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Intramolecular energy transfer between the triplet of ancillary ligand and the metal to ligand charge transfer state existed in heterocyclometalated iridium (III) complexes

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Higher efficiency red organic light emitting devices (OLEDs) were obtained by employing Ir (III) complexes with 1-phenylbutane-1, 3-dione (ba) as the second ligand than that with acetylacetone (acac) as the second ligand, which were attributed to the intramolecular energy transfer existed in these complexes. The reason were attributed to the intramolecular energy transfer existed in these complexes and were approved by their photoluminescence characteristics at 77 K, as well the phosphorescence decay lifetime. Because of the lower triplet energy level of ba (T_{ba}, 19 230 cm^{-1}) whose energy was suitable to transfer to the triplet of the metal to ligand charge transfer (MLCT) (^{3}MLCT, 16 260 cm^{-1}) state compared to T_{acac} (25 500 cm^{-1}), more efficient OLEDs were obtained (7.0 cd/A) using Ir[2-(4′-methanoxy-styryl)-benzothiazole]$_2$ba (ba-2) than Ir[2-(4′-methanoxy-styryl)-benzothiazole]$_2$acac acac-2 (6.1 cd/A). © *2009 American Institute of Physics*. [DOI: 10.1063/1.3122938]

Heterocyclometalated Ir (III) complexes are currently very important materials in phosphorescent organic light emitting diode (PhOLED) research area due to their high photoluminescence (PL) and electroluminescence (EL) efficiency in their doped PhOLEDs.[1–6] This series of cyclometalated Ir (III) complexes have two cyclometalated ligands (*C^N*) and a single monoanionic bidentate ligand as the ancillary ligand (*LX*), the *C^N* ligands can be any organometallic ligands and the *LX* ligands used for these complexes were generally all β-diketones, because of the different triplet energy (T_{LX}) of ancillary ligand and the metal to ligand charge transfer state (MLCT) (^{3}MLCT), acetylacetone (acac) was preferred to be used in green and red phosphorescent heterocyclometalated Ir (III) complexes.[1,7–10] The first notice of energy transfer in these heterocyclometalated Ir (III) complexes was by Thompson and co-workers[1] in the red phosphorescent material Ir(btp)$_2$acac, the PL quantum yield (φ) of 0.21 was observed; however, when the acac was replaced by 1-phenylbutane-1, 3-dione (ba) only 0.1 was obtained, they consider that the low triplet energy of the β-diketone may deactive the phosphorescence φ because of the nonirradiation decay of the β-diketone ligand. Though many studies on the energy transfer mechanism were reported in those complexes with chromophoric ancillary ligand;[11–13] however, the intramolecular energy transfer (IET) in complexes containing nonchromophoric ancillary ligand was reported rarely.

In this letter, four red Ir (III) complexes Ir(stybt)$_2$acac (acac-1), Ir(stybt)$_2$ba (ba-1), Ir(MeO-stybt)$_2$acac (acac-2), and Ir(MeO-stybt)$_2$ba (ba-2) containing nonchromophoric ancillary ligand were used for the study. Here Hstybt and MeO-Hstybt denote 2-styrylbenzothiazole and 2-(4′-methanoxy-styryl)-benzothiazole, respectively. Complexes ba-1 and ba-2 contain different β-diketone ligand compared to complexes acac-1 and acac-2, respectively, and the synthesis of these complexes will be reported elsewhere.

The PL quantum yield was measured with a Shimadzu UV-3101PC UV-visible-NIR scanning spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer in air. The PL excited-state lifetimes were determined by a system equipped with a TDS 3052 digital phosphor oscilloscope pulsed neodymium doped yttrium aluminum garnet laser with a THG 355 nm output. The fabrication and EL characteristics of the OLED devices were mainly carried out by the previous reported processes in our group.[10] The fabricated devices with structures of indium tin oxide/NPB (35 nm)/4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP): *x* wt % red dopant (30 nm)/BCP (10 nm)/AlQ (20 nm)/LiF (1 nm)/Al (100 nm), here NPB, BCP, and Alq_3 denote 4,4′-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]-biphenyl, 2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline and tris-(8-hydroxyquinoline)aluminum, which act as the hole transporting layer, exciton blocking layer, and electron transporting layer, respectively.

In order to determine whether all the complexes show phosphorescence coming from the same species of excited state, the UV-visible and PL spectrum were measured and shown in Fig. 1. We can see the characteristic ^{3}MLCT absorption in the range of 380–510 nm, this could be observed

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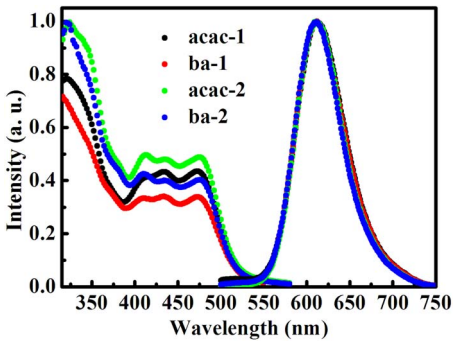

FIG. 1. (Color online) UV-visible absorption and PL spectra of acac-1, ba-2, acac-2, and ba-2 in CH_2Cl_2 solution (excited by 365 nm) at room temperature.

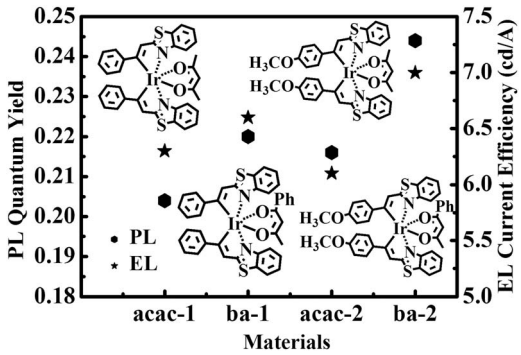

FIG. 3. The molecular structure, PL quantum yields and EL efficiencies of acac-1, ba-1, acac-2, and ba-2.

almost in all Ir (III) complexes,[5] there was no difference between acac-1 and ba-1 or acac-2 or ba-2 in this range except the π-π^* transition in the UV zone, and the emissions at room temperature were similar focused on 615 nm. So we conclude that the phosphorescence comes from the same ^{3}MLCT excited state.

The φ were measured with fac-Ir(ppy)$_3$ as the standard[14] in CH_2Cl_2 solution at room temperature, excited at 410 nm and detected at 615 nm, for which fac-Ir(ppy)$_3$ was detected at 510 nm and calculated with the formula as follows:

$$\varphi_{\text{sample}} = \varphi_{\text{standard}} \times (A_{\text{standard}}/A_{\text{sample}}) \times (I_{\text{sample}}/I_{\text{standard}}) \times (\eta_{\text{sample}}/\eta_{\text{standard}})^2.$$

Here φ, A, I, and η stand, respectively, the quantum yield, absorption intensity in the fixed wavelength, area of the emission spectrum, and the refractive index of the solution used. The corresponding φ values for acac-1, ba-1, acac-2, and ba-2 were 0.20, 0.22, 0.22, and 0.24, respectively. The result indicates that the complexes containing ba as the ancillary ligand show higher φ than the corresponding complexes employing acac as the ancillary ligand. Note that all the complexes have the same excited states, the ancillary ligand must play important role in effect on their φ.

Same disciplinarian result was found in their EL characteristics. The devices based on acac-1, ba-1, acac-2, and ba-2 have the same structure and doping concentration with 6 wt %. Figure 2 shows the current efficiency (η_c) and current density relationship of the devices, the maximum η_c of the four devices were 6.3, 6.6, 6.1, and 7.0 cd/A, respectively. The PL φ and EL η_c with the molecular structure of acac-1, ba-1, acac-2, and ba-2 were summarized in Fig. 3, both the φ and η_c of ba based complexes were higher than that of acac based complexes so we think energy transfer may exist in these complexes. In some rare earth materials such as Eu (III) complexes,[15] the triplet energy of the β-diketones have selectivity to transfer their energy to the $^5D_0$ level (17 250 cm^{-1}) of the Eu^{3+}, if the triplet energy of β-diketone (such as ba) was just above that level, efficiency energy transfer may exist; however, when the triplet energy of β-diketone (such as acac) was too high so that the energy transfer was inefficient. In Ir (III) complexes two series of triplet energy levels present, i.e., one is the phosphorescent ^{3}MLCT state, another is the nonirradiative triplet state of the β-diketone, that is T_{acac} in acac-1 and acac-2, as well as T_{ba} in ba-1and ba-2, respectively.

In order to affirm whether the energy transfer exists or not, we measured the PL spectra of ligand ba and complexes ba-2 at 77 K, which were shown in Fig. 4, also the phosphorescence decay of ligand ba at 77 K was shown in Fig. 4 (inset). One proof of the energy transfer is the longer phosphorescence lifetime of ligand ba (120 μs) which could be estimated according to the decay curve shown in Fig. 4 (inset), the phosphorescence lifetime of ba-2 was 294 ns, and we know that the longer lifetime excited state could transfer its energy to the shorter one easily. Note that there are two excited states in complex ba-2, if energy transfer between this two excited states was inefficient, the low temperature spectra of complexes ba-2 would be the stack of T_{ba} and ^{3}MLCT, the peak PL wavelength of ligand ba is about 520 nm; however, in the spectra of ba-2 we can not detect the emission of ba ligand, instead only the red emission was

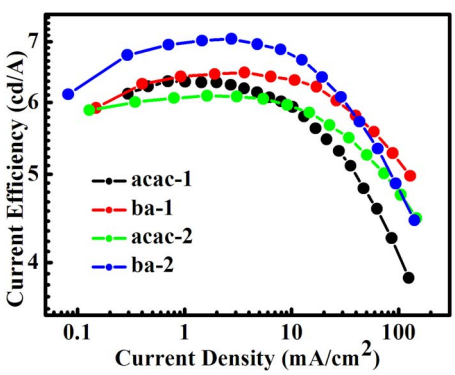

FIG. 2. (Color online) Current efficiency and current density relations of the devices with 6 wt % doped acac-1, ba-1, acac-2, and ba-2.

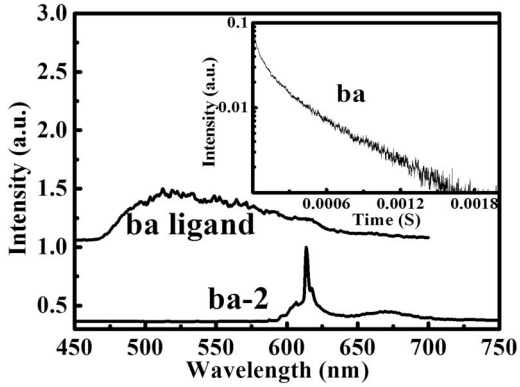

FIG. 4. The phosphorescence spectra of ba ligad and complex ba-2 at 77 K (inset: the phosphorescence decay of ligand ba).

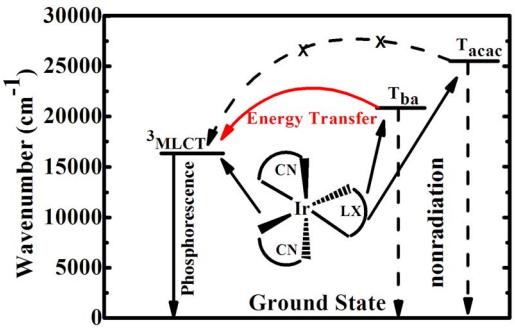

FIG. 5. (Color online) Energy transfer mechanism in heterocyclometalated complexes (real line: excitation and phosphorescence process; dashed line: nonirradiation process).

observed, so we think entirely energy transfer existed in complex ba-2, this would be the another proof of energy transfer. The intramolecular energy transfer (IET) could help us to explain why complexes ba-1 and ba-2 containing ba ligand have higher efficiency than complexes acac-1 and acac-2.

The energy transfer mechanism was shown in Fig. 5, the triplet energy of acac (T_{acac}) (Ref. 16) was 25 500 cm^{-1}, the energy of T_{ba} and ^{3}MLCT was calculated from Fig. 4, 19 230 and 16 260 cm^{-1}, respectively. When the acac-1 and acac-2 were excited, the energy of T_{acac} was too high compared with ^{3}MLCT to contribute to the room temperature phosphorescence, instead the energy decayed with nonirradiation pathway and wasted, however, in complexes ba-1 and ba-2 the energy of T_{ba} which was just above that of ^{3}MLCT could contribute to the phosphorescence though IET and was utilized adequately.

By doping ba-2 into CBP host we could obtain the best device performance with the maximum η_c of 7.0 cd/A and the highest luminance (L) of 13 804 cd/m^2 with corresponding Commission International de l'Eclairage (CIE) coordinates (0.64, 0.36). When the L rises to 1000 cd/m^2, the efficiency drops only 8.5%, the IET must play an important role in reducing the triplet-triplet annihilation, that is, excitons formed in ba ligand could compensate this efficiency rolloff.

In conclusion, we explained the IET mechanism existed in heterocyclometalated Ir (III) complexes containing nonchromophoric ancillary ligand and the energy transfer between T_{ba} and ^{3}MLCT was also proven though low temperature experiment. Efficient red OLED doped with ba-2 were attained with a maximum η_c of 7.0 cd/A and highest luminance (L) of 13 804 cd/m^2, respectively. This could be very important to develop efficient red phosphorescent materials by choosing superior ancillary ligand not only acac ligand.

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