

Polymorphism-induced dual phosphorescent emission from solid-state iridium(III) complex†

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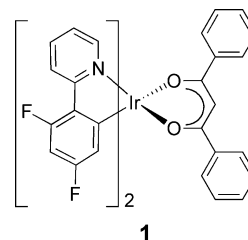
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Different molecular packing structures in the solid-state iridium(III) complex (**1**) induce unprecedented dual phosphorescent emission through ³M(LL)CT and ³M(LL)CT transitions.

Aggregation-induced emission (AIE) of solid materials has recently attracted great attention in the development of luminescent materials for various applications such as organic-light emitting diodes and sensors.¹ Particularly, the solid-state phosphorescent emission based on heavy metal ion complexes is of considerable interest owing to high quantum efficiency and color-tuning properties of molecular complexes,² which renders AIE suitable for optical device applications. It has been well established in the square-planar platinum(II) complexes that the polymorphism induced by Pt(II)–Pt(II) interactions and/or π – π stacking of the ligands gives rise to the intriguing appearance of multiple solid-state AIEs.³ For iridium(III) systems, it has been recently demonstrated that the phosphorescent AIE of heteroleptic iridium(III) complexes can be triggered by intermolecular excimer state, *i.e.*, metal-to-ligand-ligand charge-transfer (³M(LL)CT) state⁴ or restricted intramolecular relaxation⁵ in the solid-state but the observation of multiple AIEs has not been reported so far.

Since the octahedral structure of iridium(III) complex intrinsically prevents direct Ir(III)–Ir(III) interactions, the engineering of crystal packing structure through the modification of π – π interactions between the cyclometalated ligands could be a viable approach to the polymorphism-induced multiple AIEs of the iridium(III) complex. In this report, we replaced the ppy ligand in the well-known Ir(ppy)₂(DBM) complex⁶ with a ppyFF ligand (ppyFF = 2-(2,4-difluorophenyl)pyridine; DBM = dibenzoylmethane), as fluorinated arenes are known to modulate π – π interactions in the solid-state with respect to their non-fluorinated analogues.⁷ As a result, we find the unprecedented dual phosphorescence[‡] of Ir(ppyFF)₂(DBM) (**1**) complex originated from the crystal packing polymorphism.



1 was prepared in 62% yield from the reaction of DBM and dimeric [Ir(ppyFF)₂(μ -Cl)]₂ precursor⁸ *via* the modification of the literature method.^{6,9} The UV-vis absorption spectrum of **1** in a degassed chloroform solution at room temperature exhibits spin-allowed π – π^* transitions of ppyFF ligands (¹LC) below 300 nm^{6,10} and of DBM (¹LX) in the region ranging from 350 nm to 400 nm¹¹ (Fig. 1, left). While the lower energy absorption in 400–450 nm with a weak shoulder at 437 nm is attributed to spin-allowed metal-to-ligand transition (¹MLCT), the weak absorption band at 465 nm which tails to 500 nm can be assigned to the spin-forbidden MLCT (³MLCT) and DBM-centered (³LX) transitions.⁶

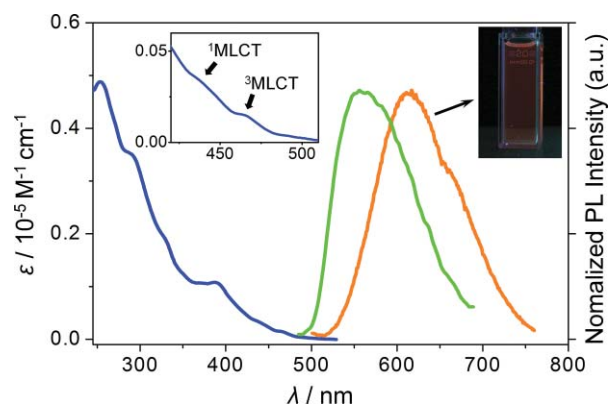


Fig. 1 UV-vis absorption (left; blue line) and PL spectra of **1** at room temperature (right; orange line) and 77 K (right; green line) (1.0×10^{-5} M in chloroform; $\lambda_{\text{ex}} = 388$ nm). Insets: Enlarged absorption spectrum (left) and photograph of **1** in chloroform under UV-lamp (right).

On the other hand, the room-temperature photoluminescence (PL) spectrum of **1** shows a very weak emission band at 611 nm (Fig. 1, right). Interestingly, this emission band is largely red-shifted compared to the ppyFF-centered ³MLCT observed for Ir(ppyFF)₃ ($\lambda_{\text{em}} = 469$ nm)^{8,12} and the emission quantum yield is also found to be very low ($\Phi_{\text{em}} = 0.03$ vs 0.77 for Ir(ppyFF)₃) indicative of inefficient phosphorescence. The low-temperature PL spectrum at 77 K exhibits a blue-shifted band at $\lambda_{\text{em}} = 555$ nm with the emission lifetime of 1.3 μ s. This emission feature is actually very consistent with that observed in the DBM anion ($\lambda_{\text{em}} = 550$ nm at

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† Electronic supplementary information (ESI) available: Experimental details and molecular structures and unit cell packing diagrams of **1A** and **1B**. CCDC reference numbers **1A**, 726166; **1B**, 726167. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b907058c

77 K),⁴ revealing that the observed weak emission originates from the DBM-based triplet excited state (³LX). The cyclic voltammetry measurement further shows the DBM-centered first reduction at −2.16 V (Fig. S2 in the ESI†) indicating the lowest-unoccupied molecular orbital (LUMO) in **1** is localized on the DBM moiety. This result also supports that the DBM ligand dominates the excited state of **1** (³LX) in solution. These findings reflect efficient energy transfer of the ³MLCT state to the ³LX of DBM of **1** in solution, as similarly found in Ir(ppy)₂(DBM).^{4,6,13}

Unlike the very weak luminescence in solution, intense luminescence was produced in the solid state of **1**. Remarkably, the crystals§ obtained from a THF/hexane solution reveal that complex **1** exists in two emitting species, *i.e.*, orange red crystals (**1A**) and yellow crystals (**1B**) (Fig. 2a). The formation of two colored species is invariably observed upon applying different crystallization methods except for a slight change of the amount ratio between the two species. For instance, cooling of either a THF/hexane or CH₂Cl₂/hexane solution of **1** resulted in a larger proportion of **1A**, but the slow evaporation of solvent at room temperature afforded more **1B**. The solid-state PL spectra of separated **1A** and **1B** exhibit an emission maximum wavelength at 605 (τ = 87 ns) and 560 nm (τ = 197 ns) that corresponds to orange red and yellow colors, respectively, (Fig. 2b) indicating the occurrence of dual phosphorescent emission in the solid-state of **1**.

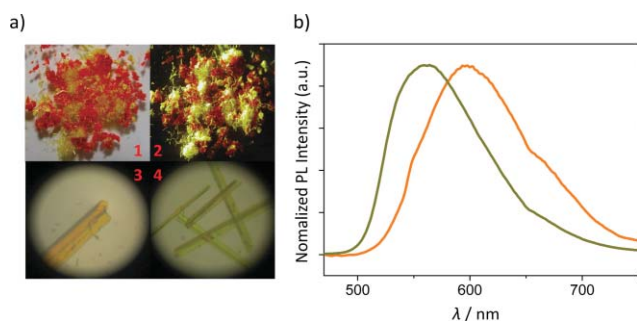


Fig. 2 (a) Photographs of solid **1** under daylight (1) and UV-lamp (2) and of crystals **1A** (3) and **1B** (4) from a THF/hexane solution. (b) Solid-state PL spectra ($\lambda_{\text{ex}} = 388$ nm) of **1A** (orange line) and **1B** (dark yellow line).

In order to clarify the origin of dual emission of **1**, the crystal structure of each species was determined from X-ray diffraction studies. While **1A** crystallizes in the space group *C2/c*, **1B** crystallizes in *P*-1, which also points to the formation of polymorphs of **1**. Although molecular structures of **1** in both crystals **1A** and **1B** show two ppyFF ligands being in a *trans* disposition of pyridine rings similar to those observed in other heteroleptic Ir(III) complexes,^{4,6,9} it is found that both crystals contain mixtures of Δ - and Λ -isomers in a 1:1 molar ratio in the unit cells (Fig. 3 and Fig. S4§). However, inspection of unit cells reveals that different kinds of π – π interactions are displayed in the crystal packing structures (Fig. 4). In the case of orange red **1A**, the π – π stacking involving four ppyFF ligands displays three types of interactions (Fig. 4a). The first two interactions are π – π interactions between the ppyFF ligands with head-to-tail ($\alpha \cdots \beta$) and tail-to-tail ($\beta \cdots \gamma$) arrangements. The orthogonally oriented ppyFF ligands afford the third type of interaction between the difluorophenyl and pyridyl rings ($\gamma \cdots \delta$). The interplanar separations between the ppyFF ligands involving each interaction are estimated to be *ca.* 3.33, 3.39, and 3.28 Å, respectively, all of which are quite short, thus indicating the presence of strong π – π interactions. It is also interesting to note that the foregoing π – π interactions displayed in **1A** take place only between the Δ - and Λ -isomers (Fig. S8§). Besides the π – π interactions between the ppyFF ligands, the isolated interactions between the DBM moieties with the short phenyl \cdots phenyl contact of *ca.* 3.45 Å are also observed (Fig. 4b).

On the other hand, in yellow **1B**, two kinds of π – π interactions between the ppyFF ligands are present. The first one is a pyridyl \cdots pyridyl interaction between the adjacent ppyFF ligands ($\alpha' \cdots \beta'$) (Fig. 4c). Although the interplanar separation of *ca.* 3.42 Å is slightly longer than those observed for **1A**, it suggests the presence of strong π – π interactions.

The other interaction, which is essentially consistent with that observed in the Ir(ppy)₂(DBM) system,^{4,13} is associated with the π – π interaction between the ppyFF ligands with a head-to-tail arrangement ($\gamma' \cdots \delta'$) (Fig. 4d). The estimated interplanar separation of *ca.* 3.40 Å is also comparable to that in Ir(ppy)₂(DBM) (3.37 Å).⁴ Different from the extended π – π stacking by four ppyFF ligands in **1A**, these interactions in **1B** are found to be isolated

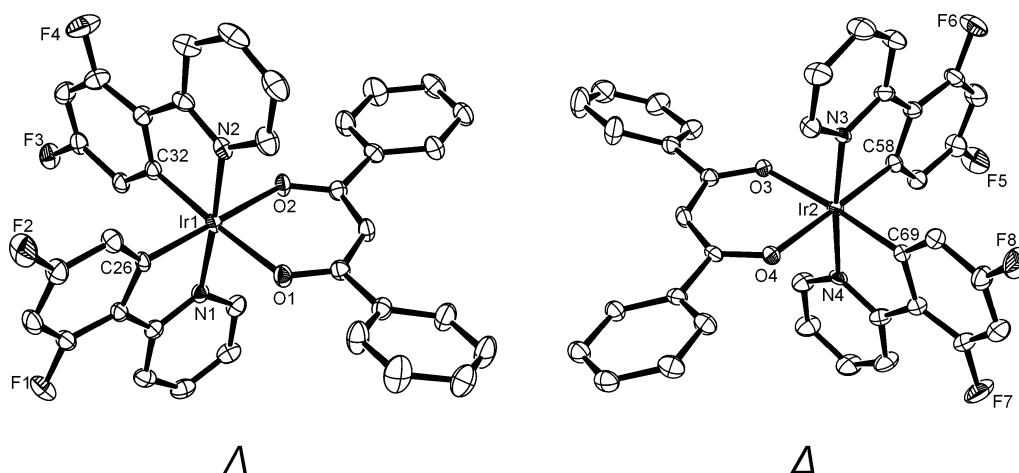


Fig. 3 Molecular structures of Λ - (left) and Δ -isomers (right) of **1A** (50% ellipsoid). The H-atoms were omitted for clarity.

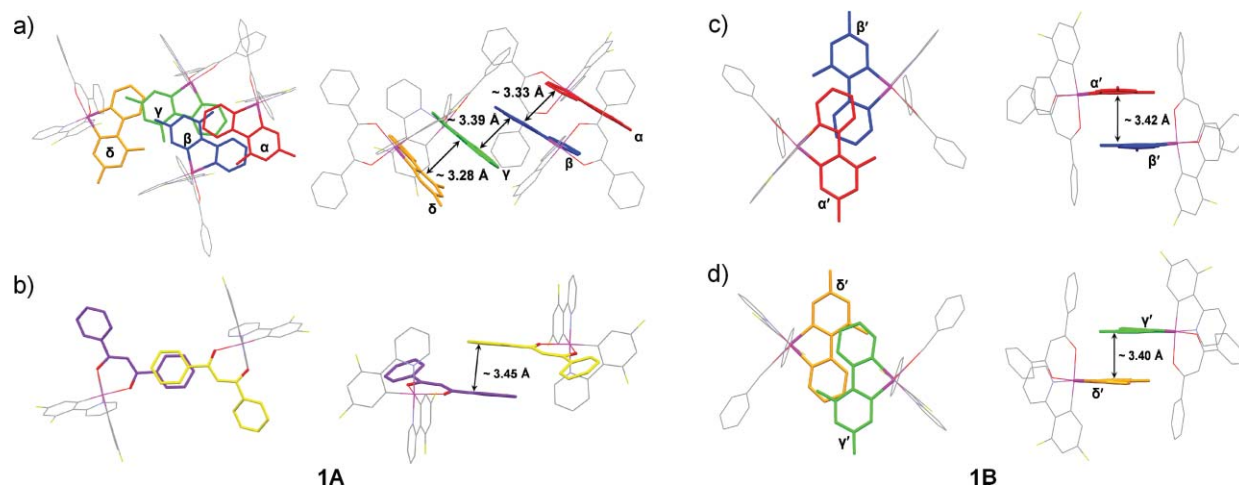


Fig. 4 Crystal packing diagrams of the orange red crystal (**1A**, left) and the yellow crystal (**1B**, right) showing π - π interactions between the ppyFF ligands (a, c, d) and between the DBM moieties (b). Greek letters denote the independent ppyFF ligands.

ones, formed between two ppyFF ligands from each Δ - and Λ -isomer (Fig. S9§). The interaction between the DBM moieties of **1B** appears to be negligible, as judged by the poor π - π overlap and relatively long separation between phenyl rings (Fig. S5§).

From these findings, it can be suggested that in the crystal packing structure of **1A**, the strong π - π interactions with the extended stacking between the four adjacent ppyFF ligands may induce the ppyFF-centered $^3\text{M}(\text{LLLL})\text{CT}$ state where the “acceptor” orbital is delocalized over four ppy ligands belonging to four different compounds and the energy of which is lower than that of the triplet states such as $^3\text{LX}_{\text{DBM}}$ and $^3\text{LX}_{\text{DBM-DBM}}$. Consequently, this state could dominate the excited state properties of the solid state **1A**, leading to the orange red emission at 605 nm (Fig. 5). In contrast, the isolated π - π interactions formed between two ppyFF ligands in **1B** may be responsible for the low-energy $^3\text{M}(\text{LL})\text{CT}$ excited state⁴ whose energy level would be higher than the $^3\text{M}(\text{LLLL})\text{CT}$ state of **1A**. The resulting emission from the $^3\text{M}(\text{LL})\text{CT}$ state could thus exhibit a blue-shifted feature corresponding to the yellow emission at 560 nm.

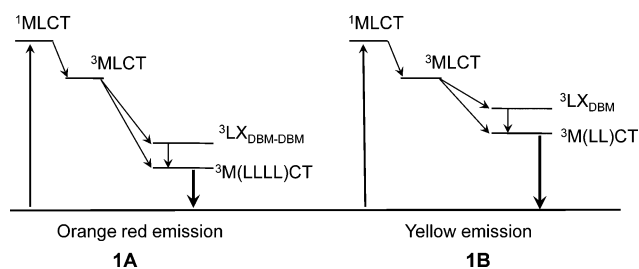


Fig. 5 Proposed mechanism of dual phosphorescent emission of solid-state **1** (**1A** and **1B**).

In conclusion, we report the polymorphism-induced dual phosphorescent emission of solid-state iridium(III) complex. It is suggested that the crystal packing polymorphism showing different π - π stacking between cyclometalated ligands is responsible for the unusual phenomenon, *i.e.*, a switch from the weakly emissive

state of molecular iridium(III) complex to both highly emissive $^3\text{M}(\text{LLLL})\text{CT}$ and $^3\text{M}(\text{LL})\text{CT}$ states in the solid-state.

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Notes and references

† The term “dual emission” usually refers to dual light emission from the same species. In this report, dual emission represents two emissions originated from two different solid state arrangements of one compound.

§ Crystal data for **1A**: $(\text{C}_{37}\text{H}_{23}\text{F}_4\text{IrN}_2\text{O}_2) \cdot (\text{C}_6\text{H}_5\text{O})_{0.5}$, $M_w = 831.84$, $\lambda = 0.74999 \text{ \AA}$ (synchrotron radiation), Monoclinic, $C2/c$, $a = 23.963(5)$, $b = 19.684(4)$, $c = 27.110(5) \text{ \AA}$, $\alpha = 90.00$, $\beta = 94.00(3)$, $\gamma = 90.00^\circ$, $V = 12756(4) \text{ \AA}^3$, $Z = 16$, $\rho_{\text{calc}} = 1.733 \text{ g cm}^{-3}$, $\mu = 4.251 \text{ mm}^{-1}$, $T = 100(2) \text{ K}$, measd reflns = 36 083, unique reflns = 19 220, $R_{\text{int}} = 0.0358$, $R1 = 0.0427$, $wR2 = 0.1186$ ($I > 2\sigma(I)$) and $\text{GOF} = 1.000$; For **1B**: $\text{C}_{37}\text{H}_{23}\text{F}_4\text{IrN}_2\text{O}_2$, $M_w = 795.79$, $\lambda = 0.74999 \text{ \AA}$, Triclinic, $P-1$, $a = 11.745(2)$, $b = 16.325(3)$, $c = 17.965(4) \text{ \AA}$, $\alpha = 113.67(3)$, $\beta = 107.93(3)$, $\gamma = 94.38(3)^\circ$, $V = 2921.4(10) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.809 \text{ g cm}^{-3}$, $\mu = 4.635 \text{ mm}^{-1}$, $T = 100(2) \text{ K}$, measd reflns = 7817, unique reflns = 7817, $R_{\text{int}} = 0.0000$, $R1 = 0.0709$, $wR2 = 0.2075$ ($I > 2\sigma(I)$) and $\text{GOF} = 1.003$.

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