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Highly efficient red electrophosphorescence from a solution-processed zwitterionic cyclometalated iridium(III) complex

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A mononuclear red-emitting zwitterionic iridium(III) complex, bis(1-(phenyl)isoquinolinato) iridium(III) (2,2′-bipyridine-3-ol-3′-olate), was synthesized and used as a triplet emitter doped in a polymeric host in solution-processed electrophosphorescent light-emitting diodes. We achieved a high luminous effieciency (LE) of 12.62 cd/A with fast response time in the device using the dopant unlike in the device using cationic irridium(III) phosphorescent materials. A hole transporting polymeric interlayer between the anode and the emitting layer improved the LE and decreased the exciton quenching at high electric fields. © *2007 American Institute of Physics*.
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Since the report of high-efficiency red phosphorescent dye by Baldo *et al.*,[1] triplet emitters have attracted a great deal of attention due to their potential application in organic light-emitting diodes (OLEDs).[2] In particular, iridium(III) phosphorescent complexes show much shorter triplet exciton lifetime, and thus lesser triplet-triplet annihilation at high currents than other transition metal complexes [e.g., platinum(II) phorphyrins] and europium(III) complexes.[2,3] Due to the strong spin-orbit coupling caused by the heavy metal ions incorporated in the complexes, they can utilize both singlet and triplet excitons for light emission, which, in principle, give internal quantum efficiency of 100%.[1,2,4]

The iridium(III) complexes can be mostly divided into two classes:[2,5,6] (i) the neutral complexes containing cyclometalated ligands and anionic ancillary ligands[5] and (ii) cationic iridium(III) complexes containing bidentate ligands (e.g., bipyridine, phenathroline, pyridnylquinoline, biquinoline, etc., derivatives).[6,7] Both the classes of irridium(III) complexes have demonstrated high quantum yields and thus high luminous efficiency (LE) in organic electrophosphorescent devices. As for the latter class of irridium(III) complexes, the ionic character makes them quite soluble in polar solvents, which enable solution process to form the film for low-cost flexible solid-state electroluminescent devices. However, the single layer devices showed a slow electroluminescence rising response time (t_r), a significant change in luminance intensity with a function of the time, and a drastic drop of LE at high current densities.[7] Therefore, they are indeed difficult to be used in full-color flexible panel displays which require fast switching. Recently, Wong *et al.* have reported multilayer yellow OLEDs using the anionic bipyridyl bis-cyclometalated Ir(III) complexes with 4,4′-dimethyl-2,2′-bipyridine. It is quite necessary to develop high-efficiency phosphorescent red materials which can be processed by solution process but show fast t_r and no drastic change of LE at high current densities.

In this letter, we report that our zwitterion-type red phosphorescent complex can provide high LE without a drastic drop of the LE at high current densities and a fast t_r in solution-processed electrophosphorescent devices. We achieved a high LE (12.62 cd/A) from the phosphorescence OLEDs using the complex as a dopant in a polymer host.

The complex was synthesized from the reaction of $(piq)_2IrCl_2Ir(piq)_2$ dimer (piq is phenylisoquinoline) and 2,2′-bipyridine-3,3′-diol [$BP(OH)_2$]. The molecular structure of the iridium complex corresponds to zwitterionic molecule carrying both the positive charge (cationic iridium center) and the negative charge (anionic ligand) (vide infrared). The molecular structure of bis[1-(phenyl) isoquinolinato] iridium(III) (2,2′-bipyridine-3-ol-3′-olate) ($(piq)_2Ir^+[BP(O^-)(OH)]$), is shown in Fig. 1. The complex has trans-N1, N2 and cis-C15, C30 (C∧N) chelate disposition similar to the previous literature.[8] The Ir–N bond lengths of C∧N ligands ($Ir-N_{av}=2.048$ Å) also fall within the range of [1.98(1)–2.07(1) Å] given in the mononuclear complexes with the "ppy_2Ir" fragment (ppy is phenypyridine).[9] In free $BP(OH)_2$ ligand, both pyridyl rings are coplanar with strong intramolecular hydrogen bonding between pyridyl nitrogen atom and hydroxy group attached to the opposite ring.[10] However, owing to N∧N coordination of $BP(O^-)(OH)$ ligand in $(piq)_2Ir^+[BP(O^-)(OH)]$, two pyridyl rings are quite distorted from the planarity because of the coordination bite

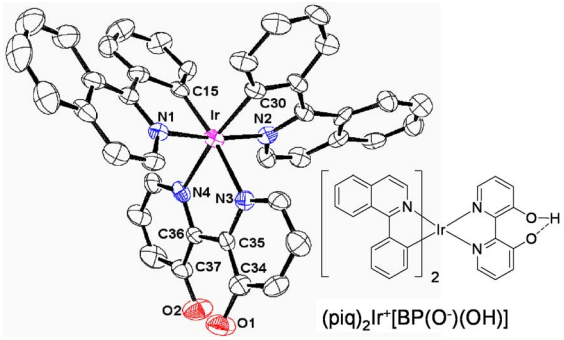

FIG. 1. (Color online) The chemical structure and Oak Ridge Thermal Ellipsoid Plot (ORTEP) diagram with partial numbering of $(piq)_2Ir^+[BP(O^-)(OH)]$. Hydrogen and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

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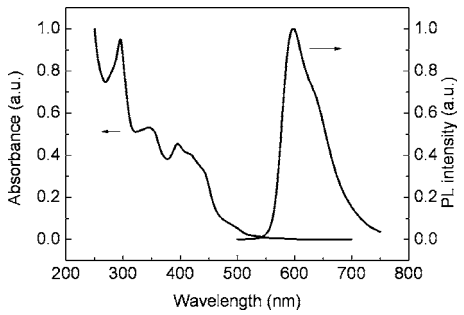

FIG. 2. UV and PL spectra of $(piq)_2Ir^+[BP(O^-)(OH)]$ in $CHCl_3$.

angle of 76.02° and repulsion between the two oxygen atoms at 5,5′-positions. Substantiated by the dihedral angles of N3–C35–C36–N4, C34–C35–C36–C37, and O1–C34–C37–O2 are −11.5°, −17.6°, and −30.9°, respectively, indicating repulsion between the two oxygen atoms at orthopositions. It is interesting to note that only one hydrogen atom from the two hydroxy groups was removed under the reaction condition, which gives a charge-neutral zwitterionic iridium complex. Strong intramolecular hydrogen bonding is suggested by very short O1–O2 and averaged C–O distances of 2.392 and 1.307 Å, respectively. In the final refinement of the structure of $(piq)_2Ir^+[BP(O^-)(OH)]$, one hydrogen atom is automatically generated onto O1 atom with a distance of 0.821 Å and H–O2 distance of 1.701 Å. The strong coordination ability of N∧N ligand and the stability of the O1−H···O2 hydrogen bond may be the driving force for the formation of zwitterionic iridium complex. Despite the easy availability of O^- coordinating site, this is an unusual example of a nonoxygen coordinated Ir(III) complex.

The UV/visible absorption and emission spectra of $(piq)_2Ir^+[BP(O^-)(OH)]$ in $CHCl_3$ solution are shown in Fig. 2. The bands below 360 nm can be assigned to the spin-allowed $^1\pi$-π^* transition of cyclometalated ligand, the broadband of 380–450 nm and the band at 492 nm can be assigned to metal ligand charge transfer (^{1}MLCT) and ^{3}MLCT, respectively. The complex shows the peak emission at 606 nm. It is worthwhile to point out that the complex $[Ir(piq)_2(bpy)]^+(PF_6)^-$ is reported[6] to have a peak emission at 586 nm, whereas the presence of the two OH groups in the 5,5′-positions of the bipyridine ligand in the complex $(piq)_2Ir^+[BP(O^-)(OH)]$ redshifts the emission to 606 nm.

Poly(N-vinyl carbazole) (PVK) was used as the host because its emission spectrum overlaps with the absorption spectrum of $(piq)_2Ir^+[BP(O^-)(OH)]$. PVK is known to be a preferentially hole transporting material. Therefore, we blended the PVK with an electron transporting material, 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) to enable the host to transport both electrons and holes. Solution-processed electrophosphorescent devices were fabricated by doping the emitter ($(piq)_2Ir^+[BP(O^-)(OH)]$) into the mixed host of PVK and PBD (40 wt %). Poly (3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS) as a hole injecting layer and 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBI) as an electron-transporting/hole-blocking layer were employed. We optionally employed poly[2,7-(9,9-di-*n*-octylfluorene)-alt-(1,4-phenylene-[(4-sec-butylphenyl)amino]-1,4-phenylene)] (TFB) as a hole transporting interlayer between PEDOT:PSS and the emitting layer (EML) in order to improve the hole transport to the EML and block electrons at the TFB/EML interface. The device structure and energy levels of each layer are shown in Fig. 3(a). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital levels (LUMO) of PVK are −5.8 and −2.2 eV, respectively.[11] The HOMO and LUMO of PBD are −5.9 and −2.4 eV, respectively.[12] In order to reduce the hole injection barrier, we used our reformulated PEDOT:PSS by adding a low molecular weight PSS (MW=48 000 g/mol) to the conventional PEDOT:PSS (Baytron P Al4083, PSS MW =0490000 g/mol) having a higher work function of 5.37 eV.

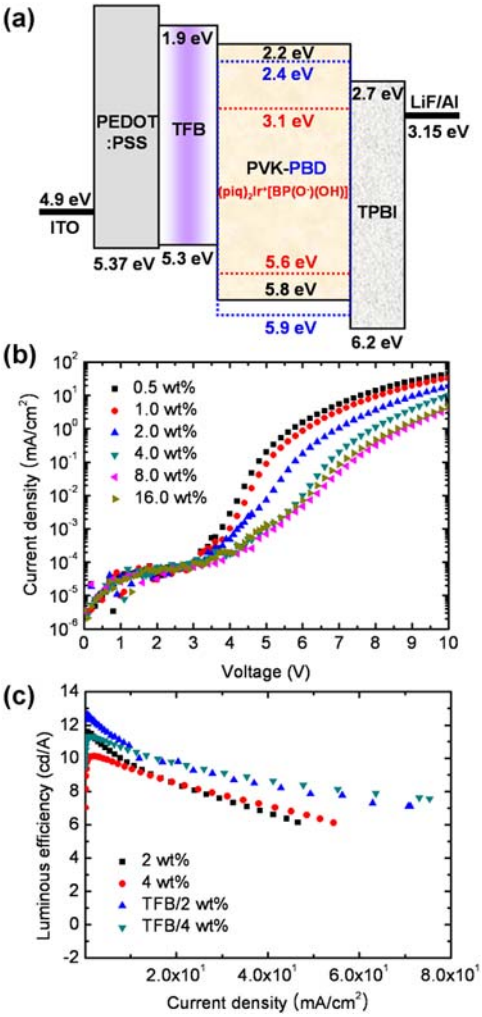

FIG. 3. (Color online) The device structure and the device characteristics of red electrophosphorescent devices using $(piq)_2Ir^+[BP(O^-)(OH)]$ as a dopant in PVK-PBD (40 wt %) host with varying dopant concentrations with or without a TFB interlayer. (a) The device structure, (b) current-density vs voltage characteristics of the luminous efficiency of red electrophosphorescent devices using $(piq)_2Ir^+[BP(O^-)(OH)]$ as a dopant in PVK-PBD (40 wt %) host with varying dopant concentrations. (c) Luminous efficiency vs current–density with varying dopant concentrations (2 and 4 wt %) with or without a TFB interlayer.

Since the HOMO and LUMO of the $(piq)_2Ir^+[BP(O^-)(OH)]$ are −5.6 and −3.1 eV, respectively, holes or electrons can be trapped by $(piq)_2Ir^+[BP(O^-)(OH)]$, and, subsequently, can recombine directly on the dopant.[13] In these devices, even at a low concentration of the dopant, the charge trapping can hugely reduce the mobility of the emitting host. It has been reported that the charge carrier mobilities in PVK are drastically reduced almost by three orders of

TABLE I. The performance of the devices using $(piq)_2Ir^+[BP(O^-)(OH)]$ doped into a PVK-PBD host as an emitting layer (EML) in the structure of ITO/PEDOT:PSS/EML/TPBI/LiF/Al and ITO/PEDOT:PSS/TFB/EML/TPBI/LiF/Al.

$(piq)_2Ir^+$ $[BP(O^-)(OH)]$ in PVK-PBD (40%)	Luminous efficiency (cd/A)	External quantum efficiency (%)	CIE at 100 cd/m^2	Turn-on voltage (V)
0.5%	2.97	2.15	0.48,0.32	4.0
1%	9.25	6.48	0.59,0.38	4.2
2%	11.61	8.01	0.61,0.38	4.4
4%	10.15	7.16	0.62,0.38	5.6
8%	7.83	6.13	0.63,0.38	5.8
16%	5.31	5.69	0.66,0.34	5.8
TFB/2%	12.62	8.60	0.61.0.38	4.0
TFB/4%	11.33	8.76	0.63,0.37	4.6
TFB/8%	8.70	7.96	0.64,0.36	5.2

magnitude by the addition of a small amount of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD).[14] We also observed similar huge reduction of the current densities in the $(piq)_2Ir^+[BP(O^-)(OH)]$ devices without a TFB interlayer, as Fig. 3(b) shows. The current densities of the devices drastically decrease from 0.5 to 4 wt % concentration owing to the charge trapping which is then saturated upon increasing the doping concentration up to 16 wt % above which the hopping transport via dopants tends to be more dominated.

Table I summarizes the performance of the devices using $(piq)_2Ir^+[BP(O^-)(OH)]$ doped into a PVK-PBD host as EML in the structure of ITO/PEDOT:PSS/EML/TPBI/LiF/Al and ITO/PEDOT:PSS/TFB/EML/TPBI/LiF/Al with varying dopant concentrations. As for the former devices, at 2 wt % $(piq)_2Ir^+[BP(O^-)(OH)]$ concentration, the LE reached the maximum. The decrease in LE at higher doping concentrations probably results from aggregation and self-quenching of the $(piq)_2Ir^+[BP(O^-)(OH)]$. Only 2 wt % doping of the guest into the PVK-PBD (40 wt %) host resulted in very high LE of 11.61 cd/A (8.01% ph/el), which is a quite high LE comparable to the best performance of solution-processed red phosphorescent devices.[15]

The device efficiency was further improved by introducing the hole-transporting interlayer (TFB) (HOMO: −5.3 eV, LUMO: −1.9 eV) between the PEDOT:PSS and the EML up to 12.62 cd/A (8.60% ph/el), as Fig. 3(c) shows. The TFB interlayer plays roles in transporting holes from the PEDOT:PSS layer and blocking electrons at the TFB/emitter interface,[11,16] which results in a more balanced electron-hole recombination and confinement of exciton in the EML. When the interlayer was employed, the rolling-off phenomena of the device efficiency at high currents were reduced which may imply that the exciton quenching by PEDOT:PSS can be removed by the interlayer at high currents.[16] Therefore, this indicates that the roll-off phenomena at high electric fields in phosphorescent OLEDs can be caused by the exciton quenching by adjacent layers such as anode, cathode, and PEDOT:PSS, as well as triplet-triplet annihilation.[3,17] We measured the transient electroluminescence of the device using 4 wt % $(piq)_2Ir^+[BP(O^-)(OH)]$ in PVK-PBD without the TFB interlayer with 6 V step voltage pulse and 10 Hz frequency which provided a fast response time of the devices (the EL onset time (t_d): 1.6 μs, the rising time (t_r): 25.9 μs) (see Fig. 4).

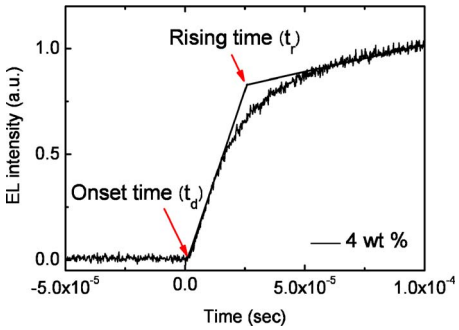

FIG. 4. (Color online) The transient electroluminescence of ITO/PEDOT:PSS/4 wt % $(piq)_2Ir^+[BP(O^-)(OH)]$ in PVK-PBD/TPBI/LiF/Al

In summary, an iridium(III) complex, $(piq)_2Ir^+[BP(O^-)(OH)]$ was synthesized and the exact configuration of $(piq)_2Ir^+[BP(O^-)(OH)]$ was confirmed using the single-crystal x-ray diffraction analysis. $BP(OH)_2$ can act as a bidentate ligand (N∧N or N∧O fashion) or as a bridging tetradentate ligand to two metal centers and can afford various zwitterionic metal complexes. The high solubility in organic solvents enables solution process for the device fabrication. We demonstrate high-efficiency red electrophosphorescent devices (12.62 cd/A) with fast response time using $(piq)_2Ir^+[BP(O^-)(OH)]$ as the dopant in the mixed host of PVK and PBD.

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