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Potential Solution Processible Phosphorescent Iridium Complexes toward Applications in Doped Light-Emitting Diodes: Rapid Syntheses and Optical and Morphological Characterizations

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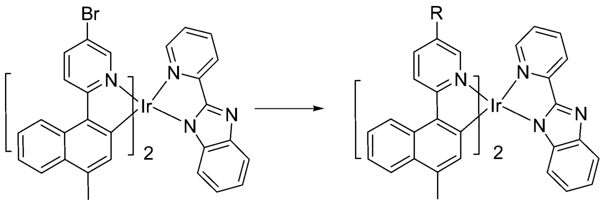

A series of carbazol-9-yl end-capped red-emitting heteroleptic iridium complexes was readily synthesized using post Suzuki coupling. The appealing solubility, photoluminescent characteristics, and morphological stability enabled the current heteroleptic iridium complexes to be highly desirable phosphorescent dopant emitters in doped light-emitting diodes for the purpose of resisting molecular aggregations in the doped emitting layers.

Electrophosphorescent molecular and polymeric materials containing platinum group metal centers are attractive active emitters in high efficiency light-emitting diodes (LEDs) due to their propensity to harvest both singlet and triplet excited states leading to a potential internal device efficiency of unity.[1,2] As triplet emitters, recent studies showed that cyclometalated organometallic iridium complexes appear of particular interest, among others.[2] They exhibit appealing characteristics such as highly emissive[3] MLCT excited states at room temperature in the doped/neat solid films and facilely tunable emission color in the visible. They are made into electroluminescent devices either via vacuum thermal deposition or solution processing techniques. At present, it is generally believed that the latter methods are more advantageous for the purposes of low cost processing and large area display.

Based on solution processing, phosphorescent iridium complexes are usually doped into semiconducting polymeric hosts. More recently, there emerged a class of electrophosphorescent dendrimers. Due to their solution-processibility, they act as host emitters or can be doped into a bipolar molecular host of CBP [4,4′-bis(*N*-carbazolyl)biphenyl].[3,4] Very high external device efficiencies have been realized in these cases.[3−5] A potential problem associated with doped LEDs is molecular crystallizations/aggregations and thus phase segregations in the doped emitting layers. With the promise of easy materials processing and high device efficiencies of doped light-emitting diodes, phosphorescent molecular/dendritic iridium complexes endowed with high solubility and amorphous morphological stability resisting the occurrence of crystallizations/aggregations would be extremely desirable as dopant emitters for solution-processed doped LEDs in terms of film homogeneity and long-term device stability.[6]

Generally, syntheses of molecular electroluminescent iridium complexes involved a chloro-bridged dimeric precursor, followed by substitution of a third ligand.[7] In the preparation of a simple green-emitting iridium complex [2-(4-*tert*-butylphenyl)pyridine]$_2$Ir(acac), we found that it appears hard to separate this heteroleptic complex from the residual dimeric presursor due to their very close polarity as a result of introduction of the solubilizing *tert*-butyl groups (acac = acetylacetonate, a coligand generally used in heterolepic iridium complexes). In the present work, we present an efficient synthesis of a new series of solution-processible red-emitting heteroleptic cyclometalated iridium(III) complexes **4a** and **4b** (Scheme 1) using the post-Suzuki coupling route.[8] Very recently, this approach has been used to prepare conjugated electrophosphorescent iridium polymers.[9,10] To effect rapid synthesis and easy separation of the highly soluble coupling products, we introduced 2-(2-pyridyl)benzimidazole as a polar coligand. The 9,9-dioctylfluorenyl groups are key to improving the solubility and thus solution processibility,[11] and the hole-transporting carbazoyl groups are key to driving the emission into the red region and increasing the morphological stability.[12] In addition, functional

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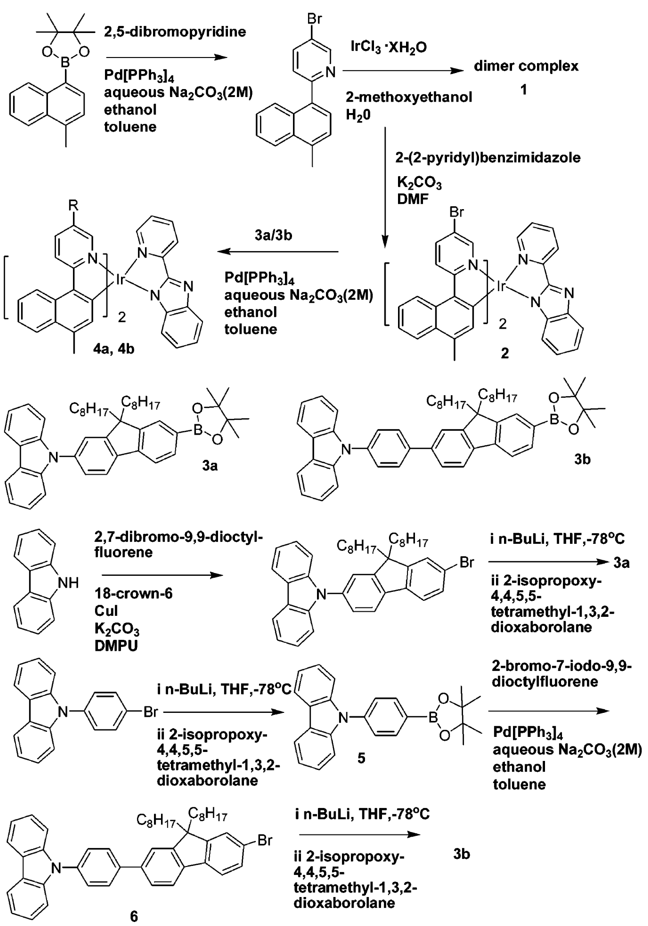
SCHEME 1. Synthetic Routes to Soluble Red-Emitting Complexes 4a and 4b



conjugated carbazole derivatives are excellent hosts for phosphorescent dopants.[13] The optical, thermal, and morphological studies showed that **4a** and **4b** are potentially highly valuable solution-processed triplet emitters for doped light-emitting diodes.

The target iridium complexes **4a** and **4b** were readily synthesized by the post-Suzuki coupling route, involving a key intermediate bis[5-bromo-2-(1-methylnaphthalen-4-yl)pyridine]-Ir[2-(2-pyridyl)benzimidazolate] **2**. Due to the differential reactivity of 2,5-dibromopyridine in the palladium-catalyzed cross-coupling reactions,[14] 5-bromo-2-(1-methylnaphthalen-4-yl)pyridine could be isolated as a white solid via Suzuki coupling using Pd(PPh$_3$)$_4$ as the catalyst and aqueous Na$_2$CO$_3$ as the base. Reflux of a mixture of the above-obtained bromide and IrCl$_3$·xH$_2$O in 3:1 (v/v) 2-methoxyethanol and H$_2$O yielded the chloro-bridged dimeric iridium complex **1**.[7] Treatment of **1** with 2-(2-pyridyl)benzimidazole using K$_2$CO$_3$ as the base in DMF afforded **2** in 72% yield without chromatography. TLC and ^{1}H NMR showed absence of the iridium dimer. Due to the marked molecular polarity upon coordination of 2-(2-pyridyl)benzimidazole, **2** could be easily separated from unreacted dimer **1** if present.

Under Ullmann reaction conditions, 9-(4-bromophenyl)-9*H*-carbazole and 9-(2-bromo-9,9-dioctylfluoren-7-yl)-9*H*-carbazole were efficiently prepared by monoamination of 1,4-dibromobenzene and 2,7-dibromo-9,9-dioctylfluorene with 9*H*-carbazole, respectively.[15] Successive treatment of the above two bromides with *n*-butyllithium and 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave the corresponding boronic esters 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole **5** and 9-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluoren-2-yl)-9*H*-carbazole **3a**. Unexpectedly, when **5** was reacted with 2,7-dibromo-9,9-dioctylfluorene in a 1:1 molar ratio under conventional Suzuki reaction conditions, the totally debrominated product 9-(4-(9,9-dioctylfluoren-7-yl)phenyl)-9*H*-carbazole was separated as the major species, instead of the monobromide product 9-(4-(2-bromo-9,9-dioctylfluoren-7-yl)-phenyl)-9*H*-carbazole **6**. Alternatively, with an excess of 2-bromo-7-iodo-9,9-dioctylfluorene[16] under similar reaction conditions, **6** was successfully isolated, emphasizing the importance of iodides in highly selective palladium-catalyzed carbon−carbon coupling reactions. Consequently, **3b** was obtained analogously to **3a**.

The boronic esters **3a** and **3b** thus obtained were reacted with the dibromide precursor **2** under conventional Suzuki coupling conditions, respectively. Target iridium complexes **4a** and **4b** were isolated by column chromatography using 1:40 (v/v) ethyl acetate/dichloromethane as the eluent and are highly soluble in common solvents such as dichloromethane, chloroform, chlorobenzene and *o*-dichlorobenzene at room temperature. The high purity of the prepared samples was confirmed by ^{1}H NMR, elemental analysis, and mass spectroscopy.

The ^{1}H NMR spectrum of the dimeric iridium intermediate **1** showed the two methyl groups on the naphthalenyls as one single signal at 2.24 ppm. Upon substitution by 2-(2-pyridyl)-benzimidazolate, the singlet was split into two peaks with an equal intensity in bis[5-bromo-2-(1-methylnaphthalen-4-yl)-pyridine]Ir[2-(2-pyridyl)benzimidazolate] **2** at 2.44 and 2.43 ppm, respectively, and thus in **4a** (2.48 and 2.47 ppm) and **4b** (2.47 and 2.46 ppm). We reason that the presence of the two signals could be attributed to the nonequivalent conjugated cyclometalated ligands induced by the asymmetric co-ligand.[17] This makes the spectra and detailed interpretation complicated.

The ESI MS of **4a** showed a molecular weight of 1932 (100), corresponding to MH$^+$ (calcd for C$_{126}$H$_{127}$IrN$_7$, 1930.98). The molecular weight of **4b** was determined by MALDI-TOF mass spectrometry using dithranol as the matrix (dithranol MW = 226). It showed a series of major peaks at 1886.8 (100) [M − 2-(2-pyridyl)benzimidazolate]$^+$ (calcd 1887.96); 2081.6 (100) [MH$^+$] (calcd 2083.04); 2305.4 (100) [MH$^+$ + dithranol] (calcd 2309.1) and 2529.1 (100) [MH$^+$ + 2-dithranol] (calcd 2535.16). The fragment peak at *m*/*z* 1886.8 resulted from the thermal process in the mass measurement.

The solution and solid UV−vis and PL spectra of **4a** and **4b** are shown in Figure 1. The absorption and emission maxima

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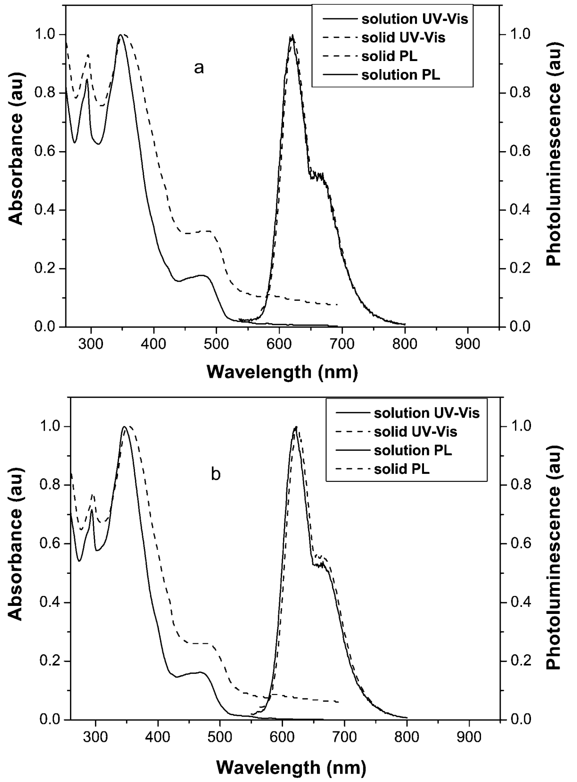

FIGURE 1. UV−vis absorption and photoluminescence spectra of **4a** (a) and **4b** (b) in CH_2Cl_2 solutions and in the films on quartz.

TABLE 1. UV−vis and PL Spectral Data

	UV−vis (λ^{abs}_{max}, nm)		PL (λ^{em}_{max}, nm)	
	solution	solid	solution	solid
4a	294, 347, 471	296, 351, 473	621 (657[a])	622 (654[a])
4b	294, 346,466	296, 353, 470	622 (650[a])	623 (652[a])

[a] Vibronic shoulder.

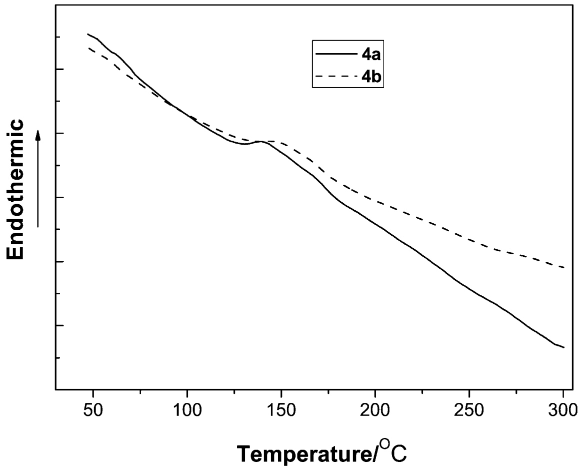

FIGURE 2. DSC curves of **4a** and **4b**.

are given in Table 1. The current UV−vis spectral characteristics led to a facile assignment of the spectra. The solution spectrum of **4a** tailed into the visible region with an emerging broad and featureless absorption band centered around 471 nm, which we attribute to the coexistent spin-allowed metal-to-ligand charge transfer ^{1}MLCT and spin-forbidden ^{3}MLCT/$^3\pi-\pi^*$ transitions as a result of iridium-induced spin-orbital coupling enhancement (heavy atom effect). Under excitation, **4a** gave a structured red emission at 621 nm with a vibronic shoulder around 657 nm, revealing that the emissive ^{3}MLCT excited states are mixed with the ligand-centered $^3\pi-\pi^*$.[18] As compared to $[(NaPy)_2Ir(acac)]$,[19] **4a** showed a nearly 20 nm bathochromic emission shift, due largely to end-capping by electron-donating and hole-transporting carbazoyl groups (NaPy = 2-(naphthalen-1-yl)-pyridine). Generally, the solid emission spectra are more sensitive to the formation of aggregates/excimers of photoluminescent materials in the solid states. The "perfect" overlap of both the solution and solid emission spectra of **4a** implies nonexistence of any appreciable aggregates in the solid state, a key merit of electroluminescent materials.

With respect to **4a**, the introduction of an additional single 1,4-phenylene group into the conjugated ligands in **4b** affected the UV−vis and PL spectra negligibly, whether in solution or in the solid state. This allows us to continue to modify this series of carbazolyl-end capped molecular structures to tune the physical properties, for instance, solubility, morphological stability, and emission quantum efficiency while not affecting substantially the emission color. The absolute photoluminescent quantum efficiencies of **4a** and **4b** in the neat films were measured in the integrating sphere. They exhibited close phosphorescent efficiencies of ca. 2.7%.

Cyclic voltammetry showed that the spin-coated films of **4a** and **4b** on the electrodes exhibited similar electrochemical behavior.[10a] The oxidation onset voltages were approximately 0.95 V vs saturated calomel electrode (SCE). The HOMO energy levels of **4a** and **4b** were then calculated to be −5.35 eV using the empirical formula HOMO $= -e(E_{ox}^{onset} + 4.4)$ eV.[20] Based on their optical band gaps of ca. 2.36 eV in the solid films, the LUMO energy levels were calculated as −2.99 eV.

Compounds **4a** and **4b** showed remarkable thermal stability. The onset decomposition temperatures are well over 350 °C. They held a high decomposition temperature of ca. 437 °C, defined by a starting 5% weight loss. DSC measurements on the as-prepared samples of **4a** and **4b** revealed an amorphous state with Tg of 123 and 127 °C, respectively (Figure 2). The slightly higher glass transition temperature of **4b** was coincident with its higher molecular size and weight. Remarkably, on heating to 300 °C, no crystallization and melting were observed. Such soluble materials are particularly useful in solution-processed light-emitting diodes where materials are more prone to aggregate and crystallize during solvent evaporation processes or in the operating devices with time. Moreover, it is worth noting that materials with high Tgs are advantageous in certain specific display devices that have to endure a higher ambient temperature.

Usually, solubilities have to be traded to the glass transition temperatures. The high amorphous morphological stabilities of **4a** and **4b** are attributed, to a large extent, to the carbazolyl end groups. The X-ray crystal structural analysis of *m*-CP, a host material for blue-emitting iridium complexes, revealed that the asymmetric bulky carbazolyl groups involved large twist

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angles of the central phenylene core of 41.8 and 112.9°, respectively [*m*-CP = 1,3-bis(carbazol- 9-yl)benzene]. This might explain why *m*-CP could exist in an amorphous state with a Tg of 55 °C for the simplest molecular structure[17] and why many other structurally closely related functional carbazoles showed more morphologically stable amorphous states.[12]

In summary, a post-Suzuki-coupling route was utilized to synthesize a series of soluble carbazolyl end-capped saturated red-emitting iridium complexes using 2-(2-pyridyl)benzimidazolate as the coligand. The appealing solubility, optical characteristics, and amorphous morphological stability promise the current hole-transporting enhanced iridium complexes great potential in solution-processible high-efficiency doped light-emitting devices to address fatal phase segregations in the doped emitting layer. The current synthetic approach can be useful in the efficient synthesis of new judiciously designed heteroleptic iridium complex for the purpose of solution-processible light-emitting devices. Intensive efforts in these directions are underway, including dedicated device engineering, and the results will be reported in due course.

Experimental Section

Synthesis of 4a. $Pd(PPh_3)_4$ (0.03 g, 0.026 mmol) was added to a mixture of **2** (0.20 g, 0.20 mmol) and **3a** (0.29 g, 0.43 mmol) in toluene (50 mL), aqueous Na_2CO_3 (2 M, 10 mL), and ethanol (5 mL) under an inert atmosphere of nitrogen. The reaction was heated at 90 °C for 48 h. After being cooled to room temperature, distilled water was added. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residual was purified on a silica gel column by gradient elution with a mixture of dichloromethane and ethyl acetate to afford a yellow solid. Yield: 0.25 g (63.6%). TLC R_f (40:1 dichloromethane/ethyl acetate v/v): 0.64. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.62 (m, 8 H), 0.80 (t, 12H, J = 6.6 Hz), 1.08−1.26 (m, 40H), 1.72−1.94 (m, 8H), 2.4663 (s, 3H), 2.4776 (s, 3H), 6.21 (d, 1H, J = 8.2 Hz), 6.49 (s, 1H), 6.53 (s, 1H), 6.69 (t, 1H, J = 7.5 Hz), 7.06−7.16 (m, 5H), 7.28−7.36 (m, 5H), 7.42−7.48 (m, 10H), 7.50−7.63 (m, 7H), 7.74−7.91 (m, 6H), 7.96−8.08 (m, 5H), 8.16−8.19 (m, 4H), 8.35 (s, 1H), 8.55−8.68 (m, 5H). Anal. Calcd for $C_{126}H_{126}IrN_7$: C, 78.39; H, 6.58; N, 5.08. Found: C, 78.12; H, 6.65; N, 5.00. ESI MS: m/z 1932 (100), MH^+ (calcd 980).

Synthesis of 4b. This compound was synthesized by a similar method for **4a**, using **2** and **3b**. Yield: 50%. TLC R_f (40:1 dichloromethane/ethyl acetate v/v): 0.62. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.62 (m, 8H), 0.80 (t, 12H, J = 6.6 Hz), 1.07 (m, 40H), 1.78−2.08 (m, 8H), 2.4643 (s, 3H), 2.4732 (s, 3H), 6.21 (d, 1H, J = 8.2 Hz), 6.50 (s, 1H), 6.53 (s, 1H), 6.70 (t, 1H, J = 7.5 Hz), 7.03−7.15 (m, 5H), 7.30 (s, 1H), 7.33 (d, 4H, J = 7.2 Hz), 7.42−7.53 (m, 10H), 7.56−7.72 (m, 12H), 7.75 (d, 1H, J = 3.0 Hz), 7.74−7.85 (m, 4H), 7.87−7.91 (m, 4H), 7.96−8.09 (m, 5H), 8.18 (d, 4H, J = 7.8 Hz), 8.35 (s, 1H), 8.55−8.68 (m, 5H). Anal. Calcd for $C_{138}H_{134}IrN_7$: C, 79.58; H, 6.48; N, 4.71. Found: C, 79.20; H, 6.70; N, 4.53. MALDI-TOF: m/z 1886.8 (100) [M − 2-(2-pyridyl)benzimidazolate]$^+$ (calcd 1887.96); 2081.6 (100) [MH^+] (calcd 2083.04); 2305.4 (100) [MH^+ + dithranol] (calcd 2309.1) and 2529.1 (100) [MH^+ + 2-dithranol] (calcd 2535.16).

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Supporting Information Available: Full experimental details and characterization of precursors to **4a** and **4b**; ^{1}H NMR and mass spectra of **4a** and **4b**; CIF file of *m*-CP. This material is available free of charge via the Internet at http://pubs.acs.org.

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