# Photophysical Properties of Hetero Oligomer Formed by Metallophilic Interaction between Dicyanogold(I) and Tetracyanoplatinum(II) Complexes in Aqueous Solution

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Gold(I) and platinum(II) complexes form oligomers due to the metallophilic interactions. These oligomers exhibit tunable emission because the emission wavelength varies greatly depending on the degrees of the oligomerization. In this work, we have studied luminescence properties of hetero-oligomers between $[Au(CN)_2]^-$ (**Au**) and $[Pt(CN)_4]^{2-}$ (**Pt**) in aqueous solutions. **Fig. 1** shows emission spectra for a 0.10 M **Au** aqueous solution (**Au**-aq), a 0.10 M **Pt** aqueous solution (**Pt**-aq), and a mixed aqueous solution of 0.10 M **Au** and 0.10 M **Pt** (**Au-Pt**-aq). The emission intensity of **Au**-aq was rather weak while **Pt**-aq showed emission with peaks at 410 nm and 520 nm. **Au-Pt**-aq showed an intense emission of which intensity was twice as high as that of **Pt**-aq though the emission spectrum was almost the same. The time-resolved emission spectra for **Au-Pt**-aq were composed of three components with lifetimes of 15 ns, 75 ns, and 493 ns (**Table.1**). The emission quantum yield of each component was estimated from the time-resolved emission spectra and the 493 ns component was found to dominantly contribute to the total emission (**Table.1**). Although the lifetime of 493 ns is close to that of the dominant component for **Pt**-aq, the quantum yield was 1.92 times higher than that of **Pt**-aq, indicating that the radiative rate of dominant emission in **Au-Pt**-aq is ~2 times higher than that in **Pt**-aq. Concentration dependence of the emission intensity and absorption intensity for **Au-Pt**-aq (**Fig.2**) revealed that the excited-state species giving dominant emission component is an oligomer of $([Au(CN)_2]^-)_2([Pt(CN)_4]^{2-})_2$ (**$Au_2Pt_2$**). Assignments of the other emission components were also made from the concentration dependence of the time-resolved emission data (**Table 1**). It was found that the **$Au_2Pt_2$** has a potential for high emission material over the homo-oligomers of the **Pt** complexes or the **Au** complexes.

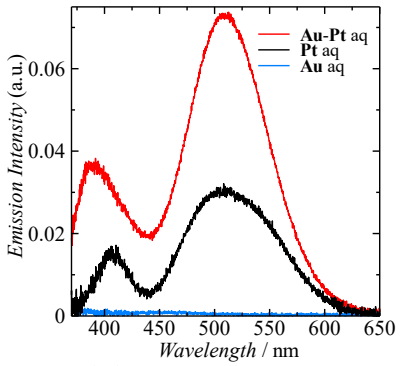


**Fig.1** Emission spectra for **Au-Pt**-aq, **Au**-aq, **Pt**-aq ($\lambda_{ex}$=337 nm). Ionic strength was adjusted to 1.0 mol/dm$^3$ with KCl.

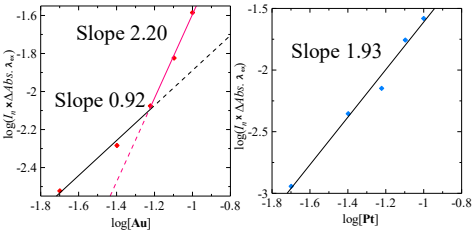


**Fig.2** Logarithmic correlation between emission intensity and concentration of **Au (Left)** or **Pt (Right)** for **Au-Pt**-aq ($\lambda_{ex}$=337 nm) ($\lambda_{em}$=510 nm). (**Left**: **[Au]** = 0.02 - 0.10 M, **[Pt]** = 0.10 M), (**Right**: **[Au]** = 0.10 M, **[Pt]** = 0.02 - 0.10 M)

**Table.1** Lifetimes, quantum yields, and radiative rates for **Au-Pt** aq. ((**[Au]**, **[Pt]**) =(0.10M,0.10M)) ($\Phi_{total}$=0.039) ($\lambda_{ex}$=337 nm)

| | $\tau$ / ns | $\Phi$ | $k_r$/ $10^5$ s$^{-1}$ |
|---|---|---|---|
| **$Au_2Pt_2$ and $Pt_{5>n}$** | 493 | 0.0305 | 6.2 |
| **Au-Pt** | 74.5 | 0.0039 | 5.2 |
| **$Pt_4$ or $Au_{5>n}$** | 14.5 | 0.0006 | 4 |

[1] M.Iwamura, *et al*., *Angew. Chem., Int. Ed.*, **2020**, 59, 23154-23161
[2] M. Iwamura, *et al*., *Phys.Chem.Chem Phys*., **2016**, 18, 5103-5107