

Chlorinated yellow phosphorescent cyclometalated neutral iridophosphors featuring broad emission bandwidths for white electroluminescence

Peng Tao^{a,d,1}, Xiao-Kang Zheng^{b,1}, Xiao-Zhen Wei^c, Mei-Tung Lau^a, Yuk-Ki Lee^a, Zi-Kang Li^a, Ze-Ling Guo^a, Fang-Qing Zhao^b, Xing Liu^c, Shu-Juan Liu^b, Qiang Zhao^{b,*}, Yan-Qin Miao^{c,*}, Wai-Yeung Wong^{a,d,*}

^a Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, P. R. China.

^b Key Laboratory for Organic Electronics and Information Displays and Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts and Telecommunications (NUPT), Nanjing, 210023, P. R. China.

^c Key Laboratory of Interface Science and Engineering in Advanced Materials of Ministry of Education, Taiyuan University of Technology, Taiyuan, 030024, P.

R. China.

^d The Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen, 518057, P. R. China.

Corresponding E-mail: iamqzhao@njupt.edu.cn (Qiang Zhao); miaoyanqin@tyut.edu.cn (Yanqin Miao); wai-yeung.wong@polyu.edu.hk (Wai-Yeung Wong).

¹P. Tao and X.-K. Zheng contributed equally to this work.

ABSTRACT

The efficient yellow phosphors with broad emission bandwidths play quite important roles for the realization of high-performance two-color white organic light-emitting devices (OLEDs). Herein, by using a chlorine-functionalization method, we designed three efficient yellow iridium(III) complexes (**Ir1-Ir3**) bearing chlorine atoms. At room temperature, these phosphors exhibit bright yellow phosphorescence with emission wavelengths of 549–574 nm and high photoluminescence efficiency of 0.49–0.73 in the N₂-saturated dichloromethane. Importantly, these complexes feature extremely broad emission bandwidths (reaching 104 nm), making them the record-high values in the yellow iridium(III) phosphors reported so far. Using these complexes as the triplet dopants, the prepared OLEDs show yellow phosphorescence with the emission maximum at 565, 548, and 551 nm, respectively. The extremely high external quantum efficiency of 23.8% was realized for the as-prepared yellow OLEDs. Furthermore, **Ir2**-based two-color white OLED with high spectra quality was also realized, and the color rendering index and CIE coordinates for two-color white OLED are 74 and (0.32, 0.34), respectively. The broad yellow emission band and high-efficiency of the device proved that these phosphors show great potentials in developing high-performance yellow and white electroluminescence.

1. Introduction

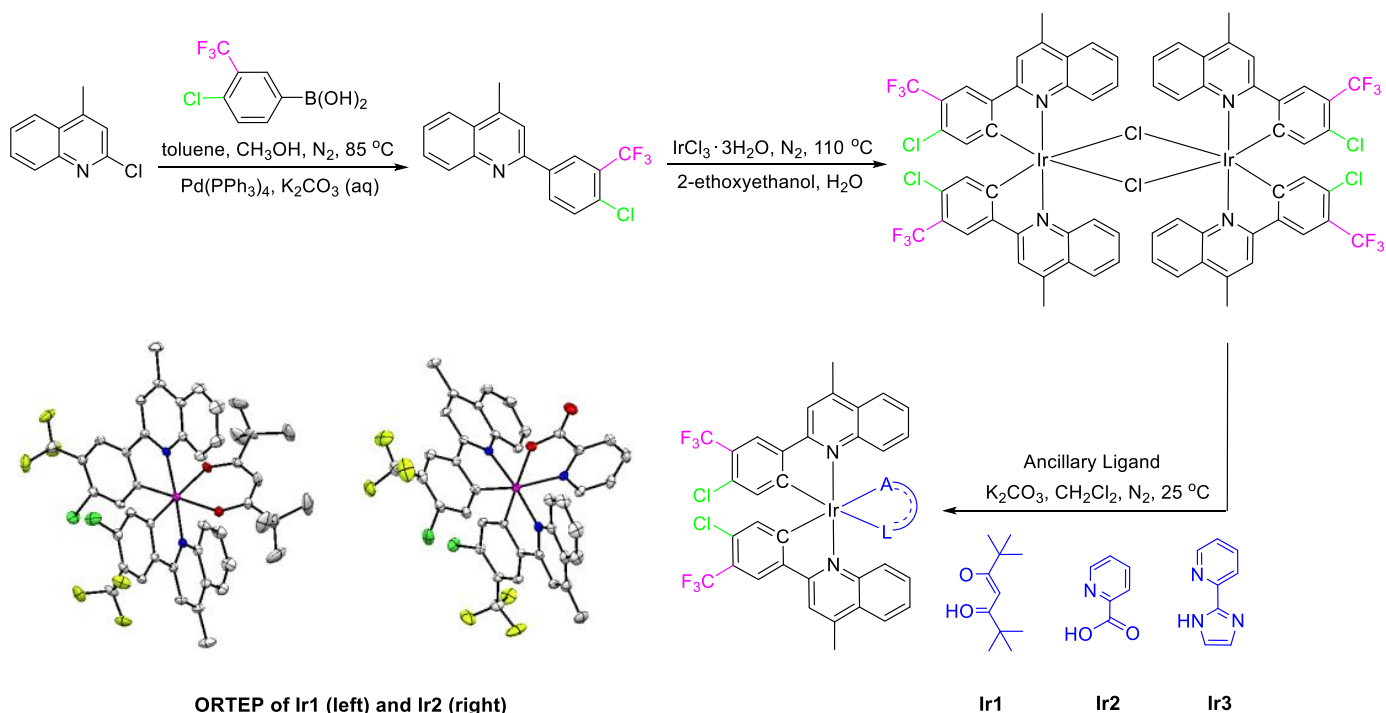
White organic light-emitting devices (OLEDs) have drawn continuous attention owing to their great potential utilizations in solid-state lightings.^[1-5] There are two main methods for the realization of white OLEDs. The first method for fabricating white OLEDs is to use multi-color emitters (such as three primary colors),^[6,7] while another method (two-color method) is to incorporate blue and complementary yellow emitters.^[8,9] Compared to the multi-color-based white OLEDs, two-color-based white OLED devices are more attractive because of their much simpler device structures.^[10] In order to improve the spectral quality of the two-color-based white devices, the performances of yellow emitters, especially the emission full width at half maximum (FWHM), are quite important.^[6,8,11,12] The broad emission bandwidth will cover more region in the white spectrum, thereby improving the color rendering index (CRI) of the white OLEDs.

The cyclometalated iridium(III) complexes, which can make full use of both triplet excitons and singlet excitons to effectively enhance the device efficiency,^[13-16] are regarded as the most popular triplet emitters for electroluminescence (EL). Compared to other metal-based triplet emitters, iridium-based emitters have

many advantages, such as tunable emission color, high chemical stability and highly efficient phosphorescence.^[12,14]

As mentioned above, in order to realize high-quality solid-state lightings, high-performance yellow light-emitting materials are necessary for two-color-based white OLEDs. However, compared with green, blue, and red iridium(III) complexes for OLEDs, the development of yellow iridium(III) complexes is still lagging behind.^[12] It is still a challenge to design the yellow neutral iridium(III) complexes featuring high luminescent efficiency and broad emission bandwidth simultaneously. The lack of high efficiency and broad emissive yellow neutral iridium(III) complexes remains an obstacle for developing high-quality two-color-based white devices.^[8]

So far, there are extremely limited examples of yellow neutral iridium(III) complexes with broad FWHMs. Jou and coworkers designed a yellow light-emitting iridium(III) complex based on fluorinated benzonaphthyridin-6-one ligand. This triplet emitter shows high photoluminescence efficiency (Φ_{PL}) of 0.71. The external quantum efficiency (EQE) of yellow device can reach 22.6%, and the FWHM of 80 nm is achieved for electroluminescence.^[17] Lee and coworkers reported a naphthylpyridine-based iridium(III) complex for preparing



Scheme 1. Synthetic routes and ORTEP plots of chlorinated iridium(III) phosphors (CCDC no. 2038562 for **Ir1**, CCDC no. 2038563 for **Ir2**).

yellow devices with broader FWHM as high as 87 nm.^[11] Recently, we modified the typical 2-phenyllepidine ligand commonly used for red iridium(III) complexes by introducing the fluorine atom and trifluoromethyl moiety into the phenyl ring of 2-phenyllepidine ligand. The obtained fluorinated 2-phenyllepidine ligand was successfully used to design high-efficiency yellow light-emitting neutral iridium(III) complexes with extremely broad FWHMs of about 100 nm in dichloromethane. The yellow OLED devices based on these emitters also produced extremely broad FWHMs analogous to that of the complexes in dichloromethane.^[8] However, due to the presence of less stable aromatic carbon-fluorine chemical bond ($C_{\text{aryl}}-F$) in the complexes, the aromatic fluorine functionalized iridium(III) complexes usually suffer from poor structural stability, leading to the reduced lifetime of the devices during operation.^[18-22] The fluorine-induced electrochemical degradation has become the challenge for the classical blue triplet emitter Firpic.^[18] To overcome this shortcoming, it is quite urgent to find an alternative showing higher structural stability. As the analogue of fluorine atom, chlorine atom has the similar properties but slightly differs in electronegativity. The chlorine atom is less electronegative, making the aromatic carbon-chlorine chemical bond ($C_{\text{aryl}}-Cl$) more stable and chemically inert. So, the chlorine atom may be the potential candidate in the ligand design. In order to ensure the emission in the yellow region, the incorporation of one trifluoromethyl group with one aromatic chlorine atom into 2-phenyllepidine cyclometalating ligand could be the possible way for designing yellow iridium(III) complexes with the improved stability. Moreover, the ancillary ligand is another important factor in finely tuning the emission energy and FWHMs of iridium(III) complex. So, the combination of well-designed cyclometalating ligand with proper ancillary ligand could realize complexes with yellow emission, high luminescent efficiency and broad FWHM simultaneously.

In this work, we developed a new chlorinated 2-phenyllepidine cyclometalating ligand for designing yellow iridium(III) complexes, and synthesized three highly efficient yellow iridium(III) complexes (**Ir1-Ir3**) with 2,2,6,6-tetramethylheptane-3,5-dione, picolinic acid, and 2-(1*H*-

imidazol-2-yl)pyridine as the ancillary ligand (**Scheme 1**). Alternation of the ancillary ligand is also used to control the emission properties of these chlorinated iridium(III) complexes, particularly in the aspect of emission wavelength, luminescent efficiency, and emission bandwidths. The prepared complexes show bright yellow phosphorescence with the photoluminescence (PL) wavelengths of 549–574 nm, the high Φ_{PL} of 0.73 and the very broad FWHMs up to 104 nm in the N_2 -saturated dichloromethane. Moreover, by using complexes as the triplet emitters, the prepared OLEDs give yellow phosphorescence peaking at 565, 548, and 551 nm, respectively. These OLEDs also exhibit broad FWHMs of 93 nm and extremely high *EQE* of 23.8%, exceeding the theoretical limit. At last, **Ir2**-based two-color white OLED showing high spectral quality was also realized, and the CRI and CIE coordinate for two-color white OLED are 74 and (0.32, 0.34), respectively.

2. Experimental section

The related information on synthesis, characterization, device preparation and performance testing in details can be found in the Supporting Information.

3. Results and discussion

3.1. Synthesis and characterization

As shown in **Scheme 1**, the chlorinated cyclometalated ligand 2-(4-chloro-3-(trifluoromethyl)phenyl)lepidine was prepared as a white solid by Suzuki coupling reaction of 2-chlorolepidine with the corresponding arylboronic acid. The iridium(III) complexes **Ir1-Ir3** were prepared easily in high yields by reaction of the different ancillary ligands with chlorinated iridium(III) μ -chloro-bridged dimer under a mild condition.^[8,23] These chlorine-bearing iridium(III) complexes show good solubility in polar organic solvents. The chemical structures of three new complexes were characterized fully by nuclear magnetic resonance (NMR) spectra, mass spectra and single crystal X-ray diffraction. The 1H NMR spectra of complexes are shown in Supporting Information. The NMR spectra clearly supported that the potential nucleophilic substitution reaction of 2-ethoxyethanol with the aromatic

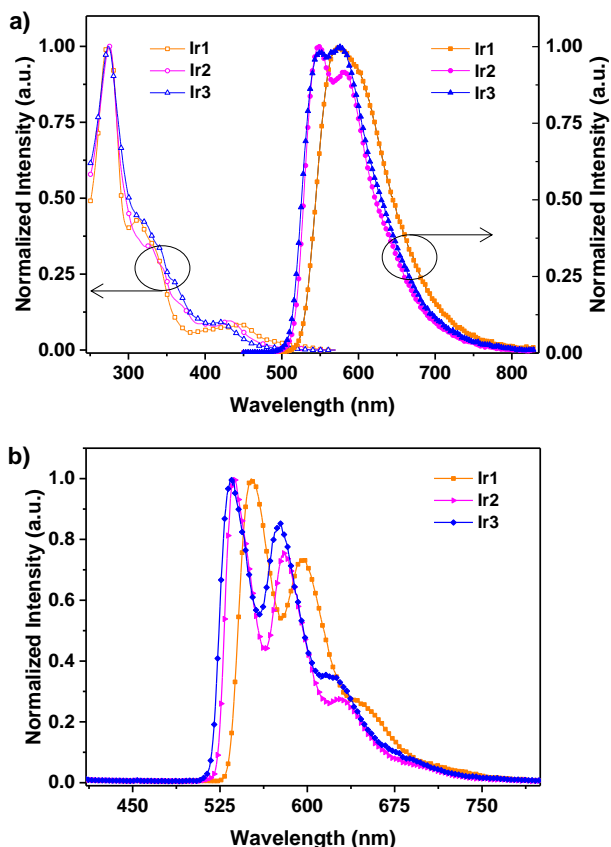


Figure 1. a) UV-visible absorption and photoluminescence spectra of **Ir1-Ir3** at 298 K in the N_2 -saturated CH_2Cl_2 ; b) low temperature photoluminescence spectra of **Ir1-Ir3** at 77 K in 2-MeTHF.

chlorine did not occur in the iridium(III) μ -chloro-bridged dimer formation reaction, indicating the high chemical stability of C_{aryl} -Cl bond. Compared with complex **Ir1** with symmetry in the molecule, complexes **Ir2** and **Ir3** show much complex well-resolved signals, supporting the absence of symmetry in the structure. In addition, complex **Ir1** shows one resonance signal (-67.81 ppm) in ^{19}F NMR spectrum, while complexes **Ir1** and **Ir2** show two slightly different resonance signals (-68.11, -68.20 ppm for **Ir1**; -68.04, -68.05 ppm for **Ir2**) in ^{19}F NMR spectra. The ^{19}F NMR spectra also implied the low structural symmetry in complex **Ir2** and **Ir3**, which is induced by the incorporation of the asymmetric ancillary ligand.

Single crystal X-ray diffraction study further confirmed the chemical structure of complexes. The single crystals of **Ir1** and **Ir2** for X-ray diffraction crystallized in the mixed solvents of methanol and dichloromethane. The ORTEP diagrams of two complexes are depicted in **Scheme 1**. The center iridium atom of each complex possesses slightly distorted octahedral coordination geometry, in which the metalated carbon atoms adopt *cis* coordination mode and the nitrogen atoms adopt *trans* coordination. The coordination configuration of these complexes

Table 1. Photophysical and electrochemical properties for **Ir1-Ir3**.

Complex	Emission ^{a)}				E_{onset}^{ox} [eV] ^{b)}	E_g [eV] ^{c)}	T_1 [eV] ^{d)}	HOMO/LUMO [eV] ^{c)}
	λ_{em} [nm]	FWHM [nm]	τ [μ s]	Φ_{PL}				
Ir1	574	101	1.00	0.62	0.81	2.55	2.25	-5.61/-3.06
Ir2	549, 582 (sh)	94	1.78	0.73	1.02	2.66	2.31	-5.82/-3.16
Ir3	550, 575 (sh)	104	1.85	0.49	1.22	2.74	2.32	-6.02/-3.28

^{a)}At a concentration of 1.0×10^{-5} mol/L in the N_2 -saturated CH_2Cl_2 , λ_{ex} = 365 nm, at 25 °C; ^{b)}In CH_2Cl_2 ; ^{c)}HOMO (eV) = $-e(E_{onset}^{ox} + 4.8)$, E_g is optical band gap, LUMO (eV) = $E_g + HOMO$; ^{d)}The triplet energy (T_1) was estimated from the highest-energy vibronic sub-band of the phosphorescence spectrum at a concentration of 1.0×10^{-5} mol/L in 2-MeTHF at 77 K, λ_{ex} = 365 nm.

are consistent with the previously reported analogues.^[8,24,25] It is clearly shown that the chlorine atoms exist in the complexes, and the bond lengths of C_{aryl} -Cl bond in complexes are in the range of 1.733-1.739 Å, which is similar to the typical C_{aryl} -Cl bond length.^[26,27] Interestingly, from the crystal structures of the complexes, the intramolecular short contacts (**Figure S1**) can be easily observed in both complexes. The interaction distances between oxygen bonded to iridium atom and proton from quinoline ring are in the range of 2.136-2.195 Å. This short contact may prevent the ligands from vibrating, thereby improving the photoluminescence of complex. It can also be found that the bulky trifluoromethyl groups in the complexes are located at the *para*-position of metal center.^[8] Moreover, the large steric hindrance of the methyl and trifluoromethyl groups in these complexes effectively increases the intermolecular distance of iridium(III) complexes, remarkably inhibiting the self-quenching of complexes.

Under N_2 atmosphere, the chemical stabilities of these complexes were explored by thermogravimetric analysis (**Figure S2**). It is found that the temperatures of weight loss in 5% of these complexes exceed 200 °C (372 °C for **Ir1**, 207 °C for **Ir2**, and 229 °C for **Ir3**), which indicates that the complexes show high thermal stabilities under vacuum evaporation. In addition, the sublimation temperature of **Ir1** is higher than these of **Ir2** and **Ir3**, indicating that the ancillary ligands have great effect on the sublimation temperature of these complexes.

3.2. Photophysical properties

Photophysical properties (**Figure 1**, **Table 1** and **Table S2**) of three iridium(III) complexes were recorded in CH_2Cl_2 by ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) spectrophotometers. As shown in **Figure 1a**, the strong absorption band in the range of 250-400 nm can be assigned to the $\pi \rightarrow \pi^*$ transition of chlorinated cyclometalating ligand of the phosphors.^[8] The relatively weak absorption band in the range of 400-550 nm should be assigned to the singlet and triplet metal-to-ligand charge-transfer transitions due to the effective spin-orbit coupling (SOC) between the singlet (S_1) and triplet (T_1) excited states induced by the heavy-atom effects of iridium atom.^[8] At 298 K, the PL spectra (**Figure 1a**) of iridium(III) complexes in CH_2Cl_2 show bright yellow phosphorescence with the maxima at 574 nm for **Ir1**, 549 nm for **Ir2**, and 550 nm for **Ir3**. The FWHM for the yellow complex is extremely broad (101 nm for **Ir1**, 94 nm for **Ir2**, 104 nm for **Ir3**). The different FWHMs of emission spectra imply that ancillary ligand can affect the intensities of shoulder emissions of these iridium(III) complexes significantly. It should be noted that, for the complex bearing 2-(1*H*-imidazol-2-yl)pyridine, the FWHM was the broadest (up to 104 nm). The Φ_{PL} of the iridium(III) complexes were recorded in the N_2 -saturated CH_2Cl_2 by using an integrating sphere, and these Φ_{PL} of **Ir1-Ir3** were determined to be 0.62, 0.73 and 0.49, respectively, indicating that the Φ_{PL} (as high as 0.73) highly related to the device efficiency can also be tuned by the ancillary

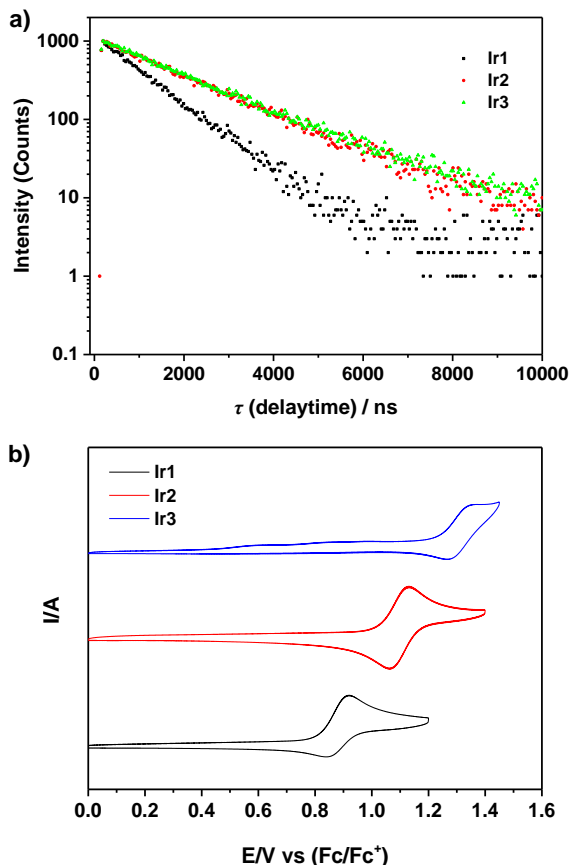


Figure 2. a) Phosphorescent decay of **Ir1-Ir3** in the N_2 -saturated CH_2Cl_2 at 298 K; b) cyclic voltammograms of **Ir1-Ir3** under a scan rate of 100 mV/s in the N_2 -saturated CH_3CN .

ligands. Moreover, the concentration quenching of complexes can also be suppressed by the steric hindrance from the methyl and trifluoromethyl moiety in the ligands for enhancing the photoluminescence efficiency.^[5] At room temperature, in the N_2 -saturated CH_2Cl_2 , the lifetimes (**Figure 2a**) of the iridium(III) complexes were recorded to be 1.00 μ s, 1.78 μ s, and 1.85 μ s for **Ir1-Ir3**, respectively, indicative of the phosphorescence nature of emission. Notably, the emission lifetimes of chlorinated iridium(III) complexes are very close to the fluorinated analogues, implying that the chlorine atom with slightly higher molecular weight almost has no effect on the excited state lifetime of iridium(III) complex.^[8]

Phosphorescence spectra (**Figure 1b**, **Table S1**) at 77 K of these complexes were measured in 2-methyltetrahydrofuran (2-MeTHF). Compared to the room temperature emission spectra, the low temperature phosphorescence spectra show blue shift to some extent, and the vibronic bands with fine structures in the low temperature emission spectra were also observed. Furthermore, there are difference in the rigidochromic shifts (difference between PL maxima recorded at 298 K and 77 K) of these chlorinated complexes. Complex **Ir1** showed the largest rigidochromic shifts of 22 nm, while complex **Ir2** and **Ir3** show slightly smaller rigidochromic shifts (12 and 16 nm), suggesting that the less polar excited states are present in complexes **Ir2** and **Ir3**.^[24-25] The triplet energies (T_1) of these complexes (**Table 1**) can be calculated according to the vibronic sub-band with the highest-energy in low temperature phosphorescence spectra.^[19] The phosphors show moderate T_1 energies (2.16 eV for **Ir1**, 2.26 eV for **Ir2**, 2.25 eV for **Ir3**). The emission energies of the complexes designed were similar to that of their fluorinated analogues,^[8] indicating that the incorporation of aromatic

chlorine and trifluoromethyl group can give rise to the yellow emission of the chlorinated iridium(III) complexes.

3.3. Electrochemical properties

The electrochemical properties of these iridium(III) complexes were investigated by cyclic voltammetry in the N_2 -saturated CH_3CN . As shown in **Figure 2b**, the complexes show oxidation waves in the oxidation process. The oxidation potential in the positive region can be attributed to the oxidations of metal center in these complexes.^[24-25] The oxidation potentials of these phosphors are quite different and are in the order of **Ir1** < **Ir2** < **Ir3** (0.81 eV for **Ir1**, 1.02 eV for **Ir2**, 1.22 eV for **Ir3**). The 2,2,6,6-tetramethylheptane-3,5-dione-based phosphor **Ir1** shows the smallest oxidation potential, while the oxidation potentials of phosphors bearing picolinic acid and 2-(1*H*-imidazol-2-yl)pyridine ligands show positive shifts of \sim 0.21-0.41 V, implying that the pyridine-type ancillary ligands could shift the oxidation potential to a more positive value. According to the oxidation potentials of the complexes, the energy levels for the highest occupied molecular orbital (HOMO) of these complexes can be determined to be -5.61 eV for **Ir1**, -5.82 eV for **Ir2**, and -6.02 eV for **Ir3**. The energy levels for the lowest unoccupied molecular orbital (LUMO) of the complexes are -3.06 eV for **Ir1**, -3.16 eV for **Ir2**, and -3.28 eV for **Ir3**.

3.4. Yellow organic light-emitting diodes

The high Φ_{PL} and broad yellow emission for the three emitters make them excellent candidates for high-efficiency electroluminescence. Thus, we designed a series of OLEDs to evaluate their electroluminescence performance, and OLEDs were fabricated with the structure (**Figure 3**) of indium-tin-oxide (ITO)/ molybdenum trioxide (MoO_3) (3 nm)/ di-(4-(*N,N*-di-*p*-tolyl-amino)-phenyl)cyclohexane (TAPC) (40 nm)/ 4,4',4''-tris(carbazol-9-yl)triphenylamine (TCTA) (5 nm)/ 4,4'-bis(9*H*-carbazol-9-yl)biphenyl (CBP): emitter (x wt% 25 nm)/ 1,3,5-tri((3-pyridyl)-phen-3-yl)benzene (TmPyPB) (50 nm)/ lithium fluoride (LiF) (1 nm)/ aluminum (Al) (120 nm). **Ir1**, **Ir2** and **Ir3** were selected as the emitters, corresponding to the devices Y1, Y2 and Y3, respectively. The device structure and energy level diagrams of the above yellow OLEDs are shown in **Figure 3**. In these devices, 180 nm ITO and 100 nm Al were used as anode and cathode, respectively; 3 nm MoO_3 layer and 1 nm-thick LiF layer were used as hole injection layer and electron injection layer, respectively; 40 nm TAPC layer and 50 nm TmPyPB layer

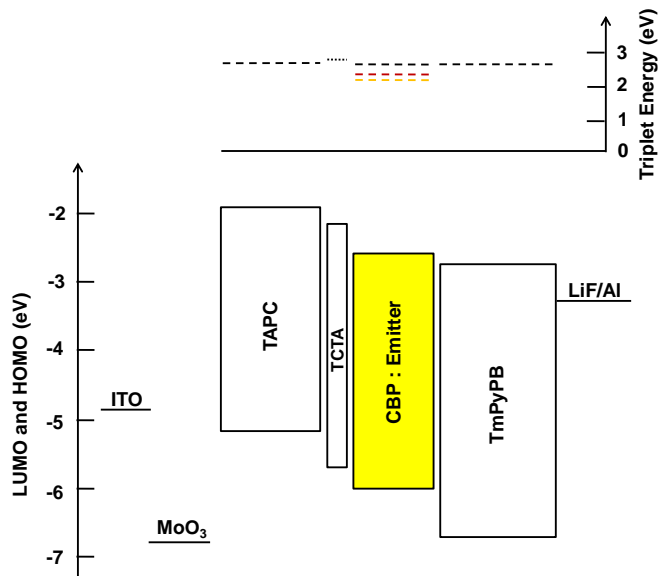


Figure 3. Schematic diagram of the energy levels of the yellow OLEDs.

were used as hole transport layer and electron transport layer, respectively; TCTA was used as exciton-blocking layer; CBP was used as host of two emitters, and 25 nm CBP doped with emitter (in 6% and 9%) layer was used as light-emitting layer (EML). Herein, TAPC and TmPyPB are excellent carriers transport materials with the hole mobility of $1.0 \times 10^{-2} \text{ cm}^2/\text{V}\cdot\text{s}$ and the electron mobility of $1.0 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$, respectively. Furthermore, TAPC has a relatively high HOMO of 5.3 eV, and TmPyPB exhibits a relatively low LUMO of 2.7 eV,^[28-29] which are favorable for the injection and transporting of hole and electron carriers to EML via the above both layers, respectively. Besides, the high energy barriers of 0.3 eV (the difference between the LUMO energy levels of TCTA and CBP) at TCTA/CBP interface and 0.7 eV (the difference between the HOMO energy levels of CBP and TmPyPB) at CBP/TmPyPB interface will well limit carrier recombination zone in EML. Moreover, the higher triplet levels of 2.8 eV for TCTA and 2.7 eV for TmPyPB than those (2.16 and 2.26 eV) for the two emitters can effectively suppress the reverse energy transfer from emitters to adjacent TCTA and TmPyPB layers, which will contribute to a high exciton utilization rate.^[30] So, it is expected that the fabricated OLEDs with these two compounds as emitters can achieve the high EL performance. First of all, the EL spectra of emitters were investigated. From **Figure 4a**, the EL spectra for all OLEDs Y1, Y2 and Y3 contain a main peak, at 565 nm for device Y1, 548 nm for device Y2, and 551 nm for device Y3, respectively. They are slightly different from the PL spectra of Ir1-Ir3, which is the result of the decrease in the shoulder intensity of the EL spectra. The EL emissions are originated from

emitters, and we do not observe emission band from host or adjacent transporting materials, implying energy transfer from host to emitters is complete, and the exciton recombination only occurs in EML.^[7] Herein, the CIE coordinates are recognized to be (0.50, 0.48) for Y1, (0.46, 0.53) for Y2, and (0.47, 0.52) for Y3, respectively, which are obviously located in the yellow light-emitting region. Particularly, the emission wavelengths for Y1 to Y3 are close to their fluorinated analogues, demonstrating that all OLEDs above give excellent yellow emissions. This is also well confirmed from the photographs of the yellow OLEDs in the inset of **Figure 4a**.

Figure 4b, **4c**, and **4d** displays the current density-voltage-luminance (*J-V-L*), current efficiency-luminance-*EQE* (*CE-L-EQE*), and power efficiency-luminance (*PE-L*) curves, and **Table 2** summarizes the main performance parameters of all fabricated yellow OLEDs. From **Figure 4b** and **S3a** and **Table 2**, the low turn-on voltages of 3.4-3.7 V were observed for all yellow OLEDs, and these devices also realize the relatively high luminance with the maximum value reaching 15,530 cd/m^2 for Y1 with the doping concentration of 9%, 13,280 cd/m^2 for Y2 with the doping concentration of 6%, and 9,235 cd/m^2 for Y3 with the doping concentration of 9%, respectively. Furthermore, from **Figures 4c**, **4d**, **S3b**, **S3c** and **Table 2**, it is found that the maximum *CE*, *PE*, and *EQE* are up to 67.5 cd/A , 47.1 lm/W and 23.8 % for Y1 with the doping concentration of 6%; 60.5 cd/A , 51.7 lm/W and 21.6 % for Y1 with the doping concentration of 9%; 71.1 cd/A , 58.7 lm/W and 22.1% for Y2 at the doping concentration of 6%; 68.1 cd/A , 53.7 lm/W and 21.3 % for Y2 at the doping concentration of 9%; 64.3 cd/A ,

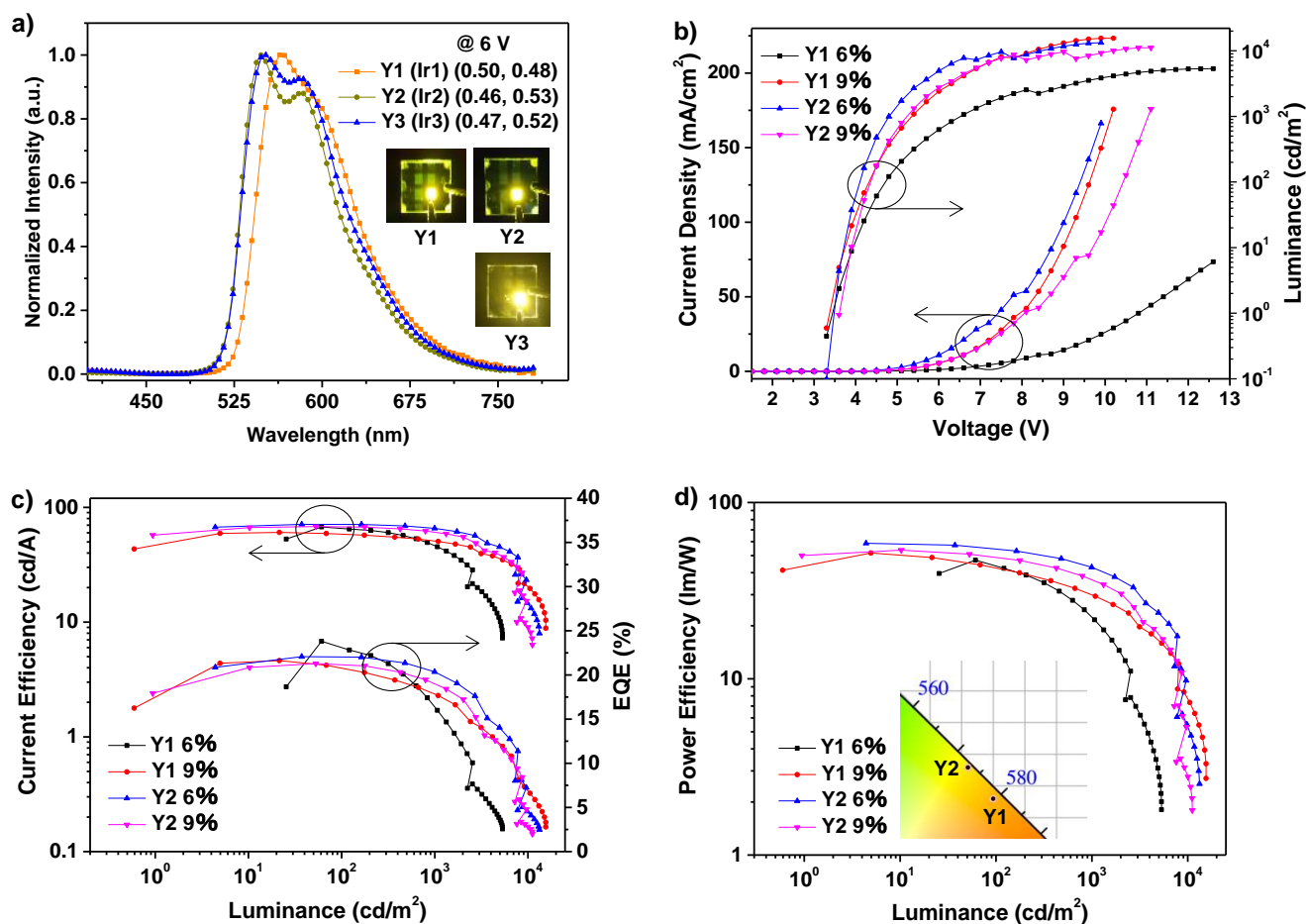


Figure 4. Normalized EL spectra (a) for the yellow devices Y1, Y2, and Y3 with 6% and 9% doping concentration (the inset shows the photographs), *J-V-L* (b), *CE-L-EQE* (c), and *PE-L* (d) curves for the yellow devices Y1 and Y2 with 6% and 9% doping concentration (the inset in (d) shows the 1931 CIE coordinates with 6% doping concentration).

6 **Table 2.** Device performances of the yellow OLEDs.

Complex	x%	$\lambda_{\text{EL}}/\text{nm}$	CIE (x, y) ^{a)}	$V_{\text{ON}}^{\text{b)}/\text{V}}$	$L_{\text{max}}/\text{cd}\cdot\text{m}^{-2}$	$CE_{\text{max}}/\text{cd}\cdot\text{A}^{-1}$	$PE_{\text{max}}/\text{lm}\cdot\text{W}^{-1}$	EQE_{max}	FWHM/nm
Ir1	6	565	(0.50, 0.48)	3.4	5,329	67.5	47.1	23.8	86
Ir1	9	565	(0.50, 0.48)	3.4	15,530	60.5	51.7	21.6	86
Ir2	6	548	(0.46, 0.53)	3.4	13,280	71.1	58.7	22.1	87
Ir2	9	548	(0.46, 0.53)	3.6	11,150	68.1	53.7	21.3	87
Ir3	6	551	(0.47, 0.52)	3.6	8,319	64.3	51.8	20.8	93
Ir3	9	551	(0.47, 0.52)	3.7	9,235	60.1	44.9	19.8	93

^{a)}At 6 V; ^{b)}Luminance is 1 $\text{cd}\cdot\text{m}^{-2}$

51.8 lm/W and 20.8% for Y3 at the doping concentration of 6%; 60.1 cd/A , 44.9 lm/W and 19.8 % for Y3 at the doping concentration of 9%, respectively. Such high $EQEs$ for Y1 to Y3 are also comparable to their fluorinated analogues.^[8] Herein, the $EQEs$ for these yellow devices obviously exceed the theoretical limit value of 20% (not considering any potential outcoupling effect) for conventional phosphorescent OLEDs from statistical mathematics,^[19] which are comparable or superior to the majority of yellow OLEDs reported in the literature.^[6,11,17,31-39] In the fluorinated analogues, it was found that the FWHMs of EL spectra of these complexes were almost the same to those of the PL spectra.^[8] However, different from their fluorinated analogues, the FWHMs of the EL spectra of these chlorinated complexes are quite different from these of the PL spectra. The FWHMs of the EL spectra for these yellow OLEDs are 86 nm for Y1, 87 nm for Y2, and 93 nm for Y3, which are smaller than those of the PL spectra (101 nm for **Ir1**, 94 nm for **Ir2**, and 104 nm for **Ir3**). The slightly narrowed FWHMs of the EL spectra may be attributed to the following reasons: 1) the intermolecular interaction between chlorinated iridium(III) complex and host material is different from the solution state; 2) the weak microcavity effect of the fabricated OLEDs affects their emission spectra.^[31] Although these iridium(III) complexes show slightly narrowed FWHMs of the EL spectra, they are still up to 87 nm, which is also superior to the majority of yellow OLEDs reported previously.^[6,11,17,32-40]

It should be noted that ancillary ligands also have remarkable effect on the device performance. The device Y1 based on **Ir1** with 2,2,6,6-tetramethylheptane-3,5-dione and Y2 based on **Ir2** with picolinic acid show higher device efficiencies than that of Y3 based on **Ir3** with 2-(1*H*-imidazol-2-yl)pyridine.

3.5. Yellow-based complementary white OLEDs

Owing to the broad emission band and high EQE for these yellow iridium(III) complexes, complex **Ir2** was selected to further fabricate white OLED to demonstrate the potential applications for these broad emissive yellow emitters in developing complementary color white OLEDs. While the newly developed pure blue emissive fluorescent emitter 4-(7-(4-(diphenylamino)phenyl)-9,9-dioctyl-9*H*-fluoren-2-yl)benzotrile (**B1**) exhibits the EL emission peak at about 450 nm, which is well complementary to the yellow light of complex **Ir2**, it was selected to fabricate white OLEDs.^[41] The complementary white OLED with the structure of ITO/ MoO_3 (3 nm)/TAPC (40 nm)/TCTA (10 nm)/**B1** (10 nm)/Bepp₂:**Ir2** (6% 5 nm)/**B1** (10 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al was designed and fabricated, and named as OLED W, where Bepp₂ is bis(2-(2-hydroxyphenyl)-pyridine)beryllium acting as host material for triplet emitter **Ir2**. The energy level diagram for the white OLED is depicted in **Figure 5a**.

The EL characteristics for the OLED W are depicted in **Figure S4**. Clearly, the EL spectra for the OLED W display two emission bands, where the blue emission band with a peak at 450 nm is from fluorescent emitter **B1**, and the yellow emission band

(peaked at 550 nm) is originated from emitter **Ir2**. It is found that the EL spectra are related closely to the applied voltage, which may be the result of recombination zone shift with the increasing voltage. With the increase of voltage from 3 V to 7 V, the gradually increasing blue emission intensity contribute to the pure white emission with balanced complementary light emissions, which was well demonstrated from the photograph of the OLED W at 7 V in the inset of **Figure 5b**. The CIE coordinates and color rendering index (CRI) is (0.32, 0.34) and 74 at 7 V. The relatively high CRI achieved can be attributed to the broad yellow emissive emitter used in this white OLED. The relatively low intensity of blue emission band at low voltages is due to the unbalanced carrier combination within **B1** layer and Bepp₂:**Ir2** layer, which could be improved by further optimization of the device structure. From **Figures S4b, S4c** and **S4d**, the device W realizes the high EL efficiencies with the maximum CE, PE and EQE reaching 46.6 cd/A , 46.9 lm/W and 16.3%, respectively. This white device with high CRI up to 74

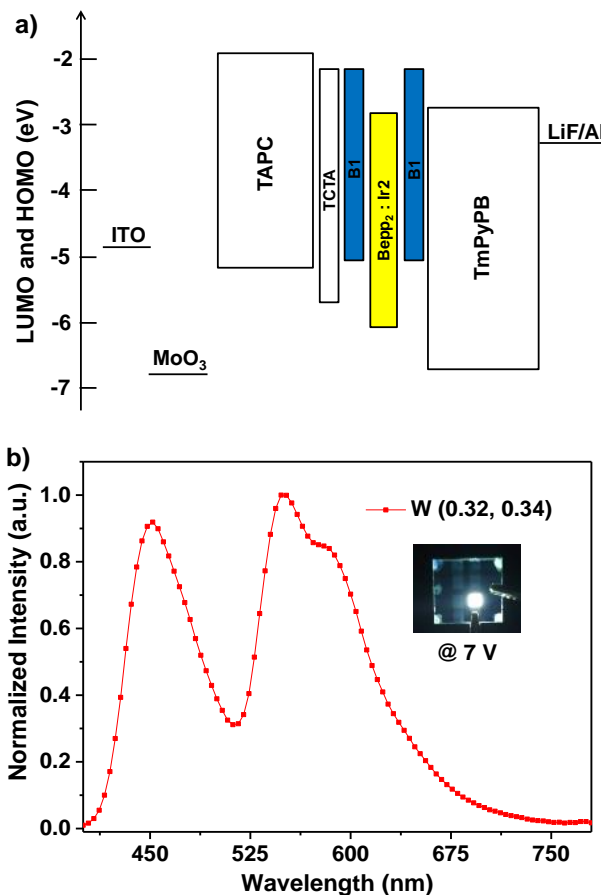


Figure 5. Schematic diagram of the energy levels (a) and EL spectrum (b) of the white OLED. The inset shows the photographs of the white OLED at 6 V.

and excellent CIE coordinates of (0.32, 0.34) indicates that the designed chlorinated yellow iridium(III) complexes with broad FWHMs have the huge application potential in the development of high-quality white OLEDs.

4. Conclusions

To conclude, three high-efficiency aromatic chlorine-based yellow neutral iridium(III) complexes have been designed and prepared in mild condition. The three phosphors obtained exhibit intense yellow emissions with very broad FWHM (as high as 104 nm) and high Φ_{PL} (reaching 0.73) in the N_2 -saturated dichloromethane. A series of yellow OLEDs based on phosphors were fabricated to evaluate their electroluminescence performance. The fabricated OLEDs emit similar yellow emissions at 565 nm (FWHM of 86 nm), 548 nm (FWHM of 87 nm), 551 nm (FWHM of 93 nm), respectively. The FWHMs for these yellow devices are slightly narrower than that of photoluminescence in solution state. Notably, the extremely high external quantum efficiency of 23.8% was achieved for the prepared yellow OLEDs, and this performance is superior or comparable to the majority of yellow OLEDs reported. Furthermore, it was demonstrated that by using the broad emissive **Ir2** as yellow emitter, the complementary white OLED with high spectral quality was also realized, and the CRI and CIE coordinates for the two-color white device are 74 and (0.32, 0.34), respectively. The results obtained revealed that these new iridium(III) complexes based on chlorinated cyclometalating ligand are a promising class of broad emissive yellow triplet emitters suitable for complementary white electroluminescence.

Author contribution

Peng Tao and Yuk-Ki Lee designed, synthesized, and characterized the ligand, complexes and wrote the manuscript. Xiao-Kang Zheng characterized the photophysical and electrochemical properties, cultured the crystals of the complexes, and collected the data of single crystal X-ray diffraction. Xiao-Zhen Wei fabricated the device. Mei-Tung Lau purified the complexes. Zi-Kang Li, Ze-Ling Guo and Fang-Qing Zhao helped the materials characterization. Xing Liu synthesized the blue fluorescent material for the white OLED. Shu-Juan Liu discussed the data and revised the manuscript. Yan-Qin Miao designed the device structure, and supervised the device fabrication. Wai-Yeung Wong and Qiang Zhao supervised the whole work and revised the manuscript. All authors contributed to the discussion of the results.

Conflict of interest

There are no conflicts to declare.

Acknowledgments

The authors acknowledge the National Natural Science Foundation of China (61905120, 51873176, 61705156), National Funds for Distinguished Young Scientists (61825503), the Hong Kong Research Grants Council (PolyU 153058/19P), the Hong Kong Polytechnic University (1-ZE1C), Ms. Clarea Au for the Endowed Professorship in Energy (847S), Guangdong-Hong Kong-Macao Joint Laboratory of Optoelectronic and Magnetic Functional Materials (2019B121205002), Natural Science Foundation of Jiangsu Province of China (BK20190740), and Key R&D program of Shanxi Province (International Cooperation, 201903D421087) for financial support.

Supplementary data

Supplementary data (details of the ligand and complex synthesis, NMR, X-ray crystallographic analysis and the device fabrication and testing) associated with this article can be found in the **Supporting Information**.

References

- [1] Z. Wu, D. Ma, Recent advances in white organic light-emitting diodes, *Mater. Sci. Eng. R* 107 (2016) 1-42.
- [2] Z. Chen, C.-L. Ho, L. Wang, W.-Y. Wong, Single-molecular white light emitters and their potential WOLED applications, *Adv. Mater.* 32 (2020), 1903269.
- [3] G. Fu, Y. He, W. Li, T. Miao, X. Lv, H. He, L. Liu, W.-Y. Wong, Efficient white polymer light-emitting diodes (WPLEDs) based on covalent-grafting of $[\text{Zn}_2(\text{MP})_3(\text{OAc})]$ into PVK, *Chem. Sci.* (11) 2020, 2640.
- [4] S. Wang, H. Zhang, B. Zhang, Z. Xie, W.-Y. Wong, Towards high-power-efficiency solution-processed OLEDs: Material and device perspectives, *Mater. Sci. Eng. R* (140) 2020, 100547.
- [5] P. Tao, Y. Miao, H. Wang, B. Xu, Q. Zhao, High performance organic electroluminescence: Design from organic light-emitting materials to devices, *Chem. Rec.* (19) 2019, 1531.
- [6] M. S. Park, H. J. Park, O. Y. Kim, J. Y. Lee, High color rendering index in phosphorescent white organic light-emitting diodes using a yellowish-green dopant with broad light emission, *Org. Electron.* (14) 2013, 1504-1509.
- [7] Y. Miao, K. Wang, B. Zhao, L. Gao, P. Tao, X. Liu, Y. Hao, H. Wang, B. Xu, F. Zhu, High-efficiency/CRI/color stability warm white organic light-emitting diodes by incorporating ultrathin phosphorescence layers in a blue fluorescence layer, *Nanophotonics* (7) 2018, 295-304.
- [8] P. Tao, W.-L. Li, J. Zhang, S. Guo, Q. Zhao, H. Wang, B. Wei, S.-J. Liu, X.-H. Zhou, Q. Yu, B.-S. Xu, W. Huang, Facile synthesis of highly efficient lepidine-based phosphorescent iridium(III) complexes for yellow and white organic light-emitting diodes, *Adv. Funct. Mater.* (26) 2016, 881-894.
- [9] S.-F. Wu, S.-H. Li, Y.-K. Wang, C.-C. Huang, Q. Sun, J.-J. Liang, L.-S. Liao, M.-K. Fung, White organic LED with a luminous efficacy exceeding $100 \text{ lm}\cdot\text{W}^{-1}$ without light out-coupling enhancement techniques, *Adv. Funct. Mater.* (27) 2017, 1701314.
- [10] X. Tang, X.-Y. Liu, Z.-Q. Jiang, L.-S. Liao, High-quality white organic light-emitting diodes composed of binary emitters with color rendering index exceeding 80 by utilizing color remedy strategy, *Adv. Funct. Mater.* (29) 2019, 1807541.
- [11] S.-L. Lai, S.-L. Tao, M.-Y. Chan, M.-F. Lo, T.-W. Ng, S.-T. Lee, W.-M. Zhao, C.-S. Lee, Iridium(III) bis[2-(2-naphthyl)pyridine] (acetylacetonate)-based yellow and white phosphorescent organic light-emitting devices, *J. Mater. Chem.* (21) 2011, 4983-4988.
- [12] C. Fan, C. L. Yang, Yellow/orange emissive heavy-metal complexes as phosphors in monochromatic and white organic light-emitting devices, *Chem. Soc. Rev.* (43) 2014, 6439-6469.
- [13] P. Tao, S.-J. Liu, W.-Y. Wong, Phosphorescent manganese(II) complexes and their emerging applications, *Adv. Optical Mater.* 2020, (20) 8, 2000985.
- [14] J. Lee, H. Chen, T. Batagoda, C. Coburn, P. I. Djurovich, M. E. Thompson, S. R. Forrest, Deep blue phosphorescent organic light-emitting diodes with very high brightness and efficiency, *Nat. Mater.* (15) 2016, 92-98.
- [15] V. W.-W. Yam, V. K.-M. M Au, S. Y.-L. Leung, Light-emitting self-assembled materials based on d^8 and d^{10} transition metal complexes, *Chem. Rev.* (115) 2015, 7589-7728.
- [16] G. Li, F. Zhan, J. Zheng, Y.-F. Yang, Q. Wang, Q. Chen, G. Shen, Y. She, Highly efficient phosphorescent tetradentate platinum(II) complexes containing fused 6/5/6 metallocycles, *Inorg. Chem.* (59) 2020, 3718-3729.
- [17] J. H. Jou, Y. X. Lin, S. H. Peng, C. J. Li, Y. M. Yang, C. L. Chin, J. J. Shyue, S. S. Sun, M. Lee, C. T. Chen, M. C. Liu, C. C. Chen, G. Y.

- Chen, J. H. Wu, C. H. Li, C. F. Sung, M. J. Lee, J. P. Hu, Highly efficient yellow organic light emitting diode with a novel wet- and dry-process feasible iridium complex emitter, *Adv. Funct. Mater.* 2014, 24, 555-562.
- [18] P. Tao, Y. Zhang, J. Wang, L. Wei, H. Li, X. Li, Q. Zhao, X. Zhang, S. Liu, H. Wang, W. Huang, Highly efficient blue phosphorescent iridium(III) complexes with various ancillary ligands for partially solution-processed organic light-emitting diodes, *J. Mater. Chem. C* (36) 2017, 5, 9306-9314.
- [19] Y. Miao, P. Tao, L. Gao, X. Li, L. Wei, S. Liu, H. Wang, B. Xu, Q. Zhao, Highly efficient chlorine functionalized blue iridium(III) phosphors for blue and white phosphorescent organic light-emitting diodes with the external quantum efficiency exceeding 20%, *J. Mater. Chem. C* (6) 2018, 6656-6665.
- [20] E. Baranoff, B. F. E. Curchod, Flrpic: archetypal blue phosphorescent emitter for electroluminescence, *Dalton Trans.* (44) 2015, 8318-8329.
- [21] Y. Zheng, A. S. Batsanov, R. M. Edkins, A. Beeby, M. R. Bryce, Thermally induced defluorination during a mer to fac transformation of a blue-green phosphorescent cyclometalated iridium(III) complex, *Inorg. Chem.* (51) 2012, 290-297.
- [22] V. Sivasubramaniam, F. Brodkorb, S. Hanning, H. P. Loeb, V. Elsbergen, H. Boerner, U. Scherf, M. Kreyenschmidt, Fluorine cleavage of the light blue heteroleptic triplet emitter Flrpic, *J. Fluorine Chem.* (130) 2009, 640-649.
- [23] M. Nonoyama, Benzo[h]quinolin-10-yl-N iridium(III) complexes, *Bull. Chem. Soc. Jpn.* (47) 1974, 767-768.
- [24] Q. Zhao, S. Liu, M. Shi, C. Wang, M. Yu, L. Li, F. Li, T. Yi, C. Huang, Series of new cationic iridium(III) complexes with tunable emission wavelength and excited state properties: Structures, theoretical calculations, and photophysical and electrochemical properties, *Inorg. Chem.* (45) 2006, 6152-6160.
- [25] Q. Zhao, C.-Y. Jiang, M. Shi, F.-Y. Li, T. Yi, Y. Cao, C.-H. Huang, Synthesis and photophysical, electrochemical, and electrophosphorescent properties of a series of iridium(III) complexes based on quinoline derivatives and different β -diketonate ligands, *Organometallics* (25) 2006, 3631-3638.
- [26] J. Qu, H. Chen, J. Zhou, H. Lai, T. Liu, P. Chao, D. Li, Z. Xie, F. He, Y. Ma, Chlorine atom-induced molecular interlocked network in a non-fullerene acceptor, *ACS Appl. Mater. Interfaces* (10) 2018, 39992-40000.
- [27] H. Yao, J. Wang, Y. Xu, S. Zhang, J. Hou, Recent progress in chlorinated organic photovoltaic materials, *Acc. Chem. Res.* (53) 2020, 822-832.
- [28] S.-J. Su, T. Chiba, T. Takeda, J. Kido, Pyridine-containing triphenylbenzene derivatives with high electron mobility for highly efficient phosphorescent OLEDs, *Adv. Mater.* (20) 2008, 2125-2130.
- [29] Y.-H. Chen, F.-C. Zhao, Y.-B. Zhao, J.-S. Chen, D.-G. Ma, Ultra-simple hybrid white organic light-emitting diodes with high efficiency and CRI trade-off: Fabrication and emission-mechanism analysis, *Org. Electron.* (13) 2012, 2807-2815.
- [30] P. Tao, Y. Miao, Y. Zhang, K. Wang, H. Li, L. Li, X. Li, T. Yang, Q. Zhao, H. Wang, S. Liu, X. Zhou, B. Xu, W. Huang, Highly efficient thienylquinoline-based phosphorescent iridium(III) complexes for red and white organic light-emitting diodes, *Org. Electron.* (45) 2017, 293-301.
- [31] C. Xiang, W. Koo, F. So, H. Sasabe, J. Kido, A systematic study on efficiency enhancements in phosphorescent green, red and blue microcavity organic light emitting devices, *Light: Sci. Appl.* (2) 2013, e74.
- [32] F. Dumur, M. Lepeltier, H. Z. Siboni, D. Gigmes, H. Aziz, Highly efficient organic light-emitting devices prepared with a phosphorescent heteroleptic iridium(III) complex containing 7,8-benzoquinoline as the cyclometalated ligand, *Adv. Optical Mater.* (2) 2014, 262-266.
- [33] B. H. Zhang, G. P. Tan, C. S. Lam, B. Yao, C. L. Ho, L. H. Liu, Z. Y. Xie, W.-Y. Wong, J. Q. Ding, L.-X. Wang, High-efficiency single emissive layer white organic light-emitting diodes based on solution-processed dendritic host and new orange-emitting iridium complex, *Adv. Mater.* (24) 2012, 1873-1877.
- [34] Y. L. Chang, B. A. Kamino, Z. B. Wang, M. G. Helander, Y. L. Rao, L. Chai, S. N. Wang, T. P. Bender, Z. H. Lu, Highly efficient greenish-yellow phosphorescent organic light-emitting diodes based on interzone exciton transfer, *Adv. Funct. Mater.* (23) 2013, 3204-3211.
- [35] H. B. Wu, G. J. Zhou, J. H. Zou, C. L. Ho, W.-Y. Wong, W. Yang, J. B. Peng, Y. Cao, Efficient polymer white-light-emitting devices for solid-state lighting, *Adv. Mater.* (21) 2009, 4181-4184.
- [36] T. Tsuzuki, N. Shirasawa, T. Suzuki, S. Tokito, Color tunable organic light-emitting diodes using pentafluorophenyl-substituted iridium complexes, *Adv. Mater.* (15) 2003, 1455-1458.
- [37] X. M. Yu, G. J. Zhou, C. S. Lam, W.-Y. Wong, X. L. Zhu, J. X. Sun, M. Wong, H. S. Kwok, A yellow-emitting iridium complex for use in phosphorescent multiple-emissive-layer white organic light-emitting diodes with high color quality and efficiency, *J. Organomet. Chem.* (693) 2008, 1518-1527.
- [38] J. H. Yao, C. Zhen, K. P. Loh, Z. K. Chen, Novel iridium complexes as high-efficiency yellow and red phosphorescent light emitters for organic light-emitting diodes, *Tetrahedron* (64) 2008, 10814-10820.
- [39] W. S. Huang, J. T. Lin, C. H. Chien, Y. T. Tao, S. S. Sun, Y. S. Wen, Highly phosphorescent bis-cyclometalated iridium complexes containing benzoimidazole-based ligands, *Chem. Mater.* (16) 2004, 2480-2488.
- [40] Y. Tao, Q. Wang, C. Yang, K. Zhang, Q. Wang, T. Zhou, J. Qin, D. Ma, Solution-processable highly efficient yellow- and red-emitting phosphorescent organic light emitting devices from a small molecule bipolar host and iridium complexes, *J. Mater. Chem.* (18) 2008, 4091-4096.
- [41] X. Liu, W. Liu, D. Wu, X. Wei, L. Wang, H. Wang, Y. Miao, H. Xu, J. Yu, B. Xu, Deep-blue fluorescent emitter based on a 9,9-dioctylfluorene bridge with a hybridized local and charge-transfer excited state for organic light-emitting devices with EQE exceeding 8%, *J. Mater. Chem. C* (8) 2020, 14117-14124.