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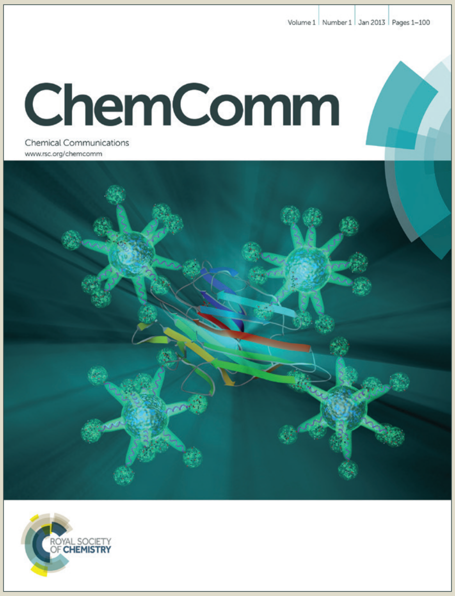

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COMMUNICATION

A cationic iridium(III) complex with aggregation-induced emission (AIE) property for highly selective detection of explosives

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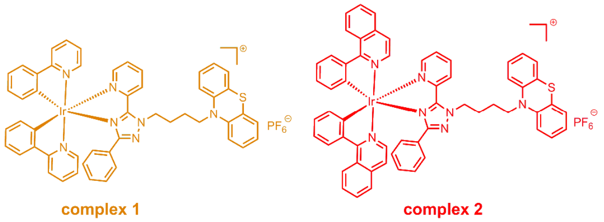
A new cationic Ir(III) complex with AIE characteristics was designed and synthesized with the help of density functional theory calculation, which exhibits highly sensitive and selective detection of explosive (2,4,6-trinitrophenol, TNP).

Rapid and highly selective detection of explosives has become an important and urgent issue in modern society since their board applications in both homeland security and environmental safety.[1] So far various detection techniques have been developed for the purpose of detecting the explosives, including gas chromatography, Raman spectroscopy, cyclic voltammetry, fluorescence sensing and so on.[2] Especially, fluorescence sensing of explosives offers several advantages such as simplicity, sensitivity, cost-effectiveness and short response time.[3] In this regard, numerous explosive sensors based on polymers, metal organic frameworks, nanomaterials and organic dyes, have been designed.[4] Despite these advances, the selective detection of nitro explosives still remains a challenge as they usually have similar electron affinity.[5] It is in great demands to design and synthesize of luminophors that are sensitive and selective for nitro-explosives.

Recently, the use of phosphorescent iridium(III) complexes as chemosensors is gaining increasing attention due to their rich photophysical properties.[6] However, the traditional aggregation-caused quenching (ACQ) effect in solid state and/or aquatic system results in drastically negative effects on the efficiency and sensitivity of the sensors. The aggregation-induced emission (AIE) phenomenon firstly reported by Tang in 2001 is precisely opposite to the ACQ effect, which provides a new strategy to construct efficient luminescent materials.[7] Since then, great efforts have been devoted to the design and synthesis of AIE-active fluorophores and the exploration of their potential application. Very recently, the phosphorescent AIE phenomenon based on iridium(III) complexes has been observed and used as chemosensors and cell imaging.[8] The recent works reported by Reddy and our group have demonstrated the potential of AIE-active iridium(III) complexes in explosives detection.[9] Although their high sensitivity towards nitro-explosive has been demonstrated, the selective detection has not been achieved so far. Among the nitro-explosive, the power of 2,4,6-trinitrophenol (TNP) is somewhat superior to that of 2,4,6-trinitroluene (TNT), but far less attention has been paid to detection of TNP.[4c, 10] Moreover, TNP is widely used in fireworks, dyes, matches and so on, whose release into the environment leads to the contamination of soil and aquatic systems[4c, 10a, 11] Consequently, the development of efficient and selective sensors for TNP is highly desirable.



Scheme 1. Chemical structures of complexes **1** and **2**.

Herein, we report the design and synthesis of a AIE-active iridium(III) complex **1** (see scheme 1) for detection of nitro explosive. For the first time, the selective detection of TNP using AIE-active iridium(III) complex has been realized. To further investigate the sensitivity of **1** towards TNP, the control experiment using another iridium(III) complex **2** was performed.

Density functional theory (DFT) calculation was performed firstly to construct efficient and stable iridium(III) complex with AIE behaviour. As shown in Fig. S1 and Table S1 (ESI†), the ancillary ligand dominates the lowest lying excited-state characters of **1** in solution. On the basis of pioneering works, the weakly emissive ^{3}ILCT or ^{3}LX characters can endow the iridium(III) complexes with AIE properties to some extent. Additionally, for transition metal-based phosphors, the metal-centered (^{3}MC) excited states are very crucial in determining the photoluminescent efficiency and stability, especially in aqueous medium.[12] The rupture of metal-ligand bonds in ^{3}MC state enhances the possibility for nucleophilic attack, resulting in detrimental degradation and hence inefficient optical sensor. Our quantum calculation results show that the ^{3}MC state of complex **1** is 0.76 eV above emitting T$_1$ state, in which only one of the N$_{ppy}$ atoms is virtually de-coordinated due to the pendant phenyl ring attached on ancillary ligands (Fig. S2, ESI†). This supramolecularly-caged structure constructed by intramolecular π-stacking can protect complex **1** from being attacked by water, leading to stable phosphors.[12a] Under the guidance of theory calculation, we elaborate a synthetic scheme for synthesizing **1** in a straightforward manner. Detailed procedures and characterization are given in the ESI.

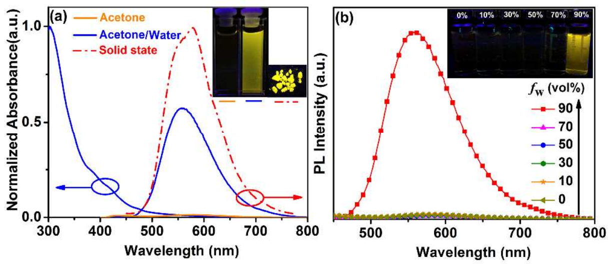


Fig. 1 (a) Normalized absorption spectra and emission spectra of complex **1** in the various states. (b) Emission spectra of **1** in acetone/water mixtures with different water fractions.

The photophysical properties of both complexes have been investigated. Interestingly, almost no emission is observed from the solution of complex **1**, however, it exhibits intense emission in the aggregation state when illuminated under 365 nm UV lamp (Fig. 1a), which is different from that of complex **2** (Fig. S3). The absolute quantum yield of **1** in acetone solution and solid state using an integrating sphere were estimated to be 0% and 15% with lifetime of ~0.20 μs, respectively. This phenomenon indicates that the aggregation has turned on the light emission of complex **1**. To probe the AIE property of **1**, its photoluminescence (PL) spectra in acetone/water mixtures have been studied. As shown in Fig. 1b, complex **1** in pure acetone solvent exhibits faint emission, the PL intensity is significantly enhanced when the water content is up to 90%, which magnifies about 60-fold than that in pure solvent. This result indicates that **1** has an obvious AIE effect. The transmission electron microscopy and electron diffraction data suggest that the amorphous nanoaggregates are formed in the mixtures with water ratio of 90% (Fig. S4, ESI†).

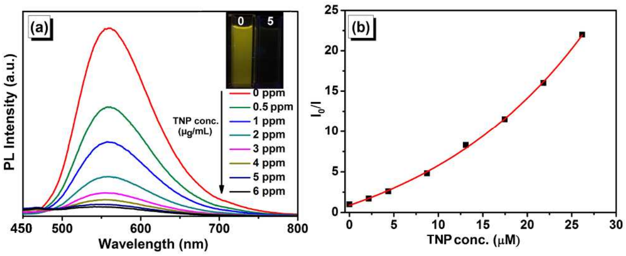


Fig. 2 (a) PL spectra of complex **1** in acetone–water (v/v = 1: 9) containing different amounts of TNP. (b) Corresponding Stern-Volmer plots of TNP.

Benefiting from the appealing AIE property of **1**, which could effectively prevent emission quenching in aqueous media, the ability of nanoaggregates of **1** to sense a trace quantity of nitro explosives was explored. As shown in Fig. 2a, complex **1** in the acetone–water (v/v = 1: 9) mixtures without TNP shows strong luminescence, while fast and visible emission quenching was observed upon increasing TNP concentration. When 0.5 ppm TNP is added to the mixtures, the emission quenching is clearly discerned. Negligible emission can be observed at a TNP concentration of 5 ppm, which quenched nearly 94% of the initial emission intensity (Fig. 2a). The phosphorescence lifetime decay profiles before and after addition of TNP were also investigated. A decrease in the lifetime was observed upon the addition of TNP, suggesting the presence of interaction between TNP and **1** in the excited state (Fig. S5, ESI†).[4f, 9b, 13]

As shown in Fig. 2b, the Stern–Volmer (SV) plots give curves bending upward, suggesting that the emission quenching becomes more efficient with increasing the TNP concentration. Combining the nonlinear SV curve and the change in excited-state lifetime, the static and dynamic quenching processes may coexist during the detection. This similar behavior was also noted by other groups.[9b, 13] The quenching constant is evaluated to be 52800 M^{-1} for **1**, which is higher than the reported fluorescent sensor for explosive detection.[11, 14] To investigate the sensing selectivity of complex **1**, the emission quenching for other nitro aromatics such as TNT, 2,4-dinitroluene (2,4-DNT), 2,6-dintritoluen (2,6-DNT), 1,3-dinitrobenzene (1,3-DNB), nitrobenzene (NB), 2-Nitrotoluene (oNT) and 3-Nitrotoluene (mNT), were also studied. As shown in Fig. 3a, in the same condition, other nitro aromatics exhibit relatively little effect on emission quenching compared with that of TNP. However, it is noted that the further addition of 5 ppm TNP into other nitro aromatics containing systems results in significant quenching of emission intensity (Fig. 3b). In order to investigate a possible concentration and solubility effect on the selectivity, the quenching efficiency for a given ratio of complex **1** to analytes (1:1, by molar) was studied (Fig. S6†).[15] Clearly, complex **1** exhibits significant emission quenching toward TNP but not obvious for other analytes. Moreover, the emission quenching of complex **1** in response to the different concentrations of analytes was also evaluated (Fig. S7†). The significant quenching efficiency was only observed for TNP. These results clearly demonstrate the unprecedented selectivity of **1** for TNP. For practical applications, selective detection of TNP in an aquatic system is highly desirable. However, various anions, cations as well as different pH values are considered as other factors influencing the efficiency and selectivity of the sensor. To this purpose, the emission response of **1** in the presence of 4 equiv of anoins and cations has been tested. As shown in Fig. S8 and Fig. S9†, the ions do not effect evidently the quenching efficiency even in their high concentrations. However, once TNP was added to the mixtures containing these ions, obvious decrease in emission intensity has been found. Other factor such as pH values on the quenching of emission **1** was studied as well (Fig. S10†). The high quenching percentage towards TNP is realized despite that pH value of water varies from 1 to 14. The highly selective detection in the presence of other nitro compounds, ions and different pH makes **1** a reliable sensor for TNP in an aqueous system.

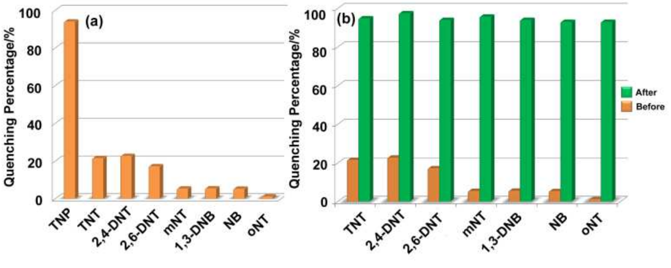


Fig. 3 (a) Quenching percentage obtained for different analytes (5 ppm. (b) Quenching percentage of **1** with analytes (5 ppm) in acetone–water (v/v = 1: 9) mixtures before and after the addition of 5 ppm TNP.

To understand the origin of the selectivity of complex **1** towards TNP, the possible quenching mechanism was investigated. Nitro compounds are usually electron-deficient. The photo-induced electron transfer (PET) from **1** to analytes may occur if the LUMO energy of **1** lies at higher than those of analytes, resulting in the emission quenching. It shows that the higher LUMO energy of **1** facilitates the jump of electron to the lower ones of the analytes (Fig. S11†), indicating that the PET may be one possible mechanism for quenching of **1** in response of the analytes. Nevertheless, the quenching caused PET is limited to the luminophors that have direct interaction with the analytes. In addition, if the absorption band of the analytes has an overlap with the emission of **1**, the resonance energy transfer will happen. Due to the fact that the energy transfer is a long-range process, the emission quenching can carry over the surrounding luminophors. Therefore, if the energy transfer is involved in quenching, the quenching efficiency can be dramatically amplified, enhancing the detection sensitivity as well as selectivity.[4c, 16] In our system, a little spectral overlap is observed for TNP, however, others analytes are no overlapping with emission of **1**, implying that the energy transfer mechanism may affect the selectivity of complex **1** for TNP (Fig. S12 and S13, ESI†).[4c, 17] To verify this assumption, a control experiment was performed using a red-emitting complex **2**. The quenching processes of **2** towards TNP and TNT were studied as an example (Fig. S14 and Fig. 15†). It is clear that complex **2** shows gradual quenching with increasing the concentration of both TNP and TNT. Due to no overlap between emission of **2** and absorption bands of TNP, the emission quenching of **2** is only caused by PET process. Furthermore, TNP is very acidic with a pK_a of 0.38 and it can readily dissociate in aqueous solvents, which might increase the electrostatic interactions between complex **1** and TNP.[5a,18] An absorption tail in the visible region is clearly observed with increasing TNP concentration (ESI, Fig. S16†), which is probably resulted from the strong interaction between **1** and TNP.[16] Such interaction will facilitate the electron transfer and energy transfer from complex **1** to TNP, and thus enhance the quenching response.[19] Moreover, the identical ^{1}H NMR spectra of **1** before and after addition of TNP indicates that no chemical reaction happens and new quenchers generate (ESI, Fig. S17†). Based on the above results, it suggests that both electron transfer and energy transfer are present in emission quenching by TNP, and the energy transfer quenching mechanism is predominant over the electron transfer for its selectivity. Furthermore, complex **1**-impregnated TLC plate can be used as portable sensor to detect the nitro explosives. The fast and remarkable quenching is observed for TNP-tested TLC plate, as shown in Fig. S18†.

In conclusion, a new AIE-active cationic iridium(III) complex has been designed and synthesized, which exhibits selective detection of TNP, even in the presence of a certain amount of anions, cations and nitro compounds as well as different pH values. The result demonstrates that both electron and energy transfer quenching mechanisms are responsible for the emission quenching of **1** towards TNP. Although various iridium(III) complexes have been synthesized, to the best of our knowledge, this is the first example for iridium(III) complex used in the sensitive and selective detection of nitro-explosives. The present study will provide a new insight into the development of effective iridium(III)-based explosive sensors in the future.

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Notes and references

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