

Piezochromic luminescent (PCL) behavior and aggregation-induced emission (AIE) property of a new cationic iridium(III) complex†

Guo-Gang Shan,^a Hai-Bin Li,^a Jun-Sheng Qin,^a Dong-Xia Zhu,^a Yi Liao^{*b} and Zhong-Min Su^{*a}

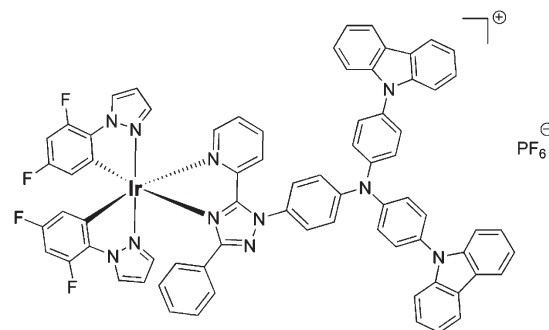
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A new cationic Ir(III) complex based on a dendritic ancillary ligand has been designed and synthesized, which simultaneously exhibits piezochromic luminescent (PCL) behavior and aggregation-induced emission (AIE) property for the first time.

The design and synthesis of solid-state organic luminescent materials have been attracting increasing attention in both scientific research and practical aspects, due to their potential applications in photonic and optoelectronic devices.¹ In the solid state, the intermolecular interactions control the molecular packing motifs of organic luminophors. In this regard, the emission properties of organic luminophors are primarily governed by the whole molecular aggregate rather than by the individual molecule.² Upon external stimulus such as pressure and mechanical grinding, alternation of solid-state arrangement and/or phase transition may occur, thus leading to a change in emission color. This process is defined as “piezochromism”.³ Since luminescence can be detected with high sensitivity, the materials with piezochromic luminescent (PCL) behavior have a wide variety of applications.^{2,3} Although compounds exhibiting PCL properties could be liquid-crystalline, polymer, organic and inorganic molecules, PCL materials are rather sparse.⁴ Further design of PCL materials and investigation of the relationship between the molecular packing and the piezochromic behavior also remain a considerable challenge.

Aggregation-induced emission (AIE),⁵ on the other hand, is an unusual phenomenon, which has no emission in the dilute solution but enhanced emission in the solid state. Since the first report of AIE material by Tang and co-workers in 2001, great efforts have been devoted to the design and synthesis of organic fluorophores with AIE properties.^{6,7} Only recently, the phosphorescent AIE phenomenon based on transition metal complexes has also been detected.⁸ Among the phosphorescent AIE compounds, the Ir(III) phosphors have been synthesized through chemical modification of the ligands by our group and others.^{8,9}



Scheme 1 Chemical structure of complex 1.

We demonstrated from our density functional theory (DFT) calculations that the weak emission of these complexes in the dilute solution might arise from the intramolecular rotation of the dendritic ancillary ligands, which induces an efficient radiationless decay pathway.⁹ A number of photoactive Ir(III) complexes have been synthesized to date.¹⁰ Zhao and coworkers also presented detailed studies on the photophysical properties of Ir(III) systems.^{10e,f} They indicated that Ir(III) complexes characterized as ³ILCT excited-state usually show very weak emission or non-emission in solution. Recently, a successful example of an Ir(III) compound [Ir(dfppz)₂(Mptz)]PF₆ exhibiting reversible piezochromic behavior has been reported by us.^{4b} It is natural to question whether this Ir(III) complex could simultaneously show the AIE behavior if a dendritic ligand, such as carbazole based dendrons, is introduced into triazole-pyridine as the ancillary ligand (See Scheme 1).

Inspired by this idea, herein, we designed and prepared a novel cationic Ir(III) complex, [Ir(dfppz)₂(L)]PF₆ (**1**), with 1-(2,4-difluorophenyl)-1H-pyrazole (dfppz) as the cyclometalated ligand and a dendritic ligand (**L**) as the ancillary ligand (Scheme 1). The quantum chemical calculations reveal that the T₁ state of complex **1** shows a predominant ³ILCT character (see Table S1 and Fig. S1, ESI†), which is different from that of our previously reported Ir(III) complex [Ir(dfppz)₂(Mptz)]PF₆, a piezochromic luminescent complex. Considering the presence of ³ILCT excited-state and dendritic ancillary ligand, we expect that complex **1** might be non-emissive in solution, but show strong emission in the solid state due to molecular stacking.^{8a,b,d} The photophysical properties of complex **1** have been investigated in detail. As expected, it is non-emissive when dissolved in good solvents, but displays enhanced emission in the solid state.

^aInstitute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun, 130024 Jilin, People's Republic of China. E-mail: zmsu@nenu.edu.cn

^bDepartment of Chemistry, Capital Normal University, Beijing, People's Republic of China. E-mail: liaoy271@nenu.edu.cn

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Additionally, the as-prepared powder of **1** obtained through recrystallization exhibits bright yellow emission and its emission color can change to orange upon grinding. In other words, complex **1** is both a PCL and AIE material. To the best of our knowledge, it is the first example of an Ir(III) complex simultaneously displaying piezochromism and aggregation-induced emission.

The ancillary ligand **L** was readily synthesized by C–N coupling of corresponding bromide with 2-(5-phenyl-2H-1,2,4-triazol-3-yl)pyridine catalyzed by copper(I) iodide. Complex **1** was prepared by reacting the dimeric iridium(III) intermediate [Ir(dfppz)₂Cl]₂ with ligand **L**, followed by a counter-ion exchange reaction (Schemes S1 and S2, ESI†). Detailed procedures and characterization data are given in the ESI.† The crystals of **1** were obtained by recrystallization from dichloromethane–petrol ether. Similar to reported cationic Ir(III) complexes,^{4b,11} complex **1** exhibits a distorted octahedral geometry around the Ir atom coordinated by two cyclometalated ligands and one ancillary ligand. Here, the two dfppz ligands adopt mutually an eclipsed configuration with two nitrogen atoms residing at *trans* locations (Fig. S4, ESI†). Close investigation of the molecular packing structure of **1** reveals that multiple intermolecular C–H... π interactions exist in the single crystal structure of **1** (Fig. S5, ESI†). Due to these weak interactions, the crystal structure of **1** would be easily destroyed, which may be triggered by packing rearrangement or phase transition under external pressure. Thus, the emission color of complex **1** changed upon grinding, which can be considered as one of the possible reasons for the present PCL behavior.^{2a,12} In addition, the ancillary ligand possesses intrinsic intramolecular rotation units. In solutions, the rotation is active and can serve as a relaxation channel, resulting in an efficient radiationless decay pathway. As a result, complex **1** would be non-luminescent in dilute solution due to the efficient radiationless decay as well as the ³ILCT excited-state character. In contrast, the intramolecular rotational motions should be effectively suppressed in the aggregation state, thereby the radiation decay would be enhanced and induce it to emit.^{5,7,13}

Under UV light irradiation of the as-prepared powder **1** (for clarity, hereafter abbreviated as the letter **1A**), the sample **1A** shows strong yellow emission (537 nm), as shown in Fig. 1. When the powder **1A** is gently ground using a pestle in the ceramic mortar, however, a significant bathochromic shift (λ_{max} = 564 nm) occurs in the orange-emitting ground sample **1G** (Fig. 1). This result indicates that complex **1** exhibits a pressure-

induced luminescence change. As a matter of fact, the ground orange-emitting powder (**1G**) can be reverted to the original yellow-emitting one through recrystallization in dichloromethane–petrol ether. Moreover, after heating the ground sample **1G** at 325 °C for 5 min, the obtained powder (**1H**) also exhibits similar emission color to sample **1A** and the recrystallized sample (**1R**) (Fig. S6, ESI†). Note that the changes in emission color are visible to the naked eye. When the powder **1A** was spread on a filter paper and the letters “AIPE” were written on that with a spatula, the marked “AIPE” can be observed clearly on the yellow “paper” under the UV lamp (Fig. 1b), implying that complex **1** has potential applications in optical recording and pressure-sensing fields.

To elucidate the PCL behavior of complex **1A**, NMR spectroscopy, differential scanning calorimetry (DSC) and powder X-ray diffraction (PXRD) studies have been performed. As shown in Fig. 2, the PXRD patterns show distinctly different patterns for the samples **1A** and **1G**. In the case of **1A**, it displays clear and sharp reflection peaks which are in good agreement with the simulated XRD from the single crystal, indicating that the **1A** molecules are packed in a relatively well-ordered structure (crystalline state). In contrast, the diffractogram of the ground sample **1G** does not show any noticeable reflections. These results demonstrated that the crystalline state **1A** was converted into an amorphous state (**1G**) after grinding. Upon heating **1A** and **1G** to 350 °C, the DSC curve of **1A** exhibited a clear endothermic melting peak, while a broad exothermic recrystallization peak at *ca.* 320 °C was detected in the case of **1G** (Fig. S7, ESI†). This exothermic peak in the DSC curve of **1G** is similar to the temperature at which thermal recrystallization starts to take place. Furthermore, ¹H NMR spectra and ¹³C magic-angle spinning nuclear magnetic resonance (¹³C CP/MAS-NMR) analysis have also been carried out to further determine whether the chemical reaction and isomer process happen. It is found that the ¹H NMR spectra for complex **1** in various states are almost identical (Fig. S8, ESI†). Additionally, the sharp resonance lines are observed in ¹³C CP/MAS NMR of **1A** (Fig. 2b), but the ground sample **1G** exhibits broader distribution compared with that of **1A**, and keeps its original conformation at the molecular level.¹⁴ Based on our experimental results, we can confidently propose that the ground sample, obtained by mechanical grinding, represents the same compound in the state of a highly amorphous powder. No chemical reaction and isomer process take place during the grinding process.

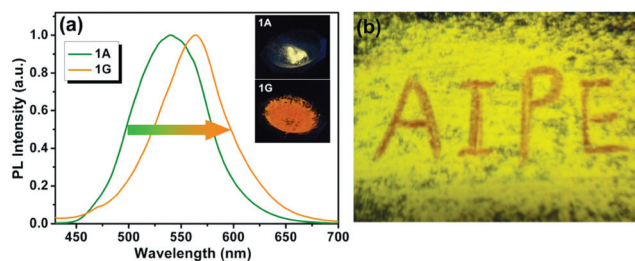


Fig. 1 (a) Emission spectra of the samples **1A** and **1G**. (b) The powder **1A** was cast on the filter paper and the letters “AIPE” were written with a spatula under UV light at room temperature.

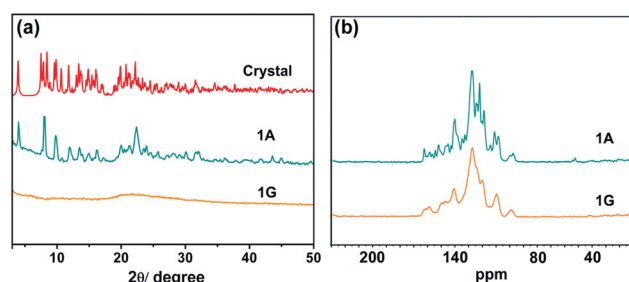


Fig. 2 (a) XRD patterns and (b) ¹³C CP/MAS-NMR spectra of the samples **1A** and **1G**.

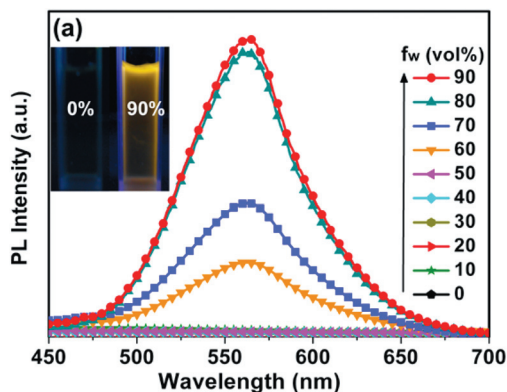


Fig. 3 Emission spectra of complex **1** in CH_3CN – H_2O mixtures with different water fractions (0–90%).

In our previous work,^{4b} the cationic Ir(III) complex, $\text{Ir}[(\text{dfppz})_2(\text{Mptz})]\text{PF}_6$ also shows an intense emission in the solid state as well as PCL behavior, which is similar to that of complex **1**. Generally, for cationic Ir(III) complexes, three excited states contribute to the observation of light emission, namely, $\text{LC } ^3\pi\text{--}\pi^*$, $^3\text{MLCT}$ and $^3\text{LLCT}$. The emission spectra from $^3\text{MLCT}$ and $^3\text{LLCT}$ states are usually broad and featureless, while the obvious vibronic emission bands are always attributed to $\text{LC } ^3\pi\text{--}\pi^*$ state. In addition, the emission spectra from $^3\text{MLCT}$ and $^3\text{LLCT}$ states depend on the polarity of solvents due to the charge transfer character of the excited state. Strong and broad emissions in CH_2Cl_2 , CH_3CN , THF and DMF solutions are observed at room temperature for complex $\text{Ir}[(\text{dfppz})_2(\text{Mptz})]\text{PF}_6$ (Fig. S9, ESI†). Moreover, the emission spectrum of complex $\text{Ir}[(\text{dfppz})_2(\text{Mptz})]\text{PF}_6$ has a dependence on the polarity of solvents, suggesting that its luminescence mainly originates from $^3\text{MLCT}$ mixed with $^3\text{LLCT}$ states.¹⁵ This conclusion is consistent with our calculated results shown in Table S1 and Fig. S1.† In sharp contrast, complex **1** can be easily dissolved in common organic solvents, such as CH_2Cl_2 , CHCl_3 , CH_3CN and DMF, it is not emissive in these solutions (Fig. S10, ESI†), but become highly emissive in the solid state as mentioned above. The absolute quantum yields of complex **1** in CH_3CN solution and in the solid state (as-prepared powder) using an integrating sphere were estimated to be 0% and 20%, respectively. This phenomenon is similar to the previously reported AIE molecules, indicating that **1** might feature the AIE property.

To probe the AIE property of complex **1**, the photoluminescence (PL) spectra of **1** in CH_3CN – H_2O mixtures with various water contents were investigated. Since **1** dissolves readily in CH_3CN solution but is insoluble in water, addition of large amounts of water into the CH_3CN solution of **1** will cause complex **1** to aggregate. If complex **1** possesses AIE activity, the PL intensity of **1** in CH_3CN – H_2O mixtures should increase due to the aggregation of **1**. As shown in Fig. 3, complex **1** in pure CH_3CN solvent exhibits faint emission, but the intensity of emission remarkably increases when the water content exceeds 60%. Adding further water up to 90%, the PL intensity is significantly enhanced, which is about 120-fold greater than that in pure CH_3CN solvent. This indicates that complex **1** has a significant AIE effect. In addition, it is noteworthy that the emission spectrum of **1** in CH_3CN – H_2O (1 : 9) mixtures is nearly identical to

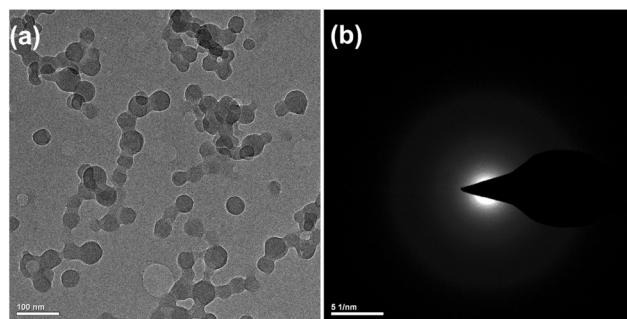


Fig. 4 (a) TEM image of nanoaggregates of complex **1** formed in CH_3CN – H_2O mixtures with 90% water fraction. (b) Electron diffraction pattern of the nanoaggregates.

that of the ground sample **1G** (Fig. S11, ESI†). This indicates that there are some amorphous molecular aggregates formed in the mixtures, which is confirmed by the results of transmission electron microscopy (TEM) and confocal luminescence experiments (Fig. 4b and Fig. S12, ESI†).¹⁶ Motivated by the existing “on–off” luminescence behavior of complex **1**, it is believed that complex **1** might serve as a chemical sensor for volatile organic vapors. As shown in Fig. S13,† the bar-like luminescence pattern formed from the CH_3CN solution of complex **1** can be observed clearly on a TLC plate. After exposure of CH_2Cl_2 solvent, the luminescence was completely turned off, demonstrating its ability to detect organic vapors.

In summary, a novel cationic Ir(III) complex has been designed and successfully prepared by employing a dendritic ancillary ligand, whose emission color of its as-prepared powder can change obviously upon grinding, and revert to the original emission *via* heating and/or recrystallization. Interestingly, it exhibits no emission in solution. This is the first example of a cationic Ir(III) complex simultaneously exhibiting PCL and AIE properties. The crystalline–amorphous phase transformation is responsible for the altered emission of the ground samples by carefully analyzing our experimental data. The design concept, the judicious modification of dendritic ancillary ligand for tuning the character of excited states, should provide valuable information for the development of multifunctional materials based on Ir(III) complexes.

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