ADVANCED MATERIALS

Strong Luminescent Iridium Complexes with C^N−N Structure in Ligands and Their Potential in Efficient and Thermally Stable Phosphorescent OLEDs

By Bao Xiu Mi, Peng Fei Wang, Zhi Qiang Gao,* Chun Sing Lee, Shuit Tong Lee,* Hui Ling Hong, Xiao Ming Chen, Man Shing Wong, Ping Fang Xia, Kok Wai Cheah, Chin Hsin Chen, and Wei Huang*

Organic luminescent materials are an important class of materials for a multitude of optoelectronic applications, such as organic light-emitting diodes (OLEDs),[1–3] luminescence-based sensors,[4] and photocatalysts.[5] According to the nature of emission, organic luminophors can be categorized as fluorescent emitters, which emit light from their singlet excited states, and phosphorescent emitters, which conduct radiative decay from their triplet excited states. It has been widely accepted that for excitons generated by carrier injection, which is exactly the case in OLEDs, the ratio of singlet and triplet exciton is 1:3. Due to this intrinsic factor, although abnormal cases exist,[6,7] the internal quantum efficiency (IQE) of OLEDs employing fluorescent emitters is generally limited to 25%, while IQE of OLEDs utilizing phosphorescent emitters (PHOLEDs) can reach almost 100%.[3] Hence, due to this higher efficiency and motivated by the

[*] Prof. Z. Q. Gao, Prof. W. Huang, Dr. B. X. Mi
Jiangsu Key Lab of Organic Electronics & Information Displays and
Institute of Advanced Materials (IAM)
Nanjing University of Posts and Telecommunications (NJUPT)
Mailbox 386, No. 9 Wenyuan Road
Yadong Xincheng Distribution Nanjing 210046 (PR China)
E-mail: iamzqgao@njupt.edu.cn; iamwhuang@njupt.edu.cn

Prof. S. T. Lee, Prof. C. S. Lee
Center of Super-Diamond & Advanced Films (COSDAF) and
Department of Physics and Materials Science
City University of Hong Kong
Tat Chee Avenue, Kowloon, Hong Kong (PR China)
E-mail: apannale@cityu.edu.hk

Prof. P. F. Wang
Technical Institute of Physics and Chemistry
Chinese Academy of Sciences
Beiyitiao No.2, Zhongguancun, Haidian District
Beijing 100080 (PR China)

Dr. H. L. Hong, Prof. X. M. Chen
School of Chemistry and Chemical Engineering
Sun Yat-Sen University, Guangzhou 510275 (PR China)

Prof. M. S. Wong, Prof. P. F. Xia, Prof. K. W. Cheah
Centre for Advanced Luminescence Materials
Waterloo Road, Kowloon Tong, Hong Kong (PR China)

Prof. C. H. Chen
Display Institute, Microelectronics and Information Systems
Research Center, National Chiao Tung University
Hsinchu, Taiwan 300 (Taiwan)

potential applications in flat panel displays (FPDs), solid-state lighting (SSL), and backlights for liquid-crystal displays (LCDs) based on OLED technology, PHOLED materials and devices have been intensively studied since the seminal work in 1998.[3] Great success has been achieved in device efficiency,[8–11] color tuning,[12–14] and also white-light emission.[15–17] In contrast, lifetimes of PHOLEDs have been less explored, and need to be further improved.[18–20] For SSL applications, OLEDs performances are far from satisfied.[15,21,22] It is believed that the OLED must have an efficiency of 50 lm W^{-1} or more and an operation lifetime of 20 kh or longer tailored to the SSL application. Thus, the design of good emitters for this demanding device performance is one of the challenging tasks.

From the practical point of view, the primary criteria for phosphorescent emitters are strong phosphorescence coupling with good thermal stability. Due to the spin conservation rule, phosphorescence is generally limited to metal complexes, where spin-orbital coupling effects exist. Usually, phosphorescence is characterized by its ^{3}MLCT (metal ligand charge transfer) nature, or has mixed $^3(\pi–\pi^*)$ and ^{3}MLCT features. Orthometalated iridium complexes are the most intensively studied materials for usage in PHOLEDs, due to several reasons: i) Benefiting from its large atomic number, Ir is a heavy metal that can offer good spin-orbital coupling leading to strong phosphorescence properties; ii) Ir has large d-orbital splitting, thus precluding the d–d transition that may deactivate the MLCT process, which is one of the important processes for room temperature phosphorescence; iii) the stable oxidation state 3+ of Ir(III) can form neutral complexes, allowing sublimation under vacuum. Regarding the thermal stability of phosphorescent emitters, forming homoleptic complexes other than their heteroleptic counterpart is one of the strategies.[23] Besides metal, organic ligands drastically influence the molecular frontier orbitals of a complex, such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which determine the emission wavelength and intensity of the complex.[24] There are two driving forces to form a complex. One is the σ-bonding between the π electron of the ligand and the empty d orbital of the metal, and the other is the π-bonding via delocalization of d-electrons from the metal to the empty orbital of the ligand. The nature and degree of interaction between metal and ligand determine the MLCT transition, and thus, partially, the emission color and intensity.

WILEY InterScience®
DISCOVER SOMETHING GREAT

Recently, we have designed a new strong phosphorescent homoleptic Ir complex with the ligand 3,6-bis (phenyl) pyridazine (BPPya). Devices based on this material have demonstrated a significantly improved performance.[25] In this work, following our previous study, we have developed another new Ir complex with the ligand 1,4-bis(phenyl) phthalazine (BPPa), an analog of BPPya, having the resemblance of an sp²-hybrid N adjacent to the chelating N atom (represented as C^N=N). Ir(BPPa)₃ proves to be a strong red-phosphorescent material with good thermal stability. PHOLED devices with Ir(BPPa)₃ as a dopant emitter exhibit a saturated red emission with high efficiency as well as good operational stability. Very recently, Tong et al. reported a promising red OLED utilizing an Ir complex with ligands also bearing the C^N=N structure.[26] Based on the results from our work and from ref. [[26]], it is reasonable to believe that ligands with a C^N=N structure are beneficial for Ir complexes. In order to have a full understanding of the various factors controlling the photophysical properties of Ir complexes, we performed quantum chemistry calculations. It was found that ligands bearing a C^N=N structure in Ir complexes could bond to the Ir atom more strongly, and could also create a "proximity effect,"[27] compared to their counterpart ligands with chelating N atoms bearing adjacent sp² C atoms (represented as C^N=CH), such as Ir(ppy)₃ (tris(2-phenylpyridine)iridium). Our result shows that for Ir complexes the ligand with a C^N=N structure is superior to the one with a C^N=CH structure, and that this kind of Ir complexes are promising for optoelectronic applications due to their strong phosphorescence and high thermal stability.

Since forming heteroleptic iridium complexes is generally easier than obtaining their homoleptic counterparts,[28] our first attempt toward forming iridium complexes utilizing the BPPa ligand was aimed at the heteroleptic form. By following route (1) in Scheme 1, the chloro-bridged diiridium precursor **1** was synthesized, in order to further develop the initial target compound, (BPPa)₂Ir(acac), where acac is 2,4-pentanedionate. After the reaction, the initially formed product, containing a yellow precipitate (main product) and a dark-red crystalline precipitate (minor product), was washed with ethanol and acetone. The red precipitate, which presented red emission under UV illumination, was later identified as Ir(BPPa)₃ by mass spectroscopy. The strong red emission of Ir(BPPa)₃ and its simple synthesis spurred our interest in preparing Ir(BPPa)₃ directly via route (2) in Scheme 1. Using Ir(acac)₃ and BPPa as the starting materials, and following a previously described method,[29] Ir(BPPa)₃ can be produced with a moderate yield of about 40%. Deep-red Ir(BPPa)₃ crystals were grown from slow solvent evaporation of a CH₂Cl₂/MeOH mixture. Characterization data from ¹H-NMR, elemental analysis, MS, and UV spectroscopy are summarized in the Experimental Section.
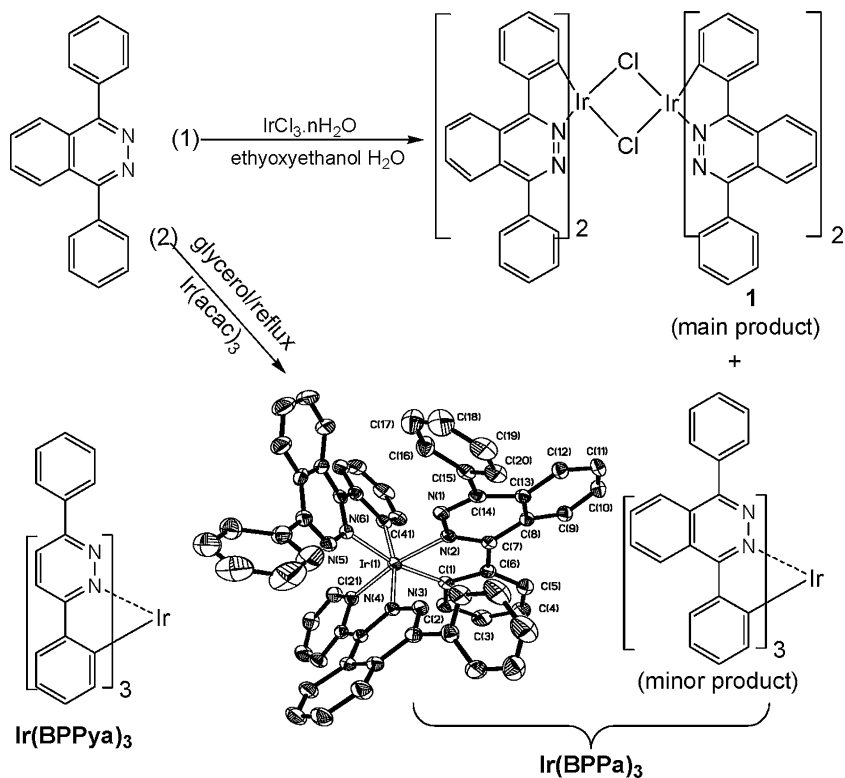
Scheme 1. Synthetic protocol and crystal structure of Ir(BPPa)₃ and Ir(BPPya)₃, iridium complexes studied in this work.

The structure of the Ir(BPPa)₃ molecule, as determined by X-ray analysis, is shown in Scheme 1. The molecule has octahedral geometry, with three BPPa ligands cyclometalated to the central iridium atom. The nonchelating phenyl part of the ligand is almost perpendicular to the phthalazine groups. This renders the molecules sterically bulky, which is generally beneficial for reducing concentration quenching of emission.

The selected bonding lengths of Ir(BPPa)₃ obtained using X-ray diffraction are compared with those calculated using density functional theory (DFT) in Table 1. The calculated bond lengths of Ir–C (2.028 Å) and Ir–N (2.152 Å) are very close to the average values from experiments, with 2.019 Å for Ir–C and 2.095 Å for Ir–N, indicating good agreement between experimental data and calculation results. The accuracy of this

Table 1. Bond Lengths of compound Ir(BPPa)₃ from X-ray crystallography data and from quantum chemical calculations.

	Ligand 1	Ligand 2	Ligand 3	Average[a]	Calcd[b]
R(Ir-C) [Å]	2.019(5)	2.021(5)	2.017(4)	2.019(5)	2.028
R(Ir-N) [Å]	2.102(4)	2.095(3)	2.089(4)	2.095(4)	2.152

[a] Average of ligands 1–3 from X-ray crystallography data; the average deviation is calculated using $\Delta = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\Delta_i^2}$. [b] Average of ligands 1–3 from quantum chemical calculation data.
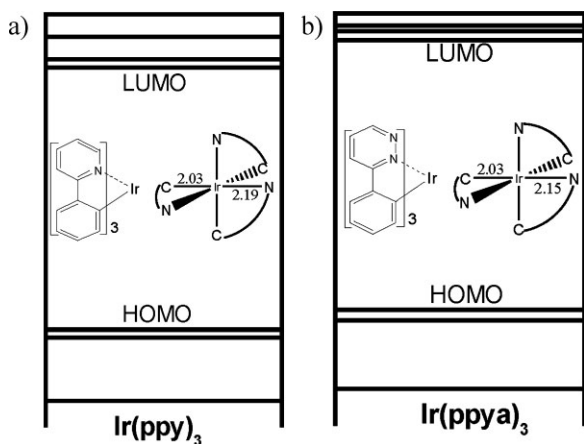
Figure 1. Calculated frontier orbital distributions from DFT for a) Ir(ppy)$_3$ and b) Ir(ppya)$_3$. Insets are their molecular structures and calculated bonding lengths (Å).

calculation method for metal complexes has also been demonstrated by works of other groups.[10,30,31]

In order to study the effect of ligands with the C^N=N structure, we compare the calculated results of Ir(ppy)$_3$ with those of model compound Ir(ppya)$_3$ (tris(3-phenylpyridazine)iridium), as shown in Figure 1. The only difference between the molecular structures of Ir(ppy)$_3$ and Ir(ppya)$_3$ arises from the atom adjacent to the chelating N in the ligand, which is C for Ir(ppy)$_3$ and N for Ir(ppya)$_3$, and which accounts for the property difference between them. It is clear from Figure 1 that, different from Ir(ppy)$_3$, the LUMO, LUMO + 1, and LUMO + 2 of Ir(ppya)$_3$ are very close to each other, leading to a larger probability of transition between the HOMO and these orbitals, hence increasing the transition cross-section, which is favorite for absorption and emission. As studied later by UV spectrometry, the more intensive absorptions of Ir(BPPya)$_3$ and Ir(BPPa)$_3$ are consistent with the above calculation results. Meanwhile, it can be noticed from Figure 1 that the HOMO and LUMO of the model compound Ir(ppya)$_3$ appear to have slightly higher energies than those of Ir(ppy)$_3$. This is understandable, taking into account the contributions corresponding to frontier orbitals from each segment in the molecules (see Fig. S1a and b in Supporting Information, and explanation therein).

Furthermore, as shown in Figure 1, while the calculated Ir–C bond lengths of the model compound Ir(ppya)$_3$ are the same as those of Ir(ppy)$_3$ (2.03 Å), the calculated Ir–N bond lengths (2.15 Å) are shorter (2.19 Å), indicating a stronger Ir–N bond in the complex with the C^N=N type ligand. In addition to a more intensive transition, the benefits of C^N=N replacing C^N=CH in the ligand include: i) strong bonding between metal and ligand, which leads to efficient mixing of the singlet and triplet excited states, and is beneficial for phosphorescence, and moreover, stronger bonding of Ir–N results in more thermally stable complexes, as confirmed by experimental data (the 5% weight loss temperature is 413 °C for Ir(ppy)$_3$,[23] 439 °C for Ir(BPPya)$_3$, and 426 °C for Ir(BPPa)$_3$, respectively); and ii) compared to C^N=N, the C^N=CH has one excess H atom, which may result in more steric hindrance toward the N chelating to the metal. Partially due to the small steric hindrance in the C^N=N type

ligand, the stable tris-cyclometalated complex is the most easily achieved form. Also, in the case of a C^N=CH type ligand, it is sometimes difficult to get stable tris-cyclometalated complex via Ir–N chelating; instead the introduction of another ancillary ligand (usually β-diketonates[28,32–35]) is generally needed.

To further illustrate the merits of complexes with C^N=N type ligands, we compared the absorption of Ir(BPPya)$_3$ and Ir(BPPa)$_3$ (as shown in Fig. 2) to that of Ir(ppy)$_3$.[36] It can be seen that due to the similarity in ligands, Ir(BPPya)$_3$ and Ir(BPPa)$_3$ exhibit similar absorption (Abs) and photoluminescence (PL) characteristics, with bathochromic shifts of approximately 40 nm for absorption and 80 nm for emission in Ir(BPPa)$_3$, which are consistent with the enlargement of the conjugated π system in the BPPa ligand. The absorption for Ir(BPPya)$_3$, with a maximum of 50 000 M^{-1} cm^{-1} at 284 nm and 14 000 M^{-1} cm^{-1} at 400 nm, and that for Ir(BPPa)$_3$, with maximum of 41 000 M^{-1} cm^{-1} at 316 nm and 12 000 M^{-1} cm^{-1} at 395–456 nm, are much more intensive than that for Ir(ppy)$_3$, with maximum of 29 000 M^{-1} cm^{-1} at 284 nm and 8 000 M^{-1} cm^{-1} at 377 nm.[36] This is in agreement with our computational calculations. According to the "proximity effect",[27] the increased absorption transition can be attributed to the nonbonding lone electron-pair located at the N atom adjacent to the chelating N in the ligand with C^N=N structure. Moreover, in the absorption of Ir(BPPya)$_3$ and Ir(BPPa)$_3$, the triplet transitions are well recognized and quite intensive, with intensities of 4500 M^{-1} cm^{-1} −1 at 471 ~475 nm for Ir(BPPya)$_3$, and at 557–564 nm for Ir(BPPa)$_3$, indicating efficient spin-orbital coupling, which is a prerequisite for phosphorescent emission. Ir(BPPa)$_3$ emits a red light peaked at 625 nm in a CH_2Cl_2 solution, with a PL quantum yield of 0.20 measured with Rhodamine B (in methanol, $\phi = 0.66$) as a calibration standard. According to computational calculations (not shown), the HOMO of Ir(BPPa)$_3$ has contributions both from the metal (M) and ligands (L, π), and the contribution in the LUMO is mainly from the ligand (L, π*), thus the emission of Ir(BPPa)$_3$ is assigned to a mixture of MLCT and ligand-centered (π–π*) transitions.

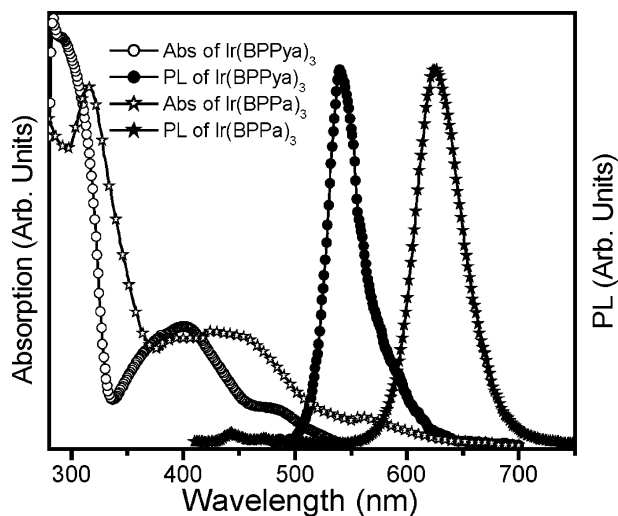With regard to the electroluminescence (EL) properties of these Ir complexes, our previous work showed that Ir(BPPya)$_3$-

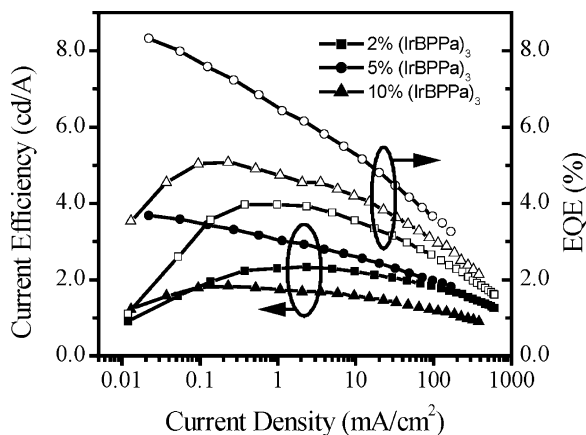**Figure 2.** Absorption and PL of Ir(BPPya)$_3$ in toluene and Ir(BPPa)$_3$ in CH_2Cl_2.

Figure 3. The efficiency of devices based on Ir(BPPa)₃.

Figure 4. Stability of Ir(BPPa)₃-based device.

based devices could achieve an efficiency of 52 cd A^{-1} with low roll-off, demonstrating its great potential in OLED applications.[25] In this study, the new Ir(BPPa)₃-based OLED devices were preliminary tested by doping Ir(BPPa)₃ into a 4,4′-dicarbazolyl-1,1′-biphenyl (CBP) host. The devices have a configuration of ITO/NPB (15 nm)/NPB:1% Ir(BBPa)₃ (5 nm)/CBP:x% Ir(BBPa)₃ (20 nm)/BCP (6 nm)/AlQ₃ (40 nm)/MgAg, where 4.4′-di-1-naphythyl-*N*,*N*′-diphenyl-biphenyl-4,4′-diamine (NPB), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), and tris(8-hydroxyquinolinato) aluminum(III) (AlQ₃) are used in the preparation of the hole-transport layer (HTL), hole-block layer (HBL), and electron-transport layer (ETL), respectively. As shown in Figure 3, devices with 2, 5, and 10% of Ir(BPPa)₃ show maximum external quantum efficiencies (EQE) of 4.0, 8.3, and 5.1%, and CIE (Commission International de L'Eclairage) coordinates of (0.64,0.32), (0.69,0.30), and (0.70,0.30), respectively. It can be seen that at the higher doping concentration of 10%, the efficiency dropped significantly, and was probably related to triplet–triplet annihilation at this high excitation density. The 5% Ir complex doped device presented the best performance, with EL efficiency of 8.3% and CIE coordinates of (0.69,0.30).

Limited to our current device study, we tentatively tested the lifetime of an Ir(BPPa)₃-based device with the structure of ITO/NPB/NPB:1% Ir(BPPa)₃/CBP:5% Ir(BPPa)₃/TPBi/AlQ₃/MgAg, where TPBi is 1,3,5-tri(phenyl-2-benzimidazolyl)-benzene. These materials are the same in the Ir(ppy)₃-based device presented in the work by Kwong et al.,[19] where a lifetime of 350 h was deduced for an initial luminance of 100 cd m^{-2}. As shown in Figure 4, our red PHOLED device achieved a lifetime of 610 h at an initial luminance of 100 cd m^{-2}, which is considerably better than the previously reported results mentioned above. As disclosed in the literature, device lifetime is strongly influenced by thermal and electrochemical stabilities of materials, as well as device structure. For example, when replacing the HBL of TPBi with the more thermally stable BAlq (bis(2-methyl-8-quinolinolato) (*p*-phenylphenolato) aluminum(III)), the lifetime of an Ir(ppy)₃-based device was observed to changed from 70 to 10 000 h at initial brightness of 500 cd m^{-2}.[19] Also, by improving the redox properties of the host for a red-emitting phosphorescent material, the decay time for a 20% brightness drop in a PHOLED device increased from 267 to 1000 h.[37] In addition, charge/
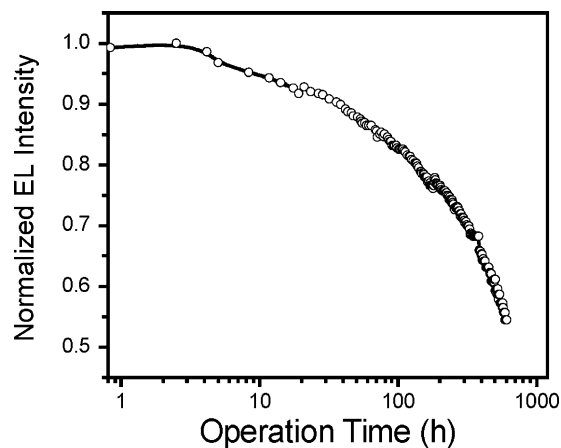
exciton confinement has been claimed to play a major role in the long-term stability of the phosphorescent device.[38] Cyclic voltammetry (CV) measurements revealed that both Ir(BPPa)₃ and Ir(BPPya)₃ are electrochemical stable, with reversible oxidation and reduction (vs. Ag/AgCl) of 1.03 and −1.88 V for Ir(BPPya)₃, and 0.91 and −1.57 V for Ir(BPPa)₃ (Fig. S2 in the Supporting Information). Taking into account the above insights, together with the fact that Ir(BPPa)₃ and Ir(BPPya)₃ are both thermally and electrochemically stable, it is reasonable to expect that the lifetimes of Ir(BPPa)₃- and Ir(BPPya)₃-based devices will be significantly improved, and may meet the requirement for commercial applications, with the optimization of the device structure using a matched host for good energy transfer and suitable layer-stacks for better carrier and exciton confinement.- Work is currently being undertaken in our laboratories, and will be reported later.

In summary, we have studied iridium complexes with ligands bearing C^N=N type ligands. It is suggested that in complexes containing these ligands the bonding strength between the N atom and iridium should be stronger compared to those bearing C^N=CH type ligands, based on the shorter Ir–N bonding length obtained from calculations. Using a newly synthesized red-emission Ir complex as an example, along with the previously reported green-emission complex, it is demonstrated that Ir complexes with C^N=N type ligands are easy to synthesize and thermally stable, and show a proximity effect and an intensive MLCT transision. Ir(BPPa)₃ is proved to be a potential material for saturated red PHOLEDs. Furthermore, by changing the conjugation length of the C^N=N type ligand, the emission color can be tuned from green to saturated red. We also expect that with minor modifications in the molecular structure of this type of ligand, efficient phosphorescent metal complexes in a wide range of colors could be obtained, with promise for optoelectronic applications.

Experimental

Instrumentation is described in the Supporting Information.

Computational Simulations: DFT calculations were performed using the B3LYP hybrid functional, with the 6–31G basis set in Gaussian 03 programs [39].

Ir(BPPa)₃ CharacterizationData: m.p. 385.3 °C; ^{1}H-NMR (300 MHz, Chloroform-d) δ (ppm): 8.81 (d, $j = 7.8$ Hz, 3H), 8.14 (d, $j = 7.8$ Hz, 3H), 7.91 (d, $j = 8.4$ Hz, 3H), 7.71 (m, 3H), 7.66 (m, 6H), 7.12 (m, 9H), 6.87 (t, $j = 7.7$ Hz, 6H), 6.78 (d, $j = 7.5$, 6H); MS: m/z 1037.0 (M + 1); Anal. calcd. for $C_{60}H_{39}N_6Ir$ (FW = 1036.32): C, 69.55; H, 3.76; N, 8.11. Found: C, 69.38; H, 3.84; N, 8.40; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 316 (41 000), 395–456 (12 000), and 557–564 nm (4500 cm^{-1} $_M{}^{-1}$).

Acknowledgements

[1] C. W. Tang, S. A. van Slyke, *Appl. Phys. Lett.* **1987**, *51*, 913.

[2] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539.

[3] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151.

[4] M. C. Derosa, D. J. Hodgson, G. D. Enright, B. Dawson, C. E. B. Evans, R. J. Crutchley, *J. Am. Chem. Soc.* **2004**, *126*, 7619.

[5] J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.* **2005**, *127*, 7502.

[6] K. Okumoto, H. Kanno, Y. Hamaa, H. Takahashi, K. Shibata, *Appl. Phys. Lett.* **2006**, *89*, 063504.

[7] H. Y. Chen, W. Y. Lam, J. D. Luo, Y. L. Ho, B. Z. Tang, D. B. Zhu, M. Wong, H. S. Kwok, *Appl. Phys. Lett.* **2002**, *81*, 574.

[8] J. Huang, T. Watanake, K. Ueno, Y. Yang, *Adv. Mater.* **2007**, *19*, 739.

[9] W.-Y. Wong, C.-L. Ho, Z.-Q. Gao, B.-X. Mi, C.-H. Chen, K.-W. Cheah, Z. Lin, *Angew. Chem. Int. Ed.* **2006**, *45*, 7800.

[10] C.-H. Yang, Y.-M. Cheng, Y. Chi, C.-J. Hsu, F.-C. Fang, K.-T. Wong, P.-T. Chou, C.-H. Chang, M.-H. Tsai, C.-C. Wu, *Angew. Chem. Int. Ed.* **2007**, *46*, 2418.

[11] M. Ilkai, S. Tokito, Y. Sakamoto, T. Suzuki, Y. Taga, *Appl. Phys. Lett.* **2001**, *79*, 156.

[12] Y. You, S. Y. Park, *J. Am. Chem. Soc.* **2005**, *127*, 12438.

[13] C. S. K. Mak, A. Hayer, S. I. Pascu, S. E. Watkins, A. B. Holmes, A. Köhler, R. H. Friend, *Chem. Commun.* **2005**, 4708.

[14] C. Yang, X. Zhang, H. You, L. Zhu, L. Chen, L. Zhu, Y. Tao, D. Ma, Z. Shuai, J. Qin, *Adv. Funct. Mater.* **2005**, *17*, 651.

[15] G. Schwartz, M. Pfeiffer, S. Reineke, K. Walzer, K. Leo, *Adv. Mater.* **2007**, *19*, 3672.

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

[17] H. Wu, J. Zou, F. Liu, L. Wang, A. Mikhailovsky, G. C. Bazan, W. Yang, Y. Cao, *Adv. Mater.* **2008**, *20*, 696.

[18] S. H. Kim, J. Jang, J. Y. Lee, *Appl. Phys. Lett.* **2007**, *90*, 203511.

[19] R. C. Kwong, M. R. Nugent, L. Michalski, T. Ngo, K. Rajan, Y.-J. Tung, M. S. Weaver, T. X. Zhou, M. Hack, M. E. Thompson, S. R. Forrest, J. J. Brown, *Appl. Phys. Lett.* **2002**, *81*, 162.

[20] B. D. Chin, C. Lee, *Adv. Mater.* **2007**, *19*, 2061.

[21] M. C. Gather, R. Alle, H. Becker, K. Meerholz, *Adv. Mater.* **2007**, *19*, 4460.

[22] E. L. Williams, K. Haavisto, J. Li, G. E. Jabbour, *Adv. Mater.* **2007**, *19*, 197.

[23] A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, *J. Am. Chem. Soc.* **2003**, *125*, 12971.

[24] M. S. Lowry, S. Bernhard, *Chem. Eur. J.* **2006**, *12*, 7970.

[25] Z. G. Gao, B. X. Mi, H. L. Tam, K. W. Cheah, C. H. Chen, M. S. Wong, S. T. Lee, C. S. Lee, *Adv. Mater.* **2008**, *20*, 774.

[26] B. Tong, Q. Mei, S. Wang, Y. Fang, Y. Meng, B. Wang, *J. Mater. Chem.* **2008**, *18*, 1636.

[27] W. Siebrand, M. Z. Zgierski, *J. Chem. Phys.* **1980**, *72*, 1641.

[28] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* **2001**, *123*, 4304.

[29] K. Dedeian, P. I. Djurovich, F. O. Garces, G. Carlson, R. J. Watts, *Inorg. Chem.* **1991**, *30*, 1685.

[30] P. J. Hay, *J. Phys. Chem.* **2002**, *106*, 1634.

[31] G. B. Rocha, R. O. Freire, A. M. Simas, G. F. de Sá, *Chem. Phys. Lett.* **2006**, *420*, 230.

[32] Y.-J. Su, H.-L. Huang, C.-L. Li, C.-H. Chien, Y.-T. Tao, P.-T. Chou, S. Datta, R.-S. Liu, *Adv. Mater.* **2003**, *15*, 884.

[33] R. J. Holmes, S. R. Forrest, Y.-J. Tung, R. C. Kwong, J. J. Brown, S. Garon, M. E. Thompson, *Appl. Phys. Lett.* **2003**, *82*, 2422.

[34] J.-P. Duan, P.-P. Sun, C.-H. Cheng, *Adv. Mater.* **2003**, *15*, 224.

[35] D. K. Rayabarapu, B. M. J. S. Paulose, J.-P. Duan, C.-H. Cheng, *Adv. Mater.* **2005**, *17*, 349.

[36] M. G. Colombo, T. C. Brunold, T. Riedener, H. U. Güdel, M. Förtsch, H.-B. Bürgi, *Inorg. Chem.* **1994**, *33*, 545.

[37] S. C. Xia, R. C. Kwong, V. I. Adamovich, M. S. Weaver, J. J. Brown, *IEEE* **2007**: 45th Annu. Int. Reliab. Phys. Symp. **2007**, p.253.

[38] B. D. Chin, C. Lee, *Adv. Mater.* **2007**, *19*, 2061.

[39] Gaussian 03, Revision B.01, Gaussian, Inc, Pittsburgh PA, USA **2003**.