Yellow/Orange Emissive Heavy-Metal Complexes as Phosphors in Monochromatic and White Organic Light-Emitting Devices

Journal:	*Chemical Society Reviews*
Manuscript ID:	CS-REV-03-2014-000110.R1
Article Type:	Review Article
Date Submitted by the Author:	26-Apr-2014
Complete List of Authors:	Fan, Cong; Wuhan University, Chemistry yang, chuluo; Wuhan University, Chemistry

Journal Name

Chemical Society Reviews

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Yellow/Orange Emissive Heavy-Metal Complexes as Phosphors in Monochromatic and White Organic Light-Emitting Devices

Cong Fan and Chuluo Yang*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Owing to the electron spin-orbit coupling (SOC) and fast intersystem crossing (ISC), heavy-metal complexes (such as iridium(III), platinum(II) and osmium(II) complexes et al.) are phosphorescence emissive at room temperature. Since 1998, heavy-metal complexes as phosphors have received considerable academic and industrial attentions in the field of organic light-emitting diodes (OLEDs), because they can harvest both the singlet (25 %) and triplet (75 %) excitons for emission during the electro-generated processes. Among all the visble colors (blue, green, yellow, orange and red), the yellow/orange heavy-metal complexes play an important role for realizing the full-color OLEDs as well as the high-efficiency white OLEDs, and thus the development of highly efficient yellow/orange heavy-metal complexes is pressing concern. In this article, we will review the progress on the yellow/orange heavy-metal complexes as phospors in OLEDs. The general principles and useful tactics for designing the yellow/orange heavy-metal complexes will be systematically summarized. The structure-property relationship and electrophosphorescence performance of the yellow/orange heavy-metal complexes in the monochromatic phosphorescent OLEDs (PhOLEDs) and white OLEDs (WOLEDs) will be comprehensively surveyed and discussed.

1. Introduction

The first electro-generated luminescence of organic compound was observed in 1963.[1] Over twenty years later, Tang and Van Slyke reported efficient green electroluminescence (EL) by using *tris*-(8-hydroxyquinolinato)aluminium (Alq_3) as emitter in organic light-emitting diodes (OLEDs).[2] Owing to the spin statistics, the singlet/triplet ratio of the electro-generated excitons is 25/75 %.[3] As a result, the internal quantum efficiency of OLEDs using fluorescent emitters can only reach the maximum value of 25 %. In 1998, Ma and Che et al. first demonstrated the electron-generated phosphorescence from the heavy-metal osimium(II) complexes.[4] In the same year, Forrest and Thompson et al. reported the high device efficiency by using the heavy-metal platinum(II) complex of PtOEP as the phosphor dopant, which can harvest both the electro-generated singlet (25 %) and triplet (75 %) excitons for emission.[5] Afterwards, the advancements of phosphorescent OLEDs (PhOLED) grow very fast in the past two decades and make revolution in the display and lighting industry, due to their outstanding merits such as high-luminance efficiency, full-color/large-area display, wide-viewing angle and low power consumption etc..[6]

The typical "sandwich" structure of PhOLEDs is shown in **Fig. 1**, which conventionally contains the multi-layer configuration as following: Anode/hole-injecting layer (HIL)/hole-transporting layer (HTL)/emitting layer (EML)/electron-transporting layer (ETL)/cathode, where the anode usually is the transparent ITO (indium tin oxide), the materials for the HIL/HTL/ETL are either organic small molecules or polymers, and the cathode is the metal (Mg, Al etc.) with low work function; while the composition in the EML of PhOLEDs incorporates organic small molecules/polymers as host materials and emissive phosphors as guest materials. To avoid competitive de-excitation pathways like triplet–triplet annihilation and/or concentration quenching, emissive phosphors are usually dispersed into host materials at low doping concentration.[7-8]

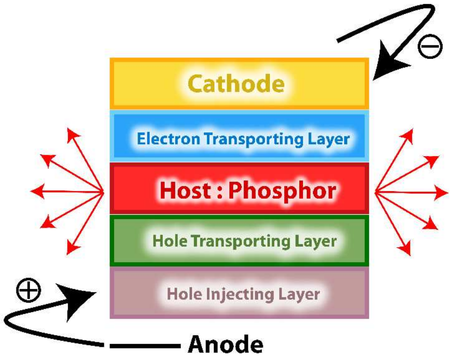


Fig. 1 Typical device configuration of PhOLEDs.

The cyclometalated heavy-metal complexes as the emissive phosphors play the core role in the EML of PhOLEDs. As the results of strong electron spin-orbit coupling (SOC) and fast intersystem crossing (ISC), the lowest triplet states (T_1) of the heavy-metal complexes are usually populated from their lowest singlet states (S_1) after photo-excitation.[9] Moreover, the lowest triplet states (T_1) of the heavy-metal complexes are found to be very sophisticated and proved to be splitted into three nondegenerate substates without the external magnetic field.[10-11] Each substate possesses relatively individual contributions from the virtual higher singlet states (S_n) involved in the configuration interaction (CI) method, which can break the spin-forbidden transition and provide the allowednesses to the electronic singlet ground states (S_0).[12] Consequently, these phosphorescent heavy-metal complexes are highly emissive at room temperature. And most ones possess radiative lifetimes in the range of microsecond (~μs), which are advantageously shorter than the typical lifetimes (ms-s) of the pure organic phosphorescence materials.[13]

For the study of heavy-metal complexes, most research works are focusing on the second- and third-row transition metal elements, such as iridium(III), platinum(II), osmium(II) and ruthenium(II) etc.. Among them, the iridium(III) complexes have been widely studied. Nowadays, using iridium(III) complexes as the emissvie phosphors, the full visible-spectrum monochromatic PhOLEDs can be easily realized. Furthermore, the external quantum efficiencies (EQE) of PhOLEDs for the three-primary colors (blue, green and red) have achieved or even exceeded the predicted upper-limit value of 20 %.[14-18] Reviews based on the heavy-metal complexes with blue, green and red emissions in PhOLEDs have been published.[19-23] However, few reviews give the systematical survey on the yellow/orange phosphorescent heavy-metal complexes, especially focusing on their designed strategies and application in monochromatic and white PhOLEDs. Not only the yellow/orange phosphorescent heavy-metal complexes are the indispensable components to fulfill the full-color display, but also they mainly contribute to realize the high-performance, two-color [blue and yellow/orange] WOLEDs, which exhibit superiority both in device efficiency and fabrication cost when compared to the three-color [blue, green and red] analogues as the solid-state lighting source. Meanwhile, in the four-color [blue, green, yellow/orange and red] WOLEDs, the yellow/orange phosphorescent heavy-metal complexes are advantageous to enhance the device efficiencies and the color rendering index (CRI)/color temperature index.

In this article, we will review the neutral-charge, yellow/orange heavy-metal complexes, particularly concentrating on the iridium(III) and platinum(II) complexes, and briefly on the osmium(II) and gold(III) complexes. The design strategies, photophysical properties of the yellow/orange heavy-metal complexes as well as their electrophosphorescence performance in the monochromatic PhOLEDs and the two-color or four-color WOLEDs will be surveyed and highlighted. In order to facilitate the survey in this context, we are focusing on the yellow/orange phosphorescent heavy-metal complexes, of which their emission peaks are mainly located between 540~610 nm in solution or in solid state/film. Subsequently, the electroluminance (EL) colors of the corresponding monochromatic PhOLEDs are roughly classified according to the Commission Internationale de L'Eclairage (CIE) coordinates of (x, y), as depicted in **Fig. 2**. For briefness, the CIE coordinates of the yellow and yellow-orange PhOLEDs are in the range of (0.45-0.55, 0.40-0.55); while the CIE coordinates of the orange and orange-red PhOLEDs are located in the scope of (0.50-0.60, 0.35-0.45).

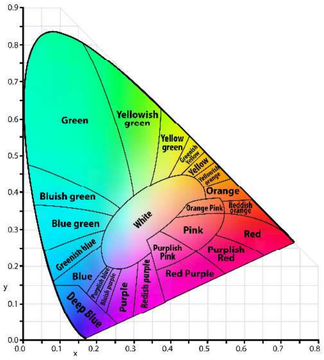


Fig. 2 CIE 1931 chromaticity diagram.

2. Iridium(III) Complexes

Owning to the d^6 electron configuration of Ir(III) ion, the neutral cyclometalated Ir(III) complexes with six chemical bonds adopt the octahedral molecular conformation. Therefore, the Ir(III) complexes are usually constituted by three bidentate ligands, either homoleptic (C^N)$_3$Ir or heteroleptic (C^N)$_2$Ir(L^X), where C^N represents the cyclometalating bidentate ligand and L^X stands for the ancillary bidentate ligand. The phosphorescence emissions of the Ir(III) complexes are found to be mainly originated from the ^{3}MLCT (metal-to-ligand charge transfer) excited states and/or the ligand-centered (LC) $^3\pi$-π^* excited states.[24] Because the strong σ-donating carbanion in the C^N ligands can elevate the d* orbitals of Ir(III) ion to avoid the non-emissive metal-centered (MC) d-d* excited states, most Ir(III) complexes are highly emissive in solution at room temperature.

Determined by the energy gaps of the cyclometalating ligands, the emission peaks (λ_{peak}) of Ir(III) complexes are easily tunable. On one hand, as shown in **Fig. 3**, using the cyclometalating ligands with large energy gaps can make Ir(III) complexes blue-emitting;[25] while using the cyclometalating ligands with large π conjugation can result in narrow energy gaps and make Ir(III) complexes red-emitting.[26] On the other hand, based on the green-emitting *tris*-(2-phenylpyridinato-*N*,*C*$^{2'}$)iridium(III) [Ir(ppy)$_3$], the HOMO level is primarily localized on the phenyl part of 2-phenylpyridine (ppy) ligand and the Ir(III) ion; while the LUMO level is mainly distributed on the pyridine part of ppy ligand.[27] Therefore, adding electron-withdrawing/electron-donating groups to the pyridine rings of Ir(III) complexes is supposed to lower/raise the LUMO level; while attaching electron-withdrawing/electron-donating groups to the phenyl rings of Ir(III) complexes is expected to decrease/increase the HOMO level. Both the methodologies can finely tune the energy gaps of Ir(III) complexes and consequently tune the emission peaks. Alternatively, in the heteroleptic cyclometalated Ir(III) complexes of (C^N)$_2$Ir(L^X), which contain two cyclometalating ligands (C^N) and one ancillary ligand (L^X), the ancillary ligand can also tune the emission peaks by its electron-accepting or electron-donating ability. Therefore, for clarity in this part, we classify the whole yellow/orange Ir(III) complexes into three categories: (i) Cyclometalating ligand-controlled Ir(III) complexes; (ii) Functional group/substituent-modified Ir(III) complexes; (iii)

Ancillary ligand-controlled Ir(III) complexes.

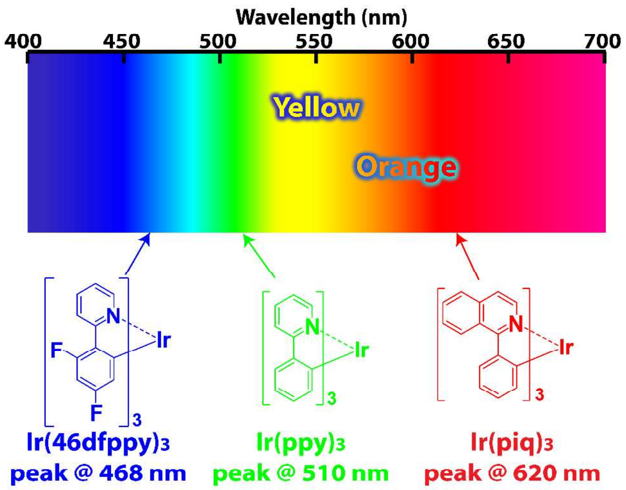
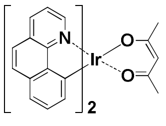


Fig. 3 The visible spectrum and the typical representatives of the blue-, green- and red-emitting homoleptic *tris*-cyclometalated Ir(III) complexes.

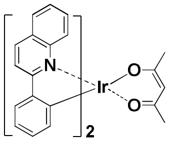
2.1. Cyclometalating ligand-controlled Ir(III) complexes

The emission peaks of Ir(III) complexes are dominantly determined by the energy gaps of the cyclometalating ligands (C^N). To successfully achieve yellow/orange emissions, the cyclometalating ligands should possess middle-size π system. Otherwise smaller or larger π system of ligands can result in the green/blue or red emissions. Noticeably, the cyclometalating ligands (C^N) are usually the aromatic heterocyclic rings containing C-, N-, S-, O-atom, etc.. Therefore, in this section, we further divide the cyclometalating ligand-controlled Ir(III) complexes into groups according to the different kinds of the hetero-atoms involved in their cyclometalating ligands (C^N).

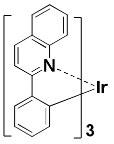
2.1.1. Ligands containing C, N-heterocyclic ring



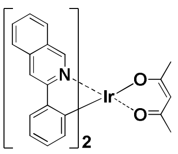
(bzq)$_2$Ir(acac)
(Ir-1)



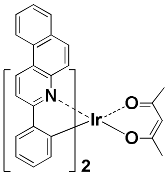
(pq)$_2$Ir(acac)
(Ir-2)



Ir(phq)$_3$
(Ir-3)



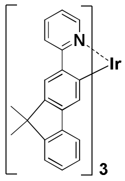
(3-piq)$_2$Ir(acac)
(Ir-4)

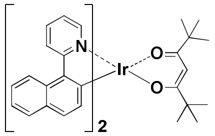


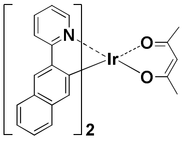
(pbq-*f*)$_2$Ir(acac)
(Ir-5)

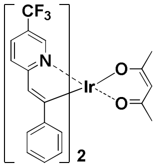
In 2001, Thompson et al. initially reported a yellow Ir(III) complex of (bzq)$_2$Ir(acac) (**Ir-1**) by using benzoquinoline (bzq) as the cyclometalating ligand, where acac stands for the ancillary ligand of acetylacetonate.[28] It was noticeable that increasing the ligand rigidity from 2-phenylpyridine (ppy) to bzq ligand enlarges the π conjugation and tunes the emission peak of green-emitting (ppy)$_2$Ir(acac) (λ_{peak} = 516 nm) to 548 nm of (bzq)$_2$Ir(acac) (**Ir-1**) in 2-methyltetrahydrofuran (2-MeTHF) solution. Meanwhile, the (bzq)$_2$Ir(acac) (**Ir-1**) possesses close quantum efficiency (Φ = 0.27) to (ppy)$_2$Ir(acac) (Φ = 0.34). Alternatively, fusing a phenyl ring into the pyridine ring of ppy ligand gave a new cyclometalating ligand of 2-phenylquinoline (pq), which made the corresponding Ir(III) complex of (pq)$_2$Ir(acac) (**Ir-2**) (Φ = 0.10) red-shift to orange-red emission of 597 nm.[28] Recently in 2011, by employing a newly developed hole-transporting material (HTL) of DCDPA [3,5-di(9*H*-carbazol-9-yl)-*N,N*-diphenylaniline], Lee et al. reported that the (pq)$_2$Ir(acac) (**Ir-2**)-based PhOLEDs hosted by BSFM {9,9'-spirobi[fluorene]-2-yl(9,9'-spirobi[fluorene]-7-yl)methanone} reached very high efficiencies (max. EQE of 19.2 %), under the device configuration of ITO/DNTPD {*N,N'*-diphenyl-*N,N'*-bis-[4-(phenyl-*m*-tolyl-amino)phenyl]-biphenyl-4,4'-diamine}/NPB [1,4-bis(1-naphthylphenylamino)-biphenyl]/DCDPA/BSFM:(pq)$_2$Ir(acac) (**Ir-2**)/TSPO1 [diphenylphosphine oxide-4-(triphenylsilyl)phenyl]/LiF/Al. Furthermore, the power efficiency (PE) reached 16.4 lm W^{-1} even at high luminance of 1000 cd m^{-2} (EQE of 17.1 %).[29] In 2004, Matsumura et al. claimed that the homoleptic *tris*-cyclometalated Ir(III) complex of Ir(phq)$_3$ (**Ir-3**) by using the same 2-phenylquinoline (phq) ligand was obtained through the microwave synthesis.[30] The Ir(phq)$_3$ (**Ir-3**) displayed orange emission of 589 nm in EL spectrum, slightly blue-shifted when compared to its heteroleptic (pq)$_2$Ir(acac) (**Ir-2**) (λ_{peak} = 597 nm). The PhOLEDs hosted by 4,4'-*N,N*'-dicarbazolylbiphenyl (CBP) achieved good efficiencies, with max. current efficiency (CE) of 33.4 cd A^{-1} and power efficiency (PE) of 11.7 lm W^{-1}. In 2005, Liu et al. unveiled that different isomers of the cyclometalating ligands can bring in different emissions. Using 3-phenylisoquinoline (3-piq) as the cyclometalating ligand, which is the isomer of 2-phenylquinoline (pq), only yellow emission of 562 nm in CH_2Cl_2 solution was observed by the resulting Ir(III) complex of (3-piq)$_2$Ir(acac) (**Ir-4**) (Φ = 0.33). The (3-piq)$_2$Ir(acac) (**Ir-4**)-based PhOLEDs hosted by CBP achieved moderate device efficiencies (max. 23.94 cd A^{-1}, 9.38 lm W^{-1} and EQE of 7.17 %).[31] However, Qiao et al. disclosed that the large π-system ligand of 1-phenyl-benzo[*f*]quinoline (pbq-*f*) by further fusing one phenyl ring on the quinoline ring of 2-phenylquinoline (pq) ligand failed to make the emission of the Ir(III) complex further red-shift.[32] The resulting Ir(III) complex of (pdq-*f*)$_2$Ir(acac) (**Ir-5**) exhibited emission peak only at 577 nm in 2-MeTHF solution, but it displayed remarkably high quantum efficiency of 0.93. Interestingly, the Ir(III) complex cyclometalated by its isomer of 2-phenyl-benzo[g]quinoline showed remarkably bathochromic emission of 708 nm in near-infrared region. Fair device efficiencies (max. 12.3 cd A^{-1} and EQE of 4.9 %) were reported for the (pdq-*f*)$_2$Ir(acac) (**Ir-5**)-based PhOLEDs hosted by CBP.

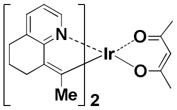
In 2003, Tsuboyama et al. issued a series of homoleptic *tris*-cyclometalated Ir(III) complexes.[33] Using rigid fluorene to replace the 2-phenyl ring in the ppy ligand caused the resulting Ir(III) complex of Ir(flpy)$_3$ (**Ir-6**) yellow emission with peak of 545 nm in toluene solution, where flpy represents the ligand of 2-(9,9-dimethyl-9*H*-fluoren-2-yl)pyridine. The Ir(flpy)$_3$ (**Ir-6**) displayed obviously red-shifted emission from Ir(ppy)$_3$ (λ_{peak} = 510 nm) due to the enlarged π conjugation. But it exhibited moderate quantum efficiency of 0.29 for its dominant ligand-center (LC) $^3\pi$-π* excited state, as confirmed by its well-resolved vibronic progressions in the low-temperature phosphorescence spectrum. Similarly, taking naphthalene ring to replace the 2-phenyl ring in the ppy ligand and using the formed 2-(naphthalen-1-yl)pyridine as the cyclometalating ligand, Holder et al. made the emission of the corresponding Ir(III) complex (**Ir-7**) (λ_{peak} = 600 nm) fall into the orange-red region in $CHCl_3$ solution, accompanying with a moderate quantum efficiency of 0.37, which was significantly red-shifted from the green-emitting $(ppy)_2Ir(acac)$ (λ_{peak} = 516 nm).[34] Afterwards, by changing the ligand from 2-(naphthalen-1-yl)pyridine to its isomer 2-(naphthalen-2-yl)pyridine (npy), Tao et al. built the yellow Ir(III) complex of $(npy)_2Ir(acac)$ (**Ir-8**), with emission peak of 551 nm in its electroluminance (EL) spectrum. The $(npy)_2Ir(acac)$ (**Ir-8**)-based PhOLEDs hosted by mCP (*N,N'*-dicarbazolyl-3,5-benzene) displayed good PE of max. 21.8 lm W^{-1}. Simultaneously, using $(npy)_2Ir(acac)$ (**Ir-8**) as the yellow phosphor and bis(2-(4',6'-difluoro)phenylpyridinato-*N*,$C^{2'}$)iridium(III) picolinate (FIrpic) as the sky-blue phosphor, the two-color WOLEDs under the device configuration of ITO/NPB/mCP:$(npy)_2Ir(acac)$ (**Ir-8**)/UGH2 [*p*-bis(triphenylsilyly)benzene]:FIrpic/BAlq [{bis(2-methyl-8-quinolinolato)-4-phenyl-phenolato}aluminum(III)]/LiF/Al with double emitting layers showed the max. PE of 29.2 lm W^{-1} (37.2 cd A^{-1} and EQE of 12.6%) with CIE coordinates around (0.32, 0.45), where UGH2 was used as the host material for the sky-blue FIrpic (E_T = 2.62 eV) for its high triplet energy (E_T = 3.18 eV).[35]


$Ir(flpy)_3$
(Ir-6)


(Ir-7)

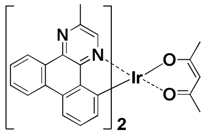

$(npy)_2Ir(acac)$
(Ir-8)

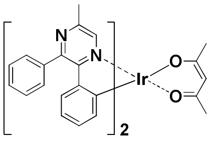

$(PETP)_2Ir(acac)$
(Ir-9)

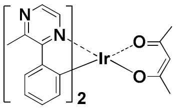

(Ir-10)

During 2004-2005, for the first time, Cheng et al. unveiled that alkenyl pyridine derivatives can functionalize as the cyclometalating ligands for orange and red Ir(III) complexes through the conventional synthetic procedures.[36-37] Among them, the Ir(III) complex of $(PETP)_2Ir(acac)$ (**Ir-9**) cyclometalated by the ligand of 2-(*E*-2-pheny-1-ethenyl)-5-(trifluoromethyl) pyridine (PETP) exhibited orange-red emission of 610 nm but fair quantum efficiency of 0.10 in CH_2Cl_2 solution. Noticeably, further changing the phenyl ring to 1-naphthyl ring in the PETP ligand failed to substantially alter the emission peak, because the aryl substitutents were not coplanar with the ethenyl (C=C) group. Fair efficiencies (max. 13.1 cd A^{-1}, 5.5 lm W^{-1} and EQE of 5.9 %) were obtained in the $(PETP)_2Ir(acac)$ (**Ir-9**)-based PhOLEDs hosted by CBP. The $(PETP)_2Ir(acac)$ (**Ir-9**) showed the emission peak of 602 nm in its EL spectrum and so the color of the resulting device fell into the orange region with a CIE coordinate of (0.59, 0.41). Later, to provide more rigidity on these alkenyl pyridine ligands, Yamashita et al. designed several bicyclic vinylpyridine-based cyclometalated Ir(III) complexes.[38] The different size of the cycloalkane rings seriously affected the photophysical properties of the Ir(III) complexes for the steric hindrance and also brought about bad quantum efficiencies. The typical Ir(III) complex (**Ir-10**) cyclometalated by the ligand of (*E*)-8-ethylidene-5,6,7,8-tetrahydroquinoline showed orange emission of 592 nm and poor quantum efficiency of ~0.06 in CH_2Cl_2 solution. Surprisingly, the Ir(III) complex (**Ir-10**)-based PhOLEDs hosted by CBP still realized moderate device efficiencies (max. 19.8 cd A^{-1}, 6.8 lm W^{-1} and EQE of 8.1 %). The above results manifested that the photoluminance (PL) properties of the Ir(III) complexes in solution were not directly related to their EL efficiencies.

2.1.2. Ligands containing N, N-heterocyclic ring


$(MDQ)_2Ir(acac)$
(Ir-11)


$(MDPP)_2Ir(acac)$
(Ir-12)

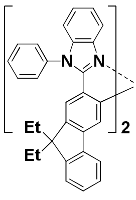

$(MPPZ)_2Ir(acac)$
(Ir-13)

In 2003, Cheng et al. presented a novel orange Ir(III) complex, named $(MDQ)_2Ir(acac)$ (**Ir-11**) by using 2-methyl-dibenzo[*f,h*]quinoxaline (MDQ) as the cyclometalating ligand.[39] The $(MDQ)_2Ir(acac)$ (**Ir-11**) displayed orange emission of 608 nm and good quantum efficiency of 0.48 in CH_2Cl_2 solution, benefiting from the highly rigid fused-pyrazine skeleton. Under the device configuration of ITO/NPB/CBP:$(MDQ)_2Ir(acac)$ (**Ir-11**)/TPBi [1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene]/Alq_3/Mg:Ag, the $(MDQ)_2Ir(acac)$ (**Ir-11**)-based PhOLEDs realized remarkably high efficiencies (max. 26.2 cd A^{-1}, 13.7 lm W^{-1} and EQE of 12.4 %) with an orange-red CIE coordinate of (0.60, 0.39) at that time. Later in 2009, Leo et al. employed $(MDQ)_2Ir(acac)$ (**Ir-11**) as the "red" component into the three-color, all-phosphor WOLEDs.[40] With the light outcoupling technology, the WOLEDs revealed the recorded PE of 90 lm W^{-1} at high luminance of 1000 cd m^{-2} at that time.

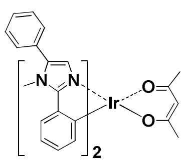
In 2005, Guo et al. reported a similar pyrazine-based Ir(III) complex of $(MDPP)_2Ir(acac)$ (**Ir-12**) by using the ligand of 5-methyl-2,3-diphenylpyrazine (MDPP).[41] The MDPP ligand expressed "broken" fused-ring structure and consequently the reduced π conjugation. As a result, the $(MDPP)_2Ir(acac)$ (**Ir-12**) showed the blue-shifted emission of 580 nm in CH_2Cl_2 solution when compared to its analogue $(MDQ)_2Ir(acac)$ (**Ir-11**) (λ_{peak} = 608 nm). Fair efficiencies (max. 9.89 lm W^{-1} and EQE of 6.02 %) were obtained for the $(MDPP)_2Ir(acac)$ (**Ir-12**)-based PhOLEDs hosted by NPB. Interestingly, cutting off the 3-phenyl ring on the ligand of MDPP still guaranteed the emission of the resulting Ir(III) complex stay in the yellow region, as later proved by the same group in 2009.[42] The newly obtained Ir(III) complex of $(MPPZ)_2Ir(acac)$ (**Ir-13**) cyclometalated by the ligand of 2-methyl-3-phenylpyrazine (MPPZ) appeared yellow emission of 575 nm in CH_2Cl_2 solution. But, its analoguous Ir(III) complex cyclometalated by 2-phenylpyrimidine, which is the similar isomer of MPPZ, only realized green emission. The $(MPPZ)_2Ir(acac)$ (**Ir-13**)-based PhOLEDs hosted by CBP displayed moderate device efficiencies (max. 37.3 cd A^{-1}, 20.3 lm

W^{-1} and EQE of 13.2 %).

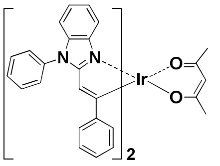
In 2004, Tao et al. established eight novel Ir(III) complexes with the emission peaks in the range of green-red by exploiting the benzoimidazole (bi) derivatives as the cyclometalating ligands.[43] However, the parent benzoimidazole-based ligand of 1,2-diphenyl-1*H*-benzoimidazole (pbi) didn't seem to possess enough π system and its related Ir(III) complex of $(pbi)_2Ir(acac)$ displayed only green emission. Combined with the rigid fluorene to increase the π conjugation in the ligand of 2-(9,9-diethyl-9*H*-fluoren-2-yl)-1-phenyl-1*H*-benzoimidazole (fbi), the resulting Ir(III) complex of $(fbi)_2Ir(acac)$ (**Ir-14**) exhibited orange emission of 563 nm and good quantum efficiency of 0.51 in toluene solution. The CBP-hosted PhOLEDs based on $(fbi)_2Ir(acac)$ (**Ir-14**) showed decent efficiencies (max. 30 cd A^{-1}, 7.8 lm W^{-1} and EQE of 10.4 %) at that time. Currently, due to its high quantum efficiency and easy processability, the $(fbi)_2Ir(acac)$ (**Ir-14**) has became one of the most used orange phosphors.[44] And recently in 2010, by developing the novel bipolar host material of *p*-BISiTPA [(4-{diphenyl[4-(1-phenyl-1*H*-benzimidazol-2-yl)phenyl]silyl}phenyl)diphenylamine], very high device efficiencies (max. 57.8 cd A^{-1}, 51.9 lm W^{-1} and EQE of 20.5 %) for the $(fbi)_2Ir(acac)$ (**Ir-14**)-based PhOLEDs were realized by our group, under the device configuration of ITO/MoO_3/NPB/TCTA [4,4',4"-tris(carbazol-9-yl)-triphenylamine]/*p*-BISiTPA:$(fbi)_2Ir(acac)$ (**Ir-14**)/TPBi/LiF/Al.[45] Meanwhile, our group fabricated the two-color WOLEDs by using $(fbi)_2Ir(acac)$ (**Ir-14**) as the orange phosphor and FIrpic as the sky-blue phosphor. Under the device configuration of ITO/MoO_3/NPB/TCTA/*p*-BISiTPA:FIrpic:$(fbi)_2Ir(acac)$ (**Ir-14**)/TPBi/LiF/Al, the resulting WOLEDs with single emitting layer reached very high efficiencies, with max. CE of 51.8 cd A^{-1}, PE of 42.7 lm W^{-1} and EQE of 19.1 %, which were among the highest results at that time.[46]



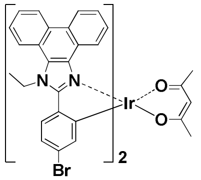
$(fbi)_2Ir(acac)$
(Ir-14)



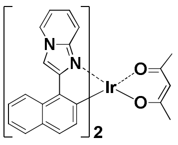
(Ir-15)



$(psbi)_2Ir(acac)$
(Ir-16)



$(pi)_2Ir(acac)$
(Ir-17)

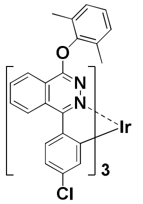


(Ir-18)

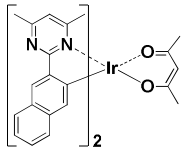
In 2010, Baranoff et al. investigated the photophysical properties of the imidazole-based Ir(III) complexes by reducing the fused benzene ring from the benzoimidazole (bi) moiety.[47] The prototype of this kind of Ir(III) complexes cyclometalated by the parent ligand of 2-phenylimidazole presented strange broad emission. Methyl groups and/or phenyl groups were added to tune the emission peaks. The represented Ir(III) complex (**Ir-15**) with 1-methyl-2,5-diphenylimidazole as the cyclometalating ligand displayed yellow emission of 557 nm and quantum efficiency of 0.32 in CH_2Cl_2 solution. It was noticeable that different methyl/phenyl groups on the different positions of the imidazole ring vastly affected the photophysical properties of these Ir(III) complexes, resulting in their various emission peaks and quantum efficiencies. In the same year of 2010, Sun et al. combined alkenyl moiety and benzoimidazole (bi) moiety together to constitute two new cyclometalating styrylbenzoimidazole ligands.[48] The resulting Ir(III) complex of $(psbi)_2Ir(acac)$ (**Ir-16**) cyclometalated by the ligand of 1-phenyl-2-styryl-1*H*-benzo[d]imidazole (psbi) appeared yellow emission of 570 nm and moderate quantum efficiency of 0.25 in CH_2Cl_2 solution. Fair efficiencies (max. 26.6 cd A^{-1} and EQE of 8.4 %) were obtained in the $(psbi)_2Ir(acac)$ (**Ir-16**)-based PhOLEDs hosted by CBP, but the device remained CE of 20.7 cd A^{-1} at extremely high luminance of 10000 cd m^{-2}.

Afterwards in 2011, Wu et al. disclosed another benzoimidazole-based ligand by fusing two more benzene rings into the benzoimidazole (bi) moiety.[49] The newly formed ligand of 2-(4-bromophenyl)-1-ethyl-1*H*-phenanthro[9,10-*d*]imidazole (pi) had enough π system and made the cyclometalated Ir(III) complex of $(pi)_2Ir(acac)$ (**Ir-17**) yellow emission of 570 nm in CH_2Cl_2 solution, where the replacement of 2-phenyl ring was no longer needed as compared to the green-emitting Ir(III) complex with the ligand of 1,2-diphenyl-1*H*-benzoimidazole (pbi). In spite of containing the bromine atom, the $(pi)_2Ir(acac)$ (**Ir-17**) still showed decent quantum efficiency of 0.28 in CH_2Cl_2 solution. However, the $(pi)_2Ir(acac)$ (**Ir-17**)-based PhOLEDs hosted by CBP exhibited poor efficiencies (max. 4.6 cd A^{-1} and 1.82 lm W^{-1}).

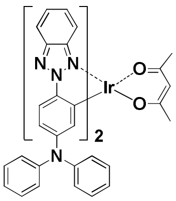
In 2007, Yamashita et al. systematically designed fourteen imidazo[1,2-*a*]pyridine-based Ir(III) complexes, aiming to tune their emissions into blue rigion.[50] The ligands of these imidazo[1,2-*a*]pyridine-based derivatives were conveniently obtained through the condensation reactions between 2-aminopyridine and the corresponding 2-bromoacetophenones. The Ir(III) complex cyclometalated by the parent ligand of 2-phenylimidazo[1,2-*a*]pyridine only accomplished green emission. Using 2-(1-naphthalenyl)imidazo[1,2-*a*]pyridine as the cyclometalating ligand, the representive Ir(III) complex (**Ir-18**) was tuned to yellow emission of 550 nm in CH_2Cl_2 solution. However, the family of these Ir(III) complexes showed unpromising quantum efficiencies with values no more than 0.01. They claimed that the metal-centered (MC) excited states in these Ir(III) complexes may be responsible for the low quantum efficiencies.



$Ir(MPCPPZ)_3$
(Ir-19)



$(NDMP)_2Ir(acac)$
(Ir-20)

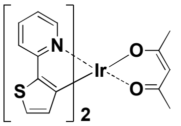


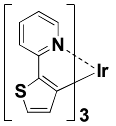
$(TBT)_2Ir(acac)$
(Ir-21)

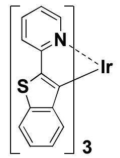
In 2008, Wang et al. issued a novel homoleptic *tris*-cyclometalated Ir(III) complex of $Ir(MPCPPZ)_3$ (**Ir-19**) based on the phthalazine-based ligand. The incorporation of phenolic group significantly improved the solubility and alleviated the self-quenching for its steric hindrance. The resulting ligand of 1-(2,6-dimethylphenoxy)-4-(4-chlorophenyl)phthalazine (MPCPPZ) made the corresponding Ir(III) complex of Ir(MPCPPZ)$_3$ (**Ir-19**) orange emission of 590 nm in the doped film co-hosted by PVK [poly(*N*-vinylcarbazole)] and CBP. Noticeably, the Ir(MPCPPZ)$_3$ (**Ir-19**) displayed astonishingly high quantum efficiency of 0.95 in the co-host film. As a consequence, a max. EQE of 20.2 % and CE of 18.4 cd A^{-1} were recorded in the Ir(MPCPPZ)$_3$ (**Ir-19**)-based PhOLEDs under the device configuration of ITO/PEDOT:PSS [poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)]/PVK:CBP:Ir(MPCPPZ)$_3$ (**Ir-19**)/TPBi/Ba/Al by solution process, which was claimed to be the first example of the polymer-based orange-red PhOLEDs with the EQE value above 20 %.[51]

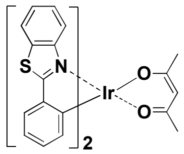
In 2011, Xu et al. revealed a pyrimidine-based Ir(III) complex of (NDMP)$_2$Ir(acac) (**Ir-20**), which was cyclometalated by the ligand of 2-(2-naphthyl)-4,6-dimethylpyrimidine (NDMP) and depicted yellow emission of 560 nm in CH_2Cl_2 solution. Obviously, as mentioned for the pyrimidine-based ligands, the 2-naphthyl moiety played the decisive role for achieving the yellow emission.[52] In 2009, Su et al. built an orange-red Ir(III) complex of (TBT)$_2$Ir(acac) (**Ir-21**) with emission peak at 598 nm in THF (tetrahydrofuran) solution by employing benzotriazole derivative as the cyclometalating ligand. The attached diphenylamine group in the ligand of 2-(4'-diphenylamine-phenyl)-2*H*-benzo[*d*][1,2,3]triazole (TBT) facilitated the hole-transporting ability and further made the emission peak red-shift ~50 nm. Although the *n*-doped layer of Bphen:Cs_2CO_3 was used to enhance the electron-transporting ability, the (TBT)$_2$Ir(acac) (**Ir-21**)-based PhOLEDs hosted by CBP exhibited only fair efficiencies (max. 15.81 cd A^{-1}, 13.8 lm W^{-1} and EQE of 9.06 %).[53]

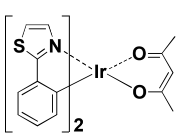
2.1.3. Ligands containing S, N-heterocyclic ring


(thp)$_2$Ir(acac)
(Ir-22)


Ir(thpy)$_3$
(Ir-23)


Ir(btpy)$_3$
(Ir-24)

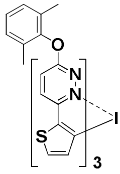

(bt)$_2$Ir(acac)
(Ir-25)


(ptz)$_2$Ir(acac)
(Ir-26)

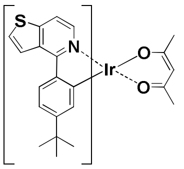
In 2001, Thompson et al. initially utilized S-containing thiophene to replace the 2-phenyl ring in the ppy ligand and synthesized 2-(2'-thienyl)pyridine (thp) as the cyclometalating ligand.[28] The resulting Ir(III) complex of (thp)$_2$Ir(acac) (**Ir-22**) succeeded in realizing red-shift to yellow emission of 562 nm in 2-MeTHF solution when compared to the green-emitting (ppy)$_2$Ir(acac) (λ_{peak} = 516 nm), which was straightforwardly attributed to the coplanar, electron-rich thiophene ring. Soon in 2003, Tsuboyama et al. used the same ligand to construct the *tris*-cyclometalated Ir(III) counterpart of Ir(thpy)$_3$ (**Ir-23**).[33] The homoleptic Ir(thpy)$_3$ (**Ir-23**) displayed slightly higher quantum efficiency (Φ = 0.17) than its heteroleptic (thp)$_2$Ir(acac) (**Ir-22**) (Φ = 0.12), but manifested a little blue-shifted emission of 550 nm from (thp)$_2$Ir(acac) (**Ir-22**) (λ_{peak} = 562 nm) in toluene solution. Simultaneously, the same group illustrated that the similar blue-shift phenomenon happened in the Ir(III) complex of Ir(btpy)$_3$ (**Ir-24**) with the ligand of 2-(2'-benzothienyl)pyridine (btpy/btp), which also showed blue-shifted emission peak of 596 nm from its Ir(III) analogue of (btp)$_2$Ir(acac) with red emission (λ_{peak} = 612 nm).[28] All the related cases unveiled that using ancillary ligand of acetylacetonate (acac) to replace one of the cyclometalating ligands in the homoleptic *tris*-cyclometalated Ir(III) complexes can make their emission peaks red-shifted, which is likely due to the electron-donating property of acac.

In the same paper mentioned above,[28] Thompson et al. also developed another kind of cyclometalating ligand based on benzothiazole derivatives. The parent benzothiazole-based ligand of 2-phenylbenzothiazole (bt) intrinsically owned the sufficient π conjugation to make its cyclometalated Ir(III) complex of (bt)$_2$Ir(acac) (**Ir-25**) yellow emission of 557 nm, along with quantum efficiency of 0.26 in 2-MeTHF solution. Apparently, displacing the 2-phenyl ring and enlarging the π conjugation with other fused aromatic rings such as thiophene and naphthalene can further tune the emission peaks into orange and red. At early stage, the (bt)$_2$Ir(acac) (**Ir-25**)-based PhOLEDs hosted by CBP only presented moderate efficiencies (max. 11 lm W^{-1} and EQE of 9.7 %). As the optimizations of the device structure are advancing and better carrier-transporting materials are exploited, currently in 2013, our group has reported that the (bt)$_2$Ir(acac) (**Ir-25**)-based PhOLEDs can reach very high efficiencies (max. 69.7 cd A^{-1}, 69 lm W^{-1} and EQE of 25.7 %) under the device configuration of ITO/MoO_3/TAPC [1,1-bis[(di-4-tolylamino)phenyl]cyclohexane]/TCTA [4,4',4''-tris(carbazol-9-yl)-triphenylamine]/CBP:(bt)$_2$Ir(acac) (**Ir-25**)/TmPyPB [1,3,5-tri(*m*-pyrid-3-yl-phenyl) benzene]/LiF/Al, where TAPC (hole mobility~10^{-2} cm^2 V^{-1} s^{-1}) and TmPyPB (electron mobility~10^{-3} cm^2 V^{-1} s^{-1}) possess high hole- and electron-transporting mobilities, respectively.[54] Moreover, the (bt)$_2$Ir(acac) (**Ir-25**)-based device remained CE of 53.5 cd A^{-1}, PE of 23 lm W^{-1} and EQE of 19.6 % at extremely high luminance of 10000 cd m^{-2}. Simultaneously, our group has also found the quantum efficiency of (bt)$_2$Ir(acac) (**Ir-25**) was as high as 0.65 in CH_2Cl_2 solution, rather than the previously reported value of 0.26. These encouraging results further assure the (bt)$_2$Ir(acac) (**Ir-25**) among one of the first choices as the yellow phosphor in the two-color WOLEDs. Recently in 2010, Kido et al. reported that the two-color WOLEDs with double emitting layers by using (bt)$_2$Ir(acac) (**Ir-25**) as the yellow phosphor revealed the max. CE of 44 cd A^{-1}, PE of 52.7 lm W^{-1} and EQE of 19 % under the device configuration of ITO/TAPC/TCTA/DCzPPy [2,6-bis(3-(carbazol-9-yl)phenyl)pyridine]:(bt)$_2$Ir(acac) (**Ir-25**)/PO9 [3,6-bis(diphenylphosphoryl)-9-phenylcarbazole]:Ir(dbfmi)/B3PyPB [3,5,3'',5''-tetra-3-pyridyl-(1,1';3',1'')terphenyl]/LiF/Al.[55] The WOLEDs exhibited the improved color rendering index (CRI) of 72.2 due to the contribution of the newly developed deep-blue Ir(III) complex of *mer*-tris(*N*-dibenzofuranyl-*N'*-methylimidazole)iridium(III) [Ir(dbfmi)].

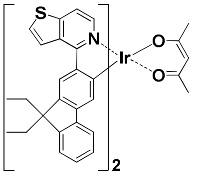
In 2009, Xu et al. diminished the π system from benzothiazole to thiazole, and the newly obtained ligand of 2-phenylthiazole (ptz) still made its cyclometalated Ir(III) complex of $(ptz)_2Ir(acac)$ (**Ir-26**) remain in yellow emission of 547 nm in CH_2Cl_2 solution, only 10 nm blue-shifted from its Ir(III) counterpart $(bt)_2Ir(acac)$ (**Ir-25**) (λ_{peak} = 557 nm). But, the quantum efficiency of $(ptz)_2Ir(acac)$ (**Ir-26**) dramatically decreased to ~0.10.[56]



Ir(PYA)$_3$
(Ir-27)



(tptpy)$_2$Ir(acac)
(Ir-28)



(EtPy)$_2$Ir(acac)
(Ir-29)

In 2010, Wang et al. built a homoleptic Ir(III) complex of $Ir(PYA)_3$ (**Ir-27**), which was *tris*-cyclometalated by the pyridazine-based ligand of 3-(2,6-dimethylphenoxy)-6-(thiophen-2-yl) pyridazine (PYA).[57] As mentioned in the literature, reducing the π system from phthalazine to pyridazine caused the resembling Ir(III) complex *tris*-cyclometalated by 3,6-bis(phenyl)-pyridazine green-emitting (λ_{peak} = 541 nm).[58] Therefore, the thiophene ring in the ligand of PYA played the critical role to tune $Ir(PYA)_3$ (**Ir-27**) into orange emission of 580 nm in CH_2Cl_2 solution. Fair efficiencies (max. 13.7 cd A^{-1} and EQE of 9.1 %) were obtained for the $Ir(PYA)_3$ (**Ir-27**)-based PhOLEDs co-hosted by PVK and PBD [2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole].

Recently in 2013, Kwon et al. reported that astonishingly high efficiencies were realized in the yellow PhOLEDs and the two-color WOLEDs by employing the novel yellow Ir(III) complex of $(tptpy)_2Ir(acac)$ (**Ir-28**).[59-60] The $(tptpy)_2Ir(acac)$ (**Ir-28**), which was cyclometalated by the thieno[3,2-c]pyridine-based ligand of 4-*p*-tolyl-thieno[3,2-c]pyridine (tptpy), exhibited emission peak at 560 nm in its EL spectrum, as previously reported in the literatures.[61-65] In the device configuration of ITO/TAPC/$Bepp_2$ [bis(2-(2-hydroxyphenyl)pyridine)beryllium]:$(tptpy)_2Ir(acac)$ (**Ir-28**)/TmPyPB/LiF/Al, the extremely high efficiencies (max. 84.4 cd A^{-1}, 90.7 lm W^{-1} and EQE of 25 %) were obtained for the $(tptpy)_2Ir(acac)$ (**Ir-28**)-based PhOLEDs.[59] Meanwhile, in the two-color, tandem WOLEDs with the complicated device configuration of ITO/TAPC/TATA [4,4',4"-(*N*-α-carbolinyl)triphenylamine]:FIrpic/TmPyPB/TmPyPB:rubidium carbonate (Rb_2CO_3)/Al/HATCN [dipyrazino[2,3-*f*:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile]/TAPC/$Bepp_2$:$(tptpy)_2Ir(acac)$ (**Ir-28**)/TmPyPB/LiF/Al, where the *n*-doped ETL/HATCN/HTL structure was used for efficient inter-connecting units (ICUs) and Rb_2CO_2 was selected as *n*-dopant material due to its high transparency in the visible range (~90 %), the super high device efficiencies (max. 129.5 cd A^{-1} and 65.4 lm W^{-1}) along with an astonishing peak EQE value of 49.5 % were realized in the WOLEDs, which are among the highest results up to the present.[60]

Afterwards, by further combining rigid fluorene moiety into the thieno[3,2-c]pyridine ring, our group disclosed an orange-red Ir(III) complex of $(EtPy)_2Ir(acac)$ (**Ir-29**), which was cyclometalated by the ligand of 4-(9,9-diethyl-9*H*-fluoren-2-yl)thieno[3,2-c]pyridine (EtPy) and displayed the red-shifted emission peak of 588 nm in CH_2Cl_2 solution for the enlarged π conjugation.[66] As shown in **Fig. 4**, despite of its fair quantum efficiency (Φ = 0.1), the $(EtPy)_2Ir(acac)$ (**Ir-29**)-based PhOLEDs still appeared satisfactory efficiencies (max. 13.4 cd A^{-1}, 5.9 lm W^{-1} and EQE of 11.2 %) under the simple device configuration of ITO/PEDOT:PSS/PVK:PBD:$(EtPy)_2Ir(acac)$ (**Ir-29**)/CsF/Al by full solution process. Moreover, the device still remained CE of 8.7 cd A^{-1} and EQE of 7.3 % at high luminance of 1000 cd m^{-2}.

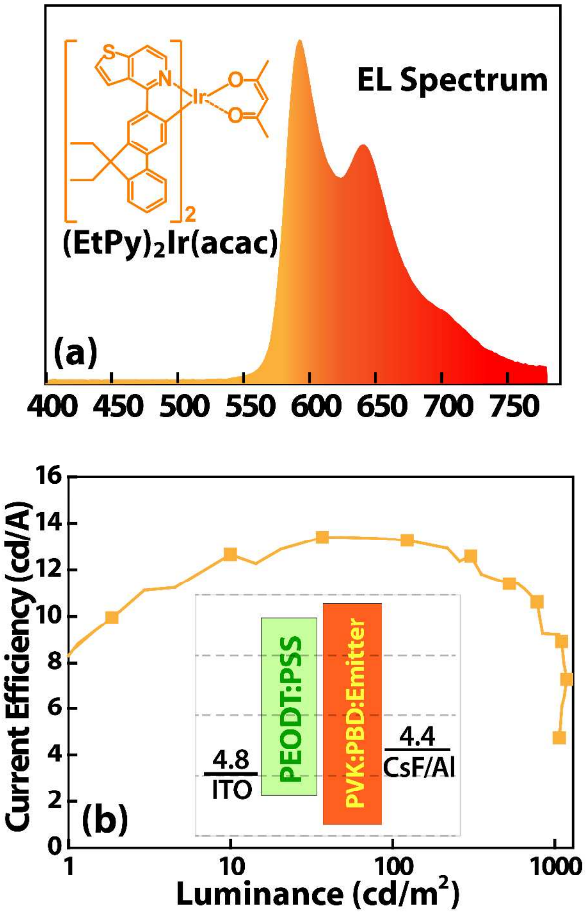
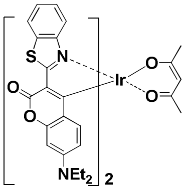
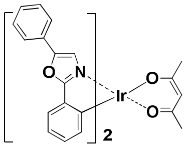


Fig. 4 (a) EL spectrum of $(EtPy)_2Ir(acac)$ (**Ir-29**); (b) Current efficiency versus luminance of the $(EtPy)_2Ir(acac)$ (**Ir-29**)-based PhOLEDs (Inset depicted the device structure).

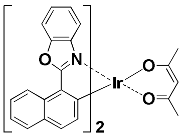
2.1.4. Ligands containing O, N-heterocyclic ring



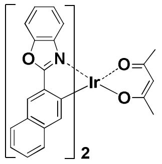
(C6)$_2$Ir(acac)
(Ir-30)



(dpo)$_2$Ir(acac)
(Ir-31)



(bon)$_2$Ir(acac)
(Ir-32)



(nbo)$_2$Ir(acac)
(Ir-33)

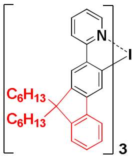
In 2001, Thompson et al. combined benzothiazole and benzopyrane together to construct the O-containing ligand of 3-(2-benzothiazolyl)-7-(diethylamino)-2*H*-1-benzopyran-2-one (C6).[28] Owning to its distinguished big π system, this C6 compound already emits strong green fluorescence in solution. The C6 could also act as the cyclometalating ligand to make the corresponding Ir(III) complex of (C6)$_2$Ir(acac) (**Ir-30**) orange emission of 585 nm and endow it with good quantum efficiency of 0.6 in 2-MeTHF solution. Meanwhile, they also manifested the Ir(III) complex of (dpo)$_2$Ir(acac) (**Ir-31**) ($\Phi = 0.10$) cyclometalated by the ligand of 2,5-diphenyloxazole (dpo) exhibited yellow emission with peak at 550 nm. But, it was notable that further fusing one phenyl ring on the oxazole ring of 2-phenyloxazole and using the obtained 2-phenylbenzoxazole (bo) as ligand can only make its cyclometalated Ir(III) complex green-emitting (λ_{peak} = 525 nm). Therefore, it was apparent that the flipping 5-phenyl ring on the 5-position of the dpo ligand increased the π system of the ligand.[28] To tune the emission peaks of these benzoxazole-based Ir(III) complexes red-shift to yellow, the aforementioned means could take effect: Using the naphthalen-1-yl to substitute the 2-phenyl group in 2-phenylbenzoxazole (bo) succeeded in making the resulting Ir(III) complex of (bon)$_2$Ir(acac) (**Ir-32**) ($\Phi = 0.11$) orange emission of 586 nm, which was cyclometalated by the newly formed ligand of 2-(naphthalen-1-yl)benzooxazole (bon).[28] Later in 2008, Chen synthesized and investigated the photophysical properties of the family of these benzoxazole-based Ir(III) complexes. The typical Ir(III) complex of (nbo)$_2$Ir(acac) (**Ir-33**) cyclometalated by the ligand of 2-(naphthalen-2-yl)benzooxazole (nbo) showed yellow emission of 568 nm but quantum efficiency no more than 0.03 in CH_2Cl_2 solution. The behind reason for the poor quantum efficiencies laid in the lack of contributions from the d orbitals of Ir(III) ion in their ligand-center (^{3}LC) π-π* excited states.[67]

2.2. Functional Group-/Substituent-Modified Ir(III) Complexes

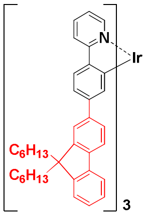
The aforementioned yellow/orange Ir(III) complexes make big contribution to the development of PhOLEDs, but there exist several deficiencies when applying these original cyclometalated Ir(III) complexes in PhOLEDs, such as poor phase compatibility with the host materials, lack of carrier-transporting abilities and unmatched HOMO/LUMO levels with nearby HTL/ETL layers et al.. To issue these problems, modifications by employing functional groups are usually adopted. The incorporation of functional groups (fluorene, triphenylamine and carbazole et al.) into the periphery of the original Ir(III) complexes can enhance the thermal/chemical stability as well as improve the carrier-balance abilities, owning to the inherent hole- and/or electron-transporting abilities of the attached functional groups. Furthermore, as the number of the attached functional groups orderly increases, the so-called "dendrons" could effectively protect the emissive Ir(III) core from luminance quenching, which is deteriorated by the aggregation and/or the triplet-triplet annihilation. Therefore, these corresponding Ir(III)-cored dendrimers can be used to fabricate the non-doped, host-free PhOLEDs.[68]

On the other hand, based on the aforementioned quantum chemistry results using the green-emitting Ir(ppy)$_3$ as the model, it is widely accepted that adding electron-withdrawing groups such as -F, -CF_3, -CN, -SO_2 and -PO et al. on the phenyl ring could lower the HOMO level, enlarge the energy gaps of Ir(III) complexes and make their emission peaks blue-shift; introducing electron-donating groups such as -NMe_2, -Me and -OMe et al. on the pyridine ring could elevate the LUMO level, increase the energy gaps of Ir(III) complexes and cause blue-shifted emission. And vice versa. The above methodologies can be used independently or cooperatively to tune the emission peaks of the original Ir(III) complexes and their HOMO/LUMO energy levels as well. The latter is advantageous for the injection of holes and/or electrons from nearby layers in OLEDs. Because simple substituents usually possess different inductive (σ_m) and resonance (σ_p) effects, it is helpful to use the quantitative Hammett parameters to give a prediction about their influence on Ir(III) complexes.[69]

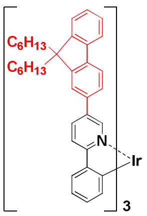
2.2.1. Modifications on parent green Ir(ppy)$_3$



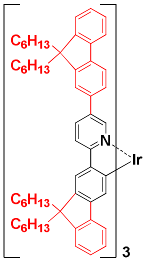
Ir(DPF)$_3$
(Ir-34)



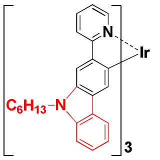
(Ir-35)



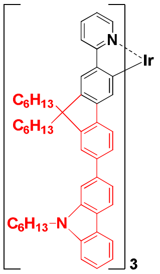
Ir(DPPF)$_3$
(Ir-36)



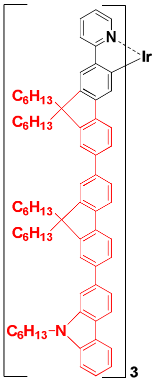
Ir(HFP)$_3$
(Ir-37)



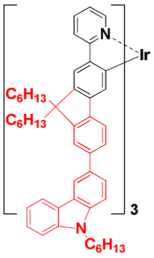
Ir(Cz-2-Py)$_3$
(Ir-38)



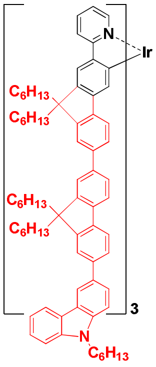
Ir(Cz-2-Fl$_1$Py)$_3$
(Ir-39)



Ir(Cz-2-Fl$_2$Py)$_3$
(Ir-40)



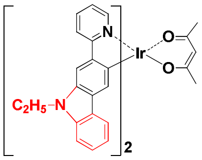
Ir(Cz-3-Fl$_1$Py)$_3$
(Ir-41)



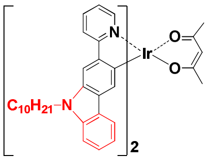
Ir(Cz-3-Fl$_2$Py)$_3$
(Ir-42)

The modifications based on the 2-phenylpyridine (ppy) ligands and the corresponding Ir(III) complexes have been widely studied. At early stage, Bazan et al. exploited a series of homoleptic *tris*-cyclometalated yellow/orange Ir(III) complexes based on Ir(ppy)$_3$. Introducing bulky, 9-alkyl substituted fluorene moiety into 2-phenylpyridine (ppy) easily made the emission peak of Ir(ppy)$_3$ (λ_{peak} = 510 nm) red-shift to 545 nm of Ir(DPF)$_3$ (**Ir-34**), 550 nm of **Ir-35**, 550 nm of Ir(DPPF)$_3$ (**Ir-36**) and 595 nm of Ir(HFP)$_3$ (**Ir-37**) in toluene solution, respectively, due to the gradually increased π system.[70] These Ir(III) complexes were expected to be highly soluble, morphologically stable and resistant to crystallization/self-quenching, which were profitable for their application in the single component, polymer PhOLEDs by full solution process. In the preliminary device configuration of ITO/PEDOT/EML/Ca/Ag, the satisfactory efficiencies (max. 36 cd A^{-1}, 2.5 lm W^{-1} and EQE of 10 %) were observed on the Ir(DPF)$_3$ (**Ir-34**)-based PhOLEDs co-hosted by PVK and PBD.[71] Simultaneously, they also observed that although the Förster energy transfer from the polymer blends of PVK and PBD to the dopants was dominate in the photo-generated process, but in fact the dominant mechanism in the electro-generated process is the charge trapping of the dopants, for very small concentration of the doped Ir(III) complexes in film blends was found to effectively quench the exciplex emission from PVK and PBD co-host.[72-73]

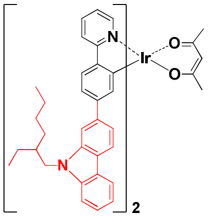
In 2007, Bryce et al. designed and synthesized two series of homoleptic Ir(III) complexes by incorporating alkyl-substituted carbazole as the end-capping group: Ir(Cz-2-Py)$_3$ (**Ir-38**) (λ_{peak} = 590 nm), Ir(Cz-2-Fl$_1$Py)$_3$ (**Ir-39**) (λ_{peak} = 560 nm), Ir(Cz-2-Fl$_2$Py)$_3$ (**Ir-40**) (λ_{peak} = 565 nm), Ir(Cz-3-Fl$_1$Py)$_3$ (**Ir-41**) (λ_{peak} = 560 nm), Ir(Cz-3-Fl$_2$Py)$_3$ (**Ir-42**) (λ_{peak} = 565 nm), where the alkyl-substituted carbazole moiety is substituted with C-2 or C-3 position to the fluorene or the pyridine unit, respectively.[74] These highly conjugated Ir(III) complexes were supposed to exhibit improved hole-transporting property from the carbazole and excellent solubility from the alkyl chains. Attractively, the different substituted positions of carbazole made different π contributions to the ligand. The C-2 substituted carbazole made its related Ir(III) complex of Ir(Cz-2-Py)$_3$ (**Ir-38**) orange emission of 590 nm in toluene solution; while the C-3 substituted carbazole made its related Ir(III) complex green-emitting (λ_{peak} = 505 nm). Although these Ir(III) complexes exhibited quantum efficiencies in the range of 0.28~0.39 in toluene solution, but low EQE values (the highest was 1.3 %) were obtained in the fabricated PhOLEDs by full solution process.



(2-PyEtCz)$_2$Ir(acac)
(Ir-43)



(2-PyDeCz)$_2$Ir(acac)
(Ir-44)



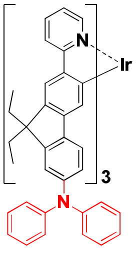
(2-PhPyCz)$_2$Ir(acac)
(Ir-45)

In the same year of 2007, using the similar carbazole-functionalized ligands, our group studied the influence of the alkyl-chain length on the morphology stability of its related heteroleptic Ir(III) complexes: (2-PyEtCz)$_2$Ir(acac) (**Ir-43**) (λ_{peak} = 594 nm), (2-PyDeCz)$_2$Ir(acac) (**Ir-44**) (λ_{peak} = 594 nm, Φ = 0.24) and (2-PhPyCz)$_2$Ir(acac) (**Ir-45**) (λ_{peak} = 548 nm, Φ = 0.26).[75] Under the identical device configuration by full solution process, the long *N*-decyl-chain (2-PyDeCz)$_2$Ir(acac) (**Ir-44**)-based PhOLEDs showed better device efficiencies (max. 6.31 cd A^{-1} and EQE of 6.59 %) than the short *N*-ethyl-chain (2-PyEtCz)$_2$Ir(acac) (**Ir-43**)-based device (max. 2.40 cd A^{-1} and EQE of 3.60 %). The results manifested the long alkyl chain was advantageous to the morphological stability of the Ir(III) complexes and the compatibility between the Ir(III) complexes and the polymer host materials. The yellow PhOLEDs based on (2-PhPyCz)$_2$Ir(acac) (**Ir-45**) showed max. CE of 21.2 cd A^{-1} and EQE of 9.41 %.

Cite this: DOI: 10.1039/c0xx00000x

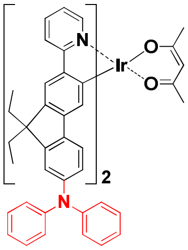
www.rsc.org/xxxxxx

ARTICLE TYPE



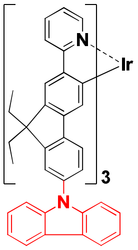
Ir(DPA-Flpy)$_3$

(Ir-46)

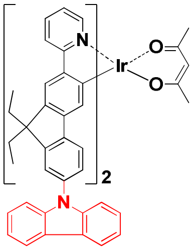


(DPA-Flpy)$_2$Ir(acac)

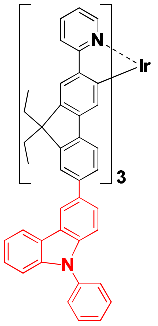
(Ir-47)



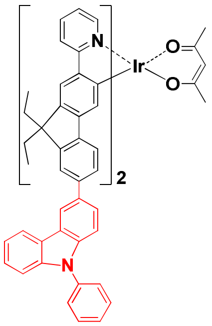
(Ir-48)



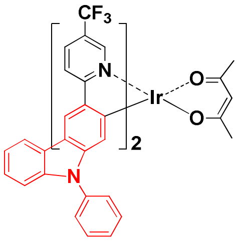
(Ir-49)



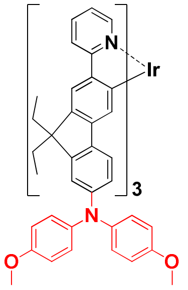
(Ir-50)



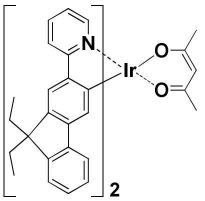
(Ir-51)



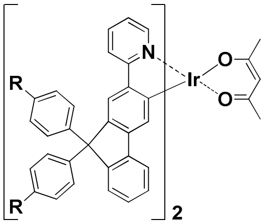
(Ir-52)



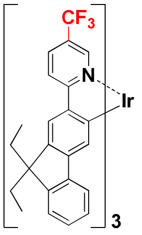
(Ir-53)



(Ir-54)



R=H, **(Ir-55)**
R=Me, **(Ir-56)**



Ir(Flpy-CF$_3$)$_3$

(Ir-57)

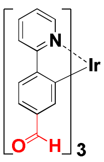
Similarly in 2006-2007, Wong et al. used the diphenylamine/carbazole end-capping, fluorene-based 2-phenylpyridine as the cycolmetalating ligands to develop three couples of homoleptic/heteroleptic Ir(III) complexes: Ir(DPA-Flpy)$_3$ (**Ir-46**) (λ_{peak} = 555 nm)/(DPA-Flpy)$_2$Ir(acac) (**Ir-47**) (λ_{peak} = 564 nm), **Ir-48** (λ_{peak} = 552 nm)/**Ir-49** (λ_{peak} = 560 nm) and **Ir-50** (λ_{peak} = 562 nm)/**Ir-51** (λ_{peak} = 566 nm).[76-77] The attached groups were expected to enhance the hole transportation and improve the amorphous stability. All the Ir(III) complexes displayed the safely-assumed, ligand-centered (LC) $^3\pi$–π* emissions in the yellow-orange range with peaks at 552-566 nm, along with fair quantum efficiencies of 0.10-0.20 in CH_2Cl_2 solution. Because of the high molecular weight of these molecules (mass/charge>1200), they were not suitable for vacuum sublimation. The alternative solution-processed PhOLEDs hosted by CBP were fabricated, and decent efficiencies (max. 11.19-29.77 cd A^{-1}, 2.79-20.78 lm W^{-1} and EQE of 3.94-9.89 %) were achieved. Meanwhile, they noticed that the efficiencies were higher in the homoleptic ones than their heteroleptic congeners, such as Ir(DPA-Flpy)$_3$ (**Ir-46**) (max. 29.77 cd A^{-1}, 20.78 lm W^{-1} and EQE of 9.89 %)/(DPA-Flpy)$_2$Ir(acac) (**Ir-47**) (max. 19.26 cd A^{-1}, 11.22 lm W^{-1} and EQE of 7.89 %), and **Ir-48** (max. 24.22 cd A^{-1}, 6.76 lm W^{-1} and EQE of 7.18 %)/**Ir-49** (max. 17.23 cd A^{-1}, 6.76 lm W^{-1} and EQE of 5.54 %). In the two-color [FIrpic/**Ir-50**] WOLEDs hosted by CBP and with double emitting layers, fair efficiencies (max. 5.2 cd A^{-1}, 2.0 lm W^{-1} and EQE of 1.9 %) were reported.

Soon in 2008, Wong and Ma et al. reported an efficient orange Ir(III) complex (**Ir-52**), which was cyclometalated by the ligand of 5-trifluoromethyl-2-[3-(*N*-phenylcarbazolyl)]pyridine.[78] The **Ir-52** showed red-shifted emission of 567 nm and quantum efficiency of 0.19 in CH_2Cl_2 solution when compared to its existing CF_3-free Ir(III) analogue (λ_{peak} = 515 nm, LUMO = -1.93 eV). Straightforwardly, this was mainly resulted from the decreased LUMO level (-2.20 eV) of the **Ir-52** caused by the attaching -CF_3 group. In the PhOLEDs hosted by CBP, the **Ir-52**-based device reached good efficiencies (max. 40.2 cd A^{-1}, 24 lm W^{-1} and EQE of 12.4 %) and outweighed by ~2 times than its green-emitting CF_3-free Ir(III) analogue (max. 19.8 cd A^{-1}, 9.6 lm W^{-1} and EQE of 6.1 %). By using fluorescent DSA-Ph [*p*-bis(*p*-*N,N*-diphenyl-aminostyryl)-benzene] as the blue emitter, the fabricated two-color [DSA-Ph/**Ir-52**] WOLEDs with double emitting layers displayed high efficiencies (max. 26.6 cd A^{-1}, 13.5 lm W^{-1} and EQE of 8.9 %) and stable EL spectra. At the current density of 100 mA cm^{-2}, the CE of the WOLEDs still remained to be ~22.3 cd A^{-1}, which were among the best results for the fluorescence/phosphorescence hybrid WOLEDs at that time.

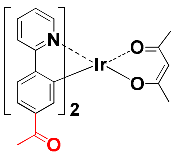
Later in 2009, Wu and Wong et al. developed two efficient yellow Ir(III) complexes (**Ir-53**) (λ_{peak} = 563 nm, Φ = 0.05) and (**Ir-54**) (λ_{peak} = 556 nm, Φ = 0.19) based on their previously designed structure of Ir(DPA-Flpy)$_3$ (**Ir-46**).[79] Fully solution-processed PhOLEDs co-hosted by PVK and PBD under the configuration of ITO/PEDOT:PSS/EML/Ba/Al were fabricated and very high efficiencies were achieved for the **Ir-53**-based device (max. 40.4 cd A^{-1}, 15.8 lm W^{-1} and EQE of 12.3 %) and

Ir-54-based device (max. 34.4 cd A^{-1}, 15.7 lm W^{-1} and EQE of 13.4 %), respectively. The higher CE value in the **Ir-53**-based device proved the functionality of the attached diphenylamine group. Meanwhile, in the fabricated two-color [FIrpic/**Ir-53**] WOLEDs [ITO/PEDOT:PSS/EML/Ba/Al] co-hosted by PVK and OXD-7 {1,3-bis[(4-*tert*-butylphenyl)-1,3,4-oxadiazolyl]phenylene} with single emitting layer, high efficiencies (max. 42.9 cd A^{-1}, 20.3 lm W^{-1} and EQE of 19.1 %) were realized in the **Ir-53**-based device. At high luminance of 1000 cd m^{-2}, these values still remained to be 41.7 cd A^{-1}, 16.8 lm W^{-1} and EQE of 18.6 %. These results were comparable to the best WOLEDs by the vacuum-deposited technology at that time. Furthermore, to simultaneously optimize the charge-carrier balance and luminous efficiency, along with two newly synthesized orange Ir(III) complexes (**Ir-55**) (λ_{peak} = 543 nm) and (**Ir-56**) (λ_{peak} = 543 nm), which were functionalized with the sterically hindered diarylfluorene chromophores, Wu and Wong et al. reported that the four-color [blue/green/orange/red], fully solution-processed WOLEDs [ITO/PEDOT:PSS 8000 (PEODT:PSS = 1:20)/PVK:OXD-7:**Ir-56**/Ba/Al] reached the recorded peak efficiencies as high as 60.1 cd A^{-1}, 37.4 lm W^{-1} and EQE of 28.8 %, which are the highest ever reported for the polymer-based WOLEDs by full solution process.[80]

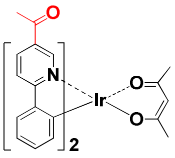
Based on the above achievements, recently in 2012, Xie et al. further reported a novel homoleptic orange Ir(III) complex by adding the -CF_3 group to the pyridine ring based on the skeleton of the reported Ir(flpy)$_3$ (**Ir-6**).[81] The modified Ir(III) complex of Ir(Flpy-CF_3)$_3$ (**Ir-57**), which was *tris*-cyclometalated by the known ligand of 2-(9,9-diethylfluoren-2-yl)-pyridine (Flpy-CF_3),[82] displayed orange emission of 569 nm and quantum efficiency of 0.35 in CH_2Cl_2 solution, 24 nm red-shifted from Ir(flpy)$_3$ (**Ir-6**) (λ_{peak} = 545 nm). In the solution-processed PhOLEDs [ITO/PEDOT:PSS/H2 (carbazole dendrimer):Ir(Flpy-CF_3)$_3$ (**Ir-57**)/SPPO13 {2,7-bis(diphenylphosphoryl)-9,9'-spirobi(fluorene)}/LiF/Al] with a vaccum-deposited electron-transporting layer, the Ir(Flpy-CF_3)$_3$ (**Ir-57**)-based device displayed significantly higher efficiencies (max. 49.7 cd A^{-1}, 43.9 lm W^{-1} and EQE of 17.6 %) than the control device based on the commonly used (fbi)$_2$Ir(acac) (**Ir-14**) (max. 23.2 cd A^{-1}, 18.2 lm W^{-1} and EQE of 9.0 %). In the following two-color [FIrpic/Ir(Flpy-CF_3)$_3$ (**Ir-57**)] WOLEDs [ITO/PEDOT:PSS 8000/H2:FIrpic:Ir(Flpy-CF_3)$_3$ (**Ir-57**)/SPPO13/LiF/Al] with single emitting layer, the best efficiencies (70.6 cd A^{-1}, 47.6 lm W^{-1} and EQE of 26.0 %) by solution process so far are recorded at the practical luminance of 100 cd m^{-2}.



Ir(fppy)$_3$
(Ir-58)

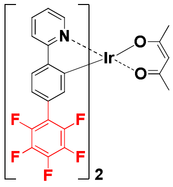


(pypAc)$_2$Ir(acac)
(Ir-59)

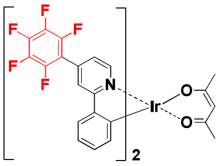


(Acppy)$_2$Ir(acac)
(Ir-60)

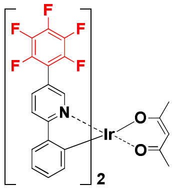
In 2003, Beeby et al. simply added aldehyde (-CHO) group into the 4'-position of the 2-phenyl ring in Ir(ppy)$_3$ and succeeded in tuning the emission peaks red-shift.[83] But the obtained Ir(III) complex of Ir(fppy)$_3$ (**Ir-58**) displayed emission peaks at 565-605 nm in different solvents. This solvatochromism manifested more charge delocalisation in the excited ^{3}MLCT state of Ir(fppy)$_3$ (**Ir-58**) due to the polar -CHO group. Afterwards in 2011, Yoon et al. added acetyl (-$COCH_3$/-Ac) group into (ppy)$_2$Ir(acac) (λ_{peak} = 516 nm) to tune its emission.[84] The attached -$COCH_3$ group worked more effectively for color tuning in the 5-position of pyridine ring for (Acppy)$_2$Ir(acac) (**Ir-60**) (λ_{peak} = 603 nm) than in the 4'-position of phenyl ring for (pypAc)$_2$Ir(acac) (**Ir-59**) (λ_{peak} = 574 nm), because it deepened the LUMO level (-3.37 eV) of (Acppy)$_2$Ir(acac) (**Ir-60**) more than that (-3.13 eV) of (pypAc)$_2$Ir(acac) (**Ir-59**). Furthermore, under the same conditions, the (Acppy)$_2$Ir(acac) (**Ir-60**)-based PhOLEDs displayed superior efficiencies (max. 31.8 cd A^{-1}, 24.6 lm W^{-1} and EQE of 13.7 %) than the (pypAc)$_2$Ir(acac) (**Ir-59**)-based device (max. 21.5 cd A^{-1}, 16.9 lm W^{-1} and EQE of 8.2 %), as well as more red CIE coordinate of (0.59, 0.44) than that of (0.52, 0.47). The distinguished quantum efficiency in CH_2Cl_2 solution between (Acppy)$_2$Ir(acac) (**Ir-60**) (Φ = 0.42) and (pypAc)$_2$Ir(acac) (**Ir-59**) (Φ = 0.27) supported the above results.



***p*-PF-ph**
(Ir-61)

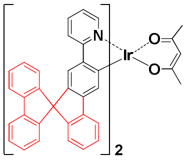


***m*-PF-py**
(Ir-62)

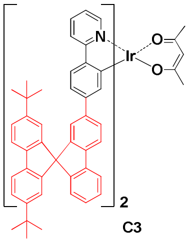


***p*-PF-py**
(Ir-63)

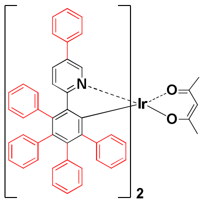
In 2003, Tsuzuki et al. disclosed four Ir(III) complexes by introducing the electron-accepting pentafluorophenyl group into the *meta-/para*-position of the phenyl/pyridine ring in (ppy)$_2$Ir(acac).[85] The emission peaks of these modified Ir(III) complexes were tuned to yellow as following: *p*-PF-ph (**Ir-61**) (λ_{peak} = 544 nm), *m*-PF-py (**Ir-62**) (λ_{peak} = 578 nm), *p*-PF-py (**Ir-63**) (λ_{peak} = 559 nm). The electron-accepting group seemed to tune the color more efficiently in the 4-position [*m*-PF-py (**Ir-62**), λ_{peak} = 578 nm] than its 5-position analogue [*p*-PF-py (**Ir-63**), λ_{peak} = 559 nm] on the pyridine ring. The PhOLEDs hosted by CBP were fabricated and decent efficiencies were obtained. At practical luminance of 100 cd m^{-2}, the *m*-PF-py (**Ir-62**)-based device appeared comparable efficiencies (43 cd A^{-1}, 28 lm W^{-1} and EQE of 16.8 %) to its analogous *p*-PF-py (**Ir-63**)-based device (47 cd A^{-1}, 29 lm W^{-1} and EQE of 14.7 %). Both the devices exhibited better efficiencies than the control device based on (ppy)$_2$Ir(acac) (42 cd A^{-1}, 23 lm W^{-1} and EQE of 11.5 %) under the same conditions.



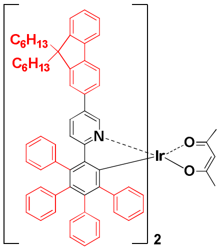
C1
(Ir-64)



C3
(Ir-65)

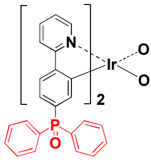


(Ir-66)

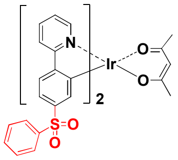


(Ir-67)

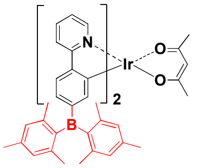
In 2008, Chen et al. established the amorphous spiro-annulated structure on $(ppy)_2Ir(acac)$ by using the spirobifluorene moiety, aiming to address the crystallization and self-quenching problems in thin film.[86] The modified Ir(III) complexes of C1 (**Ir-64**) (Φ = 0.52) and C3 (**Ir-65**) (Φ = 0.55) exhibited emission peaks at 548 nm and 555 nm in CH_2Cl_2 solution, respectively. In the PhOLEDs co-hosted by PVK and PBD by solution process, the highest efficiencies (max. 36.4 cd A^{-1} and EQE of 10.1 %) were observed in the C1 (**Ir-64**)-based device. At high current density of 100 mA cm^{-2}, the C1 (**Ir-64**)-based device remained EQE of 5.8 %, higher than the control device for $(ppy)_2Ir(acac)$ (EQE of 4.2 %). Soon in 2009, in obedience to the above idea, the same group reported polyphenyl-substituted Ir(III) complexes **Ir-66** (λ_{peak} = 557 nm) and **Ir-67** (λ_{peak} = 581 nm).[87] Further intra-connecting two of the grafted phenyl rings could tune the emissions into red. Under similar device configuration,[86] decent efficiencies (max. 46.3 cd A^{-1} and EQE of 13.9 %) were obtained for the **Ir-66**-based PhOLEDs.



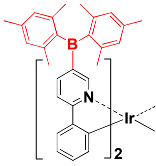
Ir-PO
(Ir-68)



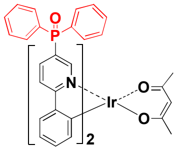
Ir-SO_2
(Ir-69)



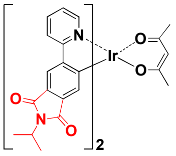
Ir-B
(Ir-70)



Ir-B-1
(Ir-71)



Ir-2
(Ir-72)

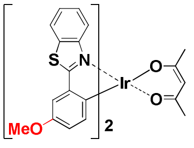


$(impy)_2Ir(acac)$
(Ir-73)

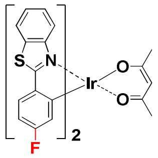
In 2008, Wong and Ma et al. systematically investigated the charge-transfer characters and color tuning of Ir(III) complexes by adding the electron-withdrawing main-group elements to the 4'-position of the 2-phenyl ring on $(ppy)_2Ir(acac)$.[88] Surprisingly, the phosphoryl-substituted Ir-PO (**Ir-68**) (λ_{peak} = 541 nm, Φ = 0.19), the sulfonyl-substituted Ir-SO_2 (**Ir-69**) (λ_{peak} = 550 nm, Φ = 0.86) and the dimesitylboron [$-B(Mes)_2$]-substituted Ir-B (**Ir-70**) (λ_{peak} = 605 nm, Φ = 0.18) appeared obviously red-shifted emission peaks when compared to $(ppy)_2Ir(acac)$ (λ_{peak} = 516 nm), which is opposite to the prediction that electron-withdrawing group on the 2-phenyl ring of ppy is supposed to lower HOMO and cause blue-shifted emissions. The phenomenon was further observed by Babudri et al. and they unveiled the sulfonyl substituent ($-SO_2$) could bring red-shifted emission when on the 2'- or 4'-position of the 2-phenyl ring, but blue-shifted once on the 3'-position of 2-phenyl ring.[89] The quantum calculation results proved that the orbitals of the -PO, $-SO_2$ and $-B(Mes)_2$ groups made contributions to the LUMO levels and consequently lowered the LUMO levels in varying degrees. Their related PhOLEDs reached moderate efficiencies, such as max. 10.31 cd A^{-1}, 5.04 lm W^{-1} and EQE of 9.36 % for the Ir-B (**Ir-70**)-based device, which were the best among the others. Currently in 2013, they added the $-B(Mes)_2$ group to the 5-position of pyridine ring on $(ppy)_2Ir(acac)$. The obtained Ir(III) complex of Ir-B-1 (**Ir-71**) still displayed orange emission with peak at 607 nm but possessed extremely high quantum efficiency of 0.95 in CH_2Cl_2 solution, much higher than its analogous Ir-B (**Ir-70**) (Φ = 0.18). After the device optimization, the Ir-B-1 (**Ir-71**)-based PhOLEDs hosted by TCTA realized attractive efficiencies (max. 21.4 cd A^{-1}, 22.2 lm W^{-1} and EQE of 14.7 %) with a red CIE coordinate of (0.64, 0.36), which were better than the control device based on the well-known $(MDQ)_2Ir(acac)$ (**Ir-11**) (max. 10.4 cd A^{-1}, 9.5 lm W^{-1} and EQE of 6.0 %) under the same conditions.[90]

In 2012, Li et al. added the diphenylphosphoryl group (-PO) to the 5-position of the pyridine ring in $(ppy)_2Ir(acac)$, the gained Ir(III) complex of Ir-2 (**Ir-72**) displayed the expected red-shifted emission at 564 nm in CH_2Cl_2 solution and lowered LUMO level of -3.06 eV when compared to $(ppy)_2Ir(acac)$ (LUMO = -2.74 eV). Good efficiencies (max. 51.6 cd A^{-1}, 27 lm W^{-1} and EQE of 14.5 %) were reported for the Ir-2 (**Ir-72**)-based PhOLEDs hosted by CBP.[91] In 2009, Kim et al. synthesized an orange Ir(III) complex of $(impy)_2Ir(acac)$ (**Ir-73**), which was cyclometalated by the ligand of 4-pyridyl-*N*-isopropylphthalimide (impy).[92] The imide-contained $(impy)_2Ir(acac)$ (**Ir-73**) showed emission peak at 560 nm and quantum efficiency of 0.32 in the CBP-hosted film. However, even with the *p-i-n* device structure and the double emitting layers, the $(impy)_2Ir(acac)$ (**Ir-73**)-based PhOLEDs still manifested moderate efficiencies (max. 36.7 cd A^{-1}, 29.2 lm W^{-1} and EQE of 14.4 %).

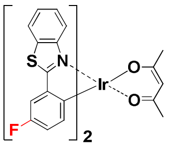
2.2.2. Modifications on parent yellow $(bt)_2Ir(acac)$



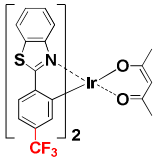
$(3\text{-}MeO\text{-}bt)_2Ir(acac)$
(Ir-74)



$(4\text{-}F\text{-}bt)_2Ir(acac)$
(Ir-75)



$(3\text{-}F\text{-}bt)_2Ir(acac)$
(Ir-76)

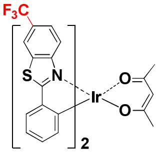


$(4\text{-}CF_3\text{-}bt)_2Ir(acac)$
(Ir-77)

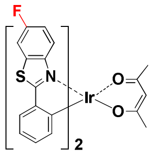
The Ir(III) complex of $(bt)_2Ir(acac)$ (**Ir-25**) cyclometalated by the ligand of 2-phenylbenzothiazole (bt) was among one of the most studied yellow Ir(III) complexes due to its excellent performance in PhOLEDs.[93] In the early year of 2004, Hu et al. and Chen et al. simultaneously initiated the systematic studies on the electronic properties of the modified Ir(III) complexes by attaching -Me, -F, -OMe and $-CF_3$ groups on $(bt)_2Ir(acac)$ (**Ir-25**).

Their investigations were mainly concentrated on the substitution in the 3'- or 4'-position of the 2-phenyl ring. The emission peaks and redox behaviours were finely tuned and well explained by the Hammett parameters. Compared to $(bt)_2Ir(acac)$ (**Ir-25**) (measured λ_{peak} = 560 nm), the emission peaks were tuned to 605 nm of $(3\text{-MeO-bt})_2Ir(acac)$ (**Ir-74**), 544 nm of $(4\text{-F-bt})_2Ir(acac)$ (**Ir-75**), 555 nm of $(3\text{-F-bt})_2Ir(acac)$ (**Ir-76**) and 567 nm of $(4\text{-}CF_3\text{-bt})_2Ir(acac)$ (**Ir-77**). At that time, the device efficiencies of the PhOLEDs based on $(4\text{-}CF_3\text{-bt})_2Ir(acac)$ (**Ir-77**) (max. 10.8 cd A^{-1} and 4.6 lm W^{-1}) were close to the one based on $(bt)_2Ir(acac)$ (**Ir-25**) (max. 9.6 cd A^{-1} and 4.7 lm W^{-1}) under the same configuration with CBP as the host.[94-95]

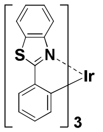
In 2011, Li et al. reported two highly efficient orange Ir(III) complexes of $(CF_3\text{-bt})_2Ir(acac)$ (**Ir-78**) (λ_{peak} = 564 nm) and $(F\text{-bt})_2Ir(acac)$ (**Ir-79**) (λ_{peak} = 554 nm) by attaching $-CF_3$ and -F groups into the 6-position of the benzothiazole ring in 2-phenylbenzothiazole (bt) ligand.[96] The two compounds displayed moderate quantum efficiencies of 0.36 and 0.32 in CH_2Cl_2 solution, respectively. Under the usual device configuration of ITO/PEDOT:PSS/EML/TPBi/LiF/Al hosted by CBP, extremely high efficiencies were realized for the $(CF_3\text{-bt})_2Ir(acac)$ (**Ir-78**)-based device (max. 76 cd A^{-1}, 39.8 lm W^{-1} and EQE of 27.2 %) and $(F\text{-bt})_2Ir(acac)$ (**Ir-79**)-based device (max. 71.6 cd A^{-1}, 44.9 lm W^{-1} and EQE of 24.9 %), respectively, which were among the highest for the vacuum-deposited yellow-orange PhOLEDs at that time. Simultaneously, in the fabricated two-color [FIrpic/(**Ir-78**)-(**Ir-79**)] WOLEDs with double emitting layers under the similar configuration of ITO/PEDOT:PSS/CBP:$(CF_3\text{-bt})_2Ir(acac)$ (**Ir-78**) or $(F\text{-bt})_2Ir(acac)$ (**Ir-79**)/CBP:FIrpic/TPBi/LiF/Al, the peak efficiencies of 68.6 cd A^{-1}, 34.0 lm W^{-1} and EQE of 26.2 % were reached for the $(F\text{-bt})_2Ir(acac)$ (**Ir-79**)-based WOLEDs, which were also among the best efficiencies at that time. Later in 2013, they initially sythesized four 2-phenylbenzothiazole-based homoleptic Ir(III) complexes with the similar ligands of 6-subsituted 2-phenylbenzothiazole (bt) derivatives. The substituents in the bt ligand were found to be unimportant to influence the performance of these Ir(III) complexes. Noticeably, in the fabricated PhOLEDs under the same structure, the iridium complex of $Ir(bt)_3$ (**Ir-80**) (λ_{peak} = 540 nm, Φ = 0.37), which was *tris*-cyclometalated by the pristine 2-phenylbenzothiazole (bt) ligand, revealed the one of the best results (max. 87.9 cd A^{-1}, 46 lm W^{-1} and EQE of 29.6 %) for the yellow PhOLEDs so far.[97]



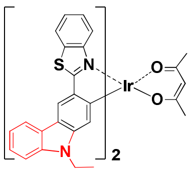
$(CF_3\text{-bt})_2Ir(acac)$
(Ir-78)



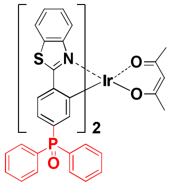
$(F\text{-bt})_2Ir(acac)$
(Ir-79)



$Ir(bt)_3$
(Ir-80)



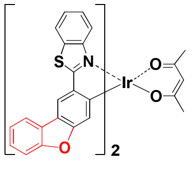
$(Btc)_2Ir(acac)$
(Ir-81)



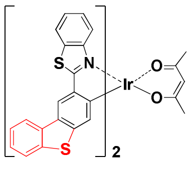
$(PO\text{-bt})_2Ir(acac)$
(Ir-82)

The electron-donating groups ($-NMe_2$,[98] carbazole) and electron-withdrawing group (-PO) were reported to be added or fused into the 4'-position of the 2-phenyl ring in bt ligand. The carbazole-fused Ir(III) complex of $(Btc)_2Ir(acac)$ (**Ir-81**) (λ_{peak} = 555 nm) cyclometalated by the ligand of 2-(9-ethyl-carbazol-3-yl)benzothiazole presented moderate efficiencies for its fabricated PhOLEDs (max. 38.1 cd A^{-1}, EQE of 12.9 %) but good efficiencies in the two-color [FIrpic/$(Btc)_2Ir(acac)$ (**Ir-81**)] WOLEDs with single emitting layer (max. 51.7 cd A^{-1} and EQE of 19.4 %).[99] However, the PO-attached Ir(III) complex of $(PO\text{-bt})_2Ir(acac)$ (**Ir-82**) (λ_{peak} = 583 nm) cyclometalated by the ligand of 2-[4-(diphenylphosphoryl)-phenyl]benzothiazole (PO-bt) displayed only low efficiency (4.3 cd A^{-1}) in its fabricated PhOLEDs.[100]

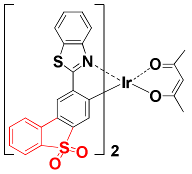
Currently in 2013, Liu et al. built novel bt-based frameworks by replacing the free 2-phenyl ring with the rigid dibenzofuran (O-bt), dibenzothiophene (S-bt) and dibenzothiophene-S,S-dioxide (SO_2-bt).[100] The modified Ir(III) complexes of $(O\text{-bt})_2Ir(acac)$ (**Ir-83**) (λ_{peak} = 551 nm), $(S\text{-bt})_2Ir(acac)$ (**Ir-84**) (λ_{peak} = 562 nm) and $(SO_2\text{-bt})_2Ir(acac)$ (**Ir-85**) (λ_{peak} = 598 nm) showed moderate quantum efficiencies of 0.1-0.29 in CH_2Cl_2 solution. Of three, the best device efficiencies (max. 58.4 cd A^{-1}, 30.6 lm W^{-1} and EQE of 19 %) were realized in the $(O\text{-bt})_2Ir(acac)$ (**Ir-83**)-based PhOLEDs hosted by CBP. While in the two-color [FIrpic/$(S\text{-bt})_2Ir(acac)$ (**Ir-84**)] WOLEDs with double emitting layers, fair efficiencies (max. 32.4 cd A^{-1} and 14.5 lm W^{-1}) were obtained.



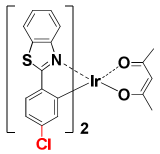
$(O\text{-bt})_2Ir(acac)$
(Ir-83)



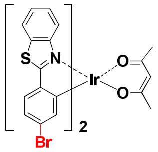
$(S\text{-bt})_2Ir(acac)$
(Ir-84)



$(SO_2\text{-bt})_2Ir(acac)$
(Ir-85)



$(4\text{-Cl-bt})_2Ir(acac)$
(Ir-86)



$(4\text{-Br-bt})_2Ir(acac)$
(Ir-87)

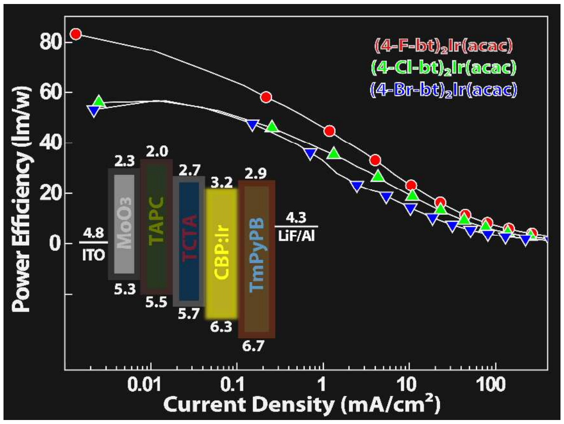
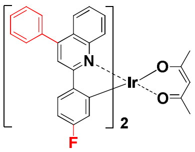


Fig. 5 Power efficiency versus current density of PhOLEDs for $(4\text{-F-bt})_2Ir(acac)$ (**Ir-75**), $(4\text{-Cl-bt})_2Ir(acac)$ (**Ir-86**), and $(4\text{-Br-bt})_2Ir(acac)$ (**Ir-**

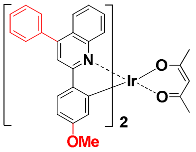
87) (Inset depicts the device configuration and the energy levels of the materials used).

Concurrently, our group initiately synthesized halogen-substituted bt ligands and systematically investigated the influence of the halogen atoms (F, Cl, Br) on the photophysical properties of the modified Ir(III) complexes, which were cyclometalated by the (2-(4'-halogen)-phenyl)benzothiazole.[54] Adding Cl and Br atoms simultaneously lowered the HOMO and LUMO levels of $(bt)_2Ir(acac)$ (**Ir-25**). As a consequence, the halogen-substituted Ir(III) complexes of (4-Cl-bt)$_2$Ir(acac) (**Ir-86**) (λ_{peak} = 554 nm) and (4-Br-bt)$_2$Ir(acac) (**Ir-87**) (λ_{em} = 555 nm) showed similar emissions to $(bt)_2Ir(acac)$ (λ_{peak} = 559 nm) (**Ir-25**). Besides, high quantum efficiencies were observed for (4-Cl-bt)$_2$Ir(acac) (**Ir-86**) (Φ = 0.59) and (4-Br-bt)$_2$Ir(acac) (**Ir-87**) (Φ = 0.46), close to $(bt)_2Ir(acac)$ (**Ir-25**) (Φ = 0.65) under the identical conditions. As shown in **Fig. 5**, after reducing the hole-injecting barrier and using better carrier-transporting materials in the optimized device configuration of ITO/MoO_3/TAPC/TCTA/EML/TmPyPB/LiF/Al hosted by CBP, very high efficiencies were achieved for the (4-Cl-bt)$_2$Ir(acac) (**Ir-86**)-based device (max. 55.9 cd A^{-1}, 55.9 lm W^{-1} and EQE of 20.2 %) and the (4-Br-bt)$_2$Ir(acac) (**Ir-87**)-based device (max. 60.3 cd A^{-1}, 56.7 lm W^{-1} and EQE of 21.6 %). Moreover, the power efficiency of the PhOLEDs based on the previously reported (4-F-bt)$_2$Ir(acac) (**Ir-75**) was enhanced to the peak value of 83.2 lm W^{-1}, which is among one of the highest results so far.

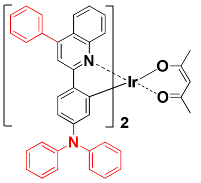
2.2.3 Modifications on parent orange $(pq)_2Ir(acac)$


$(FPPQ)_2Ir(acac)$

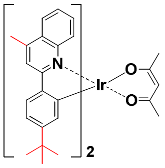
(Ir-88)


$(MeOPPQ)_2Ir(acac)$

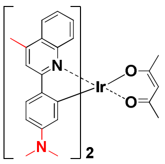
(Ir-89)


$(TPAPQ)_2Ir(acac)$

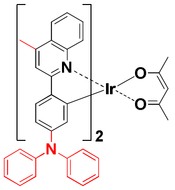
(Ir-90)


$(BuL)_2Ir(acac)$

(Ir-91)

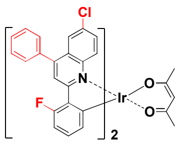

$(NMe_2L)_2Ir(acac)$

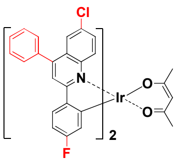
(Ir-92)

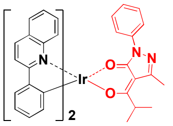

$(NPh_2L)_2Ir(acac)$

(Ir-93)

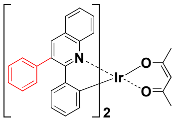
The $(pq)_2Ir(acac)$ (**Ir-2**) (λ_{peak} = 597 nm) cyclometalated by the ligand of 2-phenylquinoline (pq) is one of the best orange Ir(III) complexes nowadays.[101] As early as in 2005, Wang et al. added a phenyl ring to the 4-position of quinoline and synthesized the 2,4-diphenylquinoline (PPQ) as the parent ligand.[102] The one more phenyl ring easily made the modified $(PPQ)_2Ir(acac)$ red-shift 14 nm (λ_{peak} = 611 nm, ΔE = 2.60 eV). After adding F atom to the 4'-position of 2-phenyl ring in PPQ, it was expected to make the emission of the resulting Ir(III) complex of $(FPPQ)_2Ir(acac)$ (**Ir-88**) (λ_{peak} = 592 nm, Φ = 0.21, ΔE = 2.74 eV) blue-shift. However, it was unexpected that when adding electron-donating -OMe, -NPh_2 to the same position, the corresponding Ir(III) complexes of $(MeOPPQ)_2Ir(acac)$ (**Ir-89**) (λ_{peak} = 602 nm, Φ = 0.19, ΔE = 2.66 eV) and $(TPAPQ)_2Ir(acac)$ (**Ir-90**) (λ_{peak} = 609 nm, Φ = 0.17, ΔE = 2.62 eV) still exhibited blue-shifted emissions, as further confirmed by their energy gaps (ΔE). In the PhOLEDs hosted by CBP, good efficiencies were reported for the $(FPPQ)_2Ir(acac)$ (**Ir-88**)-based device (13.7 cd A^{-1}, 7.1 lm W^{-1} and EQE of 6.7 % at 100 cd m^{-2}) and $(TPAPQ)_2Ir(acac)$ (**Ir-90**)-based device (12.2 cd A^{-1}, 7.5 lm W^{-1} and EQE of 9.0 % at 100 cd m^{-2}) at that time, respectively. In 2005, Lin et al. developed several lepidine-based Ir(III) complexes by using 2-phenyl-4-methyl-quinoline as the parent ligand.[103] The emission peaks of some Ir(III) complexes were tuned to red. In coincidence with the phenomenon reported above, the modified Ir(III) complexes of $(BuL)_2Ir(acac)$ (**Ir-91**) (λ_{peak} = 599 nm, Φ = 0.17), $(NMe_2L)_2Ir(acac)$ (**Ir-92**) (λ_{peak} = 598 nm, Φ = 0.10) and $(NPh_2L)_2Ir(acac)$ (**Ir-93**) (λ_{peak} = 593 nm, Φ = 0.16) exhibited close emissions to $(pq)_2Ir(acac)$ (λ_{peak} = 597 nm), when adding the electron-donating *t*-butyl, -NMe_2 and -NPh_2 groups to the 4'-position of 2-phenyl ring in the ligand of 2-phenyl-4-methyl-quinoline. Among all the fabricated PhOLEDs hosted by CBP, very good efficiencies were obtained for $(BuL)_2Ir(acac)$ (**Ir-91**)-based device (26.4 cd A^{-1} and 6.7 lm W^{-1} and EQE of 12.1 %) at high current density of 100 mA cm^{-2}.


(Ir-94)

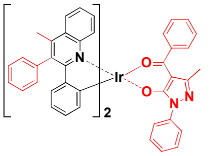

(Ir-95)


$(pq)_2Ir(PMIP)$

(Ir-96)


$(23dpq)_2Ir(acac)$

(Ir-97)


$(4\text{-Me-}2,3\text{-dpq})_2Ir(przl\text{-}C_6H_5)$

(Ir-98)

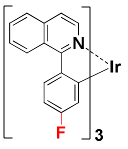
In 2006, our group initially introduced Cl atom to the 6-position of quinoline ring in the ligand of 2,4-diphenylquinoline.[104] And the additional F atom on the 2-phenyl ring could make sure the modified Ir(III) complexes orange emissions. In the Ir(III) complexes with the basic ligand of 6-chloro-2,4-diphenylquinoline, adding F atom on the 4'-position of 2-phenyl ring in the Ir(III) complex (**Ir-94**) (λ_{peak} = 587 nm) worked more efficiently than its 2'-position analogue of **Ir-95** (λ_{peak} = 602 nm) for color tuning. The **Ir-94** and **Ir-95** showed good quantum efficiencies of 0.34 and 0.32 in CH_2Cl_2 solution, respectively. Moderate device efficiencies were obtained for their PhOLEDs hosted by CBP, with max. 9.34 cd A^{-1}, 5.20 lm W^{-1} for **Ir-94** and max. 11.12 cd A^{-1}, 4.97 lm W^{-1} for **Ir-95**.

In the same year of 2006, Li et al. unveiled that the replacement of acetylacetonate (acac) in $(pq)_2Ir(acac)$ (**Ir-2**) by the new ancillary ligand of 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolonate (PMIP) could improve the quantum efficiency from $(pq)_2Ir(acac)$ (**Ir-2**) (Φ = 0.13, λ_{peak} = 600 nm) to the resulting $(pq)_2Ir(PMIP)$ (**Ir-96**) (Φ = 0.21, λ_{peak} = 596 nm) in CH_2Cl_2 solution.[105] In 2009, Yang et al. reported the synthetic routes for the novel cyclometalating ligand of 2,3-diphenylquinoline (23dpq).[106] The newly resulting Ir(III) complex of $(23dpq)_2Ir(acac)$ (**Ir-97**) exhibited emission peak at 608 nm in CH_2Cl_2 solution but poor device efficiencies (max. 11.4 cd A^{-1}

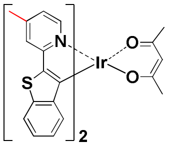
and 2.4 lm W^{-1}) in its fabricated PhOLEDs. At the same time, Ha et al. built several Ir(III) complexes with the similar 4-methyl-2,3-diphenylquinoline (4-Me-2,3-dpq) ligand but the prazolone derivatives as the ancillary ligand.[107] But the PhOLEDs fabricated from the representative Ir(III) complex of $(4\text{-Me-}2,3\text{-dpq})_2Ir(przl\text{-}C_6H_5)$ (**Ir-98**) (λ_{peak} = 601 nm) showed fair efficiency (max. 11.38 cd A^{-1}).

2.2.4. Modifications on other parent Ir(III) complexes

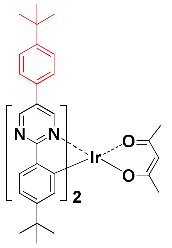
In 2003, Tao et al. added F atom to the 4'-position of 1-phenyl ring in the ligand of 1-phenylisoquinoline (piq) to obtain 1-(4'-fluorophenyl)isoquinoline (piq-F).[108] The resulting homoleptic Ir(III) complex of $Ir(piq\text{-}F)_3$ (**Ir-99**) displayed orange emission of 595 nm in CH_2Cl_2 solution, blue-shifted from its red Ir(III) analogue of $Ir(piq)_3$ (λ_{peak} = 620 nm). And the decreased quantum efficiency from 0.26 of $Ir(piq)_3$ to 0.15 of $Ir(piq\text{-}F)_3$ (**Ir-99**) was observed. Satisfactory device efficiencies (10.36 cd A^{-1}, 3.8 lm W^{-1} and EQE of 5.81 % at 20 mA cm^{-2}) were realized for the $Ir(piq\text{-}F)_3$ (**Ir-99**)-based PhOLEDs hosted by CBP. In 2007, Xu et al. introduced methyl group (-Me) to the 4-position of pyridine ring in the ligand of 2-benzothiophen-2'-yl-pyridine (btp), which made the emission peak blue-shift to 604 nm of $(btmp)_2Ir(acac)$ (**Ir-100**) from $(btp)_2Ir(acac)$ (λ_{peak} = 612 nm).[109] In 2009, to expand the π system of 2-phenylpyrimidine (PPM) by simply adding a phenyl ring on the 5-position of pyrimidine, Lin et al. used the newly obtained 2,5-bis-(4-*tert*-butylphenyl)pyrimidine as the cyclometalating ligand and easily tuned the resulting Ir(III) complex (**Ir-101**) yellow emission of 544 nm in toluene solution, red-shifted from the green-emitting $(PPM)_2Ir(acac)$ (λ_{peak} = 527 nm).[110]



$Ir(piq\text{-}F)_3$
(Ir-99)

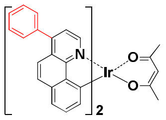


$(btmp)_2Ir(acac)$
(Ir-100)

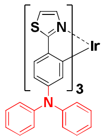


(Ir-101)

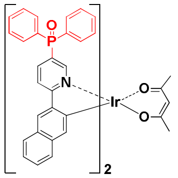
In 2009, Li et al. appended a phenyl ring to the 4-position of benzoquinoline (bzq) to synthesize the ligand of 4-phenybenzoquinoline (PBQ).[111] Its cyclometalated Ir(III) complex of $(PBQ)_2Ir(acac)$ (**Ir-102**) exhibited orange emission of 579 nm in CH_2Cl_2 solution, red-shifted from the previous yellow-emitting $(bzq)_2Ir(acac)$ (**Ir-1**) (λ_{peak} = 548 nm). Besides, $(PBQ)_2Ir(acac)$ (**Ir-102**) showed higher quantum efficiency of 0.35 than 0.27 of $(bzq)_2Ir(acac)$ (**Ir-1**). Good efficiencies (max. 44 cd A^{-1}, 37 lm W^{-1} and EQE of 14.6 %) were obtained for the $(PBQ)_2Ir(acac)$ (**102**)-based PhOLEDs hosted by CBP. In 2012, Zhou et al. attached the electron-donating diphenylamine group to the 4'-position of 2-phenyl ring in 2-phenylthiazole (ptz), to provide better hole-injection/-transporting abilities.[112] The corresponding homoleptic Ir(III) complex of IrTZ1 (**Ir-103**), which was *tris*-cyclometalated by the newly formed ligand of (2-(4'-diphenylamine)-phenyl)thiazole, presented the expected red-shifted emission of 562 nm from $(ptz)_2Ir(acac)$ (**Ir-26**) (λ_{peak} = 547 nm) in CH_2Cl_2 solution. Despite of its unsatisfactory quantum efficiency of 0.14, good device efficiencies (max. 39.97 cd A^{-1}, 34.95 lm W^{-1} and EQE of 14.82 %) were obtained in the IrTZ1 (**Ir-103**)-based PhOLEDs hosted by CBP. They also used IrTZ1 (**Ir-103**) as the orange phosphor for the two-color WOLEDs with double emitting layers, but the WOLEDs using FIrpic as the sky-blue phosphor showed moderate and similar efficiencies (max. 18.07 cd A^{-1}, 19.57 lm W^{-1} and EQE of 7.2 %) with the device employed the DPAVBi [4,4'-bis{4-(di-4-tolylamino)styryl}biphenyl] as the blue fluorescent emitter (max. 22.72 cd A^{-1}, 17.28 lm W^{-1} and EQE of 9.06 %). In the same year of 2012, Li et al. reported the tailoring of the pyridine ring by adding electron-withdrawing diphenylphosphoryl (-PO) group to its 3-position based on the ligand of 2-(naphthalen-2-yl)pyridine (npy).[91] Evidently, the modified **Ir-104** exhibited lower LUMO level of -3.03 eV than that (-2.80 eV) of $(npy)_2Ir(acac)$ (**Ir-8**) but similar HOMO level of -5.11 eV with $(npy)_2Ir(acac)$ (**Ir-8**) (-5.10 eV). As a consequence, **Ir-104** showed red-shifted emission peak of 600 nm from $(npy)_2Ir(acac)$ (**Ir-8**) (λ_{peak} = 551 nm) in CH_2Cl_2 solution. Fair efficiencies were reported for the **Ir-104**-based PhOLEDs (max. 27.2 cd A^{-1}, 15.5 lm W^{-1} and EQE of 9.7 %) and the two-color [FIrpic/**Ir-104**] WOLEDs (max. 23.9 cd A^{-1}, 13.9 lm W^{-1} and EQE of 5.4 %) with double emitting layers and hosted by CBP.



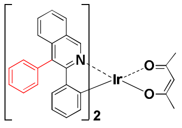
$(PBQ)_2Ir(acac)$
(Ir-102)



IrTZ1
(Ir-103)



Ir-4
(Ir-104)



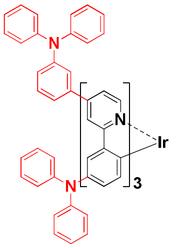
$(dpiq)_2Ir(acac)$
(Ir-105)

Currently in 2013, Cheng et al. developed an efficient orange Ir(III) complex of $(dpiq)_2Ir(acac)$ (**Ir-105**) cyclometalated by the ligand of 3,4-diphenylisoquinoline (dpiq), which was derived by simply adding a phenyl ring to the already-existing ligand of 3-phenylisoquinoline (3-piq).[113] The $(dpiq)_2Ir(acac)$ (**Ir-105**) exhibited orange emission of 578 nm in CH_2Cl_2 solution, red-shifted 16 nm from $(3\text{-piq})_2Ir(acac)$ (**Ir-4**) (λ_{peak} = 562 nm). Although the fair quantum efficiency of 0.23 for $(dpiq)_2Ir(acac)$ (**Ir-105**) was observed, its PhOLEDs hosted by CBP appeared extremely high efficiencies (max. 68.3 cd A^{-1}, 49.7 lm W^{-1} and EQE of 21.6 %). Furthermore, in the two-color WOLEDs under the configuration of ITO/NPB/TCTA/CBP:$(dpiq)_2Ir(acac)$ (**Ir-105**)/CzSi [9-(4-*tert*-butylphenyl)-3,6-bis(triphenylsilyl)-9*H*-carbazole]:$(fmoppy)_2Ir(tfpypz)$/CBP:$(dpiq)_2Ir(acac)$ (**Ir-105**)/BSB [4,4'-bis-triphenylsilanyl-biphenyl]/TAZ [3-(4-biphenyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole]/LiF/Al, which featured the triple emitting layers and a newly synthesized Ir(III) complex of $(fmoppy)_2Ir(tfpypz)$ as the blue phosphor, the peak efficiencies of the WOLEDs reached as high as 68.8 cd A^{-1}, 45.0 lm W^{-1} and EQE of 21.5 %. Meanwhile, using the independent triple emitting layers, the CIE coordinates of (0.44, 0.45) in the WOLEDs shifted by only (0.02, ≤0.01) within the luminance range of 1000-10000 cd m^{-2}.

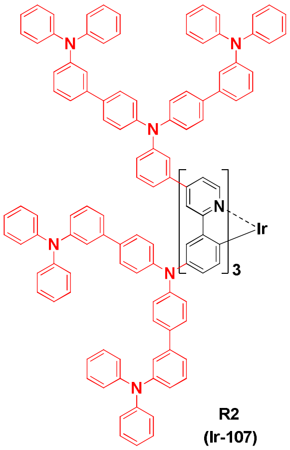
2.2.5. Yellow/orange Ir(III) dendrimers

The emissive Ir(III) complexes usually can't be directly used as the sole emitting layer in PhOLEDs, because the severe concentration quenching and triplet–triplet annihilation will drastically decrease the device efficiencies. In addition, the phase seperation between the doped Ir(III) complexes and the related host materials could probably happen due to the poorly matched compatibility. To simultaneouly address the issues, the corresponding dendrimers of Ir(III) complexes are developed. Their merits are as following: i) Most employed dendrons are functional groups possessing high triplet energies, which can prevent the back energy transfer from the emissive Ir(III) core to the grafted dendrons; ii) A large number of dendrons could bring in bulky steric hindrance, which is effective to eliminate intermolecular interaction; iii) The dendrons usually possess excellent charge-transporting ability and could improve device efficiencies. As a consequence, highly efficient, non-doped PhOLEDs could be fabricated.[114-116]

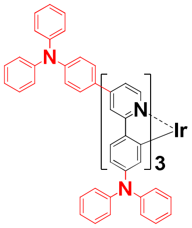
Recently in 2012, our group developed two categories of orange Ir(III) dendrimers based on the homoleptic $Ir(ppy)_3$ by using triphenylamine as the dendron. The high generation dendrimers of these Ir(III) complexes were obtained by traditionally convergent strategy, along with satisfactory product yields. The introduction of triphenylamine group into the periphery of the emissive $Ir(ppy)_3$ core facilely tuned the emission peaks red-shifted. Meanwhile, the electron-donating triphenylamine with high HOMO level (-5.2 eV) possesses excellent hole-transporting ability, which could facilitate the EL performance.



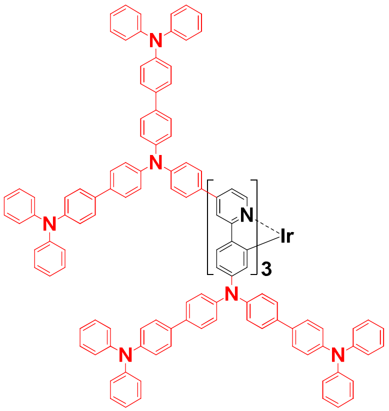
R1
(Ir-106)



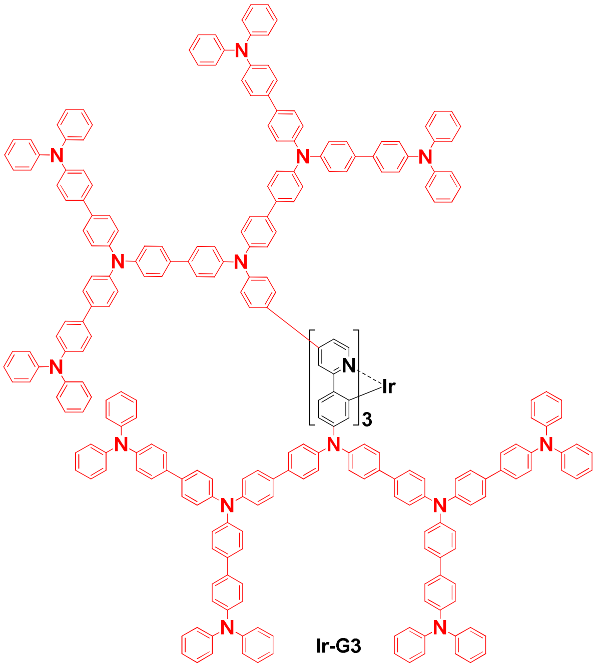
R2
(Ir-107)



Ir-G1
(Ir-108)



Ir-G2
(Ir-109)



Ir-G3
(Ir-110)

The first category is through the *meta*-linkage of triphenylamine to the $Ir(ppy)_3$ core and the obtained two Ir(III) dendrimers R1 (**Ir-106**) (λ_{peak} = 608 nm) and R2 (**Ir-107**) (λ_{peak} = 608 nm) showed identical emissions in toluene solution. Noticeably, in neat film, their PL spectra only exhibited slightly red shifts [6 nm for **Ir-106** and 5 nm for **Ir-107**]. High quantum efficiencies [Φ = 0.28 for **Ir-106** and Φ = 0.34 for **Ir-107**] were still observed in film, which indicated the triphenylamine-functionalized dendrimers effectively suppress the detrimental intermolecular interaction. In the PhOLEDs of ITO/PEDOT:PSS/PVK:PBD:**Ir-106**/Ba/Al by full solution process, the peak EQE of 15.3 % was realized for **Ir-106**-based device with dopant concentration of 30 w.t.%; while EQE of 13.8 % for the low dopant concentration of 10 w.t.%.[117-118]

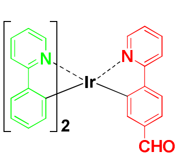
The second category is through the *para*-linkage of triphenylamine to the $Ir(ppy)_3$ core and the obtained three Ir(III) dendrimers of Ir-G1 (**Ir-108**) (λ_{peak} = 561 nm), Ir-G2 (**Ir-109**) (λ_{peak} = 561 nm) and Ir-G3 (**Ir-110**) (λ_{peak} = 561 nm) were attached by 6, 18, 42 triphenylamine units, respectively. Moreover, 50 % of yield was obtained for Ir-G3 (**Ir-110**) bearing 42 triphenylamine branching units without difficulty from steric crowding. All the three dendrimers displayed nearly the same emissions of 561 nm. Besides, the quantum efficiencies in toluene solution increased from Ir-G1 (**Ir-108**) (Φ = 0.29), Ir-G2 (**Ir-109**) (Φ = 0.40) to Ir-G3 (**Ir-110**) (Φ = 0.44). In all the three non-doped PhOLEDs of ITO/PEDOT:PSS/Ir dendrimers/TPBi/Ba/Al, the efficiency order was Ir-G1 (**Ir-108**)≈Ir-G2 (**Ir-109**)>>Ir-G3 (**Ir-110**). The best efficiencies were achieved for the Ir-G1 (**Ir-108**)-based device (max. 40.9 cd A^{-1}, 39.5 lm W^{-1} and EQE of 16.4 %), which were close to its doped device under identical conditions except using the blended PVK:PBD:Ir-G1 (**Ir-108**) as the emitting layer (max. 41.7 cd A^{-1}, 13.6 lm W^{-1} and EQE of 16.7 %). Soon, after employing PEDOT:PSS 8000 in the fully solution-processed PhOLEDs of ITO/PEDOT:PSS 8000/PVK:PBD:Ir-G2 (**Ir-109**)/Ba/Al, the efficiencies for the Ir-G2 (**Ir-109**)-based device were futher improved to max. 52.4 cd A^{-1}, 21.6 lm W^{-1} and EQE of 21 %. At high luminance of 1000 cd m^{-2}, the values still remained to be 51 cd A^{-1}, 17.2 lm W^{-1} and EQE of 20.4 %, which are among the highest results ever reported for dendrimer-based PhOLEDs. Moreover, under the similar device configuration of ITO/PEDOT:PSS 8000/PVK:OXD-7:FIrpic:Ir-G1 (**Ir-108**)/Ba/Al, the fabricated two-color WOLEDs with single emitting layer displayed the astonishing peak efficiencies of 62.4 cd A^{-1}, 36.3 lm W^{-1} and EQE of 31.2 %.[119-120]

2.3. Ancillary Ligands-Controlled Ir(III) Complexes

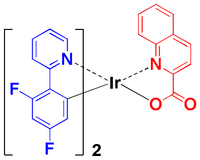
Besides the color tuning by the above-mentioned substitution and/or functional groups, in the heteroleptic cyclometalated Ir(III) complexes with the skeleton of $(C^\wedge N)_2Ir(L^\wedge X)$, the emission peaks could be probably dominated by the narrow π-π* energy gap of the ancillary ligand ($L^\wedge X$), which consequently can make these Ir(III) complexes emit longer emission peaks. The behind mechanism was interpreted by Chi and Chou: After an initial $S_0 \rightarrow S_1$ Franck-Condon excitation, an ultrafast $S_1 \rightarrow T_n$ intersystem crossing occurred with rate constant being $>10^{12}$ s^{-1} in these Ir(III) complexes.[19] Due to the large π-π* energy gap of the cyclometalating ligand (main ligand), the LUMO of the Ir(III) complexes was mostly contributed by the ancillary ligand. Consequently, when populated at the triplet manifold, the following $T_n \rightarrow T_1$ internal conversion rested on the ancillary ligand, which finally accounted for the origin of the red-shifted emission peaks.

2.3.1. Color-tuning from blue and green Ir(III) complexes

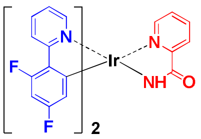
In 2003, Beeby et al. initially unveiled that simply adding an aldehyde (-CHO) group into one of the 2-phenyl rings in $Ir(ppy)_3$ facilely tuned the emission peak to 580 nm of the Ir(III) complex of $(ppy)_2Ir(fppy)$ (**Ir-111**).[83] Afterwards in 2005, Park et al. developed several Ir(III) complexes by using 2-(2',4'-difluorophenyl)pyridine (dfppy) as the large energy-gap cyclometalating ligand and different ancillary ligands based on pyridine-/pyrazine-structures (quinaldinate, pyrazinate et al.).[121] They found the absorptions of the corresponding Ir(III) complexes were almost the same, but the emission colors were facileyl tuned to green, orange and red, depending on the π conjugation of the ancillary ligands. On account of the different π system in the ancillary ligands, it was feasible to tune the emission peaks from sky blue of the parent FIrpic (λ_{peak} = 470 nm) to the orange of FIrqnd (**Ir-112**) (λ_{peak} = 573 nm), FIrpca (**Ir-113**) (λ_{peak} = 574 nm), FIriq (**Ir-114**) (λ_{peak} = 581 nm) and FIrprz (**Ir-115**) (λ_{peak} = 587 nm) in CH_2Cl_2 solution. Meanwhile, the quantum efficiences of these orange Ir(III) complexes (Φ = 0.04-0.35) were decreased relative to the FIrpic (Φ = 0.42). They deduced that the triplet energy transfer from the cyclometalating ligand to the lower triplet state of the ancillary ligand probably occurred.



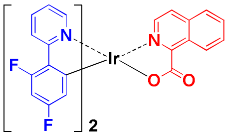
$(ppy)_2Ir(fppy)$
(Ir-111)



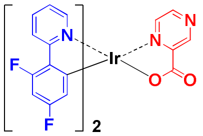
FIrqnd
(Ir-112)



FIrpca
(Ir-113)



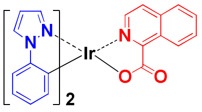
FIriq
(Ir-114)

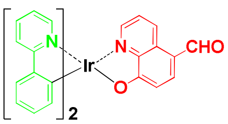


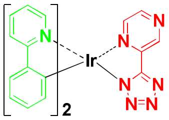
FIrprz
(Ir-115)

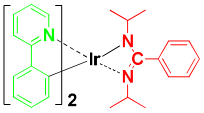
In the same year of 2003, Hong et al. synthesized sixteen Ir(III) complexes with *N*-phenylpyrazole (ppz) as the cyclometalating ligand and 1-isoquinolinecarboxylic/3-isoquinolinecarboxylic acids (1iq/3iq) as the ancillary ligands.[122] One or more methyl groups (-Me) were further added to the ppz ligand to tune the emission peaks. All the compounds exhibited very low quantum efficiencies (Φ < 0.002). The parent Ir(III) complex of $(ppz)_2Ir(1iq)$ (**Ir-116**) showed orange emission of 574 nm in CH_2Cl_2 solution, dramatically red-shifted from its homoleptic Ir(III) analogue of $Ir(ppz)_3$ (λ_{peak} = 414 nm at 77 K).[123] In 2007, Slugovc et al. reported three Ir(III) complexes of $(ppy)_2Ir(L^\wedge X)$ by employing 2-phenylpyridine (ppy) as the cyclometalating ligand and 8-hydroxyquinoline as the ancillary ligand.[124] 8-Hydroxyquinoline was rarely used as the ancillary ligand before, and the formed parent Ir(III) complex was not luminescent at first. After adding an aldehyde (-CHO) group, the newly obtained Ir(III) complex (**Ir-117**) started to show weak emission with peak at 603 nm. In 2008, Stagni et al. used 2-(1*H*-tetrazol-5-yl)pyrazine (PzTz) as the ancillary ligand in $(ppy)_2Ir(L^\wedge X)$ and succeeded in tuning emission peak from 516 nm of $(ppy)_2Ir(acac)$ to 601 nm of Ir(PzTz) (**Ir-118**) in CH_2Cl_2 solution.[125]

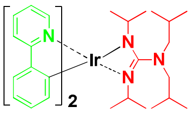
In 2009, Liu et al. reported a novel Ir(III) complex of $(ppy)_2Ir(dipba)$ (**Ir-119**) by using amidinate as the ancillary ligand in $(ppy)_2Ir(L\^{}X)$.[126] The resulting $(ppy)_2Ir(dipba)$ (**Ir-119**) showed emission peak of 543 nm (553 in neat film) and quantum efficiency of 0.3 in CH_2Cl_2 solution. But, PE of max. 32.5 lm W^{-1} was realized in the non-doped PhOLEDs of ITO/NPB/$(ppy)_2Ir(dipba)$ (**Ir-119**)/BCP/Alq_3/LiF/Al, which was better than its CBP-hosted device (max. 29.5 lm W^{-1}) and among the highest results for the non-doped PhOLEDs at that time. The PE value remained to be 22 lm W^{-1} at high luminance of 1000 cd m^{-2}. Afterwards in 2011, they further developed guanidinate derivatives as the ancillary ligands to synthesize eleven Ir(III) complexes.[127] These Ir(III) complexes showed emission peaks in range of 535-548 nm in CH_2Cl_2 solution and quantum efficiencies of 0.16-0.37 in THF solution. Among all the CBP-hosted PhOLEDs with the structure mentioned above, the representative Ir(III) complex of $(ppy)_2Ir\{(N^iPr)_2C(N^iBu_2)\}$ (**Ir-120**) (λ_{peak} = 548 nm, Φ = 0.17) appeared the recorded current efficiency of max. 137.4 cd A^{-1}, which was ascribed to the steric hindrance and the improved hole-injecting/-transporting abilities of the ancillary ligand. In 2010, Ren et al. disclosed a new class of coumarin-based Ir(III) complexes.[128] Using the coumarin-based 6*H*-[2]benzopyrano[4,3-b]pyridin-6-one (bppo) as the ancillary ligand to replace acac in the $(ppy)_2Ir(L\^{}X)$ molecule, the resulting Ir(III) complex of $(ppy)_2Ir(bppo)$ (**Ir-121**) showed orange emission of 570 nm in CH_2Cl_2 solution with high quantum efficiency of 0.82. In the fabricated PhOLEDs co-hosted by TPBi and TCTA, high efficiencies (max. 65.7 cd A^{-1}, 44.7 lm W^{-1} and EQE of 19.3 %) were reported for the $(ppy)_2Ir(bppo)$ (**Ir-121**)-based device.

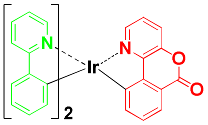

$(ppz)_2Ir(1iq)$
(Ir-116)

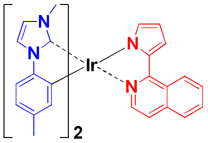

(Ir-117)


Ir(PzTz)
(Ir-118)


$(ppy)_2Ir(dipba)$
(Ir-119)


$(ppy)_2Ir\{(N^iPr)_2C(N^iBu_2)\}$
(Ir-120)

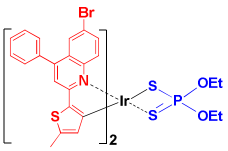

$(ppy)_2Ir(bppo)$
(Ir-121)

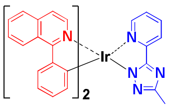

$(mpmi)_2Ir(priq)$
(Ir-122)

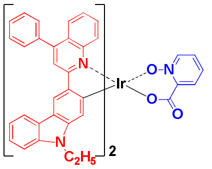
Recently in 2011, Cheng et al. reported four Ir(III) complexes based on the carbene derivatives [H_2mpmiI = 1-(4-tolyl)-3-methyl-imidazolium iodide] as the cyclometalating ligand.[129] The carbene ligand possessed high energy gap and consequently the emission peaks could be tuned from blue to red by employing proper ancillary ligands.[130] Using 1-(1*H*-pyrrol-2-yl)isoquinoline (Hpriq) as the ancillary ligand, its cyclometalated Ir(III) complex of $(mpmi)_2Ir(priq)$ (**Ir-122**) showed orange-red emission of 599 nm in CH_2Cl_2 solution and good quantum efficiency of 0.55 in the doped film. The $(mpmi)_2Ir(priq)$ (**Ir-122**)-based PhOLEDs reached peak efficiencies of 55.4 cd A^{-1}, 43.6 lm W^{-1} and EQE of 24.9 %, which are among one of the best results ever reported for the orange-red PhOLEDs so far.

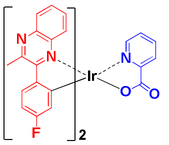
2.3.2. Color-tuning from red Ir(III) complexes

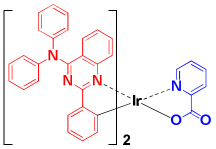
When using electron-accepting moieties as the ancillary ligands (L^X), the previously red-emitting Ir(III) complexes, which were cyclometalated by the large π-conjugation ligands with narrow energy gaps, could tune emission peaks blue-shifted to the orange or yellow region, because the electron-accepting ancillary ligands can disperse the electron density from the d orbitals of Ir(III) ion, consequently resulting in the deepened HOMO level and the enlarged HOMO-LUMO energy gaps.[131-132]


$(TPQ)_2Ir(Et_2dtp)$
(Ir-123)


G0
(Ir-124)


(Et-CVz-PhQ)$_2$Ir(pic-N-O)
(Ir-125)


$(fpmqx)_2Ir(pic)$
(Ir-126)


$(PQxD)_2Ir(pic)$
(Ir-127)

Early in 2006, our group investigated several bromine-substituted Ir(III) complexes with 4-phenylquinoline derivatives as the cyclometalating ligands.[133] Using electron-deficient *O*,*O*'-diethyldithiophosphine (Et_2dtp) as the ancillary ligand to replace the acac in the Ir(III) complex with the large π-system ligand of 6-bromo-2-(5-methylthiophen-2-yl)-4-phenylquinoline (TPQ), the emission peak was blue-shifted from the parent $(TPQ)_2Ir(acac)$ (λ_{peak} = 631 nm) to the 606 nm of the modified $(TPQ)_2Ir(Et_2dtp)$ (**Ir-123**) in CH_2Cl_2 solution. But the $(TPQ)_2Ir(Et_2dtp)$ (**Ir-123**) showed low quantum efficiency of only ~0.03, probably quenched by the bromine atom. In 2007, Cao et al. represented high-efficiency red Ir(III) dendrimers based on the 2-phenylisoquinoline (piq) as the cyclometalating ligand.[134] In the zero-generation Ir(III) dendrimer, they used the electron-accepting 5-methyl-3-(pyridin-2'-yl)-1*H*-1,2,4-triazole as the ancillary ligand to replace acac in $(piq)_2Ir(L\^{}X)$. The corresonding Ir(III) complex of G0 (**Ir-124**) showed significantly blue-shifted emission peak of 593 nm when compared to its red-emitting $(piq)_2Ir(acac)$ (λ_{peak} = 622 nm). In the fully solution-processed PhOLEDs, good efficiencies (max. 6.1 cd A^{-1} and EQE of 8.2 %) were obtained for the G0 (**Ir-124**)-based device at that time. In 2009, Lee et al. synthesized several solution-processable orange and red Ir(III) complexes with the carbazole (CVz)-containing 4-phenylquinoline (PhQ) derivatives as the cyclometalating ligands.[135] In the skeleton of Ir(III) complex (Et-CVz-PhQ)$_2$Ir(L^X), where Et-CVz-PhQ stands for the ligand of 9-ethyl-3-(4-phenylquinolin-2-yl)-9*H*-carbazole, the Ir(III) complex of (Et-CVz-PhQ)$_2$Ir(pic-N-O) (**Ir-125**) using picolinic acid *N*-oxide (pic-N-O) as the ancillary ligand displayed the expected blue-shifted emission of 595 nm in $CHCl_3$ solution and decreased HOMO level of -5.14 eV than its acac analogue (λ_{peak} = 619 nm, HOMO = -5.02 eV, Φ = 0.05), but the improved quantum efficiency (Φ = 0.20) for $(Et\text{-}CVz\text{-}PhQ)_2Ir(pic\text{-}N\text{-}O)$ (**Ir-125**) was observed. In the solution-processed PhOLEDs, the $(Et\text{-}CVz\text{-}PhQ)_2Ir(pic\text{-}N\text{-}O)$ (**Ir-125**)-based device exhibited fair efficiencies (max. 8.36 cd A^{-1}, 3.50 lm W^{-1} and EQE of 4.98 %). Afterwards, the efficiencies were enhanced to max. 13.86 cd A^{-1}, 4.32 lm W^{-1} and EQE of 8.74 % by an optimized device configuration.[136]

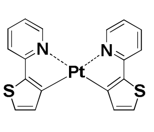
In 2010, Johannes et al. issued three Ir(III) complexes bearing 2-(4'-fluorophenyl)-3-methyl-quinoxaline (fpmqx) as the cyclometalating ligands and triazolylpyridine (trz)/picolinate (pic)/acetylacetonate (acac) as the ancillary ligands, respectively.[137] The basic Ir(III) complex of $(fpmqx)_2Ir(acac)$ manifested red emission (λ_{peak} = 628 nm), even containing the F atom in the 4'-postion of its 2-phenyl ring. After placing electron-accepting pic into the acac position of $(fpmqx)_2Ir(L\hat{}X)$, the resulting Ir(III) complex of $(fpmqx)_2Ir(pic)$ (**Ir-126**) appeared blue-shifted emission peak of 606 nm in CH_2Cl_2 solution. It was observed that the HOMO level of $(fpmqx)_2Ir(pic)$ (**Ir-126**) (-5.67 eV) was lower than that of $(fpmqx)_2Ir(acac)$ (HOMO = -5.54 eV). Despite that, both $(fpmqx)_2Ir(acac)$ and $(fpmqx)_2Ir(pic)$ (**Ir-126**) possessed good quantum efficiencies of 0.39 and 0.41, respectively. In their fabricated PhOLEDs hosted by TCTA, the $(fpmqx)_2Ir(pic)$ (**Ir-126**)-based device exhibited higher efficiencies (max. 13.4 cd A^{-1}, 14.6 lm W^{-1} and EQE of 11.5 %) than its $(fpmqx)_2Ir(acac)$ analogue (max. 5.4 cd A^{-1}, 5.7 lm W^{-1} and EQE of 7.2 %). Recently in 2012, Mei et al. presented a novel Ir(III) complex of $(PQxD)_2Ir(pic)$ (**Ir-127**), which was cyclometalated by the ligand of *N*,*N*,2-triphenylquinazolin-4-amine (HPQxD) and the ancillary ligand of pic.[138] The $(PQxD)_2Ir(pic)$ (**Ir-127**) displayed orange emission of 599 nm and fair quantum efficiency of 0.12 in CH_2Cl_2 solution. But the quantum efficiency was improved to 0.55 in the doped film. In the solution-processed PhOLEDs co-hosted by PVK and PBD, satisfactory efficiencies (max. 20.7 cd A^{-1} and EQE of 18.4 %) were achieved for the $(PQxD)_2Ir(pic)$ (**Ir-127**)-based device.

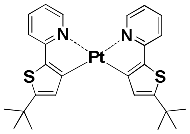
3. Platinum(II) Complexes

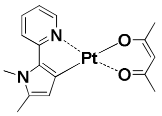
With the d^8 electron configuration of Pt(II) ion, the neutral cyclometalated Pt(II) complexes with four chemical bonds prefer the square planar conformation.[139-140] Due to the ligand-field stabilisation, the unoccupied d_{x2-y2} orbital of Pt(II) ion is usually antibonding or mainly contributed to the antibond. When the Pt(II) ion is coordinated with weak-field ligands such as bipyridine (bpy), the energy level of the antibonding d_{x2-y2} orbital can probably lie close to the π* orbitals of the ligands. Consequently, the promotion from the emissive ^{3}MLCT (d–π*) or ^{3}LC (π–π*) excited states to the non-emissive metal-centered (MC) d-d* excited states can be easily achieved through the isoenergetic crossing point of the potential energy surfaces with the offset of thermal energy, ultimately leading to the non-emissive Pt(II) complexes in solution at room temperature.[141-142] Meanwhile, owning to the square planar structure and the unsaturated 18-electron configuration of Pt(II) complexes, the intermolecular stacking generally appears in the solid state through the Pt-Pt interaction and/or the ligand π-π interaction.[143] Therefore, when the intermolecular aggregation occurs, the resulting excimer and/or dimer could make much richer photophysic properties, particularly bringing in the remarkably red-shifted emission relative to the isolated, mononuclear emission spectrum.[144] These transition states are usually assigned as either metal-metal-to-ligand charge transfer (MMLCT) or excimeric ligand-to-ligand charge transfer.[145]

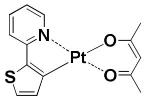
In this part, we will focus on the emission peaks of Pt(II) complexes both in solution and solid state/film. According to the coordinating number of the ligands, we divide the yellow/orange Pt(II) complexes into three groups: i) Containing bidentate ligand; ii) Containing tridentate ligand; iii) Containing tetradentate ligand.

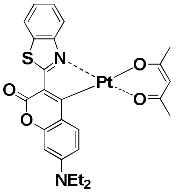
3.1. Containing Bidentate Ligand


Pt(thpy)$_2$
(Pt-1)


Pt(thpy-SiMe$_3$)$_2$
(Pt-2)

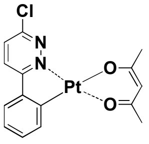

(pyrpy)Pt(acac)
(Pt-3)


(thpy)Pt(acac)
(Pt-4)

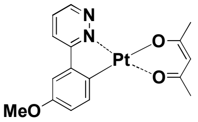

(C6)Pt(acac)
(Pt-5)

In principle, the aforementioned bidentate cyclometalating ligands (C^N) for the Ir(III) complexes can be used in the Pt(II) complexes as well. In early 2001, Thompson et al. reported a homoleptic Pt(II) complex of $Pt(C\hat{}N)_2$, namely *cis*-bis[2-(2'-thienyl)pyridine-*N*,*C*^{3}]platinum(II) [$Pt(thpy)_2$] (**Pt-1**).[146] The strong σ-donating carbanion in the C^N ligand can elevate the d-d* energy gap of Pt(II) ion to avoid the non-emissive MC excited states. The $Pt(thpy)_2$ (**Pt-1**) showed orange emission of 578 nm and quantum efficiency of 0.18 in toluene solution. And the $Pt(thpy)_2$ (**Pt-1**)-based device co-hosted by PVK and PBD acquired fair efficiencies (max. 6.0 cd A^{-1} and EQE of 2.2 %). Afterwards, the EQE of the $Pt(thpy)_2$ (**Pt-1**)-based device was improved to 5.4 % by Cocchi et al..[147] Meanwhile, they synthesized a modified Pt(II) complex of $Pt(thpy\text{-}SiMe_3)_2$ (**Pt-2**) (λ_{peak} = 590 nm, Φ = 0.35), which was the derivative of **Pt-1** by adding trimethylsilanyl group to the 5-position of 2'-thienyl ring. The EQE of the $Pt(thpy\text{-}SiMe_3)_2$ (**Pt-2**)-based PhOLEDs reached the value of 11.5 %. Soon in 2002, Thompson et al. synthesized dozens of heteroleptic Pt(II) complexes by employing the same bidentate ligands they previously used for the Ir(III) complexes.[28] These Pt(II) complexes have the general structure of $(C\hat{}N)Pt(O\hat{}O)$, where C^N represents the cyclometalating ligands such as 2-phenylpyridine (ppy), 2-(2'-thienyl)pyridine (tpy) and O^O is a *β*-diketonato ligand [acetyl acetone (acacH) or dipivaloylmethane (dpmH)].[148] The strong σ-donating carbanion of these C^N ligands elevated the d-d* energy gap of Pt(II) ion and assure that most of the Pt(II) complexes were emissive in solution at room temperature. The quantum calculations demonstrated similar results as the Ir(III) analogues: The HOMO levels were a mixture of Pt(II) d orbitals and ligand π orbitals;

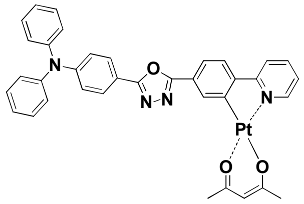
while the LUMO is predominantly based on C^N ligands. Therefore, the emission peaks of Pt(II) complexes can be manipulated by the π conjugation of the cyclometalating C^N ligands and also be finely tuned by adding electron-withdrawing/-donating groups. Proved by the well-resolved vibronic emission spectra at room temperature and 77 K, their excited states were found to be a mixed ^{3}LC/^{3}MLCT excited states. Consequently, the quantum efficiencies were depend on the contributions from the ^{3}MLCT excited states. The typical Pt(II) complexes of (pyrpy)Pt(acac) (**Pt-3**) (λ_{peak} = 603 nm), (thpy)Pt(acac) (**Pt-4**) (λ_{peak} = 575 nm) and (C6)Pt(acac) (**Pt-5**) (λ_{peak} = 589 nm) displayed quantum efficiencies of 0.02, 0.11 and 0.25 in 2-MeTHF solution, respectively.



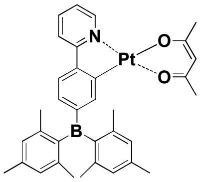
(6clppdz)Pt(acac)
(Pt-6)



(5'meoppdz)Pt(acac)
(Pt-7)



(Pt-8)



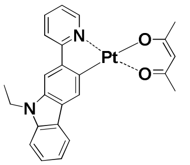
Pt-B
(Pt-9)

In 2004, Lee et al. presented several Pt(II) complexes by using 3-phenylpyridazine (ppdz) as the cyclometalating ligand.[149] The parent Pt(II) complex of (ppdz)Pt(acac) is green-emitting (λ_{peak} = 516 nm). Attaching functional groups could tune the emission peaks: Adding Cl atom to the 6-position of pyridazine ring could lower the LUMO level, and thus the emission peak of the resulting Pt(II) complex (6clppdz)Pt(acac) (**Pt-6**) was red-shifted to 541 nm in *n*-hexane solution. Simultaneously, adding methoxy group (-OMe) to the 3'-position of the 3-phenyl ring could increase the HOMO level, and thus the emission peak of the resulting Pt(II) complex (5'meoppdz)Pt(acac) (**Pt-7**) was red-shifted to 573 nm.

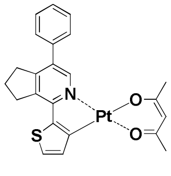
In 2005, Wong et al. demonstrated a multi-functional Pt(II) complex based on the skeleton of (ppy)Pt(acac)[150] by adding both hole-transporting triphenylamine and electron-transporting oxadiazole groups.[151] The corresponding Pt(II) complex (**Pt-8**) showed dominating ^{3}LC emission, with structured emission peaks at 471, 533 (sh) and 570 (sh) nm in CH_2Cl_2 solution (Φ = 0.02). But in neat film, its emission peaks was red-shifted to 550, 590 (sh), 668 (sh) nm, as the dimeric Pt-Pt stacking was observed in its crystal structure. Simple non-doped PhOLED [ITO/CuPc/(**Pt-8**)/Ca/Al] was constructed and max. CE of 1.2 cd A^{-1} was acquired. Later in 2010, they tailored the cyclometalating ppy ligand by attaching main-group elements to the *para*-position of the 2-phenyl ring and obtained a series of Pt(II) complexes, similar to the reported Ir(III) analogues. Adding the following main-group elements [-B(Mes)$_2$, -SiPh$_3$, -GePh$_3$, -NPh$_2$, -POPh$_2$, -OPh, -SPh, -SO$_2$Ph] not only tuned the emission peaks, but also improved the hole-/electron-transporting abilities.[152] Among these Pt(II) complexes, the boron-substituted Pt(II) complex of Pt-B (**Pt-9**) displayed the emission peak of 542 nm along with a good quantum efficiency of 0.42 in CH_2Cl_2 solution. In the fabricated PhOLEDs hosted by CBP, the **Pt-9**-based device showed the best efficiencies (max. 30 cd A^{-1}, 8.36 lm W^{-1} and EQE of 9.52 %) among them.

In 2007, our group synthesized a yellow Pt(II) complex of (C^N)Pt(O^O) by using the 2-pyridinyl-*N*-ethylcarbazole (2-PEC) as the cyclometalating ligand.[153] We found that the 2-position C atom of the carbazole coordinating to the Pt(II) atom made more contributions to the π system than the 3-position C atom of the carbazole. The resulting Pt(II) complex of (2-PEC)Pt(acac) (**Pt-10**) displayed emission peak of 560 nm and fair quantum efficiency of 0.19 in CH_2Cl_2 solution, whereas its counterpart Pt(II) complex of (3-PEC)Pt(acac) cyclometalated by 3-pyridinyl-*N*-ethylcarbazole (3-PEC) exhibited bluish-green emission (λ_{peak} = 493 nm). In the fabricated PhOLEDs hosted by CBP, the (2-PEC)Pt(acac) (**Pt-10**)-based device achieved satisfactory efficiencies (max. 35.8 cd A^{-1}, 25.0 lm W^{-1} and EQE of 13.1 %), which were among the highest results for the Pt(II)-based PhOLEDs at that time.

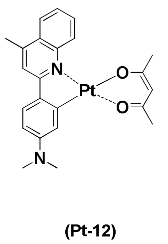
In 2009, Yersin et al. reported a series of modified heteroleptic Pt(II) complexes of (C^N)Pt(acac) based on (thpy)Pt(acac), where C^N represents the substituted 2-(2'-thienyl)pyridine (thpy) ligands.[154] All the Pt(II) complexes were orange or red emissions with quantum efficiencies in the range of 0.04-0.28 in CH_2Cl_2 solution, lower than that of (thpy)Pt(acac) (**Pt-4**) (Φ = 0.42). The represented Pt(II) complex (**Pt-11**) showed orange emission of 577 nm and the highest quantum efficiency of 0.28 among them. Highly resolved emission and excitation spectra were obtained and analysed for the Pt(II) complex (**Pt-11**) under low temperature (T = 1.2 K) and high magnetic fields (B = 10 T) in the Shpol'skii matrix [the complexes are dissolved in *n*-octane]. The small energy difference (Δ<1 cm^{-1}) of Pt(II) complex (**Pt-11**) at zero magnetic field for its three substates of the lowest triplet state (T_1) manifested that the triplet states of these Pt(II) complexes were largely ligand-centered (LC) $^3\pi$-π* character, which was originated from the weak spin-orbit couplings and consequently brought about the low quantum efficiencies.[155-156]



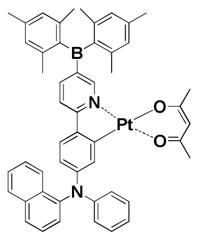
(2-PEC)Pt(acac)
(Pt-10)



(Pt-11)



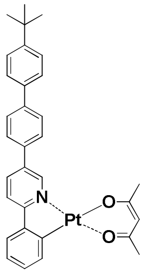
(Pt-12)



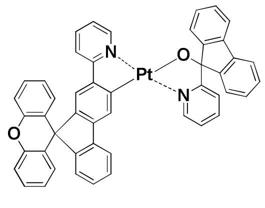
Pt-BNPB2
(Pt-13)

In 2010, Lin et al. synthesized seven Pt(II) complexes

(C^N)Pt(O^O) bearing lepidine-based ligands, which covered emission range from yellow to saturated red.[157] The typical Pt(II) complex (**Pt-12**) cyclometalated by *N*,*N*-dimethyl-4-(4-methylquinolin-2-yl)aniline displayed orange emission of 597 nm and high quantum efficiency of 0.87 in toluene solution. In the fabricated PhOLEDs hosted by CBP, the **Pt-12**-based device showed satisfactory efficiencies (max. 29.83 cd A^{-1}, 11.79 lm W^{-1} and EQE of 15.21 %) with an orange-red CIE coordinate of (0.60, 0.40). In 2011, Wang et al. designed an efficient orange Pt(II) complex of (C^N)Pt(O^O) by simultaneously incorporating electron-transporting triarylboron moiety and hole-transporting triarylamine moiety into the ppy ligand.[158] The resulting Pt(II) complex of Pt-BNPB2 (**Pt-13**) exhibited the orange emission of 590 nm and extremely high quantum efficiency of 0.91 in CH$_2$Cl$_2$ solution.[159] The high quantum efficiency was believed to be originated from the bulky boron group, which increased energy gap between the emissive excited state and the quenching d-d* state. In the device configuration of ITO/MoO$_3$/CBP/CBP:**Pt-13**/TPBi:**Pt-13**/TPBi/Cs$_2$CO$_3$/Al, the Pt-BNPB2 (**Pt-13**)-based PhOLEDs with double emitting layers showed satisfactory efficiencies (max. 35 cd A^{-1}, 36.6 lm W^{-1} and EQE of 10.1 %).

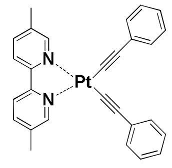


(Pt-14)



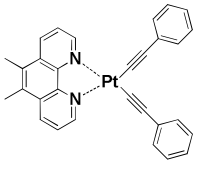
(SFXPy)Pt(PyFO)

(Pt-15)



Pt(5,5'-dmbpy)(C≡CPh)$_2$

(Pt-16)

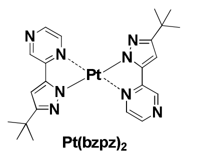


Pt(5,6-dmphen)(C≡CPh)$_2$

(Pt-17)

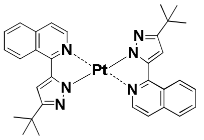
In 2011, Adachi et al. synthesized a linear-shaped Pt(II) complex based on (ppy)Pt(acac), with the aim to form horizontal orientation in the amorphous film.[160] The corresponding Pt(II) complex (**Pt-14**) cyclometalated by 5-[4-(4-*tert*-butylphenyl)phenyl]-2-phenylpyridine exhibited yellow emission of 550 nm and good quantum efficiency of 0.5 in THF solution. Polarized emission from the edge of the fabricated thin film confirmed the horizontal orientation of the Pt(II) complex (**Pt-14**). The max. EQE of 15.8 % was achieved for the **Pt-14**-based PhOLEDs hosted by mCP, and the light out-coupling efficiency of the device was estimated to be at least Φ = 32 %. Recently in 2012, Huang et al. disclosed a spiro-functionalized heteroleptic Pt(II) complex of (C^N)Pt(C'^N').[161] The resulting Pt(II) complex of (SFXPy)Pt(PyFO) (**Pt-15**) was cyclometalated by the ligand of 2-(spiro[fluorene-9,9'-xanthene])pyridine (SFXPy) and the ancillary ligand of 9-(pyridin-2-yl)-9*H*-fluoren-9-ol (PyFO). The (SFXPy)Pt(PyFO) (**Pt-15**) showed orange emission peak of 548 nm in its EL spectrum and no excimer emission or Pt-Pt interaction was observed, due to the three-dimensional spiro-containing bulky configuration of the ligands. However, fair efficiencies (max. 16 cd A^{-1}, 19.2 lm W^{-1} and EQE of 5.2 %,) were reported for the **Pt-15**-based PhOLEDs.

In early 2001, Che et al. reported two series of bis(arylacetylide) Pt(II) complexes (N^N)Pt(L)$_2$ with aromatic diimine (bipyridine or phenanthroline) (N^N) as the ligands, where L represents the phenylacetylide ligand.[162] The strong-field acetylide ligands could spit up the d-d* energy gap of Pt(II) ion and make the dominate formation of ^{3}MLCT [d(Pt)→π*(phen)] excited states, resulting in their high quantum efficiencies in the range of 0.35-0.64. Meanwhile, the low LUMO energy levels contributed largely from the π-accepting aromatic diimine ligands (N^N) caused these Pt(II) complexes yellow or orange emissions. Adding alkyl/phenyl groups to the aromatic diimine ligands could further tune the emission. The representative Pt(II) complexes (**Pt-16**) and (**Pt-17**) showed emission peaks of 545 nm and 554 nm in CH$_2$Cl$_2$ solution, respectively. Although the similar Pt(II) complexes have been reported by other groups before,[163-165] Che et al. initially used these Pt(II) complexes as emissive phosphors in the PhOLEDs by solution process and acquired fair device efficiencies.



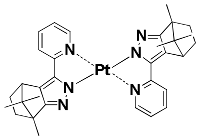
Pt(bzpz)$_2$

(Pt-18)



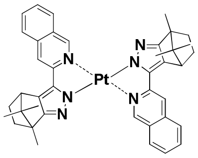
Pt(bqpz)$_2$

(Pt-19)



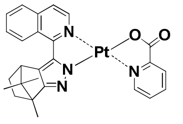
Pt(pydz)$_2$

(Pt-20)



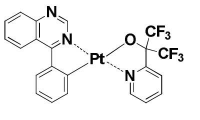
Pt(3-iqdz)$_2$

(Pt-21)



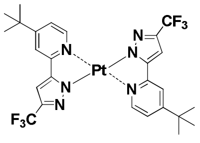
(1-iqdz)Pt(pic)

(Pt-22)

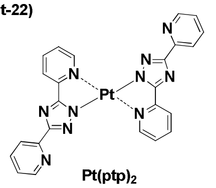


(nazo)Pt(pyF6O)

(Pt-23)



(Pt-24)



Pt(ptp)$_2$

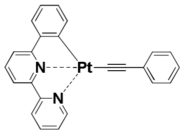
(Pt-25)

In 2005, Chi et al. issued several homoleptic Pt(II) complexes of Pt(N^N)$_2$ with pyridyl azolate-based ligands.[166] The N^N ligands adopted the *trans*-configuration in these Pt(II) complexes, which was believed to be caused by the unusual intra-molecular H-bonding.[167] The parent Pt(II) complex cyclometalated by 3-methyl-5-(2-pyridyl)-pyrazole showed green emission, and the replacement of pyrazole by 1,2,4-triazole made emission peak further blue-shift. On the contrary, using the ligands of 3-*tert*-butyl-5-(2-pyrazine)-pyrazole (bzpzH) and 1-(5-*tert*-butyl-2H-pyrazol-3-yl)-isoquinoline (bqpzH) could make the corresponding Pt(II) complexes of Pt(bzpz)$_2$ (**Pt-18**) and Pt(bqpz)$_2$ (**Pt-19**) orange emissions of 576 nm (Φ = 0.82) and 584 nm (Φ = 0.74) in THF solution, respectively, probably attributed to the reduced LUMO level and the enlarged π conjugation. In the same year of 2005, Chi et al. reported two homoleptic Pt(II) complexes bearing isoquinolinyl indazole (iqdzH) or pyridyl indazole (pydzH) as the cyclometalating ligands, which possessed bulky, rigid camphor-like architecture to prevent molecular aggregates or excimers.[168] The two Pt(II) complexes adapted *trans*-configuration for the existence of the intra-molecular H-bond interaction. The Pt(II) complex of Pt(pydz)$_2$ (**Pt-20**) showed emission peak of 553 nm and high quantum efficiency of 0.64 in CH_2Cl_2 solution. Fusing another phenyl ring on the pyridine moiety (isoquinoline) made emission peak red-shift to 635 nm. Later in 2007, Chi et al. investigated the synthetic pathway for the heteroleptic Pt(II) complex of (N^N)Pt(L^X), where N^N is 1- or 3-isoquinolinyl indazolate ligand (1-iqdz or 3-iqdz) and L^X is pic or 3-trifluoromethyl-5-(2-pyridyl)-pyrazole (fppz).[169] As in the case for the Ir(III) analogues,[31] the homoleptic Pt(II) complex of Pt(3-iqdz)$_2$ (**Pt-21**) showed orange emission of 567 nm (Φ = 0.24) in CH_2Cl_2 solution, blue-shifted from its red-emitting isomer of Pt(1-iqdz)$_2$ (λ_{peak} = 624 nm). By changing the ligand to the electron-accepting pic ligand, the resulting heteroleptic Pt(II) complex of (1-iqdz)Pt(pic) (**Pt-22**) displayed blue-shifted emission peak of 587 nm (Φ = 0.64). In the fabricated PhOLEDs hosted by CBP, decent efficiencies (12.19 cd A^{-1}, 6.12 lm W^{-1} and EQE of 4.93 % at 20 mA cm^{-2}) were achieved for the (1-iqdz)Pt(pic) (**Pt-22**)-based device. In 2008, Chi et al. developed several Pt(II) complexes bearing 2-pyridyl hexafluoropropoxide (pyF6O) as the ancillary ligand.[170] With 4-phenyl quinazoline (nazo) as the cyclometalating ligand, the heteroleptic Pt(II) complex of (nazo)Pt(pyF6O) (**Pt-23**) showed orange emission of 595 nm and decent quantum efficiency of 0.48 in CH_2Cl_2 solution. Recently in 2013, Chi et al. further developed three Pt(II) complexes bearing spatially encumbered pyridinyl pyrazolate as the cyclometalating ligands.[171] In spite of that they were hardly emissive in dilute solution, they were highly emissive in the powdery sample. The homoleptic Pt(II) complex (**Pt-24**) cyclometalated by the ligand of 4-(*tert*-butyl)-2-(3-trifluoromethyl-1*H*-pyrazol-5-yl)-pyridine displayed orange-red emission of 606 nm and high quantum efficiency of 0.73 in solid phase. In the fabricated PhOLEDs hosted by POCz3 [3,3',3''-phosphoryl tris(9-phenyl-9*H*-carbazole)], the Pt(II) complex (**Pt-24**)-based device showed very high efficiencies (max. 47.6 cd A^{-1}, 50.8 lm W^{-1} and EQE of 20.0 %). Combined with the newly synthesized homoleptic blue-emitting Pt(II) complex, which was cyclometalated by 4-(2,6-diisopropylphenyl)-2-(3-trifluoromethyl-1*H*-pyrazol-5-yl)pyridine, the corresponding two-color WOLEDs with single emitting layer reached good efficiencies as high as 44.8 cd A^{-1}, 46.2 lm W^{-1} and EQE of 15.0 %.

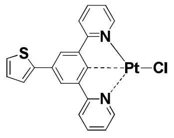
In 2009, Omary designed one Pt(II) complex of Pt(ptp)$_2$ with 3,5-bis(2-pyridyl)-1,2,4-triazole (N^N) as the cyclometalating ligand. The Pt(II) complex of Pt(ptp)$_2$ (**Pt-25**) displayed bluish-green emission from its isolated monomer, but exhibited orange emission of 580 nm in neat film for the common "metallophilic interactions" from the excimer. At the beginning, they fabricated the corresponding PhOLEDs hosted by CBP. At high dopant concentration of 45 w.t.%, the Pt(ptp)$_2$ (**Pt-25**)-based device showed orange EL spectrum but poor efficiencies (max. 2.38 lm W^{-1}).[172-173] But later in 2013, they reported that the power efficiency for the Pt(ptp)$_2$ (**Pt-25**)-based PhOLEDs was astonishingly improved to be max. 63 lm W^{-1}, along with the peak EQE of 20.3 %, under the simple, non-doped device configuration of ITO/TAPC/Pt(ptp)$_2$ (**Pt-25**)/LiF/Al, which are among the highest efficiencies for the non-doped, Pt(II)-based orange PhOLEDs so far.[174] Furthermore, compared to the doped PhOLEDs, the EQE roll-off in the device decreased by less than 5 % at a high luminance of 1000 cd m^{-2}. To explain this, they performed exhaustively quantitative analysis for the annihilation mechanism in these devices. Their results demonstrated that the triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA) played the dominating role for the roll-off at high current density. Meanwhile, the short lifetime of Pt(ptp)$_2$ (**Pt-25**) in the neat film was a key for the reduction of triplet excitons quenching.

3.2 Containing Tridentate Ligand

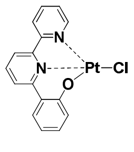
In 2002, Che et al. disclosed a series of Pt(II) complexes of (C^N^N)Pt(C≡C-R) with a tridentate 6-aryl-2,2'-bipyridine (C^N^N) ligand and a strong σ-donating alkynyl ligand (-C≡C-R).[175] The strong σ-donating alkynyl ligand increased the HOMO levels of the Pt(II) complexes and caused the red-shifted emissions when compared to the related ionic $[(C^\wedge N^\wedge N)Pt(L)]^+$ derivatives (L = phosphine, pyridine, isocyanide or Fischer carbene ligands).[176-177] Their emission peaks could be tuned by the π-conjugation length of the oligoynyl moiety and/or by adding the electron-withdrawing/-donating groups. The typical Pt(II) complex (**Pt-26**) displayed orange emission of 582 nm with poor quantum efficiency of 0.04 in CH_2Cl_2 solution, and its related PhOLEDs showed fair efficiencies (max. 4.2 cd A^{-1} at 2 % doping ratio). Owing to the existence of multi-modification sites on the Pt(II) complex (**Pt-26**), its emission peak can be further tuned into red by further enlarging the π-conjugation.[178-179]



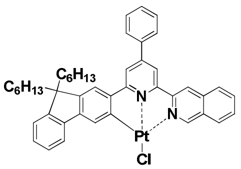
(Pt-26)



HL8
(Pt-27)



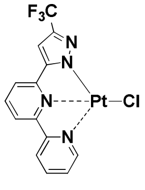
(Pt-28)



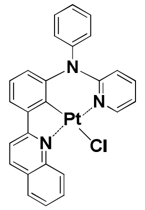
(Pt-29)

In 2005, Williams et al. reported several Pt(II) complexes of (N^C^N)Pt(Cl) containing tridentate 1,3-dipyridylbenzene (N^C^N) as the cyclometalating ligands.[180-181] The strong σ-donating carbanion in these N^C^N ligands could avoid the non-emissive MC excited states even that a weak-field Cl atom was included. The excited states of these Pt(II) complexes were dominating ^{3}LC states. And the parent 1,3-dipyridylbenzene-cyclometalated Pt(II) complex showed bluish-green emission. Their emission peaks were further tuned by incorporating pendent aryl groups on the 5-position of the phenyl ring. By adding a thienyl ring, the resulting Pt(II) complex of HL8 (**Pt-27**) showed yellow emission of 548 nm and good quantum efficiency of 0.54 in CH_2Cl_2 solution. Later in 2007, the device efficiencies of these Pt(II) complexes in the PhOLEDs were improved, with the EQE values ranging from 4 to 16 % and the CE values ranging from 15 to 40 cd A^{-1}.[182]

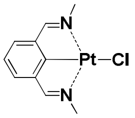
In 2005, Che et al. unraveled a family of Pt(II) complexes (O^N^N)Pt(X), where O^N^N is the tridentate ligand of 6-(2-hydroxyphenyl)-2,2'-bipyridine or its derivatives; and X is Cl, Br, I, or −C≡C−Ph.[183] Modifications on the tridentate ligands were easily carried out. Although these Pt(II) complexes showed emission peaks in the region of orange-red, they showed too low quantum efficiencies to be measured. The Pt(II) complex (**Pt-28**) showed emission peak of 606 nm in DMF (*N,N'*-dimethylformamide) solution. The PhOLEDs hosted by CBP were fabricated, but fair efficiencies (max. 7.8 cd A^{-1} among all) were obtained due to their low quantum efficiencies. Later in 2010, Che et al. further developed and systematically investigated a family of Pt(II) complexes containing tridentate cyclometalating C^N^N ligands fusing with fluorene units, where C^N^N is 6-phenyl-2,2'-bipyridine or π-extended 3-[6'-(naphthalen-2''-yl)pyridin-2'-yl]isoquinoline.[184] Adding or fusing 9,9'-dihexylfluorene group can enhance the solubility or rigidity, which was favorable to the device fabrication and improved the quantum efficiency. The typical Pt(II) complex (**Pt-29**) displayed orange emission peak of 568 nm and high quantum efficiency of 0.73 in CH_2Cl_2 solution. The **Pt-29**-based PhOLEDs displayed the best efficiencies (max. 14.7 cd A^{-1}, 9.2 lm W^{-1} and EQE of 5.5 %) among them.



(fpbpy)Pt(Cl)
(Pt-30)



(Pt-31)

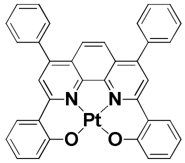


(Pt-32)

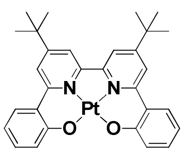
In 2008, Chi et al. synthesized three Pt(II) complexes of (N^N^N)Pt(L) cyclometalated by the ligand of 6-(5-trifluoromethyl-pyrazol-3-yl)-2,2'-bipyridine (fpbpy).[185] The electron-withdrawing -CF_3 group not only increased the pyrazolic N-H acidity and activity, but also minimized the unwanted side reaction by blocking the coordination to the adjacent nitrogen atom. The parent Pt(II) complex of (fpbpy)Pt(Cl) (**Pt-30**) showed greenish-yellow emission of 524 (sh), 560 nm in dilute CH_2Cl_2 solution. Using (fpbpy)Pt(Cl) (**Pt-30**) as the dopant, the PhOLEDs hosted by TPSi-F [triphenyl-(4-(9-phenyl-9*H*-fluoren-9-yl)phenyl)] were fabricated. At the dopant concentration of 28 w.t.%, the (fpbpy)Pt(Cl) (**Pt-30**)-based device achieved decent efficiencies (max. 18.5 cd A^{-1}, 4.9 lm W^{-1} and EQE of 8.5 %), with a yellow CIE coordinate of (0.53, 0.46). At the 100 w.t.% dopant concentration, the emission peak of the EL spectrum was red-shifted to 630 nm. In 2011, Huo et al. reported several luminescent tridentate Pt(II) complexes of (N^C*N)Pt(L) featured in fused five/six-membered metallacycle.[186] The representative Pt(II) complex (**Pt-31**) displayed orange emission peak of 595 nm and decent quantum efficiency of 0.39 in CH_2Cl_2 solution.[187] In 2012, Coe et al. synthesized six Pt(II) complexes of (N^C^N)Pt(Cl) bearing 5-substituted 1,3-bis(*N*-methylimino)benzene (bIBH) derivatives as the tridentate ligands. The parent Pt(II) complex (**Pt-32**) cyclometalated by 1,3-bis(*N*-methylimino)benzene displayed orange emission peak of 562 nm but low quantum efficiency (Φ < 0.01) in CH_2Cl_2 solution.[188]

3.3 Containing Tetradentate Ligand

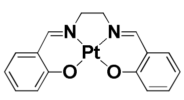
In 2003, Che et al. developed two Pt(II) complexes of (N^N^O^O)Pt bearing the tetradentate bis(phenoxy)diimine as the ligands.[189] The tetradentate quinoline-containing ligands of bis(2'-phenol)-bipyridine and -phenanthrolines included sufficient electron mobility and steric hindrance, but the resulting Pt(II) complexes were unstable in solution. Both the two Pt(II) complexes (**Pt-33**) (Φ = 0.60) and (**Pt-34**) (Φ = 0.12) showed orange emission peaks of 586 nm and 595 nm in CH_2Cl_2 solution, respectively. Their emissions were tentatively assigned to the mixed ^{3}MLCT and ^{3}[lone pair→π*(diimine)] excited states. Fair PhOLEDs efficiencies were reported.



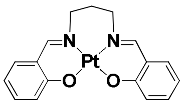
(Pt-33)



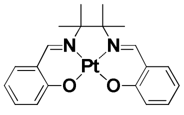
(Pt-34)



(Pt-35)

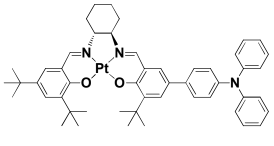


(Pt-36)

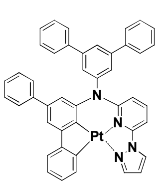


(Pt-37)

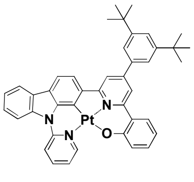
Soon in 2004, Che et al. disclosed three Pt(II) complexes by using the well-known tetradentate *N,N'*-bis(salicylidene)-1,2-ethylenediamine (H_2salen) as the parent ligand.[190] The Pt(II) complexes [**Pt-35**, **Pt-36** and **Pt-37**] bearing the Schiff base as the tetradentate ligands showed yellow or orange emissions in acetonitrile solution at 298 K, with maximum peaks at 550 nm (Φ = 0.19), 592 nm (Φ = 0.09) and 541 nm (Φ = 0.18), respectively. The **Pt-37**-based device showed satisfactory efficiencies (max. 31 cd A^{-1}, 14 lm W^{-1} and EQE of 11 %). The corresponding two-color WOLEDs with single emitting layer were fabricated under the configuration of ITO/NPB/$Bepp_2$: **Pt-35**/LiF/Al, where $Bepp_2$ was used as both host material and blue fluorescent material. Peak PE of 0.79 lm W^{-1} and a CIE coordinate of (0.33, 0.35) were obtained. Later in 2010, Che et al. further expanded this series of Schiff-based Pt(II) complexes and gave a detailed account for their photophysical properties.[191] By increasing the π conjugation of the Schiff-based ligands, the emission peak was tuned to 649 nm. Meanwhile, highly resolved emissions and lifetimes for the lowest triplet excited states (T_1) have been performed. The small energy difference (Δ~20 cm^{-1}) of Pt(II) complex (**Pt-37**) at zero magnetic field for its three substates of T_1 could explain its moderate quantum efficiency.



(Pt-38)



(Pt-39)



Y-Pt
(Pt-40)

In 2012, Wong and Ma et al. further developed several Pt(II) complexes of (N^N^O^O)Pt with the asymmetric Schiff base as ligand.[192] And the emission peaks could be tuned into saturate red. The representative Pt(II) complex (**Pt-38**) displayed orange emission of 568 nm and fair quantum efficiency of 0.17 in CH_2Cl_2 solution. In the fabricated PhOLEDs hosted by TCTA, the Pt(II) complex (**Pt-38**)-based device exhibited the best efficiencies (max. 23 cd A^{-1}, 17 lm W^{-1} and EQE of 8.3 %) among them. In the two-color [FIrpic/**Pt-38**] WOLEDs hosted by TCTA with single emitting layer, fair efficiencies (max. 21 cd A^{-1}, 17 lm W^{-1} and EQE of 7.7 %) were obtained. Recently in 2013, Huo et al. gave a detailed synthetic investigation on the synthesis of tetradentate Pt(II) complex (C^C*N^N)Pt.[193] The typical Pt(II) complex (**Pt-39**) displayed orange emission peak of 555 nm and quantum efficiency of 0.17 in CH_2Cl_2 solution. And changing the pyrazole ring to phenyl ring in the tetradentate ligand could further tune the emission into saturate red. In the same year of 2013, Che et al. developed five Pt(II) complexes of (O^N^C^N)Pt by employing the tetradentate ligands.[194] Due to the rigidity of the ligands, all the Pt(II) complexes showed high quantum efficiencies of 0.47-0.86. The typical Pt(II) complex of Y-Pt (**Pt-40**) (Φ = 0.86) display yellow emission peak of 553 nm in CH_2Cl_2 solution. With the configuration of ITO/NPB/mCP:**Pt-40**)/BAlq/LiF/Al, the device achieved very high efficiencies (max. 74.9 cd A^{-1} and 52.1 lm W^{-1}), which are among the highest results so far. In the two-color WOLEDs with triple emitting layers under the configuration of ITO/MoOx/NPB/TCTA:Y-Pt (**Pt-40**)/mCP:FIrpic/UGH2:FIrpic/BAlq/LiF/Al, high efficiencies (max. 45.6 cd A^{-1} and 35.8 lm W^{-1} and EQE of 16 %) were also realized.

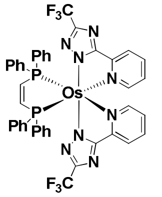
4. Other Organometallic Complexes

Besides Ir(III) and Pt(II) complexes, the other emissive organometallic compounds usually include Re(I) complexes,[195] Ru(II) complexes,[196] Cu(I) complexes,[197-198] Os(II) complexes[199] and Au(III) complexes.[200] In this part, we are selectively focusing on the yellow/orange Os(II) and Au(III) complexes and briefly introduce their application in PhOLEDs.

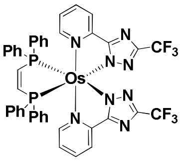
4.1 Osmium(II) Complexes

The neutral d^6 Os(II) complexes were isoelectronic to the Ir(III) analogues, which usually adopted six-coordinated, octahedral configuration and possessed high thermal stability. The disadvantageous intermolecular packing and/or excimer formation rarely exist.[201] In Os(II) complexes, owing to the much contribution of its d orbitals for the lowest excited triplet states (T_1), the dominating ^{3}MLCT excited states and subsequent high quantum efficiencies could be feasibly achieved. As reported in the literature, the energy difference (ΔE) for the three substates of T_1 in the typical ionic Os(II) complex $[Os(bpy)_3]^{2+}$ at zero magnetic field was found to be as high as 211 cm^{-1}.[202] At present, tunable emission peaks from green to near-infrared for Os(II) complexes have been successfully achieved,[203-204] while obtaining efficient blue-emitting Os(II) complexes is still difficult.[205]

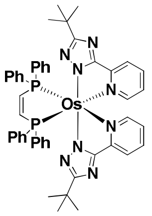
In 2008, Chi et al. developed several Os(II) complexes bearing pyridyl azolates as the cyclometalating liangds, and either bis(diphenylphosphino)methane (dppm) or *cis*-1,2-bis(diphenylphosphino)ethene (dppee) as the bidentate ligands.[206] When employing dppm ligand, the resulting Os(II) complexes exhibited unique molecular configuration; while the usage of dppee as the bidentate ligand brought in the formation of the two isomeric products, where the azolate fragments of the cyclometalating ligands were resided at the mutual *trans*- (isomer A) and *cis*-disposition (isomer B), respectively. The two isomers displayed different photophysical properties, the *trans*-$Os(fptz)_2(dppee)$ (**Os-1**), which was cyclometalated by the ligand of 2-pyridyl-3-trifluoromethyl-1,2,4-triazole (fptz), showed orange emission of 572 nm and nearly unitary quantum efficiency of 0.9 in CH_2Cl_2 solution, while the *cis*-$Os(fptz)_2(dppee)$ (**Os-2**) displayed yellow emission of 547 nm and low quantum efficiency (Φ = 0.01). They reasoned that the stronger electron-donating, *trans*-located azolate moieties could elevate the energy level of the d* orbital in Os(II) ion more effectively than the *cis*-isomer. In the solution-processed PhOLEDs co-hosted by PVK and PBD, the *trans*-$Os(fptz)_2(dppee)$ (**Os-1**)-based device realized satisfactory efficiencies (max. 48.9 cd A^{-1}, 16.8 lm W^{-1} and EQE of 13.3 %). Later in 2010, Wu and Chi et al. developed a wide-bandwidth, yellow-emitting Os(II) complex of *trans*-$Os(bptz)_2(dppee)$ (**Os-3**) based on the ligand of 3-*tert*-butyl-5-(2-pyridyl)-1,2,4-triazolate (bptz).[207] Compared to the above *trans*-$Os(fptz)_2(dppee)$ (**Os-2**) (HOMO = -5.2 eV), the electron-donating *tert*-butyl group in bptz elevated the HOMO level and caused the red-shifted emission peak of 612 nm for the *trans*-$Os(bptz)_2(dppee)$ (**Os-3**) (HOMO = -4.8 eV). However, the featureless emission of the *trans*-$Os(bptz)_2(dppee)$ (**Os-3**) (Φ = 0.30) with full-width at half-maximum (FWHM) of 120 nm made it yellow emitter. Combined with the blue-emitting Ir(III) complex of $Ir(dfbppy)(fbppz)_2$ (λ_{peak} = 449 nm, Φ = 0.68), where dfbppy and fbppz stand for 4-*tert*-butyl-2-(2,4-difluorophenyl)pyridine and 3-(trifluoromethyl)-5-(4-*tert*-butylpyridyl) pyrazole, respectively, the two-color WOLEDs with triple emitting layers were fabricated. Fair device efficiencies (max. 22.9 cd A^{-1}, 20 lm W^{-1} and EQE of 9.5 %) were reported, but the WOLEDs displayed nearly pure white EL spectrum with stable CIE coordinates of (0.311, 0.327)-(0.314, 0.332) and a high-CRI value of 81.



***trans*-Os(fptz)$_2$(dppee)**
(Os-1)



***cis*-Os(fptz)$_2$(dppee)**
(Os-2)

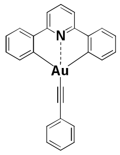


***trans*-Os(bptz)$_2$(dppee)**
(Os-3)

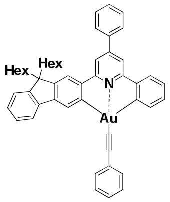
4.2 Gold(III) Complexes

The d^8 Au(III) complexes were isoelectronic to the Pt(II) analogues. Rich luminescence properties have been found early for its related Au(I) congeners, but few examples showed emission in solution at room temperature.[208] For the luminescent Au(III) complexes, the research is in its infancy and most reported Au(III) complexes displayed low quantum efficiencies in solution at room temperature.[209] The reason for the lack of luminescent Au(III) complexes is as following: The high electrophilicity of Au(III) ion makes the unoccupied d_{x2-y2} orbital low-lying, and thus the low-energy ligand-to-metal charge transfer (LMCT) excited states are close and thermally accessable to the emissive intraligand excited states, ultimately leading to the luminescence quenching.[210-211] Similarly like the Pt(II) analogues, the strategies to overcome the problems are to employ strong-field ligands [such as cyclometalating ligands, acetylide or *N*-heterocyclic carbene (NHC)], with the sole purpose to elevate the d–d* energy gap in Au(III) ion.[212] Meanwhile, partial Au-Au interaction and/or aromatic π-π stacking interaction could be probably observed in solid state, because of the four-coordinated, square-planar configuration.

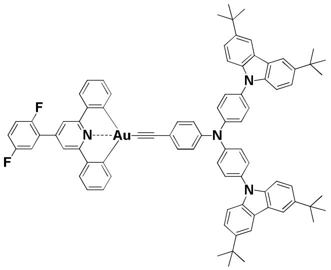
In 2005, Yam et al. initially reported five emissive Au(III) complexes of (C^N^C)Au(C≡CR), which were cyclometalated by the tridentate ligand of 2,6-diphenylpyridine (C^N^C).[213] Although they all possessed low quantum efficiencies (Φ<0.01) at room temperature in CH_2Cl_2 solution, the strong σ-donating alkynyl ligands (-C≡CR) made big contribution for their luminescence, as compared to the low-temperature emission observed for its chloro counterpart (C^N^C)Au(Cl). The prototypical Au(III) complex (**Au-1**) displayed emission peak of 476 nm in CH_2Cl_2 solution, but exhibited orange emission peak of 568 in thin film. In 2013, Che et al. developed several Au(III) complexes of (C^N^C)Au(C≡CR) by incorporating fluorene moiety as one σ-donating carbanion in the tridentate cyclometalating C^N^C ligands.[214] Although their long excited state lifetimes (over 200 μs) at room temperature manifested little metal character was involved in their excited states, they possessed unprecedentedly high quantum efficiencies up to max. 0.58 in CH_2Cl_2 solution. The typical Au(III) complex (**Au-2**) displayed yellow emission of 540 nm and good quantum efficiency of 0.51 in CH_2Cl_2 solution. Recently in 2013, Yam et al. reported the first example of emissive Au(III) dendrimers (C^N^C)Au(C≡CR) for the solution-processed PhOLEDs.[215] The three Au(III) dendrimers with carbazole as the dendrons displayed broad and structureless emission bands at approximate 620-695 nm and low quantum efficiencies (Φ≤ 0.1) in CH_2Cl_2 solution. Their emissions were tentatively assigned as ligand-to-ligand-charge-transfer (^{3}LLCT) excited states and gradually blue-shifted by incorporating more carbazole units in the higher generation dendrimers. Their emissions were also concentration-dependent in doped thin film for the excimers formation. In the fabricated PhOLEDs under the device configuration of ITO/PEDOT:PSS/mCP:Au(III) complex (**Au-3**)/3TPYMB [tris(2,4,6-trimethyl-3-(pyridine-3-yl)phenyl)borane]/TmPyPB/LiF/Al, the first-generation dendrimer of Au(III) complex (**Au-3**) with the dopant concentration of 10 w.t.% exhibited the best efficiencies (max. 24 cd A^{-1}, 14.5 lm W^{-1} and EQE of 7.8 %) among them, along with a yellow CIE coordinate of (0.40, 0.54).



(Au-1)



(Au-2)



(Au-3)

5. Conclusions and Outlooks

In this review article, we systematically summarize the design tactics for yellow/orange heavy-metal complexes, and their application as phosphors in yellow/orange monochromatic PhOLEDs as well as the WOLEDs. The selective photophysical and electroluminescent data for the representative yellow/orange heavy-metal complexes are collected in Table 1.

To make sure high quantum efficiency in heavy-metal complexes, the metal-centred (MC) d-d* excited states must be avoided and the d orbitals of heavy metals must make contribution as much as possible to the HOMO levels and the ^{3}MLCT excite states. The latter can be quantitatively described by the energy difference values (cm^{-1}) between the three substates in the lowest triplet states (T_1) at zero magnetic field. To succeed in obtaining yellow/orange heavy-metal complexes, using the cyclometalating ligands with proper π system can be a direct and feasible way. Modifications by the functional groups/substituents or finely tuning with the proper ancillary ligands can also be applicable.

To realize high-performance monochromatic PhOLEDs and WOLEDs, besides the high-quality yellow/orange heavy-metal complexes with high quantum efficiency and short decay lifetime, the other materials (such as hole-/electron-transporting materials and host materials) in device structures should be optimized. If the power efficiency of the yellow/orange PhOLEDs could exceed 100 lm W^{-1} at high luminance and have the small efficiency roll-off value, they can play an important role in the high power-efficiency WOLEDs for pratical lighting application. With the development of elegant materials and elaborate device structures, we believe that the satisfactory yellow/orange PhOLEDs and the WOLEDs incorporating yellow/orange phosphors as component will fulfill the requirements for both device efficiency and service lifetime in the near future.

Tab. 1 Selective photophysical and electroluminescence data for the representative yellow/orange heavy-metal complexes

Emitter	λ_{peak} (nm)[a]	Φ[b]	Active Layers[c]	η_c (cd A^{-1})[d]	η_p (lm W^{-1})[d]	η_{ext} (%)[d]	Ref.[e]
Ir-2	597	0.1	NPB/DCDPA/BSFM:$(pq)_2Ir(acac)$/TSPO1	-	-/-/16.4	19.2/-/17.1	28,29
Ir-14	563	0.51	NPB/TCTA/*p*-BISiTPA:$(fbi)_2Ir(acac)$/TPBi	57.8/57.3/53.2	51.9/43.9/29.3	20.5/20.4/18.9	43,45
			W: NPB/TCTA/*p*-BISiTPA:FIrpic:$(fbi)_2Ir(acac)$/TPBi	51.8/51.7/47.3	42.7/37.8/25.2	19.1/19.1/17.4	46
Ir-19	590, 630 (sh)	0.95	PEDOT:PSS/PVK:CBP:$Ir(MPCPPZ)_3$/TPBi	18.4/-/-	-	20.2/-/-	51
Ir-25	559, 595 (sh)	0.65	TAPC/TCTA/CBP:$(bt)_2Ir(acac)$/TmPyPB	69.7/69.1/66.5	69/62/42.6	25.7/25.5/24.4	28,54
			W: TAPC/TCTA/DCzPPy:$(bt)_2Ir(acac)$ /PO9:Ir(dbfmi)/B3PyPB	44.0/44.4/38.7	52.7/45.4/33.2	19.0/19.1/15.9	55
Ir-28	560	-	TAPC/$Bepp_2$:$(tptpy)_2Ir(acac)$/TmPyPB	84.4/-/80.3	90.7/-/54.1	25.0/-/-	59
			W: TAPC/TATA:FIrpic/TmPyPB/TmPyPB:Rb_2CO_3/Al/ HATCN/TAPC/$Bepp_2$:$(tptpy)_2Ir(acac)$/TmPyPB	129.5/-/128.8	65.4/-/63.1	49.5/-/49.2	60

Ir-52	567	0.19	NPB/CBP:**Ir-52**/BCP/Alq$_3$	40.2/38.5/39.1	23.9/23.6/19.3	12.4/12.0/12.1	78
			W: NPB/CBP:**Ir-52**/NPB/ADN:DSA-Ph/BAlq	26.6/25.8/26.5	13.5/12.4/7.8	8.9/8.8/8.6	78
Ir-53	563, 603 (sh)	0.05	PEDOT:PSS/PVK:PBD:**Ir-53**	40.4/-/38.8	15.8/-/11.9	12.3/-/11.8	79
			W: PEDOT:PSS/PVK:OXD-7:FIrpic:**Ir-53**	42.9/-/41.7	20.3/-/16.8	19.1/-/18.6	79
Ir-56	543, 584 (sh)	-	W: PEDOT:PSS 8000/PVK:OXD-7: FIrpic:Ir(mppy)$_3$:**Ir-56**:Ir-G2	60.1/58.6/53.5	37.4/30.7/20.7	28.8/-/-	80
Ir-57	569	0.35	PEDOT:PSS/H2:Ir(Flpy-CF$_3$)$_3$/SPPO13	49.7/-/40.9	43.9/-/19.7	17.6/-/14.4	81
			W: PEDOT:PSS 8000/H2:FIrpic:Ir(Flpy-CF$_3$)$_3$/SPPO13	-/70.6/44.3	-/47.6/23.3	-/26.0/-	81
Ir-75	540, 574 (sh)	0.56	TAPC/TCTA/CBP:(4-F-bt)$_2$Ir(acac)/TmPyPB	76.8/69.9/61.6	83.2/62.8/41.2	24.3/22.1/19.4	54
Ir-79	554, 592 (sh)	0.32	PEDOT:PSS/CBP:(F-bt)$_2$Ir(acac)/TPBi	71.6/-/-	44.9/-/-	24.9/-/-	96
			W: PEDOT:PSS/CBP:(F-bt)$_2$Ir(acac)/CBP:FIrpic/TPBi	68.6/-/-	34.0/-/-	26.2/-/-	96
Ir-80	540, 580 (sh)	0.37	PEDOT:PSS/CBP:Ir(bt)$_3$/TPBi	87.9/-/-	46.0/-/-	29.6/-/-	97
Ir-81	555	-	PEDOT:PSS/α-NPD/TCTA/CBP:(Btc)$_2$Ir(acac)/BCP/Alq$_3$	38.1/38.1/35.4	-	12.9/12.9/12.0	99
			W: TAPC/DCzPPy:FIrpic:(Btc)$_2$Ir(acac)/Bphen	51.7/45.9/38.6	-	19.4/17.2/14.5	99
Ir-86	554, 591 (sh)	0.59	TAPC/TCTA/CBP:(4-Cl-bt)$_2$Ir(acac)/TmPyPB	55.9/54.3/49.5	55.9/46.7/33	20.2/19.6/17.8	54
Ir-87	555, 592 (sh)	0.46	TAPC/TCTA/CBP:(4-Br-bt)$_2$Ir(acac)/TmPyPB	60.3/59.2/40.8	56.7/47.6/23.3	21.6/21.2/14.6	54
Ir-105	578	0.23	NPB/TCTA/CBP:(dpiq)$_2$Ir(acac)/BCP/Alq$_3$	68.3/-/-	49.7/-/-	21.6/-/21.0	113
			W: NPB/TCTA/CBP:(dpiq)$_2$Ir(acac)/CzSi: (fmoppy)$_2$Ir(tfpypz)/CBP:(dpiq)$_2$Ir(acac)/BSB/TAZ	68.6/-/-	45/-/-	21.5/-/18.9	113
Ir-108	561	0.29	PEDOT:PSS/**dendrimer**/TPBi	40.9/-/35.7	39.5/-/31.6	16.4/-/14.6	120
			W: PEDOT:PSS 8000/PVK:OXD-7:FIrpic:**dendrimer**	62.4/-/47.7	36.3/-/20.0	31.2/-/23.9	119
Ir-119	543	0.30	NPB/(ppy)$_2$Ir(dipba)/BCP/Alq$_3$	-	32.5/28/22	-	126
Ir-120	548	0.17	NPB/CBP:(ppy)$_2$Ir(dipba)/BCP/Alq$_3$	137.4/-/-	39.2/-/-	-	127
Ir-121	570	0.82	CFx/NPB/TCTA/TPBi:TCTA:(ppy)$_2$Ir(bppo)/TPBi/Alq$_3$	65.7/-/-	44.7/-/-	19.3/-/-	128
Ir-122	599	0.55	NPB/TCTA/CBP:(mpmi)$_2$Ir(priq)/BCP/Alq$_3$	55.4/48.9/35.7	43.6/27.9/15.0	24.9/22.0/16.0	129
Ir-127	599	0.12	PEDOT:PSS/PVK:PBD:(PQxD)$_2$Ir(pic)/TPBi	20.7/-/-	-	18.4/-/-	138
Pt-13	590	0.91	CBP/CBP:Pt-BNPB2/TPBi:Pt-BNPB2/TPBi	35.0/-/-	36.6/-/-	10.6/-/-	158
Pt-24	606	0.73	DTAF/TCTA/POCz3:**Pt-24**/3TPYMB	47.6/-/-	50.8/-/-	20.0/-/18.8	171
			W: DTAF/TCTA/POCz3:**blue-Pt:Pt-24**/3TPYMB	44.8/-/-	46.2/-/-	15.0/-/12.4	171
Pt-25	580	-	TAPC/Pt(ptp)$_2$		63.0/-/39.4	20.3/-/19.8	174
Pt-40	553, 587 (sh)	0.86	NPB/mCP:Y-Pt/BAlq	74.9/-/-	52.1/-/-		194
			W: NPB/TCTA:Y-Pt/mCP:FIrpic/UGH2:FIrpic/BAlq	45.6/36.2/16.4	35.8/21.6/6.9	16.0/14.1/6.7	194
Os-1	572	0.90	PEDOT/PVK:PBD:*trans*-Os(fptz)$_2$(dppee)/TPBi	48.9/-/-	16.8/-/-	13.3/-/-	206
Os-3	611	0.3	W: α-NPD/TCTA/TCTA:*trans*-Os(bptz)$_2$(dppee)/ CzSi:Ir(dfbppy)(fbppz)$_2$/BCP:Os(bptz)$_2$(dppee)/BCP	22.9/15.0/-	20.0/8.7/-	9.5/7.0/-	207
Au-3	548	0.57	PEDOT:PSS/mCP:**dendrimer**/3TPYMB/TPBi	24.0/-/-	14.5/-/-	7.8/-/-	215

[a] Emission peaks measured in solution or solid state/film. [b] Quantum efficiencies in solution or solid state/film. [c] Active layers in the fabricated monochromatic and white (W) PhOLEDs. [d] Device efficiencies measured for the order: Maximum/100 cd m^{-2}/1000 cd m^{-2}. [e] References.

6. Acknowledgements

We thank the National Basic Research Program of China (973 Program 2013CB834805) and the National Science Fund for Distinguished Young Scholars of China (No. 51125013) for financial support.

7. Notes

Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Department of Chemistry, Wuhan University, Wuhan, 430072, People's Republic of China.
E-mail: clyang@whu.edu.cn

8. References

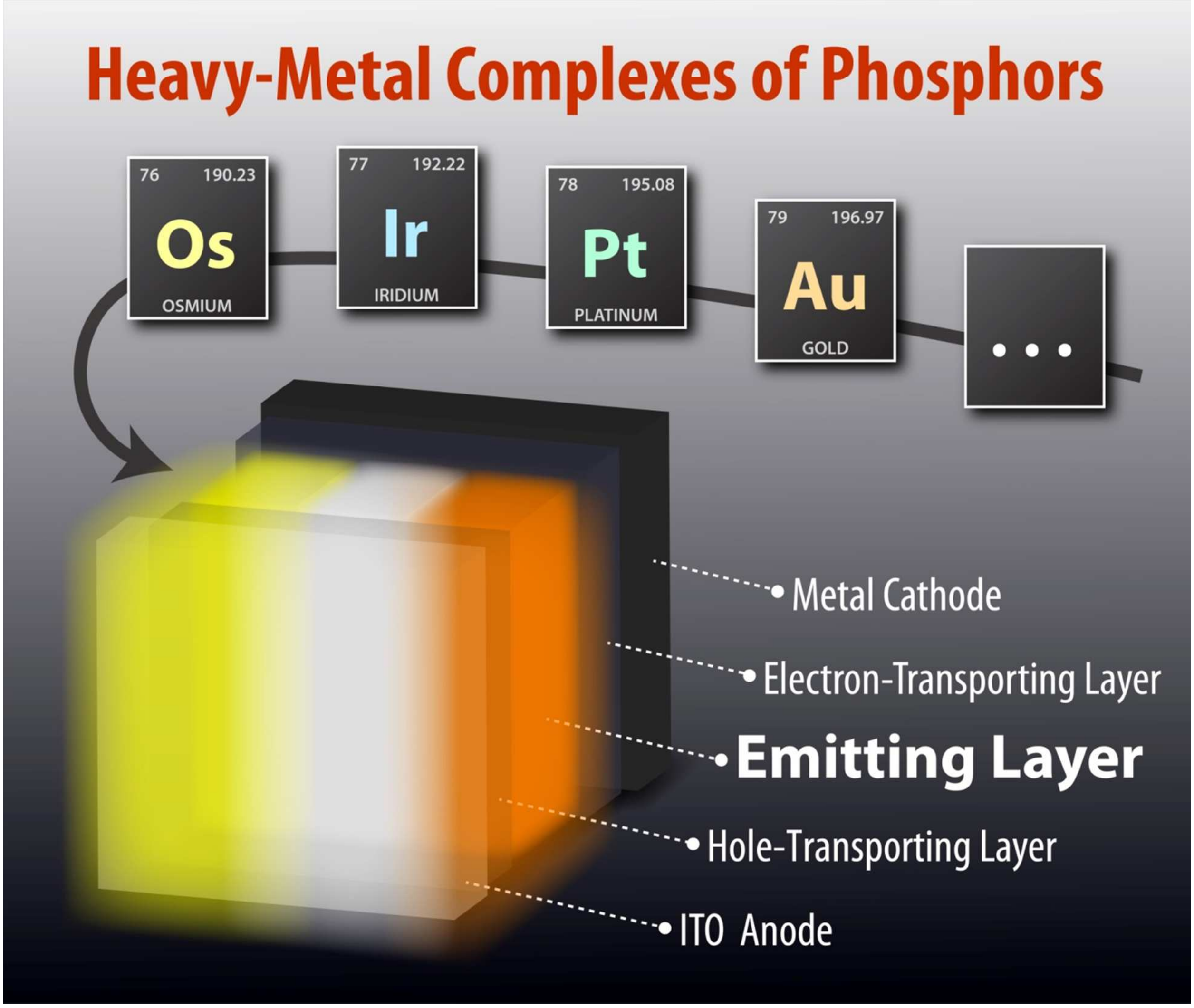
1. W. Helfrich and W. G. Schneider, *Phys. Rev. Lett.*, 1965, 14, 229-231.
2. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, 51, 913-915.
3. M. Wohlgenannt, K. Tandon, S. Mazumdar, S. Ramasesha and Z. V. Vardeny, *Nature*, 2001, 409, 494-497.
4. Y. Ma, H. Zhang, J. Shen and C. Che, *Synth. Met.*, 1998, 94, 245-248.
5. M. A. Baldo, D. F. Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, 395, 151-154.
6. K. T. Kamtekar, A. P. Monkman and M. R. Bryce, *Adv. Mater.*, 2010, 22, 572-582.
7. Y. Tao, C. Yang and J. Qin, *Chem. Soc. Rev.*, 2011, 40, 2943-2970.
8. A. Chaskar, H.-F. Chen and K.-T. Wong, *Adv. Mater.*, 2011, 23, 3876-3895.
9. B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, 2001.
10. W. J. Finkenzeller, M. E. Thompson and H. Yersin, *Chem. Phys. Lett.*, 2007, 444, 273-279.
11. T. Hofbeck and H. Yersin, *Inorg. Chem.*, 2010, 49, 9290-9299.
12. H. Yersin, A. F. Rausch, R. Czerwieniec, T. Hofbeck and T. Fischer, *Coord. Chem. Rev.*, 2011, 255, 2622-2652.
13. Q. Zhang, J. Li, K. Shizu, S. Huang, S. Hirata, H. Miyazaki and C. Adachi, *J. Am. Chem. Soc.*, 2012, 134, 14706-14709.
14. Y. J. Cho and J. Y. Lee, *Adv. Mater.*, 2011, 23, 4568-4572.
15. Y. Tao, Q. Wang, C. Yang, Q. Wang, Z. Zhang, T. Zou, J. Qin and D. Ma, *Angew. Chem. Int. Ed.*, 2008, 47, 8104-8107.
16. C.-H. Fan, P. Sun, T.-H. Su and C.-H. Cheng, *Adv. Mater.*, 2011, 23, 2981-2985.
17. C. Fan, F. Zhao, P. Gan, S. Yang, T. Liu, C. Zhong, D. Ma, J. Qin and C. Yang, *Chem.-Eur. J.*, 2012, 18, 5510-5514.
18. H.-H. Chou and C.-H. Cheng, *Adv. Mater.*, 2010, 22, 2468-2471.
19. Y. Chi and P.-T. Chou, *Chem. Soc. Rev.*, 2010, 39, 638-655.
20. P.-T. Chou and Y. Chi, *Chem.-Eur. J.*, 2007, 13, 380-395.
21. W.-Y. Wong and C.-L. Ho, *Coord. Chem. Rev.*, 2009, 253, 1709-1758.
22. L. Xiao, Z. Chen, B. Qu, J. Luo, S. Kong, Q. Gong and J. Kido, *Adv. Mater.*, 2011, 23, 926-952.
23. C.-L. Ho and W.-Y. Wong, *New J. Chem.*, 2013, 37, 1665-1683.
24. I. M. Dixon, J.-P. Collin, J.-P. Sauvage, L. Flamigni, S. Encinas and F. Barigelletti, *Chem. Soc. Rev.*, 2000, 29, 385-391.
25. C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 2001, 79, 2082-2084.
26. X. Chen, J.-L. Liao, Y. Liang, M. O. Ahmed, H.-E. Tseng and S.-A. Chen, *J. Am. Chem. Soc.*, 2002, 125, 636-637.
27. P. J. Hay, *J. Phys. Chem. A*, 2002, 106, 1634-1641.

28. S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, 123, 4304-4312.
29. Y. J. Cho and J. Y. Lee, *Adv. Mater.*, 2011, 23, 4568-4572.
30. K. Saito, N. Matsusue, H. Kanno, Y. Hamada, H. Takahashi and T. Matsumura, *Jpn. J. Appl. Phys.*, 2004, 43, 2733-2734.
31. 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.
32. J. Qiao, L. Duan, L. Tang, L. He, L. Wang and Y. Qiu, *J. Mater. Chem.*, 2009, 19, 6573-6580.
33. A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino and K. Ueno, *J. Am. Chem. Soc.*, 2003, 125, 12971-12979.
34. N. Tian, D. Lenkeit, S. Pelz, L. H. Fischer, D. Escudero, R. Schiewek, D. Klink, O. J. Schmitz, L. González, M. Schäferling and E. Holder, *Eur. J. Inorg. Chem.*, 2010, 2010, 4875-4885.
35. S. L. Lai, S. L. Tao, M. Y. Chan, T. W. Ng, M. F. Lo, C. S. Lee, X. H. Zhang and S. T. Lee, *Org. Electron.*, 2010, 11, 1511-1515.
36. B. M. J. S. Paulose, D. K. Rayabarapu, J. P. Duan and C. H. Cheng, *Adv. Mater.*, 2004, 16, 2003-2007.
37. D. K. Rayabarapu, B. M. J. S. Paulose, J. P. Duan and C. H. Cheng, *Adv. Mater.*, 2005, 17, 349-353.
38. S.-y. Takizawa, Y. Sasaki, M. Akhtaruzzaman, H. Echizen, J.-i. Nishida, T. Iwata, S. Tokito and Y. Yamashita, *J. Mater. Chem.*, 2007, 17, 841-849.
39. J.-P. Duan, P.-P. Sun and C.-H. Cheng, *Adv. Mater.*, 2003, 15, 224-228.
40. S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem and K. Leo, *Nature*, 2009, 459, 234-238.
41. G. Zhang, H. Guo, Y. Chuai and D. Zou, *Mater. Lett.*, 2005, 59, 3002-3006.
42. G. Ge, J. He, H. Guo, F. Wang and D. Zou, *J. Organomet. Chem.*, 2009, 694, 3050-3057.
43. W.-S. Huang, J. T. Lin, C.-H. Chien, Y.-T. Tao, S.-S. Sun and Y.-S. Wen, *Chem. Mater.*, 2004, 16, 2480-2488.
44. H. Huang, Y. Wang, S. Zhuang, X. Yang, L. Wang and C. Yang, *J. Phys. Chem. C,* 2012, 116, 19458-19466.
45. S. Gong, Y. Chen, J. Luo, C. Yang, C. Zhong, J. Qin and D. Ma, *Adv. Funct. Mater.*, 2011, 21, 1168-1178.
46. S. Gong, Y. Chen, C. Yang, C. Zhong, J. Qin and D. Ma, *Adv. Mater.*, 2010, 22, 5370-5373.
47. E. Baranoff, S. Fantacci, F. De Angelis, X. Zhang, R. Scopelliti, M. Gra□tzel and M. K. Nazeeruddin, *Inorg. Chem.*, 2010, 50, 451-462.
48. G. Zhang, F.-I. Wu, X. Jiang, P. Sun and C.-H. Cheng, *Synth. Met.*, 2010, 160, 1906-1911.
49. S. Wang, Y. Duan, C.-X. Du and Y.-J. Wu, *Inorg. Chem. Commun.*, 2011, 14, 1393-1395.
50. S.-y. Takizawa, J.-i. Nishida, T. Tsuzuki, S. Tokito and Y. Yamashita, *Inorg. Chem.*, 2007, 46, 4308-4319.
51. B. Tong, Q. Mei, S. Wang, Y. Fang, Y. Meng and B. Wang, *J. Mater. Chem.*, 2008, 18, 1636-1639.
52. Z.-Q. Wang, C. Xu, X.-M. Dong, Y.-P. Zhang, X.-Q. Hao, J.-F. Gong, M.-P. Song and B.-M. Ji, *Inorg. Chem. Commun.*, 2011, 14, 316-319.
53. Z.-Y. Xia, X. Xiao, J.-H. Su, C.-S. Chang, C. H. Chen, D.-L. Li and H. Tian, *Synth. Met.*, 2009, 159, 1782-1785.
54. C. Fan, L. Zhu, B. Jiang, Y. Li, F. Zhao, D. Ma, J. Qin and C. Yang, *J. Phys. Chem. C*, 2013, 117, 19134-19141.
55. H. Sasabe, J.-i. Takamatsu, T. Motoyama, S. Watanabe, G. Wagenblast, N. Langer, O. Molt, E. Fuchs, C. Lennartz and J. Kido, *Adv. Mater.*, 2010, 22, 5003-5007.
56. M. Xu, R. Zhou, G. Wang and J. Yu, *Inorg. Chim. Acta*, 2009, 362, 515-518.
57. Y. Fang, Y. Li, S. Wang, Y. Meng, J. Peng and B. Wang, *Synth. Met.*, 2010, 160, 2231-2238.
58. Z. Q. Gao, B. X. Mi, H. L. Tam, K. W. Cheah, C. H. Chen, M. S. Wong, S. T. Lee and C. S. Lee, *Adv. Mater.*, 2008, 20, 774-778.
59. Y. J. Kim, Y. H. Son and J. H. Kwon, *J. Inf. Display*, 2013, 14, 109-113.
60. Y. H. Son, Y. J. Kim, M. J. Park, H.-Y. Oh, J. S. Park, J. H. Yang, M. C. Suh and J. H. Kwon, *J. Mater. Chem. C*, 2013, 1, 5008-5014.
61. K. H. Shen, S. T. Yeh, H. L. Huang, I. H. Shen, M. T. Chu and T. S. Shieh, *T. W. Patent*, 2004, I242999.
62. K. H. Shen, S. T. Yeh, H. L. Huang, I. H. Shen, M. T. Chu and T. S. Shieh, *U. S. Patent*, 2008, 7445857.
63. S.-Y. Huang, H.-F. Meng, H.-L. Huang, T.-C. Chao, M.-R. Tseng, Y.-C. Chao and S.-F. Horng, *Synth. Met.*, 2010, 160, 2393-2396.
64. H.-C. Yeh, H.-F. Meng, H.-W. Lin, T.-C. Chao, M.-R. Tseng and H.-W. Zan, *Org. Electron.*, 2012, 13, 914-918.
65. Y.-F. Chang, Y.-C. Chiu, H.-C. Yeh, H.-W. Chang, C.-Y. Chen, H.-F. Meng, H.-W. Lin, H.-L. Huang, T.-C. Chao, M.-R. Tseng, H.-W. Zan and S.-F. Horng, *Org. Electron.*, 2012, 13, 2149-2155.
66. C. Fan, J. Miao, B. Jiang, C. Yang, H. Wu, J. Qin and Y. Cao, *Org. Electron.*, 2013, 14, 3392-3398.
67. T.-R. Chen, *J. Organomet. Chem.*, 2008, 693, 3117-3130.
68. S.-C. Lo, R. E. Harding, C. P. Shipley, S. G. Stevenson, P. L. Burn and I. D. W. Samuel, *J. Am. Chem. Soc.*, 2009, 131, 16681-16688.
69. C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, 91, 165-195.
70. J. C. Ostrowski, M. R. Robinson, A. J. Heeger and G. C. Bazan, *Chem. Commun.*, 2002, 784-785.
71. X. Gong, M. R. Robinson, J. C. Ostrowski, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2002, 14, 581-585.
72. X. Gong, S.-H. Lim, J. C. Ostrowski, D. Moses, C. J. Bardeen and G. C. Bazan, *J. Appl. Phys.*, 2004, 95, 948-953.
73. X. Gong, J. C. Ostrowski, G. C. Bazan, D. Moses, A. J. Heeger, M. S. Liu and A. K.-Y. Jen, *Adv. Mater.*, 2003, 15, 45-49.
74. S. Bettington, M. Tavasli, M. R. Bryce, A. Beeby, H. Al-Attar and A. P. Monkman, *Chem.-Eur. J.*, 2007, 13, 1423-1431.
75. K. Zhang, Z. Chen, C. Yang, X. Zhang, Y. Tao, L. Duan, L. Chen, L. Zhu, J. Qin and Y. Cao, *J. Mater. Chem.*, 2007, 17, 3451-3460.
76. W.-Y. Wong, G.-J. Zhou, X.-M. Yu, H.-S. Kwok and B.-Z. Tang, *Adv. Funct. Mater.*, 2006, 16, 838-846.
77. C.-L. Ho, W.-Y. Wong, G.-J. Zhou, B. Yao, Z. Xie and L. Wang, *Adv. Funct. Mater.*, 2007, 17, 2925-2936.
78. C.-L. Ho, W.-Y. Wong, Q. Wang, D. Ma, L. Wang and Z. Lin, *Adv. Funct. Mater.*, 2008, 18, 928-937.
79. H. Wu, G. Zhou, J. Zou, C.-L. Ho, W.-Y. Wong, W. Yang, J. Peng and Y. Cao, *Adv. Mater.*, 2009, 21, 4181-4184.
80. J. Zou, H. Wu, C.-S. Lam, C. Wang, J. Zhu, C. Zhong, S. Hu, C.-L. Ho, G.-J. Zhou, H. Wu, W. C. H. Choy, J. Peng, Y. Cao and W.-Y. Wong, *Adv. Mater.*, 2011, 23, 2976-2980.
81. B. Zhang, G. Tan, C.-S. Lam, B. Yao, C.-L. Ho, L. Liu, Z. Xie, W.-Y. Wong, J. Ding and L. Wang, *Adv. Mater.*, 2012, 24, 1873-1877.
82. W. Zhang, Y. Wang, Z. He, L. Mu, Y. Zou, C. Liang and S. Zhao, *Synth. Met.*, 2010, 160, 354-360.
83. A. Beeby, S. Bettington, I. D. W. Samuel and Z. Wang, *J. Mater. Chem.*, 2003, 13, 80-83.
84. K. H. Lee, H. J. Kang, S. J. Lee, J. H. Seo, Y. K. Kim and S. S. Yoon, *Synth. Met.*, 2011, 161, 1113-1121.
85. T. Tsuzuki, N. Shirasawa, T. Suzuki and S. Tokito, *Adv. Mater.*, 2003, 15, 1455-1458.
86. J. H. Yao, C. Zhen, K. P. Loh and Z.-K. Chen, *Tetrahedron*, 2008, 64, 10814-10820.
87. C. Huang, C.-G. Zhen, S. P. Su, Z.-K. Chen, X. Liu, D.-C. Zou, Y.-R. Shi and K. P. Loh, *J. Organomet. Chem.*, 2009, 694, 1317-1324.
88. G. Zhou, C.-L. Ho, W.-Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T. B. Marder and A. Beeby, *Adv. Funct. Mater.*, 2008, 18, 499-511.
89. R. Ragni, E. Orselli, G. S. Kottas, O. H. Omar, F. Babudri, A. Pedone, F. Naso, G. M. Farinola and L. De Cola, *Chem.-Eur. J.*, 2009, 15, 136-148.
90. X. Yang, N. Sun, J. Dang, Z. Huang, C. Yao, X. Xu, C.-L. Ho, G. Zhou, D. Ma, X. Zhao and W.-Y. Wong, *J. Mater. Chem. C*, 2013, 1, 3317-3326.
91. L. Deng, T. Zhang, R. Wang and J. Li, *J. Mater. Chem.*, 2012, 22, 15910-15918.
92. D.-S. Leem, S. O. Jung, S.-O. Kim, J.-W. Park, J. W. Kim, Y.-S. Park, Y.-H. Kim, S.-K. Kwon and J.-J. Kim, *J. Mater. Chem.*, 2009, 19, 8824-8828.
93. M. Li, H. Zeng, Y. Meng, H. Sun, S. Liu, Z. Lu, Y. Huang and X. Pu, *Dalton Trans.*, 2011, 40, 7153-7164.
94. W.-C. Chang, A. T. Hu, J.-P. Duan, D. K. Rayabarapu and C.-H. Cheng, *J. Organomet. Chem.*, 2004, 689, 4882-4888.

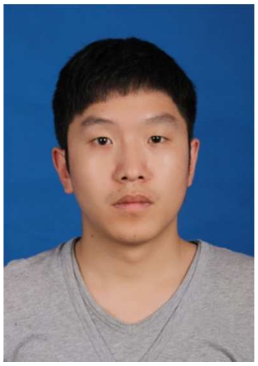
95. I. R. Laskar and T.-M. Chen, *Chem. Mater.*, 2004, 16, 111-117.
96. R. Wang, D. Liu, H. Ren, T. Zhang, H. Yin, G. Liu and J. Li, *Adv. Mater.*, 2011, 23, 2823-2827.
97. R. Wang, D. Liu, H. Ren, T. Zhang, X. Wang and J. Li, *J. Mater. Chem.*, 2011, 21, 15494-15500.
98. G. Xiao, X. Li, H. Chi, Y. Lu, Y. Dong, Z. Hu, J. Yu and M. Kimura, *Synth. Met.*, 2012, 162, 497-502.
99. F. Xu, J.-Y. Kwon, J.-H. Kim, H. U. Kim, J. M. Lim, H. Cho, C. Lee, J. Lee, J.-I. Lee and D.-H. Hwang, *Synth. Met.*, 2012, 162, 1421-1428.
100. D. Liu, H. Ren, L. Deng and T. Zhang, *ACS Appl. Mater. Interfaces*, 2013, 5, 4937-4944.
101. Y. H. Park and Y. S. Kim, *Thin Solid Films*, 2007, 515, 5084-5089.
102. J. Ding, J. Gao, Q. Fu, Y. Cheng, D. Ma and L. Wang, *Synth. Met.*, 2005, 155, 539-548.
103. K. R. J. Thomas, M. Velusamy, J. T. Lin, C.-H. Chien, Y.-T. Tao, Y. S. Wen, Y.-H. Hu and P.-T. Chou, *Inorg. Chem.*, 2005, 44, 5677-5685.
104. X. Zhang, J. Gao, C. Yang, L. Zhu, Z. Li, K. Zhang, J. Qin, H. You and D. Ma, *J. Organomet. Chem.*, 2006, 691, 4312-4319.
105. Q. Zhao, C.-Y. Jiang, M. Shi, F.-Y. Li, T. Yi, Y. Cao and C.-H. Huang, *Organometallics*, 2006, 25, 3631-3638.
106. T.-H. Chuang, C.-H. Yang and P.-C. Kao, *Inorg. Chim. Acta*, 2009, 362, 5017-5022.
107. H. S. Lee, S. Y. Ahn, H. S. Huh and Y. Ha, *J. Organomet. Chem.*, 2009, 694, 3325-3330.
108. Y.-J. Su, H.-L. Huang, C.-L. Li, C.-H. Chien, Y.-T. Tao, P.-T. Chou, S. Datta and R.-S. Liu, *Adv. Mater.*, 2003, 15, 884-888.
109. M. Xu, G. Wang, R. Zhou, Z. An, Q. Zhou and W. Li, *Inorg. Chim. Acta*, 2007, 360, 3149-3154.
110. C.-F. Lin, W.-S. Huang, H.-H. Chou and J. T. Lin, *J. Organomet. Chem.*, 2009, 694, 2757-2769.
111. C. Li, H.-H. Shih, X. Jiang, P. Sun, Y. Pan and C.-H. Cheng, *Synth. Met.*, 2009, 159, 2070-2074.
112. X. Yang, Y. Zhao, X. Zhang, R. Li, J. Dang, Y. Li, G. Zhou, Z. Wu, D. Ma, W.-Y. Wong, X. Zhao, A. Ren, L. Wang and X. Hou, *J. Mater. Chem.*, 2012, 22, 7136-7148.
113. H.-H. Chou, Y.-K. Li, Y.-H. Chen, C.-C. Chang, C.-Y. Liao and C.-H. Cheng, *ACS Appl. Mater. Interfaces*, 2013, 5, 6168-6175.
114. G. Zhou, W.-Y. Wong, B. Yao, Z. Xie and L. Wang, *Angew. Chem. Int. Ed.*, 2007, 46, 1149-1151.
115. J. Ding, B. Wang, Z. Yue, B. Yao, Z. Xie, Y. Cheng, L. Wang, X. Jing and F. Wang, *Angew. Chem. Int. Ed.*, 2009, 48, 6664-6666.
116. D. Xia, B. Wang, B. Chen, S. Wang, B. Zhang, J. Ding, L. Wang, X. Jing and F. Wang, *Angew. Chem. Int. Ed.*, 2014, 53, 1048-1052.
117. M. Zhu, Y. Li, S. Hu, C. g. Li, C. Yang, H. Wu, J. Qin and Y. Cao, *Chem. Commun.*, 2012, 48, 2695-2697.
118. M. Zhu, Y. Li, C. g. Li, C. Zhong, C. Yang, H. Wu, J. Qin and Y. Cao, *J. Mater. Chem.*, 2012, 22, 11128-11133.
119. M. Zhu, J. Zou, S. Hu, C. Li, C. Yang, H. Wu, J. Qin and Y. Cao, *J. Mater. Chem.*, 2012, 22, 361-366.
120. M. Zhu, J. Zou, X. He, C. Yang, H. Wu, C. Zhong, J. Qin and Y. Cao, *Chem. Mater.*, 2012, 24, 174-180.
121. Y. You and S. Y. Park, *J. Am. Chem. Soc.*, 2005, 127, 12438-12439.
122. T.-H. Kwon, H. S. Cho, M. K. Kim, J.-W. Kim, J.-J. Kim, K. H. Lee, S. J. Park, I.-S. Shin, H. Kim, D. M. Shin, Y. K. Chung and J.-I. Hong, *Organometallics*, 2005, 24, 1578-1585.
123. A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau and M. E. Thompson, *J. Am. Chem. Soc.,* 2003, 125, 7377-7387.
124. S. Kappaun, S. Sax, S. Eder, K. C. Möller, K. Waich, F. Niedermair, R. Saf, K. Mereiter, J. Jacob, K. Müllen, E. J. W. List and C. Slugovc, *Chem. Mater.*, 2007, 19, 1209-1211.
125. S. Stagni, S. Colella, A. Palazzi, G. Valenti, S. Zacchini, F. Paolucci, M. Marcaccio, R. Q. Albuquerque and L. De Cola, *Inorg. Chem.*, 2008, 47, 10509-10521.
126. Y. Liu, K. Ye, Y. Fan, W. Song, Y. Wang and Z. Hou, *Chem. Commun.*, 2009, 3699-3701.
127. V. K. Rai, M. Nishiura, M. Takimoto, S. Zhao, Y. Liu and Z. Hou, *Inorg. Chem.*, 2011, 51, 822-835.
128. X. Ren, M. E. Kondakova, D. J. Giesen, M. Rajeswaran, M. Madaras and W. C. Lenhart, *Inorg. Chem.*, 2010, 49, 1301-1303.
129. K.-Y. Lu, H.-H. Chou, C.-H. Hsieh, Y.-H. O. Yang, H.-R. Tsai, H.-Y. Tsai, L.-C. Hsu, C.-Y. Chen, I. C. Chen and C.-H. Cheng, *Adv. Mater.*, 2011, 23, 4933-4937.
130. C.-H. Hsieh, F.-I. Wu, C.-H. Fan, M.-J. Huang, K.-Y. Lu, P.-Y. Chou, Y.-H. O. Yang, S.-H. Wu, I. C. Chen, S.-H. Chou, K.-T. Wong and C.-H. Cheng, *Chem.-Eur. J.*, 2011, 17, 9180-9187.
131. P. Coppo, E. A. Plummer and L. De Cola, *Chem. Commun.*, 2004, 1774-1775.
132. H.-J. Seo, K.-M. Yoo, M. Song, J. S. Park, S.-H. Jin, Y. I. Kim and J.-J. Kim, *Org. Electron.*, 2010, 11, 564-572.
133. L. Chen, H. You, C. Yang, X. Zhang, J. Qin and D. Ma, *J. Mater. Chem.*, 2006, 16, 3332-3339.
134. B. Liang, L. Wang, Y. H. Xu, H. H. Shi and Y. Cao, *Adv. Funct. Mater.*, 2007, 17, 3580-3589.
135. S.-J. Lee, J.-S. Park, M. Song, I. A. Shin, Y.-I. Kim, J. W. Lee, J.-W. Kang, Y.-S. Gal, S. Kang, J. Y. Lee, S.-H. Jung, H.-S. Kim, M.-Y. Chae and S.-H. Jin, *Adv. Funct. Mater.*, 2009, 19, 2205-2212.
136. M. Song, J. S. Park, Y.-S. Gal, S. Kang, J. Y. Lee, J. W. Lee and S.-H. Jin, *J. Phys. Chem. C*, 2012, 116, 7526-7533.
137. D. Schneidenbach, S. Ammermann, M. Debeaux, A. Freund, M. Zöllner, C. Daniliuc, P. G. Jones, W. Kowalsky and H.-H. Johannes, *Inorg. Chem.*, 2009, 49, 397-406.
138. Q. Mei, L. Wang, Y. Guo, J. Weng, F. Yan, B. Tian, B. Tong, *J. Mater. Chem.*, 2012, 22, 6878-6884.
139. C.-W. Chan, L.-K. Cheng and C.-M. Che, *Coord. Chem. Rev.*, 1994, 132, 87-97.
140. V. H. Houlding and M. Miskowski, *Coord. Chem. Rev.*, 1991, 111, 145-152.
141. W. B. Connick, D. Geiger and R. Eisenberg, *Inorg. Chem.*, 1999, 38, 3264-3265.
142. J. Garethwilliams, S. Develay, D. Rochester and L. Murphy, *Coord. Chem. Rev.*, 2008, 252, 2596-2611.
143. W. Lu, M. C. W. Chan, K.-K. Cheung and C.-M. Che, *Organometallics*, 2001, 20, 2477-2486.
144. B. Ma, J. Li, P. I. Djurovich, M. Yousufuddin, R. Bau and M. E. Thompson, *J. Am. Chem. Soc.,* 2004, 127, 28-29.
145. V. W.-W. Yam, K. M.-C. Wong and N. Zhu, *J. Am. Chem. Soc.,* 2002, 124, 6506-6507.
146. S. Lamansky, R. C. Kwong, M. Nugent, P. I. Djurovich and M. E. Thompson, *Org. Electron.*, 2001, 2, 53-62.
147. M. Cocchi, D. Virgili, C. Sabatini, V. Fattori, P. D. Marco, M. Maestri and J. Kalinowski, *Synt. Met.*, 2004, 147, 253-256.
148. J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2002, 41, 3055-3066.
149. S. J. Lee, S. Kang, S. H. Lee, K. J. Hwang, N. K. Park and Y. S. Kim, *Mat Sci Eng C.*, 2004, 24, 221-224.
150. P. I. Djurovich, D. Murphy, M. E. Thompson, B. Hernandez, R. Gao, P. L. Hunt and M. Selke, *Dalton Trans.,* 2007, 3763-3770.
151. W.-Y. Wong, Z. He, S.-K. So, K.-L. Tong and Z. Lin, *Organometallics*, 2005, 24, 4079-4082.
152. G. Zhou, Q. Wang, X. Wang, C.-L. Ho, W.-Y. Wong, D. Ma, L. Wang and Z. Lin, *J. Mater. Chem.,* 2010, 20, 7472-7484.
153. 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.
154. D. N. Kozhevnikov, V. N. Kozhevnikov, M. M. Ustinova, A. Santoro, D. W. Bruce, B. Koenig, R. Czerwieniec, T. Fischer, M. Zabel and H. Yersin, *Inorg. Chem.*, 2009, 48, 4179-4189.
155. H. Yersin and D. Donges, *Top. Curr. Chem.*, 2001, 214, 81-186.
156. H. Yersin and J. Strasser, *Coord. Chem. Rev.*, 2000, 208, 331–364.
157. M. Velusamy, C.-H. Chen, Y. S. Wen, J. T. Lin, C.-C. Lin, C.-H. Lai and P.-T. Chou, *Organometallics*, 2010, 29, 3912-3921.
158. Z. M. Hudson, M. G. Helander, Z. H. Lu and S. Wang, *Chem. Commun.,* 2011, 47, 755-757.
159. W. L. Jia, X. D. Feng, D. R. Bai, Z. H. Lu, S. Wang and G. Vamvounis, *Chem. Mater.*, 2004, 17, 164-170.
160. M. Taneda, T. Yasuda and C. Adachi, *Appl. Phys. Express*, 2011, 4, 071602-(1-3).

161. X. H. Zhao, G. H. Xie, Z. D. Liu, W. J. Li, M. D. Yi, L. H. Xie, C. P. Hu, R. Zhu, Q. Zhao, Y. Zhao, J. F. Zhao, Y. Qian and W. Huang, *Chem. Commun.*, 2012, 48, 3854-3856.
162. S.-C. Chan, M. C. W. Chan, Y. Wang, C.-M. Che, K.-K. Cheung and N. Zhu, *Chem.–Eur. J.*, 2001, 7, 4180-4190.
163. A. Klein and W. Kaim, *Organometallics*, 1995, 14, 1176-1186.
164. C. J. Adams and P. R. Raithby, *J. Organomet. Chem.*, 1999, 578, 178-185.
165. M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte and R. Eisenberg, *Inorg. Chem.*, 2000, 39, 447-457.
166. S.-Y. Chang, J. Kavitha, S.-W. Li, C.-S. Hsu, Y. Chi, Y.-S. Yeh, P.-T. Chou, G.-H. Lee, A. J. Carty, Y.-T. Tao and C.-H. Chien, *Inorg. Chem.*, 2005, 45, 137-146.
167. M. Gianini, A. Forster, P. Haag, A. von Zelewsky and H. Stoeckli-Evans, *Inorg. Chem.,* 1996, 35, 4889-4895.
168. J. Kavitha, S. Y. Chang, Y. Chi, J. K. Yu, Y. H. Hu, P. T. Chou, S. M. Peng, G. H. Lee, Y. T. Tao, C. H. Chien and A. J. Carty, *Adv. Funct. Mater.*, 2005, 15, 223-229.
169. S.-Y. Chang, J. Kavitha, J.-Y. Hung, Y. Chi, Y.-M. Cheng, E. Y. Li, P.-T. Chou, G.-H. Lee and A. J. Carty, *Inorg. Chem.*, 2007, 46, 7064-7074.
170. S. Y. Chang, Y. M. Cheng, Y. Chi, Y. C. Lin, C. M. Jiang, G. H. Lee and P. T. Chou, *Dalton Trans.*, 2008, 6901-6911.
171. L.-M. Huang, G.-M. Tu, Y. Chi, W.-Y. Hung, Y.-C. Song, M.-R. Tseng, P.-T. Chou, G.-H. Lee, K.-T. Wong, S.-H. Cheng and W.-S. Tsai, *J. Mater. Chem. C*, 2013, 1, 7582–7592.
172. M. Li, W.-H. Chen, M.-T. Lin, M. A. Omary and N. D. Shepherd, *Org. Electron.,* 2009, 10, 863-870.
173. M. Li, M.-T. Lin, W.-H. Chen, R. McDougald, R. Arvapally, M. Omary and N. D. Shepherd, *Phys. Status Solidi A*, 2012, 209, 221-225.
174. Q. Wang, I. W. H. Oswald, M. R. Perez, H. Jia, B. E. Gnade and M. A. Omary, *Adv. Funct. Mater.*, 2013, 23, 5420-5428.
175. W. Lu, B.-X. Mi, M. C. W. Chan, Z. Hui, N. Zhu, S.-T. Lee and C.-M. Che, *Chem. Commun.*, 2002, 206-207.
176. S.-W. Lai, M. C.-W. Chan, T.-C. Cheung, S.-M. Peng and C.-M. Che, *Inorg. Chem.,* 1999, 38, 4046-4055.
177. S.-W. Lai, M. C.-W. Chan, K.-K. Cheung and C.-M. Che, *Organometallics*, 1999, 18, 3327-3336.
178. W. Lu, B.-X. Mi, M. C. W. Chan, Z. Hui, C.-M. Che, N. Zhu and S.-T. Lee, *J. Am. Chem. Soc.*, 2004, 126, 4958-4971.
179. P. Shao, Y. Li, J. Yi, T. M. Pritchett and W. Sun, *Inorg. Chem.*, 2010, 49, 4507-4517.
180. S. J. Farley, D. L. Rochester, A. L. Thompson, J. A. K. Howard and J. A. G. Williams, *Inorg. Chem.*, 2005, 44, 9690-9703.
181. A. F. Rausch, L. Murphy, J. A. Williams and H. Yersin, *Inorg. Chem.*, 2009, 48, 11407-11414.
182. M. Cocchi, D. Virgili, V. Fattori, D. L. Rochester and J. A. G. Williams, *Adv. Funct. Mater.*, 2007, 17, 285-289.
183. C.-C. Kwok, H. M. Y. Ngai, S.-C. Chan, I. H. T. Sham, C.-M. Che and N. Zhu, *Inorg. Chem.*, 2005, 44, 4442-4444.
184. M.-Y. Yuen, S. C. F. Kui, K.-H. Low, C.-C. Kwok, S. S.-Y. Chui, C.-W. Ma, N. Zhu and C.-M. Che, *Chem.-Eur. J.*, 2010, 16, 14131-14141.
185. J. L. Chen, S. Y. Chang, Y. Chi, K. Chen, Y. M. Cheng, C. W. Lin, G. H. Lee, P. T. Chou, C. H. Wu, P. I. Shih and C. F. Shu, *Chem.-Asian J.* 2008, 3, 2112-2123.
186. D. A. Vezzu, D. Ravindranathan, A. W. Garner, L. Bartolotti, M. E. Smith, P. D. Boyle and S. Huo, *Inorg. Chem.*, 2011, 50, 8261-8273.
187. D. Ravindranathan, D. A. K. Vezzu, L. Bartolotti, P. D. Boyle and S. Huo, *Inorg. Chem.*, 2010, 49, 8922-8928.
188. O. A. Blackburn, B. J. Coe, M. Helliwell and J. Raftery, *Organometallics*, 2012, 31, 5307-5320.
189. Y.-Y. Lin, S.-C. Chan, M. C. W. Chan, Y.-J. Hou, N. Zhu, C.-M. Che, Y. Liu and Y. Wang, *Chem.–Eur. J.*, 2003, 9, 1263-1272.
190. C.-M. Che, S.-C. Chan, H.-F. Xiang, M. C. W. Chan, Y. Liu and Y. Wang, *Chem. Comm.*, 2004, 1484-1485.
191. C.-M. Che, C.-C. Kwok, S. W. Lai, A. F. Rausch, W. J. Finkenzeller, N. Zhu and H. Yersin, *Chem.-Eur. J.*, 2010, 16, 233-247.
192. J. Zhang, F. Zhao, X. Zhu, W.-K. Wong, D. Ma and W.-Y. Wong, *J. Mater. Chem.,* 2012, 22, 16448-16457.
193. S. Huo, C. F. Harris, D. A. K. Vezzu, J. P. Gagnier, M. E. Smith, R. D. Pike and Y. Li, *Polyhedron*, 2013, 52, 1030-1040.
194. S.-L. Lai, W.-Y. Tong, S. C. F. Kui, M.-Y. Chan, C.-C. Kwok and C.-M. Che, *Adv. Funct. Mater.*, 2013, 23, 5168-5176.
195. X. Gong, P. K. Ng and W. K. Chan, *Adv. Mater.*, 1998, 10, 1337-1340.
196. S. Bernhard, J. A. Barron, P. L. Houston, H. D. Abruña, J. L. Ruglovksy, X. Gao and G. G. Malliaras, *J. Am. Chem. Soc.,* 2002, 124, 13624-13628.
197. Q. Zhang, Q. Zhou, Y. Cheng, L. Wang, D. Ma, X. Jing and F. Wang, *Adv. Mater.*, 2004, 16, 432-436.
198. X.-L. Chen, R. Yu, Q.-K. Zhang, L.-J. Zhou, X.-Y. Wu, Q. Zhang and C.-Z. Lu, *Chem. Mater.*, 2013, 25, 3910-3920.
199. Y.-L. Tung, S.-W. Lee, Y. Chi, Y.-T. Tao, C.-H. Chien, Y.-M. Cheng, P.-T. Chou, S.-M. Peng and C.-S. Liu, *J. Mater. Chem.*, 2005, 15, 460-464.
200. K. M.-C. Wong, X. Zhu, L.-L. Hung, N. Zhu, V. W.-W. Yam and H.-S. Kwok, *Chem. Commun.*, 2005, 2906-2908.
201. S. Bernhard, X. Gao, G. G. Malliaras and H. D. Abruña, *Adv. Mater.*, 2002, 14, 433-436.
202. H. Yersin, E. Gallhuber and G. Hensler, *Chem. Phys. Lett.*, 1987, 140, 157-162.
203. T.-C. Lee, J.-Y. Hung, Y. Chi, Y.-M. Cheng, G.-H. Lee, P.-T. Chou, C.-C. Chen, C.-H. Chang and C.-C. Wu, *Adv. Funct. Mater.*, 2009, 19, 2639-2647.
204. B.-S. Du, J.-L. Liao, M.-H. Huang, C.-H. Lin, H.-W. Lin, Y. Chi, H.-A. Pan, G.-L. Fan, K.-T. Wong, G.-H. Lee and P.-T. Chou, *Adv. Funct. Mater.*, 2012, 22, 3491-3499.
205. C.-C. Hsu, C.-C. Lin, P.-T. Chou, C.-H. Lai, C.-W. Hsu, C.-H. Lin and Y. Chi, *J. Am. Chem. Soc.*, 2012, 134, 7715-7724.
206. Y. M. Cheng, G. H. Lee, P. T. Chou, L. S. Chen, Y. Chi, C. H. Yang, Y. H. Song, S. Y. Chang, P. I. Shih and C. F. Shu, *Adv. Funct. Mater.*, 2008, 18, 183-194.
207. C.-H. Chang, C.-C. Chen, C.-C. Wu, S.-Y. Chang, J.-Y. Hung and Y. Chi, *Org. Electron.*, 2010, 11, 266-272.
208. A. Vogler and H. Kunkely, *Coord. Chem. Rev.*, 2001, 219–221, 489-507.
209. V. K.-M. Au, W. H. Lam, W.-T. Wong and V. W.-W. Yam, *Inorg. Chem.*, 2012, 51, 7537-7545.
210. C. Bronner and O. S. Wenger, *Dalton Trans.*, 2011, 40, 12409-12420.
211. W.-P. To, G. S.-M. Tong, W. Lu, C. Ma, J. Liu, A. L.-F. Chow and C.-M. Che, *Angew. Chem. Int. Ed.*, 2012, 51, 2654-2657.
212. J. A. Garg, O. Blacque, T. Fox and K. Venkatesan, *Inorg. Chem.*, 2010, 49, 11463-11472.
213. V. W.-W. Yam, K. M.-C. Wong, L.-L. Hung and N. Zhu, *Angew. Chem. Int. Ed.*, 2005, 44, 3107-3110.
214. W.-P. To, K. T. Chan, G. S. M. Tong, C. Ma, W.-M. Kwok, X. Guan, K.-H. Low and C.-M. Che, *Angew. Chem. Int. Ed.*, 2013, 52, 6648-6652.
215. M.-C. Tang, D. P.-K. Tsang, M. M.-Y. Chan, K. M.-C. Wong and V. W.-W. Yam, *Angew. Chem. Int. Ed.*, 2013, 52, 446-449.

This article reviews the development of the yellow/orange emissive heavy-metal complexes used in organic light-emitting devices.



Cong Fan received his Bachelor's degree in Chemistry from Wuhan University (P. R. China) in 2008. After five-year study as the graduate student under the supervision of Prof. Chuluo Yang, he received his PhD degree in Chemistry from Wuhan University in 2013, focusing on the research for the emitting layer of phosphorescent organic light-emitting diodes. Currently, he joined the group of Assoc Prof. Qichun Zhang as a Post Doctor in the School of Materials Science & Engineering, Nanyang Technological University (Singapore).



Chuluo Yang received his Ph.D. degree in Organic Chemistry from Wuhan University in 1997 and joined Wuhan University as a lecturer in the same year. From 1999 to 2000, he was a visiting scholar at the Hong Kong University of Science and Technology. From 2000 to 2002, he was a postdoctoral fellow at University of New Orleans and University of Rochester. Since 2003, he has been full professor at Wuhan University. His research interests cover the synthesis, structures, properties, and device performance of organic/polymeric optoelectronic materials.