A X-ray Excitable Vibrational AIE System Based on Platinum

(II) Salts

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Abstract: Aggregation-induced emission luminogen excited by X-ray is highly advantageous for imaging and diagnosis but has not been achieved. Herein, we demonstrated BaPt(CN)₄ as the first inorganic salt based AIE system which can be excited by X-ray. The AIE mechanism of BaPt(CN)₄ is studied and the X-ray luminescence of BaPt(CN)₄ is tested.

Introduction

Molecular motion responsive luminescent materials have attracted great attention due to their significant roles in affording multifunctional materials and broadening the fundamental understanding of dynamic molecular systems.^{1–5} In this regard, one of the most fascinating concepts is aggregation-induced emission (AIE) proposed by Tang and co-workers.^{6,7} Typical AIE luminogens (AIEgens) show strong emission in aggregated/solid state but are non-emissive in their monodispersed state. Further underlying mechanism study unveiled that luminescence of AIE system basically depends on the intramolecular motion extent that influenced by the surrounding environment of the molecules.⁸ In monodispersed state, the active intramolecular motion including rotation and vibration accelerates the non-radiative decay process of the excitons and quenches the emission, while in the solid state or other media that can restriction the intramolecular motion, the non-radiative decay will be suppressed and consequently enhance the emission. The solid-state emission and environmental sensitivity of AIEgens enable them highly advantageous as nano imaging agents for long-term tracing and as sensors or imaging probes for biological species detection.^{8–12}

So far, large amounts of AIEgens with different colors have been developed and successfully utilized for cell and microbial imaging, biomarker detection, physiological process monitoring and imaging guided surgery etc.^{5,6,9} However, an unignored limitation of these AIEgens is that their excitation wavelengths are mostly located in the UV/vis range, which has the disadvantages of significant auto-fluorescence resulting in poor signal-to-noise ratio, and poor tissues penetration depth. Although some near-infrared absorption and two-photo excitable AIEgens have been developed to improve this problem, they may suffer quite low luminescence quantum yield and still have limited penetrative power in living tissues.^{13–16}

On the other hand, Luminogens excited by X-ray are attracting more and more attention recently since X-ray can easily penetrate biological tissues and thus improve both limitations of auto-fluorescence and poor penetration depth of common luminogens.^{17–24} For instance, the luminescence signal of some inorganic system can be detected even in 5 cm thick porcine tissues under X-ray irradiation.²⁵ Furthermore, since X-ray computed tomography had been widely used in clinic for imaging the anatomy, luminogens with X-ray luminescence thus are advantageous for dual-modal X-ray/X-ray excited fluorescence imaging wherein optical signal and anatomical information was simultaneously obtained.¹⁷ Therefore, it is highly advantageous to develop X-ray excitable AIEgens, which potentially integrated both the advantages of AIEgens and X-ray excitation and possibly open a new door for fluorescence imaging in bio-applications.

Platinum (II) salts have been widely investigated as luminescent materials for optoelectronics and bio-imaging applications.^{26–30} While $\text{Pt}(\text{CN})_4^{2-}$ complexes possibly are among the earliest luminescent Platinum (II) salts, since their luminescence has been observed by Sir Stokes as early as in 1853, when the term “fluorescence” was coined.³¹ However, the luminescence phenomenon of these $\text{Pt}(\text{CN})_4^{2-}$ complexes were not deeply investigated at that time possibly due to the limitation people’s knowledge to luminescence. Until 1970s, scientists began to systematically study the electronic structure and spectroscopy properties of these $\text{Pt}(\text{CN})_4^{2-}$ complexes and their derivatives.^{32–36} Currently, research interest in these inorganic complexes is continuing with new understanding and applications are continuously developed, a recent study just explored the application of $\text{ZnPt}(\text{CN})_4$ in ammonia detection.^{36,37} Since the research on luminescent materials and photophysical mechanism have made great achievements in the past four decades, re-investigation these old compounds based on current understanding on luminescence is interesting and of big scientific value, which possibly results in some new discovery or new understanding on these old luminescent materials. In this work, we found the inorganic salts, $\text{BaPt}(\text{CN})_4$ showed typical AIE characteristic, which showed no emission in water solution but bright luminescence in aggregates and solid state. Spectroscopy study indicates that the intramolecular vibration should be responsible for the non-luminescent characteristic of $\text{BaPt}(\text{CN})_4$ in solution state, while crystal structure analysis suggests multiple intermolecular hydrogen bonding and electrostatic interactions as well as Pt...Pt interactions contribute greatly to the solid state emission efficiency and emission wavelength. The influence of intermolecular Pt...Pt interactions on emission wavelength was further confirmed by hydrostatic pressure depended fluorescence experiment. More importantly, we found $\text{BaPt}(\text{CN})_4$ could be excited by X-ray and emit bright green luminescence. To the best of our knowledge, this is the first AIE system based on inorganic salts and also the first X-ray excitable AIEgen, which opens a new door for the AIE research.

Figure 1. (A) PL spectra of BaPt(CN)₄ in H₂O/THF mixtures with different THF fractions (f_H) (2 μ M). (B) The plot of the emission maximum and the relative emission intensity ($\alpha_{AIE} = I/I_0$) versus the composition of the aqueous mixture of BaPt(CN)₄. Inset: Fluorescence photographs of BaPt(CN)₄ in water and in $f_H = 99\%$ mixture taken under 365 UV irradiation.

Results and Discussion

BaPt(CN)₄ was purified by recrystallization three times before the optical properties measurement. Slow evaporation of the saturated aqueous solution of BaPt(CN)₄ generates green crystals. These green crystals show brightly green emission with an emission maximum of 516 nm and a quantum yield of 47.9%, while their dilute solution shows non-emission, suggesting their AIE activity. The AIE characteristic of BaPt(CN)₄ is further demonstrated by studying its Photoluminescence (PL) behavior in the H₂O/THF mixture (Fig. 1). In aqueous solution, BaPt(CN)₄ is non-emissive, with adding THF into the aqueous solution until the THF fraction up to 99%, molecules of BaPt(CN)₄ begin to aggregate which turns on its emission. The aggregates at 99% THF fraction was confirmed by DLS measurement, which gives a particle size of about 250 nm (Fig. S1). According to the AIE mechanism proposed by Tang and co-workers, the emission quenching in dilute was generally resulted by the active intramolecular motion.⁷ We thus speculated the emission quench of BaPt(CN)₄ in aqueous solution was resulted by the active intramolecular vibration of the CN group of Pt(CN)₄²⁻ since CN group shows strong vibrational signal in their IR spectra (Fig. S2).

To elucidate the role of intramolecular motion in contributing the AIE phenomenon of BaPt(CN)₄, we measure its PL spectra in dilute solution (2×10^{-5} M) at 77K, at which the intramolecular vibration will be greatly suppressed (Fig. S3). As expected, the dilute solution of BaPt(CN)₄ show bright blue emission at 77K with two emission peaks at 410 nm and 450nm, respectively. Interestingly, further increasing the concentration to 2×10^{-4} M, a new emission peak at around 550 nm emerged, suggesting some aggregates seems formed. At a concentration of 2×10^{-3} M, the shorter emission peaks disappeared and the emission peak at 550 nm show a slightly blue shift. These results indicate that when located at low temperature, the dye incline to aggregate possibly due to the

decrease of the solubility. We also measured the UV spectra changes of BaPt(CN)₄ solution with different concentrations at room temperature, which implies that even at room temperature, the dye has some aggregates since new absorption band emerge at a dye concentration of 2×10^{-4} M.^{38,39} However, at this concentration, the solution shows non-emission at room temperature. These results suggest that both the dye aggregates formed at low temperature and room temperature can influence their spectra wavelength, while only the dye aggregates formed at low temperature can emit brightly, which should be ascribed to the restriction of the intramolecular motion. And the non-emissive aggregates formed at room temperature possibly is due to the loose packing can't effectively restrict the molecular motion. It is worthy to note that Schindle et al. had also observed the dye concentration depended emission wavelength of BaPt(CN)₄ at 77K, which they assigned as dimer emission and cluster/oligomer emission resulted by the intermolecular Pt...Pt interaction.^{32,33} While they didn't consider the role of intramolecular motion, which consequently can't explain the non-emissive characteristic of BaPt(CN)₄ aggregates at room temperature reasonably.

To deeply understand this photophysical phenomenon, we analyzed the crystal structure of BaPt(CN)₄. As shown in Fig. 2, the Pt(CN)₄²⁻ show a square planar configuration without obvious rotation unit, suggesting intramolecular vibration should be the main molecular motion style. In addition, there is a strong Pt...Pt interaction exist in the crystal packing with a Pt...Pt distance of 3.319 Å. These Pt atoms can form orderly arranged Pt channel which should contribute greatly the wavelength red-shift of the aggregation. Additionally, multiple intermolecular hydrogen bonding (H–O–H...N≡C) and electrostatic interactions exist in the crystal which help rigidify the molecular structure, resulting the bright solid-state emission. Destroy these intermolecular interactions by grinding the crystal greatly decrease the emission intensity (Fig. S4).

Figure 2. (A) Top-view and Side-view of the single crystal of $\text{Pt}(\text{CN})_4^{2-}$. (B) Intermolecular Pt...Pt distance within the single crystal of $\text{BaPt}(\text{CN})_4$ with hiding the Ba^{2+} cation and H_2O molecules. (C) The long-range orderly intermolecular Pt...Pt interactions within the single crystal of $\text{BaPt}(\text{CN})_4$. (D) Various intermolecular interactions in crystals of $\text{BaPt}(\text{CN})_4$.

Hydrostatic pressure depended PL measurement provide a suitable platform to study the influence of intermolecular interaction on the luminescence because it enables tuning the intermolecular distance through changing the hydrostatic pressure.^{8,40,41} Since the intermolecular Pt...Pt interactions possibly contribute greatly to the emission wavelength, we thus implemented the hydrostatic pressure experiment to investigate the PL changes upon high pressure. As shown in Fig. 3, within a pressure range from 0 GPa to 3.4 GPa, the luminescence intensity of $\text{BaPt}(\text{CN})_4$ crystal generally decrease while the emission wavelength gradually red-shifted from 516 nm to about 660 nm, which is consistent well with the low temperature PL data. Therefore, the emission red-shift of the high concentration aggregates relative to the low concentration aggregates is mainly due to the enhanced intermolecular Pt...Pt interactions.

Figure 3. (A) Micrographs of the crystal of BaPt(CN)₄ under varied hydrostatic pressure. (B) Emission spectra recorded during the compression process in the range of 0–3.4 GPa. (C) Plot of the PL intensity and emission wavelength vs. the hydrostatic pressure.

Based on these results, we propose a hypothetical diagram sketch which fit the data to describe the AIE process of BaPt(CN)₄. In general, in solution state, BaPt(CN)₄ exhibit active intramolecular vibration including stretching and swing upon photoirradiation, which accelerates the non-radiative decay of the exciton to quench the emission. While in the crystal, the multiple intermolecular interactions including hydrogen bonding, electrostatic interactions and Pt...Pt interactions help rigidify the molecular configuration and suppress the non-radiative decay, resulting the bright

luminescence. Additionally, the intermolecular Pt...Pt interactions also contribute to decrease the energy gap between the HOMO and LUMO, benefiting the emission wavelength red shift of BaPt(CN)₄ in aggregates, which also helps understanding the unconventional clusteroluminescence of some non-conjugated luminescent system.

Figure 4. (A) PL spectra of BaPt(CN)₄ under irradiation of X-ray with varied dose by fiber optic spectrometer. (B) The plot of the relative emission intensity ($\alpha_{\text{AIE}} = I/I_0$) versus the dose of X-ray. Inset: Fluorescence photographs of BaPt(CN)₄ taken under varied X-ray irradiation.

Materials with X-ray luminescence are highly advantageous in improving the problem of auto-fluorescence and tissue penetration depth *in vivo*.¹⁷ However, most of the organic luminescent materials show poor absorption to X-ray, let alone the emission. According to the X-ray attenuation formula, molecules with high atomic number usually have strong absorption to X-ray, which can be used as CT imaging and X-ray luminescence imaging. We thus measured the response of BaPt(CN)₄ to X-ray irradiation since both Ba and Pt have large atomic number. The results indicate that in solution state, BaPt(CN)₄ has no response to X-ray irradiation, while in the solid state, BaPt(CN)₄ show obvious X-ray luminescence whose intensity was enhanced with the increase the voltage of the X-ray. As a contrast, TPE shows no signal to X-ray irradiation. We further measured the response of Na₂Pt(CN)₄ and K₂Pt(CN)₄ to X-ray irradiation, it shows that the crystal of K₂Pt(CN)₄ show strong blue emission upon X-ray excitation. Therefore, Pt atom possibly plays a more important role for the X-ray luminescence of BaPt(CN)₄.

In summary, we have demonstrated the AIE property of BaPt(CN)₄ for the first time, which can be extended to other Pt(CN)₄²⁻ complexes. The underlying mechanism has been investigated which indicates that the intramolecular motion such as the vibration of the CN is responsible for the AIE phenomenon of BaPt(CN)₄. Furthermore, the influence of the intermolecular Pt...Pt interaction on the emission wavelength has been well elucidated by concentration-depended PL measurement and hydrostatic depended PL measurement, which indicates that intermolecular Pt...Pt interaction contribute greatly to the emission wavelength red-shift of BaPt(CN)₄. This to some extent helps

understanding the unconventional clusteroluminescence of some non-conjugated luminescent system. More importantly, we found BaPt(CN)₄ can be excited by X-ray, which fundamentally is highly significant since it can overcome the excitation limitation resulted auto-fluorescence and poor tissues penetration depth of AIEgens. To the best of our knowledge, this is the first reported AIEgen which could be excited by X-ray. The current work possibly opens a new door for AIE research.

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