#### Accepted Manuscript

Title: Tuning the photophysical properties of heteroleptic Ir(III) complexes through ancillary ligand substitution: Experimental and theoretical investigation

Authors: Aravind Babu Kajjam, V. Sivakumar



PII:	S1010-6030(17)31208-X
DOI:	https://doi.org/10.1016/j.jphotochem.2017.09.054
Reference:	JPC 10901
To appear in:	Journal of Photochemistry and Photobiology A: Chemistry
Received date:	17-8-2017
Revised date:	21-9-2017
Accepted date:	23-9-2017

Please cite this article as: Aravind Babu Kajjam, V.Sivakumar, Tuning the photophysical properties of heteroleptic Ir(III) complexes through ancillary ligand substitution: Experimental and theoretical investigation, Journal of Photochemistry and Photobiology A: Chemistry https://doi.org/10.1016/j.jphotochem.2017.09.054

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Tuning the photophysical properties of heteroleptic Ir(III) complexes through ancillary ligand substitution: Experimental and theoretical investigation.

Aravind Babu Kajjam, and V. Sivakumar\*

Optoelectronics laboratory, Department of Chemistry, National Institute of Technology, Rourkela, India.

\* To whom correspondence should be addressed. Email: vsiva@nitrkl.ac.in (V. Sivakumar)

Tel: +91-661-2462654;

#### **Graphical abstract**



#### **Highlights:**

• Successfully synthesised three phosphorescent heteroleptic Ir(III) complexes with three different auxiliary ligands.

- Photophysical and electrochemical properties of Ir(III) complexes were studied and verified by DFT analysis.
- Among all the Ir(III) complexes Ben-Ir-acac complex shows yellow emission with high PLQY (0.29).
- From the DFT analysis, compare to all Ir(III) complexes Ben-Ir-acac acts a potential emitter for OLED applications.

#### Abstract:

A series of new phosphorescent heteroleptic Iridium(III) complexes with 2-phenylpyridine, acetylacetone and 2-picolinic acid as ancillary ligands have been designed and synthesized. The photophysical and electrochemical properties have been investigated experimentally and theoretically. The UV-Visible absorption and photoluminescence (PL) emission spectra of the complexes were carried out in solution as well as thin film. The PL study indicates that the Iridium complexes show broadband emission ranging from green to yellowish-green in solution and greenish-yellow to yellow emission in PMMA films with appropriate CIE color gamut. The PLQY of the complexes were found to be in the range of 0.12 - 0.29. Singlet and triplet energy levels were calculated by using time dependent DFT (TD-DFT) calculations. The excited triplet energy was estimated and correlated to structural and energetic characteristics of the reported host materials. Further, investigations have been performed to explore the optical, electronic, charge transport, and stability properties of Ir(III) complexes as charge transport and emissive materials for organic light emitting devices (OLEDs). Furthermore, all the complexes are promising luminescent and its hole transporting performance is more favorable than electron transport performances. According to theoretical

calculations, it is clearly indicating that, Ben-Ir-acac complex is a more potential emitter for OLED applications.

Keywords: Benzil/ ppy/ acac/ pic/ Ir(III) metal ion/ DFT.

#### Introduction:

Luminescent metal complexes have great attention in the field of different application like optoelectronics, photochemistry, biological applications and chemo sensors, etc. [1] The phosphorescent transition metal complexes have revolutionized the field of optoelectronics due to the advantages they possess over the other alternative emissive materials [2]. In particular, the second and third row transition metals with d<sup>6</sup> configuration have been extensively studied due to the spectroscopic and photophysical properties they exhibit that can be conveniently modified according to the desired objective [3]. Due to the mixing of singlet and triplet energy levels in these complexes, theoretically it is predicted that they provide 100% internal quantum efficiencies unlike the case in fluorescent metal complexes [4-5]. Among them, the cyclometalated Iridium (III) complexes show high phosphorescent efficiencies and relatively short lifetimes and are thus considered one of the most promising candidates as emissive materials for phosphorescent OLEDs [6-9]. Hence in recent years, a significant amount of work is being carried out on the development of cyclometalated ( $C^{\Lambda}N$ ) Ir(III) complexes. The efficiency, brightness and emission wavelengths of Iridium(III) complexes depend strongly on the structure of the cyclometalated ligand [10]. The emission

wavelength of the Ir(III) complexes can be normally tuned by changing the electronic nature and the position of the substituents on the ligands [11]. Several groups have demonstrated the tuning of photoluminescence emission wavelength from blue to red by appropriate functionalization of the electron withdrawing and electron donating substituents in the ligand structure [12–14].

Previous works have shown that the highest occupied molecular orbitals (HOMOs) are located on the phenyl groups of the cyclometalating ligands and the 5d orbitals of the Ir(III) ion, whereas the lowest unoccupied molecular orbitals (LUMOs) are found on the ancillary ligands [15-20]. Hence an emission shift from blue to greenish-yellow can be obtained by stabilizing the HOMO or destabilizing the LUMO levels [21]. A large number of Iridium complexes were found conducive to this desired target which are mostly based on the cyclometalating ligand 2-phenylpyridine (ppy) with ancillary ligands such as acetylacetonate (acac) or picolinate (pic) [22 - 29].

T. Fei *et al.*, reported Phenylpyrazole based iridium(III) complexes, Ir(ppz)<sub>3</sub>, that show deep blue emission at 77 K in CH<sub>2</sub>Cl<sub>2</sub> but a quite poor emission at room temperature [12a,30a]. Their picolinate complex (Ir(ppz)<sub>2</sub>(pic)) and acetylacetonate complex (Ir(ppz)<sub>2</sub>(acac)), have shown a relatively stronger green emission (507 and 514 nm) at room temperature [30b]. The advances in technology simulataneously led to raised concern over the environmental issues which perturbed the energy conservation and the utilization of depleting natural resources. This demanded energy efficient lighting systems (solid state lighting (SSL), which include white OLEDs), that can help to conserve energy and reduce the overall lighting costs. In this scenario, white OLEDs are considered as potential candidates for future solid-state lighting applications and backplane illumination in large-area smart displays. One of the general approaches in obtaining white light involves the combination of blue and orange-red or yellow emitters in the active layer [31]. Till date a lot of blue emitting Ir(III) complexes were

explored for white OLEDs [32] however, the complimentary yellow emitting Ir(III) complexes are scarcely reported. The design and synthesis of novel yellow emitting Ir(III) complexes is considered as an active research area in the field of white OLEDs. Our group has perpetuated the work by developing a series of heteroleptic Ir(III) complexes with benzilimidazole as cyclometalating ligand and three commonly used ancillary ligands (acetylacetonate ( $O^{\Lambda}O$ ), picolinate ( $O^{\Lambda}N$ ) and phenyl pyridine ( $C^{\Lambda}N$ ) (Fig. 1). We found that the alterations in the ancillary ligands in the complex had a note-worthy impact on the electronic and phosphorescent properties (as well as emission color tuning). These results provide a well-defined pathway to use the ancillary ligand modification in controlling the phosphorescence emission in Ir-based emitters and offer a powerful tool in the design of the emitter architecture. Herein, we report the systematic design, synthesis, and characterization of green/yellow-emitting Ir(III) benzilimidazole complexes through the variation of ancillary ligands. The emission peak wavelength can be fine-tuned in greenish-yellow range (over the 540-555 nm range in solution and 530-560 nm range in PMMA films). All the complexes exhibited high photoluminescence quantum efficiency (PLQE). The HOMO and LUMO energy levels are calculated by using cyclic voltammetry analysis and the values are verified by using B3LYP method, 6-31G(d) basis set for ligands and LANL2DZ basis set for an Iridium atom. In addition, we have explored the possibility of using the currently synthesized Ir(III) complexes for OLED as an emitters or host materials. We have calculated the other electronic properties, such as ionization potentials (IPs), electronic affinities (EAs) and reorganization energy (\lambda hole/electron) to shed light on the photophysical properties. And also, we report the investigation of both host-guest interaction and signaling properties from theoretical point of view for these Ir(III) complexes. Further in-depth interpretations of the available reported electron and hole transporting materials electronic characteristics have been discussed by the investigation of the optical and electronic properties of this system.

Furthermore, quantum-chemical studies of the auxiliary ligand effect on the electronic and optical properties of these systems are also studied.

#### **Experimental:**

<sup>1</sup>H NMR and <sup>13</sup>C NMRspectra were measured on a BRUKER AV 400 Avance-III (400MHz) in CDCl<sub>3</sub> using tetramethylsilane as an internal reference. UV–Vis absorption spectra were recorded using a Shimadzu UV-2450 spectrophotometer. Emission spectra were measured on a Horiba Jobin Yvon, Fluoromax 4P fluorescence spectrophotometer. Lifetime measurements are measured in DCM solution at 298K with Edinburgh instruments FLS 980 and pulsed xenon lamp was used as excitation source. Cyclic voltammetry studies were performed with a computer-controlled EG&G potentiostat/galvanostat Metrohm model in a one-compartment electrolysis cell consisting of a platinum bottom working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. Cyclic voltammograms were monitored at a scan rate of 100 mV/ s and recorded in dimethylformamide. The concentration of the complex was maintained at 1.0 mM and each solution contained 0.1 M of tetrabutylammonium perchlorate (TBAP) as the electrolyte. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy level were calculated by assuming the energy level of ferrocene/ferrocenium to be 4.4 eV.

#### **Computational Methods:**

**Molecular orbital calculations:** The ground and low-lying excited electronic states of Ir(III) complexes were calculated using the Gaussian 09 and 03 program package. For the calculated ground state geometries, the electronic structure is examined in terms of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). Based on Becke-LeeYoung-Parr composite exchange-correlation functional (B3LYP) method with the 6–31G(d) basis set were used for the geometry optimization and the energy level

calculation of the ground state of those ligands, respectively [33]. Calculations on the electronic ground states of the Ir(III) complexes have been carried out using the same calculation method except LANL2DZ basis set for an Ir atom. The electronic populations on the central atom were calculated to show the significant admixture of ligand  $\pi$  character with the amount of iridium 5d character in the occupied molecular orbitals related to those MLCT transitions. The UV-visible spectra, singlet and triplet energy levels were calculated by using TD-DFT calculations [34]. In addition to these, other electronic properties, such as ionization potentials (IPs), electronic affinities (EAs) and reorganization energy ( $\lambda$ hole/electron) were also calculated to shed light on the photophysical properties of these Ir(III) complexes. All calculations were carried out using Gaussian09 and Gauss View 05 suite of programs.

Synthesis: General procedure for the synthesis of benzillimidazole ligand: [35] A mixture of benzil (1gm, 4.75mmol, 1 eq), benzaldehyde (0.555 gm, 5.23 mmol, 1.1 eq), ammonium acetate (3.65 gm, 47.5 mmol, 10 eq) and aniline (0.442 gm, 4.756 mmol, 1eq) in the presence of glacial acetic acid (20 mL) were heated up to 120 - 130 <sup>o</sup>C for 12 hrs under N<sub>2</sub> atmosphere in a round bottomed flask equipped with a reflux condenser. After cooling to room temperature, the reaction mixture was poured into distilled water with continuous stirring. The separated solid was filtered off and washed with water. The obtained solid was dried to give expected product with good yield 95%). <sup>1</sup>H – NMR data (CDCl<sub>3</sub>, 400 MHz):  $\delta = (7.48 - 7.50 \text{ (d, 2H)}, 7.202 - 7.359 \text{ (m, 18 H)}. ^{13}C-NMR Data (CDCl<sub>3</sub>, 100MHz): <math>\delta = 126.6, 127.42, 127.95, 128.10, 128.25, 128.35, 128.97, 129.06.6, 130.53, 130.65, 130.86, 131.13, 134.44, 137.11, 138.29, 146.94 ppm.$ 

General procedure for the synthesis of the iridium complexes: All synthetic procedures involving  $IrCl_3 \cdot 3H_2O$  and other Ir(III) species were carried out in inert gas atmosphere despite the air stability of the compounds, the main concern being the oxidative stability of

intermediate complexes at the high temperatures used in the reactions [36a]. Cyclometalated Ir(III)-chloro-bridged dimers of general formula  $(C^{\Lambda}N)_2Ir(\mu-Cl)_2Ir(C^{\Lambda}N)_2$ , where  $C^{\Lambda}N$  represents the cyclometalated ligand, were synthesized by the same method reported by Nonoyama [36]. The crude products of these dimers were used for the subsequent preparation of  $(C^{\Lambda}N)_2Ir(C^{\Lambda}X)$ ,  $C^{\Lambda}X$  represents the ancillary ligand.

Cyclometalated Ir(III)-chloro-bridged dimers [(Ben)<sub>2</sub>IrCl]<sub>2</sub> were synthesized according to the Nonoyama route [36a], A mixture of benzilimidazole ligand (100 mg, 0.27 mmol), Iridium chloride trihydrate (47 mg, 0.135 mmol), 2 – ethoxyethanol (6 mL), water (2mL) were refluxed under nitrogen for 24 hrs. The precipitate was collected by filtration, washed with water and methanol, and dried. A mixture of chloro-bridged dimer, 0.125 mL (1.2 mmol) of 2,4-pentanedione, and 0.322 g (3.0 mmol) of sodium carbonate was refluxed under a nitrogen atmosphere in 10 mL of 2-ethoxyethanol for 12 h. After the reaction mixture was cooled to room temperature, the mixture was poured into water for extraction with dichloromethane. The organic extracts were collected by using column chromatography (yield 35%). The NMR spectra of the synthesized Ir(III) complexes were mentioned in supplementary information.

**Ben-Ir-ppy:** <sup>1</sup>H – NMR data (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.32$  (d, 2H), 8.30 (d, 2H), 7.89 – 7.99 (d, 4H) 7.79 – 7.88 (m, 10H), 7.69 (d, 6H), 7.66 - 7.67 (m, 8H), 7.50 – 7.58 (m, 8H), 7.33 – 7.34 (m, 6H). <sup>13</sup>C NMR data (100MHz, CDCl<sub>3</sub>):  $\delta = 149.18$ , 146.45, 137.77, 136.57, 136.31, 133.92, 130.62, 130.36, 130.11, 129.99, 129.18, 128.58, 128.48, 128.27, 127.93, 127.85, 127.77, 127.68, 127.68, 127.62, 127.47, 126.93, 126.44, 126.13, 121.64, 120.14. (CHNS): Anal. calcd for C<sub>68</sub>H<sub>46</sub>IrN<sub>8</sub>:C, 69.96; H, 3.97; N, 9.60 Found: C, 69.51; H, 3.89; N, 9.54.

Ben-Ir-pic: <sup>1</sup>H-NMR Data (CdCl<sub>3</sub>, 400MHz): δ = 8.02 (d, 4H), 7.72 – 7.76 (m, 5H), 7.61 (d, 7H), 7.50 – 7.51 (m, 5H), 7.30 – 7.48 (m, 8H), 7.13 – 7.21 (d, 6H), 7.05 – 7.10 (d, 2H), 6.82
- 6.92 (m, 5H). <sup>13</sup>C-NMR Data (CdCl<sub>3</sub>, 100MHz): δ = 169.45, 146.45, 137.77, 136.59,

8

133.92, 130.84, 130.62, 130.36, 130.13, 130.01, 129.72, 129.48, 128.56, 128.48, 128.56, 128.48, 128.48, 127.94, 127.85, 127.76, 127.66, 127.60, 127.46, 127.22, 126.93, 126.11. (CHNS): Anal. calcd for C<sub>61</sub>H<sub>42</sub>IrN<sub>8</sub>: C, 65.93; H, 3.81; N, 10.08. Found: C, 65.99; H, 3.79; N, 10.18.

**Ben-Ir-acac:** <sup>1</sup>H – NMR data (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.98$  (d, 4H), 7.87 (d, 3H), 7.74 – 7.73 (m, 2H), 7.58-7.68 (m, 5H), 7.65 (d, 3H), 7.54 (t, 3H), 7.50 – 7.52 (m, 6H), 7.41-7.49 (m, 6H), 7.25-7.27 (d, 2H), 6.85 – 6.92 (m, 5H), 5.24 (s, 1H), 2.33 (s, 6H). <sup>13</sup>C NMR data (100MHz, CDCl<sub>3</sub>-d6):  $\delta = 150.00$ , 147.45, 146.76, 137.71, 137.66, 131.12, 130.15, 129.35, 128.99, 128.93, 128.83, 128.75, 128.25, 128.19, 127.82, 127.34, 126.61, 126.42, 126.34, 125.98, 125.69, 124.92, 124.45, 123.52, 123.35, 122.91, 121.58, 120.20, 118.06, 60.85, 28.25. (CHNS): Anal. calcd for C<sub>61</sub>H<sub>48</sub>IrN<sub>5</sub>O<sub>3</sub>: C, 67.14; H, 4.43; N, 6.42; Found: C, 67.03; H, 4.29; N, 6.12.

#### **Results and discussion:**

#### **Photophysical properties:**

The UV–Vis absorption spectra of the heteroleptic Ir-complexes are shown in Fig. 2. The major absorptions observed at 220-320 were appear to be  $\pi$ - $\pi$ \* absorptions of aromatic moiety present in the ligand and the absorption at 330-475 nm can be assigned to singlet metal-to-ligand charge transfer (<sup>1</sup>MLCT) band and triplet metal-to-ligand charge transfer (<sup>3</sup>MLCT) band, respectively. In general, the absorption and excitation spectrum should be similar. However, in the presently studied complexes, we have observed the intensity difference in the organic ligand absorption as well as metal ligand charge transfer spectral range. In the excitation spectra it is clearly showing that, the  $\pi$ - $\pi$ \* excited states are non-emissive, whereas the MLCT is emissive. From the DRS spectra of the PMMA films showed (Fig. S10) that, the band gap from the DRS spectra of the Ir(III) complexes are 2.50 eV for Ben-Ir-acac, 2.52 eV for Ben-Ir-pic and 2.88 eV for Ben-Ir-ppy. Fig. 3 shows the

photoluminescence (PL) spectrum of the Ir-complex in 10<sup>-4</sup> M CH<sub>2</sub>Cl<sub>2</sub> solution and PMMA films. The Ir- complexes shows strong photoluminescence at 533- 561 nm, which is much red shifted from that of the free ligand (at 462 nm). As the change in ancillary ligand from ppy to pic the luminescence is shifted towards higher spectral region (red-shift), which could be attributed due to the alteration in the electronic structure of the ancillary ligand and formation of aggregates in the PMMA matrix and strong intermolecular interactions are present in the PMMA matrix [37]. The changes in the PL spectrum of the complexes (spectral data's) are tabulated in Table 1. The low-energy MLCT band in Ben-It-acac complex (542 nm) is significantly red-shifted compared to that of Ben-Ir-ppy and Ben-Ir-pic complexes (Fig. 3). The Ben-Ir-ppy emits green light with a maximum peak at 523 nm, whereas the Ben-Ir-pic emits greenish yellow light with a maximum peak at 534 nm (Fig. 3) which is in good consistency with their absorption spectra. The small Stokes shift between emission signal and the lowest energy absorption band in the Iridium complexes, in combination with a structure less spectral feature, suggest that the phosphorescence originates primarily from the <sup>3</sup>MLCT state, together perhaps with a lesser contribution from the  ${}^{3}\pi - \pi *$  excited states. Similarly, compared with Ben-Ir-acac, Ben-Ir-pic also shows a ~10 nm blue-shift of the emission band. The results imply that the orientation of  $\pi$  conjugation would exert a large effect on the photophysical properties of the phosphorescent Ir (III) complexes. Compared to the complexes Ir(ppz)<sub>2</sub>(pic) and Ir(ppz)<sub>2</sub>(acac), the synthesized complexes show emission towards red and have high PLQY [33a, b]. It clearly indicates that the modification of an ancillary ligand is certainly followed by the change in emission spectra. Compared to emission in the solution, emissions with a small red shift were observed (in PMMA films) in the case of Ben-Ir-ppy to Ben-Ir-pic. By changing the auxiliary ligand from pic (Ben-Ir-pic) complex to acac (Ben-Ir-acac) there is a bathochromic shift (~20 nm) in PMMA films. Similar observations were also been reported by Yafei Wang et al., in Ir(III) complexes with

pic and acac as auxiliary ligands [33c]. The emission values of the PMMA films were shown in table 1.

#### Photoluminescence Quantum yield calculations:

Quantum yields of the Ir(III) complexes were calculated by using  $Ir(ppy)_3$  (PLQY=0.97) as standard according to equation 1 [38].

I (sample) and I' (standard) are the integrated emission peak areas, A (sample) and A' (standard) are the absorbance at the excitation wavelength, and n (sample) and n' (standard) are the refractive indices of the solvents. Based on the above equation, the PLQY of the heteroleptic Ir(III) complexes were calculated and corresponding values are mentioned in Table. 1. The observed quantum yields for the synthesized Ir complexes in solution and PMMA films in the range of 0.12 - 0.29 and 0.15-0.28, respectively.

#### Lifetime measurements:

Lifetime decay curve analysis of Iridium(III) complexes are shown in the Figure 4. The measured data was fitted with the bi-exponential function given by below equation. [39a,b]

$$(\tau) = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$$

Where, ( $\tau$ ) is the mean lifetimes,  $\tau_1$ ,  $\tau_2$  are short- and long decay components, and A<sub>1</sub>, A<sub>2</sub> are weight factors, respectively. Compared to the well know Ir complex (FIrpic, 1.69 µs) [39c], all the novel Ir(III) complexes have shown slightly higher decay times. The luminescent decay time values ( $\tau$ ) of Ben-Ir-ppy, Ben-Ir-pic and Ben-Ir-acac were found to be 1.48, 1.76 and 1.82 µs, respectively.

**Electrochemical properties:** The HOMO and LUMO energy levels were calculated by using equation reported by de Leeuw *et al* [40].

$$E_{HOMO} = -(E_{onset \rightarrow SCE}^{Oxi} + 4.4) \text{ eV}$$
$$E_{LUMO} = -(E_{onset \rightarrow SCE}^{Red} + 4.4) \text{ eV}$$

Cyclic voltammetry (CV) was employed to investigate the electrochemical behavior of the iridium complexes. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the materials were estimated according to the electrochemical performance. As shown in Fig.5, the oxidation potential was measured relative to a ferrocenium/ferrocene reference (Fc<sup>+</sup>/Fc). The HOMO energy values for these Iridium complexes were calculated based on the value of -4.4 eV for Fc with respect to zero vacuum level. The electrochemical data and energy levels of the complexes are summarized in Table 2. The oxidation of the three substituted heteroleptic Ir(III) complexes (ben-Ir-ppy, Ben-Ir-pic and Ben-Ir-acac) are generally chemically irreversible and appear at more positive potentials (1.25, 1.30 and 1.45 V). The irreversibility in such cases is generally attributed to the susceptibility of the electrogenerated Ir(III) species to nucleophilic attack by the solvent. Thus, the chemical reversibility in the present instance, as well as the substantially lower potential of the oxidation, suggests that the resulting charge may be more delocalized over the cyclo-metallating ligand than in the auxiliary ligands. The reduction irreversibility of Ir(III) complexes might be attributed to the ancillary ligand environment [41]. The HOMO-LUMO level of these Ir (III) complexes is also affected by the ancillary ligand. This was revealed by the fact that substitution of the acac ligand by the ppy ligand markedly raised the LUMO energy from -2.87 eV of Ben-Ir-ppy to -3.04 eV of Ben-Ir-pic, while the replacement of ppy ligand with pic led to a shift from -2.87 eV to -3.06 eV was observed. It should be noted that major changes at the HOMO were also observed i.e, when replacement of ppy ligand with pic ligand the shifting was observed from -5.85 eV to -5.70 eV, while in

the case of ppy to acac the shifting was observed from -5.85 eV to -5.65 eV. It is concluded that, by changing the auxiliary ligand there is a affect in the HOMO and LUMO levels were absorbed.

#### **DFT analysis:**

The optimized structures of the synthesized Ir(III) complexes (Ben-Ir-acac, Ben-Ir-ppy and Ben-Ir-pic) are depicted in Fig.6. All the Ir(III) complexes are coordinated with two primary ligands (Benzilimidazole) and one ancillary ligand (acac/ppy/pic). The representation structures of the Ir(III) complexes are shown in Fig. S9 along with the numbering of some key atoms. The lowest lying ground state (S0) energy levels were calculated to observe the changes in the geometry structures upon excitation, and the corresponding values are enumerated in Table 4. The results indicating that, there is no much deviation on bond distances around Ir(III) atoms by introduction of different substitutions on the primary ligands. In addition, for all the three complexes, the bond lengths of  $Ir-N_1/N_2$  are about 0.02– 0.06 Å longer than that of  $Ir-C_1/C_2$ , which is due to the different features of the N and C atoms. There is a possibility to form a Ir-N coordination bond through a pair of electrons from N (lone-pair of electrons for the hybrid N atom) entering the unoccupied orbit of the Ir(III) ion, whereas the Ir-C bond is formed by sharing electrons because of the absence of the lone-pair of electrons for the hybrid C atom [42]. The shorter distances indicate a stronger interaction between the benzilimidazole rings and the metal center. Moreover, both the benzilimidazole ligands are almost perpendicular to the ancillary ligand with the bond angles of N<sub>1</sub>-Ir-N<sub>1</sub> and N<sub>2</sub>-Ir-N<sub>1</sub> being 78°-79° and 79°-80°, respectively. To explore the influence of different ancillary ligands on the electronic structures especially for the FMOs (Frontier Molecular Orbitals), the contour plots of the FMOs and energy levels for all complexes are shown in Table 5. The HOMOs of all complexes present similar features which are principally localized on the Ir(III) d-orbital and and the relatively electron rich phenyl group

of the cyclometalated ligand. In addition, the LUMOs primarily distribute over the the Nheterocyclic part of the cyclometalated ligand and the ancillary ligand. Based on the HOMO, LUMO energy level band gap was calculated and tabulated in table 3.

#### **Absorption spectra:**

To provide a suitable inference on the electronic transition properties of the Ir(III) complexes has been done by using TD-DFT. The absorption process were performed by TD-DFT calculations with PCM in gas phase with the basis of the optimized ground-state geometry (Fig. 8). The absorption spectra of the theoretical DFT functional with the same basis set 6-31G(d)-LANL2DZ, i.e., TD-B3LYP were employed to perform the calculations for the three heteroleptic Ir(III) complexes, whose corresponding experimental values are shown in Table.1. For all the three complexes, the experimental absorption spectra show intense absorption bands around 320 - 400 nm and an obscure long absorption band at 400 - 475 nm. Neither the band shape nor the position obtained at the TD-B3LYP level agrees well with the experimental results. According to Kasha's rule (photoluminescence (PL) occurs from the lowest relaxed excited state) and due to spin orbit coupling (heavy metal ion effect), all the excited energies in the higher excited levels of the heavy metal complexes tend to reach  $T_1$ state through internal conversion (IC) or intersystem crossing (ISC), thus, it is reasonable to investigate only the T<sub>1</sub> excited state here. The obtained corresponding singlet and triplet energy levels are tabulated in Table. 3. By changing the ppy ligand with pic ligand there is a red shift was observed from 379 to 392 nm. Simultaneously, compared with Ben-Ir-pic complex with Ben-Ir-acac, there is a red shift observed from 392 - 399 nm which suggests that, the substitution of the ancillary ligand can influence the absorption properties of synthesized Ir(III) complexes. The vertical transitions, their oscillator strengths and configurations of the heteroleptic Ir(III) complexes are tabulated in table 6.

<sup>a</sup>Orbital contributions below 10% are omitted.

#### **Charge transport properties:**

The balance between charge injection and transfer character of molecules is very important in deciding the electronic properties of OLEDs [43]. Thus, it is necessary to evaluate the energy barrier for the hole and electron injection and transfer mobility. Ionization potential (IP) and electron affinity (EA) can be used to evaluate the energy barrier for hole and electron injections [44]. In general lower IP (large EA) value suggests an easy injection of holes (electrons).

To evaluate the charge transfer rate and balance properties, the reorganization energy ( $\lambda$ ) is estimated for all the synthesized Ir(III) complexes. A small  $\lambda$  value is essential for an efficient charge transport process. Generally, the  $\lambda$  for hole and electron transfers can be simply defined by the following eqs 1 and 2 and is schematically presented in Scheme 3.

$$\lambda_{hole} = [E^{+}(M)] - E(M)] + [E^{+}(M^{+}) - E(M^{+})] \text{ or } [\lambda_{1} + \lambda_{2}] = IP_{v} - HEP \dots (1)$$

$$\lambda_{\text{electron}} = [E(M^{-})] - E^{-}(M^{-})] + [E(M) - E^{-}(M)] \text{ or } [\lambda_{3} + \lambda_{4}] = EEP - EA_{v} \dots (2)$$

where E,  $E^+$ , and  $E^-$  represent the energies of the neutral, cation, and anion species, respectively, and M, M<sup>+</sup>, and M<sup>-</sup> denote the optimized geometries of neutral, cation, and anion, respectively. HEP and EEP are hole and electron extraction potentials, respectively. Here the HEP and EEP are the expressions of IP and EA, respectively. HEP is the energy

difference from M<sup>+</sup>(cationic) to M (neutral molecule), using M<sup>+</sup> geometric structure in the calculation and EEP is the energy difference from M<sup>-</sup>(anionic) to M, using M<sup>-</sup> geometric structure in calculation. E(M) and E<sup>+</sup>(M<sup>+</sup>) represent the energies of the neutral and cation species in their lowest energy geometries respectively, while E(M<sup>+</sup>) and E<sup>+</sup>(M) represent the energies of the cation and neutral species, respectively. In the table 7, the calculated IP<sub>v</sub> values increase in the following order: Ir-Ben-ppy<Ir-Ben-acac<Ir-Ben-pic. For all the complexes, the reorganization energies of hole transport ( $\lambda_{hole}$ ) are lower than those for electron transport ( $\lambda_{electron}$ ), which reveals that the hole transport performance of these complexes is slightly better than the electron transport ability. Moreover, when the acac group introduced is in the complex, the imbalances between  $\lambda_{hole}$  and  $\lambda_{electron}$  for Ben-Ir-acac are smaller than the remaining complexes, demonstrating that the performance of the OLED device is more affected on substituted ligand. In addition, the  $\Delta\lambda$  of Ben-Ir-acac is the smallest one among the other Ir(III) complexes, revealing that Ben-Ir-acac is a more potential emitter for OLED applications.

#### **Comparison of performance in OLEDs:**

The investigation on the matching relationship between the guest and host materials is an important subject for research on the efficiency of OLED devices. We have taken CPB, TCTA and TPBI host materials to compare the efficiency of our studied complexes [45]. TCTA is a typical hole transport (HT) host material and TPBI is mostly used as an electron transport (ET) type host in a mixed host system or a double emissive layer. As seen from Fig. 5, the triplet energies of the three complexes acting as guest materials (phosphorescent dopant) in the OLED devices are smaller than those of the host materials. To achieve efficient electrophosphorescence, the host should also have the high triplet energies than those of the

guest emitters, so that the triplet excitons confine in the emissive layer. It will also prevent the reverse energy transfer from the guest back to the host. Based on the results obtained from the calculations, the triplet energy levels of the complexes are in the range of 2.37-2.62 eV. Thus CBP can be proposed as the best host material for the synthesized Ir(III) complexes.

According to the Marcus theory, Dexter energy transfer plays a important role in obtaining triplet excitons for the guest materials, and the consistent transfer rate is usually associated with the changes of Gibbs free energy ( $\Delta G^0$ ) [45]. When the values of  $\Delta G^0$  approach 0, the corresponding electron-transfer rates were reaches to their highest values, whereas when the values approaches far from 0, then Dexter energy transfer velocities will be very slow. Here,  $\Delta G^0$  can be considered as the triplet energy difference between the host and guest materials [46]. Furthermore, large free energy changes can help the exciton confinement. If  $\Delta G^0 \ll 0$ , the triplets can be strongly confined on the guest material, whereas if  $\Delta G^0 \gg 0$ , triplet excitons will be strongly confined on the host material. And in the latter case, the studied systems need to have a long host lifetime in order to achieve high electroluminescent quantum efficiency [46]. Based on the theoretical results, the triplet energy levels of the host and guest are calculated and shown in Fig. 9.

Fig. 9, shows that all the synthesized complexes acting as guest materials in the OLED devices having lower triplet energies than CBP host material. It clearly demonstrates that, Dexter energy transfer from the host to the guest has taken place for the synthesized Ir(III) complexes. On comparing with FIrpic ( $E_T$ =2.82 eV) [47], all the Ir(III) complexes increases the values of  $\Delta G^0$ , which indicates that the triplet excitons can be more confined on the guest materials.

#### **Stability properties:**

Stability is a useful criterion to evaluate the nature of devices for charge transport and luminescent materials. To predict the stability of the Ir(III) complexes from a viewpoint of molecular orbital theory, the absolute hardness  $\eta$  of Ir(III) complexes were calculated using the operational definitions [48] given by:

$$\eta = \frac{1}{2} \left[ \frac{\delta \mu}{\delta N} \right] = \left[ \frac{\delta \mu}{\delta N} \right] \left[ \frac{\delta^2 \mu}{\delta N^2} \right] = \frac{\text{IP} - \text{EA}}{2}$$

Where  $\mu$  is the chemical potential and N is the total electron number. In this work, the values for IP (ionization potential) and EA (electron affinity) were determined according to the equation 1 and 2. The absolute hardness  $\eta$  is the resistance of the chemical potential to change in the number of electrons. The results displayed in Table 7 reveals that the  $\eta$  values of all Ir(III) complexes in the range of Ir(III) complexes are 2.64-3.12.

#### **CIE color coordinates:**

CIE chromaticity coordinates were calculated for Ir(III) complexes from emission spectral data of solution as well as PMMA films. The calculated the CIE coordinates for the complexes are shown in Fig.10 and the corresponding x, y values are tabulated in Table 8. Based on this data, the Ben-Ir-ppy and Ben-Ir-pic complexes shows greenish emission and the Ben-Ir-acac shows greenish-yellow emission (0.370, 0.574) in solution but in the case of PMMA films the emission of Ben-Ir-ppy and Ben-Ir-pic was in greenish-yellow, Ben-Ir-acac shows yellow emission (0.450, 0.540). Based on the CIE values we can conclude that, the complexes are showing green to greenish-yellow emission in the CIE gamut color space in three phases and close to NTSC (National Television System Committee) standards.

#### **Conclusion:**

In summary, we have reported the synthesis, photophysical and electrochemical properties of three novel heteroleptic Ir(III) complexes with benzilimidazole as cyclometalated ligands and ppy, acac and pic as ancillary ligands. All the complexes have shown broad emission with PLQYs in the range of 0.125-0.291 in CH<sub>2</sub>Cl<sub>2</sub> and PMMA films at 298 K. We have calculated the HOMO-LUMO energy levels by using cyclic voltammetry and further they were correlated with DFT analysis. The electron densities of the frontier molecular orbital distributions are also influenced by different auxiliary ligand substitutions of these complexes and hence their effect on the phosphorescent properties and OLED performance was studied through theoretical calculations. The obtained results suggest the effect of different auxiliary ligands on the electron density distributions, the phosphorescent properties and the OLED performance. Besides, Ben-Ir-acac is superior to other Ir(III) complexes in view of the charge balance and its excellent hole trapping and hole injection capability through Dexter energy The results from theoretical calculations reveal that, there is a well transfer rate. interpretation on structure property relationships and matching rules between host and guest materials in OLED devices. Hence, these Ir(III) complexes can be used as hole transport materials for OLEDs. And further, it clearly indicates that, Ben-Ir-acac complex is a more potential emitter for OLED applications.

#### **Acknowledgements:**

This work is funded by the Department of Science and Technology (DST), Government of India (SERB/F/4895/2012-13 and INSPIRE award no IFA12-CH-48).

#### **References:**

 a) Chenfu Liu, Chao Yang, Lihua Lu, Wanhe Wang, Weihong Tan, Chung-Hang Leung and Dik-Lung Ma, *Chem. Commun.*, 2017, 53, 2822. b) Holger Braunschweig, Theresa Dellermann, Rian D. Dewhurst, Benjamin Hupp, Thomas Kramer, James D. Mattock, Jan Mies, Ashwini K. Phukan, Andreas Steffen, and Alfredo Vargas, *J. Am. Chem. Soc.* 2017, 139, 4887–4893. c) Minhee Lee, Niko G. Gubernator, David Sulzer and Dalibor Sames, *J. Am. Chem. Soc.*, 2010, 132 (26), 8828–8830. d) Dik-Lung Ma, Sheng Lin, Wanhe Wang, Chao Yang and Chung-Hang Leung, *Chem. Sci.*, 2017, 8,878.

[2] a) Baldo, M. A.; Lamaneky, S. *Appl. Phys. Lett.* 1999, 4. 75-77. b) Yoshikawa, N.; Sakamoto, J.; Matsumura-Inoue, T. ; Takashima, H.; Tsukahara, K.; Kanehisa, N.; Kai, Y. *Anal. Sci.* 2004, 711-716.

[3] Dedeian, K.; Shi, J.; Shepherd, N.; Forsythe, E.; Morton, D. C. *Inorg. Chem.* 2005, 44, 4445-4447.

[4] a) E. Holder, B. M. W. Langeveld, U. S. Schubert, *Adv. Mater.* 2005, 17, 1109. b) Highly Efficient OLEDs with Phosphorescent Materials, (Ed: H. Yersin), *Wiley-VCH, Weinheirm, Germany* 2008.

[5] Collin, J.-P.; Dixon, I. M.; Sauvage, J.P.; Williams, J. A. G.; Barigelletti, F.; Flamigni, L. J. Am. Chem. Soc. 1999, 121, 5009-5016. Stagni, S.; Colella, S.; Palazzi, A.; Valenti, G.; Zacchini, S.; Paolucci, F.; Marcaccio, M.; Albuquerque, R. Q.; Cola, L. De, *Inorg. Chem.* 2008, 47, 10509-10521. Bandini, M.; Bianchi, M.; Valenti, G.; Piccinelli, F.; Paolucci, F.; Monari, M.; Ronchi, A. U.; Marcaccio, M, *Inorg. Chem.* 2010, 49, 1439-1448. B. S. Brunschwig, C. Creutz and N. Sutin, *Chem. Soc. Rev.*, 2002, 31, 168, J. P. Launay, Chem. Soc. Rev., 2001, 30, 386. E. Baranoff, J. P. Collin, L. Flamigni and J. P. Sauvage, *Chem. Soc. Rev.*, 2004, 33, 147. I. M. Dixon, J. P. Collin, J. P. Sauvage, L. Flamigni, S. Encinas and F. Barigelletti, *Chem. Soc. Rev.*, 2000, 29, 385. F. Barigelletti and L. Flamigni, *Chem. Soc. Rev.*,

2000, 29, 1. W. R. Browne, N. M. O'Boyle, J. J. McGarvey and J. G. Vos, *Chem. Soc. Rev.*, 2005, 34, 641. D. M. D'Alessandro and F. R. Keene, *Chem. Soc. Rev.*, 2006, 35, 424. Aravind Babu Kajjam, V. Sivakumar, *Chemical Record*, 2017 (Accepted for publication).

[6] Lee, K. H.; Seo, J. H.; Kim, Y. K.; Yoon, S. S. J. Nanosci. Nanotechnol. 2009, 9, 7099.

[7] Lee, K. H.; Kim, J. H.; Seo, J. H.; Kim, Y. K.; Yoon, S. S. J. Nanosci. Nanotechnol.2010, 10, 3193.

[8] a) Lee, K. H.; Kang, H. J.; Kim, H. M.; Seo, J. H.; Kim, Y. K.; Yoon, S. S. J. Nanosci. Nanotechnol. 2010, 11, 1499. b) Lee, K. H.; Kim, S. O.; Seo, J. H.; Kim, Y. K.; Yoon, S. S. J. Nanosci. Nanotechnol. 2011, 11, 4471.

[9] a) Kim, J. H.; Nam, E. J.; Hong, S. Y.; Kim, B. O.; Kim, S. M.; Yoon, S. S.; Suh, J. H.;
Ha, Y. K.; Kim, Y. K. *Mater. Sci. & Eng. C* 2004, 24, 167. b) C. Yang, X. Zhang, H. You, L.
Zhu, L. Chen, L. Zhu, Y. Tao, D. Ma, Z. Shuai and J. Qin, *Adv. Funct. Mater.*, 2007, 17, 651–661.

[10] Jayaraman Jayabharathi, Venugopal Thanikachalam and Ramalingam Sathishkumar, *NewJ.Chem.*, 2015, 39, 235.

[11] P. Coppo, E. A. Plummer and L. De Cola, Chem. Commun., 2004, 1774.

[12] a) T. Sajoto, P. I. Djurovich, A. B. Tamayo, M. Yousufuddin, R. Bau, M. E. Thompson,
R. J. Holmes and S. R. Forrest, *Inorg. Chem.*, 2005, 44, 7992. b) X. Gong, M. R. Robinson, J.
C. Ostrowski, D. Moses, G. C. Bazan and A. Heeger, J. *Adv. Mater.*, 2002, 14, 581–585. c)
R. N. Bera, N. Cumpstey, P. L. Burn and I. W. Samuel, Adv. Funct. Mater., 2007, 17, 1149–1152. d) Z. W. Xu, Y. Li, X. M. Ma, X. D. Gao and H. Tian, *Tetrahedron*, 2008, 64, 1860–1867.

[13] a). Y. You and S. Y. Park, J. Am. Chem. Soc., 2005, 125, 12438. b) H. J. Bolink, E. Coronado, R. D. Costa, N. Lardiés, E. Ortí, Inorg. Chem. 2008, 47, 9149–9151.

[14] a) J. D. Slinker, C. Y. Koh, G. G. Malliaras, M. S. Lowry, S. Bernhard, *Appl. Phys. Lett.* 2005, 86, 173506. b) Z. Y. Xia, X. Xiao, J. H. Sua, C. S. Chang, C. H. Chen, D. L. Li and H. Tian, *Synth. Met.*, 2009, 159, 1782–1785. c) Jung-Bum Kim, Seung-Hoon Han, Kiyull Yang, Soon-Ki Kwon, Jang-Joo Kim and Yun-Hi Kim *Chem. Commun.*, 2015, 51, 58. d) Seungjun Yi, Jin-Hyoung Kim, Yang-Jin Cho, Jiwon Lee, Tae-Sup Choi, Dae Won Cho, Chyongjin Pac, Won-Sik Han, Ho-Jin Son, and Sang Ook Kang, *Inorg. Chem.* 2016, 55, 3324–3331.

[15] D. Tordera, M. Delgado, E. Ortí, H. J. Bolink, J. Frey, M. K. Nazeeruddin, E. Baranoff, *Chem. Mater*.2012, 24, 1896–1903.

[16] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, S. Bernhard, *Chem. Mater*. 2005, 17, 5712–5719.

[17] H. C. Su, F. C. Fang, T. Y. Hwu, H. H. Hsieh, H. Chen, G. Lee, S. Peng, K. T. Wong, C.C. Wu, *Adv. Funct. Mater*. 2007, 17, 1019–1027.

[18] R. Terki, L. P. Simoneau, A. Rochefort, J. Phys. Chem. A 2009, 113, 534-541.

[19] a) J. D. Slinker, J. Rivnay, J. S. Moskowitz, J. B. Parker, S. Bernhard, H. D. Abruña, G. G. Malliaras, *J. Mater. Chem.* 2007, 17,2976–2989; b). T. Hu, L. He, L. Duan, Y. Qiu, *J. Mater. Chem.* 2012,22, 4206–4215; c). R. D. Costa, E. M. Lepeltier, F. Dumur, G. Wantz, N. Vila, I. Mbomekalle, D. Bertin, D. Gigmes, C.R. Mayer, *J. Lumin.* 143, 2013, 145.

[20] M. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli and M. Graetzel, J. Am. Chem. Soc., 2003, 125, 8790.

[21] E. Holder, B. M. W. Langeveld and U. S. Schubert, Adv. Mater., 2005, 17, 1109.

[22] Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson and S. R. Forrest, *Nature*, 2006, 440, 908.

- [23] S. Lamansky, P. I. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2001, 40, 1704.
- [24] M. S. Lowry, W. R. Hudson, R. A. Pascal and S. Bernhard, J. Am. Chem. Soc., 2004, 126, 14129.
- [25] M. Lepeltier, F. Dumur, G. Wantz, D. Bertin, D. Gigmes, C.R. Mayer, *Opt. Data Process. Storage*, 2014, 1, 6.
- [26] Becke, A. J. Chem. Phys. 1993;98:5648; Lee, C.; Yang, W.; Parr, R. G, *Phys. Rev. B* 1988;37:785-789.
- [27] P. Coppo, E. A. Plummer and L. De Cola, Chem. Commun., 2004, 1774–1775.
- [28] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, 395, 151–154.

[29] a) C. L. Li, Y. J. Su, Y. T. Tao, P. T.Chou, C. H. Chien, C. C. Cheng and R. S. Liu, *Adv. Funct. Mater.*, 2005, 15, 387–395. b) L. L. Wu, I. W. Sun and C. H. Yang, *Polyhedron*, 2007, 26, 2679–2685.

[30] a) R. S. Lumpkin, E. M. Kober, L. A. Worl, Z. Murtaza and T. J. Meyer, *J. Phys. Chem.*, 1990, 94, 239–243. b) T. Fei, X. Gu, M. Zhang, C. Wang, M. Hanif, H. Zhang and Y. Ma, *Synth. Met.*, 2009, 159, 113–118.

[31] a) M. C. Gather, A. Ko"hnen and K. Meerholz, Adv. Mater., 2011, 23, 233. (a) Y. Kawamura, S. Yanagida and S. R. Forrest, *J. Appl. Phys.*, 2002, 92, 87; (b) H. Wu, G. Zhou, J. Zou, C.-L. Ho, W.-Y. Wong, W. Yang, J. Peng and Y. Cao, *Adv. Mater.*, 2009, 21, 4181; (c) Y. Li, Z. Wang, X. Li, G. Xie, D. Chen, Y.-F. Wang, C.-C. Lo, A. Lien, J. Peng, Y. Cao and S.-J. Su, *Chem. Mater.*, 2015, 27, 1100; (d) J. Jiang, Y. Xu, W. Yang, R. Guan, Z. Liu, H.

Zhen and Y. Cao, Adv. Mater., 2006, 18, 1769; (e) G. L. Tu, C. Y. Mei, Q. G. Zhou, Y. X. Cheng, Y. H. Geng, L. X. Wang, D. G. Ma, X. B. Jing and F. S. Wang, Adv. Funct. Mater., 2006, 16, 101. f) H. J. Bolink, F. De Angelis, E. Baranoff, C. Klein, S. Fantacci, E. Coronado, M. Sessolo, K. Kalyanasundaram, M. Gr<sup>-</sup>atzel and M. K. Nazeeruddin, Chem. Commun., 2009, 4672. g) I. Oner, E. Stathatos and C. Varlikli, Adv. Opt. Technol., 2011, 1. [32] a) Chiu, Y.-C.; Chi, Y.; Hung, J.-Y.; Cheng, Y.-M.; Yu, Y.-C.; Chung, M.-W.; Lee, G.-H.; Chou, P.-T.; Chen, C.-C.; Wu, C.-C.; Hsieh, H.-Y. ACS Appl. Mater. Interfaces 2009, 1, 433. b) Chiu, Y.-C.; Hung, J.-Y.; Chi, Y.; Chen, C.-C.; Chang, C.-H.; Wu, C.-C.; Cheng, Y.-M.; Yu, Y.-C.; Lee, G.-H.; Chou, P.-T. Adv. Mater. 2009, 21, 2221. c) Hung, J.-Y.; Chi, Y.; Pai, I.-H.; Yu, Y.-C.; Lee, G.-H.; Chou, P.-T.; Wong, K.-T.; Chen, C.-C.; Wu, C.-C. Dalton Trans. 2009, 6472. d) Yang, C.-H.; Cheng, Y.-M.; Chi, Y.; Hsu, C.-J.; Fang, F.-C.; Wong, K.-T.; Chou, P.-T.; Chang, C.-H.; Tsai, M.-H.; Wu, C.-C. Angew. Chem., Int. Ed. 2007, 46, 2418. e) Chang, C.-H.; Chen, C.-C.; Wu, C.-C.; Yang, C.-H.; Chi, Y. Org. Electron. 2009, 10, 1364. f) Chang, C.-F.; Cheng, Y.-M.; Chi, Y.; Chiu, Y.-C.; Lin, C.-C.; Lee, G.-H.; Chou, P.-T.; Chen, C.-C; Chang, C.-H.; Wu, C.-C. Angew. Chem., Int. Ed. 2008, 120, 4618. g) Sasabe, H.; Takamatsu, J.; Motoyama, T.; Watanabe, S.; Wagenblast, G.; Langer, N.; Molt, O.; Fuchs, E.; Lennartz, C.; Kido, J. Adv. Mater. 2010, 22, 5003. h) Hsieh, C.-H.; Wu, F.-I.; Fan, C.-H.; Huang, M.-J.; Lu, K.-Y.; Chou, P.-Y.; Ou Yang, Y.-H.; Wu, S.-H.; Chen, I. -C.; Chou, S.-H.; Wong, K.-T.; Cheng, C.-H. Chem. Eur. J. 2011, 17, 9180. i) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. J. Am. Chem. Soc. 2003, 125, 7377. j) Lo, S.-C.; Shipley, C. P.; Bera, R. N.; Harding, R. E.; Cowley, A. R.; Burn, P. L.; Samuel, I. D. W. Chem. Mater. 2006, 18, 5119. k) Yeh, Y.-S.; Cheng, Y.-M.; Chou, P.-T.; Lee, G.-H.; Yang, C.-H.; Chi, Y.; Shu, C.-F.; Wang, C.-H. Chem. Phys. Chem 2006, 7, 2294. 1) Tsai, J.-Y.; Yager, W.; Brooks, J.; Beers, S.; Kottas, G. S.; Barron, E.; Kwang, R (Universal Display Corporation, USA) US2010/ 0148663 A1, 2010.

m) Lee, S. J.; Park, K.-M.; Yang, K.; Kang, Y. *Inorg. Chem.* 2009, 48, 1030. n) Yang-Jin Cho, So-Yoen Kim, Jin-Hyoung Kim, Douglas W. Crandell, Mu-Hyun Baik, Jiwon Lee, Chul Hoon Kim, Ho-Jin Son, Won-Sik Han and Sang Ook Kang *J. Mater. Chem. C*, 2017, 5, 4480. o) Ganguri Sarada, Woosum Cho, Athithan Maheshwaran, Vijaya Gopalan Sree, Ho-Yeol Park, Yeong-Soon Gal, Myungkwan Song, and Sung-Ho Jin., *Adv. Funct. Mater.* 2017, 27, 170100.

[33] a). Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* 1996, 256, 454–464. b). Scalmani,
G.; Frisch, M. J.; Mennucci, B.; Tomasi, J.; Cammi, R.; Barone, V, *J. Chem. Phys.* 2006, 124, 094107 (1–15). c) Yafei Wang, Ning Sun, Basile F. E. Curchod, Louise Male, Dongge
Ma, Jiang Fan, Yu Liu, Weiguo Zhu and Etienne Baranoff., *J. Mater. Chem. C*, 2016, 4, 3738.

[34] S. Lamansky, P. Djarovich, D. Murphy, F.A. Razzaq, R. Kwong, I. Tsyba, M. Bortz, B.Mui, R. Bau, M.E. Thompson. J. Am. Chem. Soc., 123 (2001), p. 4304.

[35] Oyama Y, Kumaoka H, Uwada K, Yoshida K., Tetrahedron. 65 (2009) 8336-43.

[36] a) M.B. Nonoyama. *Chem. Soc. Jpn.*, 47 (1974), p. 767. b) Kawamura, Y.; Sasabe, H.;
Adachi, C. *Jpn. J. Appl. Phys., Part 1* 2004, 43, 7729–7730.

[37] (a) J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y. Tang and B. Z. Tang, *Adv. Mater.*, 2014, 26, 5429–5479; (b) Y. Q. Zhang, G. Y. Zhong and X. A. Cao, *J. Appl. Phys.*, 2010, 108, 083107; (c) Adam F. Henwood, Ashu K. Bansal, David B. Cordes, a Alexandra M. Z. Slawin, Ifor D. W. Samuelb and Eli Zysman-Colman, *J. Mater. Chem. C*, 2016, 4, 3726.

[38] a) G. A. Crosby and J. N. Demas, J. Phys. Chem, 1971, 75, 991-1024. b) D. M. de Leeuw, M. M. J. Simenon, A. R. Brown and R. E. F. Einerhand, Synth. Met., 1997, 87, 53-59.
[39] a) Cathrin D. Ertl, Cristina Momblona, Antonio Pertegás, JoséM. Junquera-Hernández, Maria-Grazia La-Placa, Alessandro Prescimone, Enrique Ortí, Catherine E. Housecroft,

Edwin C. Constable, and Henk J. Bolink., *J. Am. Chem. Soc.* 2017, 139, 3237–3248. b) S. Buddhudu, M. Morita, S. Murakami, D. Rau, J. Lumin. 1999, 8384, 199203. c) E. Baranoff, B. F. E. Curchod, F. Monti, F. Steimer, G. Accorsi, I. Tavernelli, U. Rothlisberger, R. Scopelliti, M. Gra<sup>--</sup>tzel and M. K. Nazeeruddin, *Inorg. Chem.*, 2012, 51, 799.

[40] L. L. Shi, T. Li, S. S. Zhao, H. Li and Z. Su, Theor. Chem. Acc., 2009, 124, 29-36.

[41] L. He, J. Qiao, L. Duan, G. F. Dong, D. Q. Zhang, L. D. Wang and Y. Qiu, Adv. Funct. Mater., 2009, 19, 2950.

[42] G. S. M. Tong and C. M. Che, Chem. - Eur. J., 2009, 15, 7225-7237.

[43] X. N. Li, Z. J. Wu, Z. J. Si, H. J. Zhang, L. Zhou and X. J. Liu, *Inorg. Chem.*, 2009, 48, 7740–7749.

[44] Y. Q. Liu, G. Gahungu, X. B. Sun, X. C. Qu and Z. J. Wu, J. Phys. Chem. C., 2012, 116, 26496–26506.

[45] E. Orselli, G. S. Kottas, A. E. Konradsson, P. Coppo, R. Frohlich, L. D. Cola, D. V. Dijken, M. Buchel and H. Borner, *Inorg. Chem.*, 2007, 46, 11082–11093,

[46] Li Wang, Yong Wu, Guo-Gang Shan, Yun Geng, Jian-Zhao Zhang, Dong-Mei Wang,Guo-Chun Yang and Zhong-Min Su., J. Mater. Chem. C, 2014, 2, 2859–2868.

[47] Y. Tao, C. Yang, and J. Qin, Chem. Soc. Rev. 2011, 40, 2943.

[48] a) Parr RG, Pearson RG, J. Am. Chem. Soc., 1983, 105, 7512–7516 82. b) Chattaraj PK,
Lee H, Parr RG, J. Am. Chem. Soc., 1991, 113, 1856–1857. c) Yang W, Parr RG, (1985)
Proc. Natl. Acad. Sci. USA., 1985, 82, 6723–6726. d) Chermette. H, J. Comput. Chem., 1999,
20, 129–154. e) Parr RG, Chattaraj PK, J. Am. Chem. Soc., 1991, 113, 1855–1857.

Figures



Fig.1. Chemical structure of heteroleptic Ir(III) complexes.



**Fig.2.** UV-Visible (left) and excitation (right) spectra of heteroleptic Ir(III) complexes in 10<sup>-4</sup> M CH<sub>2</sub>Cl<sub>2</sub> solution.



Fig. 3. Emission spectra of heteroleptic Ir(III) complexes in solution (left) in  $10^{-4}$  M CH<sub>2</sub>Cl<sub>2</sub> solution and PMMA films (right).



Fig. 4. Lifetime of heteroleptic Ir(III) complexes.



**Fig.5.** Cyclic voltammetry curves of the three Ir(III) complexes ( $E_{pa}$  and  $E_{pc}$  are the cathodic and anodic potential, respectively).



Fig.6. Optimized structures of heteroleptic Ir(III) complexes.



Fig.7. Energy level diagrams of heteroleptic Ir(III) complexes.



Fig. 8. Absorption spectra of the heteroleptic Ir(III) complexes in gas phase.



Fig. 9. Calculated triplet energies of the host and different guest materials at their optimized  $S_0$  geometries through TD-DFT method. (The triplet energies for host materials and FIrpic are taken from [46].)



**Fig.10.** CIE color coordinates of heteroleptic Ir(III) complexes (A=solution, B=PMMA film). Where, a = Ben-Irppy, b = Ben-Ir-pic and c = Ben-Ir-acac.



Scheme1: A general procedure for benzilimidazole preparation.



Scheme 2: Synthetic route for the heteroleptic Ir(III) complexes.



Scheme 3. Internal reorganization energy for holes  $(\lambda_h)$  in arbitrary units.

Table 1:	Photophysical	properties of	Ir(III)	complexes.
----------	---------------	---------------	---------	------------

Complex	Absorption peaks (nm)	Emission peak (nm)		Quantum yield (%)		τ (μs)
	()	sol <sup>n</sup>	PMMA film	sol <sup>n</sup>	PMMA film	
Ben-Ir-ppy	245, 276, 369	523	533	0.125	0.152	1.47
Ben-Ir-pic	232, 289, 378	534	542	0.291	0.285	1.76
Ben-Ir-acac	230, 292, 378	542	561	0.264	0.198	1.82

**Table 2:** Electrochemical data of heteroleptic Ir(III) complexes.

Complex	E <sub>red</sub> (eV)	E <sub>ox</sub> (eV)	HOMO (eV)	LUMO (eV)	Band gap (eV)
Ben-Ir-ppy	-1.520	1.450	-5.850	-2.879	2.97
Ben-Ir-pic	-1.359	1.309	-5.709	-3.040	2.66

Ben-Ir-acac	-1.339	1.258	-5.658	3.060	2.59
-------------	--------	-------	--------	-------	------

**Table 3:** Summarized data of heteroleptic Ir(III) complexes in DFT analysis.

Complex	HOMO (eV)	LUMO (eV)	Band gap (eV) DFT	Band gap (eV) Exp.	S1 gas	T <sub>1</sub> gas
Ben-Ir-ppy	-4.508	-1.188	3.32	2.97	2.96	2.62
Ben-Ir-pic	-4.581	-1.158	3.30	2.66	2.55	2.39
Ben-Ir-acac	-4.858	-1.594	3.26	2.59	2.50	2.37

**Table 4:** Main optimized geometric parameters of all investigated Ir(III) complexes in the  $S_0$  states determined at the B3LYP/6-31G(d)(E)-LANL2DZ(Ir) level of theory.

	Ben-Ir-acac	Ben-Ir-ppy	Ben-Ir-pic				
	Bond length (A°)						
Ir-N <sub>1</sub>	2.061	2.092	2.083				
Ir-N <sub>2</sub>	2.201	2.238	2.199				
Ir-N <sub>3</sub>	-	2.064	2.055				
Ir-O <sub>1</sub>	2.177	-	2.176				
Ir-O <sub>2</sub>	2.077	-	-				
Ir-C1	2.020	2.024	2.028				
Ir-C <sub>2</sub>	2.016	2.113	2.030				
Ir-C3	-	2.088	-				
	Bond	angle (°)					
N <sub>1</sub> -Ir-C <sub>1</sub>	79.90	79.53	78.94				
N2-Ir-C2	79.42	77.19	79.75				
N <sub>3</sub> -Ir-C <sub>3</sub>	-	79.45	-				
N <sub>3</sub> -Ir-O <sub>1</sub>	-	-	79.08				

O <sub>1</sub> -Ir-O <sub>2</sub>	89.43	-	-

**Table 5:** HOMO – LUMO energy diagrams of heteroleptic Ir(III) complexes.

Complex	Ben-Ir-ppy	Ben-Ir-acac	Ben-Ir-pic
НОМО			
LUMO			
HOMO-1			
LUMO+1			

**Table 6:** Computed Vertical Transitions and Their Oscillator Strengths and Configurations in gas phase<sup>a</sup>.

Complex	λ <sub>max</sub> nm	f	Configuration (%)
Ben-Ir-ppy	417	0.03	HOMO→LUMO (0.64)

			HOMO→LUMO+1 (0.12)
			HOMO→LUMO+2 (0.12)
			HOMO→LUMO+7 (0.45)
	405	0.02	HOMO→LUMO (0.54)
	403	0.05	HOMO→LUMO+2 (0.61)
			HOMO→LUMO+6 (0.28)
			HOMO→LUMO+9 (0.12)
	381	0.08	HOMO-1→LUMO (0.53)
			HOMO→LUMO+3 (0.39)
	377	0.01	HOMO-1→LUMO+2 (0.48)
			HOMO→LUMO+4 (0.32)
			HOMO-1→LUMO+5 (0.17)
Ben-Ir-acac	484	0.01	HOMO→LUMO (0.69)
	426	0.03	HOMO→LUMO+1 (0.66)
			HOMO→LUMO+5 (0.18)
	422	0.07	HOMO-1→LUMO (0.68)
	413	0.02	HOMO→LUMO+2 (0.65)
	385	0.01	HOMO→LUMO+4 (0.57)
			HOMO→LUMO+3 (0.30)
	380	0.05	HOMO-1→LUMO+1 (0.63)
			HOMO-1→LUMO+5 (0.16)
Ben-Ir-pic	495	0.01	HOMO→LUMO (0.69)
	446	0.01	HOMO-2→LUMO (0.67)
			HOMO-1→LUMO (0.17)
	408	0.02	HOMO→LUMO+1 (0.65)
	390	0.02	HOMO→LUMO+2 (0.64)
			HOMO→LUMO+5 (0.13)

		HOMO→LUMO+8 (0.13)
386	0.01	HOMO-2→LUMO (0.639)
382	0.02	HOMO $\rightarrow$ LUMO+5 (0.61)
		HOMO $\rightarrow$ LUMO+2 (0.17)
		HOMO $\rightarrow$ LUMO+5 (0.13)
		HOMO→LUMO+7 (0.13)
377	0.02	HOMO-1→LUMO+1 (0.64)
361	0.08	HOMO-4→LUMO (0.60)
		HOMO-2→LUMO $(0.14)$
		HOMO $\rightarrow$ LUMO+4 (0.15)

**Table 6:** Calculated ionization potentials (IP in eV), electronic affinities (EAs in eV),extraction potentials (eV), reorganization energies (eV) of Ir(III) complexes.

Compound	Ben-Ir-ppy	Ben-Ir-pic	Ben-Ir-acac
IPv	5.48	5.87	5.62
IPa	5.39	5.793	5.56
HEP	5.18	5.797	5.48
SPE(h)	0.21	-0.004	0.07
-EA <sub>v</sub>	0.19	-0.384	-0.105
-EAa	0.29	0.495	0.245
LHE	0.022	0.108	0.045
SPE(e)	0.65	1.113	0.132
EEP(e)	-0.36	-0.618	-0.377
λhole	0.30	0.081	0.138
λelectron	0.564	0.233	0.272
Δspe	0.447	1.117	0.06
Δλ	0.264	0.152	0.133

[			
n	2 64	3 1 2	2.86
- <b>'</b> l	2.04	5.12	2.00

 Table 8. CIE color coordinates of heteroleptic Ir(III) complexes.

Complex	x, y (solution)	x, y (PMMA film)
Ben-Ir-ppy	0.287, 0.487	0.325, 0.635
Ben-Ir-pic	0.338, 0.547	0.373, 0.601
Ben-Ir-acac	0.370, 0.574	0.450, 0.540