DOI: 10.1002/ejic.201000275

## Dinuclear Iridium(III) Complexes Linked by a Bis(β-diketonato) Bridging Ligand: Energy Convergence versus Aggregation-Induced Emission

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Keywords: Aggregation / Dimetallic complexes / Phosphorescence / Iridium / Platinum

Novel iridium(III)/iridium(III) and iridium(III)/platinum(II) dinuclear complexes,  $[{Ir(ppyFF)_2}_2(\mu_2-L)]$  (4) and  $[{Ir(ppyFF)_2} (\mu_2-L){Pt(ppy)}$  (5) [ppyFF = 2-(2,4-difluorophenyl)pyridine, ppy = 2-phenylpyridine, L = 1,3-bis(3-phenyl-3-oxopropanoyl)benzene], linked by an L bridging ligand were prepared, and their photophysical properties were investigated in solution and in the solid state. The photophysical properties of mononuclear iridium(III) and platinum(II) complexes, [Ir(ppyFF)<sub>2</sub>(dbm)] (1) and [Pt(ppy)(dbm)] (2) bearing a dibenzoylmethane (dbm) ligand were also compared. Whereas the UV/Vis absorption spectra of 4 and 5 show independent light absorption at each metal-centered moiety, the photoluminescence spectra of  ${\bf 4}$  and  ${\bf 5}$  display almost identical features, but very weak emissions in solution at both room temperature and 77 K. The weak emission in solution is found to mainly originate from a <sup>3</sup>LX state of the L bridging ligand,

## Introduction

Luminescent solid materials have recently attracted great attention in the areas of optoelectronic device applications such as organic light-emitting diodes and sensors.<sup>[1]</sup> Although the majority of organic dyes and luminescent metal complexes are highly emissive in their molecular state, aggregation into the solid state often has detrimental effects on their light-emitting properties like emission quenching, which may render them less suitable for many optical applications. Thus, it would be highly desirable to construct an emissive solid state or to enhance the light emission of molecular species by means of aggregation-induced emission (AIE).<sup>[2]</sup> Although a number of AIEs of organic solid materials that constitute fluorescent emission have been reported, the solid-state emission based on heavy-metal ion

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 Supporting information for this article is available on the

WWW under http://dx.doi.org/10.1002/ejic.201000275.

which reflects the occurrence of efficient energy convergence from the triplet states of the Pt(ppy) and Ir(ppyFF) moieties to the <sup>3</sup>LX state of **L**. By contrast, intense orange-red emission, that is, aggregation-induced emission, is produced in the solid state of **4** and **5**. Inspection of the crystal-packing structures of **5** reveals that strong intermolecular  $\pi$ - $\pi$  interactions between the adjacent pyridine rings of ppyFF ligands in the Ir-centered moieties are responsible for the emissive metal-to-ligand-ligand charge-transfer [<sup>3</sup>M(LL)CT] state of the solid-state dinuclear systems. The electrochemical properties of **4** and **5** further indicate that the first two reductions occur at the dbm moieties of the **L** bridging ligand linked to each metal center, which is consistent with the fact that the lowest-energy excited state of the **L** bridging ligand dominates the excited-state properties of **4** and **5** in solution.

complexes may be of particular interest owing to the excellent emitting properties of molecular complexes<sup>[3]</sup> such as the high quantum efficiency of their phosphorescent emission.<sup>[4]</sup>

It has been well established in the square-planar platinum(II) complexes that  $Pt^{II}-Pt^{II}$  interactions and/or  $\pi-\pi$ stacking of the ligands gives rise to the appearance of AIE or in some cases to the multiple AIEs induced by polymorphism.<sup>[5]</sup> In contrast, the phosphorescent AIEs of iridium(III) systems have been relatively less investigated owing to the octahedral structure of the iridium(III) complex.<sup>[6–11]</sup> Regarding the AIE phenomena, Zhao and Huang et al. demonstrated that the phosphorescent AIEs of heteroleptic iridium(III) complexes such as [Ir(ppy)<sub>2</sub>(dbm)] (ppy = 2-phenylpyridine, dbm = dibenzoylmethane)<sup>[11]</sup> can be induced by the intermolecular excimer state, that is, the metal-to-ligand charge-transfer [<sup>3</sup>M(LL)CT] state (Scheme 1).<sup>[8,9]</sup> Park and You et al. also suggested that the restricted intramolecular relaxation in the solid state is responsible for the AIE of the heteroleptic iridium(III) complexes such as [Ir(ppyFF)<sub>2</sub>(pip)] [pip = 2-(phenyliminomethyl)phenol] bearing an imine ancillary ligand<sup>[10]</sup> although the proposed mechanism has been recently refuted by Chou and Chi et al.<sup>[12]</sup> and Huang et al.<sup>[8]</sup> Verv recently. we have also reported that the dual phosphorescent emis-



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Scheme 1.

sion from a solid-state iridium(III) complex could be achievable through the crystal-packing polymorphism induced by the modification of  $\pi$ - $\pi$  interactions between the cyclometalated ligands of [Ir(ppyFF)<sub>2</sub>(dbm)] (1) [ppyFF = 2-(2,4-difluorophenyl)pyridine].<sup>[7]</sup> These examples of the iridium(III) systems reveal that the very weakly emissive or nonemissive <sup>3</sup>LX excited state of the ancillary ligand can be switched into emissive states if a proper manipulation of the crystal-packing structure is allowed in the solid state.

In a continuous effort to develop novel AIE, we turned our attention to the dinuclear iridium(III) systems bearing photoactive cyclometalated ligands, as the multinuclearity could lead to facile modulation of  $\pi$ - $\pi$  stacking and/or metal-metal interactions in the solid state. Furthermore, whereas the earlier investigations of phosphorescence have been extensively directed toward mononuclear Ir<sup>III</sup> complexes,<sup>[13–15]</sup> there have been few reports on the photophysical properties of dinuclear Ir<sup>III</sup> complexes.<sup>[16]</sup> Since the solid-state AIE derived from dinuclear complexes could also be useful for the development of color-tunable emitters for full-color and white-light display applications,<sup>[17]</sup> it would be intriguing to investigate the photophysical properties and AIE of dinuclear complexes. In this regard, we designed novel Ir<sup>III</sup>/Ir<sup>III</sup> homodinuclear and Ir<sup>III</sup>/Pt<sup>II</sup> heterodinuclear complexes that are linked by means of a bridging ligand comprising two  $\beta$ -diketonato binding sites. As noted in previous reports, a  $\beta$ -diketonato ligand such as dbm can act as an energy-converging unit through its low-energy <sup>3</sup>LX excited state in the mononuclear systems. By the same analogy, we chose 1,3-bis(3-phenyl-3-oxopropanoyl)benzene (H<sub>2</sub>L),<sup>[18,19]</sup> which possesses two  $\beta$ -diketonato binding sites connected by a 1,3-phenylene spacer as the bridging ligand.

In the present study, the synthesis and characterization of neutral Ir<sup>III</sup>/Ir<sup>III</sup> homodinuclear and Ir<sup>III</sup>/Pt<sup>II</sup> heterodinuclear complexes linked by a bis( $\beta$ -diketonato) bridging ligand (L) are described to investigate the electronic energy convergence from the metal centers to the bridging ligand in the molecular state, as well as the solid-state AIE.

#### **Results and Discussion**

#### Synthesis and Crystal Structure

The mononuclear platinum complex [Pt(ppy)(dbm)] (2) was obtained in good yield (68%) according to the analo-



Scheme 2. Reaction conditions: (i) 2-ethoxyethanol, Na<sub>2</sub>CO<sub>3</sub>, 25 °C, 24 h, 45%; (ii) 2-ethoxyethanol, Na<sub>2</sub>CO<sub>3</sub>, 130 °C, 24 h, 70%; (iii) 2-ethoxyethanol, Na<sub>2</sub>CO<sub>3</sub>, 25 °C, 24 h, 40%.

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gous method applied to the synthesis of 1. The synthesis of mono- and diiridium complexes of [Ir(ppyFF)<sub>2</sub>(HL)] (3) and  $[{Ir(ppyFF)_2}_2(\mu_2-L)]$  (4) was achieved through the reaction of the H<sub>2</sub>L ligand and a dimeric precursor,  $[{Ir(ppyFF)_2(\mu-Cl)}_2]$ , by varying the reaction temperature and the stoichiometry of the reactants according to the procedures outlined in Scheme 2. It is noteworthy that the reaction temperature plays an important role in the syntheses of 3 and 4. When  $[{Ir(ppyFF)_2(\mu-Cl)}_2]$  was treated with H<sub>2</sub>L (1–3 equiv.) at room temperature, monosubstituted  $\beta$ diketonato complex 3 was the sole product. In contrast, the same reaction at 130 °C gave disubstituted 4 as the major product. This result may indicate that 4 is a thermodynamic product of the reaction between  $[{Ir(ppyFF)_2(\mu-Cl)}_2]$  and H<sub>2</sub>L. Indeed, **3** was slowly changed to **4** upon heating of the solution. The reaction between 3 and the  $[{Pt(ppy)(\mu-$ Cl)<sub>2</sub> precursor at room temperature afforded an orange solid of heterodinuclear complex  $[{Ir(ppyFF)_2}(\mu_2 - \mu_2 - \mu_2)]$ L {Pt(ppy)}] (5) linked by an L bridge in 40% yield. All the complexes were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis. In particular, an X-ray diffraction study was performed on single crystals of 5.

The molecular structure of 5 and selected interatomic distances and angles are shown in Figure 1. The structure of 5 clearly shows the heterodinuclear connectivity between the Ir- and Pt-centered moieties by means of the L bridging ligand. The Ir-centered moiety adopts a A-configuration and bears two ppyFF ligands with a trans disposition of pyridine rings. In the Pt-centered moiety, the N3-Pt-C16 angle of 81.6(3)° and the O2-Pt-O1 angle of 91.42(18)° indicate a distorted square-planar geometry around the Pt center similar to that of the reported cyclometalated Pt complexes.<sup>[20]</sup> When compared to the dihedral angle between the phenyl rings in dbm of 1 (20.25°),<sup>[7]</sup> the dbm fragment at the Ir center of 5 forms a much larger angle of 53.97° probably due to the steric hindrance exerted by the adjacent ppy ligand of the Pt-centered moiety. In addition, the planes defined by O3-Ir-O4 and O1-Pt-O2 are linked to the central phenylene plane of the L bridging ligand by a relatively small dihedral angle of 18.74 and 10.68°, respectively, which indicates the presence of electronic conjugation between the planes. This feature may suggest that efficient electronic interactions can occur between the metal-centered moieties and the L bridging ligand through a  $\pi$ -orbital overlap.<sup>[21]</sup> It seems that Ir and Pt atoms do not interact with each other as judged by the large Ir...Pt separation of 9.926 Å.

#### **Photophysical Properties and Solid-State Emission**

The absorption spectra of the complexes were recorded in degassed solutions of chloroform at room temperature (Figure 2 and Table 1). The intense high-energy bands below the 300 nm region can be assigned to singlet spin-allowed  $\pi$ - $\pi$ \* ligand-centered (<sup>1</sup>LC) transitions of ppy and ppyFF ligands.<sup>[15,20,22]</sup> The broad bands in the region rang-



Figure 1. Molecular structure of **5** (50% thermal ellipsoid). Hydrogen atoms and solvent molecules (THF) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir–C41 1.992(7), Ir–C52 1.994(6), Ir–N1 2.043(5), Ir–N2 2.045(5), Ir–O4 2.120(5), Ir–O3 2.145(4), Pt–N3 1.911(8), Pt–C16 1.982(6), Pt–O2 2.034(5), Pt–O1 2.039(4); C41–Ir–N1 82.1(2), C52–Ir–N2 81.2(3), O4–Ir–O3 87.95(17), N3–Pt–C16 81.6(3), C16–Pt–O2 94.9(2), N3–Pt–O1 92.1(2), O2–Pt–O1 91.42(18).

ing from 350 to 400 nm are caused by  $\pi - \pi^*$  transitions  $(^{1}LX)$  on the  $\beta$ -diketonato bridging ligands (L and dbm).<sup>[19]</sup> Whereas the lower energy absorption in 400-500 nm is weak for 2, the Ir-centered species 1, 4, and 5 exhibit more intense bands with two shoulders in this region. The weak shoulder at 437 nm is assignable to the spin-allowed MLCT transition (<sup>1</sup>MLCT), and the other one at 465 nm, which tails to 500 nm, can be assigned to the spin-forbidden MLCT transition (<sup>3</sup>MLCT). These features of <sup>1</sup>MLCT and <sup>3</sup>MLCT transitions are very similar to those of the reported phosphorescent Ir complexes.<sup>[15,23]</sup> In particular, the absorption spectrum of 4 shows an identical absorption band with an intensity twice that of the spectrum of 1. Heterodinuclear 5 also exhibits an absorption feature corresponding to the sum of the independent spectra of 1 and 2. These results indicate that the electronic transition at each metalcentered moiety in 4 and 5 is not affected by the L bridging ligand.



Figure 2. Absorption spectra of 1, 2, 4, and 5 in CHCl<sub>3</sub> at room temperature. Inset: enlarged absorption spectra.

The room-temperature photoluminescence (PL) spectra of solutions of 1, 2, 4, and 5 in degassed chloroform are shown in Figure 3, and the photophysical data are summarized in Table 1. The selective excitation at a wavelength of

	Table	1.	Photophysical	data
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	Absorption <sup>[a]</sup>	Emission at 293 K <sup>[b]</sup>					Emission at 77 K <sup>[b]</sup>	
	$\lambda_{abs} [nm] (\epsilon [10^{-4} M^{-1} cm^{-1}])$		Solution	[a]	Solic	1		
		$\lambda_{\max}$ [nm]	τ [ns]	$\Phi_{\rm em}{}^{\rm [c]}$	$\lambda_{\max}$ [nm]	τ [ns]	$\lambda_{\max}$ [nm]	τ [μs]
1	254 (4.88), 290 (3.51), 330 (1.88), 388 (1.08), 437 (0.34), 465 (0.15)	611	23	$3.0 \times 10^{-2}$	605 <sup>[d]</sup>	n.d. <sup>[e]</sup>	555	1.3
2	261 (3.72), 280 (3.12), 314 (1.88), 365 (1.56)	540	180	$2.3 \times 10^{-1}$	548, 570	n.d.	495, 527, 555 (sh)	4.9
4	253 (10.0), 290 (6.75), 328 (4.07), 388 (2.17), 435 (0.76), 465 (0.31)	615	22	$3.0 \times 10^{-2}$	597	67	570	1.3
5	259 (8.58), 281 (6.81), 327 (3.83), 369 (2.72), 388 (2.43), 437 (0.58), 465 (0.21)	615	22	$2.3 \times 10^{-2}$	597	56	570	1.4

[a] In degassed CHCl<sub>3</sub>. [b]  $\lambda_{ex} = 388$  nm. [c] [Ir(ppy)<sub>3</sub>] ( $\Phi_{em} = 0.40$ ) was used as a standard. [d] For the orange-red crystals of 1. [e] Not determined.

388 nm provides the most feasible quantitative explanation of the electronic energy relaxation since the Ir- and Pt-centered moieties are estimated to absorb nearly an equal quantity of light at that wavelength, as judged from the similar absorption coefficients of mononuclear complexes 1 and 2 ( $\varepsilon_1 = 10804 \text{ m}^{-1} \text{ cm}^{-1}$ ;  $\varepsilon_2 = 11319 \text{ m}^{-1} \text{ cm}^{-1}$ ). As reported earlier, the very weak emission band at 611 nm in 1 could be assignable to the major contribution from the <sup>3</sup>LX state of the dbm ligand.<sup>[7,9]</sup> Moreover, although weak in intensity, the observation of the emission band of 1 ( $\Phi_{\rm em}$  = 0.03) with a relatively short emission lifetime ( $\tau = 23$  ns for 1) may further indicate the possible involvement of the <sup>3</sup>MLCT state, thus leading to the proper description of the lowest-energy excited state of 1 in solution as the mixed <sup>3</sup>MLCT-<sup>3</sup>LX state. The absence of a <sup>3</sup>MLCT band is likely due to the large  $\pi - \pi^*$  energy gap of the ppyFF ligand, which causes the LUMO to be located mostly at the dbm ligand, thus allowing the <sup>3</sup>LX state of the dbm ligand to dominate the lowest-lying excited state. Chou and Chi et al. very recently demonstrated that all higher-energy excited states of relevant heteroleptic Ir<sup>III</sup> complexes are strongly coupled with each other.<sup>[12]</sup> In contrast, 2 exhibits an intense emission band at 540 nm with high quantum efficiency ( $\Phi_{\rm em} = 0.23$ ), which indicates that the emission from an excited state of the Pt(ppy) moiety is not quenched despite the presence of the dbm moiety in 2 (vide infra). The emission spectrum of homodinuclear complex 4 exhibits a very weak emission band at 615 nm with low quantum efficiency ( $\Phi_{\rm em} = 0.03$ ) indicative of inefficient phosphorescence. This feature is in fact very similar to that observed in the mononuclear complex 1 ( $\lambda_{em}$  = 611 nm,  $\Phi_{em}$  = (0.03),<sup>[7]</sup> which suggests that the observed weak emission in 4 is dominated by the L-based triplet excited state  $({}^{3}LX)$ . Interestingly, heterodinuclear 5 also exhibits a weak emission band at 615 nm with low quantum efficiency ( $\Phi_{\rm em}$  = 0.023) as observed in 4. The characteristic emission band around 540 nm that appeared in the mononuclear Pt complex 2 is not observed in the emission spectrum of 5, pointing to the quenching of the Pt(ppy)-based emission. One order of magnitude decrease in quantum efficiency  $(\Phi_{\rm em} = 0.23 \text{ for } 2 \text{ vs. } 0.023 \text{ for } 5)$  and a much reduced emission lifetime of 5 relative to that of 2 ( $\tau = 180$  ns for 2 vs. 22 ns for 5) are in agreement with this observation. Furthermore, a comparison of the emission intensities for 1 and 5 at the same molar concentration reveals that the 615 nmband intensity of 5 is increased 1.5-fold. This result may suggest that the internal conversion of the  $T_n$  state, which is contributed mainly by the Pt(ppy) moiety, into an energy state of 615 nm, that is, the  $T_1$  state, dominated by the <sup>3</sup>LX state of the L bridging ligand, effectively takes place in 5.



Figure 3. Emission spectra of 1, 2, 4, and 5 in CHCl<sub>3</sub> ( $1.0 \times 10^{-5}$  M;  $\lambda_{ex} = 388$  nm) at room temperature.

To clarify the electronic energy convergence, low-temperature PL experiments were performed in chloroform rigid matrices at 77 K. The emission spectra of **2**, **4**, and **5** are displayed in Figure 4, and that of **1** is shown for comparison. The mononuclear Pt complex **2** shows a structured band at 495 nm with a long emission lifetime of 4.9 µs, thus confirming that the emission is originated from a mixed MLCT–<sup>3</sup>LC(ppy) excited state<sup>[20]</sup> (Figure 4a). In addition, the weak shoulder around 555 nm that was not observed in the room-temperature spectrum could be attributed to a dbm-based excited state (<sup>3</sup>LX) as similarly found in **1** ( $\lambda_{em}$ = 555 nm at 77 K).<sup>[7,9]</sup>

This result indicates that the lowest-energy excited state of **2** could be described as a mixed MLCT $^{3}LC(ppy)$ –  $^{3}LX(dbm)$  state presumably due to a small difference in energy between these states. In contrast, the emission band of the Pt(ppy) moiety in heterodinuclear **5** is completely quenched at 77 K, only giving rise to a 570 nm band. This feature is actually similar to that observed at room tempera-



Figure 4. Emission spectra ( $\lambda_{ex} = 388$  nm) of 1, 2, 4, and 5 in (a) a CHCl<sub>3</sub> rigid matrix at 77 K and (b) the solid state. The solid-state spectrum of 1 was taken from an orange polymorph reported in the literature.<sup>[10]</sup>

ture. Since the emission spectra of an equimolar mixture of 1 and 2 contain all of the emission bands derived from the Pt complex 2 (Figure S1 in the Supporting Information), this finding signifies the occurrence of an efficient  $T_n \rightarrow T_1$  internal conversion from the Pt(ppy) moiety to the L bridging ligand in 5. Moreover, the shapes of emission bands and the maximum emission wavelength of the dinuclear complexes 4 and 5 are virtually identical, and the maximum peak positions are also redshifted by 15 nm in comparison with mononuclear 1. This feature further indicates that the lowest-excited state of 4 and 5 is mainly involved with the

<sup>3</sup>LX state of the L bridging ligand, the energy level of which would be lower than that of dbm probably owing to a longer conjugation length. Consequently, as depicted in the schematic energy-level diagram of **5** (Figure 5), all these results together with the electrochemical data (vide infra) may suggest that in the given molecular dinuclear Ir<sup>III</sup> systems linked by the bis( $\beta$ -diketonato) L bridging ligand, energy convergence effectively takes place from the T<sub>n</sub> states contributed by metal-centered moieties to the T<sub>1</sub> state dominated by the L bridging ligand, which thus plays the role of an energy "collector" or a "converging unit".



Figure 5. Schematic energy-level diagram and proposed emission processes of 5 in solution. IC: internal conversion; ISC: intersystem crossing; VR: vibrational relaxation.



Figure 6. Crystal-packing structures of 5. (a) Overall packing structure. (b)  $\pi - \pi$  interaction between Ir-centered moieties. (c) Extended  $\pi - \pi$  stacking structure between Pt-centered moieties. (d) Top views showing two kinds of  $\pi - \pi$  interaction between Pt-centered moieties: left, Pt(A)L···Pt(B)L interactions; right, Pt(B)(ppy)···Pt(C)(ppy) interactions.

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Unlike the very weak luminescence of 4 and 5 in solution, the intense orange-red emission (i.e., AIE) centered at 597 nm is observed in the solid state (Figure 4b and Figure S2 in the Supporting Information). This feature is in accord with those observed in solid-state iridium complexes such as [Ir(ppy)<sub>2</sub>(dbm)]<sup>[9]</sup> and 1.<sup>[7]</sup> To elucidate the origin of the AIE, the crystal-packing structures of heterodinuclear 5 were examined. The packing structures illustrated in Figure 6 clearly show that each metal-centered moiety forms  $\pi$ - $\pi$  interactions in the crystal (Figure 6a). One is the effective overlap between the ppyFF ligands of the Ir-centered moieties in adjacent molecules (Figure 6b), and the other is  $\pi - \pi$ stacking of the Pt-centered moieties (Figure 6c). In the Ircentered moieties, the interplanar separation between the adjacent pyridine rings of ppyFF ligands is estimated to be approximately 3.40 Å, comparable to those observed in mononuclear [Ir(ppy)<sub>2</sub>(dbm)]  $(3.37 \text{ Å})^{[9]}$  and 1  $(3.40 \text{ Å})^{[7]}$ which reflects the presence of sufficiently strong  $\pi$ - $\pi$  interactions. The Pt-centered moieties, on the other hand, pack as an extended  $\pi$ - $\pi$  stacking structure consisting of two kinds of alternating  $\pi$ - $\pi$  interactions, that is, Pt(A)L... Pt(B)L and Pt(B)(ppy)···Pt(C)(ppy) interactions (Figure 6c and d). This feature is quite different from the isolated ppyFF...ppyFF interactions observed in the Ir-centered moieties. Along with the apparent incorporation of Pt centers into the stacking structures, this could be ascribed to the planar geometry of the Pt moiety. Whereas a direct Pt...Pt interaction appears absent as judged by the long separations [6.575 Å in Pt(A)L···Pt(B)L and 4.299 Å in Pt(B)-(ppy)···Pt(C)(ppy)], the short interplanar separations of approximately 3.36 and 3.42 Å, respectively, indicate the presence of strong  $\pi$ - $\pi$  interactions between the Pt-centered moieties.<sup>[20]</sup> Therefore, it can be suggested that in the solid state of 5, the strong  $\pi - \pi$  interactions between the adjacent ppyFF ligands induce the ppyFF-centered triplet excited state, that is, the  ${}^{3}M(LL)CT$  state, which is lower in energy than <sup>3</sup>LX of the L bridging ligand. As a result, the <sup>3</sup>M(LL)CT state dominates the lowest-energy excited state leading to the intense emission. Furthermore, the essentially identical emission features observed for both 4 and 5 in terms of emission wavelength ( $\lambda_{em} = 597 \text{ nm}$ ) and lifetime  $(\tau = 67 \text{ ns for 4 and 56 ns for 5})$  imply the quenching of the Pt(ppy)-based emission in the solid state of 5 (Figure 4b). We attribute this to the extended  $\pi$ - $\pi$  stacking structure comprised of alternating Pt(A)L···Pt(B)L and Pt(B)-(ppy)...Pt(C)(ppy) interactions. Although the Pt(B)(ppy)... Pt(C)(ppy) interactions may lead to an emissive <sup>3</sup>M(LL)CT excited state, the energy of such a state appears to be efficiently converged into the weakly emissive triplet state (<sup>3</sup>LLX) formed by adjacent Pt(A)L···Pt(B)L interactions.

#### **Electrochemical Properties**

The electrochemical properties of the complexes were examined by cyclic voltammetry (Table 2 and Figure 7). The mononuclear Ir complex 1 shows reversible oxidation at 0.73 V, whereas Pt complex 2 exhibits an irreversible oxi-

dation feature with an onset potential of 0.48 V. In the case of heterodinuclear **5**, two successive oxidations are observed. Whereas the irreversible first oxidation ascribable to the Pt-centered moiety in **5** occurs at a potential identical to that of **2**, the reversible second oxidation potential of the Ir-centered moiety (0.78 V) is slightly higher than that of **1**. This result indicates a stabilization of the filled d orbitals of the Ir center in **5** due to the electron-withdrawing effect caused by the first oxidation of the linked Pt moiety as similarly found in an Ru<sup>II</sup>/Os<sup>II</sup> system.<sup>[24]</sup> In contrast, **4** undergoes a single two-electron reversible oxidation process consistent with identical environments of both Ir-centered moieties and thereby simultaneous oxidation. Hence, the increase of the Ir-centered oxidation potential in **4** (0.76 V) relative to the potential of **1** is less apparent than that in **5**.

Table 2. Electrochemical data.[a]

Complexes	Oxid $E_{ m ox}^{2 m nd}$ [V] (Ir <sup>III</sup> /Ir <sup>IV</sup> )	ation $E_{ m ox}^{ m 1st}$ [V] (Pt <sup>II</sup> /Pt <sup>III</sup> )	$E_{\rm red}^{\rm 1st}$ [V]	Reduction $E_{\rm red}^{2nd}$ [V]	$E_{\rm red}^{\rm 3rd}$ [V]
1	0.73	_	-2.16	-2.77 <sup>[b]</sup>	_
2	_	0.48 <sup>[b]</sup>	-2.00	-2.58	_
4	0.76 <sup>[c]</sup>	_	-2.06	-2.27	-2.68 <sup>[b]</sup>
5	0.78	0.48 <sup>[b]</sup>	-1.94	-2.23	$-2.64^{[b]}$

[a] Conditions:  $10^{-3}$  M in CH<sub>3</sub>CN, 0.1 M [ $nBu_4$ N][PF<sub>6</sub>], scan rate 50 mV s<sup>-1</sup>, redox potential reported versus  $E_{\frac{1}{2}}$ (ferrocene/ferrocenium). [b] Irreversible redox. [c] Single two-electron wave.



Figure 7. Cyclic voltammograms of 1, 2, 4, and 5 showing (a) oxidation and (b) reduction.

However, mononuclear 1 undergoes a two-step reduction process with first and second reduction potentials of -2.16and -2.77 V, respectively. Since the second reduction potential falls in the typical range observed for Ir–ppy derivatives<sup>[13]</sup> and it is known that the LUMO of the [Ir(ppy)<sub>2</sub>-(dbm)] complex is distributed mainly on the dbm ligand,<sup>[9]</sup> the first and second reductions of 1 can be assigned to the dbm and ppyFF ligand-based reduction. In the case of 2, two-step reduction processes take place at a less negative potential (–2.00 and –2.58 V) than those observed for 1, but the reduction features are quite similar to those of 1.

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Scheme 3. First and second reduction processes in 4 and 5.

Moreover,  $[(ppy)Pt(O^{\cap}O)]^{[20]}(O^{\cap}OH)$  = acetylacetone, dipivaloylmethane) and  $[Pt(ppy)_2]^{[25]}$  complexes are reported to have a ppy ligand-based reduction at around -2.4 to -2.5 V. Although the second reduction potential of 2 is slightly more negative than the reported values, presumably due to the already reduced state of 2, these results indicate that the first and second reductions of 2 are the dbm and ppy ligand-based reductions, respectively. The dinuclear complexes 4 and 5 undergo a three-step reduction process with a comparable reduction potential at each reduction step. The first and third reductions could be assignable to the reduction at the dbm moiety in the L bridging ligand and at the ppyFF or ppy ligand in the metal-centered moieties, respectively. The second reduction, which exhibits a reversible feature, has its potential close to the first reduction potentials of 1 and 2, which suggests that the second reduction also occurs at the dbm moiety in the L bridging ligand. Furthermore, the first reduction potentials of 4 and 5 show an anodic shift, to a similar extent, with respect to those of 1 and 2, respectively, implying that the LUMO localized on the dbm moiety of the L bridging ligand has a lower energy than that of the monomeric dbm complexes. This feature is in accord with the extended conjugation in the L bridging ligand. In addition to the anodic shift of the first reduction potential of 5 (-1.94 V) with respect to that of 4 (-2.06 V), as similarly shown in 1 and 2, these findings indicate that the initial two reduction processes in 4 and 5 involve the first reduction at the dbm moiety of the L bridging ligand linked to the Ir and Pt centers, respectively, and is followed by the second reduction at the dbm moiety linked to the remaining Ir centers in the first reduced state of 4 and 5 (Scheme 3). These reduction behaviors are also in good agreement with the fact that the L bridging ligand dominates the lowest-energy excited state of 4 and 5 in solution.

## Conclusion

Novel  $Ir^{III}/Ir^{III}$  homodinuclear and  $Ir^{III}/Pt^{II}$  heterodinuclear complexes linked by a bis( $\beta$ -diketonato) bridging ligand (L) were synthesized and characterized. According to the photophysical results in solution, it was found that the

lowest-energy excited state of dinuclear complexes receives its major contribution from the <sup>3</sup>LX state of the L bridging ligand, and hence the absorbed energy was efficiently converged into the energy acceptor, the L bridging ligand between Ir<sup>III</sup>/Ir<sup>III</sup>- and Ir<sup>III</sup>/Pt<sup>II</sup>-based luminophores. In contrast to the weak luminescence in solution, intense emission (i.e., aggregation-induced emission) was produced in the solid state. It is suggested from the crystal-packing structures that strong  $\pi$ - $\pi$  intermolecular interactions between adjacent pyridine rings of ppyFF ligands in the Ir-centered moieties are responsible for the emissive <sup>3</sup>M(LL)CT state of the solid-state dinuclear systems. The electrochemical properties of 4 and 5 further indicate that the first two reductions occur at the dbm moieties of the L bridging ligand linked to each metal center, which supports evidence that the L bridging ligand dominates the lowest excited state of 4 and 5 in solution.

### **Experimental Section**

General: All manipulations were performed under nitrogen by using standard Schlenk and glove-box techniques. Anhydrousgrade solvents (Aldrich) were purified by passing them through an activated alumina (Acros, 50-200 micron) column. All reagents were used without any further purification after being purchased from Aldrich (dimethyl isophthalate, acetophenone, 2-phenylpyridine, 2-bromopyridine, 2,4-difluorophenylboronic acid, dibenzoylmethane, 2-ethoxyethanol), Fluka (anhydrous Na<sub>2</sub>CO<sub>3</sub>), and Strem [iridium(III) chloride hydrate, potassium tetrachloroplatinate]. The compounds 2-(2,4-difluorophenyl)pyridine,<sup>[13]</sup> 1,3bis(3-oxo-3-phenylpropanoyl)benzene (H<sub>2</sub>L),<sup>[19]</sup> [{Ir(ppyFF)<sub>2</sub>(µ- $Cl)_{2}^{[13]} [{Pt(ppy)(\mu-Cl)}_{2}^{[20]} and [Ir(ppyFF)_{2}(dbm)] (1)^{[7]} were$ prepared according to modified literature procedures. Deuterated solvents (Cambridge Isotope Laboratories) were dried with activated molecular sieves (5 Å). <sup>1</sup>H and <sup>13</sup>C NMR spectra of the compounds were recorded with a Bruker Spectrospin 400 spectrometer at ambient temperature. All chemical shifts are reported in  $\delta$  with reference to the residual peaks of CDCl<sub>3</sub> for proton ( $\delta$  =7.24 ppm) and carbon ( $\delta$  =77.0 ppm) chemical shifts. Elemental analyses (EA) were carried out with an EA1110-FISONS (CE Instruments) instrument by the Environmental Analysis Laboratory at KAIST. MALDI-TOF MS were measured with a Voyager DE-STR 4700 proteomics analyzer at the Korea Basic Science Center (KBSC).



UV/Vis and PL spectra were obtained with a Jasco V-530 spectrophotometer and a Spex Fluorog-3 luminescence spectrometer, respectively. Solution PL experiments were performed by using HPLC-grade chloroform. All solutions in chloroform were degassed by several freeze-pump-thaw cycles using a diffusion pump. The emission quantum yields of the complexes were calculated by using degassed *fac*-[Ir(ppy)<sub>3</sub>] in toluene ( $\Phi = 0.40$ ) as a reference. Low-temperature measurements were recorded in 5 mm diameter quartz tubes that were placed in a quartz-walled Dewar flask filled with liquid nitrogen (77 K). Emission lifetimes were determined by using a third-harmonic generator of an Nd:YAG laser (Spectra-Physics LAB170, 10 Hz). A laser beam collected through a fused silica window was applied to excite the sample, and the delay time (310 µs) between the flash lamp and Q-switch was used to reduce the laser output power. The final power of the laser beam to the pump samples was about 100 µJ pulse<sup>-1</sup>. A monochromator (Dongwoo Optron, DM150i) and a general photomultiplier tube (PMT; Hamamatsu, R928) were employed to select the wavelength of the emission and to detect the strength of the emission. The signals from the PMT were spread on an oscilloscope (Lecroy waverunner 104Xi, 1 GHz bandwidth) and recorded. Cyclic voltammetry was performed by using an AUTOLAB/PGSTAT12 model system with a three-electrode cell configuration consisting of platinum working and counter electrodes and an Ag/AgNO<sub>3</sub> (0.1 M in acetonitrile) reference electrode at room temperature. Anhydrous acetonitrile was used as the solvent, and 0.1 M tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. The redox potentials were recorded at a 50 mV s<sup>-1</sup> scan rate and reported against the ferrocene/ferrocenium ( $Cp_2Fe/Cp_2Fe^+$ ; Cp = cyclopentadienyl) redox couple that was used as an internal standard.

**Synthesis of [Pt(ppy)(dbm)] (2):**  $[{Pt(ppy)(\mu-Cl)}_2]$  (0.45 g, 0.58 mmol), dibenzoylmethane (0.39 g, 1.74 mmol), and Na<sub>2</sub>CO<sub>3</sub> (0.62 g, 5.8 mmol) were mixed in 2-ethoxyethanol (30 mL) at room temperature. The mixture was stirred and heated at reflux overnight. After cooling to room temperature, water (30 mL) was added, and the mixture was then filtered to give a dark crude product, which was washed with water (30 mL) and diethyl ether (30 mL). The pure complex was obtained by flash chromatography on a silica column by using dichloromethane as the eluent to yield 2 (0.45 g) as a yellow solid in 68% yield. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.11 (d,  $J_{H,H}$  = 5.7 Hz, 1 H), 8.02–8.08 (m, 4 H), 7.75– 7.82 (m, 2 H), 7.63 (d,  $J_{\rm H,H}$  = 8.0 Hz, 1 H), 7.53–7.56 (m, 2 H), 7.45–7.50 (m, 5 H), 7.25 (td,  $J_{\rm H,H}$  = 7.3, 0.9 Hz, 1 H), 7.10–7.16 (m, 2 H), 6.75 (s, 1 H) ppm. <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>):  $\delta$  = 179.92, 178.94, 168.49, 147.28, 144.77, 140.27, 139.30, 138.88, 138.24, 130.90, 130.87, 130.74, 129.36, 128.63, 128.57, 127.11, 126.98, 123.74, 123.08, 121.35, 118.47, 97.55 ppm. MALDI-TOF MS:  $m/z = 571.80 \text{ [M^+]}$ . C<sub>26</sub>H<sub>19</sub>NO<sub>2</sub>Pt (572.51): calcd. C 54.55, H 3.35, N 2.45; found C 54.49, H 3.19, N 2.44.

**Synthesis of [Ir(ppyFF)<sub>2</sub>(HL)] (3):** [{Ir(ppyFF)<sub>2</sub>(µ-Cl)}<sub>2</sub>] (1.22 g, 1.0 mmol), H<sub>2</sub>L (1.11 g, 3.0 mmol), and Na<sub>2</sub>CO<sub>3</sub> (1.06 g, 10 mmol) were mixed in 2-ethoxyethanol (30 mL) and stirred at room temperature for 24 h. Addition of water (30 mL) followed by filtration and flash column chromatography (eluent; ethyl acetate/hexane, 1:4) yielded **3** as an orange solid (0.85 g, 45%). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 16.83 (br., 1 H), 8.51 (d, *J*<sub>H,H</sub> = 6.2 Hz, 2 H), 8.3 (t, *J*<sub>H,H</sub> = 1.7 Hz, 1 H), 8.26 (d, *J*<sub>H,H</sub> = 8.3 Hz, 2 H), 8.07 (d, *J*<sub>H,H</sub> = 8.1 Hz, 1 H), 7.90–7.93 (m, 3 H), 7.75–7.81 (m, 4 H), 7.4–7.60 (m, 5 H), 7.33 (t, *J*<sub>H,H</sub> = 7.2 Hz, 2 H), 7.08–7.13 (m, 2 H), 6.73 (s, 1 H), 6.63 (s, 1 H), 6.35–6.43 (m, 2 H), 5.75–5.80 (m, 2 H) ppm. <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>):  $\delta$  = 186.07, 185.58, 185.34, 184.79, 180.01, 177.93, 165.19, 164.29, 162.47, 160.90, 159.05, 151.37, 151.16, 147.99, 141.17, 140.48, 138.28, 137.90, 135.76,

135.23, 130.81, 129.15, 128.76, 128.37, 127.28, 126.97, 126.71, 126.27, 125.40, 122.82, 122.56, 122.35, 121.88, 121.68, 115.39, 115.21, 97.61, 97.27, 96.91, 95.14, 93.13 ppm. MALDI-TOF MS: m/z = 941.99 [M<sup>+</sup>]. C<sub>46</sub>H<sub>29</sub>F<sub>4</sub>IrN<sub>2</sub>O<sub>4</sub> (941.94): calcd. C 58.65, H 3.10, N 2.97; found C 59.49, H 3.09, N 2.91.

Synthesis of  $[{Ir(ppyFF)_2}_2(\mu_2-L)]$  (4):  $[{Ir(ppyFF)_2(\mu-Cl)}_2]$  (0.61 g, 0.5 mmol), H<sub>2</sub>L (0.19 g, 0.5 mmol), and Na<sub>2</sub>CO<sub>3</sub> (0.53 g, 5.0 mmol) were mixed in 2-ethoxyethanol (30 mL), and the mixture was heated at 130 °C for 24 h. Workup followed by flash column chromatography (eluent: dichloromethane) yielded 4 as an orange solid (0.53 g, 70%). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ = 8.46–8.51 (m, 4 H), 8.23 (t,  $J_{H,H}$  = 6.8 Hz, 4 H), 8.15 (d,  $J_{H,H}$  = 19 Hz, 1 H), 7.81–7.86 (m, 2 H), 7.67–7.74 (m, 8 H), 7.44 (t,  $J_{H,H}$  = 7.0 Hz, 2 H), 7.30–7.35 (t,  $J_{H,H}$  = 7.7 Hz, 4 H), 7.26 (dd,  $J_{H,H}$  = 10.1, 1.8 Hz, 1 H), 7.07 (t,  $J_{H,H}$  = 6.2 Hz, 2 H), 7.00–7.04 (m, 2 H), 6.51 (s, 2 H), 6.32-6.42 (m, 4 H), 5.70-5.79 (m, 4 H) ppm. <sup>13</sup>C NMR  $(100.62 \text{ MHz}, \text{CDCl}_3): \delta = 179.50, 178.77, 178.67, 165.28, 164.66,$ 164.35, 164.19, 162.55, 160.98, 160.80, 159.11, 158.94, 151.59, 151.19, 147.89, 141.06, 140.50, 138.26, 137.85, 130.61, 129.15, 128.75, 128.51, 128.33, 127.15, 126.93, 126.38, 122.51, 121.64, 121.00, 115.31, 115.09, 97.62, 97.27, 96.90, 95.13 ppm. MALDI-TOF MS:  $m/z = 1514.15 \text{ [M^+]}$ . C<sub>68</sub>H<sub>40</sub>F<sub>8</sub>Ir<sub>2</sub>N<sub>4</sub>O<sub>4</sub> (1513.49): calcd. C 53.96, H 2.66, N 3.70; found C 53.57, H 2.57, N 3.73.

Synthesis of  $[{Ir(ppyFF)_2}(\mu_2-L){Pt(ppy)}]$  (5): Compound 3 (0.43 g, 0.46 mmol), [{Pt(ppy)(µ-Cl)}<sub>2</sub>] (0.18 g, 0.23 mmol), and Na<sub>2</sub>CO<sub>3</sub> (0.49 g, 4.6 mmol) were mixed in 2-ethoxyethanol (30 mL) and stirred at room temperature for 24 h. Workup followed by flash column chromatography (eluent: ethyl acetate/hexane, 1:4) yielded 5 as an orange solid (0.23 g, 40%). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.07 (d,  $J_{H,H}$  = 5.6 Hz, 0.5 H), 9.02 (d,  $J_{H,H}$  = 5.5 Hz, 0.5 H), 8.53–8.59 (m, 2.5 H), 8.43 (s, 0.5 H), 8.26 (d,  $J_{H,H}$  = 8.4 Hz, 2 H), 8.09–8.11 (m, 1 H), 7.96–8.00 (m, 3 H), 7.86 (d,  $J_{H,H}$  = 7.6 Hz, 1 H), 7.81 (d, J<sub>H,H</sub> = 7.6 Hz, 1 H), 7.72–7.76 (m, 4 H), 7.56 (t,  $J_{H,H}$  = 7.7 Hz, 2 H), 7.40–7.48 (m, 5 H), 7.32 (t,  $J_{H,H}$  = 7.6 Hz, 2 H), 7.24 (t, J = 7.5 Hz, 0.5 H), 7.07–7.12 (m, 4 H), 6.90 (t,  $J_{H,H}$ = 7.5 Hz, 0.5 H), 6.76 (s, 0.5 H), 6.67 (t,  $J_{H,H}$  = 7.4 Hz, 1.5 H), 6.36-6.43 (m, 2 H), 5.78-5.83 (m, 2 H) ppm. <sup>13</sup>C NMR  $(100.62 \text{ MHz}, \text{CDCl}_3)$ :  $\delta = 180.06, 179.63, 179.01, 178.58, 177.92,$ 168.35, 165.24, 163.85, 162.05, 161.31, 159.47, 151.46, 151.25, 148.03, 147.21, 147.00, 144.77, 141.06, 140.62, 140.41, 140.04, 139.19, 138.78, 138.22, 138.05, 131.00, 130.84, 130.67, 130.57, 129.43, 128.96, 128.75, 128.62, 128.46, 127.03, 126.89, 125.10, 123.66, 123.12, 122.67, 122.48, 121.79, 121.36, 118.45, 115.32, 115.15, 97.52, 97.20, 97.02, 95.19, 95.07 ppm. MALDI-TOF MS:  $m/z = 1289.78 \text{ [M^+]}$ . C<sub>57</sub>H<sub>36</sub>F<sub>4</sub>IrN<sub>3</sub>O<sub>4</sub>Pt (1290.20): calcd. C 53.06, H 2.81, N 3.26; found C 53.86, H 2.73, N 3.28.

X-ray Crystallography: Single crystals of 5 suitable for X-ray diffraction studies were obtained by slow cooling of solutions of 5 in THF/hexane. Crystals were coated with Paratone oil, and diffraction data were measured at 100 K with synchrotron radiation ( $\lambda$  = 0.74999 Å) by a 4AMXW ADSC Quantum-210 detector equipped with a silicon double-crystal monochromator at the Pohang Accelerator Laboratory in Korea. The reflection data were collected as  $\pi$ -scan frames with a width of 1° per frame and an exposure time of 1 s per frame. HKL2000 (version 0.98.698)<sup>[26]</sup> was used for data collection, cell refinement, reduction, and absorption correction. The structure was solved by direct methods and refined by fullmatrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters.

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**Crystal Data for 5·(thf)<sub>3</sub>:**  $C_{69}H_{60}F_4IrN_3O_7Pt$ ,  $M_r = 1506.49$ ,  $\lambda = 0.74999$  Å (synchrotron radiation), triclinic, PI, a = 10.599(2) Å, b = 13.534(3) Å, c = 21.654(4) Å,  $a = 72.87(3)^\circ$ ,  $\beta = 78.33(3)^\circ$ ,  $\gamma = 79.76(3)^\circ$ , V = 2883.8(10) Å<sup>3</sup>, Z = 2,  $\rho_{calcd.} = 1.735$  gcm<sup>-3</sup>,  $\mu = 4.801$  mm<sup>-1</sup>, F(000) = 1484, T = 100 K, measured reflections = 12793 in h(0/14), k(-17/18), l(-27/29), unique reflections = 12793,  $R_{int} = 0.000$ , refined parameters = 766,  $R_1 = 0.0626$ ,  $wR_2 = 0.1829$   $[I > 2\sigma(I)]$  and GOF on  $F^2 = 1.008$ ,  $\rho_{final}$  (max./min.) = 2.150/-4.541 e Å<sup>-3</sup>.

CCDC-756977 (5) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Supporting Information (see footnote on the first page of this article): Emission spectrum of a mixture of 1 and 2 in solution and MALDI-TOF MS spectra of complexes.

## Acknowledgments

We gratefully acknowledge the Korea Research Foundation (no. KRF-2008-313-C00454 for Y. D.) and the Priority Research Centers Program of the National Research Foundation of Korea (no. 2009-0093818 for M. H. L.) for financial support and the Pohang Accelerator Laboratory (PAL) for beam-line use (grant 2008-2041-05).

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Received: March 10, 2010 Published Online: July 1, 2010