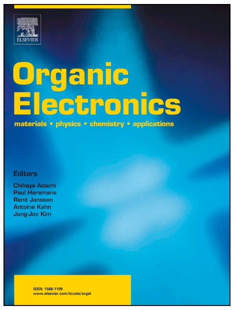


Highly-efficient solution-processed deep-red organic light-emitting diodes based on heteroleptic Ir(III) complexes with effective heterocyclic Schiff base as ancillary ligand

Meha J. Prajapati, Rohit Ashok Kumar Yadav, Sujith Sudheendran Swayamprabha, Deepak Kumar Dubey, Jaydip D. Solanki, Jwo-Huei Jou, Kiran R. Surati

PII: S1566-1199(20)30271-8

DOI: https://doi.org/10.1016/j.orgel.2020.105885

Reference: ORGELE 105885

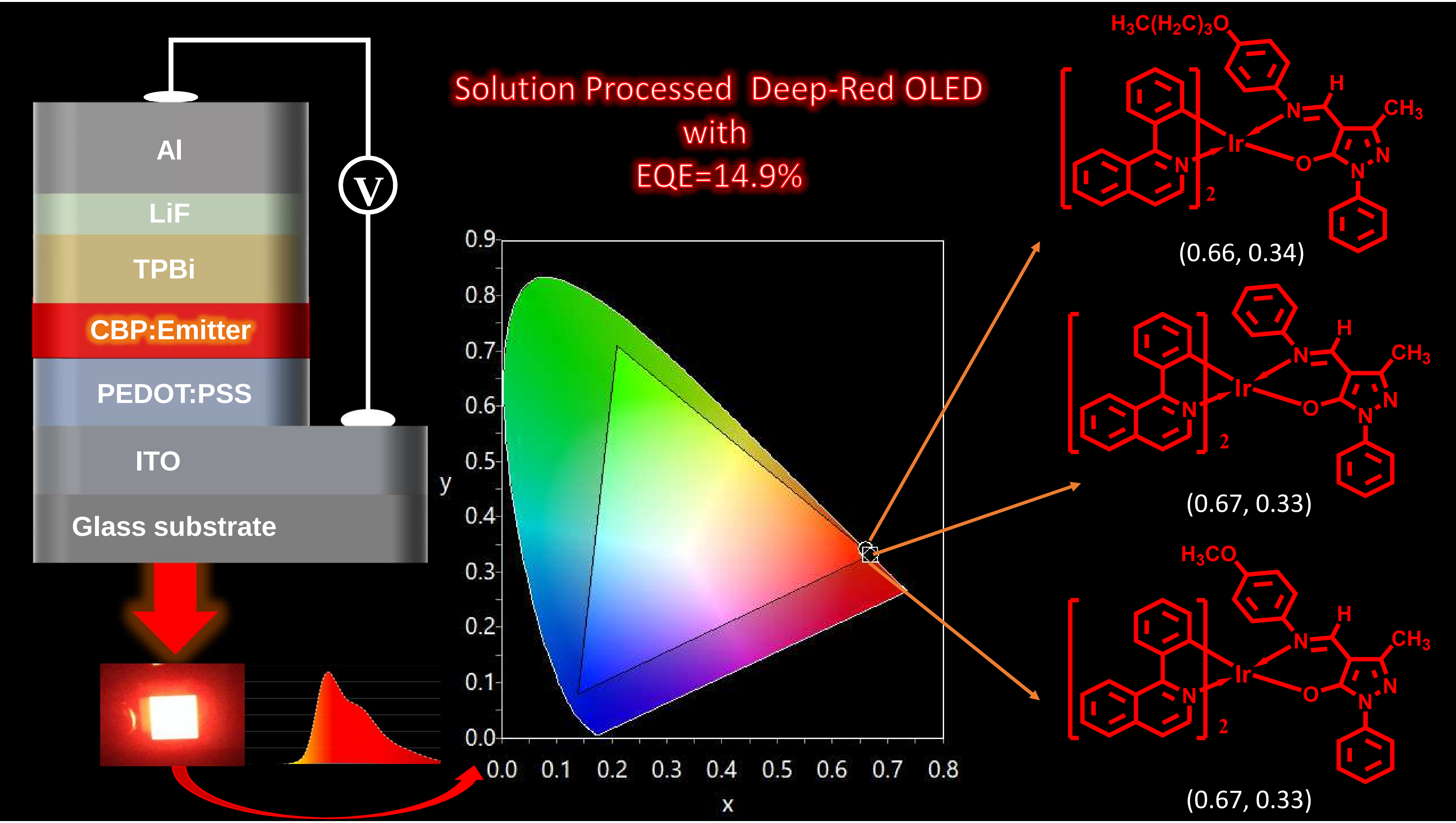
To appear in: *Organic Electronics*

Received Date: 13 April 2020

Revised Date: 21 June 2020

Accepted Date: 21 June 2020

Please cite this article as: M.J. Prajapati, R.A. Kumar Yadav, S.S. Swayamprabha, D.K. Dubey, J.D. Solanki, J.-H. Jou, K.R. Surati, Highly-efficient solution-processed deep-red organic light-emitting diodes based on heteroleptic Ir(III) complexes with effective heterocyclic Schiff base as ancillary ligand, *Organic Electronics* (2020), doi: https://doi.org/10.1016/j.orgel.2020.105885.



Solution Processed Deep-Red OLED
with
EQE=14.9%

Highly-Efficient Solution-Processed Deep-Red Organic Light-Emitting Diodes Based on Heteroleptic Ir(III) Complexes with Effective Heterocyclic Schiff Base as Ancillary Ligand

Meha J. Prajapati[a,§], Rohit Ashok Kumar Yadav[b,§], Sujith Sudheendran Swayamprabha[b], Deepak Kumar Dubey[b], Jaydip D. Solanki[a], Jwo-Huei Jou[b]* and Kiran R. Surati[a]*

[a]Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388120, Anand, Gujarat, India

[b]Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan, Republic of China

*Corresponding authors: jjou@mx.nthu.edu.tw and kiransurati@yahoo.co.in

§: Both authors contributed equally to this work.

Abstract

Three new deep-red heteroleptic phosphorescent iridium(III) complexes Ir(piq)$_2$(L$_1$), Ir(piq)$_2$(L$_2$), and Ir(piq)$_2$(L$_3$), comprising cyclometalated ligand 1-pheynylisoquionoloine(piq) and heterocyclic Schiff base ancillary ligands 3-methyl-1-phenyl-4-(phenylimino)methyl-1H-pyrazol-5-ol(L$_1$), 3-methyl-1-phenyl-4-(phenylimino)methyl-1H-pyrazol-5-ol (L$_2$), and 4-(4-methoxyphenyl)imino-methyl-3-methyl-1-phenyl-1H-pyrazol-5-ol (L$_3$) have been designed, synthesized, and characterized. All the compounds emit deep red emission with λ_{max} values in the spectral range of 602-620 nm, high quantum yield 0.44 to 0.52 and short excited state lifetime τ (0.51-0.55 μs) due to dominant strong field ligands, resulting an efficient triplet metal-ligand charge transfer (^{3}MLCT) excited state. Time dependent density functional theory (TD-DFT) calculations and electrochemical measurements of the compounds strongly support their genuine deep red phosphorescent emission. The combination of ancillary and cyclometalated ligands significantly influence the molecular orbitals of Ir(III) complex, leading to clearly distinct electron density distributions of the LUMO and HOMO. The compounds show good thermal stability and quantum yield, these characteristics making them an ideal candidate to exploit in phosphorescent organic light emitting diodes (PhOLEDs). Highly-efficient PhOLEDs were developed by using Ir(piq)$_2$(L$_1$), Ir(piq)$_2$(L$_2$), and Ir(piq)$_2$(L$_3$) in solution process as deep red emitters and device composed of Ir(piq)$_2$(L$_3$) exhibited an excellent external quantum efficiency of 14.9% and current efficiency of 10.8 cd/A with the stable CIE coordinates of (0.67,0.33).

Keywords: Heteroleptic iridium(III) complex, deep red, solution process, PhOLED.

Introduction

Phosphorescent organic light emitting diodes (PhOLEDs) have drawn potential attention in last few decades as most promising alternatives in next generation display and solid-state lighting technology [1-7]. Compared to the conventional well established liquid crystal display (LCD) and light emitting diodes (LED) technology, the advantage of OLEDs includes high speed vide rate, wide visual angle, high contrast, and cold resistance [8]. Moreover, OLEDs technology also capable of flexible/transparent devices and extremely thin light screens.

The OLED technology has been unfolding from single heterojunction structure into a double heterojunction structure, taking advantage of the severance of the carrier transport and light emitting layers into two territories. Besides these multi-heterojunction architectures, it facilitates more confine the charge carriers and improves the performance [9-10]. To achieve high performance OLEDs development of various materials including electrodes, electron/hole transport, host, and emitters are of the key issues drawing extensive academic-industrial interest. Among all these compounds for OLEDs, Ir(III) based compounds are consider to be the most promising candidates for the facile chemical modification, tunable photophysical characteristics and superior stability.

A huge research has been carried out aimed to develop Ir(III) complexes for different applications in OLEDs. However, development of an efficient deep red phosphorescent device is a formidable challenge as it experienced the energy gap law and luminous flux drop in the saturated red region [11-16]. Good efficiency of deep red phosphorescent OLED (PhOLEDs) with the maximum luminescence in the region 640-680 nm and the Commission International de L'Eclairage (CIE) coordinates of $x \geq 0.70$ and $y \leq 0.30$ are rare so far [17-20]. Therefore, developing novel high-performance red phosphorescent emitters through an effective molecular design strategy will revamp the color purity, luminescence quantum yield, and lifetime, hence better OLED efficiency devices. Numerous attempts have been reported with the derivatives of phenyl quinoline or phenyl iso-quinolone as cyclometalated ligands and other ancillary ligands such as acetylacetonate (acac), picolinate(pic), and N,N′-diisopropylbenzamidinate (dipba) etc. However, these compounds suffer from the limitations that lower the luminescence quantum yield, excited lifetime, and device efficiency [21-33].

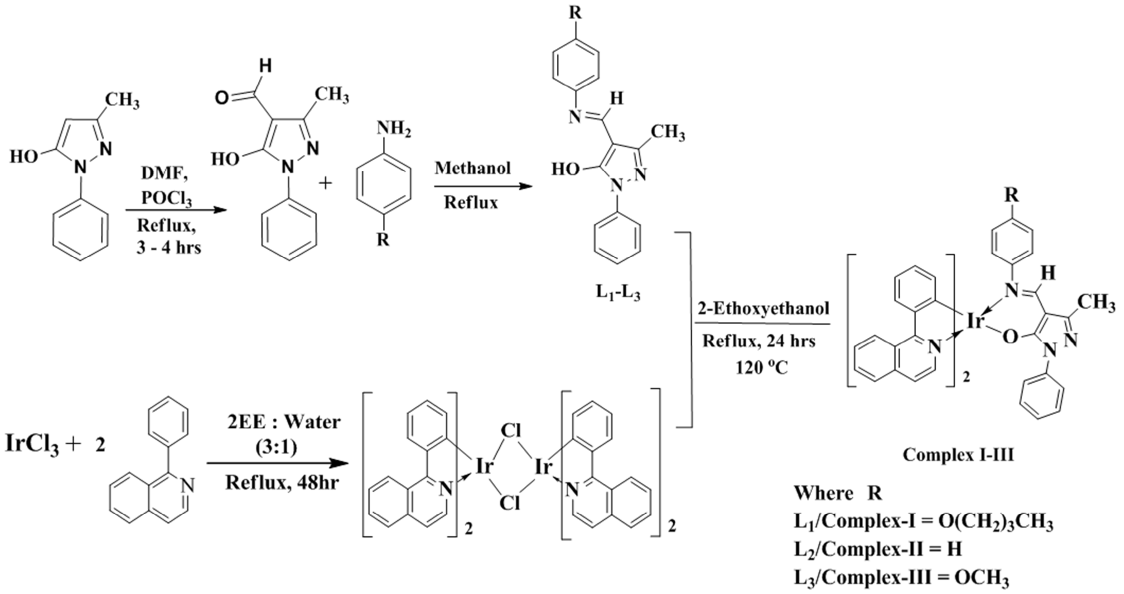
In the present study, we have designed and synthesized three new heteroleptic Ir(III) complexes, namely $Ir(piq)_2(L_1)$, $Ir(piq)_2(L_2)$, and $Ir(piq)_2(L_3)$. The photophysical and electrochemical characteristics were studied and reveals that the synthesized compounds possess significant potential towards deep red emission along with good luminescence quantum yield. The compounds emit deep red emission with λ_{max} values in the spectral range of 602-620 nm, high quantum yield 0.44 to 0.52 and short excited state lifetime (0.51-0.55 μs) due to dominant strong field ligands, resulting an efficient triplet metal-ligand charge transfer (^{3}MLCT) excited state. The pyrazolone based ligand offers several important features to the compounds such as enhancing luminescence quantum yield due to strong field effect of the ligands as well as good film forming properties [10, 34-35]. Density functional theory (DFT), time dependent DFT (TD-DFT) calculations, and electrochemical measurements of the compounds strongly support their genuine deep red phosphorescent emission. The compounds show good thermal stability and high glass transition temperature. These Ir(III) compounds employed as dopant for the deep red PhOLEDs, a maximum EQE of 14.9% with CIE coordinate of (0.67, 0.33) was recorded for the Ir(piq)$_2$(L$_3$) dopant. All the devices display very stable electroluminescent emission, low turn-on and high luminance.

Results and discussion

All synthesized ancillary compounds were stable at room temperature, soluble in common organic solvents and further characterized through different spectroscopic techniques. The results were in good agreement with the proposed structures.

Structural description

The synthesis route of ancillary ligand L$_1$, L$_2$, and L$_3$ are shown in Scheme 1. Intermediate 1-phenyl-4-formyl pyrazolone derivatives were synthesized according to our previous reports [36,37]. The ligands were characterized by ^{1}H-NMR, APT and ESI-MS. The ^{1}H-NMR spectra of the ligands showed the characteristics of an enolic proton at δ 11.34-11.40, which disappeared during complexation with the Ir(III) metal ion [36,38]. FT-IR spectra of the complexes show band between 1504-1535 cm^{-1} which is assigned to aromatic C=C bond. Strong bands observed in the range of 1612-1620 cm^{-1} is due to C=N azomethine group. The lower bands between 500-800 cm^{-1} is due to the Ir-O and Ir-N [39]. The mass spectra of complexes L_1, L_2, and L_3 showed the characteristic molecular ion signals at 949, 877.4 and 907 m/z, respectively (Fig. S1-S11). X-ray structure of ligands determines and its crystallographic data are summarized in (Table S1-S2 and Fig. S12).



Scheme 1: Synthesis of ancillary ligands and Ir(III) complexes.

Photophysical properties

Figure 1 displays the UV-Vis absorption spectra of the Ir(III) compounds measured at room temperature in dichloromethane (DCM) solution. The absorption spectra can be considered as composed of two parts, the broad and intense absorption bands observed below 350 nm closely resembled that of cyclometalated and ancillary ligand that are assigned to spin allowed $^1\pi$- π^* transition [40-42]. These transitions are also known as ligand centered (LC) transitions [25]. The peaks at around 350-420 nm could be as a result of the spin allowed inter ligand charge transfer (^{1}ILCT) between the cyclometalated and ancillary ligands. However, the weaker absorption band observed above 450-500 nm could be assigned to the spin allowed transitions metal-to-ligand charge transfer band (^{1}MLCT), while spin forbidden (^{3}MLCT) transition bands appeared at 550-650 nm [43-44].

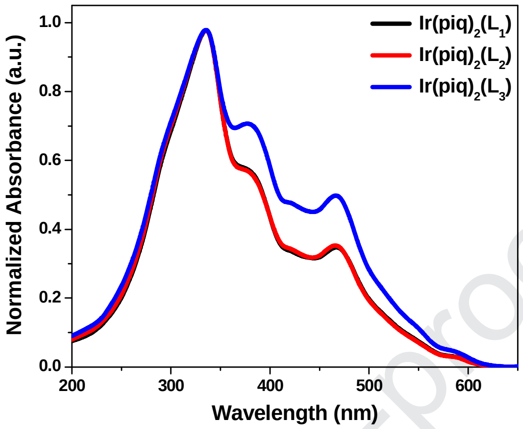


Figure 1: Electronic absorption spectra of the compounds in DCM.

The emission spectra of the Ir(III) compounds at room temperature were carried out in DCM solution and solid-state by using integrating sphere are shown in Figure 2. All complexes display deep-red luminescence peak in the range of 602-621 nm, data are summarized in Table 1. The compound displays deep red PL emission ranging 601-603 nm in the DCM solution. The complexes show good quantum yield in the range of 0.44-0.52 with reference to Ir(ppy)$_3$.

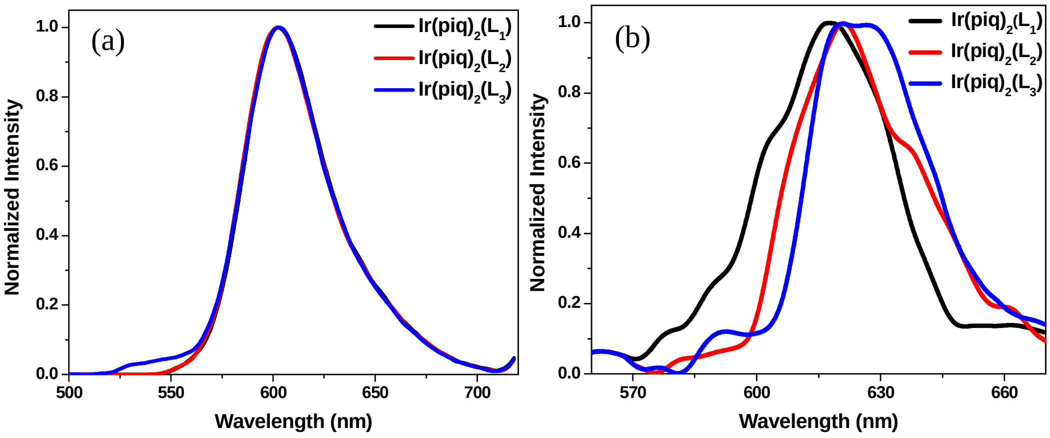


Figure 2: PL spectra of compounds in (a) DCM and (b) solid state.

Our rational design complexes show superior quantum yield as compared with the homoleptic and heteroleptic iridium(III) complexes such as Ir(piq)$_3$ (0.26) and Ir(piq)$_2$(acac) (0.20) at 620 and 622 nm, respectively [14,45]. Our compounds show excellent Φ_{PL} as compared with other reported complexes [15,18,46]. Due to such limitations, this homoleptic and heteroleptic complexes do not show significant properties and device performance too. Our designed heteroleptic complexes are superior in terms of Φ_{PL} and lifetime in the range of 0.50-0.55 μs, which may be due to the superior excited MLCT characters over the other complexes. Here the increasing MLCT character subsequently enhances the spin-orbit coupling (SCO) and leads to larger radiative rate k_r as summarized in Table 1. These complexes also show good solid state luminescence in the range of 618-621 nm. All these complexes show a stronger bathochromic shift and broad emission spectrum in solid state than those discerned in the solution state, which may be due to presence of the packed molecules interact and the formation of excimer in solid state [47-48]. It is believed that intermolecular interactions arising from π-π stacking in the thin-film or solid-state have always led to small red shifts in the emission spectra. In the solid state, the quantum yields of complexes were calculated using integrating sphere method and were found to be 0.39, 0.48 and 0.49 respectively. All the emitters show nearly same emission in toluene, chloroform and acetone with a shift of 2 nm [49]. Representative spectra of complex L_1, L_2, and L_3 are shown in Fig. S13-S15. It is interesting to note optical bandgap of complex Ir(piq)$_2$(L_3) is higher than that of other counterparts, which may be attributed to presence of relatively less bulky group (-OCH$_3$) and lower possibilities of steric hindrance in the Schiff base units in complex, Ir(piq)$_2$(L_3).

Table 1: Photophysical, electrochemical and thermal properties of iridium compounds.

Compounds	**λ_{PL}**^{a} **[nm]**	**λ_{PL}**^{b} **[nm]**	**λ_{abs}**^{c} **[nm]**	**λ_{onset}**^{d} **[nm]**	**E_g**^{e} **[eV]**	**E_{onset}**^{f} **[eV]**	**HOMO**^{g} **[eV]**	**LUMO**^{h} **[eV]**	**T_d**^{i} **[°C]**	**Φ_{PL}**^{j}	**Φ_{PL} (Solid state)**	**Lifetime τ (μs)**	**k_r**^{k} **($10^7\ s^{-1}$)**	**k_{nr}**^{l} **($10^6\ s^{-1}$)**
$Ir(piq)_2(L_1)$	602	618	340	623	1.99	0.496	-5.59	-3.60	310	0.44	0.39	0.51	0.862	1.098
$Ir(piq)_2(L_2)$	602	621	335	618	2.00	0.522	-5.62	-3.62	292	0.51	0.48	0.55	0.927	0.890
$Ir(piq)_2(L_3)$	603	620	336	629	1.97	0.503	-5.60	-3.63	318	0.52	0.49	0.53	0.981	0.905

[*a*] measured in dichloromethane

[*b*] measured in solid state

[*c*] measured in dichloromethane at concentration 5×10^{-6}mol/lit

[*d*] estimated from absorption spectra

[*e*] estimated from absorption onset from UV-visible

[*f*] estimated from cyclic voltammetry

[*g*] estimated from $E_{1/2oxd}$ and E_{onset} obtained from cyclic voltammetry

[*h*] estimated using HOMO and E_g

[*i*] estimated from TGA (5% weight loss)

[*j*] in dichloromethane

[*k*] the radiative $k_r = \Phi_{PL}\ \tau$-1

[*l*]the non-radiative $k_{nr} = (1-\Phi_{PL})\ \tau$-1

Electrochemical properties

Cyclic voltammetry (CV) was conducted to study the electrochemical characteristics of the iridium compounds and carried out by three-electrode system on CHI660E electrochemical workstation (Ocean Optics, USA). The measurements were carried out at room temperature in DCM solutions with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The cyclic voltammograms of calibration compound ferrocene obtained with reference to Ag/Ag$^+$ electrode is shown in Figure 3. The cyclic voltammograms are obeying quasi reversible nature and by using onset oxidation potential values which are ranging from -0.359 to 0.564 V, the HOMO and LUMO energy levels of the compounds are calculated and summarized in Table 1.

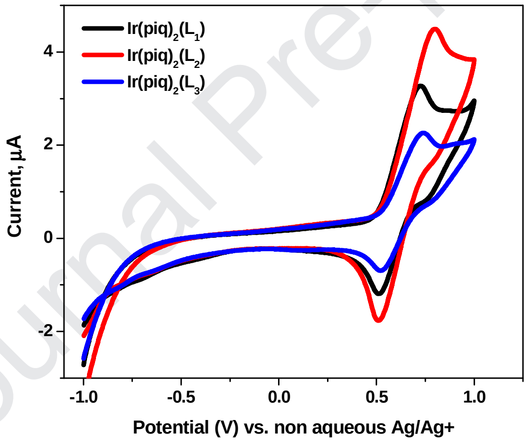


Figure 3: Cyclic voltammograms of compounds.

Thermal properties

The thermal behavior of the compounds was investigated by the thermogravimetric analysis (TGA) under nitrogen atmosphere with a heating rate of 10 °C/min from room temperature to 500 °C as shown in Figure 4. The characteristic provides information such as thermal stability, glass transition temperature and melting assay of the materials. Such parameter is crucial in terms of fabrication of device using materials which are essential for the fabrication of OLED by a vapor deposition method [50]. All the iridium complexes exhibit good thermal stability (T_d) in the range of 292-318 °C. Differential scanning calorimetry (DSC) analysis was performed from 30 to 250 ºC at a heating rate of 10 ºC/min under the nitrogen atmosphere (Fig. S16). As indicated by the DSC curves, no obvious glass transition temperatures were observed which suggests that these Ir(III) complexes are highly amorphous. These complexes showed excellent thermal stabilities high enough for OLED device fabrication [51-53].

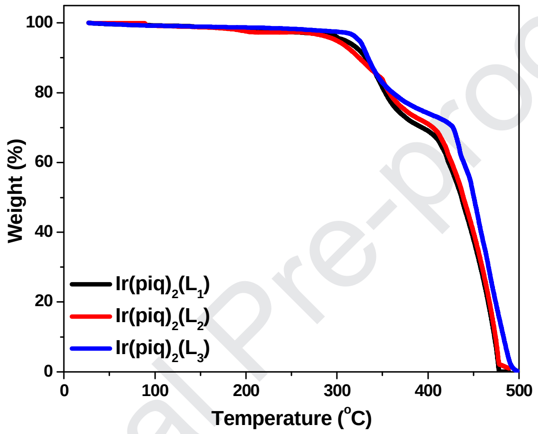


Figure 4: TGA curves of synthesized iridium(III) complexes.

Theoretical calculation

The density functional theory (DFT) and time dependent DFT (TD-DFT) calculations of complexes were performed using the Becke's three parameters and Lee-Yang-Parr (B3LYP) hybrid exchange-correlation method with LANL2DZ basis set for the iridium atom and 6-31G* for the other atoms. To more understand about the spatial distribution of the frontier molecular orbitals, the contour plots of LUMO + 2 to HOMO - 2 of iridium complexes in Figure5. All calculations are performed in Spartan'18 Software. As shown in Figure 5, HOMO of L_1, L_2, and L_3 are mainly localized on the pyrazolone ring of ancillary ligand and iridium center. Meanwhile, the LUMO of all complexes are localized on the two cyclometalated ligands, along with a minor contribution of iridium center. The other heteroleptic and homoleptic complexes were also carried out with the same basic set to establish the more understanding regarding the behavior of these ligands and their contribution in the formation of FMOs (Table S3-S5). The ancillary ligands acac and pic of complex Ir(SQ)$_2$(acac), Ir(CTBT)$_2$(acac), Ir(MTPQ)$_2$(pic), and Ir(BTP)$_2$(acac) (Table S6) are not contributing in the formation of frontier molecular orbitals (FMOs), whereas the designed ancillary ligands L$_1$-L$_3$ in complex are largely effects on the FMOs and subsequently enhances the radiative process by tuning the band-gap which is also support by the device data shows in Table S3.

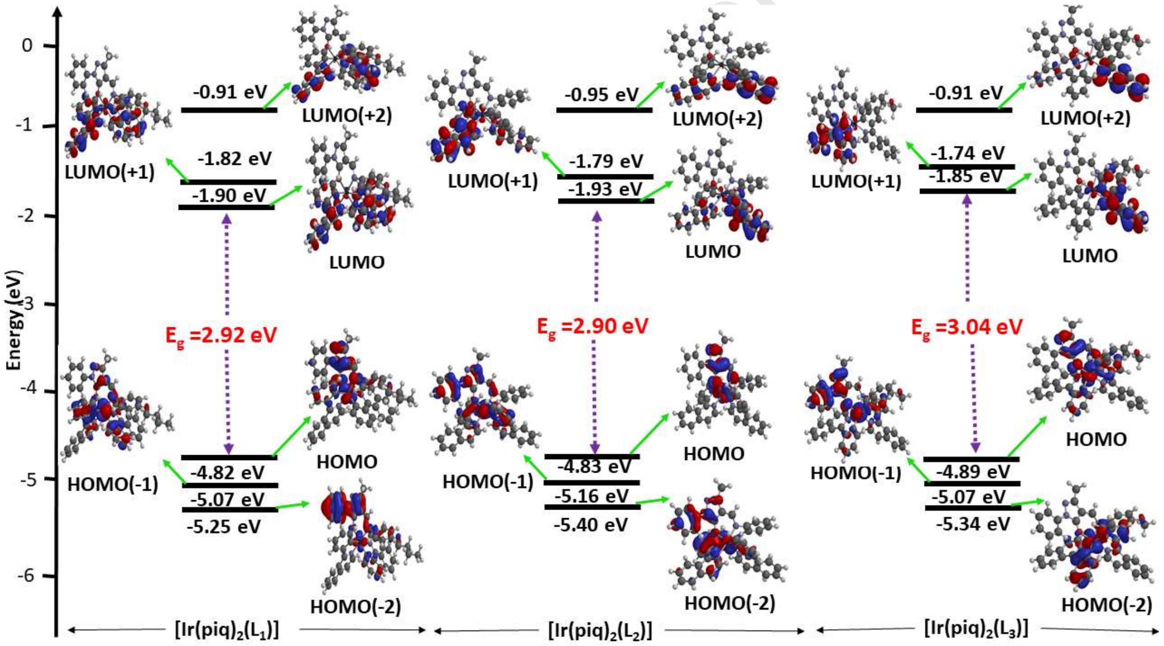


Figure 5: Frontier molecular orbitals (FMOs) of the iridium complexes.

Device electroluminescent characteristics

Inspired by the excellent photophysical characteristics and comprehensive abilities of the emitters, we have evaluated the potential application of the iridium compounds as dopant in the solution processed PhOLED with CBP host. Single emissive layer electroluminescent (EL) devices with a structure ITO/ poly(3,4-ethylene-dioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS; 35 nm)/ CBP: *x* wt% emitter (22 nm)/ 1,3,5-tris(N-phenylbenzimidazol-2-yl)-benzene (TPBi; 40 nm)/ LiF (1.5 nm)/ Al (150 nm) were fabricated by solution processing. Herein, ITO acts as an anode, PEDOT:PSS serves as the hole injection/transporting layer (HIL/HTL), TPBi serve as an electron transporting/hole blocking layer (HTL/HBL), LiF acts as the electron injecting layer (EIL), and Al as a cathode. In order to achieve high performance PhOLEDs, different doping concentration of the Ir(III) emitters (x = 5.0, 7.5, 10, and 12.5 wt%) in the host CBP matrix were deployed. The studied device structure and molecular energy level alignment between the layers are displayed in Figure 6.

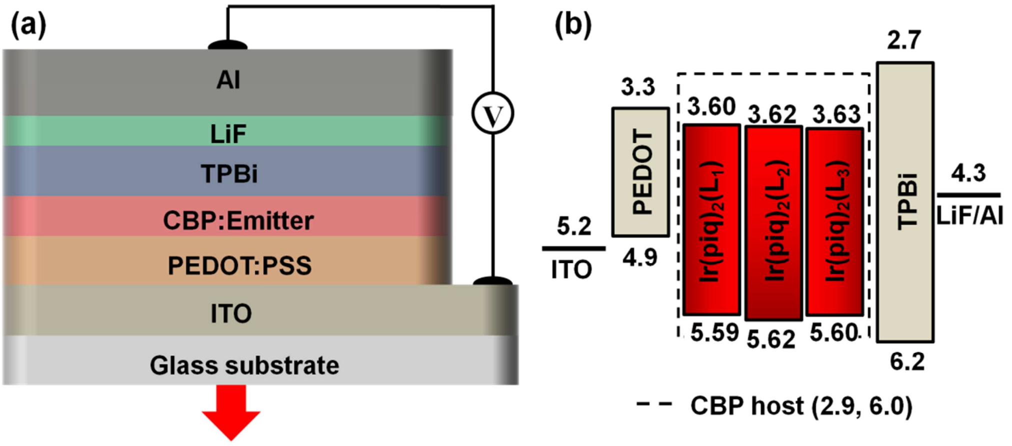


Figure 6: (a) Schematic device structure and (b) energy level diagram of the studied solution processed deep red PhOLEDs.

The current density-voltage-luminance, efficiency characteristics and normalized EL spectra of the deep red PhOLED are shown in Figure 7 and data are summarized in Table 2. The $Ir(piq)_2(L_1)$, $Ir(piq)_2(L_2)$, and $Ir(piq)_2(L_3)$ compounds showed deep red electroluminescence emission having maxima spectral λ_{max} value at 616, 617 and 620 nm with CIE coordinates of

(0.66, 0.34), (0.67, 0.33) and (0.67, 0.33), respectively. Devices exhibit very stable EL emission spectra without any effect on the CIE coordinates when increasing the dopant concentration. The main peak in the EL spectra of the devices was well consistent with the corresponding photoluminescence spectra of the films. A shoulder peak was observed in the lower energy region of EL spectra around 660 nm and became gradually drop with increasing dopant concentration, which may be seeded by the excimer formation in solid state.

Furthermore, the red shifted EL peak with an increasing doping concentration was also confirmed. No emission from the CBP host and adjacent charge transporting layers were observed which indicates an efficient energy transfer mechanism from host to dopant and effective confinement of charges. The doping concentration strongly influences the device performance. Table S7 and Figures S17-S19 summarizes the effects of doping concentration on power efficiency (PE), current efficiency (CE), external quantum efficiency (EQE), CIE coordinates, and maximum luminance.

A deep red emitting PhOLED devices with stable CIE coordinates of (0.67, 0.33), a maximum CE of 10.8 cd/A and a maximum EQE of 14.9% was achieved for the Ir(piq)$_2$(L$_3$) (10 wt%) based device featured the highest performance. This is the highest EQE among the simple design solution processed Ir(III) based PhOLEDs (Table S8). The EQE is approximately 1.5 and 2 times higher than that of the device based on Ir(piq)$_2$(L$_1$) and Ir(piq)$_2$(L$_2$), respectively. For Ir(piq)$_2$(L$_1$) and Ir(piq)$_2$(L$_2$), a decent maximum EQE of 9.6% and 7.3% was realized, respectively. The Ir(piq)$_2$(L$_3$) based device showed an increased EQEs from 7.1% to 10.4% as the doping concentration increased from 5.0 wt% to 10.0 wt%, respectively. As the concentration of the dopant is increased to 12.5wt% the EQE dropped to 8.0%, this decline in EQE might cause from the doping concentration quenching and triplet-triplet annihilation process. The Ir(piq)$_2$(L$_3$)

based device showed an EQE of 11.7% and 9.9% at 100 and 1000 cd/m^2, respectively. Herein, it is interesting to note that the devices do not suffer from the efficiency roll-off, which is a major issue faced in PhOLEDs. The surface morphologies of the thin films were studied using AFM in trapping mode. The root mean square values of the films were recorded 0.67 nm and 0.65 nm for 7.5 wt% and 10 wt% of $Ir(piq)_2(L_3)$ dopant with CBP host matrix, respectively. The AFM images display a uniform and homogenous distribution of the film surface illustrated in Fig. S20. Remarkably, no major changes have been observed in the emission spectra of molecules by introducing the alkoxy group in the Schiff base units. However, molecular orbital energy level and quantum yield of the compounds has been slightly altered. The quantum yield of the compounds and EQE of the reported devices are quite good when compared with the complexes those reported in the literature. The observed 14.9% EQE for the OLED device based on complex $Ir(piq)_2(L_3)$ may also be attributed to the presence of less bulky ($-OCH_3$) group in the Schiff base units.

It is also noticeable that observed PE and CE of the resultants OLED devices lower than that of EQE. The reason beside this may be high PLQY value of emitters, efficient energy transfer between host and guest molecules, generation of radiative exciton in the sufficient amount, and balanced charge carrier in the recombination zone. The PE of OLED is inversionally proportional to driving voltage of the device, a hole enriched device leads to low driving voltage and high PE. However, the EQE of an OLED device depends on many factors and can be determined by the optical out-coupling factor (η_{op}), photoluminescence quantum yield (PLQY), exciton generation (η_r), and carrier balance factor (γ).

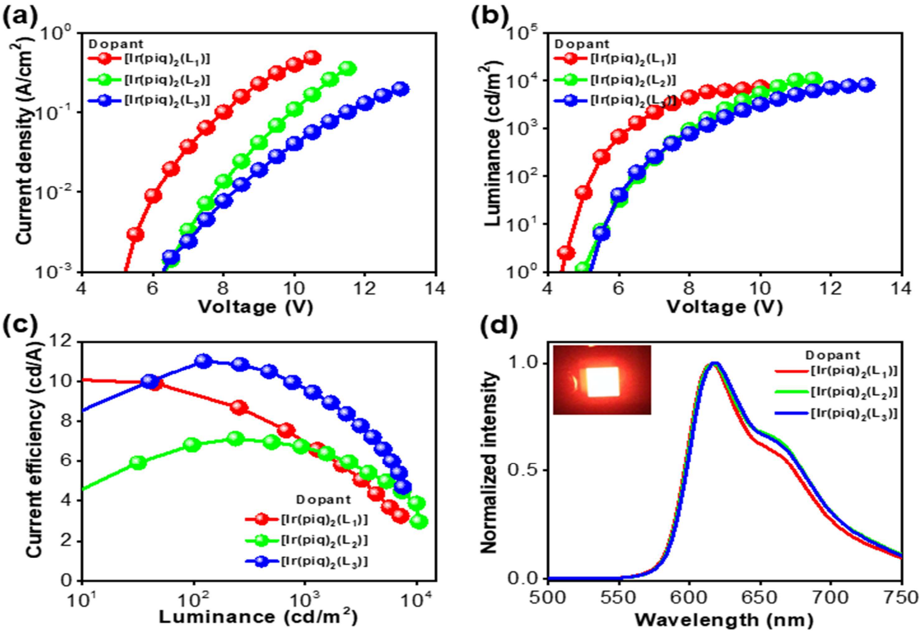


Figure 7. (a) Current density-voltage, (b) luminance-voltage, (c) current efficiency-luminance, and (d) EL spectra plots of the solution processed deep red PhOLEDs.

Table 2. Electroluminescence performances of the deep red solution processed PhOLEDs.

Dopant	**Dopant conc. (wt%)**	**PE$_{max}$ (lmW^{-1})**	**CE$_{max}$ (cdA^{-1})**	**EQE$_{max}$ (%)**	**CIE Coordinates**
Ir(piq)$_2$(L$_1$)	7.5	6.2	9.9	9.6	(0.66, 0.34)
Ir(piq)$_2$(L$_2$)	10	3.3	7.1	7.3	(0.67, 0.33)
Ir(piq)$_2$(L$_3$)	10	4.8	10.8	14.9	(0.67, 0.33)

Conclusion

In summary three new heteroleptic deep red iridium(III) phosphorescent compounds were designed with cyclometalated ligand (piq) and heterocyclic Schiff bases as ancillary ligands. All the compounds are well characterized by spectroscopy techniques. The photophysical properties of the complexes show excellent Φ_{PL} 0.44 to 0.52 and short excited-state lifetime τ (0.51-0.55 μs) due to dominant strong field ligands, L_1-L_3 resulting in efficient triplet metal-ligand charge transfer (^{3}MLCT) existed state. These results further support by the spin forbidden ^{3}MLCT bands 550-650 nm. The DFT and TD-DFT calculations strongly support the involvement of ancillary ligands in formation of FMOs and the resulting complexes offer radiative process with band gap fine tuning. These complexes show excellent thermal stability and high glass transition temperature. Highly efficient solution processed PhOLEDs were developed by using Ir(piq)$_2$(L$_1$), Ir(piq)$_2$(L$_2$), and Ir(piq)$_2$(L$_3$) as deep red emitters. Device composed of Ir(piq)$_2$(L$_3$) exhibited an excellent external quantum efficiency of 14.9% and current efficiency of 10.8 cd/A with the stable CIE coordinates of (0.67,0.33).

Acknowledgments

Authors express sincere thanks to Science and Engineering Research Board (SERB), New Delhi, India (Ref. No. SB/EMEQ-204/2014), scheme of Young Scientist &Technologist (SYST)(Ref. No.SP/YO/008/2014(G)), Department of Science and Technology (DST), New Delhi under the Technology System Group (TSG) program (Ref. No. DST/TSG/PT/2011/194-G)for the financial support. Authors are thankful to the Head, Department of Chemistry, Sardar Patel Universityfor providing basic infrastructural and instrumental facility, Saurashtra University, Rajkot for instrumental facility. Special thanks to Dr. S. S. Soni and his group for cyclic voltammetry measurements. MJPand JDS acknowledges financial support as INSPIRE fellowship (DST/INSPIRE Fellowship/2015/IF-150296) and SYST(Ref. No.SP/YO/008/2014(G))from the DST.

Conflicts of interest

There are no conflicts to declare.

References

[1] Li, T.-Y.; Wu, J.; Wu, Z.-G.; Zheng, Y.-X.; Zuo, J.-L.; Pan, Y. (2018). Rational design of phosphorescent iridium(III) complexes for emission color tunability and their applications in OLEDs. *Coord. Chem. Rev.* 374, 55.

[2] Wang, L., Zhao, Z., Wei, C., Wei, H., Liu, Z., Bian, Z., Huang, C. (2019). Review on the electroluminescence study of lanthanide complexes, *Adv. Opt. Mater.* 7, 1801256.

[3] Liu, C.-F., Liu, X., Lai, W.-Y., Huang, W. (2018). Organic light-emitting field-effect transistors: device geometries and fabrication techniques. *Adv. Mater.* 30, 1802466.

[4] Li, G, Congrave, D.G., Zhu, D., Su, Z., Bryce, M.R. (2018).Recent advances in luminescent dinucleariridium(III) complexes and their application in organic electroluminescent devices. *Polyhedron.* 140, 146.

[5] Jou, J.-H., Sahoo, S., Dubey, D.K., Yadav, R.A.K., Swayamprabha, S. S., Chavhan, S. D. (2018) Molecule-based monochromatic and polychromatic OLEDs with wet-process feasibility.*J. Mater. Chem. C.* 6, 11492.

[6] Lee, S. M., Kwon, J. H., Kwon, S., Choi, K. C. (2017). A review of flexible oleds toward highly durable unusual displays. *IEEE Trans. Electron Devices* 64, 1922.

[7] Ou, Q., Tang, J. (2016). Recent advances in light manipulation for organic light-emitting diodes, *Materials China* 35, 606.

[8] Liu, X., Yao, B., Zhang, Z., Zhao, X., Zhang, B., Wong, W. Y., Cheng, Y.,Xie, Z. (2016). Power-efficient solution-processed red organic light-emitting diodes based on an exciplex host and a novel phosphorescent iridium complex. *J. Mater. Chem. C.* 4, 5787.

[9] Fu, H., Cheng, Y.-M., Chou, P.-T., Chi, Y. (2011). Feeling blue? blue phosphors for OLEDs. *Mater. Today* 14, 472.

[10] Pereira, L. (2012). Organic light emitting diodes: the use of rare earth and transition metals. PanStandford Publisher, USA.

[11] Caspar, J. V., Meyer, T. J. (1983). Application of the energy gap law to nonradiative, excited-state decay. *J. Phys. Chem.* 87, 952.

[12] Cummings, S. D.; Eisenberg, R. (1996). Tuning the excited-state properties of platinum(ii)diiminedithiolate complexes. *J. Am. Chem. Soc.* 118, 1949.

[13] Chen, C. T. (2004). Evolution of red organic light-emitting diodes: materials and devices.*Chem. Mater.*16, 4389.

[14] Su, Y. J., Huang, H. L., Li, C. L.,Chien, C. H., Tao, Y. T., Chou, P. T., Datta, S., Liu, R. S. (2003). Highly efficient red electrophosphorescent devices based on iridium isoquinoline complexes: remarkable external quantum efficiency over a wide range of current. *Adv. Mater.*15, 884.

[15] Li, C. L., Su, Y. J., Tao, Y. T., Chou, P. T., Chien, C. H., Cheng, C. C., Liu, R. S. (2005). Yellowand red electrophosphors based on linkage isomers of phenylisoquinolinyliridium complexes: distinct differences in photophysical and electroluminescence properties. *Adv. Funct. Mater.*15, 387.

[16] Fan, C. H., Sun, P.,Su, T. H., Cheng, C. H. (2011). Host and dopant materials for idealized deep-red organic electrophosphorescence devices. *Adv. Mater.*23, 2981.

[17] Song, Y. H., Yeh, S. J., Chen, C. T., Chi, Y., Liu, C. S., Yu, J. K., Hu, Y. H., Chou, P. T., Peng, S. M., Lee, G. H. (2004). Bright and efficient, non-doped, phosphorescent organic red-light- emitting diodes. *Adv. Funct. Mater.*14, 1221.

[18] Sree, V. G., Cho, W., Shin, S., Lee, T., Gal, Y. S., Song, M.,Jin, S. H. (2017). Highly efficient solution-processed deep-red emitting heteroleptic thiophene-phenylquinoline based Ir(iii) complexes for phosphorescent organic light-emitting diodes. *Dyes and Pigments*139, 779.

[19] Bae, H. J., Chung, J., Kim, H., Park, J., Lee, K. M., Koh, T. W., Lee, Y. S., Yoo, S., Do, Y., Lee, M. H. (2014). Deep red phosphorescence of cyclometalated iridium complexes by o-carborane substitution. *Inorg. Chem.*53, 128.

[20] You, Y., An, C. G., Kim, J. J., Park, S. Y. (2007). A deep red phosphorescent Ir(iii) complex foruse in polymer light-emitting diodes: role of the arylsilyl substituents. *J. Org. Chem.* 72, 6241.

[21] Kim, D.H., Cho, N.S., Oh, H.-Y., Yang, J. H., Jeon, W. S., Park, J. S., Suh, M. C., Kwon, J. H. (2011). Highly efficient red phosphorescent dopants in organic light-emitting devices. *Adv. Mater.*23, 2721.

[22] Su, T.-H., Fan, C.-H., Ou-Yang, Y.-H., Hsu, L.-C., Cheng, C.-H. (2013). Highly efficient deep-red organic electrophosphorescent devices with excellent operational stability using bis (indoloquinoxalinyl) derivatives as the host materials. *J. Mater. Chem. C.*1, 5084.

[23] Ho, C. L., Wong, W. Y., Gao, Z. Q., Chen, C. H., Cheah, K. W., Yao, B.,Xie, Z. Y., Wang, Q., Ma, D. G., Wang, L. X., Yu, X. M., Kwok, H. S., Lin, Z.Y. (2008). Red-light-emitting iridium complexes with hole-transporting 9-arylcarbazole moieties for

electrophosphorescence efficiency/color purity trade-off optimization. *Adv. Funct. Mater.*18, 319.

[24] Niu, Z.-G., Yan, L.-P.,Wu, L.,Chen, G.-Y.,Sun, W.,Liang, X.,Zheng, Y.-X.,Li, G.-N., Zuo, J.-L. (2019). Iridium(III) complexes adopting thienylpyridine derivatives for yellow-to-deep red OLEDs with low efficiency roll-off.*Dyes and Pigments*162, 863.

[25] Li, Q., Shi, C., Huang, M.,Wei, X.,Yan, H.,Yang, C.,Yuan, A.(2019). B- and N-embedded color-tunable phosphorescent iridium complexes and B-N Lewis adducts with intriguing structural and optical changes.*Chem. Sci.* 10, 3257.

[26] Lu, K.-Y., Chou, H.-H., Hsieh, C.-H., Yang, Y.H. O., Tsai, H.- R., Tsai, H. Y., Hsu, L. C., Chen, C.-Y., Chen, I. C., Cheng, C.-H. (2011). Wide-range color tuning of iridium biscarbene complexes from blue to red by different N̂ N ligands: an alternative route for adjusting the emission colors. *Adv. Mater.*23, 4933.

[27] Li, G., Li, P., Zhuang, X., Ye, K., Liu, Y., Wang, Y. (2017) Rational design and characterization of heteroleptic phosphorescent complexes for highly efficient deep-red organic light-emitting devices. *ACS Appl. Mater. Interfaces*9, 11749.

[28] Lai, P.-N., Teets. T. S. (2019). Ancillary ligand effects on redemitting cyclometalated iridium complexes. *Chem. Eur. J.* 25, 6026.

[29] Chao, Y., Huang, S., Chen, C., Chang, Y., Meng, H., Yen, F., Lin, I., Zan, H., Horng, S. (2011). Highly efficient solution-processed red organic light-emitting diodes with long-side-chained triplet emitter. *Synth. Met.* 161, 148.

[30] Kim, H. U., Jang, J.-H., Xu, F., Lee, J. Y., Hwang, D.-H. (2016). A new iridium(III) complex as a deep-red phosphorescent emitter in organic light-emitting diodes. *J. Nanosci. Nanotechnol.* 16, 2773.

[31] Cho, W., Reddy, S.S., Kim,J., Cho, Y.-R., Jin, S.-H. (2018). All solution-processed red organic light-emitting diode based on a new thermally cross-linked heterolepticIr(III) complex. *J. Mater. Chem. C.* 6, 11714.

[32] Sree, V. G., Park, H.-Y., Gal, Y.-S., Lee, J. W., Jin, S.-H. (2018). Highly efficient deep-red emitting methyl substituted thiophenylquinoline based Ir(III) complexes for solution-processed organic light-emitting diodes. *Mol. Cryst. Liq. Cryst.*660, 1.

[33] Chang, Y.-F., Yang, L.-S., Su, H.-T., Liao, S.-Y., Niu, M.-C., Mahesh, K. P. O., Chen, C.-H, Chao, Y.-C., Meng, H.-F., Huang, H.-L., Chao, T.-C., Tseng, M.-R., Luo, C.-W., Zan, H.-W.,Horng, S.-F. (2019). Allsolutionprocessed red and orangered organic lightemitting diodes with highefficiencies: the effect of mixedhost emissive layers and thermal annealing treatment. *ChemPlusChem.*84, 1375.

[34] Kido, J., Hayase, H., Hongawa, K., Nagai, K., Okuyama, K. (1994) Bright red light□emitting organic electroluminescent devices having a europium complex as an emitter. Appl. Phys. Lett. 65, 2124.

[35] Binnemans, K. (2005) Rare-earth beta-diketonates. In Handbook of the Physics and Chemistry of Rare Earths;Gschneidner, K.A., Jr., Bünzli, J.-C.G., Pecharsky, V.K., Eds.; North Holland: Amsterdam, Holland,Elsevier, Volume 35, pp. 107–272. DOI: https://doi.org/10.1016/S0168-1273(05)35003-3.

[36] Kumar, S., Surati, K.R., Lawrence, R., Vamja, A.C., Yakunin, S., Kovalenko, M. V., Santos, E. J. G., Shih, C.-J. (2017). Design and synthesis of heterolepticIridium(III) phosphors for efficient organic light-emitting devices. *Inorg. Chem.*56, 15304.

[37] Surati, K.R., Thaker, B.T. (2010) Synthesis, spectral, crystallography and thermal investigations of novel Schiff base complexes of manganese(III) derived from heterocyclic β-diketone with aromatic and aliphatic diamine. *Spectrochim. Acta Part A*75, 235.

[38] Prajapati M. J., Surati, K.R., (2019). Aggregation induced emission (AIE) properties of heterolepticIr(III) complexes with non-chromophoric ligand effect:synthesis, characterization and photophysical investigations.*ChemistrySelect*4, 8263.

[39] Nakamoto. K. (1978). Infrared and raman spectra of inorganic and coordination compounds. 3rd Edn., John Wiley and Sons, New York.

[40] H. Yersin, H. (2007). Highly efficiency OLEDs with phosphorescent materials.Wiley-VCH Verlag GmbH & Co. KGaA.

[41] Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F.,Kwong, R.,Tsyba, I., Bortz, M., Mui, B., Bau, R., Thompson, M.E. (2001) Synthesis and characterization of phosphorescent cyclometalated iridium complexes. *Inorg. Chem.* 40, 1704.

[42] Colombo, M.G., Hauser, A., Gudel, H.U. (1994).Competition between ligand centered and charge transfer lowest excited states in bis cyclometalated Rh3+ and Ir3+ complexes. *T. Curr. Chem.*171, 143.

[43] Kim, H.U., Jang, H.J., Choi, W., Kim, M., Park, S., Park, T., Lee, J.Y., Bejoymohandas, K.S. (2019). Ancillary ligand-assisted robust deep-red emission in iridium(III) complexes for solution-processable phosphorescent OLEDs. *J. Mater. Chem. C.*7, 4143.

[44] Lai, P.-N., Brysacz, C. H., Alam, M. K., Ayoub, N. A., Gray, T. G., Bao, J., Teets, T. S. (2018). Highly efficient red-emitting biscyclometalated iridium complexes. *J. Am. Chem. Soc.* 140, 10198.

[45] Tsuboyama, A., Iwawaki, H., Furugori, M., Mukaide, T., Kamatani, J., Igawa, S., Moriyama, T., Miura, S., Takiguchi, T., Okada, S., Hoshino, M. (2003). Homoleptic cyclometalated iridium complexes with highly efficient red phosphorescence and application to organic light-emitting diode. *J. Am. Chem. Soc.* 25, 12971.

[46] Zhou, G., Wong, W.-Y., Yao, B., Xie, Z., Wang, L. (2007). Triphenylamine-dendronized pure red iridium phosphors with superior OLED efficiency/color purity trade-offs. *Angew. Chem., Int. Ed.* 46, 1149.

[47] Thaker, B. T., Surati, K. R., Oswal, S., Jadeja, R. N., Gupta, V. K. (2007). Synthesis, spectral, thermal and crystallographic investigations on oxovanadium(IV) and manganese(III) complexes derived from heterocyclic β-diketone and 2-amino ethanol. *Structural Chem.*18, 295.

[48] Thakur, D., Dubey, D. K., Yadav, R., Venkateswarulu, M., Banik, S., Jou, J. H., Ghosh, S. A (2020) Way to Clinch High Triplet Energy with Admirable Current and Power Efficiency Devoiding Outcoupling Mode for RG Phosphorescent OLED. *J. Mater. Chem. C* 8 228-239.

[49] Huang, S.F., Sun, H.Z., Shan, G.G., Wu, Y., Zhang, M., Su, Z.M. (2016). Towards an efficient blue emission cationic Ir(III) complex with azole-type ancillary ligands: a joint theoretical and experimental study. *New J. Chem.*40, 4635.

[50] Schols, S. (2011). Device architecture and materials for organic light emitting devices.Springer.

[51] Haines, P.J. (1995). Thermal method of analysis principle, application and problems.Blackie academic & professional publisher, UK.

[52] Cao, X., Hu, J., Tao, Y., Yuan, W., Jin, J., Ma, X., Zhang, X., Huang, W. (2017). Alkyl effects on the optoelectronic properties of bicarbazole/cyanobenzene hybrid host materials:

Double delayed fluorescent host/dopant systems in solution-processed OLEDs. *Dyes and Pigments* 136, 543.

[53] Kim, H. U., Sohn, S., Choi, W., Kim, M., Ryu, S. U., Park, T., Jung, S., Bejoymohandas, K. S. (2018). Substituents engineered deep-red to near-infrared phosphorescence from tris-heteroleptic iridium(III) complexes for solution processable red-NIR organic light-emitting diodes. *Journal of Materials Chemistry C* 6(39), 10640.

Highlights

- Novel deep-red heteroleptic phosphorescent iridium(III) complexes is designed and synthesized.
- High thermal stabilities, excellent photophysical and electroluminescent features of the complexes.
- The solution-processed deep-red device shows CIE of (0.67, 0.33) and EQE of 14.9%.

Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: