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Carbazole and arylamine functionalized iridium complexes for efficient electro-phosphorescent light-emitting diodes

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ABSTRACT

We report the synthesis and characterization of four cyclometalated iridium complexes based on carbazole and arylamine modified 2-phenylpyridine. The carbazole and arylamine groups are linked to 2-phenyl pyridine backbone to enhance the energy harvesting and transfer from host to guest materials. The electrochemical and photophysical properties of the complexes are studied and electroluminescent devices are fabricated. The results show that the complexes with ligands containing carbazole moieties have desirable phosphorescent properties. The device with complex **3** doped PVK (poly (vinylcarbazole)) as emission layer achieves maximum luminous efficiency of 6.56 cd A^{-1} and maximum brightness of 14448 cd m⁻².

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1. Introduction

In the past decades, organic light-emitting diodes (OLEDs) based on phosphorescent complexes have attracted increasing attentions. The phosphorescent materials are doped as emitting guests into charge-transporting host materials to obtain high efficiency. The presence of a heavy-metal atom in the phosphorescent complex provides a significant spin–orbit interaction that allows the decay of normally spin-forbidden radiative triplet to happen. Due to both singlet and triplet excited states participating in the emission, the internal quantum efficiency can potentially reach as high as 100% [1–6].

Of all these phosphorescent complexes, cyclometalated iridium (III) complexes are the most promising candidates. Because of the comparatively short excited state and high phosphorescent efficiency, the quenching of the triplet excitons is decreased, leading to the effective phosphorescent emission in OLEDs [7–14]. Generally, it is necessary to disperse the iridium complexes as guest into a suitable host material to reduce triplet–triplet annihilation and concentration quenching so that the efficiency of energy-harvesting and the completeness of energy transfer from hosts to guests are can be effectively improved for highly efficient electrophosphorescent devices.

4,4'-Bis(N-carbazolyl)biphenyl (CBP) is a commonly used host material, and many excellent devices with CBP as host exhibiting high efficiencies were reported [15-20]. The green phosphorescent device with heteroleptic complex, Ir(ppy)₂acac, doped into CBP has been reported with a high η_{ext} of 19% and a power efficiency (η_{p}) of 60 lm W^{-1} (ppy = 2-phenyl pyridine, acac = acetylacetone) [21,22]. However, these devices have a complicated structure and consist of multiple layers deposited sequentially by thermal evaporation under high vacuum conditions. PLEDs that are made by processing polymeric materials from solution, such as by spin-coating or ink-jet printing techniques, have the advantages of easy fabrication and low cost. This inspires the exploration of the solution processable approach by incorporation of iridium complexes either by physical blending in polymeric host materials like PVK [23-29] or chemical bonding on polymer chains [30-34]. However, polymeric materials have disadvantages such as uncertain molecular structure and purity. In contrast, small molecule materials have defined molecular structure and can be easily purified. In order to combine both the advantages of small molecules with high purity and the convenience of solution-processible PLEDs, we synthesized a series of iridium complexes that can form uniform films through spin-coating. Owing to the high solubility, high thermal stability of the complexes and fine film morphology, the devices with solution-processible phosphorescent light-emitting layers show excellent properties.

In addition, because the balanced injection and transport of holes and electrons are key factors in the high efficiency OLED devices, it would be desirable to prepare phosphorescent complexes



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Scheme 1. Synthetic route to the iridium complexes 1-4.

containing structures that are beneficial for charge injection and transport. Carbazole- and arylamine-based compounds are commonly used as host materials for both small-molecule OLEDs (such as CBP) and PLEDs (such as PVK), because of their good hole-transporting ability and high triplet energy that effectively confines triplet excitons on phosphorescent dopants [14,35-40]. In this work, we introduced carbazole and arylamine functionalized groups directly into the ligands to increase energy transfer efficiency and hole-transporting ability. A series of novel iridium complexes with formula $Ir(L)_2(acac)$ (L = 2,5-bis(4,4"-N,N-diphenylamino) phenyl pyridine (1); L = 2-(4'-(4"-N,N-dipheny-lamino)phenyl)phenyl-5-(4^{"'}-N,N-diphenylamino)phenyl-pyridine (2); (9H-9-carbazolyl)phenyl)phenyl-5-(4^{'''}-(9H-9-carbazole))phenyl pyridine (4) have been synthesized. The photophysical and electro-chemical properties were studied and electroluminescent devices were fabricated. The device based on complex 3 showed a maximum luminous efficiency of $6.56 \text{ cd } \text{A}^{-1}$ and a maximum brightness of 14448 cd m^{-2} .

2. Results and discussion

2.1. Synthesis

The target compounds were synthesized through typically four key steps (Scheme 1). First, 4-*N*,*N*-diphenylaminophenylboronic acid and 4-(9*H*-9-carbazole)phenylboronic acid were synthesized in good yields. Then, the ligands were obtained via Suzuki coupling under mild conditions. The third step was to obtain μ -chlorobridged dimers of a general formula (C^N)₂ Ir(μ -Cl)₂Ir(C^N)₂. Finally, the complexes were obtained through the reaction of the μ -chlorobridged dimmers with the second ligand, acac β -diketone. The overall yield for complexes **1–4** over these steps was about 30%.

2.2. Photophysical properties

The absorption spectra of $Ir(ppy)_2$ (acac) and complexes **1–4** are shown in Fig. 1a. Complexes **1–4** have characteristic absorptions

shorter than 400 nm due to the π - π * transition of the ligands. The π - π * bands are accompanied by weaker, lower energy absorptions extending into the visible region longer than 450 nm, which can be assigned to MLCT transitions. The complexes with carbazole-substituted phenyl pyridine ligands showed more



Fig. 1. Absorption spectra (a) and photoluminescence spectra (b) of iridium complexes 1-4 in CHCl₃ at 293 K with $Ir(ppy)_2$ (acac) as a reference.

distinguishable MLCT absorption features at about 460 nm, which are likely due to the ³MLCT transitions [18]. The similarity of MLCT energies for complexes 1, 2 and complexes 3, 4 is not surprising, since each pair of complexes has MLCT states involving very similar acceptors. Meanwhile, the absorption spectra matched well with the emission spectra of the host material PVK (main peak at 370 nm), ensuring efficient energy transfer from host materials to guest materials. The PL spectra of complexes 1-4 are shown in Fig. 1b. All the complexes have two emission peaks with one at the longer wavelength and another at the shorter wavelength. The high energy emission at shorter wavelength can be assigned to the ligand emission and the low energy emission at longer wavelength can be assigned to the ³MLCT emission. The corresponding maximum emission wavelengths of complex 1 in CH₂Cl₂ are near 475 and 580 nm. For complex 2, the main emissions are near 450 and 580 nm. Complexes **3** and **4** have similar maximum emission wavelengths, with peaks at near 410 and 550 nm. All complexes emit from a mixed ${}^{3}MLCT {}^{-3}\pi {}^{-}\pi$ state with more ${}^{3}\pi {}^{-}\pi$ characteristics than those in the known complex Ir(ppy)₂(acac) and have an emission wavelength longer than the PL wavelength of $Ir(ppy)_2(acac)$ (518 nm), due to the enlarged conjugation system and increased size of the ligands.

The phosphorescence quantum yields of complex **3** and complex **4** are high (0.18 and 0.29), measured by using $Ir(ppy)_2(acac)$ as a reference, which has a value of 0.34 [19]. Complexes **1** and **2** have a relatively low quantum yield (about 0.038 and 0.10). The results show that the phosphorescence emissions of complex **3** and complex **4** are stronger due to the rigid carbazole group.

2.3. Electrochemical properties

Cyclic voltammetry (CV) was used to evaluate the electrochemical behavior of the four complexes and the results were shown in Fig. 2. It was recorded with a glass-carbon electrode in CH_2Cl_2 solutions containing 0.001 M of the Ir-complex and 0.10 M n-Bu₄NClO₄ against Ag/AgCl using ferrocene (Fc) as the internal standard.



Fig. 2. Cyclic voltammograms of complexes 1, 2, 3, 4, with $n-Bu_4NCIO_4$ as electrolytes.

 Table 1

 Electrochemical potentials and energy levels of the iridium complexes.

	HOMO/LUMO(eV)	$E_g(eV)$
Complex 1	-5.04/-2.65	2.39
Complex 2	-5.13/-2.77	2.36
Complex 3	-5.19/-2.76	2.43
Complex 4	-5.23/-2.58	2.38
Ir(ppy) ₂ (acac)	-5.15/-2.34	2.81

According to the literature [41,42], the HOMO energy level can be estimated from the onset potentials (E_{onset}^{ox}) through the follow-



Fig. 3. (a) EL spectra of devices using iridium complexes as guest and PVK as host with a concentration of 5 wt% and (b and c) current–voltage and luminance–voltage characteristics (d) current efficiency–current density characteristics.

Table 2EL performance of devices

Complex	$U_{\text{onset}}(V)$	$L_{\rm max}$ (cd m ⁻²)	$\eta_{ m Lmax} (m lm W^{-1})$	$\eta_{ m Imax}$ (cd A ⁻¹)	CIE coordinate	$\eta_{\mathrm{ext}\ \mathrm{max}}$ (%)	λ (nm) (low voltage)
1	8.3	2264	0.49	1.84	(0.54, 0.45)	0.69	581
2	10.75	2800	0.38	1.76	(0.58, 0.45)	0.64	589
3	7.6	14448	1.70	6.56	(0.42, 0.57)	1.81	550
4	7.8	5768	0.81	2.75	(0.44, 0.53)	0.80	557

ing equation: $E_{HOMO} = -(4.8 + E_{ref} + E_{onset}^{ox})$ eV, where E_{ref} is the potential of the Fc reference. The energy levels of LUMO and the HOMO-LUMO energy gap were calculated from the spectroscopic and electrochemical data, as shown in Table 1. The complexes with high electron density moieties have relatively high HOMO levels, thus high hole-transfer abilities. Consistent with the description of pyridine-localized LUMO and metal-involved HOMO [43,44], the direct linkage of the iridium atoms to pyridine in these complexes leads to discrete striking difference in HOMO levels. In addition, the iridium complexes 1-4 show similar energy band gap due to the similar electron-donating ability of carbazole, triphenylamine and diphenylamine moieties. However, complex 4 has a narrower energy gap due to the much higher LUMO, which attributes to the modification of pyridine with 9-phenyl-carbazole that has relatively lower electron-donating ability. As a result, the LUMO in complex **4** is stabilized more than other complexes. Moreover, the results showed that the complexes with the cyclometalated ligands containing phenylamine moieties have higher HOMO levels than that of $Ir(ppy)_2$ (acac) (-5.15 eV). This result confirms the improved hole-transporting ability of complexes 1-2 comparing with $Ir(ppy)_2$ (acac). These frontier orbital levels match closely with the energy levels for PEDOT:PSS (HOMO: -5 eV) and TPBI (LUMO: -2.9 eV) so that the electronic-structure requirements for the OLED devices can be satisfied.

2.4. Device properties

To evaluate the electroluminescent property of the iridium complexes in OLEDs, devices using these complexes as dopant emitters were fabricated. These phosphors are used as phosphorescent dopants rather than a single emission layer in OLEDs to prevent the severe self-quenching expected in the solid. PVK is used as the polymer host material for the electrophosphor because of the excellent overlap of the absorption spectra of the iridium complexes with the PL spectrum of PVK. Such a guest-host system allows efficient Forster energy transfer from the PVK host singlet to the iridium guest complex. TPBi acts as both a hole blocker and an electron transporter, and LiF as an electron-injection layer. Compared with the commonly used electron transporting materials 2,9-dimethyl-4,7-diphenyl-1, 10-phenanthroline (BCP) or tris(8aluminum hydroxyquinolinato) $(Alq_3),$ 1,3,5-tris(N-phenylbenzimidazol-2-yl) benzene (TPBi) was adopted for the devices since it shows a higher electron mobility and can efficiently confine excitons within the emission layer.

The electroluminescence (EL) spectra, current-voltage, luminance-voltage characteristics and current efficiency versus current density curve of devices using iridium complexes as guest at a concentration of 5% (wt) and PVK as host are shown in Fig. 3. Complexes **3** and **4** emit green light with the peak of the featureless spectrum at about 550 nm, while complexes **1** and **2** emit orange light with λ_{max} at 580 nm and a shoulder at around 640 nm. The maximum emission wavelengths of complexes **2** and **4** show slight red shifts compared to those of complexes **1** and **3** due to the increased π -conjugated system of the ligands. In addition, it should be noted that the EL emission at the high energy region, the blue emission from the ligand, is weak for all the complexes. This further proves the correct assignment of the high- and low-energy emissions of the PL emission and that the electrophosphorescent efficiency is higher than the electroluminescent efficiency.

The device with complex **3** as the doped material exhibits the best performance with the lowest turn-on voltage at 7.6 V. The maximum luminous efficiency reaches 6.56 cd A^{-1} , with a peak external quantum efficiency of 1.8%, while the maximum luminance reaches 14448 cd m⁻². These excellent properties are mainly attributed to the high phosphorescence quantum yields and electrochemical stability. Although complex **4** also has relatively high phosphorescence quantum yields, the device with which as the dopant shows comparatively lower performance with maximum brightness of 5768 cd m⁻², a maximum external quantum efficiency of 0.81%, and a luminance efficiency of 2.75 cd A⁻¹, due to its irreversible electrochemical process.

The devices with complex **1** and **2** as emitters exhibit similar performance, not as good as the other two. It demonstrates that the iridium complexes with carbazole moiety based ligands have much better electrophosphorescent properties than with the phenylamine moiety. These results shown in Table 2 also agree well with the quantum efficiencies of the complexes.

3. Conclusions

A series of iridium complexes were synthesized. Experimental results indicate that the complexes with carbazole-substituted 2-phenyl pyridine ligands have more desirable phosphorescent properties due to the rigid carbazole group harvesting and transferring energy efficiently to guest. The absorption and photo-luminescence spectra of the complexes show characteristic phosphorescent features. The increased HOMO level indicates that the modification of 2-phenylpyridine ligand with carbazole or phenyl-amine moieties increases hole-transporting ability of the phosphorescent center. The complexes have good solubility and can form uniform films for device fabricating. Especially, the device with complex **3**:PVK as emission layer shows the highest brightness (14448 cd m⁻²) and luminous efficiency (6.56 cd A⁻¹). This work provides a lead for future design of the ligand structures of iridium complexes.

4. Experimental part

4.1. Materials

Carbazole, n-BuLi, B(OCH₃)₃, were from Alfa Aesar. Pd(AcO)₂, Pd(PPh₃)₄, t-BuONa were from Acros. Diphenylamine, 4-bromoaniline, 4-bromophenylboronic acid, 1,4-dibromobenzene, 2,5-dibromopyridine were purchased from Sinopharm Chemical Reagent (SCRC).

4.2. Characterization and measurements

¹H NMR was collected by a Bruker 400 MHz spectrometer. Absorption spectra and photoluminescence (PL) spectra were recorded on a JASCO V-500 spectrophotometer and a JASCO FP-6200 spectrofluorometer, respectively in degassed CHCl₃ solutions. The phosphorescence quantum yields were determined in CHCl₃ at 293 K with Ir (ppy)₂(acac) as a reference ($\phi = 0.34$) [19]. Cyclic voltammetry was performed using a Model 283 potentiostat/galvanostat (Princeton Applied Research) with a scan rate of 50 mV/s.

Fabrication of light-emitting devices: The etched ITO $(20 \,\Omega/\Box)$ glass substrate was rinsed with detergent, deionized water, acetone, and ethanol in sequence, and then treated with UV-ozone. Next, poly(ethlyenedioxythiophene): poly (styrene-sulfonicacid) (PEDOT:PSS) was spin-coated on the surface of the ITO substrate, followed by thermal annealing at 120 °C for 2 h. On top of it, the solution of the mixture of complex and PVK in chloroform (10 mg/mL) was spin-coated through a 0.45 μ m teflon filter, followed by thermal annealing at 120 °C for 2 h. Finally, a thin layer of TPBi (20 nm) was used as the hole-blocking layer. A LiF layer (1 nm) and an Al layer (80 nm) were deposited successively in a vacuum evaporation chamber. The voltage-current density-luminance curve was measured by a measuring system composed of the R6145 (Advantest), the multimeter 2000 (Keithley), the luminance meter LS-110 (Minolta), and the power meter 1835-C (Newport), while the electroluminescence (EL) spectra were recorded by the fiber optic spectrometer S2000 (Ocean Optics). All measurements were carried out by a computer under ambient environment.

4.3. Synthesis experiment

4.3.1. General procedure for the synthesis of 4-(N,N-

diphenylamino)phenyl boronic acid (a) and 4-(N-carbazolyl)phenyl boronic acid (b)

To a three-necked flask containing 10 mmol Ar–Br and 50 ml THF protected by N₂ and cooled by dry-ice (-78 °C), was slowly added 16 mmol n-BuLi and the reaction was kept at -78 °C for 1 h. 30 mmol B(OCH₃)₃ was added to the flask rapidly and the reaction was continued for 2 h. As the temperature was raised to 0 °C, 50 ml 2 M HCl was added to the flask and the reaction continued for another 3 h. Ether was used to extract the product and the organic layer was evaporated to dryness. White powder was obtained.

Yield for **a**: 70%. m.p. 218 °C, ¹HNMR(CDCl₃, 400 MHz), δ: 8.02– 7.99 (d, 2H); 7.31–7.25 (m, 6H); 7.16–7.14 (d, 4H); 7.10–7.04 (m, 4H). Yield for **b**: 80%. m.p. 261–262 °C.

4.3.2. General procedure for the synthesis of 2,5-bis(4',4"-N,Ndiphenylamino) phenyl pyridine (bppp, **c**), 2,5-bis(4',4"-9H-9carbazolyl)phenyl pyridine (bcpp, **d**), and 5-bromo-2-(4'bromophenyl)pyridine (**e**)

To a three-necked flask protected by N₂ containing 2 mmol 2,5dibromopyridine, 4.57 mmol **a**, **b**, or 4-bromophenylboronic acid, was added 20 ml toluene and 10 ml ethanol, 0.2 mmol Pd (PPh₃)₄ and 20 mmol saturated K₂CO₃ solution. After refluxing for 36 h, the product was extracted and the organic phase was collected and evaporated to dryness. Chromatography of the resulting residue on 200–400 mesh silica gel eluting with dichloromethane affords **c**, **d** and **e**. The solvent was evaporated and the solid was recrystallized in ethanol. Pale green crystals were obtained.

For **c**, yield 70%. m.p. 217 °C. ¹H NMR (CDCl₃, 400 MHz), δ : 8.87 (s, 1H, Py–H); 7.91–7.90 (t, 3H); 7.72 (s, 1H); 7.51–7.50 (d, 2H); 7.30–7.26 (m, 8H); 7.18–7.14 (m, 12H); 7.07–7.04 (m, 4H). *Anal.* Calc. for C₄₁H₃₁N₃: C, 87.05; H, 7.43; N, 5.52. Found: C, 86.5; H, 7.31; N, 5.33%.

For **d**: yield: 55%. m.p. 272–27 °C, ¹H NMR (CDCl₃, TMS), δ : 9.11 (s, 1H); 8.34–8.32 (d, 2H); 8.19–8.17 (2, 4H); 8.08–8.07 (d, 1H); 7.93–7.90 (d, 1H); 7.87–7.85 (d, 2H); 7.76–7.73 (d, 4H); 7.53–7.51 (d, 4H); 7.47–7.43 (t, 4H); 7.35–7.32 (m, 4H). *Anal.* Calc. for C₄₁H₂₇N₃: C, 87.67; H, 4.99; N, 7.48. Found: C, 88.22; H, 4.85; N, 7.17%.

For **e**, as indicated in the Scheme, the starting materials were 4-bromophenylboronic acid and 2,5-dibromopyridine and the ratio is 1:1.5. The product was white needles, yield: 61%. m.p. 78–79 °C. ¹HNMR (CDCl₃, 400 MHz, δ : 8.73-8.72(s, H); 7.89–7.83 (m, 3H); 7.61–7.59 (d, 2H).

The synthesis of **f**, 2-(4'-(4''-N,N-diphenylamino)phenyl)phenyl-5-(4'''-N,N-diphenylamino)phenyl-pyridine (**apppp**) and**g**, <math>2-(4'-(4''-(9H-9-carbazolyl)phenyl) phenyl-5-(4'''-(9H-9-carbazolyl))phenyl pyridine (**cpppp**) is similar to that of **c** and **d**.

For **f**, **appp**, yellow needles, yield: 58%. m.p. 234–236 °C, ¹H NMR(CDCl₃, 400 MHz), δ : 8.92 (s, H); 8.11–8.09 (d, 2H); 7.93–7.91 (d, H); 7.83–7.81 (d, 2H); 7.71–7.69 (d, 2H); 7.56–7.51 (t, 4H); 7.31–7.28 (m, 8H); 7.18–7.14 (m, 12H); 7.08–7.02 (t, 4H). *Anal.* Calc. for C₄₇H₃₅N₃: C, 87.99; H, 5.46; N, 6.55. Found: C, 87.95; H, 5.82; N, 6.01%.

For **g**, **cpppp**, white flakes, yield: 56%. m.p. $302-304 \degree C$. ¹H NMR (CDCl₃, 400 MHz), δ : 9.11 (s, H); 8.36–8.32 (d,2H); 8.18–8.16 (t, 4H); 7.92–7.90 (d, 2H); 7.85–7.83 (d, 2H); 7.81–7.79 (d, 2H); 7.75–7.73 (d, 4H); 7.52–7.50 (m, 6H); 7.46–7.43(t, 4H); 7.34–7.30(t, 4H). *Anal. Calc.* for C₄₇H₃₁N₃: C, 88.54; H, 4.87; N, 6.59. Found: C, 88.37; H, 4.63; N, 6.55%.

4.3.3. General procedure for the synthesis of complex 1-4 [18,19]

The synthetic procedures for complex **1–4** were quite similar. The following is the procedure for complex **2**:

First, the synthesis of apppp₂Ir(μ -Cl)₂Irapppp₂ dimer: to a 50 mL three-necked flask protected by N₂ containing 15 mL 2-eth-oxyethanol, 5 mL water, 1.224 g (2.2 mmol) of **apppp** was added. The solution was stirred for 30 min. Then, 0.299 g (1 mmol) of IrCl₃·3H₂O was added and the solution was refluxed for 25 h. After cooling, the solution was filtered and washed by methanol, ether and hexane. 0.88 g of yellow powder was obtained, yield: 70%. m.p. > 300 °C.

Secondly, the complex: to a 50 mL three-necked flask equipped with a magnetic stirrer and protected by N₂, containing 15 mL 2ethoxyethanol, 0.06 mL (0.4 mmol) of acetylacetone (acac), 0.24 g Na₂CO₃, was added to 0.534 g (0.2 mmol) apppp₂lr(μ -Cl)₂Irapppp₂, after refluxing for 48 h under N₂, the solution was cooled to room temperature, red solid powers were obtained. The powders were filtered and washed buy water, methanol, ether and hexane. The red residues were chromatographed on a 200–400 mesh silica gel with dichloromethane mobile phase to yield –0.3 g (63%) pure apppp₂Ir(acac). ¹H NMR(CDCl₃, 400 MHz), δ : 7.367–6.874 (m, 68 H); 1.280 (s, 6H). *Anal.* Calc. for C₉₉H₇₅IrN₆O₂: C, 75.60; H, 4.81; N, 5.34. Found: C, 74.97; H, 5.55; N, 4.72%. ESI-MS: *m/z* 1572.6 [M]⁺.

For **(bppp)₂Ir(acac)**, **1**: yellow powder, yield: 63%. m.p. > 300 °C, dec. ¹H NMR (CDCl₃, 400 MHz), 7.363–7.324 (t, 7H); 7.260 (s, 9H); 7.205–7.186 (d, 7H); 7.164–7.068 (m, 12H); 7.013–6.992 (d, 6H); 6.943–6.904 (t, 7H); 6.829–6.810 (d, 6H) 6.753–6.731 (d, 3H); 6.703–6.667 (t, 3H), 1.558 (s, 6H). *Anal.* Calc. for $C_{87}H_{67}IrN_6O_2$: C, 73.57; H, 4.75; N, 5.92. Found: C, 73.61; H, 4.72; N, 6.09%. ESI-MS: *m/z* 1390.5 [M–2CH₃]⁺; 1321.5 [M–acac]⁺.

For **(bcpp)**₂ **Ir(acac)**, **3**, yellow powder, yield: 65%. ¹H NMR (CDCl₃, TMS), *δ*: 7.561–7.077 (m, 52H); 1.574 (s, 6H). *Anal.* Calc. for C₈₇H₆₃IrN₆O₂: C, 73.97; H, 4.21; N, 5.95. Found: C, 73.87; H, 4.74; N, 6.10%. ESI-MS: *m/z* 1382.4 [M–CH₃]⁺; 1413.4 [M–acac]⁺.

For **(cpppp)**₂**Ir(acac)**, **4**, yellow powder, yield: 66.0%. ¹H NMR (CDCl₃, 400 MHz), δ : 8.175–7.185 (m, 60H); 1.258 (s, 6H). *Anal.* Calc. for C₉₉H₆₇IrN₆O₂: C, 75.99; H, 4.32; N, 5.37. Found: C, 74.41; H, 4.11; N, 5.68%. ESI-MS: *m*/*z* 1548.4 [M–H–CH₃]⁺.

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References

- [1] I.E. Pomestcheako, C.R. Luman, M. Hissler, R. Ziessel, F.N. Castellano, Inorg. Chem. 42 (2003) 1394.
- R.C. Kwong, S. Sibley, T. Dubovoy, M.A. Baldo, S.R. Forrest, M.E. Thompson, [2] Chem. Mater. 11 (1999) 3709.
- [3] W. Lu, B.X. Mi, M.C.W. Chan, Z. Hui, N. Zhu, S.T. Lee, C.M. Che, Chem. Commun. 3 (2002) 206.
- [4] Y.G. Ma, H.Y. Zhang, J.C. Shen, C.M. Che, Synth. Met. 94 (1998) 245.
- [5] J.H. Kim, M.S. Liu, A.K.Y. Jen, B. Carlson, L.R. Dalton, C.F. Shu, R. Dodda, Appl. Phys. Lett. 83 (2003) 776. [6] Y.L. Tung, P.C. Wu, C.S. Liu, Y. Chi, J.K. Yu, Y.H. Hu, P.T. Chou, S.M. Peng, G.H. Lee,
- Y. Tao, A.J. Carty, C.F. Shu, F.I. Wu, Organometallics 23 (2004) 3745. [7] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R.
- Forrest, Nature 395 (1998) 151. [8] I.P. Duan, P.P. Sun, C.H. Cheng, Adv. Mater, 15 (2003) 224.
- [9] X. Gong, T.C. Ostrowski, G.C. Bazan, D. Moses, A.J. Heeger, M.S. Liu, Adv. Mater. 15 (2003) 45.
- [10] X. Chen, J.L. Liao, Y.M. Liang, M.O. Ahmed, H.E. Tseng, S.A. Chen, J. Am. Chem. Soc. 125 (2003) 636.
- [11] A. Tsubovama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, J. Am. Chem. Soc. 125 (2003) 12971.
- [12] Z.W. Liu, M. Guan, Z.Q. Bian, D.B. Nie, Z.L. Gong, Z.B. Li, C.H. Huang, Adv. Funct. Mater. 16 (2006) 1441.
- [13] C. Adachi, M.A. Baldo, S.R. Forrest, M.E. Thompson, Appl. Phys. Lett. 77 (2000) 904
- [14] M.A. Baldo, M.E. Thompson, S.R. Forrest, Nature 403 (2000) 750.
- [15] M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett 75 (1999) 4
- [16] M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, Y. Taga, Appl. Phys. Lett. 79 (2001) 156
- [17] S. Lamansky, P. Diurovich, D. Murphy, F. Abdel-Razzag, H.E. Lee, C. Adachi, P.E. Buttows, S.R. Forrest, M.E. Thompson, J. Am. Chem. Soc. 123 (2001) 4304.
- [18] D.K. Rayabarapu, B.M.J.S. Paulose, J.-P. Duan, C.-H. Cheng, Adv. Mater. 17 (2005) 349.
- [19] C.-H. Yang, C.-C. Tai, I.-W. Sun, J. Mater. Chem. 14 (2004) 947.
- [20] S. Takizawa, Y. Sasaki, M. Akhtaruzzaman, H. Echizen, I. Nishida, T. Iwata, S. Tokito, Y. Yamashita, J. Mater. Chem. 17 (2007) 841.
- [21] S. Lamansky, P. Djarovich, D. Murphy, F.A. Razzaq, H.E. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompson, J. Am. Chem. Soc. 123 (2001) 4304.

- [22] S. Lamansky, P. Djurovich, D. Murphy, F.A. Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M.E. Thompson, Inorg. Chem. 40 (2001) 1704
- K. Zhang, Z. Chen, C. Yang, X. Zhang, Y. Tao, L. Duan, L. Chen, L. Zhu, J. Qin, Y. Cao, J. Mater. Chem. 17 (2007) 3451.
- C.-H. Ku, C.-H. Kuo, C.-Y. Chen, M.-K. Leung, K.-H. Hsieh, J. Mater. Chem. 18 (2008) 1296
- [25] C.Y. Jiang, W. Yang, J.B. Peng, S. Xiao, Y. Cao, Adv. Mater. 16 (2004) 537.
- [26] X. Gong, J.C. Ostrowski, M.R. Robinson, D. Moses, G.C. Bazan, A.J. Heeger, Adv. Mater. 14 (2002) 581.
- Y. You, C.-G. An, D.-S. Lee, J.-J. Kim, S.Y. Park, J. Mater. Chem. 16 (2006) 4706. [28] F.-I. Wu, H.-J. Su, C.-F. Shu, L. Luo, W.-G. Diau, C.-H. Cheng, J.-P. Duan, G.-H. Lee,
- J. Mater. Chem. 15 (2005) 1035. [29] S.-P. Huang, T.-H. Jen, Y.-C. Chen, A.-E. Hsiao, H.Sh. Yin, H.-Y. Chen, S.-A. Chen, J. Am. Chem. Soc. 130 (2008) 4699.
- [30] X.-H. Yang, F.-I. Wu, D. Neher, C.-H. Chien, C.-F. Shu, Chem. Mater. 20 (2008) 1629.
- [31] K. Zhang, Z. Chen, C. Yang, S. Gong, J. Qin, Y. Cao, Macromol. Rapid Commun. 27 (2006) 1926.
- [32] Y. Zhang, Y. Xu, Q. Niu, J. Peng, W. Yang, X. Zhu, Y. Cao, J. Mater. Chem. 17 (2007) 992.
- [33] N.R. Evans, L.S. Devi, C.S.K. Mak, S.E. Watkins, S.I. Pascu, A. Kähler, R.H. Friend, C.K. Williams, A.B. Holmes, J. Am. Chem. Soc. 128 (2006) 6647.
- [34] S.-J. Liu, Q. Zhao, Y. Deng, Y.-J. Xia, J. Lin, Q.-L. Fan, L.-H. Wang, W. Huang, J. Phys. Chem. C. 111 (2007) 1167.
- [35] S.Y. Chang, J. Kavitha, S.W. Li, C.S. Hsu, Y. Chi, Y.S. Yeh, P.T. Chou, G.H. Lee, A.J. Carty, Y.T. Tao, C.H. Chien, Inorg. Chem. 45 (2006) 137
- [36] J.W. Hua, G.H. Zhang, H.H. Shih, X.Q. Jiang, P.P. Sun, C.H. Cheng, J. Organomet. Chem, 693 (2008) 2798.
- W.Y. Wong, G.J. Zhou, X.M. Yu, H.S. Kwok, B.Z. Tang, Adv. Funct. Mater. 16 (2006) 838.
- [38] W.Y. Wong, C.L. Ho, Coord. Chem. Rev. 253 (2009) 1709.
- [39] W.Y. Wong, C.L. Ho, J. Mater. Chem. 19 (2009) 4457.
- [40] Y. You, C.G. An, J.J. Kim, S.Y. Park, J. Org. Chem. 72 (2007) 6241.
- [41] R. Fink, Y. Heischkel, M. Thelakkat, H.W. Schmidt, C. Jonda, M. Huppauff, Chem. Mater. 10 (1998) 3620.
- [42] R. Zhu, G.A. Wen, J.C. Feng, R.F. Chen, L. Zhao, H.P. Yao, Q.L. Fan, W. Wei, B. Peng, W. Huang, Macromol. Rapid Commun. 26 (2005) 1729.
- [43] J. Brooks, Y. Babayan, S. Lamansky, P.I. Djurovich, I. Tsyba, R. Bau, M.E. Thompson, Inorg. Chem. 41 (2002) 3055.
- [44] K. Zhang, Z. Chen, C. Yang, X.W. Zhang, Y.T. Tao, L. Duan, L. Chen, L. Zhu, J.G. Qin, Y. Cao, J. Mater. Chem. 17 (2007) 3451.