



Luminescent properties of dicyanoaurate(I) aggregates based on electrostatic assembly along poly(allylamine hydrochloride)

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ABSTRACT

Poly(allylamine hydrochloride) (PAA) bearing positively charged side chains along the polymer chain was demonstrated to serve as a polymeric spatially aligned scaffold for aggregation and self-association of negatively charged $[\text{Au}(\text{CN})_2]^-$ through the electrostatic and aurophilic bonding interactions to afford the luminescent $[\text{Au}(\text{CN})_2]^-$ aggregates.

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The utilization of polyelectrolytes has been recognized to be a reliable strategy for the assembly of oppositely charged functional groups along polyelectrolytes through electrostatic interaction.¹ The anionic polyelectrolyte-induced metal–metal interaction and concomitant luminescence have been reported with platinum(II) complexes.^{1d,e,f} We have also demonstrated that redox-active ferrocenes, bearing a long alkylene chain, are aggregated along the backbone of anionic double helical DNA, presenting the

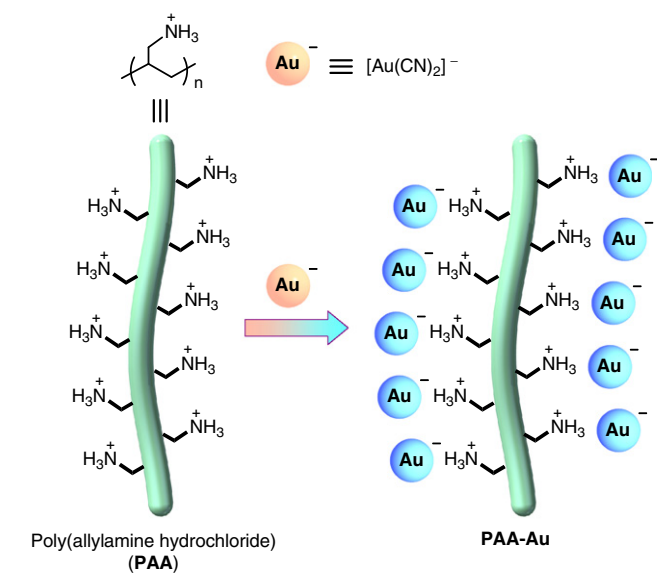


Figure 1. Schematic representation of PAA-induced aggregation and self-association of $[\text{Au}(\text{CN})_2]^-$.

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redox-active (outer) and hydrophobic (inner) spheres around the double helical core.² On the other hand, an architectural design of luminescent aggregated gold(I) complexes^{3,4} based on the self-association properties through $d^{10}\cdots d^{10}$ closed shell aurophilic bonding interaction^{3b,d,5} has attracted growing attention. Efficient control for aggregation is required for this kind of architecture. In an aqueous media, emission of dicyanoaurate(I) ions, $[\text{Au}(\text{CN})_2]^-$, has been reported to be tunable based on the self-association through aurophilicity as a function of concentration⁶ although $[\text{Au}(\text{CN})_2]^-$ exists as a monomer at a low concentration probably due to weak aurophilic bonding interaction (7–11 kcal/mol) comparable to hydrogen bonding. Poly(allylamine hydrochloride) (PAA) decorates positively charged side chains along the polymer chain, which is envisioned to serve as a polymeric spatially aligned scaffold for the aggregation and self-association of negatively charged $[\text{Au}(\text{CN})_2]^-$ through the electrostatic interaction. We

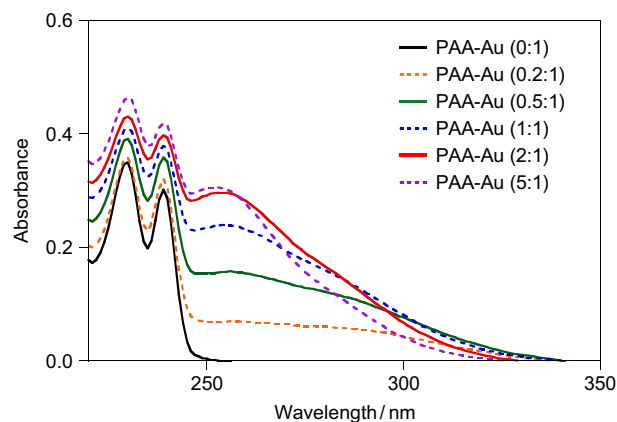


Figure 2. UV/vis spectra of $\text{K}[\text{Au}(\text{CN})_2]$ (1.0×10^{-3} M) in an ultra-pure water solution containing various amounts of PAA ($0, 0.2, 0.5, 1.0, 2.0,$ and 5.0×10^{-3} M PAA unit, respectively) at 298 K.

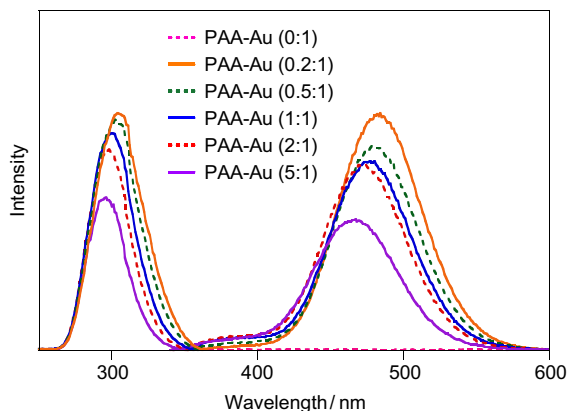


Figure 3. Emission (right, $\lambda_{\text{ex}} = 290 \text{ nm}$) and excitation (left) of $\text{K}[\text{Au}(\text{CN})_2]$ ($1.0 \times 10^{-3} \text{ M}$) in an ultra-pure water solution containing various amounts of PAA (0, 0.2, 0.5, 1.0, 2.0, and $5.0 \times 10^{-3} \text{ M}$ PAA unit, respectively) at 298 K.

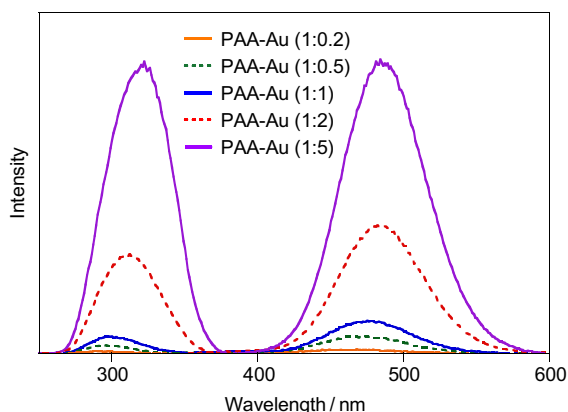


Figure 4. Emission (right, $\lambda_{\text{ex}} = 290 \text{ nm}$) and excitation (left) spectra of various amounts of $\text{K}[\text{Au}(\text{CN})_2]$ (0.2, 0.5, 1.0, 2.0, and $5.0 \times 10^{-3} \text{ M}$, respectively) in the presence of PAA ($1.0 \times 10^{-3} \text{ M}$ PAA unit) in an ultra-pure water solution at 298 K.

herein report the luminescent properties of $[\text{Au}(\text{CN})_2]^-$ aggregates based on electrostatic assembly along PAA (Fig. 1).

PAA-induced aggregation and self-association of $[\text{Au}(\text{CN})_2]^-$ through the electrostatic interaction were investigated by UV/vis spectroscopy. The addition of PAA (MW $\sim 15,000$ as obtained from Aldrich) to an ultra-pure water $1.0 \times 10^{-3} \text{ M}$ solution

of $\text{K}[\text{Au}(\text{CN})_2]$ exhibited the appearance of a new lower energy absorption in the region of approximately 250–320 nm, and increasing the ratio of the PAA unit to $\text{K}[\text{Au}(\text{CN})_2]$ resulted in a gradual increase of the peak in the UV/vis spectra (Fig. 2). These observations indicate the aggregation and self-association of $[\text{Au}(\text{CN})_2]^-$ induced by the electrostatic interaction with the positively charged side chains of PAA and aurophilic bonding interaction.

The aggregation and self-association of $[\text{Au}(\text{CN})_2]^-$ around the backbone of positively charged PAA exhibited the unique luminescent properties as shown in Figure 3. The addition of 0.2 mol equiv of PAA (based on the PAA unit) to an ultra-pure water $1.0 \times 10^{-3} \text{ M}$ solution of $\text{K}[\text{Au}(\text{CN})_2]$ resulted in the appearance of the emission band at 484 nm. Such luminescence was not observed in the absence of PAA. Interestingly, further addition of PAA (0.5–5 mol equiv of PAA unit) caused a decrease of the emission intensity with a continuous blue shift of the emission band. High loading of PAA per $\text{K}[\text{Au}(\text{CN})_2]$ might lead to the arrangement of $[\text{Au}(\text{CN})_2]^-$ separately to the backbone of positively charged PAA, which prevents the aggregation, and thus causes the blue shift of the emission band with a decrease of the emission intensity. When PAA loading per $\text{K}[\text{Au}(\text{CN})_2]$ is lowered, the ratio of $[\text{Au}(\text{CN})_2]^-$ aggregates around the backbone of positively charged PAA is increased, which induces a red shift of the emission band. The aggregation and self-association of $[\text{Au}(\text{CN})_2]^-$ by increasing concentration are known to induce the red shift of the emission band of $[\text{Au}(\text{CN})_2]^-$.^{6a,b} Our results are consistent with the above-mentioned report. A gradual blue shift of the excitation band was observed by the continuous addition of PAA (Fig. 3), supporting the PAA-induced self-association and luminescence of $[\text{Au}(\text{CN})_2]^-$. The order of the emission intensity is correlated with the intensity of a new lower energy absorption shoulder at around 290 nm (Fig. 2).

The reverse addition was performed as follows. The addition of 0.2–5 mol equiv of $\text{K}[\text{Au}(\text{CN})_2]$ to an ultra-pure water $1.0 \times 10^{-3} \text{ M}$ solution of PAA (based on PAA unit) led to a gradual increase of the emission intensity and a red shift of the emission band with a red shift of the excitation band as shown in Figure 4, indicating the aggregation of anionic $[\text{Au}(\text{CN})_2]^-$ around the backbone of positively charged PAA. From the above-mentioned results, the aggregation and self-association of $[\text{Au}(\text{CN})_2]^-$ are envisioned to be tunable by changing the ratio of PAA and $\text{K}[\text{Au}(\text{CN})_2]$.

PAA-Au complex could be isolated in a high concentration. The reaction of 5 mol equiv of an ultra-pure water 0.5 M solution of $\text{K}[\text{Au}(\text{CN})_2]$ and an ultra-pure water 0.1 M solution of PAA afforded

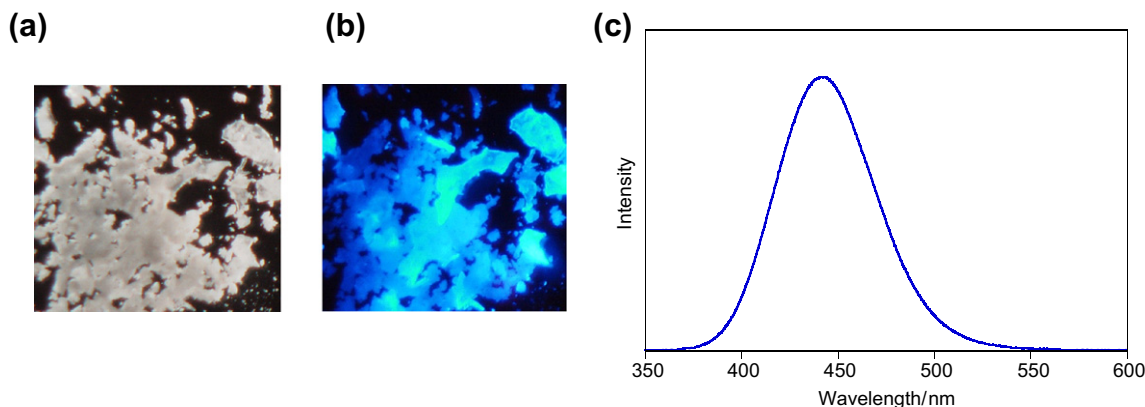


Figure 5. Photographs of **PAA-Au** (a) under ambient light, (b) under UV irradiation with black light (365 nm). (c) Solid-state emission spectrum ($\lambda_{\text{ex}} = 340 \text{ nm}$) of **PAA-Au** at 298 K.

PAA-Au complex as a white precipitate (Fig. 5a). **PAA-Au** complex exhibited an intense blue emission with a maximum at 441 nm in a solid state at 298 K as depicted in Figure 5c, which is blue shifted as compared to that in a solution state. This observation is probably due to the formation of various aggregates, which is consistent with the results of Patterson and co-workers.^{6a,b} A distinct blue luminescence was observed in the solid state upon exposure to UV irradiation, $\lambda = 365$ nm, (Fig. 5b). The quantum yield of **PAA-Au** complex at room temperature, measured in an integrating sphere for the packed powder sample, is 0.52 using $\lambda_{\text{ex}} = 340$ nm.

In conclusion, poly(allylamine hydrochloride) (PAA) bearing multiple positively charged side chains as a polymeric spatially aligned scaffold was found to induce the aggregation and self-association of negatively charged $[\text{Au}(\text{CN})_2]^-$ through the electrostatic and aurophilic bonding interactions, wherein tunable luminescent properties of $[\text{Au}(\text{CN})_2]^-$ aggregates were demonstrated. Studies on the application of polymer-induced metal ion aggregates, including functional materials and catalysts are now in progress.

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Supplementary data

Supplementary data (general information and procedure) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.05.087.

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