

Red Phosphorescent Bis-Cyclometalated Iridium Complexes with Fluorine-, Phenyl-, and Fluorophenyl-Substituted 2-Arylquinoline Ligands

Jwajin Kim,^[a] Kum Hee Lee,^[a] Seok Jae Lee,^[b] Ho Won Lee,^[b] Young Kwan Kim,^{*[b]} Young Sik Kim,^{*[c]} and Seung Soo Yoon^{*[a]}

Abstract: Red phosphorescent iridium(III) complexes based on fluorine-, phenyl-, and fluorophenyl-substituted 2-arylquinoline ligands were designed and synthesized. To investigate their electrophosphorescent properties, devices were fabricated with the following structure: indium tin oxide (ITO)/4,4',4''-tris[2-naphthyl(phenyl)amino]triphenylamine (2-TNATA)/4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl

(NPB)/4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP): 8% iridium

Introduction

Recently, in both industry and academia, organic light-emitting diodes (OLEDs) are focused on the next generation flat-panel displays and solid-state lighting.^[1,2] In OLEDs, holes and electrons are injected and recombined at the emitting layer (EML) when it is operated electrically. During this process, singlet and triplet excitons occur statistically in a ratio of 1:3. OLEDs that use only fluorescence can only use singlet excitons for emission, but phosphorescence OLEDs (PHOLEDs) can use both singlet and triplet excitons, and thus, their internal quantum efficiency can be four times higher than that of fluorescence OLEDs. Their ability of using triplet excitons for emission is originated from spin–orbital coupling derived from third-row transition-metal elements, such as Ir or Pt.^[3,4] PHOLEDs, which use iridium complexes with an efficient emission of the whole visible area have been reported for several years.^[5–8]

[a] J. Kim, Dr. K. H. Lee, Prof. S. S. Yoon	
Department of Chemistry, Sungkyunkwan University	
2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do (Korea)	
Fax: (+82)031-290-7075	
E-mail: ssyoon@skku.edu	

[b] Dr. S. J. Lee, Dr. H. W. Lee, Prof. Y. K. Kim Department of Information Display, Hongik University 94, Wausan-ro, Mapo-gu, Seoul (Korea) Fax: (+ 82) 2-3141-8928; E-mail: kimyk@hongik.ac.kr

[c] Prof. Y. S. Kim
Department of Information Display, Hongik University
94, Wausan-ro, Mapo-gu, Seoul (Korea)
Fax: (+82)2-3142-0335
E-mail: youngkim@hongik.ac.kr

(III) complexes/bathocuproine (BCP)/tris(8-hydroxyquinolinato)aluminum (Alq₃)/8-hydroxyquinoline lithium (Liq)/Al. All devices, which use these materials showed efficient red emissions. In particular, a device exhibited a saturated red emission with a maximum luminance, external quantum efficiency, and luminous efficiency of 14200 cd m⁻², 8.44%, and 6.58 cd A⁻¹ at 20 mA cm⁻², respectively. The CIE (*x*, *y*) coordinates of this device are (0.67, 0.33) at 12.0 V.

Many researchers have designed and synthesized a series of iridium(III) complexes, which have substituted 2-phenylpyridines as the cyclometalating ligands. By changes of the substituent position and the electronic nature of the substituents in the aromatic ligands, the emissive colors of the iridium complexes could be fine-tuned.^[9-15] As early as 2001, the 2-phenylquinoline (pq) ligand was applied to the synthesis of phosphorescent cyclometalated iridium complexes called [Ir(pq)₂(acac)] (acac = acetylacetonate) that presents an orange-red emission at $\lambda = 597$ nm.^[16] In order to get deep-red emission, modified pq ligands with a variety of aromatic segments were designed and cyclometalated iridium complexes, which use these ligands have been prepared. In accordance with the structures of the quinoline ligands, iridium complexes emitting phosphorescence from orange to red with an emission wavelength range from $\lambda = 590$ to 660 nm have been developed.^[17–19]

As continuing efforts to search for the efficient deep-red phosphorescent emitters for OLEDs, the iridium(III) complexes 1–9 based on fluorine-, phenyl-, and fluorophenyl-substituted 2-arylquinoline ligands were designed and synthesized, and their photophysical and electrophosphorescent properties were investigated. In the ligands of iridium complexes 2, 3, 5, 6, and 9 the electron-withdrawing fluorine atoms were introduced to tune the band gap of the iridium complexes by the control of the HOMO or LUMO energy levels.^[20,21]

Furthermore, fluorine atoms in the ligands would affect to carrier transporting abilities, molecular packing tendencies, and luminescent properties of the corresponding iridium complexes,^[21] which play significant roles in the electro-luminescence (EL) performances of the devices, which use these materials. The additional phenyl groups in the quinoline

Chem. Eur. J. 2016, 22, 4036-4045

Wiley Online Library



moiety of the iridium complexes **1–9** and the fluorene moieties of the iridium complexes **4–6** would extend the π -conjugation length of these complexes, and thus induce the red shifts of the phosphorescent emissions of the corresponding complexes to the saturated red region in comparison with [(pq)₂lr(acac)].

Multilayered organic light-emitting diodes were fabricated to explore their electroluminescent properties by employing the complexes as a dopant. This study revealed that these iridium(III) complexes (i.e., complexes **1–9**) had highly efficient red electroluminescent properties. The influence of the systematic changes of the substituent in the ligands of these iridium complexes to their photophysical properties and the electrophosphorescent properties will be discussed.

Results and Discussion

Synthesis of iridium complexes

Figure 1 shows the structures of the iridium complexes **1–9** and Scheme 1 exhibits their synthetic routes. Detail conditions of each synthesis are explained in the Experimental Section (see below). Newly synthesized red-emitting materials (set 1: complexes **1**, **2**, and **3**; set 2: complexes **4**, **5**, and **6**; and set 3: complexes **7**, **8**, and **9**) were purified further by train sublimation at a reduced pressure, below 10^{-3} Torr, and fully characterized by using ¹H and ¹³C NMR as well as infrared (IR) spectroscopy, and low- and high-resolution mass spectrometry. High-performance liquid chromatography (HPLC) analysis revealed that the purity of the orange- to red-emitting materials (i.e., complexes **1–9**) was at least 99.0%.

Physical and photophysical properties of the complexes

Figure 2 shows the UV/Vis absorption and photoluminescence (PL) emission spectra of the iridium complexes 1-9 in CH₂Cl₂



A European Journal Full Paper

Figure 1. Structures of the iridium(III) complexes 1-9.

solutions. All complexes exhibit a strong UV/Vis absorption in the range of $\lambda = 250-400$ nm with distinct vibronic features, which were assigned to the spin-allowed ${}^{1}\pi - \pi^{*}$ transition of the cyclometalated ligands in the complexes.^[22] In the range of $\lambda = 400-470$ nm, the weak absorption from spin-allowed metal-to-ligand charge-transfer (${}^{1}MLCT$) transitions of all the complexes **1–9** are exhibited.^[23]

Over $\lambda = 470$ nm, according to the band position and size, all iridium complexes have weak absorptions due to spinforbidden metal-to-ligand charge-transfer (³MLCT) and ³ π - π *



Scheme 1. Synthetic route of the ligands L1–L9 and the corresponding iridium(III) complexes 1–9. Reaction conditions: i [Pd(PPh₃)₄], 2 \times Na₂CO₃, ethanol, toluene, heating to reflux for two hours at 90 °C; ii) peracetic acid, CHCl₃, heating to reflux for four hours at 70 °C; iii) POCl₃, heating to reflux for one hour at 100 °C; iv) IrCl₃·H₂O, H₂O, H₂O, H₂O, 2-ethoxyethanol, heating to reflux for 24 h at 120 °C; v) 2,4-pentanedione, Na₂CO₃, 2-ethoxyethanol, heating to reflux for six hours at 100 °C; 6 h;¹⁽⁶⁾ v) sulfuric acid, acetic acid.

Chem. Eur. J. 2016, 22, 4036-4045

www.chemeuri.ora





Figure 2. UV/Vis absorption and PL emission spectra of a) set 1, b) set 2, and c) set 3.

transitions caused by spin-orbital coupling.^[24] As shown in Table 1, all complexes 1–9 show totally slightly red-shifted absorption spectra compared with the absorption spectrum of [(pq)₂Ir(acac)] due to the extended π -conjugation lengths of the ligands by substitution of the aryl groups in complexes 1 and 3–9, and the electron- withdrawing effect of the fluorine atom of the ligand in complex 2. Particularly, the absorption spectra of complexes 4–6 and 9 show more red-shifted maximum absorption wavelengths than the other complexes 1–3, 7, and 8 due to the fluorene unit in complexes 4–6 and the additional phenyl units in complex 9, which make the π -conjugation lengths longer than those of complexes 1–3, 7, and 8.

The maximum emission wavelength λ_{max} for the complexes 1-9 ranged from $\lambda = 603$ to 622 nm in the red region of the visible spectra. The trends in the emission spectra of complexes 1-9 are similarly observed in the absorption spectra of complexes 1-9. For examples, the PL spectra of all the complexes 1-9 are red shifted compared with [(pq)₂lr(acac)], and those of complexes 4-6 and 9 show largely red-shifted maximum emission wavelengths in comparison with the other complexes 1-3, 7, and 8.

By using $[Ir(ppy)_3]$ (ppy = 4-pyrrolidinopyridine) as a standard material with a quantum yield (Φ) of 0.4,^[24] the quantum yields for all complexes **1–9** were measured and are summarized in Table 1 together with the other physical properties of complexes **1–9**. Especially, complex **6** showed a highly luminescent capability with the value of Φ as high as 0.67. This observation indicates that it can be a promising phosphorescent dopant for high-performance PHOLEDs. The highest occupied molecular orbital (HOMO) energy levels of complexes **1–9** were measured with an AC-2 photoelectron spectrometer, and the lowest unoccupied molecular orbital (LUMO) energy levels were calculated by subtracting the corresponding optical band-gap energies from the HOMO values. The HOMO and LUMO energy levels for complexes **1–9** varied from –5.24 to –5.57 eV and from –2.96 to –3.30 eV, respectively.

Figure 3 shows the cyclic voltammogram of complex 1 in CH_2Cl_2 solution. Cyclic voltammetry (CV) was used to examine

Table 1. Optical properties of the iridium complexes 1–9.								
Sample	$\lambda_{Abs}^{[b]}$ [nm] ($arepsilon$)	$\lambda_{\rm Em}^{\rm [b]}$ [nm]	FWHM ^[b] [nm]	$\Phi^{[\rm c]}$	HOMO ^[d] /LUMO ^[e] [eV]	$E_g^{[f]}$ [eV]	HOMO ^[g] /LUMO ^[g] [eV]	
1	262 (9.87), 348 (3.32), 434 (1.05), 472 (0.79)	607	73	0.47	-5.26/-2.99	2.27	-4.79/-1.76	
2	262 (15.0), 434 (0.93), 473 (0.85)	609	70	0.37	-5.57/-3.30	2.27	-4.95/-1.92	
3	279 (8.80), 428 (0.75), 473 (0.71)	600	69	0.49	-5.37/-3.08	2.29	-4.87/-1.85	
4	283 (2.89), 316 (3.28), 370 (2.56), 487 (0.35)	614	52	0.34	-5.25/-3.06	2.19	-4.72/-1.80	
5	284 (6.20), 313 (7.04), 326 (6.88), 371 (6.47), 489 (0.85)	622	56	0.24	-5.40/-3.22	2.18	-4.87/-1.95	
6	286 (18.6), 314 (11.0), 374 (8.81), 487 (1.27)	618	53	0.67	-5.33/-3.13	2.20	-4.79/-1.88	
7	280 (18.6), 353 (6.67), 407 (1.39), 477 (1.46)	603	66	0.45	-5.24/-2.96	2.28	-4.81/-1.83	
8	279 (11.6), 353 (4.06), 407 (0.87), 477 (0.86)	603	65	0.46	-5.42/-3.15	2.27	-4.88/-1.91	
9	283 (12.1), 359 (4.51), 484 (1.04)	618	70	0.58	-5.44/-3.20	2.24	-4.76/-1.85	
reference ^[a]	270 (10.6), 425 (0.93), 464 (0.89)	596	66	0.86	-5.11/-2.50	2.61	-4.81/-1.77	

[a] [(pq)₂Ir(acac)]. [b] Measured in CH_2CI_2 at a concentration of 10^{-5} M. The molar extinction coefficient (ε) values (in $[10^4 \text{ m}^{-1} \text{ cm}^{-1}]$) are shown in parentheses. [c] In degassed CH_2CI_2 relative to *fac*-[Ir(ppy)₃] (Φ =0.40), λ_{ex} =470 nm. [d] Measured with a low-energy photo-electron spectrometer (Riken-Keiki, AC-2). [e] Calculated by subtracting the corresponding optical band gap energies from the HOMO energy values. [f] Determined from the intersection of the absorption and PL spectra. [g] Calculated values by using the Gaussian 03 program.^[34]



Figure 3. Cyclic voltammogram of complex 1.

the electrochemical behavior as well as the HOMO energy level of complex **1**.

The conventional three-electrode cell with ferrocene as the internal standard, allowed an estimation of the electrochemical behavior of complex 1. The cyclic voltammogram was recorded in a single compartment glass cell in CH₂Cl₂ with ferrocene as the internal standard and nBu₄NPF₆ as a supporting electrolyte. The CV curve of this complex showed a clean reversible one-electron oxidation wave at $E_{1/2}^{OX} = 0.50 \text{ V}$ versus the Fc/Fc⁺ (ferrocene/ferrocenium) couple reference, indicating the good electrochemical stability of the complex. Based on the onset potentials of the oxidation, the respective HOMO energy level of complex 1 was estimated to be -5.30 eV, with regard to ferrocene (-4.80 eV in vacuum).^[25,26] This suggests that the estimation of the HOMO energy levels by using AC-2 photoelectron spectroscopy (-5.26 eV in Table 1) and the electrochemical study (-5.30 eV) is comparable to each other within the experimental error.

The introduction of substituents with the different electronic properties in the ligands of the iridium complexes has an effect on the HOMO and LUMO energy levels. In this kinds of iridium complexes, the electronic properties of Ir-carbon-coordinated aromatic groups/hetero aromatic rings of the cyclometalating ligands have major effects on the HOMO/LUMO energy levels, respectively.^[11,25] The iridium complexes 1-3 and 7-9 with the substituent at the heteroaromatic ring of the cyclometalating ligands exhibit lower LUMO energy levels than $[(pq)_2 lr(acac)]$ due to the extended π -conjugation lengths of the ligands by substitution of the aryl groups in complexes 1, 3, and 7-9, and the electron-withdrawing effect of the fluorine atom of the ligand in complex **2**. Compared to $[(pq)_2 lr(acac)]$, the HOMO energy levels of the iridium complexes 1-3 and 7-9 also decreased by the relatively small amounts in comparison with those of the LUMO energy levels. This implies that the substituent at the heteroaromatic ring of the cyclometalating ligand have great effects on the LUMO energy levels of the iridium complexes. However, there are small influences on the HOMO energy levels due to the conjugation between the two aromatic groups in the ligands of the iridium complexes. In the iridium complexes 4-6, the substitutions at both the aromatic groups in the ligands and the resulting conjugation and electronic effects would lead to large decreases in the band-gap energies of complexes 4-6 in comparison with $[(pq)_2 lr(acac)]$. Therefore, the iridium complexes 4-6 showed deep-red emissions with maximum emission wavelengths λ_{max} of 614, 622 and 618 nm, respectively.

DFT calculations

DFT calculations of the iridium complexes **1–9** were performed by using the Gaussian 03 program.^[34] To obtain their HOMO/ LUMO energy levels and to optimize the molecular structures of the iridium(III) complexes, the B3LYP density functional theory was employed, by using the LANL2DZ and 6-31G(d) basis sets^[35] for iridium and the other atoms in the iridium complexes **1–9**, respectively.

Geometry optimizations were performed on all possible isomers of the iridium complexes. Ideally, there would be three diastereomers of the iridium complexes. From the geometry optimization of the iridium complexes **1–9**, the structures with "N–N *trans* and C–C *cis*" relations between the iridium and the nearest carbon/nitrogen atoms were the most stable ones. As shown in Figure 4, the HOMOs of all iridium complexes are mainly localized on the phenyl ring of the pq ligand and the centric iridium atom. Especially, the donation of the d orbital of the iridium atom is significant. The LUMOs of all iridium complexes are seen to be localized on the quinoline ring of the pq ligand. The calculated HOMO and LUMO levels are given in Table 1, in comparison with the experimental ones.

It can be clearly seen that the HOMO and LUMO energy levels become lower by introduction of a fluorine atom in the pq ligands. Thus, the iridium complexes 2 and 5 showed lower HOMO/LUMO energy levels in comparison with those of complexes 1 and 4. The iridium complexes 3, 6, and 8, due to substitution of the aryl group with the electron-withdrawing fluorine atom, also exhibit lower HOMO/LUMO energy levels in comparison with those of complexes 1, 4 and 7, respectively. The HOMO and LUMO energy levels of the iridium complexes 3 and 6 decreased by the relatively small amounts in comparison with iridium complexes 2 and 5. This implies that the electron-withdrawing effect of the fluorine atom decreased with extending the conjugation length of the heteroaromatic ring of the cyclometalating compound. Although the experimentally obtained energy levels are somewhat different from the calculated ones, their trends are almost consistent. The calculated HOMO and LUMO levels are slightly influenced by the substitution of the aryl group and the fluorine atom and this is also consistent with the experimental results.

Electrophosphorescent characterization of the PHOLEDs

To investigate the performances of the iridium(III) complexes **1–9** in devices, the multilayered PHOLEDs **A–I** and the reference device **J** (the corresponding dopants and devices are represented in Table 2) were fabricated by using a thin hole and exciton blocking layer (HBL) composed of bathocuproine (BCP) placed between 4,4'-bis(*N*-carbazolyI)-1,1'-biphenyI (CBP) (as EML), and aluminum-tris(8-hydroxychinolin) (Alq₃) (as ETL). The performances of the devices are summarized in Table 2.

As shown in Figure 5, the devices A-J, which are based on the iridium complexes 1-9 and $[(pq)_2 lr(acac)]$ show electrolumi-

Chem	Fur	1	2016	22	4036 - 4045
Chem.	Lui.	٦.	2010,	ZZ ,	4030 - 4043





Figure 4. Calculated spatial distributions of the HOMOs and LUMOs of complexes 1–9.

nescence emission in the red region around $\lambda = 602-627$ nm. Among the devices **A**–**J**, the devices **E** and **F** exhibit excellent values of the Commission Internationale de l'Eclairage (CIE) coordinates with (0.67, 0.32) and (0.67, 0.33) at 12 V, respectively. These values are well matching with the National Television System Committee (NTSC) standard red, that is, (0.67, 0.33). The trend in the EL spectra of the devices is similar to that in the PL spectra of the iridium complexes 1–9, which are used as dopants in the corresponding devices. This similarity between the PL and EL emission spectra indicates that the EL emission is originating from the phosphorescence of the iridium dopants.^[27]

Figure 6 shows plots of a) the current density J and the luminance L versus the voltage V (J–V–L), b) the luminous efficiency (LE) and the power efficiency (PE) versus the current density, and c) the external quantum efficiency versus the current density plots of the devices A-J. The EL efficiency data of the devices A-J showed interesting trends upon changes in the structures of the dopants in the emitting layer. In the devices A-C, which are built from the iridium complexes 1-3 based on pq ligands with substituents at the C-5 atom of the quinoline moiety, the external quantum efficiencies at 20 mA cm⁻² increased in the order B < C < A. The devices A-C as well as the devices **D-I** have large hole-injection barriers (0.5 eV) as shown in Figure 7, in comparison with the electroninjection barriers (0.1 eV).^[28] These suggest that the direct hole trapping from HTL into the dopants in the emitting layers would play an important role in the EL efficiencies of devices, which use the corresponding dopants. Interestingly, the HOMO energy levels of the dopants 1-3 increased in the order 2 (-5.57 eV) < 3 (-5.37 eV) < 1 (-5.27 eV).

This implies that the direct hole trapping into the dopants in the devices A-C becomes effective in the order B < C < A. This trend is well compatible with that of the EL efficiencies of the devices A-C.

In the devices **G** and **H**, which are built from the iridium complexes based on pq ligands with substituents at the C-6 atom of the quinoline moiety, the trend in the external quantum efficiencies at 20 mA cm⁻² (**G** > **H**) is well compatible with that of the HOMO energy levels of the corresponding dopants [i.e., **7** (-5.24 eV) > **8** (-5.42 eV)]. This suggests that the effective direct hole trapping into the dopant **7** in device **G** would

Table 2. EL performance characteristics of the devices A–J.								
Device	Dopant	λ_{\max}^{EL} [nm]	$V_{on}^{[a]}$ [V]	$L^{[b]} [cd m^{-2}]$	$LE^{[c]/[d]}$ [cd A^{-1}]	$PE^{[c]/[d]}$ [Im W ⁻¹]	EQE ^{[c]/[d]} [%]	$CIE^{[e]}(x,y)$
A	1	604 (73)	4.0	18800	9.24/8.36	4.90/2.69	6.93/6.88	(0.61, 0.38)
В	2	613 (76)	4.2	12100	7.40/6.95	5.15/2.18	12.5/5.50	(0.63, 0.37)
c	3	606 (77)	4.1	14200	7.74/7.12	4.45/2.16	10.0/6.68	(0.62, 0.37)
D	4	623 (52)	4.4	9930	4.42/3.90	3.19/1.31	5.96/4.42	(0.61, 0.31)
E	5	627 (52)	4.2	11 400	4.99/4.31	6.50/1.38	12.4/5.91	(0.67, 0.32)
F	6	612 (71)	3.7	14200	9.69/6.54	6.86/2.11	15.9/8.44	(0.67, 0.33)
G	7	611 (70)	3.6	22600	12.7/9.31	8.09/3.15	12.4/8.10	(0.64, 0.36)
н	8	616 (70)	4.1	13 100	12.1/8.52	7.98/2.55	14.5/7.99	(0.64, 0.36)
1	9	624 (74)	3.9	12300	9.69/7.15	4.61/2.20	13.9/6.25	(0.66, 0.33)
J	(pq) ₂ lr(acac)	605 (78)	3.7	35700	17.9/16.0	10.9/5.18	13.7/11.3	(0.61, 0.39)
[a] Turn-on voltage at 1 cd m ⁻² .[b] Maximum value at 16.0 V. [c] Maximum value. [d] At 20 mA cm ⁻² . [e] At 12.0 V.								

Chem. Eur. J. 2016, 22, 4036-4045

www.chemeurj.org

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



CHEMISTRY A European Journal Full Paper



Figure 5. Normalized EL emission spectra of the devices a) A-C, b) D-F, and c) G-J.

lead to improved EL efficiencies of the device **G** compared with the device **H**. Compared to $[(pq)_2 lr(acac)]$, the low HOMO energy level and the resulting ineffective hole trapping ability of the iridium complex **9** reduced the external quantum efficiency of the device **I** in comparison with the device **J**.

Intriguingly, the external quantum efficiencies of the device **D**–**F**, which were built from the iridium complexes based on fluorenylquinoline ligands showed an incompatible trend with the HOMO energy levels of the iridium complexes **4**–**6**, which were used as dopants. Among the complexes **4**–**6**, the highest phosphorescent quantum yield of complex **6** would contribute the most efficient EL properties of the device **F** compared with

Figure 6. a) Current density and luminance versus voltage plot and b) luminous efficiency, c) power efficiency and d) external quantum efficiency versus current density plots of the devices A–J.

the devices **D** and **E**. This suggests that the phosphorescent quantum yields as well as the direct hole trapping tendencies

Chem. Eu	ır. J. 20	16, 22,	4036 -	4045
----------	-----------	---------	--------	------

Figure 7. Device structure and energy diagrams of the materials used in the devices.

of the iridium complexes **1–9** would significantly contribute to the EL efficiencies of devices, which use them.

For example, in the devices A–C, the higher phosphorescent quantum yield of complexes 1 and 3 would contribute to the improved efficient EL properties of the devices A and C compared with device B. Also, the higher phosphorescent quantum yield of [(pq)₂lr(acac)] compared to complex 9 provides the more efficient EL properties of the devices J than device I.

These observations reflect the very complex natures of the EL emission processes in phosphorescent OLEDs (i.e., devices A–J). Presumably, the subtle combinations of the intrinsic luminescent capability and the carrier trapping property of the iridium complexes 1–9 and [(pq)₂Ir(acac)] would control the EL efficiencies of devices, which use them. These factors would affect the complex trends in the EL efficiencies of the devices A–J.

Conclusion

A series of red phosphorescent iridium(III) complexes were synthesized and their electroluminescent properties were examined. By using these red phosphorescent iridium(III) complexes as dopants (i.e., complexes **1–9**), the efficient red phosphorescent OLEDs were demonstrated. Particularly, a device, which uses an iridium complex based on 2-(9,9-dimethyl-9*H*-fluoren-2-yl)-5-(4-fluorophenyl)quinoline ligand, showed a maximum luminance of 14200 cdm⁻², a luminous efficiency of 6.58 cd A⁻¹, and an external quantum efficiency of 8.44% at 20 mA cm⁻², with CIE coordinates of (0.67, 0.33), a saturated red region. In comparison with the other red emitters,^[29] this material has a high potential to be a candidate for an efficient red emitter in PHOLEDs in terms of the EL efficiencies and color purities.

Experimental Section

Materials and measurements: Phenylboronic acid, 4-fluorophenylboronic acid, 5-bromo-quinoline, and acetophenone were used as received from Aldrich or TCI. 5-Phenylquinoline,^[30] 2-chloro-5-

2-amino-5-bromobenzaldehyde,^[31] fluoro-quinoline (13),^[28] 2amino-5-bromobenzophenone,[32] and 6-bromo-2,4-diphenylquinoline $(16)^{[33]}$ were synthesized as previously reported. The solvents were dried by using standard procedures. All reagents were used as received from commercial sources, unless otherwise stated. All reactions were performed under a N₂ atmosphere. ¹H- and ¹³C NMR spectra were obtained by using a Varian (Unity Inova 300NB) or Varian (Unity Inova 500NB) spectrometer at 300 and 500 MHz, respectively. FTIR spectra were recorded by using a Thermo Nicolet Avatar 320 FTIR spectrometer. Low- and high-resolution mass spectra were recorded by using a Jeol JMS-AX505WA spectrometer in the FAB mode or a Jeol JMS-600 spectrometer in the EI mode. Elemental analyses (EA) were determined by a Flash 2000 auto analyzer. The UV/Vis absorption measurements of the materials in dichloromethane $(10^{-5} M)$ were acquired with a Scinco S-3100 in a quartz cuvette (1.0 cm path length). The PL spectra were measured on an AMINCO-Bowman Series 2 Luminescence Spectrometer. The phosphorescence quantum yields were determined in CH_2CI_2 solutions at 293 K against $[Ir(ppy)_3]$ as reference $(\Phi_{ph} =$ 0.40).^[24] Electrochemical measurements were made by using a CHI 600C potentiostat (CH Instruments) at a scan rate of 100 mV s⁻¹. A conventional three-electrode configuration consisting of a glassy carbon working electrode and a Pt wire as counter and reference electrodes was used. The supporting electrolyte was 0.1 M of tetra*n*-butylammoniumhexafluorophosphate (nBu_4NPF_6) solution in anhydrous CH₂Cl₂. The HOMO energy levels were determined by using a low-energy photoelectron spectrometer (Riken-Keiki, AC-2). The energy band gaps were determined from the intersection of the absorption and the PL spectra. The LUMO energy levels were calculated by subtracting the corresponding optical band-gap energies from the HOMO energy values.

The ligands **L1–L6** were synthesized by using Suzuki cross coupling reactions with moderate yields. Three 2-arylquinoline derived ligands, **L7**, **L8**, and **L9** were conveniently synthesized by using the acid-catalyzed Friedländer condensation reaction^[19,33] of acetophenone with the corresponding 2-aminobenzaldehyde compounds.

General procedures for the Suzuki cross-coupling reaction: Arylboronic acid (1.2 mol), the corresponding aryl bromide derivatives (1.0 mol), $[Pd(PPh_3)_4]$ (0.04 mol), aqueous 2.0 m solution of K₂CO₃ (10.0 mol), ethanol, and toluene were mixed in a flask, and the mixture was heated to reflux for 4 h. After the reaction was complete, the reaction mixture was extracted with ethyl acetate and washed with water. The combined organic layers were dried with anhydrous MgSO₄ and evaporated to dryness. The crude product was further purified by silica gel column chromatography with 6:1 CH₂Cl₂/hexane as eluent.

5-Phenylquinoline (10): Yield: 98%; ¹H NMR (500 MHz, CDCl₃): δ = 8.93 (d, *J*=3.5 Hz, 1 H), 8.24 (d, *J*=7.8 Hz, 1 H), 8.13 (d, *J*=8.5 Hz, 1 H), 7.76 (t, *J*=8.5 Hz, 1 H), 7.52–744 (m, 5 H), 7.35 (dd, *J*=4.2, 8.5 Hz, 1 H), 7.17 ppm (d, *J*=4.5 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃): δ = 150.5, 148.8, 140.7, 139.6, 134.6, 130.3, 129.2, 129.1, 128.7, 127.9, 127.5, 126.9, 121.3 ppm; MS (EI): *m/z*: 205 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₁₅H₁₁N: 205.0891; found: 205.0889.

5-(4-Fluorophenyl)quinoline (11): Yield: 57%; ¹H NMR (300 MHz, CDCl₃): δ = 8.93 (dd, *J* = 1.6, 4.1 Hz, 1 H), 8.20–8.16 (m, 1 H), 8.15–8.12 (m, 1 H), 7.75 (t, *J* = 7.0 Hz, 1 H), 7.48 (dd, *J* = 1.2, 7.2 Hz, 1 H), 7.42 (dd, *J* = 5.4, 8.3 Hz, 2 H), 7.36 (dd, *J* = 4.1, 8.5 Hz, 1 H), 7.20 ppm (t, *J* = 8.7 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ = 162.7 (d, *J*(F,C) = 247.1 Hz), 150.6, 148.8, 139.6, 135.5 (d, *J*(F,C) = 3.3 Hz), 134.3, 131.8 (d, *J*(F,C) = 7.7 Hz), 129.4, 129.1, 127.6, 127.0, 121.4, 115.7 ppm (d, *J*(F,C) = 21.6 Hz); FTIR (ATR): $\tilde{\nu}$ = 3041, 2970, 1739, 1512, 1366, 1228, 798 cm⁻¹; MS (EI): *m/z*: 223 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₁₅H₁₀NF: 223.0797; found: 223.0796.

Chem. Eur. J. 2016, 22, 4036 – 4045

2,5-Diphenylquinoline (L1): Yield: 89%; ¹H NMR (300 MHz, CDCl₃): δ =8.30 (d, *J*=8.9 Hz, 1H), 8.21–8.16 (m, 3H), 7.82 (d, *J*=8.9 Hz, 1H), 7.76 (dd, *J*=8.5, 7.5 Hz, 1H), 7.56–7.44 ppm (m, 9H); ¹³C NMR (125 MHz, CDCl₃): δ =157.4, 148.8, 140.5, 139.8, 135.3, 130.3, 129.6, 129.5, 129.4, 129.1, 128.7, 127.9, 127.8, 127.7, 127.2, 125.8, 119.2 ppm; FTIR (ATR): $\tilde{\nu}$ =2970, 1738, 1366, 1216, 822, 780, 702 cm⁻¹; MS (EI): *m/z*: 281 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₂₁H₁₅N: 281.1204; found: 281.1205.

5-Fluoro-2-phenylquinoline (L2): Yield: 87%; ¹H NMR (300 MHz, CDCl₃): δ = 8.50 (d, *J* = 8.8 Hz, 1H), 8.19–8.16 (m, 2H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.68–7.61 (m, 1H), 7.57–7.48 (m, 3H), 7.19 ppm (d, *J* = 8.7 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 158.4, 158.2 (d, *J*(F,C) = 254.3 Hz), 149.4 (d, *J*(F,C) = 2.8 Hz), 139.5, 130.3 (d, *J*(F,C) = 3.9 Hz), 129.1, 129.8, 125.8 (d, *J*(F,C) = 3.9 Hz), 119.3 (d, *J*(F,C) = 2.8 Hz), 118.1 (d, *J*(F,C) = 16.6 Hz), 110.1 ppm (d, *J*(F,C) = 19.4 Hz); FTIR (ATR): $\tilde{\nu}$ = 3016, 2970, 1738, 1441, 1366, 1216, 771, 691 cm⁻¹; MS (EI): *m/z*: 223 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₁₅H₁₀FN: 223.0797; found: 223.0798.

5-(4-Fluorophenyl)-2-phenylquinoline (L3): Yield: 82%; ¹H NMR (300 MHz, CDCl₃): δ = 8.24 (dd, *J* = 0.8, 8.9 Hz, 1 H), 8.21–8.15 (m, 2 H), 7.83 (d, *J* = 8.9 Hz, 1 H), 7.75 (dd, *J* = 7.1, 8.5 Hz, 1 H), 7.56–7.51 (m, 3 H), 7.50–7.44 (m, 4 H), 7.21 ppm (t, *J* = 8.8 Hz, 2 H); ¹³C NMR (125 MHz, CDCl₃): δ = 162.7 (d, *J*(F,C) = 247.1 Hz), 157.5, 148.8, 139.7, 139.4, 135.7 (d, *J*(F,C) = 3.3 Hz), 135.1, 131.8 (d, *J*(F,C) = 7.7 Hz), 129.7, 129.6, 129.4, 129.2, 127.8, 127.3, 125.8, 119.3, 115.7 ppm (d, *J*(F,C) = 21.6 Hz); MS (EI): *m/z*: 299 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₂₁H₁₄FN: 299.1110; found: 299.1111.

2-(9,9-Dimethyl-9*H***-fluoren-2-yl)-5-phenylquinoline (L4)**: Yield: 76%; ¹H NMR (300 MHz, CDCl₃): δ = 8.31 (d, *J* = 8.6 Hz, 2 H), 8.14 (dd, *J* = 1.8, 8.4 Hz, 1 H), 7.88 (t, *J* = 8.1 Hz, 3 H), 7.81–7.75 (m, 3 H), 7.54–7.45 (m, 5 H), 7.40–7.33 (m, 3 H), 1.60 ppm (s, 6 H);¹³C NMR (125 MHz, CDCl₃): δ = 157.6, 154.6, 154.5, 148.9, 140.8, 140.5, 139.9, 138.9, 138.8, 135.2, 130.3, 129.5, 129.3, 128.7, 127.9, 127.8, 127.3, 127.1, 127.0, 125.7, 122.9, 122.1, 120.6, 120.5, 119.4, 47.3, 27.5 ppm; FTIR (ATR): $\hat{\nu}$ = 3016, 2970, 1738, 1444, 1366, 1216, 762, 739 cm⁻¹; MS (EI): *m/z*: 397 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₂₁H₁₅N: 281.1204; found: 281.1203.

2-(9,9-Dimethyl-9*H***-fluoren-2-yl)-5-fluoroquinoline (L5)**: Yield: 77%; ¹H NMR (300 MHz, CDCl₃): δ =8.50 (dd, *J*=0.7, 8.8 Hz, 1 H), 8.29 (d, *J*=1.1 Hz, 1 H), 8.15 (dd, *J*=1.7, 8.0 Hz, 1 H), 8.01 (d, *J*= 8.8 Hz, 2 H), 7.87 (d, *J*=8.0 Hz, 1 H), 7.81–7.74 (m, 1 H), 7.69–7.62 (m, 1 H), 7.50–7.47 (m, 1 H), 7.39–7.34 (m, 2 H), 7.22–7.16 (m, 1 H), 1.60 ppm (s, 6 H); ¹³C NMR (125 MHz, CDCl₃): δ =158.7, 158.2 (d, *J*(F,C)=254.8 Hz), 154.6, 154.5, 149.6 (d, *J*(F,C)=2.8 Hz), 141.1, 138.8, 138.5, 130.2 (d, *J*(F,C)=4.4 Hz), 129.3 (d, *J*(F,C)=9.4 Hz), 128.0, 127.4, 127.8, 125.8 (d, *J*(F,C)=3.9 Hz), 122.9, 122.2, 120.7, 120.6, 119.5 (d, *J*(F,C)=2.8 Hz), 117.9 (d, *J*(F,C)=16.6 Hz), 109.9 (d, *J*(F,C)=19.4 Hz), 47.3, 27.5 ppm; FTIR (ATR): $\tilde{\nu}$ =3016, 2970, 1738, 1366, 1216, 834, 737 cm⁻¹; MS (EI): *m/z*: 339 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₂₄H₁₈FN: 339.1423; found: 339.1421.

2-(9,9-Dimethyl-9 H-fluoren-2-yl)-5-(4-fluorophenyl)quinoline

(L6): Yield: 83%; ¹H NMR (300 MHz, CDCl₃): δ = 8.28 (d, *J* = 1.5 Hz, 1 H), 8.24 (t, *J* = 8.8 Hz, 2H), 8.13 (dd, *J* = 1.8, 7.8 Hz, 1 H), 7.90 (d, *J* = 8.8 Hz, 1 H), 7.86 (d, *J* = 7.9 Hz, 1 H), 7.81–7.76 (m, 2 H), 7.50–7.44 (m, 4 H), 7.39–7.35 (m, 2 H), 7.26–7.19 (m, 2 H), 1.59 ppm (s, 6 H); ¹³C NMR (125 MHz, CDCl₃): δ = 162.7 (d, *J*(F,C) = 245.8 Hz), 157.2, 154.6, 154.5, 148.9, 140.8, 139.4, 138.8, 138.6, 135.7 (d, *J*(F,C) = 2.8 Hz), 134.9, 131.9 (d, *J*(F,C) = 7.8 Hz), 129.4, 129.3, 127.9, 127.3, 127.1, 126.8, 125.7, 122.9, 121.9, 120.6, 120.4, 119.1, 115.5 (d, *J*(F,C) = 21.6 Hz), 47.3, 27.2 ppm; FTIR (ATR): $\tilde{\nu}$ = 3016, 2970, 1738, 1366, 1217, 901, 764, 740 cm⁻¹; MS (EI): *m/z*: 415 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₃₀H₂₂FN: 415.1736; found: 415.1737. **2,6-Diphenylquinoline (L7)**: Yield: 78%; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.28$ (d, J = 8.7 Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H), 8.21–8.17 (m, 2H), 8.02–7.99 (m, 2H), 7.92 (d, J = 8.5 Hz, 1H), 7.77–7.74 (m, 2H), 7.55–7.48 (m, 5H), 7.44–7.39 ppm (m, 1H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 157.6$, 147.9, 140.7, 139.9, 139.3, 137.2, 130.4, 129.6, 129.6, 129.2, 129.1, 127.9, 127.8, 127.7, 127.6, 125.4, 119.6 ppm; FTIR (ATR): $\tilde{\nu} = 3028$, 2970, 1738, 1595, 1366, 1216, 764, 677 cm⁻¹; MS (EI): m/z: 281 [M^+]; HRMS (EI⁺): m/z calcd for C₂₁H₁₅N: 281.1204; found: 281.1203.

6-(4-Fluorophenyl)-2-phenylquinoline (L8): Yield: 82%; ¹H NMR (300 MHz, CDCl₃): δ = 8.25 (t, *J* = 8.7 Hz, 2 H), 8.21–8.17 (m, 2 H), 7.95 (s, 1 H), 7.91 (d, *J* = 8.7 Hz, 2 H), 7.69 (dd, *J* = 5.3, 8.8 Hz, 2 H), 7.57–7.47 (m, 3 H), 7.19 ppm (t, *J* = 8.7 Hz, 2 H); FTIR (ATR): $\tilde{\nu}$ = 3016, 2970, 1738, 1366, 1217, 762, 655 cm⁻¹; MS (EI): *m/z*: 299 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₂₁H₁₄FN: 299.1110; found: 299.1107.

2,4,6-Triphenylquinoline (L9): Yield: 59%; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.30$ (d, J = 8.7 Hz, 1 H), 8.20 (d, J = 7.0 Hz, 2 H), 8.09 (d, J = 1.9 Hz, 1 H), 7.98 (dd, J = 1.9, 8.7 Hz, 1 H), 7.83 (s, 1 H), 7.62–7.57 (m, 5 H), 7.55–7.50 (m, 4 H), 7.48–7.40 (m, 3 H), 7.34 ppm (d, J = 7.2 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 157.1$, 149.6, 148.5, 140.9, 139.9, 139.3, 138.7, 130.8, 129.8, 129.6, 129.5, 129.1, 129.0, 129.9, 128.7, 127.8, 127.6, 126.2, 123.6, 120.0 ppm; FTIR (ATR): $\hat{v} = 3016$, 2970, 1738, 1366, 1216, 761, 697 cm⁻¹; MS (EI): *m/z*: 357 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₂₇H₁₉N 357.1517; found: 357.1516.

2-Chloro-5-phenylquinoline (12): To a mixture of 5-phenylquinoline (1.0 g, 4.28 mmol) in anhydrous CHCl₃ (20 mL) at 0 °C was added dropwise peracetic acid (32%) (30.0 mmol) in CHCl₃ (10 mL) under a N₂ atmosphere. The reaction mixture was heated to refluxed at 70 $^{\circ}$ C for 4 h. Subsequently, the solution was stirred at room temperature for 4 h. A solution of anhydrous quinoline Noxide in phosphoryl trichloride (10 mL, 34.0 mmol) was prepared by slow addition at -5 °C. The mixture was heated to reflux for 3 h and then poured on ice, neutralized with aqueous sodium hydroxide, and extracted with dichloromethane. The extracts were dried over sodium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane, 1:4), giving 2-chloro-5-phenylquinoline (12) (0.55 g, 60%) as a white solid. ¹H NMR (300 MHz, $CDCI_3$): $\delta = 8.23$ (d, J = 8.8 Hz, 1 H), 8.09 (d, J = 8.5 Hz, 1 H), 7.83 (t, J=8.5 Hz, 1 H), 7.58-7.47 (m, 6 H), 7.38 ppm (d, J=8.8 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 150.9$, 148.5, 140.8, 139.2, 137.6, 130.3, 130.1, 128.8, 128.2, 128.1, 127.9, 125.6, 122.5 ppm; MS (EI): *m*/*z*: 240 [*M*⁺+H]; HRMS (EI⁺): *m*/*z* calcd for C₁₅H₁₁CIN: 240.0580; found: 240.0579.

2-Chloro-5-(4-fluorophenyl)quinoline (14): Yield: 60%; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.12$ (d, J = 8.8 Hz, 1 H), 8.05 (d, J = 8.5 Hz, 1 H), 7.77 (t, J = 7.2 Hz, 1 H), 7.49 (dd, J = 0.9, 7.2 Hz, 1 H), 7.41 (dd, J = 5.4, 8.5 Hz, 2 H), 7.34 (d, J = 8.8 Hz, 1 H), 7.21 ppm (t, J = 8.6 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 162.9$ (d, J(F,C) = 247.7 Hz), 151.0, 148.5, 139.7, 137.3, 135.1 (d, J(F,C) = 3.3 Hz), 131.7 (d, J(F,C) =8.3 Hz), 130.3, 128.5, 128.0, 125.6, 122.6, 115.8 ppm (d, J(F,C) =21.6 Hz); FTIR (ATR): $\tilde{\nu} = 3017$, 2970, 1739, 1509, 1366, 1224, 1218, 845, 805 cm⁻¹; MS (EI): m/z: 257 [M^+]; HRMS (EI⁺): m/z calcd for C₁₅H₉NCIF: 257.0407; found: 257.0410.

6-Bromo-2-phenylquinoline (15): 5-Bromo-2-aminobenzo-phenone (0.4 g, 1.99 mmol) and acetophenone (0.25 g, 2.02 mmol) were dissolved in acetic acid (8 mL) and then concentrated H_2SO_4 (0.13 mL) was added. After heating to reflux for 12 h under an argon atmosphere, the solution was poured into a mixture of concentrated NH_3 · H_2O (30 mL) and ice water (30 g). The resulting precipitate was filtered and washed with water. The pure compounds were recrystallized from THF/ethanol. Compound **15** was obtained as pale yellow crystals (0.26 g, 46%). ¹H NMR (300 MHz, CDCl₃): δ =

Chem. Eur. J. 2016, 22, 4036 – 4045

CHEMISTRY A European Journal Full Paper

8.17–8.13 (m, 3 H), 8.04 (d, J=9.0 Hz, 1 H), 8.00 (d, J=2.1 Hz, 1 H), 7.91 (d, J=8.7 Hz, 1 H), 7.79 (dd, J=2.1, 9.0 Hz, 1 H), 7.54–7.48 ppm (m, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ =157.9, 147.1, 139.4, 136.1, 133.4, 131.7, 129.8, 129.7, 129.2, 128.5, 127.8, 120.3, 120.1 ppm; MS (EI): *m/z*: 283 [*M*⁺]; HRMS (EI⁺): *m/z* calcd for C₁₅H₁₀BrN: 282.9996; found: 282.9995.

General procedure of the [(CN)2lr(acac)] complexes: The corresponding ligand (4.46 mmol) was dissolved in 2-ethoxyethanol (18.0 mL) in a 50 mL round-bottom flask. IrCl₃·3 H₂O (2.01 mmol) and water (6.0 mL) were then added to the flask. The mixture was stirred under nitrogen at 120 °C for 24 h and cooled to room temperature. The precipitate formed in the mixture was collected and washed with methanol and hexane, and dried in a vacuum to give the corresponding cyclometalated Ir^{III} - μ -chloro-bridged dimer. In a 50 mL flask, the dimmer complex, acetylacetone (3.02 mmol) and Na₂CO₃ (6.03 mmol) were mixed with 2-ethoxyethanol (20 mL), and the mixture was heated to $100\,^\circ\text{C}$ for 6 h. After cooling to room temperature, the precipitated solid was collected by filtration and washed with ethanol and hexane. The residue was dissolved in dichloromethane and the solid was filtered. The solution was concentrated in vacuo and the residue was purified on a silica gel column by using dichloromethane and methanol as the eluent. The product was obtained after recrystallization from dichloromethane/ethanol. Similar procedures were also used to synthesize the other iridium(III) complexes. The yields and spectral data of all iridium complexes are as follows.

Complex 1: Red solid; yield: 48%; ¹H NMR (300 MHz, CDCl₃): $\delta =$ 8.53 (dd, J = 1.1, 8.1 Hz, 2 H), 8.26 (d, J = 9.0 Hz, 2 H), 7.99 (d, J =9.2 Hz, 2 H), 7.80 (d, J=7.9 Hz, 2 H), 7.56–7.41 (m, 14 H), 6.91 (td, J= 1.5, 7.3 Hz, 2 H), 6.65-6.58 (m, 4 H), 4.72 (s, 1 H), 1.53 ppm (s, 6 H); ^{13}C NMR (125 MHz, CDCl₃): $\delta\!=\!186.2,\;169.8,\;150.8,\;150.4,\;149.8,\;$ 147.7, 138.0, 136.1, 130.6, 130.0, 129.1, 129.0, 128.9, 128.8, 126.9, 126.5, 126.3, 126.2, 121.3, 117.4, 100.4, 28.3 ppm; FTIR (ATR): $\tilde{\nu} =$ 3028, 2970, 1739, 1578, 1518, 1365, 926, 762, 738 cm⁻¹; MS (FAB): *m/z*: 852 [*M*⁺]; HRMS (FAB⁺): *m/z* calcd for C₄₇H₃₅IrN₂O₂: 852.2328; found: 852.2321; elemental analysis calcd (%) for $C_{47}H_{35}IrN_2O_2$ (*M*_w=852): C 66.26, H 4.14, N 3.29; found: C 66.03, H 4.11, N 3.26. Complex 2: Red solid; yield: 34%; ¹H NMR (300 MHz, CDCl₃): $\delta =$ 8.46 (d, J=8.9 Hz, 2 H), 8.25 (d, J=9.0 Hz, 2 H), 8.11 (d, J=9.0 Hz, 2H), 7.84 (d, J=7.0 Hz, 2H), 7.39-7.31 (m, 2H), 7.15 (dd, J=1.6, 8.6 Hz, 2 H), 6.95 (dd, J=1.2, 7.5 Hz, 2 H), 6.62 (td, J=1.3, 7.4 Hz, 2H), 6.50 (dd, J=1.1, 7.7 Hz, 2H), 4.66 (s, 1H), 1.50 ppm (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ = 186.2, 171.5, 158.2 (d, J(F,C) = 252.5 Hz), 150.9, 150.0 (d, J(F,C) = 3.9 Hz), 147.0, 136.1, 131.4 (d, J(F,C) = 6.1 Hz), 130.4 (d, J(F,C) = 9.4 Hz), 129.4, 126.8, 122.4 (d, J(F,C) = 3.9 Hz), 121.5, 118.1 (d, J(F,C) = 18.3 Hz), 117.1, 110.0 (d, J(F,C) = 18.9 Hz, 100.4, 28.1 ppm; FTIR (ATR): $\tilde{v} = 3015$, 2970, 1738, 1578, 1366, 1216, 1046, 912, 722, 738 cm⁻¹; MS (FAB): (*m/z*: 736 $[M^+]$; HRMS (FAB⁺): m/z calcd for $C_{35}H_{25}F_2IrN_2O_2$: 736.1513; found: 736.1512; elemental analysis calcd (%) for $C_{35}H_{25}F_2IrN_2O_2$ ($M_w =$ 736): C 57.13, H 3.42, N 3.81; found: C 56.97, H 3.38, N 3.79.

Complex **3**: Red solid; yield: 42%; ¹H NMR (300 MHz, CDCl₃): δ = 8.53 (dd, J=0.9, 8.6 Hz, 2H), 8.21 (d, J=9.0 Hz, 2H), 8.01 (d, J= 9.2 Hz, 2H), 7.81 (d, J=7.8 Hz, 2H), 7.51 (dd, J=5.4, 8.7 Hz, 4H), 7.48–7.38 (m, 4H), 7.27–7.22 (m, 4H), 6.95 (td, J=1.3, 7.8 Hz, 2H), 6.68–6.57 (m, 4H), 4.72 (s, 1H), 1.53 ppm (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ =186.2, 170.3, 162.9 (d, J(F,C)=246.9 Hz), 150.4, 149.8, 147.4, 139.8, 136.5, 136.1, 135.6 (d, J(F,C)=3.3 Hz), 132.1 (d, J(F,C)=7.7 Hz), 130.1, 129.0, 127.2, 126.4, 126.2, 125.9, 121.3, 116.9, 115.7 (d, J(F,C)=21.6 Hz), 100.4, 28.2 ppm; FTIR (ATR): $\hat{\nu}$ =3006, 2970, 1738, 1578, 1521, 1365, 1014, 978, 777, 739 cm⁻¹; MS (FAB): m/z: 888 [M^+]; HRMS (EI⁺): m/z calcd for C₄₇H₃₃F₂IrN₂O₂: 888.2139; found: 888.2130; elemental analysis calcd (%) for

 $C_{47}H_{33}F_2 lrN_2 O_2 \ (M_w\!=\!888):$ C 63.57, H 3.75, N 3.81; found: C 63.47, H 3.78, N 3.78.

Complex **4**: Red solid; yield: 26%; ¹H NMR (300 MHz, CDCl₃): δ = 8.60 (d, *J*=8.1 Hz, 1H), 8.41 (d, *J*=9.0 Hz, 1H), 8.33 (d, *J*=9.9 Hz, 1H), 8.12 (dd, *J*=4.5, 4.8 Hz, 2H), 7.85 (s, 2H), 7.62–7.58 (m, 7H), 7.55–7.52 (m, 3H), 7.48–7.41 (m, 4H), 7.30 (d, *J*=7.8 Hz, 3H), 6.93 (s, 1H), 6.75 (s, 1H), 2.16 (s, 6H), 1.49 ppm (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ = 154.9, 136.7, 136.0, 130.5, 129.9, 128.7, 127.9, 127.5, 127.1, 126.8, 126.5, 122.6, 120.5, 116.9, 89.9, 86.5, 78.7, 46.3, 31.2, 28.6, 27.9, 27.7, 27.5 ppm; FTIR (ATR): $\tilde{\nu}$ = 3016, 2970, 1738, 1599, 1519, 1366, 875, 760, 740 cm⁻¹; MS (FAB): *m/z*: 1084 [*M*⁺]; HRMS (FAB⁺): *m/z* calcd for C₆₅H₅₁IrN₂O₂: 1084.3580; found: 1084.3577; elemental analysis calcd (%) for C₆₅H₅₁IrN₂O₂ (*M*_w = 1084): C 72.00, H 4.74, N 2.58; found: C 71.74, H 4.69, N 2.55.

Complex **5**: Red solid; yield: 57%; ¹H NMR (300 MHz, CDCl₃): δ = 8.50 (d, J=9.0 Hz, 2H), 8.29 (d, J=8.8 Hz, 2H), 8.23 (d, J=9.0 Hz, 2H), 7.89 (s, 2H), 7.38–7.29 (m, 4H), 7.14 (d, J=8.4 Hz, 4H), 7.06–7.03 (m, 4H), 6.85 (s, 2H), 4.70 (s, 1H), 1.55 (s, 6H), 1.52 (s, 6H), 1.46 ppm (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ =186.2, 171.5, 158.2 (d, J(F,C)=251.8 Hz), 155.1, 150.0 (d, J(F,C)=3.6 Hz), 149.5, 147.2, 145.9, 140.9, 138.5, 131.1 (d, J(F,C)=6.2 Hz), 130.3 (d, J(F,C)=9.1 Hz), 127.8, 127.0, 126.7, 122.6, 122.3 (d, J(F,C)=3.9 Hz), 121.2, 120.6, 117.9 (d, J(F,C)=18.0 Hz), 117.3, 109.8 (d, J(F,C)=19.2 Hz), 100.5, 46.4, 28.1 ppm; FTIR (ATR): $\tilde{\nu}$ =3004, 2970, 1738, 1584, 1518, 1364, 1020, 920, 763, 738 cm⁻¹;MS (FAB) (m/z): 968 [M⁺];HRMS (EI⁺) calcd for C₅₃H₄₁F₂IrN₂O₂: 968.2765 found: 968.2760; elemental analysis calcd (%) for C₅₃H₄₁F₂IrN₂O₂ (M_w =968): C 65.75, H 4.27, N 2.89; found: C 64.98, H 4.24, N 2.84.

Complex **6**: Red solid; yield: 50%; ¹H NMR (300 MHz, CDCl₃): δ = 8.54 (d, J=8.7 Hz, 2H), 8.26 (d, J=9.1 Hz, 2H), 8.12 (d, J=9.2 Hz, 2H), 7.85 (s, 2H), 7.59–7.56 (m, 4H), 7.44 (d, J=6.9 Hz, 2H), 7.39 (d, J=6.6 Hz, 2H), 7.32–7.25 (m, 8H), 7.13–7.03 (m, 4H), 6.92 (s, 2H), 4.73 (s, 1H), 1.55 (s, 6H), 1.54 (s, 6H), 1.45 ppm (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ =186.5, 170.3, 162.9 (d, J(F,C)=246.6), 155.1, 149.9, 148.9, 147.1, 146.4, 140.6, 139.7, 138.8, 136.3, 135.8 (d, J(F,C)=3.3 Hz), 132.2 (d, J(F,C)=8.1 Hz), 130.0, 127.6, 127.1, 126.6, 126.1, 125.7, 122.6, 120.8, 120.5, 117.1, 115.6 (d, J(F,C)=21.6 Hz), 100.4, 46.4, 28.2, 27.5, 27.4 ppm; FTIR (ATR): $\tilde{\nu}$ =3050, 2961, 1690, 1599, 1521, 1358, 975, 769, 740 cm⁻¹; MS (FAB): m/z: 1120 [M^+]; HRMS (FAB⁺): m/z calcd for C₆₅H₄₉F₂IrN₂O₂: 1120.3391; found: 1120.3387; elemental analysis calcd (%) for C₆₅H₄₉F₂IrN₂O₂ (M_w = 1120): C 69.69, H 4.41, N 2.50; found: C 68.85, H 4.39, N 2.49.

Complex 7: Red solid; yield: 41%; ¹H NMR (300 MHz, CDCl₃): $\delta =$ 8.56 (d, J = 9.2 Hz, 2 H), 8.24 (d, J = 8.6 Hz, 2 H), 8.11 (d, J = 8.8 Hz, 2H), 8.00 (d, J=1.9 Hz, 2H), 7.85 (d, J=7.6 Hz, 2H), 7.71 (d, J= 8.2 Hz, 6 H), 7.49 (t, J=7.4 Hz, 4 H), 7.40 (d, J=7.2 Hz, 2 H), 6.96 (t, J=6.7 Hz, 2H), 6.67-6.56 (m, 4H), 4.69 (s, 1H), 1.54 ppm (s, 6H); $^{13}\mathrm{C}\;\mathrm{NMR}$ (125 MHz, CDCI_3): $\delta\!=\!185.8,\;170.6,\;151.4,\;149.1,\;147.3,\;$ 140.2, 138.6, 138.3, 136.4, 130.1, 129.2, 128.9, 127.9, 127.7, 127.5, 127.4, 126.1, 125.6, 121.2, 117.3, 100.5, 28.5 ppm; FTIR (ATR): $\tilde{\nu} =$ 3057, 2979, 1684, 1579, 1516, 1342, 965, 760, 734 cm⁻¹; MS (FAB): *m/z*: 852 [*M*⁺]; HRMS (FAB⁺): *m/z* calcd for C₄₇H₃₅IrN₂O₂: 852.2328; found: 852.2319; elemental analysis calcd (%) for C47H35IrN2O2 (M_w=852): C 66.26, H 4.14, N 3.29; found: C 65.87, H 4.10, N 3.25. *Complex* **8**: Red solid; yield: 36%; ¹H NMR (300 MHz, CDCl₃): $\delta =$ 8.55 (d, J=9.2 Hz, 2H), 8.19 (d, J=8.6 Hz, 2H), 8.09 (d, J=8.8 Hz, 2H), 7.92 (s, 2H), 7.83 (d, J=7.9 Hz, 2H), 7.66-7.61 (m, 6H), 7.15 (t, J=8.6 Hz, 4H), 6.95 (t, J=7.3 Hz, 2H), 6.63 (d, J=7.5 Hz, 2H), 6.56 (d, J=7.5 Hz, 2 H), 4.69 (s, 1 H), 1.52 ppm (s, 6 H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 185.8$, 170.6, 151.3, 148.9, 147.2, 145.1 (d, J(F,C) =281.4 Hz), 138.3, 137.6, 136.3, 129.9, 129.2 (d, J(F,C) = 7.2 Hz), 128.9 (d, J(F,C) = 3.9 Hz), 127.7, 127.4, 126.1, 125.4, 124.2, 121.2, 117.4, 116.1 (d, J(F,C) = 21.5 Hz), 100.5, 28.5 ppm; FTIR (ATR): $\tilde{\nu} = 3062$,

Chem. Eur. J. 2016, 22, 4036-4045

1689, 1578, 1517, 1344, 964, 749, 737 cm⁻¹; MS (FAB): m/z: 888 [M^+]; HRMS (EI⁺): m/z calcd for C₄₇H₃₃F₂IrN₂O₂: 888.2139; found: 888.2135; elemental analysis calcd (%) for C₄₇H₃₃F₂IrN₂O₂ (M_w = 888): C 63.57, H 3.75, N 3.15; found: C 62.96, H 3.71, N 3.12.

Complex **9**: Red solid; yield: 62%; ¹H NMR (500 MHz, CDCl₃): δ = 8.68 (d, J=9.2 Hz, 2H), 8.06 (d, J=2.0 Hz, 2H), 8.04 (s, 2H), 7.85 (d, J=8.1 Hz, 2H), 7.74–7.70 (m, 6H), 7.64 (t, J=7.5 Hz, 4H), 7.59–7.57 (m, 6H), 7.41 (t, J=7.6 Hz, 4H), 7.33 (t, J=7.4 Hz, 2H), 6.97–6.94 (m, 2H), 6.68–6.66 (m, 4H), 4.76 (s, 1H), 1.6 ppm (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ = 185.9, 169.9, 151.3, 150.4, 149.4, 147.5, 140.5, 138.6, 138.3, 136.5, 130.1, 129.9, 129.1, 129.0, 128.9, 127.8, 127.5, 126.3, 126.1, 123.9, 121.2, 117.8, 100.6, 28.7 ppm; FTIR (ATR): $\tilde{\nu}$ = 3026, 1738, 1579, 1366, 878, 760, 738 cm⁻¹; MS (FAB): m/z: 1004 [M^+]; HRMS (FAB⁺): m/z calcd for C₅₉H₄₃IrN₂O₂: 1004.2954; found:1004.2953; elemental analysis calcd (%) for C₅₉H₄₃IrN₂O₂ (M_w =1004): C 70.57, H 4.32, N 2.79; found: C 69.97, H 4.30, N 2.72.

Fabrication and characterization of the devices: For the OLED fabrication, indium tin oxide (ITO) thin films coated on glass substrates were used, which were 12 Ω square⁻¹ of the sheet resistivity with 1000 Å of thickness. The ITO-coated glass was cleaned in an ultrasonic bath by the following sequence: acetone, methyl alcohol, distilled water, followed by storage in isopropyl alcohol for 20 min and drying with a N₂ gas gun. The substrates were treated with O₂ plasma argon environment. Organic layers were deposited by thermal evaporation from resistively heated alumina crucibles onto the substrate at a rate of 1.0 Å s⁻¹. All organic materials and the metal were deposited under high vacuum (5.0×10^{-7} Torr). Devices were fabricated in the following structure: ITO/4,4',4"-tris[2naphthyl(phenyl)amino]triphenylamine (2-TNATA) (60 nm)/4,4'bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) (20 nm)/CBP: 8 % iridium(III) complexes (30 nm)/BCP (10 nm)/Alq₃ (20 nm)/8-hydroxyquinoline lithium (Liq) (2 nm)/Al (100 nm). The current density J, the luminance L, the luminous efficiency LE, and the CIE chromaticity coordinates of the OLEDs were measured with a Keithly 2400, Chroma meter CS-1000A. The electroluminance (EL) was measured by using a Roper Scientific Pro 300i.

Acknowledgements

This research was supported by the Basic Science Research Program through the NRF funded by the Ministry of Education, Science and Technology, South Korea (NRF-2013R1A1A2A10008105).

Keywords: 2-arylquinoline ligands · iridium · OLEDs · phosphorescence · red electroluminescence

- J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, *347*, 539–541.
- [2] J. Kido, M. Kimura, K. Nagai, Science 1995, 267, 1332–1334.
- [3] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151–154.
- [4] M. A. Baldo, M. E. Thompson, S. R. Forrest, Nature 2000, 403, 750-753.
- [5] K. H. Lee, H. J. Kang, S. J. Lee, J. H. Seo, Y. K. Kim, S. S. Yoon, Synth. Met. 2011, 161, 1113–1121.
- [6] K. H. Lee, S. O. Kim, J. H. Seo, Y. K. Kim, S. S. Yoon, J. Nanosci. Nanotechnol. 2011, 11, 4471–4475.
- [7] C. Adachi, M. A. Baldo, S. R. Forrest, S. Lamansky, M. E. Thompson, R. C. Kwong, Appl. Phys. Lett. 2001, 78, 1622–1624.
- [8] J. V. Caspar, T. J. Meyer, J. Phys. Chem. 1983, 87, 952-957.
- [9] H. J. Kang, K. H. Lee, S. J. Lee, J. H. Seo, Y. K. Kim, S. S. Yoon, Bull. Korean Chem. Soc. 2010, 31, 3711–3717.

- [10] K. H. Lee, H. J. Kang, J. K. Park, J. H. Seo, Y. K. Kim, S. S. Yoon, *Thin Solid Films* 2010, *518*, 6188–6194.
- [11] M. S. Lowry, S. Bernhard, Chem. Eur. J. 2006, 12, 7970-7977.
- [12] K. H. Lee, W. Lee, M. K. Kim, J. H. Seo, Y. K. Kim, S. S. Yoon, *Thin Solid Films* 2010, 518, 3972–3977.
- [13] H. J. Kang, K. H. Lee, S. J. Lee, J. H. Seo, Y. K. Kim, S. S. Yoon, *Thin Solid Films* 2011, *519*, 6544–6549.
- [14] D. H. Kim, N. S. Cho, H.-Y. Oh, J. H. Yang, W. S. Jeon, J. S. Park, M. C. Suh, J. H. Kwon, Adv. Mater. 2011, 23, 2721–2726.
- [15] K. H. Lee, J. H. Kim, J. H. Seo, Y. K. Kim, S. S. Yoon, J. Nanosci. Nanotechnol. 2010, 10, 3193–3197.
- [16] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. E. Thompson, *Inorg. Chem.* 2001, 40, 1704–1711.
- [17] Q. Zhao, C.-Y. Jang, M. Shi, F.-Y. Li, T. Yi, Y. Cao, C.-H. Huang, Organometallics 2006, 25, 3631–3638.
- [18] F. I. Wu, H. J. Su, C. F. Shu, L. Y. Luo, W. G. Diau, C. H. Cheng, J. P. Duan, G. H. Lee, J. Mater. Chem. 2005, 15, 1035–1042.
- [19] L. Chen, H. You, C. Yang, X. Zhang, J. Qin, D. Ma, J. Mater. Chem. 2006, 16, 3332-3341.
- [20] W. Mróz, R. Ragni, F. Galeotti, E. Mesto, C. Botta, L. De Cola, G. M. Farinola, U. Giovanella, *J. Mater. Chem. C* **2015**, *3*, 7506–7512.
- [21] H.-W. Hong, T.-M. Chen, Mater. Chem. Phys. 2007, 101, 170.
- [22] V. V. Grushin, N. Herron, D. D. LeCloux, W. J. Marshall, V. A. Petrov, Y. Wang, Chem. Commun. 2001, 16, 1494–1495.
- [23] M. Thelakkat, H. W. Schmidt, Adv. Mater. 1998, 10, 219-223.
- [24] H. Y. Chen, C.-H. Yang, Y. Chi, Y.-M. Cheng, Y.-S. Yeh, P.-T. Cheu, H.-Y. Hsieh, C.-S. Liu, S.-M. Peng, G.-H. Lee, *Can. J. Chem.* **2006**, *84*, 309–318.
- [25] H. Jang, C. H. Shin, N. G. Kim, K. Y. Hwang, Y. Do, Synth. Met. 2005, 154, 157–160.
- [26] C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **2001**, *79*, 2082–2084.
- [27] C.-L. Ho, W.-Y. Wong, Z. Q. Gao, C. H. Chen, K. W. Cheah, B. Yao, Z. Xie, Q. Wang, D. Ma, L. Wang, X. M. Yu, H. S. Kwok, Z. Lin, *Adv. Funct. Mater.* 2008, *18*, 319–331.
- [28] N. C. Greenham, R. H. Friend, D. D. C. Bradley, *Adv. Mater.* **1994**, *6*, 491–494.
- [29] G. Sarada, J. Yoon, W. Cho, M. Cho, D. W. Cho, S. O. Kang, Y. Nam, J. Y. Lee, S.-H. Jin, J. Mater. Chem. C 2016, 4, 113–120.
- [30] M. Karramkam, F. Dolle, H. Valette, L. Besret, Y. Bramoullé, F. Hinnen, F. Vaufrey, C. Franklin, S. Bourg, C. Coulon, M. Ottaviani, M. Delaforge, C. Loc'h, M. Bottlaender, C. Crouzel, *Bioorg. Med. Chem.* 2002, 10, 2611–2623.
- [31] Y.-Z. Hu, G. Zhang, R. P. Thummel, Org. Lett. 2003, 5, 2251-2253.
- [32] S. Atechian, N. Nock, R. D. Norcross, H. Ratni, A. W. Thomas, J. Verron, R. Masciadri, *Tetrahedron* 2007, 63, 2811–2823.
- [33] X. Zhang, J. Gao, C. Yang, L. Zhu, Z. Li, K. Zhang, J. Qin, H. You, D. Ma, J. Organomet. Chem. 2006, 691, 4312–4319.
- [34] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [35] P. J. Hay, J. Phys. Chem. A 2002, 106, 1634-1641.

Received: November 2, 2015 Published online on February 16, 2016