Aggregation-induced phosphorescent emission (AIPE) of iridium(III) complexes†

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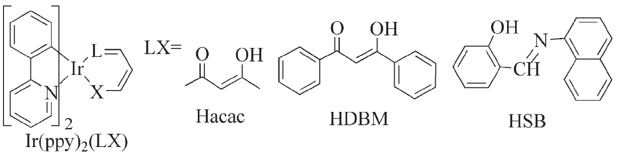
A novel aggregation-induced phosphorescent emission (AIPE) was observed for iridium(III) complexes. This interesting phenomenon was attributed to the intermolecular packing, resulting in a switch from the non-emissive ^{3}LX excited state to the emissive ^{3}MLLCT transition, which is confirmed by X-ray diffraction studies as well as theoretical calculations.

The design and synthesis of purely organic dyes and metal complexes as optical materials have attracted a great deal of interest because of their possible applications in molecule-based devices.[1] The performance of organic molecule-based devices strongly depends on the molecular-assembly structures.[2] Therefore, understanding and controlling molecular arrangements in the solid state are fundamental issues for solid organic materials. Unfortunately, aggregate formation often quenches light emission,[3] which has been a thorny problem in the development of photoluminescent materials that exhibit strong solid-state emission properties. Recently, aggregation-induced emission (AIE) has attracted more and more attention, and many chromophores with AIE have been reported.[4,5] However, the output signal of AIE is still mainly limited to fluorescence emission.

Recently it has been found that, owing to their planar structures, platinum(II) complexes readily undergo π–π stacking through Pt–Pt interactions, and a few platinum(II) complexes exhibited solid-state phosphorescent emission.[6] The solid-state phosphorescent emission primarily originates from metal–metal-to-ligand charge-transfer transition (^{3}MMLCT).[6] However, the phosphorescent mechanism of ^{3}MMLCT is not suitable for the design of cyclometalated iridium(III) complexes because of the octahedral structure of iridium(III) complexes. Up to now, little work has been reported on the influence of intermolecular interactions on the solid-state luminescent properties of octahedral iridium(III) complexes,[8] although iridium(III) complexes are still the best phosphorescent dyes due to their high photoluminescence efficiency and excellent color tuning.[8,9] Herein, we describe the intense aggregation-induced phosphorescent emission (AIPE) of two iridium(III) complexes Ir(ppy)$_2$(DBM) and Ir(ppy)$_2$(SB) (Scheme 1, where ppy = 2-phenylpyridine, DBM = 1,3-diphenyl-1,3-propanedione, acac = acetylacetonate and SB = 2-(naphthalen-1-yliminomethyl)-phenol), and demonstrate a novel phosphorescence mechanism of metal-to-ligand–ligand charge-transfer transition (MLLCT).



Scheme 1 Chemical structures of iridium(III) complexes.

All complexes were synthesized according to a previously reported method,[7] and were further characterized by an X-ray diffraction study.†‡ The UV-Vis absorption spectra of the complexes in solution show weak absorption tails above 500 nm (see ESI†), which are attributed to spin-forbidden metal-to-ligand charge transfer (^{3}MLCT) and ligand centered (^{3}LX) transitions. Moreover, it should be mentioned that no obvious change was observed for the absorption of all complexes in solution and in the solid state.

The photoluminescence properties of all complexes in dilute solution were investigated. In contrast to the intense luminescence of Ir(ppy)$_2$(acac) (Scheme 1), no luminescence was observed for Ir(ppy)$_2$(DBM) and Ir(ppy)$_2$(SB) in different dielectric constant solvents (such as DMF, CH_3CN, C_2H_5OH, acetone, CH_2Cl_2, THF and toluene) (Fig. 1 and ESI†). This is in agreement with the work of Thompson and colleagues.[9a] In light of the same cyclometalated ligand (ppy) being present in these three complexes, the different photoluminescence properties in solution are attributed to the variation in ancillary ligands (LX).

To explain the significant difference in emission properties, the triplet energy levels of the three ancillary ligands DBM, SB and acac (Scheme 1) were estimated by referring to the lower wavelength emission edges of their corresponding phosphorescence spectra. The triplet energy level of the ligand is scarcely affected by the lanthanide ion, and the lowest lying excited level ($^6P_{7/2} \rightarrow {}^8S_{7/2}$) of Gd(III) is located at 32150 cm^{-1}.[10] On this basis, the phosphorescence spectra of Gd(DBM)$_3$(H$_2$O)$_2$, Gd(SB)$_3$(H$_2$O)$_2$ and Gd(acac)$_3$(H$_2$O)$_2$ allow one to evaluate the $^3\pi\pi^*$ energy levels of corresponding ligand anions DBM, SB, and acac. The phosphorescence spectra of Gd(DBM)$_3$(H$_2$O)$_2$, Gd(SB)$_3$(H$_2$O)$_2$ and Gd-(acac)$_3$(H$_2$O)$_2$ at 77 K have bands with maxima at approximately

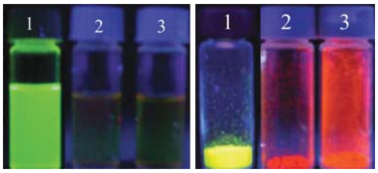


Fig. 1 Luminescence photographs of Ir(ppy)$_2$(acac) (1), Ir(ppy)$_2$(DBM) (2) and Ir(ppy)$_2$(SB) (3) in CH_2Cl_2 solution (left) and solid state (right) (λ_{ex} = 365 nm).

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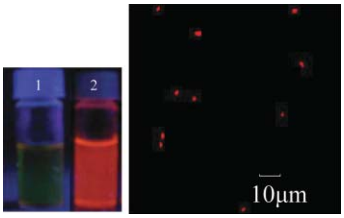


Fig. 2 (Left) Luminescent photograph of Ir(ppy)$_2$(SB) (2 × 10^{-5} mol L^{-1}) in pure CH_3CN (1) and H_2O–CH_3CN (4 : 1, v/v) mixture (2) at 298 K. (Right) Confocal fluorescence microscope image of Ir(ppy)$_2$(SB) in H_2O–CH_3CN (4 : 1, v/v) mixture.

550, 542 and 483 nm (see ESI†), respectively. We compared them with the phosphorescent emission peak of Ir(ppy)$_3$ (515 nm), which was assumed to be essentially dominated by the excited triplet energy of ppy-centered ^{3}MLCT.[3d] So, we can conclude that the energetic positions of ppy-centered ^{3}MLCT and the triplet energy levels ^{3}LX of ancillary ligands are as follows: ^{3}LX(acac) > ppy-centered ^{3}MLCT > ^{3}LX(SB) ≈ ^{3}LX(DBM). Thus, for Ir(ppy)$_2$(DBM) and Ir(ppy)$_2$(SB), the ancillary ligands DBM or SB instead of ppy dominate the excited state properties, leading to inefficient emission.

An unusual observation was made in that Ir(ppy)$_2$(DBM) and Ir(ppy)$_2$(SB), in powder, emitted moderately intense emissions (Fig. 1) with emission wavelengths of 625 and 610 nm and with quantum efficiencies of 7.6% and 7.9%, respectively. Furthermore, addition of non-solvent water into the dilute CH_3CN solutions can turn on the photoluminescent emission of the two complexes (see ESI†). For example, Ir(ppy)$_2$(SB) in the H_2O–CH_3CN mixture (4 : 1, v/v) exhibits intense photoluminescence (Fig. 2). As determined using confocal laser scanning fluorescence microscopy, the intense emissions of the two complexes in the H_2O–CH_3CN mixture originate from molecular micro-aggregates (Fig. 2 and ESI†). Evidently, taking the absence of emission of these two complexes in solution into account, we can conclude that Ir(ppy)$_2$(DBM) and Ir(ppy)$_2$(SB) are aggregation-induced phosphorescent emission (AIPE) active.

Furthermore, single crystals of Ir(ppy)$_2$(DBM) and Ir(ppy)$_2$(SB) were obtained and analyzed to study the molecular packing structures (Fig. 3). Interestingly, there are strong π–π interactions, involving the offset pyridine ring of adjacent ppy ligands, in both Ir(ppy)$_2$(DBM) and Ir(ppy)$_2$(SB), with an interplanar separation of ∼3.37 Å.

To understand the unusual solid-state photoluminescence properties of these iridium(III) complexes, periodic density functional theory (DFT) calculations on Ir(ppy)$_2$(DBM) (as an example) were carried out using SIESTA code.[11] By referring to the X-ray diffraction data, we have calculated the complex in a series of different unit cell sizes, which effectively mimics the environment change from the solution (well-separated) to the solid state (closely-packed). The optimized structures were found to be very consistent with the X-ray data. Then, the wavefunctions of all of the structures were viewed state-by-state.

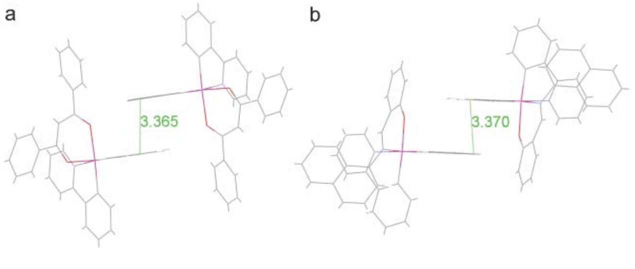
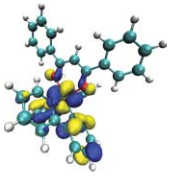
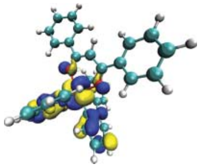
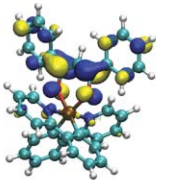
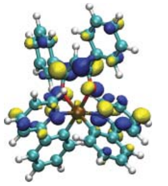
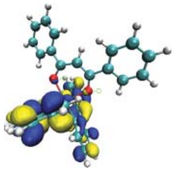


Fig. 3 Molecular packing of Ir(ppy)$_2$(DBM) (a) and Ir(ppy)$_2$(SB) (b).

Table 1 HOMO, LUMO and LUMO + 1 distributions of Ir(ppy)$_2$(DBM) calculated by DFT calculations in State I and State II

X	State I	State II
HOMO		
LUMO		
LUMO + 1		

Although similar HOMO and LUMO + 1 distributions were observed for State I and II (Table 1), we have found that the characteristics of the LUMO are largely modified when the adjacent pyridyl rings of ppy ligands are close. When the complex molecules are well-separated as they are in dilute solution, *i.e.* the distance between adjacent pyridyl groups being 20.4 Å (State I), the LUMO distribution of Ir(ppy)$_2$(DBM) was found to be mainly centered on the DBM ligand (Table 1), indicating that the DBM ligand dominates the excited state of Ir(ppy)$_2$(DBM) in State I. In contrast, when the distance between adjacent pyridyl groups is shortened to 3.4 Å (State II), the LUMO in State II delocalizes onto both the DBM ligand and the pyridyl groups of the ppy ligands (Table 1). Herein, State II mimics the solid state situation: the crystal-packing of Ir(ppy)$_2$(DBM) exhibits a strong π–π interaction between adjacent pyridyl rings of ppy ligands with a face-to-face separation of 3.37 Å. It is obvious that, due to the interaction of adjacent pyridyl groups, the ppy ligands participate intensively in the excited state of Ir(ppy)$_2$(DBM) in State II.

As shown in Fig. 4, the total density of states (TDOS) of State I, State II and State III (with the intermediate distance of adjacent pyridyl groups being 5.4 Å) from DFT calculations clearly indicates that the LUMO orbital gradually mixes with LUMO + 1 on going from State I to State III and to State II. In State I, the LUMO and LUMO + 1 distributions can be distinguished clearly and the energy level of the LUMO is the lowest. In conjunction with the orbit distribution calculated using DFT, we can clearly conclude that the triple excited state of the DBM ligand participates in the excited state of Ir(ppy)$_2$(DBM) in State I. However, in State II, the LUMO orbital strongly mixes with LUMO + 1. The LUMO + 1 distribution in State II from the DFT calculations entirely delocalizes onto the pyridyl groups of

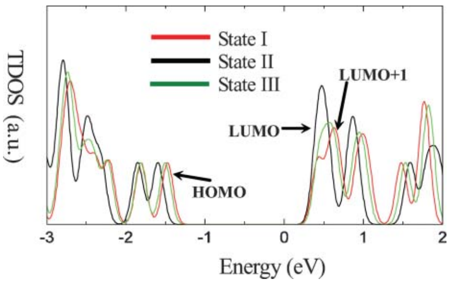


Fig. 4 Energy levels of Ir(ppy)$_2$(DBM) in different States I, II and III from DFT calculations.

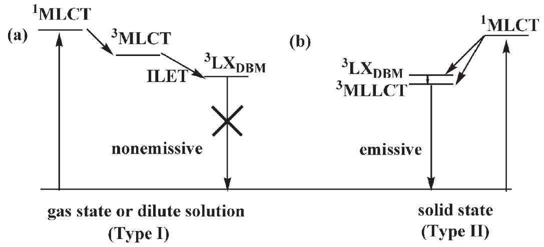


Fig. 5 Possible mechanism of phosphorescence emission in State I (a) and State II (b).

ppy (Table 1), and the LUMO in State II delocalizes onto both the DBM ligand and the pyridyl groups of the ppy ligands (Table 1). Therefore, the ppy ligands participate extensively in the excited state of Ir(ppy)$_2$(DBM) in State II when the adjacent pyridyl rings of ppy ligands are close.

On the basis of experimental observations and DFT calculations, the mechanism of phosphorescence emission from Ir(ppy)$_2$(DBM) in the solid state may be explained as follows (Fig. 5). After the ^{1}MLCT excitation from iridium to ppy in the singlet, highly efficient inter-system crossing to ^{3}MLCT occurs, owing to strong spin–orbit coupling. This ppy-centered ^{3}MLCT state of Ir(ppy)$_2$(DBM) has different fates in solution and solid state (Types I and II), depending on the difference between the energy level of the ^{3}MLCT state and the triplet energy level of the DBM ligand (^{3}LX$_{DBM}$), as depicted in Fig. 5. In a solution of Ir(ppy)$_2$(DBM), the DBM ligand instead of the ppy ligand dominates the excited state properties due to the lower energy level of ^{3}LX$_{DBM}$ (Table 1), which switches the phosphorescent decay of the ppy-centered ^{3}MLCT state (Type I, Fig. 5a), leading to very weak emissions in solution.[7] However, in the solid state, strong π–π interactions between the adjacent pyridyl rings of ppy ligands elongates the overall π-conjugation degree and reduces the energy level of π^*_{ppy}, compared with that in solution. As a result, the triplet energy level of the charge transfer state from iridium to the interacting ppy [denoted as ^{3}MLLCT] is reduced and the ppy ligands participate in the excited state of Ir(ppy)$_2$(DBM) in the solid state. Therefore, the emission of ^{3}MLLCT based on the interaction of ppy is observed (Type II, Fig. 5b). Moreover, this ^{3}MLLCT-mediated phosphorescent emission is strongly supported by the fact that the emission (λ_{max} = 625 nm) of Ir(ppy)$_2$(DBM) in the solid state is red-shifted significantly in comparison to that of Ir(ppy)$_2$(acac) in solution with a typical ppy-centered ^{3}MLCT emission.

In conclusion, for the first time, we have discovered the aggregation-induced phosphorescent emission (AIPE) of iridium(III) complexes. By analyzing the influence of molecular packing on photophysical properties with the help of first-principles DFT calculations, we found that this interesting phenomenon could be explained by a new mechanism of ^{3}MLLCT-mediated phosphorescent emission, that is, the formation of excimers by π–π stacking of adjacent pyridyl rings of ppy ligands can significantly change the excited state properties of iridium(III) complexes.

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‡ CCDC 610633 and 611152. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712416c

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