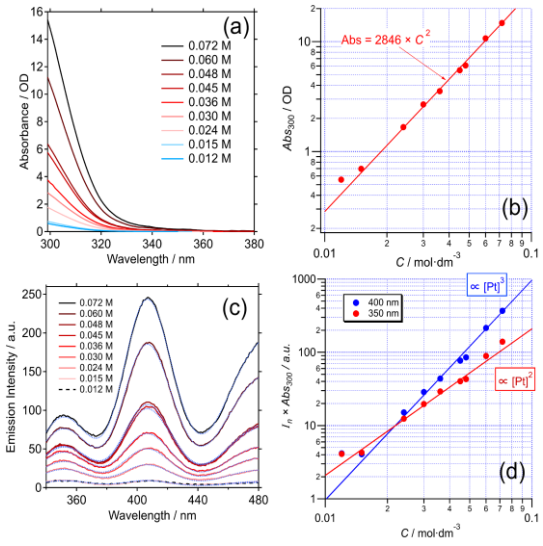

Figure 1. Concentration dependence of absorption spectra (a) and absorbance at 300 nm (b) of $K_2[Pt(CN)_4]$ aqueous solution. (c) Steady-state fluorescence spectra of $K_2[Pt(CN)_4]$ aqueous solution at various concentrations. (d) Concentration dependence of $I_n \times Abs_{300}$ (the product of intensities of the 407-nm or 350-nm emission band and absorbance at 300 nm). ([Pt] = 0.012-0.072 mol/dm^3, μ = 1.8 mol/dm^3, λ_{ex} = 300 nm d = 1 mm)[2]

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