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Synthesis and optoelectronic properties of a heterobimetallic Pt(II)–Ir(III) complex used as a single-component emitter in white PLEDs[†]

Xiaoshuang Li, Yu Liu, Jian Luo, Zhiyong Zhang, Danyan Shi, Qing Chen, Yafei Wang,* Juan He, Jianming Li, Gangtie Lei and Weiguo Zhu*

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To tune aggregation/excimer emission and obtain a single active emitter for white polymer light-emitting devices (PLEDs), a heterobimetallic Pt(II)–Ir(III) complex of FIr(pic)-C₆DBC₆-(pic)PtF was designed and synthesized, in which C₆DBC₆ is a di(phenyloxyhexyloxy) bridging group, FIr(pic) is an iridium(III) bis [(4,6-difluorophenyl)pyridinato-N,C²'] (picolinate) chromophore and FPt(pic) is a platinum(II) [(4,6-difluorophenyl)pyridinato-N,C²'] (picolinate) chromophore. Its physical and opto-electronic properties were investigated. Interestingly, the excimer emission was efficiently controlled by this heterobimetallic Pt(II)–Ir(III) complex compared to the PL profile of the mononuclear FPt(pic) complex in the solid state. Near-white emissions were obtained in the single emissive layer (SEL) PLEDs using this heterobimetallic Pt(II)–Ir(III) complex as a single dopant and poly(vinylcarbazole) as a host matrix at dopant concentrations from 0.5 wt% to 2 wt%. This work indicates that incorporating a non-planar iridium(III) complex into the planar platinum(II) complex can control aggregation/excimer emissions and a single phosphorescent emitter can be obtained to exhibit white emission in SEL devices.

Introduction

Since Kido and his coworkers reported the first white organic light-emitting diode in 1994,¹ white organic and polymer light-emitting diodes (OLEDs/PLEDs) have attracted tremendous attention in both academic and industrial communities for their intrinsic characteristics, such as low driving voltages, non-glare light, homogenous illumination, and for their potential applications in energy saving solid-state lighting sources.² Up to now, various white OLEDs/PLEDs with single-emissive-layers (SEL),^{1,3,4} multiple-emissive-layers (MEL),⁵ tandems,^{6–9} and microcavity structures,^{10,11} have been reported. In these devices, the SEL-based white OLEDs and PLEDs can be made with a simple process technique and were considered a class of promising commercial lighting sources.

There are often two approaches to construct the emitting layer in the SEL-based white OLEDs/PLEDs. The first way is doping multi-emitters with various emissive colors into a host matrix.^{12–16} However, this type of device has an inherent color stability problem as the blue emitters have shorter lifetimes than the green and red ones. The second way is employing only a single emitter with a wide-band emission in a host matrix.^{17–23} These single phosphorescent emitters mainly contain copolymers with different phosphors,^{17–19} and small molecular compounds with a mononuclear platinum complex unit.^{20–23} By mixing the blue-emitting monomolecule and its aggregation/excimer emissions, or different phosphor emissions, the SEL OLEDs/PLEDs exhibit white or near-white emissions. However, it is more difficult to present pure white emission in SEL devices with single small molecular phosphorescent emitters than copolymers.

As the structure and optoelectronic properties of the single small molecular active emitters are easily tuned in order to control the formation of the aggregation/excimer and to obtain stable white emission, we previously reported an alkyltrifluorene-modified mononuclear platinum complex and another dinuclear cyclometalated platinum(II) complex of (dfppy)₂-Pt₂(dipic) as single active emitters in white SEL PLEDs.⁴ In this paper, to further study the structure-property relationship of the platinumcontaining complexes, we designed and synthesized a heterobimetallic platinum-iridium complex of FIr(pic)-C₆DBC₆-(pic) PtF, in which the C_6DBC_6 is a di(phenyloxyhexyloxy) bridged group. FIr(pic) and FPt(pic), blue-emitting phosphorescent chromophores, are iridium(III) bis[(4,6-difluorophenyl)-pyridinato-N, C^{2} (picolinate) and platinum(II) [(4,6-diffuorophenyl)-pyridinato-N,C²'](picolinate), respectively. Here, incorporating an unconjugated C_6DBC_6 unit between the FIr(pic) and FPt(pic) chromophores is expected to efficiently manage intramolecular energy transfer, and partly control the excimer formation as the biphenyl unit in C₆DBC₆ has a distorted configuration. Introducing a non-planar iridium complex unit into the planar platinum

College of Chemistry, Key Lab of Environment-Friendly Chemistry and Application in Ministry of Education, Xiangtan University, Xiangtan, 411105, China. E-mail: zhuwg18@126.com, qij8304@hotmail.com; Fax: +86 731 58292251; Tel: +86 731 58298280 ‡Electronic_supplementary_information_(ESI)_available_See_DOI

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complex is hoped to further tune aggregation/excimer formation. The synthetic route of this FIr(pic)-C₆DBC₆-(pic)PtF complex is shown in Scheme 1. Its photophysical, electrochemical and electroluminescent properties were studied. The results showed that this heterobimetallic platinum–iridium complex presented stable near-white emission in the SEL PLEDs using poly(*N*-vinylcarbazole) (PVK) as a host matrix at different dopant concentrations from 0.5 wt% to 2 wt%. Therefore, attaching a non-planar blue-emitting iridium complex to a planar blue-emitting platinum complex by the unconjugated C₆DBC₆ unit can effectively tune the aggregation/excimer formation and a single active phosphorescent emitter can be obtained to exhibit white emission in SEL-based PLEDs.

Results and discussion

Synthesis and characterization

Compounds of 1, 2, 5, 8, FIr(pic) and FPt(pic) were prepared following literature procedures.^{4a,24–26} The methyl picolinate derivative 3 with a hydroxyl was synthesized *via* a Williamson

ether-forming reaction under a strict ratio of 4,4'-dihydroxybiphenyl and methyl 3-(6-bromohexyloxy) picolinate. Picolinic acid derivative **4** was obtained by a hydrolysis of methyl picolinate derivative **3** in sodium carbonate aqueous solution and methanol. The mononuclear Pt(II) complex **9** was synthesized by a debridging reaction of the chloride-bridged dimer **8** in the presence of sodium carbonate. The heterobimetallic platinumiridium complex of FIr(pic)-C₆DBC₆-(pic)PtF was obtained by a similar ether-forming reaction between compounds **7** and **9**, in which DMF was used as the solvent instead of acetone to improve the solubility of reactants. The molecular structure of FIr(pic)-C₆DBC₆-(pic)PtF was confirmed by ¹H NMR spectra and elemental analysis.

Photophysical properties

The UV-vis absorption spectra of FIr(pic)-C₆DBC₆-(pic)PtF, FIr(pic) and FPt(pic) in dichloromethane (DCM) are shown in Fig. 1, and their UV-vis absorption data are listed in Table 1. Similar UV-vis absorption spectra with a strong high-lying



Scheme 1 Synthetic route of the heterobimetallic cyclometalated platinum-iridium complex of $FIr(pic)-C_6DBC_6-(pic)PtF$.



Fig. 1 UV/vis absorption spectra of $FIr(pic)-C_6DBC_6-(pic)PtF$, FIr(pic) and FPt(pic) in dilute DCM (10⁻⁵ M) at 298 K.

absorption band below 300 nm and a weak low-lying absorption band between 350 nm and 450 nm are observed for FIr(pic)-C₆DBC₆-(pic)PtF and FIr(pic), in which the high-lying absorption band is assigned to be ligand-centered (LC) π - π * electron transition, and the low-lying absorption band is attributed to the mixing singlet and triplet metal-to-ligand charge transfer (MLCT) transitions.^{27a} However, FPt(pic) exhibited two new moderate absorption peaks in the range of 328 nm-350 nm. These moderate absorption peaks probably originate from the intraligand $\pi - \pi^*$ electron transition and the ligand to ligand charge transfer (LLCT) transition.^{27b} Compared to the UV-vis absorption spectrum of FPt(pic), the absorption peaks of the intraligand π - π * and LLCT transitions from this heterobimetallic platinum-iridium complex have not been observed. This implies that incorporating a non-planar FIr(pic) unit into a planar platinum complex by the unconjugated C₆DBC₆ unit can reduce the molecular aggregation and result in the disappearance of absorption from the LLCT transition for the resulting heterobimetallic platinum-iridium complex in DCM.

The photoluminescence (PL) spectra of FIr(pic)-C₆DBC₆-(pic)PtF, FIr(pic) and FPt(pic) in DCM and their neat films are shown in Fig. 2 and their PL data are also listed in Table 1. Almost identical PL spectra are observed between the heterobimetallic platinum–iridium complex and the mono-nuclear FIr(pic) complex at 10^{-5} M in DCM. For FIr(pic)-C₆DBC₆-(pic)PtF, an intense emission peak at 469 nm with a shoulder at 496 nm is presented. According to the literature,²⁸ this blue emission is assigned to the mixing singlet and triplet MLCT transitions of this complex. We noted that the FIr(pic)-C₆DBC₆-(pic)PtF complex has a PL quantum yield (Φ_{PL}) of 0.53 in

degassed DCM at room temperature using FIr(pic) as the standard ($\Phi_{PL} = 0.60$).²⁹ This indicates that the heterobimetallic platinum-iridium complex has a higher emission efficiency than FPt(pic) in DCM. To further understand the effect of the unconjugated C₆DBC₆ linking unit clearly in FIr(pic)-C₆DBC₆-(pic) PtF, the PL spectrum of a mixture of FPt(pic) and FIr(pic) was examined in DCM for comparison and shown in Figure S1.[†] A analogous PL spectrum with a 2 nm blue shift is found for the mixture instead of FIr(pic)-C₆DBC₆-(pic)PtF at 10⁻⁵ M in DCM. However, we found that the mixture film exhibited much weaker emission compared to that of the FIr(pic)-C₆DBC₆-(pic)-PtF neat film. It implies that the unconjugated C₆DBC₆ linking unit plays an important role in the emission.

On the other hand, the PL spectra in the neat films display only a minor red shift for FIr(pic)-C₆DBC₆-(pic)PtF and FIr(pic) compared to their corresponding PL spectra in DCM. The maximum emission peaks around 495 nm and 502 nm are observed in the PL spectra for FIr(pic)-C₆DBC₆-(pic)PtF and FIr(pic) in their neat films, respectively. However, a significantly red-shifted PL spectrum with an emission peak around 599 nm is exhibited only for FPt(pic) in its neat film. The remarkably different PL spectra between FIr(pic)-C₆DBC₆-(pic)PtF and FPt(pic) in their neat films can be ascribed to their different aggregated state. A non-planar structure of the FIr(pic) unit and a distorted unconjugated linkage of the C₆DBC₆ unit make their resulting heterobimetallic platinum-iridium complex hardly aggregate in the neat film. Therefore, it is difficult for FIr(pic)-C₆DBC₆-(pic)PtF to give aggregation/excimer emissions under this solid state.

Thermal and dispersibility properties

The thermal properties were examined by thermgravimetric analysis (TGA) under a nitrogen atmosphere at a scan rate of 20 °C min⁻¹. The thermal decomposition temperatures at 292 °C were observed for FIr(pic)-C₆DBC₆-(pic)PtF. This means that FIr(pic)-C₆DBC₆-(pic)PtF has high stability at the same time.

In order to make clear their dispersibility in a polymer matrix, the films of FIr(pic)-C₆DBC₆-(pic)PtF, FIr(pic) and FPt(pic) doped into PVK at 1 wt% doping concentration were made. The surface morphologies were recorded by atomic force microscopy (AFM) and are shown in Fig. 3. Roughnesses with $R_a =$ 0.45 nm, 0.37 nm and 0.34 nm are observed in the FIr(pic)-C₆DBC₆-(pic)PtF, FIr(pic) and FPt(pic)-doped films, respectively. Therefore, this heterobimetallic cyclometalated platinumiridium complex likewise has a good dispersibility in the PVK matrix.

Table 1 Photophysical and electrochemical properties of FIr(pic)-C₆DBC₆-(pic)PtF, FIr(pic) and FPt(pic)

Compounds	UV-vis (nm)	Emission (nm) ^a	Emission $(nm)^b$	$E_{\rm HOMO}~({\rm eV})$	$E_{\rm LUMO}~({\rm eV})$	$E_{\rm g}~({\rm eV})$
Flr(pic)	258, 385	471, 496	501	-5.62	-3.20	2.42
FPt(pic)	250, 328 352, 385	475, 502	599	-6.63	-3.46	3.17
Flr(pic)-C ₆ DBC ₆ -(pic)PtF	250, 280 374	469, 496	495	-5.51	-3.08	2.43

^a Measured in DCM at room temperature. ^b Measured in the neat film at room temperature.

1.00



Fig. 2 PL spectra of FIr(pic)-C₆DBC₆-(pic)PtF, FIr(pic) and FPt(pic) in DCM (10⁻⁵ M) and their neat films at 298 K.

Electrochemical properties

The electrochemical behaviors of FIr(pic)-C₆DBC₆-(pic)PtF were investigated by cyclic voltammetry (CV), and the resulting CV data are listed in Table 1. A reversible onset oxidation potential (E_{ox}) in a range from 1.23 to 1.25 V and an onset reduction potential (E_{red}) in a range from -1.16 to -1.18 V were observed. Based on the literature, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels (E_{HOMO} and E_{LUMO}) were calculated by the following equation: $E_{HOMO} = -(E_{ox} + 4.34)$, $E_{LUMO} = -(E_{red} + 4.34)$.³⁰ As a result, the HOMO and LUMO energy levels are located at -5.51 eV and -3.08 eV for FIr(pic)-C₆DBC₆-(pic) PtF, respectively. Compared to FIr(pic) and FPt(pic), this heterobimetallic platinum–iridium complex presented incremental E_{HOMO} and E_{LUMO} levels.

Electroluminescence properties

The electroluminescence (EL) spectra of the FIr(pic)-C₆DBC₆-(pic)PtF-doped PVK devices at the different dopant concentrations from 0.5 wt% to 2 wt% at 10 V are shown in Fig. 4, and their CIE chromaticity diagrams are also inserted in Fig. 4. Four distinct emission peaks at 410, 474, 500 and 598 nm are observed in these EL spectra, in which the emission peaks at 474 and 500 nm are assigned to both chromophores of the iridium and platinum complexes, and the emission peak at 598 nm is attributed to the excimers. Compared to the reported mononuclear platinum complex or its analogous dinuclear platinum complexes,⁴ the FIr(pic)-C₆DBC₆-(pic)PtF complex exhibited a decreased excimer emission at the dopant concentrations from 0.5 wt% to 2 wt% in the PLEDs. Furthermore, with increasing dopant concentrations, the excimer emission weakened little by little. This decreased excimer emission is attributed to the combined effects of a non-planar structure of the FIr(pic) unit and a distortedly unconjugated linkage of the C_6DBC_6 unit. As a result, a near-white emission was observed in the devices at low dopant concentrations from 0.5 wt% to 2.0 wt% under 10V, which corresponds to CIE coordinates from (0.24, 0.30) to (0.22, 0.36). In addition, the EL spectra have a minor change with increasing driving voltages from 9 V to 14 V in the device at 0.5 wt% doping concentration (Fig. 5). The



Fig. 3 Atomic force microscope images for the complex-doped PVK films (70 nm) at 1wt% doping concentration. (a) $FIr(pic)-C_6DBC_6-(pic)$ PtF, (b) FIr(pic) and (c) FPt(pic).

highest luminance of 245 cd m^{-2} and a current efficiency of 0.04 cd A^{-1} is achieved in the device at a 1 wt% doping level, respectively. Although these preliminary results are inferior to those of the reported white OLEDs, to the best of our knowledge, this is the first example on a heterobimetallic platinum–iridium complex as a single-emitting component in white



Fig. 4 EL spectra and CIE 1931 chromaticity diagrams of the FIr(pic)- C_6DBC_6 -(pic)PtF-doped PLEDs at different dopant concentrations from 0.5 wt% to 2 wt%.



Fig. 5 EL spectra and CIE 1931 chromaticity diagrams of the FIr(pic)- C_6DBC_6 -(pic)-PtF-doped PLEDs at 0.5 wt% dopant concentration under different applied voltages.

PLEDs. Compared to the mononuclear cyclometalated platinum complex of FPt(pic) and the homobimetallic platinum complex of $(dfppy)_2Pt_2(dipic)$,⁴ as expected, introducing a non-planar iridium complex into the planar platinum complex by an unconjugated linkage of the C₆DBC₆ unit plays a more important role in controlling aggregation/excimer emissions for their resulting heterobimetallic platinum–iridium complex. Therefore, this FIr(pic)-C₆DBC₆-(pic)PtF complex exhibited a more decreased excimer emission than $(dfppy)_2Pt_2(dipic)$ and FPt(pic) in the devices and should become another promising single phosphorescent emitter to exhibit white-emission in the SEL-based PLEDs.

Conclusions

In summary, a heterobimetallic platinum–iridium complex of $FIr(pic)-C_6DBC_6-(pic)PtF$ was prepared. Introducing a nonplanar FIr(pic) unit into the planar FPt(pic) unit by an unconjugated linkage can effectively control the excimer emission for the heterobimetallic platinum–iridium complex. Near-white emission was obtained in the SEL-based PLEDs using this

Experimental

Methods

All ¹H NMR spectra were acquired using a Bruker Dex-400 NMR instrument. UV absorption spectra were recorded with a HP-8453UV-visible system. PL spectra were recorded on a fluor-escence spectrophotometer (HITACHI-850). Cyclic voltammetry was carried out on a CHI660A electrochemical workstation in a 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution at a 100 mV s⁻¹ scan rate under nitrogen protection. A micro-platinum spar ($\emptyset = 0.8$ mm), a platinum wire and KCl saturated Hg/HgO were used as the work electrode, counter electrode and reference electrode, respectively. The thermogravimetric analysis (TGA) was carried out with a NETZSCH STA449 from 25 °C to 700 °C at a 20 °C min⁻¹ heating rate under a nitrogen atmosphere.

Device fabrication and characterization

Electroluminescence spectra were recorded with an InstaSpec IV CCD system (Oriel). Luminance was measured with a Si photodiode and calibrated by a PR-705 SpectraScan spectrophotometer (Photo Research). The SEL devices were fabricated with a structure of ITO/PEDOT: PSS (40–50 nm)/emitting layer (70–75 nm)/CsF (1.5 nm)/Al (100 nm), in which indium tin oxide (ITO) and poly(3,4-ethylenedioxy-thiophene)-poly (styrenesulfonate) (PEDOT: PSS) (Bayer AG) were used as the anode and hole-injection layer. Cesium fluoride (CsF) and Al were employed as the electron-injection layer and cathode, respectively. The emitting layer consists of the FIr(pic)-C₆DBC₆-(pic)PtF dopant and PVK host matrix. The dopant weight concentrations vary from 0.5 wt%, 1 wt% to 2 wt%.

Synthesis of FIr(pic)-C₆DBC₆-(pic)PtF

General information. All solvents were carefully dried and distilled prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were performed under a nitrogen atmosphere and were monitored by thin-layer chromatography (TLC). Flash column chromatography and preparative TLC were carried out using silica gel from Merck (200–300 mesh).

Methyl-3-(6-(4'-hydroxybiphenyl-4-oxy)hexyloxy)picolinate (3). A mixture of compound 2 (1.7 g, 5 mmol), biphenyl-4,4'diol (1.5 g, 7.5 mmol), potassium carbonate (3.7 g, 27 mmol), potassium iodide (0.1 g, 0.6 mmol) and 100 mL acetone were stirred at 65 °C for 48 h. After the mixture was cooled to room temperature (RT), 100 mL deionized water was added. The formed precipitate was filtered off, and washed with water, followed by ethanol. The precipitate was then purified on a silica column using a mixture of hexane and ethyl acetate (1 : 2, v/v) as eluent to provide compound **3** (1.3 g, 61.9%) as a white solid. ¹H NMR (DMSO, 400 MHz) δ : 9.42 (s, 1H), 8.17 (d, J = 4.19 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.40–7.63 (m, 5H), 6.95 (d, J = 8.41 Hz, 2H), 6.81 (d, J = 8.28 Hz, 2H), 4.10 (t, J = 6.10 Hz, 2H), 3.98 (t, J = 6.3 Hz, 2H), 3.83 (s, 3H), 1.75–1.82 (m, 4H), 1.26–1.37 (m, 4H).

3-(6-(4'-Hydroxybiphenyl-4-oxy)hexyloxy)picolinic acid (4). A mixture of compound **3** (0.5 g, 1.19 mmol), 10 mL sodium carbonate aqueous solution (2 M) and 50 mL methanol were stirred at 70 °C for 6 h. After the mixture was cooled to RT, 20 mL HCl solution (2 M) was added (pH = 2). The resulting precipitate was filtered off, washed with water, and by ethanol to present compound **4** (0.38 g, 76.0%) as a white solid. ¹H NMR (DMSO, 400 MHz) δ : 13.09 (s, 1H), 9.42 (s, 1H), 8.17 (d, *J* = 4.19 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.40–7.63 (m, 5H), 6.95 (d, *J* = 8.41 Hz, 2H), 6.82 (d, *J* = 8.28 Hz, 2H), 4.10 (t, *J* = 6.10 Hz, 2H), 3.98 (t, *J* = 6.3 Hz, 2H), 1.72–1.84 (m, 4H), 1.24–1.34 (m, 4H).

Iridium[111]bis[(4,6-difluorophenyl)-pyridinato-N,C²][(3hydroxy)picolinate] (6). A mixture of iridium trichloride hydrate (0.3 g, 0.85 mmol), compound 5 (0.5 g, 2.62 mmol), 15 mL 2ethoxyethanol and 5 mL deionized water were stirred at 100 °C for 12 h. After the mixture was cooled to RT, the resulting precipitate was filtered off, washed with water, followed by hexane to provide chloro-bridged dimer as a yellow solid. Then the mixture of the chloro-bridged dimer (0.35 g, 0.28 mmol), 3hydroxypicolinic acid (0.11 g, 0.84 mmol), sodium carbonate (0.45 g, 4.2 mmol) and 30 mL 2-ethoxyethanol was stirred at 130 °C for 12 h. After the mixture was cooled to RT, 20 mL deionized water and 5 mL HCl solution (2 M) were added (pH = 6), the resulting precipitate was filtered off, and washed with water, followed by hexane. The precipitate was then purified on a silica column using a mixture of hexane and ethyl acetate (2:1, v/v) as the eluent to present the compound 6 (0.49 g, 86.1%) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz) δ : 13.59 (s, 1H), 8.70 (d, J = 5.4 Hz, 1H), 8.23–8.68 (m, 2H), 7.80 (t, J = 7.76 Hz, 2H), 7.44–7.50 (m, 2H), 7.24–7.29 (m, 4H), 7.0 (d, J= 5.2 Hz, 1H), 6.40–6.54 (m, 2H), 5.81 (d, J = 8.64 Hz, 1H), 5.59 (d, J = 6.6 Hz, 1 H).

Iridium[111]bis[(4,6-difluorophenyl)-pyridinato-N,C²] [3-(6-bromohexyloxy)picolinate](7)

A mixture of compound **6** (0.5 g, 0.7 mmol), 1,6-dibromohexane (1.6 g, 6.56 mmol), cesium carbonate (1.0 g, 3.0 mmol), potassium iodide (0.1 g, 0.6 mmol) and 15 mL acetone was stirred at 65 °C for 6 h. After the mixture was cooled to RT, 20 mL deionized water was added. The resulting mixture was extracted with DCM (30 mL × 3). The organic layer was combined and dried over anhydrous MgSO₄. After removal of the solvent, the residue was purified on a silica column using a mixture of hexane and ethyl acetate (1 : 4, v/v) as eluent to obtain the compound of 7 (0.53 g, 85.5%) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz) δ : 8.84 (d, *J* = 5.2 Hz, 1H), 8.23–8.29 (m, 2H), 7.76 (t, *J* = 7.64 Hz, 2H), 7.41–7.50 (m, 3H), 7.21–7.23 (m, 2H), 6.99–7.01 (m,1H), 6.40–6.53 (m, 2H), 5.81 (d, *J* = 8.64 Hz,

1H), 5.53 (d, J = 6.6 Hz, 1H), 4.11 (t, J = 6.5 Hz, 2H), 3.43 (t, J = 6.7 Hz, 2H), 1.89–1.99 (m, 4H), 1.23–1.27 (m, 4H).

Platinum[II][(4,6-difluorophenyl)-pyridinato-N,C²] [3-(6-(4'-hydroxybiphenyl-4-oxy)hexyloxy)picolinate] (9)

A mixture of platinum dimer **8** (0.21 g, 0.25 mmol), compound **4** (0.26 g, 0.62 mmol), sodium carbonate (0.33 g, 3.1 mmol) and 15 mL 2-ethoxylethanol was stirred at 100 °C for 12 h. After the mixture was cooled to RT, 30 mL deionized water was added. The resulting precipitate was filtered off, and washed with water, followed by hexane. The precipitate was then dried and purified on a silica column using a mixture of hexane and ethyl acetate (1 : 8, v/v) as eluent to present compound **9** (0.18 g, 89.6%) as a yellow solid. ¹H NMR (DMSO, 400 MHz) δ : 9.42 (s, 1H), 9.08 (d, J = 6.63 Hz, 2H), 8.18 (d, J = 4.19 Hz, 2H), 7.95–8.02 (m, 2H), 7.70–7.73 (m, 1H), 7.41–7.54 (m, 5H), 6.95 (d, J = 8.41 Hz, 2H), 6.82 (d, J = 8.28 Hz, 2H), 6.62–6.67 (m, 1H), 4.09 (t, J = 6.10 Hz, 2H), 3.98 (t, J = 6.3 Hz, 2H), 1.72–1.84 (m, 4H), 1.24–1.34 (m, 4H).

Heterobimetallic iridium-platinum complex of FIr(pic)-C₆DBC₆-(pic)PtF. A mixture of iridium complex 7 (0.09 g, 0.1 mmol), platinum complex 9 (0.08 g, 0.1 mmol), cesium carbonate (0.17 g, 0.5 mmol), potassium iodide (0.01 g, 0.06 mmol) and 10 mL of DMF was stirred at 80 °C for 30 h. After the mixture was cooled to RT, 30 mL deionized water was added, and the resulting mixture was extracted with DCM (30 mL \times 3). The organic layer was combined and then dried over anhydrous MgSO₄. After removal of the solvent, the residue was purified on a silica column using a mixture of hexane and ethyl acetate (1:10, v/v) as eluent to provide $FIr(pic)-C_6DBC_6-(pic)PtF$ (0.058 g, 36.2%) as a yellow solid. ¹H NMR: (CDCl₃, 400 MHz) δ : 8.83 (d, J = 5.5 Hz, 3H), 8.23-8.25 (m, 4H), 7.72-7.80 (m, 5H), 7.40-7.49 (m, 4H), 7.21–7.33 (m, 6H), 7.00–7.02 (m, 4H), 6.65 (t, J = 1.6 Hz, 2H), 6.40–6.53 (m, 2H), 5.81 (d, J = 8.64 Hz, 1H), 5.53 (d, J = 6.6Hz, 1H), 4.16 (t, J = 6.5 Hz, 2H), 3.90 (t, J = 6.8 Hz, 2H), 3.58 (t, J = 6.5 Hz, 2H), 3.44 (t, J = 6.5 Hz, 2H), 1.84–1.99 (m, 6H), 1.23-1.27 (m, 12H). Anal. calcd for C₆₉H₅₆F₆IrN₅O₈Pt: C, 52.31; H, 3.54; N, 4.42; Found: C, 52.51; H, 3.74; N, 4.56%.

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