Emission and morphology change of supramolecular platinum(II) complex via the incorporation of a polymeric electrolytic

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Abstract. A novel polymeric hybrids can be produced by the electrostatic assembly of polymeric electrolytic and the platinum(II) complex, which could readily be probed by luminescence spectra and transmission electron microscope. An interesting aggregation and a morphological transformation from unstable fibers to stable spheres have been demonstrated. The emission spectra demonstrating that the excimers luminescence have enhanced in the new nanostructures.

1. Introduction
Supramolecular self-assembly is a powerful way to construct large architectures. In the past few decades, square-planar platinum(II) complexes have drawn considerable attention because of their intriguing spectroscopic properties and ability to assemble. The square-planar coordination geometry of platinum(II) complexes aids the formation of regular aggregates in concentrated solutions and thin films via Pt–Pt and/or electrostatic interactions. For example, Che\textsuperscript{4, 8} and Yam\textsuperscript{9, 10} have reported a variety of organized supramolecular aggregates assembled from platinum(II) complexes and polymeric electrolytic, which show potential for use in biological detection. Through controlling the above-mentioned intermolecular interactions, the luminescence properties and morphology of platinum(II) complexes can be tuned purposively.

On the other hand, amphiphilic platinum complex were very advantageous self-assembling units due to their strong hydrophobic interactions of alkyl chains in aqueous medium. Recently, we investigated supramolecular nanostructures that emitted bright monomer emission from a platinum(II) complex in water and the solid state. This system consisted of an amphiphilic platinum complex (FPtNC\textsubscript{3}) (Chart 1) and dodecyltrimethylammonium bromide (DTAB). In another work, we demonstrated that solvent evaporation induce self-assembly of the amphiphilic platinum(II) complex FPTNC\textsubscript{12} to form ordered supramolecular nanostructures that exhibit bright monomer emission. We herein reported that the incorporation of polymeric electrolytic induced self-assembly of the complex FPTNC\textsubscript{3} to form ordered supramolecular nanostructures. The photophysical properties of the mixtures of FPTNC\textsubscript{3} and polymeric electrolytic in solution and the solid state, and their assembly behaviors are described. Of interest is that its morphology and emission could be controlled by the incorporation of polymeric electrolytic, which led to a morphological transformation from fibers to spheres.
The structure of the platinum complexes FPtNC₃ is shown in Chart 1. The complexes contained the bidentate ligand 2-(4,6-difluorophenyl) pyridine (CN) and an ancillary β-diketonato ligand. The β-diketonato ligand of FPtNC₃ was functionalized with a DTAB group. The hydrophilic nature of the ancillary ligands combined with the hydrophobic character of the main chelate endowed the compounds with amphiphilic features, which led to a tendency to self-assemble into discrete entities.¹⁴

Scheme 1. Chemical structures of FPt1, FPtNC₃ and PAA.

2. Experiment
We recently described the synthesis and photophysical properties of FPtNC₃.¹⁴ The platinum(II) complex FPtNC₁₂ was synthesized according to the routine shown in our previous literature and fully characterized by ¹H and ¹³C NMR spectra together with high-resolution electrospray ionization mass spectra.¹⁴

We dissolved FPtNC₃ in deionized water (2× 10⁻⁴ M). The resulting aqueous solution showed a yellowish color under ambient light and emitted weak orange light under UV irradiation. The quantum yield (2%) measurements of FPtNC₃ showed similar results with FPt1 described in previous reports.¹⁶,¹⁷ Upon excitation at 385 nm, the aqueous solution showed four emission bands with comparable intensities, which were centered at 471 nm, 501 nm, 540 nm and 645 nm, respectively (Fig. 1a). According to the previous reports about FPt1 and its analogues,¹⁶,¹⁷ the fore three bands originated from the monomer emission while the latter one the excimer emission. Fluorescence microscopic images showed that the complex FPtNC₃ in water self-assembled into fibrous micelles with a length of several ten micrometers, which emitted weak orange light (Fig. 1b). It was noted that TEM and SEM images (Fig. 5) revealed that after water evaporated, the complexes disaggregated to form fibers (Fig. 1c, 1d). According to previous studies of surfactants,¹⁴,¹⁵ we deduced that the amphiphilic feature of FPtNC₃ played an important role in its self-assembly. For the detailed explanation, please refer to our previous article.¹⁴,¹⁵

Figure 1 (a) Emission spectra of FPtNC₃ aqueous solution (λ<sub>exc</sub>=385 nm); (b) Fluorescence microscopic images of FPtNC₃ aqueous solution; (c) TEM and (d) SEM images of FPtNC₃ after water evaporated; (e) Schematic representation of self-assembled structure of FPtNC₃.
To explore polymeric electrolytic induced self-assembly, aqueous solution of PAA/NaOH was prepared (COO' : NaOH=1:1 (0.01 M). Then FPtNC₃/PAA aqueous solution (FPtNC₃/COO' =1:1, 0.2 mM) was prepared by injecting the concentrated PAA/NaOH solution into the FPtNC₃ aqueous solution. The resultant yellow solution was not stable. After aging for a while, the system became green suspension. Microscope measurement was firstly employed to investigate the aggregates. A drop (6 uL) of the green suspension was placed on slide glass and covered with a cover slide. Microscopic images of the mixture system revealed spheres with some water droplets adhere to the surface (Fig. 2c, 2d). We can’t find any sphere under fluorescence microscopic images, because the emission was quenched.

![Figure 2. (a, b) TEM image images of FPtNC₃/PAA mixture system in dry state; (c, d) Microscopic images of FPtNC₃/PAA mixture system in water.](image)

To investigate the influence of solvent evaporation on assembly formation, a drop (6 uL) of the suspension of FPtNC₃/PAA system was placed on copper net. After the water was evaporated, the spheres were observed by TEM images (Fig. 2a, 2b). This result demonstrated that the solvent evaporation process did not change aggregated structure formed in water. In addition, the spheres in the TEM images showed nuclear shell structure. The average diameter of the spheres were determined to be ca. 300 nm and the average thickness of shell were ca. 50 nm through TEM measurements.

These results confirmed that, there were no signs of collapse in any sphere, which proved that the spheres were solid sphere. A possible model of the solid sphere is presented in Fig. 4. The hydrophobic part forms the core and the hydrophilic part forms the shell.

According to previous studies of surfactants, we deduced that the amphiphilic feature played an important role in its self-assembly. In water, as a result of the electrostatic interaction and solvophobic effect, the FPtNC₃/PAA system formed the spheres. The hydrophobic part was formed by the electrostatic interaction of FPtNC₃ and COO', the hydrophilic part was composed of the remaining COO' groups. The other part of FPtNC₃, which is not combined with COO electrostatic, still existed in the water system in fibers form.

To explore the detailed luminescent features of the spheres, the green suspension was filtered to get green solid powder (Fig. 3 insert). The green solid powder displayed three emission bands at 467, 498, and 610 nm (Fig. 1b). The first two bands originated from monomeric species of the platinum complex. The band at 610 nm was excimers emission band. The yellow FPtNC₃ solid (Fig. 3 insert) displayed three emission bands at 467, 498, and 625 nm (Fig. 1b). Compared with the yellow FPtNC₃ solid, the monomeric species of the FPtNC₃/PAA system powder were decreased, and the excimers emission band increased and blue shift. Inside of the hydrophobic core, the platinum(II) complexes were close enough to form the excimers. Additionally, with the dual effect of hydrophobic interaction and electrostatic interaction, the platinum(II) complex squares became closer, resulting in the blue shift of the excimers emission band.
In summary, we have demonstrated that the incorporation of polymeric electrolytic into the amphiphilic platinum(II) complex FPtNC₃ could tune the spectroscopic and luminescence properties of complex efficiently. Besides this, the aggregate structures of the mixtures transformed from fibres to ordered spheres in solution and dry state. Such approach will provide an entry to new classes of 3D supermolecular nano materials.

3. Conclusion

4. References

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