**Organic Light-Emitting Diodes** 



# Synthesis and Characterization of Highly Efficient Solution-Processable Green Ir(III) Complexes with High Current Efficiency and Very Low Efficiency Roll-Off

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Three new highly efficient green-emitting heteroleptic phosphorescent iridium(III) complexes are designed and synthesized for the fabrication of solution-processable phosphorescent organic light-emitting diodes (PHOLEDs). Their photophysical, thermal, and electroluminescent (EL) properties are systematically investigated. The Ir(III) complexes comprise an amide-bridged trifluoromethyl (-CF<sub>3</sub>)-substituted phenylpyridine unit as the main ligand and picolinic acid (pic) and tetraphenylimidodiphosphinate (tpip) as ancillary ligands. In addition, the 2-ethoxyethnol (EO<sub>2</sub>-) solubilizing group is attached to the 4-position of pic ancillary ligand via tandem reaction, which improved the absolute photoluminescence quantum yields (PLQYs) and EL performance. The high-performance solution-processable PHOLEDs based on the bis[5-methyl-8-trifluoromethyl-5H-benzo(c)(1,5)naphthyridin-6-one](4-(2-ethoxyethoxy picolinate) iridium(III) (Ir1) complex exhibit a maximum external quantum efficiency (EQE) of 24.22% and a maximum current efficiency (CE) of 92.44 cd A<sup>-1</sup>, with the latter being among the best reported CEs achieved though solution processing. In contrast, PHOLEDs with the bis[5-hexyl-8-trifluoromethyl-5H-benzo(c)(1,5)naphthyridin-6-one] (tetraphenylimidodiphosphinato)iridium (Ir3) complex show extremely low efficiency roll-off, with an EQE<sub>max</sub> of 19.40% and an EQE of 19.29% at 10 000 cd m<sup>-2</sup>.

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# **1. Introduction**

In recent years, phosphorescent organic light-emitting diodes (PHOLEDs) have attracted extensive academic and commercial attention for display and lighting devices. As a display technology that has matured over the recent decades, vacuumprocessed organic light-emitting diodes (OLEDs) have achieved external quantum efficiencies (EQEs) over 30%.<sup>[1,2]</sup> Although multiavered device architecture with notable efficiencies has been fabricated, the low material utilization and easy processing of solution-processed OLEDs have made them more attractive than vacuumprocessed counterparts.<sup>[3,4]</sup> However, the prerequisite is to design solution-processable materials with the integrated properties achievable with vacuum-processed OLEDs. Among the three primary components of white light sources, efficient electroluminescent (EL) green color emitters are critical for achieving efficient white light, as human eyes are sensitive to green light (555 nm).<sup>[5,6]</sup> Solution-processable green emitters with excellent EL

properties are the optimal solution for attaining cost-effective large-scale manufacturing and high-performance products.

Heteroleptic Ir(III) complexes [(C^N)2Ir(LX)] bearing two 2-arylpyridinate(C^N) and one ancillary (LX) ligands are among the most promising phosphorescent emitters for optoelectronics and lighting applications.<sup>[7-10]</sup> With the strong spin-orbit coupling of heavy metal phosphors, they have high quantum efficiencies<sup>[11,12]</sup> and easier synthetic accessibility than their homoleptic Ir(III) complex  $[Ir(C \land N)_3]$  counterparts, <sup>[13,14]</sup> along with an emission wavelength that is conveniently tunable by systematic design and functionalization of the organic ligands.<sup>[15-19]</sup> From the perspective of the molecular design, an efficient phosphorescent emitter with the ability to harvest both singlet and triplet excitons could be designed using heavy metals by achieving 100% internal quantum efficiency.<sup>[20-22]</sup> Recent reports have indicated that further enhancing the charge injection and transporting characteristics of phosphorescent emitters will require the introduction of additional special functional



groups to the cyclometalated ligands of these emitters in order to

shorten the excited-state lifetime and/or increase the quantum vield.<sup>[23,24]</sup> Moreover, it should be considered that attaching

PHOLEDs with a low efficiency roll-off. Herein, the tetraphenylimidodiphosphinate acid (Htpip) was used as the ancillary

ligand which consist of more polar P=O and bulky aromatic groups which may improve the electron mobility and effectively

reduce the triplet-triplet annihilation (TTA) and triplet-polaron

quenching (TPQ) effects.<sup>[30-32]</sup> Founded on these research

results, herein we design and synthesize three new heteroleptic

green emitting Ir(III) complexes based on an amide-bridged

trifluromethyl (-CF<sub>3</sub>)-substituted phenylpyridine skeleton with

a solubilizing group. Furthermore, -CF<sub>3</sub> is introduced in the

main ligand not only to reduce the vibrational frequency, but also

to minimize the radiation-less deactivation and thus improve the

EL performance. In addition, the electron-accepting -CF<sub>3</sub> sub-

stituents in the cyclometalated ligand prevent the suppression of

self-quenching action in phosphorescence emitters as they may produce a steric factor around the metal and thereby improve the

device performance.<sup>[33,34]</sup> Moreover, the introduction of a longer

alkyl chain into the metal complexes affords some interesting

properties. We achieved Ir(III) complexes with extremely high

solubility toward organic solvents and reduced intermolecular

interaction, which are major factors necessary to enhance the

device performance of solution-processed PHOLEDs. The synthesized Ir(III) complexes showed better quantum yield than

did the well-known fac-tris(2-phenylpyridine)Ir(III), Ir(ppy)<sub>3</sub>. Via

solution processing, the resulting PHOLEDs achieved a remark-

ably high  $CE_{max}$  of 92.44 cd A<sup>-1</sup> with a corresponding EQE<sub>max</sub> of

24.22%. One of the other Ir(III) complexes also achieved respect-

able  $CE_{max}$  and  $EQE_{max}$  results of 85.31 cd  $A^{-1}$  and 19.40%,



2. Results and Discussion

#### 2.1. Synthesis and Characterization

functional units on the phosphorescent emitters as steric hin-Recently, our group has first reported Ir(III) complexes with drance could efficiently suppress intermolecular interaction and thus reduce self-quenching effects, thereby further optia solubilizing electron-donating ethylene oxide group intromizing these phosphorescent emitters for high-performance duced into the ancillary ligand in order to improve device nondoped PHOLEDs.<sup>[25-27]</sup> For instance, Wong and co-workers performance without compromising the color purity.<sup>[35,36]</sup> Here, introduced a phenoxy group on the cyclometalated ligand of a in order to develop highly efficient solution-processable green green Ir(III) complex-based emitter and achieved a maximum PHOLEDs and to prove the enhancing effect of the solubilizing power efficiency (PE) of 77.6 lm W <sup>-1.[23]</sup> Park et al. achieved group on the device performance, three Ir(III) complexes, a maximum PE of 25.6 lm W<sup>-1</sup> by using side chain-bearing bis[5-methyl-8-trifluoromethyl-5*H*-benzo(c)(1,5)naphthyridinhost and guest units in solution-processed PHOLEDs.<sup>[24]</sup> By 6-one](4-(2-ethoxyethoxy picolinate) iridium(III) (Ir1), bis[5-ethylhexyl-8-trifluoromethyl-5*H*-benzo(c)(1,5)naphthyridin-6-one] using carbazole and diphenylphosphoryl-functionalized Ir(III) complexes as active components, Su and co-workers fabricated (picolinate)iridium(III) (Ir2), and bis[5-hexyl-8-trifluoromethylnondoped PHOLEDs with a maximum current efficiency (CE) 5*H*-benzo(c)(1,5)naphthyridin-6-one] (tetraphenylimidodiand PE of 29.7 cd A<sup>-1</sup> and 31.1 lm W<sup>-1</sup>, respectively.<sup>[28]</sup> In most phosphinato)iridium(III) (Ir3), were designed and successfully of the reported the solution-processed PHOLEDs, the Ir(III) synthesized according to the route shown in Scheme 1 and complexes with oligomeric or polymeric ligand system or den-Scheme S1 (Supporting Information). Most reported solutiondrimers are extensively used in PHOLEDs to enhance the device processable Ir(III) complexes have been synthesized by mulperformance. Moreover, it is the greatest challenge to introduce tiple steps, and complex synthetic processes with additional this macromolecular system into Ir(III) complexes, and addipurification techniques are required.<sup>[35]</sup> Here, the solubilizing tional multistep reaction sequences are required to achieve this group in Ir1 was attached through a tandem reaction, which macromolecular system.<sup>[29]</sup> To overcome this issue, the Ir(III) eliminates the isolation and complicated purification steps. The three Ir(III) complexes, Ir1, Ir2, and Ir3, were purified complexes with the solubilizing 2-ethoxyethnol ( $EO_2$ -) group is more desirable and is an emerging strategy to improve the perby column chromatography and/or recrystallized using suitformance of solution-processed PHOLEDs. In general, the hole able solvents. The structures of these Ir(III) complexes were confirmed by <sup>1</sup>H, mass, and <sup>13</sup>C NMR spectroscopic methods mobility is  $\approx 2-3$  orders of magnitude higher than the electron mobility in OLED.<sup>[30-32]</sup> Furthermore, the Ir(III) complexes with (Figure S1, Supporting Information). high electron mobility is highly preferred to fabricate efficient

#### 2.2. Photophysical and Electrochemical Properties

The emission quantum yields were measured in degassed dichloromethane (DCM) at room temperature (RT) and the well-known green emitter *fac*-Ir(ppy)<sub>3</sub> was used as a reference. Interestingly, Ir1, Ir2, and Ir3 showed higher quantum yield of 80%, 75%, and 47%, respectively. The quantum yields were much higher than that of the standard green emitter fac-Ir(ppy)<sub>3</sub> (40%).<sup>[32]</sup> Furthermore, the study results reveal that the addition of solubilizing group into metal complexes at a suitable position not only improves the solubility but also increases the photoluminescence quantum yield (PLQY) compared to those of previously reported similar molecular structures.<sup>[37,38]</sup> As a result, Ir1 showed maximum EQE among the three Ir(III) complexes as evident from its higher PLQY. The triplet lifetime ( $\tau$ ) was measured in deaerated DCM (1 × 10<sup>-5</sup> M), as shown in Figure S2 (Supporting Information). The measured  $\tau$  values were 0.66, 0.75, and 0.40 us for Ir1, Ir2, and Ir3, respectively. The smallest lifetime of Ir3 may have reduced the TTA, TPQ, and self-quenching, resulting in extremely low efficiency roll-off at high current densities.<sup>[32]</sup> The electrochemical behavior of Ir1, Ir2, and Ir3 was carried out by cyclic voltammetry (CV), as shown in Figure S3 (Supporting Information). The oxidation potential ( $E_{ox}$ ) was calculated by the onset peak at (1.38 eV) with respect to Fc/Fc+, which could be ascribed to metal-centered Ir<sup>III</sup>/Ir<sup>IV</sup> oxidation couple. Therefore, as estimated from the optical band gap  $(E_g)$ , the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)

respectively, with a very low efficiency roll-off.







Scheme 1. Synthetic route of metal complexes.

were -5.7 and -3.2 eV, respectively (Table 1). The Ir3 complex showed a reversible oxidation with a redox potential, which is very similar that for previously reported tpip-based Ir(III) complexes.<sup>[30,37]</sup> Figure 1 shows the molecular orbital distribution from the density functional theory (DFT) calculation of the three green Ir(III) complexes, Ir1, Ir2, and Ir3. The HOMOs of Ir1, Ir2, and Ir3 were mainly distributed over Ir(III) d-orbitals and from a  $\pi$ -orbital localized on the -CF<sub>3</sub>-substituted ppy ligand. For all three complexes, LUMO was mainly located on their ancillary ligand and Ir atom. HOMO-1 of Ir1 and Ir3 is distributed over main ligand and Ir atom while HOMO-1 for Ir2 is distributed mainly in main ligand and Ir atom, and little in ancillary ligand. LUMO-1 for Ir1 and Ir2 is distributed over ancillary, and one of the main ligands while LUMO-1 of Ir3 is mainly located in ancillary ligand and minorly in metal atom and main ligand. Moreover, our computation study was in good agreement with our experimentally calculated energy levels.

IrCl<sub>2</sub>,3H<sub>2</sub>O

2-EtO.EtOH:H<sub>2</sub>O

Figure 2 shows the UV–vis absorption spectra and photoluminescence (PL) spectra measured in DCM solution  $[10^{-5} M]$  and neat film of Ir1, Ir2, and Ir3 at RT, while the low-temperature spectra were measured in 2-methyltetrahydrofuran matrix at

77 K. The detailed photophysical, electrochemical, and thermal properties are summarized in Table 1. The absorption spectra of Ir1, Ir2, and Ir3 showed intense absorption peaks at 334 and 345 nm, which was assigned to the spin-allowed  ${}^{1}\pi - \pi^{*}$  transitions of cyclometalated ligands. The next long tail absorption in the region of 400-460 nm was reasonably assigned to a mixed state of metal-to-ligand charge transfer <sup>1</sup>MLCT and <sup>3</sup>MLCT resulting from spin-orbital coupling. The introduction of the 2-ethoxyethnol (EO<sub>2</sub>-) group in Ir1 did not affect the optical properties, possibly because the EO<sub>2</sub>- group was attached to the ancillary ligand by ether linkage.<sup>[35,36]</sup> Thus, this additional solubilizing group may have enhanced the solubility of the Ir(III) complexes, resulting in homogeneous and tightly packed films. The optical band gaps ( $E_g^{opt}$ ) of the three Ir(III) complexes were measured from the UV-vis absorption edge (Table 1). The three new Ir(III) complexes emitted bright green light upon UV irradiation. Upon photoexcitation at corresponding MLCT absorption band, the Ir1, Ir2, and Ir3 complexes exhibit almost featureless emission spectra with maximum PL (PLmax) at 514, 510, and 534 nm, respectively, which clearly reveals that the emissions of the three Ir(III) complexes originated from the

Table 1. Thermal, photophysical, and electrochemical properties of the Ir(III) complex.

Complexes	$T_{\rm g}/T_{\rm d}$ [°C]	$\lambda_{PL}^{a)}$ [nm]		λ <sub>PL</sub> [nm]	PLQY <sup>b)</sup> [%]	<i>Τ</i> [μs]	HOMO [eV]	LUMO [eV]	$E_{\rm g}^{\rm c)}$ [eV]
		CH <sub>2</sub> Cl <sub>2</sub>	Neat film	77 K	CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>			
lrl	112/353	514	523	502	80%	0.66	-5.7	-3.2	2.5
lr2	147/364	510	515	501	75%	0.75	-5.7	-3.2	2.5
lr3	161/340	530	536	516	47%	0.40	-5.6	-3.3	2.3

<sup>a)</sup>Measured in CH<sub>2</sub>Cl<sub>3</sub> solution at RT ( $1 \times 10^{-5}$  M); <sup>b)</sup>Relative PLQY; <sup>c)</sup>HOMO is calculated from the onset oxidation potentials from CV, LUMO =  $E_g$  (optical) + HOMO.





Figure 1. Contours and contributions of the frontier molecular orbitals of the studied Ir(III) complexes.

<sup>3</sup>MLCT or <sup>3</sup>ligand to ligand charge transfer (LLCT) state and not from ligand center (LC) <sup>3</sup> $\pi$ – $\pi$ <sup>\*</sup>, which always show vibronically structured emission spectra.<sup>[39]</sup> Furthermore, a small PL redshift was observed in the neat film, which revealed the aggregation and/or strong intermolecular interactions between the Ir(III) complexes in thin films. At low-temperature emission spectra at 77 K, both Ir(III) complexes show much structured emission spectra, which display rigidochromic blueshifts relative to RT emission spectra ensuring that LC  ${}^{3}\pi$ - $\pi$ \* nature of the emissive excited state.<sup>[39]</sup> As shown in Figure S4 (Supporting Information), the UV-vis spectrum of the guests and the PL spectra of the mixed hosts show a large overlapping area, and thus the host materials can effectively transfer their energy to the green emitters, leading to a higher device efficiency.<sup>[40]</sup> The transient PL results revealed that the triplet lifetimes ( $\tau$ ) of the host films doped with the three Ir(III) complexes decreased in the order, Ir2 > Ir1 > Ir3, which is in agreement with those measured in solution and nondoped film.

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#### 2.3. Thermal Properties

The thermal properties of Ir1, Ir2, and Ir3 were investigated under nitrogen atmosphere using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) as shown in Figures S5 and S6 (Supporting Information). The decomposition temperatures of Ir1, Ir2, and Ir3 corresponding to 5% weight loss were 353, 364, and 340 °C, respectively, indicating their good thermal stability of the Ir(III) complexes, which is essential for the efficient fabrication of OLEDs. Compared to Ir1 and Ir3, the DSC analysis of Ir2 revealed a higher glass transition temperature ( $T_g$ ) in the range of 112–161 °C, which



Figure 2. UV-vis and PL spectra of a) Ir1, b) Ir2, and c) Ir3 in solution and in film state.

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supported its good film morphological stability at RT (Table 1). The lower  $T_{\rm g}$  value of Ir1 is due to presence of solubilizing chain.<sup>[36]</sup>

# 2.4. Electroluminescent Properties of Green PHOLEDs via Solution Processing

Figure S7 (Supporting Information) shows the atomic force microscope (AFM) 3D images of single (4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP)) and mixed (4,4',4"-tris(N-carbazolyl)triphenvlamine (TCTA) and 1,3,5-tris(N-phenyl-benzimidazol-2-yl) benzene (TPBi)) host films containing the corresponding Ir(III) complexes by spin coating. The respective root mean square (RMS) surface roughness values of films with CBP as host were 0.62, 0.66, and 0.69 nm for Ir1, Ir2, and Ir3, respectively, while RMS values for mixed host with the respective complexes (Ir1, Ir2, and Ir3) were measured to be 0.48, 0.50, and 0.56 nm, respectively. All six films exhibited a homogeneous and smooth morphology with barely any significant surface morphological difference among them. To understand the EL properties of the three different Ir(III) complexes, we fabricated devices A (Ir1), B (Ir2), and C (Ir3) with CBP chosen as the host because of its favorable factors such as low electron injection barrier, effective host-to-guest energy transfer, ability to generate excitons in both host and guest, and effective hole confining function.<sup>[41]</sup> From Figure 3 (energy level), the dopant molecules favor the minority carriers (electrons) leading to the generation of excitons in the guest by the balanced carrier injection. However, increased efficiency requires that sufficiently numerous excitons are generated in the host. The lower injection barrier for electrons facilitates the injection of electrons leading to a desirable and balanced carrier injection on the host. As the applied bias voltage is increased, more electrons could be trapped in the host due to the saturating electrons being trapped by the scarcity of guest molecules. Thus, the electrons trapped in the CBP host assist in attracting holes, which increases the number of excitons generated in host and thus facilitates effective energy transfer from host to guest. Devices were fabricated with a device structure of indium tin oxide (ITO)/PEDOT:PSS (40 nm)/EML (30 nm)/TPBi (40 nm)/LiF (1 nm)/Al (120 nm), while TPBi was the electron transport layer (ETL). Table 2 summarizes the EL performances of the PHOLEDs using different dopants in single- and double-host systems. Figure 4 shows the current density-voltage-luminance (I-V-L) characteristic of the devices fabricated using CBP as the host. Devices with the Ir1, Ir2, and Ir3 complexes exhibited a maximum luminance of 22 083, 34 729, and 16 993 cd  $m^{-2}$ , respectively. Figure 4 shows that device A exhibits a maximum EQE and CE of 18.51% and 70.18 cd A<sup>-1</sup> with a commission internationale de l'éclairage (CIE) of (0.33, 0.61), respectively, compared to 17.20% and 61.22 cd  $A^{-1}$  for device B with a CIE of (0.34, 0.61), 7.19% and 26.31 cd  $A^{-1}$  for device C with a CIE of (0.38, 0.58), respectively. Devices A and B show  $\text{EL}_{\text{max}}$  values of 523 and 522 nm (Figure 4d), respectively, while device C's emission peak is at 534 nm.

Further, a double host with different carrier transport properties, i.e., one material with better hole-transporting properties and one with better electron-transporting properties, was chosen to fabricate the devices. The mixed host was







Figure 3. a) Energy level diagram and b) chemical structures of the employed materials.

comprised of TCTA and an electron-transporting host, TPBi in 1:1 weight ratio doped with 15 wt% of Ir1 and Ir2, and 12 wt% of Ir3. Devices D (Ir1), E (Ir2), and F (Ir3) were fabricated with a device structure of ITO/PEDOT:PSS (40 nm)/EML (50 nm)/ TPBi (40 nm)/LiF (1 nm)/Al (120 nm). These mixed host emitting layer (EML) provided balanced charge carrier transport in the EML, improved device lifetime behavior<sup>[42]</sup> and prevented charge accumulation at the interfaces.<sup>[43]</sup> In the *I-V-L* characteristics shown in Figure 5, devices D, E, and F showed maximum luminance of 42 249, 35 292, and 29 745 cd  $\mathrm{m}^{-2}$ with turn-on voltages (Von) of 5.3, 5.0, and 5.4 V, respectively. Figure 5b,c shows the EQE versus luminance and the CE-current density-PE curve of devices D-F. Device D showed an excellent  $CE_{\rm max}$  of 92.44 cd  $A^{-1}$  and a maximum EQE of 24.22% with a CIE of (0.33, 0.61). This is one of the best reported CE results for solution-processed green PHOLEDs. Similarly, PHOLEDs with Ir2 also showed a high CE of 84.25 cd A<sup>-1</sup> and a maximum EQE of 23.53% with a CIE of (0.34, 0.61). Although device F showed a maximum EQE

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Device	Host	Guest	OV [V]	EQE [%] Max., @10 000 cd m <sup>-2</sup>	CE [cd A <sup>-1</sup> ]	PE [lm W <sup>-1</sup> ]	CIE [x, y]	CIE [x, y] EL <sub>max</sub> [nm]	Maximum luminance [cd m <sup>-2</sup> ]
					Max., @30 mA cm <sup>-2</sup>		@30 mA cm <sup>-2</sup>		-
A	CBP	lr1	5.6 <sup>a)</sup> , 7.3 <sup>b)</sup>	18.51, 11.47	70.18, 39.52	22.88, 13.94	0.335, 0.615	521	22 083
В		lr2	5.7 <sup>a)</sup> , 8.2 <sup>b)</sup>	17.20, 15.50	61.22, 47.40	17.49, 12.34	0.340, 0.612	522	34 729
С		lr3	5.7 <sup>a)</sup> , 8.7 <sup>b)</sup>	7.19, 7.07	26.31, 26.20	6.75, 6.49	0.380, 0.587	534	16 993
D	ТСТА:ТРВі	lr1	5.3 <sup>a)</sup> , 8.5 <sup>b)</sup>	24.22, 22.91	92.44, 60.53	26.43, 17.98	0.331, 0.617	520	42 249
E		lr2	5.0 <sup>a)</sup> , 7.6 <sup>b)</sup>	23.53, 16.71	84.25, 49.56	33.08, 15.01	0.340, 0.612	522	35 292
F		lr3	5.4 <sup>a)</sup> , 8.7 <sup>b)</sup>	13.58, 13.27	46.22, 44.24	13.19, 11.47	0.382, 0.587	534	29 745
G		lr1	4.6 <sup>a)</sup> , 7.82 <sup>b)</sup>	25.91, 19.22	89.11, 84.79	32.69, 30.56	0.330, 0.617	520	51 808
н		lr2	4.5 <sup>a)</sup> , 9.2 <sup>b)</sup>	25.12, 19.31	87.10, 86.77	37.96, 37.49	0.340, 0.612	522	39 618
I		lr3	5.1 <sup>a)</sup> , 8.3 <sup>b)</sup>	19.40, 19.29	85.31, 81.91	20.30, 17.72	0.383, 0.596	534	54 914

 Table 2. Device performance of green PHOLEDs using Ir1, Ir2, and Ir3 complexes as guests.

 $^{a)}\mbox{Operation}$  voltage (OV) at 1 cd m  $^{-2};$   $^{b)}\mbox{OV}$  at 10 000 cd m  $^{-2}.$ 

of 13.58%, it exhibited a very low efficiency roll-off of 13.27% (EQE) at 10 000 cd m<sup>-2</sup>. Additionally, devices G-I were fabricated using an interlayer 4,4'cyclohexylidenebis[N,N-bis(4methylphenyl)benzenamine] (TAPC) at the interface of holeinjecting layer (HIL) and EML with the dopants Ir1, Ir2, and Ir3, respectively, with the device structure of ITO/PEDOT:PSS (40 nm)/TAPC (8 nm)/EML (60 nm)/TPBi (50 nm)/LiF (1 nm)/ Al (120 nm). Figure 6 and Figure S8 (Supporting Information) show the electro-optical characteristics (J-V-L, CE-current density-PE, and EQE-luminance) of Ir1, Ir2, and Ir3 with TAPC interlayer. Devices G and H achieved maximum brightness values of 51, 808, and 39 618 cd  $m^{-2}$  with EQE<sub>max</sub> of 25.91% and 25.12%, respectively. Device I showed a maximum luminance of 54 914 cd m<sup>-2</sup>. PHOLEDs with the Ir3 achieved a maximum EQE of 19.40%, 19.29% at 10 000 cd  $m^{-2}$ , and a maximum CE of 85.31 and 81.91 cd A<sup>-1</sup> at 30 mA cm<sup>-2</sup>. It could be seen that the EL efficiency roll-off in device I was very low and the resulting high efficiencies at relatively high current densities was observed. For device I, the CE values at the practical luminance of 10 000 and 50 000 cd m<sup>-2</sup> were 84.81 and 69.03 cd A<sup>-1</sup>, respectively. Device I also achieved EQE of 19.29% and 15.73% at 10 000 and 50 000 cd m<sup>-2</sup>, respectively. This efficiency roll-off of devices with Ir3 was attributed to the application of tpip as the ancillary ligand (presence of more polar P=O) and bulky substituents ( $-CF_3$ ) in the main ligand, which decreased the self-quenching and improved the hole–electron balance in charge injection. This balanced charge transport facilitated the injection and broadened the recombination zone.

Roll-off in PHOLEDs is usually resulted due to the possible quenching process: TTA and TPQ.<sup>[44]</sup> To figure out this issue, the TTA model was employed to fit J–EQE curves using the equation



Figure 4. a) J-V-L characteristics, b) CE-luminance-PE curves, c) EQE versus luminance, and d) EL spectra of devices A-C.





Figure 5. a) J–V–L characteristics, b) CE–luminance–PE curves, and c) EQE versus luminance curves of devices D–F.

$$\frac{\eta}{\eta_0} = \frac{J_0}{4J} \left( \sqrt{1 + 8\frac{J}{J_0}} - 1 \right) \tag{1}$$

where  $\eta$  and  $\eta_0$  refer to EQE with and without TTA and  $J_0$  is the critical current density at  $\eta = \eta_0/2$ . EQE curves fitted for complex Ir1 and Ir2 were in agreement with the TTA model (Figure S9, Supporting Information), indicating that the TTA process is responsible for efficiency roll-off at high current densities.  $J_0$  values, defined as the current density at  $\eta = \eta_0/2$  for devices with Ir1 and Ir2, were 91.86 and 84.2 mA cm<sup>-2</sup>, respectively.

Lifetime of PHOLEDs with the synthesized complexes was tested and is shown in Figure S10 (Supporting Information). Device structure of devices D–F was used for the stability measurement. Lifetime measurements were carried out for devices after encapsulation under continuous electrical stress. With the initial luminance of 6000 cd m<sup>-2</sup>, devices with Ir3 showed better stability while Ir1 and Ir2 exhibited a similar lifetime stability.

These study results demonstrate that the addition of a solubilizing group to the Ir(III) complex at a suitable position not only improves the overall solubility of the Ir(III) complex, but also increases the emission quantum yield.<sup>[38]</sup> In particular, the balanced charge injection and broadened recombination zone suppress TTA and TPQ, and improve the recombination probability with low EL efficiency roll-off.<sup>[43]</sup>

#### 3. Conclusion

In summary, we designed and synthesized three new highly efficient green emitting Ir(III) complexes for high-performance solution-processed PHOLEDs. The introduction via tandem reaction of an EO<sub>2</sub>- solubilizing group into the ancillary ligand in the Ir(III) complexes did not affect the optical and electrical properties of the Ir(III) complexes and improved the PLQY and EL performance of solution-processed PHOLEDs without compromising the color characteristics. Photophysical, thermal, electrochemical, and electro-optical studies were conducted to understand the characteristics of the Ir(III) complexes. The Ir1 complex showed a high PLQY of 80%. PHOLEDs were fabricated using CBP as the single host and TCTA:TPBi (1:1) as the mixed host to evaluate their PHOLED performances. An impressively high  $CE_{max}$  of 92.44 cd  $A^{-1}$  and an EQE of 24.22% were achieved using Ir1 and the mixed host system. These are among the best reported CE results for solution-processed green PHOLEDs. PHOLEDs incorporating the complex Ir3 achieved an EQE\_{max} of 19.40% and a CE\_{max} of 85.31 cd  $A^{-1},$ while still retaining exceptionally low efficiency roll-off, with CE and EQE of 84.81 cd  $A^{-1}$  and 19.29% at 10 000 cd  $m^{-2}\!,$  and 69.03 cd  $A^{-1}$  and 15.73% at 50 000 cd  $m^{-2}$ , respectively. This low-efficiency roll-off effect is exceptionally favorable for the commercial fabrication of solution-processed devices.

#### 4. Experimental Section

Synthesis of 2-Chloro-N-methylpyridin-3-amine (a): A solution of 3-amino-2-chloropyridine (2.46 g, 19.2 mmol) in anhydrous tetrahydrofuran (THF) (50 mL) was added to a suspension of sodium hydride (NaH) (0.78 g, 19.2 mmol, 60% dispersion in oil) and THF (50 mL) under nitrogen atmosphere. The reaction mixture was stirred at RT for 3 h. Afterward, iodomethane (1.2 mL, 19.2 mmol) was added, and the reaction mixture was heated to 40 °C for 9 h. After cooling to RT, the solvent was removed and the crude material was dissolved in DCM and filtered to remove any salt. The filtrate was purified by column chromatography on silica gel using ethyl acetate (EtOAc): *n*-hexane (10:90% as an eluent (v/v) to afford compound **a** as a pale-yellow liquid (1.52 g). (yield: 62%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, $\delta$ ): 7.72 (d, 1H), 7.18–7.0 (m, 1H), 6.8 (d, 1H), 4.2 (s, 1H), 3.16 (d, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 141.8, 137.0, 136.2, 123.6, 116.9, 30.0.

Synthesis of (N-(2-Chloropyridin-3-yl)-N-methyl-3-(trifluoromethyl) benzamide) (b): NaH (2.8 g, 7.1 mmol) was added to anhydrous







Figure 6. a) J-V-L characteristics, b) CE-luminance-PE curves, c) EQE versus luminance, and d) EL spectra of device I.

THF (30 mL) and the mixture was cooled to 0 °C under nitrogen atmosphere. Compound (a) (5 g, 3.5 mmol) was added into the reaction mixture and stirred for 1 h. After that, 3-(trifluoromethyl)benzoyl chloride (10.97 g, 52.59 mmol) was added and stirred for 8 h at RT. After reaction completion, water (50 mL) was added into the reaction mixture to quench the reaction. Finally, the organic layer was extracted with DCM, washed with brine solution, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:*n*-hexane (20:80% v/v) as an eluent to afford **b** as a white solid (3.5 g,). (yield: 70%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, $\delta$ ): 8.25 (s, 1H), 7.63 (s, 1H), 7.54 (d, 3H), 7.38–7.29 (s, 1H), 7.18 (s, 1H) 3.33 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 169.6, 149.5, 138.8, 139.4, 134.5, 132.3, 131.1, 130.8, 129.1, 123.8, 123.7, 123.6, 128.5, 37.5.

Synthesis of (5-Methyl-8-(trifluoromethyl)benzo[c][1, 5]naphthyridin-6(5H)-one) (c): The mixture of compound (b) (2 g, 6.0 mmol), Pd (PPh<sub>3</sub>)<sub>4</sub> (0.7 g, 0.59 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.18 g, 30 mmol), and 2-(dimethylamino) ethyl methacrylate (DMA) (30 mL) was stirred at 150 °C for 4 h. After that, the reaction mixture was cooled to RT and water (50 mL) was added. The resulting mixture was extracted with DCM (100 mL), and the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:*n*-hexane (8:92% v/v) as an eluent to afford **c** as a white solid (1.5 g). (yield: 75%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, $\delta$ ): 8.96 (s, 1H), 8.80 (s, 1H), 8.62 (s, 1H), 8.05 (s, 1H), 7.77 (d, 1H), 7.58 (s, 1H) 3.88 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 161.1, 146.5, 144.9, 138.4, 137.8, 132.9, 130.7, 129.0, 128.2, 124.7, 124.3, 122.7, 122.6, 38.0.

Synthesis of 2-Chloro-N-(2-ethylhexyl)pyridin-3-amine (d): A solution of 3-amino-2-chloropyridine (5 g, 38.89 mmol) in anhydrous THF (50 mL) was added to a suspension of NaH (1.65 g, 38.89 mmol, 60% dispersion in oil) and THF (50 mL) under nitrogen atmosphere. After the reaction mixture was stirred at RT for 3 h, 2-ethylhexyl bromide (5.78 mL, 38.89 mmol) was added, and the reaction mixture was heated to 40 °C for 9 h. After cooling to RT, the solvent was removed and the crude material was dissolved in DCM and filtered to remove any salt. The filtrate was purified by column chromatography on silica gel using EtOAc:*n*-hexane (10:60% v/v) as an eluent to afford compound d as a pale-yellow liquid (3.1 g). (yield: 62%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,

 $\delta):$  7.64–7.63 (d, 1H), 7.06–7.02 (m, 1H), 6.84–6.81 (d, 1H), 4.33 (s, 1H), 3.01 (t, 2H), 1.57–1.55 (d, 1H), 1.41–1.28 (m, 8H), 0.87 (m, 6H).  $^{13}\text{C}$  NMR (75 MHz, CDCl3,  $\delta):$  146.8, 140.5, 139.8, 124.7, 123.6, 55.1, 40.8, 32.0, 29.3, 26.0, 23.2, 14.1, 12.6.

Synthesis of N-(2-Chloropyridin-3-yl)-N-(2-ethylhexyl)-3-(trifluoromethyl) benzamide (e): NaH (1.39 g, 58.14 mmol) was added to anhydrous THF (30 mL) and the mixture was cooled to 0 °C under nitrogen atmosphere. Compound (d) (5 g, 29.07 mmol) was added to the reaction mixture and stirred for 1 h. After that, 3-(trifluromethyl)benzoyl chloride (9.09 g, 43.61 mmol) was added and stirred for 8 h at RT. After completion of the reaction, the reaction mixture was quenched by the addition of water (50 mL). Finally, the organic layer was extracted with DCM, washed with brine solution, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:n-hexane (10:40% v/v) as an eluent to afford **e** as a white solid (3.5 g). (yield: 70%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> δ): 8.25 (s, 1H), 7.45–7.56 (d, 4H), 7.32 (d, 1H), 7.18 (s, 1H), 7.18 (s, 1H), 4.15 (s, 1H), 3.25-3.23 (t, 1H), 1.32-1.22 (d, 8H), 0.98 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 169.3, 149.5, 138.8, 139.4, 134.5, 132.3, 131.1, 130.8, 129.1, 128.5, 124.8, 123.7, 123.6, 49.2, 37.1, 32.0, 29.3, 26.0, 23.0, 14.1, 11.6.

Synthesis of 5-(2-Ethylhexyl)-8-(trifluoromethyl)benzo[c][1,5]naphthyridin-6(5H)-one (f): The mixture of compound (e) (4 g, 10.62 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.6 g, 0.53 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.18 g, 53.10 mmol), and of DMA (30 mL) was stirred at 150 °C for 4 h. Then the reaction mixture was cooled to RT and water (50 mL) was added. The resulting mixture was extracted with DCM (100 mL) and the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:*n*-hexane (10:60% v/v) as an eluent to afford f as a white solid (3 g). (yield: 75%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.99–8.96 (d, 1H), 8.79 (s, 1H), 8.61 (s, 1H), 8.03–8.01 (d, 1H), 7.73–7.70 (d, 1H), 7.51 (s, 1H), 4.38–4.27 (d, 2H), 1.90 (s, 1H), 1.40–1.29 (m, 8H), 0.94–0.87 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 161.8, 146.5, 144.9, 138.4, 137.8, 132.9, 130.7, 129.0, 128.0, 124.7, 124.3, 122.7, 122.6, 50.7, 37.1, 32.0, 29.3, 26.0, 23.0, 14.1, 12.6.

Synthesis of 2-Chloro-N-hexylpyridin-3-amine (g): A solution of 3-amino-2-chloropyridine (5 g, 38.9 mmol) in anhydrous THF (50 mL) was added to a suspension of sodium hydride (NaH) (1.5 g, 38.9 mmol, 60% **1DVANCED** 

dispersion in oil) and THF (50 mL) under nitrogen atmosphere. The reaction mixture was stirred at RT for 3 h. Afterward, 1-bromohexane (5.4 mL, 38.9 mmol) was added and the reaction mixture was heated to 40 °C for 9 h. After cooling to RT, the solvent was removed and the crude material was dissolved in DCM and filtered to remove any salt. The filtrate was purified by column chromatography on silica gel using EtOAc:*n*-hexane (10:90% v/v) as an eluent to afford compound **g** as pale-yellow liquid (3.1 g). (yield: 62%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> $\delta$ ): 7.62–7.61 (d, 1H), 7.04–6.99 (m, 1H), 6.81–6.78 (d, 1H), 4.27 (s, 1H), 3.09–302 (q, 2H), 1.61–1.54 (m, 2H), 1.36–1.26 (6H, m), 0.86–0.82 (t, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> $\delta$ ): 146.8, 140.5, 139.8, 124.7, 124.6, 51.8, 32.7, 31.5, 27.7, 23.7, 14.1.

N-(2-Chloropyridin-3-yl)-N-hexyl-3-(trifluoromethyl) Synthesis of benzamide (h): NaH (1.88 g, 47.41 mmol) was added to anhydrous THF (30 mL) and the mixture was cooled to 0 °C under nitrogen atmosphere. Compound (g) (5 g, 23.50 mmol) was added to the reaction mixture and stirred for 1 h. After that, 3-(trifluoromethyl)benzoyl chloride (7.353 g, 35.25 mmol) was added and stirred for 8 h at RT. After completion of the reaction, the reaction mixture was guenched by the addition of water (50 mL). Finally, the organic layer was extracted with DCM, washed with brine solution, and dried over anhydrous  $\mathsf{Na_2SO_4}$ The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:*n*-hexane (10:40 v/v) as an eluent to afford h as a white solid (3.5 g). (yield: 70%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> δ): 8.24 (s, 1H), 7.54–7.46 (d, 4H), 7.27–7.25 (t, 1H), 7.17 (s, 1H), 4.12-4.07 (s, 1H), 3.59-3.49 (m, 1H), 1.59-1.56 (d, 2H), 1.27 (s, 6H), 0.84 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 169.3, 149.5, 139.8, 139.4, 134.5, 132.3, 131.8, 131.1, 129.1, 128.5, 124.8, 124.7, 124.6, 44.0, 31.5, 27.4, 27.7, 22.7, 14.1.

Synthesis of 5-Hexyl-8-(trifluoromethyl)benzo[c][1,5]naphthyridin-6(5H)one (i): The mixture of compound (h) (4 g, 10.39 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.6 g, 0.519 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.18 g, 51.97 mmol), and DMA (30 mL) was stirred at 150 °C for 4 h. Then the reaction mixture was cooled to RT and water (50 mL) was added. The resulting mixture was extracted with DCM (100 mL) and the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:*n*-hexane (10:60 v/v) as an eluent to afford i as a white solid (3 g). (yield: 75%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.99–8.96 (d, 1H), 8.78 (s, 1H), 8.61 (s, 1H), 8.03–8.01 (d, 1H), 7.72–7.69 (d, 1H), 7.53 (m, 1H), 4.34–4.32 (m, 2H), 1.77–1.68 (m, 2H), 1.47–1.35 (m, 6H), 0.90 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 161.8, 146.5, 144.9, 138.4, 137.8, 132.9, 130.7, 129.0, 128.0, 124.7, 124.3, 122.7, 122.6, 45.5, 32.5, 27.7, 27.4, 23.7, 14.1.

Synthesis of Iridium Dimer Complex: Compounds (c, f, or i) (1.5 g, 53.91 mmol) and  $IrCl_3$ · $3H_2O$  (0.76 g, 134.77 mmol) were added to a mixture of 2-ethoxyethanol and water (40 mL, 3:1 v/v). The reaction mixture was stirred at 140 °C for 20 h and a yellow precipitate was obtained and cooled to RT. The precipitate was filtered and washed with water (60 mL) and methanol (10 mL) and subsequently dried under vacuum to afford a compound as yellow solid.

Synthesis of bis[5-Methyl-8-trifluoromethyl-5H-benzo(c)(1,5)naphthyridin-6-one](4-(2-ethoxyethoxy picolinate)iridium(III), Ir1 via Tandem Reaction: A solution of compound (j) (1 g, 0.63 mmol), 4-chloropicolinic acid (0.504 g, 3.19 mmol), and  $Na_2CO_3$  (0.67 g, 6.39 mmol) in 2-ethoxyethanol (25 mL) was stirred at 120 °C under nitrogen atmosphere for 12 h. After cooling to RT, the reaction mixture was poured into water and extracted with DCM. The organic layer was dried over anhydrous Na2SO4 and concentrated under vacuum, giving a residue that was purified by column chromatography silica gel using methanol (MeOH): EtOAc (30:70% v/v) as an eluent to afford compound Ir1 as a yellow solid (0.5 g). (yield: 50%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>  $\delta$ ): 8.70 (d, J = 5.4 Hz, 1H), 8.18 (s, 1H), 8.12 (s, 1H), 7.86 (d, J = 2.6Hz, 1H), 7.76 (d, J = 8.6 Hz, 2H), 7.57–7.52 (m, 1H), 7.44 (d, J = 5.6Hz, 2H), 7.38-7.33 (m, 1H), 6.93-6.90 (m, 1H), 6.83 (s, 1H), 6.62 (s, 1H), 4.25 (d, J = 2.9 Hz, 2H), 3.84 (s, 6H), 3.79–3.76 (m, 2H), 3.56 (q, J = 7.0 Hz, 2H), 1.20 (t, J = 7.0 Hz, 3H).<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 173.0, 167.0, 161.5, 161.4, 153.5, 150.3, 149.2, 148.8, 147.1, 144.9, 142.9, 142.0, 135.3, 134.8, 132.4, 132.0, 131.9, 131.5, 131.2, 131.2,

130.8, 130.7, 126.7, 126.4, 125.5, 125.4, 124.7, 124.5, 123.1, 123.0, 121.9, 121.8, 118.6, 118.6, 118.0, 118.0, 116.7, 113.7, 68.9, 68.1, 67.1, 30.0, 29.9, 15.2. FAB<sup>+</sup> MS (m/z): [M + H]<sup>+</sup> calcd. for C<sub>38</sub>H<sub>28</sub>F<sub>6</sub>IrN<sub>5</sub>O<sub>6</sub>, 957.16.32; found 958.16.

Synthesis of bis[5-Ethylhexyl-8-trifluoromethyl-5H-benzo(c)(1,5)naphthyridin-6-one] (picolinate)iridium(III) Ir2: A solution of compound (k) (1 g, 0.63 mmol), 2-picolinic acid (0.504 g, 3.19 mmol), and Na<sub>2</sub>CO<sub>3</sub> (0.67 g, 6.39 mmol) in 2-ethoxyethanol (25 mL) was stirred at 120 °C under nitrogen atmosphere for 12 h. After cooling to RT, the reaction mixture was poured into water and extracted with DCM. The organic layer was dried over anhydrous Na2SO4 and concentrated under vacuum, giving a residue that was purified by column chromatography silica gel using MeOH:EtOAc (40:60% v/v) as an eluent to afford compound Ir2 as a yellow solid (0.5 g). (yield: 50%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>  $\delta$ ): 8.72 (d, J = 5.4 Hz, 1H), 8.38 (d, J = 7.7 Hz, 1H), 8.19 (s, 1H), 8.12 (s, 1H), 7.99 (t, / = 7.7 Hz, 1H), 7.78–7.72 (m, 3H), 7.58–7.53 (m, 1H), 7.46-7.42 (m, 1H), 7.38-7.30 (m, 2H), 6.82 (s, 1H), 6.53 (s, 1H), 4.49-4.24 (m, 4H), 2.02-1.86 (m, 2H), 1.60-1.25 (m, 17H), 1.00-0.82 (m, 11H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 173.0, 167.0, 161.5, 161.4, 153.5, 150.3, 149.2, 148.8, 147.1, 144.9, 142.9, 142.0, 135.3, 134.8, 132.4, 132.0, 131.9, 131.5, 131.2, 131.2, 130.8, 130.7, 126.7, 126.4, 125.5, 125.4, 124.7, 124.5, 123.1, 123.0, 121.9, 121.8, 118.6, 118.6, 118.0, 118.0, 116.7, 113.7, 68.9, 68.1, 67.1, 30.0, 29.9, 15.2. FAB<sup>+</sup> MS (m/z): [M + H]<sup>+</sup> calcd. for C<sub>48</sub>H<sub>48</sub>F<sub>6</sub>IrN<sub>5</sub>O<sub>4</sub>, 1065.32; found, 1066.33.

Synthesis of bis[5-Hexyl-8-trifluoromethyl-5H-benzo(c)(1,5)naphthyridin-6-one](Tetraphenylimidodiphosphinato)Iridium(III). Ir3: A solution of compound (I) (1 g, 0.54 mmol) and ktpip<sup>[32]</sup> (0.617 g, 1.35 mmol) in 2-ethoxyethanol (25 mL) was stirred at 140 °C under nitrogen atmosphere for 24 h. After cooling to RT, the reaction mixture was poured into water and extracted with DCM. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum, giving a residue that was purified by column chromatography silica gel using MeOH:EtOAc (20:80% v/v) as an eluent to afford compound, Ir3 as a yellow solid (0.3 g). (yield: 40%) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.83 (d, J = 5.1 Hz, 2H), 8.06 (s, 2H), 7.78–7.72 (m, 4H), 7.41–7.30 (m, 7H), 7.26-7.24 (m, 1H), 7.19-7.08 (m, 6H), 7.06-6.99 (m, 2H), 6.91-6.82 (m, 4H), 6.52 (s, 2H), 4.40-4.25 (m, 4H), 1.90-1.80 (m, 4H), 1.62-1.36 (m, 13H), 0.95 (t, J = 6.4 Hz, 5H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 161.4, 149.5, 148.2, 143.5, 140.4, 139.9, 138. 4, 133.2, 130.8, 130.1, 130.6, 130.6, 130.5, 129.9, 128.3, 128.1, 127.5, 127.3, 125.7, 123.2, 122.1, 117.5, 117.4, 43.0, 31.8, 27.1, 26.9, 22.8, 14. 4. FAB<sup>+</sup> MS (*m*/*z*): [M + H]<sup>+</sup> calcd. for C<sub>62</sub>H<sub>56</sub>F<sub>6</sub>IrN<sub>5</sub>O<sub>4</sub>P<sub>2</sub>, 1303.33; found, 1304.34.

Theoretical Calculation: The calculations reported here were carried out by using the Gaussian  $09^{[45]}$  software package. Ground state DFT calculations were performed to understand the molecular distributions of the Ir(III) complexes. The DFT calculations of the Ir(III) complexes were performed using the B3LYP functional with the 6–31G (d,p) basis set for C, H, N, O, and F, and LANL2DZ for the Ir atom. To understand the spatial distribution of the frontier molecular orbitals clearly, the contour plots of LUMO + 1 to HOMO – 1 of Ir1, Ir2, and Ir3 were simulated, and the calculated energies are provided in Table S1 (Supporting Information).

Device Fabrication and Measurement: The HIL, poly(3,4-ethylened ioxythiophene):polystyrenesulfonate (PEDOT:PSS) was spin-coated onto the UV–ozone-treated ITO-coated glass substrate, followed by annealing in air for 15 min at 150 °C, respectively. The EML was then spin-coated onto the HILs and annealed at 100 °C for 30 min in nitrogen atmosphere. ETL, LiF, and Al were sequentially deposited over the EML layer in vacuum at a pressure of  $5 \times 10^{-6}$  Torr. All measurements of devices were carried out under ambient condition at RT. The thickness of each layer was measured by an Alpha-step IQ surface profiler (KLA Tencor, San Jose, CA).

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

### **Keywords**

green iridium complexes, high current efficiency, organic light-emitting diodes, solubilizing group, very low efficiency roll-off

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