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White emission from dinuclear cyclometalated platinum(II) complex in single-emitting layer PLEDs

Yafei Wang^a, Xianping Deng^a, Yu Liu^{a,*}, Meijun Ni^a, Ming Liu^a, Hua Tan^a, Xiaoshuang Li^a, Weiguo Zhu^{a,*}, Yong Cao^{b,*}

^a College of Chemistry, Key Lab of Environment-Friendly Chemistry and Application of the Ministry of Education, Xiangtan University, Xiangtan 411105, China ^b Institute of Polymer Optoelectronic Material and Devices, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

A dinuclear platinum(II) complex of $(dfppy)_2Pt_2(dipic)$ has been prepared, where dfppy is 2,4difluorophenylpyridine and dipic is a biphenyl-bridged bi-picolinic acid derivative. Its physical and optoelectronic properties, as well as molecular orbitals calculation have been investigated and compared with those of its mono-nuclear (dfppy)Pt(pic) complex. Both platinum(II) complexes exhibited almost identical photoluminescence (PL) spectra with deep blue emission in dilute dichloro-methane $(10^{-5} M)$ and different PL spectra with red emission in their neat films. Stable white emissions were obtained in the $(dfppy)_2Pt_2(dipic)$ -doped polymer light-emitting devices using a blend of poly(vinylcarbazole) and 2-(4-biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole as a host matrix at dopant concentrations from 1 wt % to 10 wt %. In contrast, the (dfppy)Pt(pic)-doped devices exhibited orange-red emissions in the same device configuration. It indicates that dinuclear platinum(II) complex with a non-planar structure is an effective way to control formation excimers of platinum(II) complex and get white-emitting PLEDs with single dopant.

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1. Introduction

White organic light-emitting devices (WOLEDs) have been attracting much interest because of their great potential applications for flat-panel displays with low-cost, high efficiency, and flexible property.^{1–4} Usually, white light emission can be obtained from two kinds of device structures. One is multiple-emissive-laver (MEL) structure, 5-12 in which different layers emit different light in visible spectral regions. The other is single-emissive-layer (SEL) structure where multi-emitters are doped in the same emissive laver.^{13–16} In the MEL-based WOLEDs, a charge-blocking layer is usually inserted between emissive layer and cathode in order to confine the charges and excitons within the MEL regions for achieving high-efficiency emission. However, this approach often causes expensive processing cost, high driving voltage, and low efficiencies. In contrast, the SEL-based WOLEDs have simple process and lower cost than the MEL-based WOLEDs. Nevertheless, it is a crucial challenge to get pure white emission and color stability because of phase separation and undesired Förest energy transfer in the SEL-based WOLEDs.

Recently, another kind of the SEL-based WOLEDs with single dopant has been developed, in which white light emission results from a mixing emission of high-lying monomer emission and lowlying excimer emission. The reported excimer-emitting materials are mostly blue-emitting fluorescence^{17,18} and phosphorescence materials with planar molecular structure.^{19–23} Compared to fluorescence materials, phosphorescence materials, such as platinum (II) complexes have higher efficient luminescence as they can harvest single and triplet excitons leading to 100% internal quantum efficiency in theory. To our best knowledge, most of the reported phosphors used as single dopant in the SEL-based WOLEDs are bidentate platinum(II) complex of (dfppy)Pt(acac)²⁰ and N^C^Ncoordinated tridentate platinum(II) complex of PtL²Cl.²¹⁻²³ For example, Jabbour et al. made a (dfppy)Pt(acac)-doped WOLED using 2,6-bis(N-carbazolyl)-pyridine (26mCPy) as a host matrix, which exhibited near-white emission with a power efficiency of 29.1 Im W^{-1} and a Commission Internationale de l'éclairage (CIE) 1931 chromaticity coordinates of (0.46, 0.47).²⁰ Cocchi et al. used PtL²Cl and its derivatives as dopant to fabricate another WOLED with an external quantum efficiency (EQE) of 18.3%, a power efficiency of 11.8 $\text{Im} \hat{W}^{-1}$, and a CIE 1931 chromaticity coordinates of (0.33, 0.38).²³ Nevertheless, there are few reports on the white polymer light-emitting devices (WPLEDs) using dinuclear platinum (II) complex as single dopant.





^{*} Corresponding authors. Tel.: +86 731 58298280; fax: +86 731 58292251 (W.Z., Y.L.); tel.: +86 20 87114635 (Y.C.); e-mail addresses: liuyu03b@126.com (Y. Liu), zhuwg18@126.com (W. Zhu), poycao@scut.edu.cn (Y. Cao).

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In order to achieve novel excimer-emitting platinum(II) complex and its doped WPLEDs with stable white emission, here we reported a dinuclear platinum(II) complex of (dfppy)₂Pt₂(dipic), in which dfppy is 2,4-difluorophenylpyridine and dipic is a biphenylbridged bi-picolinic acid derivative. For comparison, its mononuclear platinum(II) complex of (dfppy)Pt(pic) was synthesized. where pic is picolinic acid. The synthetic route of both platinum(II) complexes is shown in Scheme 1. The photophysical, electrochemical, and electroluminescent properties, as well as molecular orbitals calculated by density functional theory (DFT) for both of platinum(II) complexes were studied. We found that the binuclear platinum(II) complex of (dfppy)₂Pt₂(dipic) presented stable white emission in the PLEDs using a blend of poly(N-vinylcarbazole) (PVK) and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) as a host matrix with increasing dopant concentrations from 1 wt% to 10 wt% and tuning applied voltages from 7 V to 12 V. However, the mononuclear (dfppy)Pt(pic) complex exhibited only red emission in the PLEDs with the same configuration at different concentrations from 1 wt% to 10 wt%.

2.2. Photophysical properties

The UV/vis absorption spectra of (dfppy)Pt(pic) and (dfppy)₂Pt₂(dipic) in dilute dichloromethane (DCM, 10⁻⁵ M) at 298 K are shown in Fig. 1, and their pertinent UV/vis absorption data are summarized in Table 1 for comparison. As a nearly linear and isolated arrangement between the Pt–Pt segments, dinuclear platinum(II) complex exhibits a similar UV/vis spectral pattern to that of mononuclear counterpart.^{25,26} Two moderate UV absorption bands are observed at around 325 nm and 350 nm from the spin-allowed and spin-forbidden metal-to-ligand charge transfer transitions (¹MLCT and ³MLCT), respectively. However, the dinuclear platinum(II) complex exhibits an increased extinction coefficient of MLCT absorption compared to the mononuclear platinum(II) complex. It is suggested to be relative to the additional intramolecular acceptor(A)-donor (D)-acceptor(A) interaction of $(dfppy)_2Pt_2(dipic)$, where acceptor(A) is a (dfppy)Pt(pic) chromophore and donor(D) is biphenyl unit.

Fig. 1 also depicts the photoluminescence (PL) spectra of these two platinum(II) complexes in dilute DCM (10^{-5} M) and the neat



Scheme 1. Synthesis of cyclometalated platinum(II) complexes.

2. Results and discussion

2.1. Syntheses and characterization

The methyl bi-picolinate derivative (**4**) was synthesized via a Williamson etherforming reaction between 4,4'-dihydroxybiphenyl and methyl 3-(6-bromohexyloxy) picolinate (**3**) in the presence of K₂CO₃ with a moderate yield of 38.5%. The bi-picolinic acid derivative of H₂dipic (**5**) was obtained by hydrolysis of methyl bi-picolinate derivative (**4**) under NaOH aqueous solution with a high yield of 87%. The mononuclear platinum(II) complex of (dfppy)Pt(pic) and binuclear platinum(II) complex of (dfppy)₂Pt₂(dipic) were obtained according to our previous work²⁴ by a chloride cleavage of the (dfppy)₂Pt₂Cl₂ dimmer with picolinic acid and its di-picolinic acid derivative, respectively. (See Supplementary data). The ¹H NMR spectra (Fig. S1), elemental analysis, and TOF-MS data confirm that both of the platinum(II) complexes were successfully obtained.



Fig. 1. The UV/vis absorption and PL spectra in dilute DCM (10^{-5} M) and the PL spectra in the neat films for (dfppy)₂Pt₂(dipic) and (dfppy)Pt(pic) at 298 K.

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Table 1

Photophysical and electrochemical properties of (dfppy)₂Pt₂(dipic) and (dfppy)Pt(pic)

Compounds	UV/vis (nm)	Emission ^b (nm)	Emission ^c (nm)	HOMO (eV)	LUMO (eV)	$E_{\rm g}({\rm eV})$
(dfppy)Pt(pic)	264, 325(0.652), ^a 350(0.652) ^a	418	601	-6.63	-3.46	3.17
(dfppy) ₂ Pt ₂ (dipic)	258, 322(2.03), ^a 353(1.54) ^a	425	438, 627	-5.83	-2.69	3.14

^a Absorption extinction coefficient (10⁴).

^b Measured in dilute DCM (10^{-5}) at room temperature.

^c Measured in the neat film at room temperature.

films at room temperature. All of the PL data are also summarized in Table 1. Both mono- and di-nuclear platinum(II) complexes exhibit a similar PL profile in dilute DCM. The maximum emission peaks at 425 nm and 418 nm are observed for the dinuclear platinum(II) complex and mononuclear platinum(II) complex, respectively, which are assigned to the electronic transition from ³MLCT to ground state. Furthermore, the PL spectra exhibit varieties with increasing (dfppy)₂Pt₂(dipic) concentrations from 10^{-5} M to 10^{-1} M in DCM, in which low-energy emission band exhibits an increased intensity accompanying with another red-shift band from high-energy emission (Fig. S2). The variety in PL profiles of (dfppy)₂Pt₂(dipic) is attributed to its different aggregation state at different concentrations in DCM.

At the same time, the PL spectra in the $(dfppy)_2Pt_2(dipic)$ and (dfppy)Pt(pic) neat films exhibit two resolved emission bands with a high-lying one at around 440 nm and a low-lying one at about 600 nm. However, distinct differences in the emission intensity and location are present in the two PL spectra. For the PL spectrum of $(dfppy)_2Pt_2(dipic)$, the intensity from the high-lying energy emission

peaked at 440 nm is stronger than that from the low-lying energy emission peaked at 628 nm. In contrast, for the PL spectrum of (dfppy)-Pt(pic), the intensity from the high-lying energy emission peaked at 440 nm is much weaker than that from the low-lying energy emission peaked at 601 nm. It is obvious that the (dfppy)Pt(pic) complex exhibits stronger excimer emission than the (dfppy)_2Pt2(dipic) complex. Therefore, this A–D–A-based dinuclear platinum(II) complex is available to display a decreased excimer emission due to the distorted interaction of two (dfppy)Pt(pic) chromophores at terminal.

2.3. DFT calculations

In order to investigate the effect of electronic transitions on PL property, the molecular orbital calculations by density functional theory (DFT: b3lyp/6-31g**: lanl2dz) were performed for both platinum(II) complexes. The resulting high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) graphs are shown in Fig. 2 and their energy levels are listed in



Fig. 2. Molecular orbitals of (dfppy)₂Pt₂(dipic) and (dfppy)Pt(pic).

Table 2 Energies for the frontier orbitals of (dfppy)₂Pt₂(dipic) and (dfppy)Pt(pic) calculated by DFT

Compounds	HUMO-1 (eV)	HUMO (eV)	LUMO (eV)	LUMO+1 (eV)	LUMO+2 (eV)
(dfppy)Pt(pic)	-6.302	-6.138	-2.356	-1.973	-1.562
(dfppy) ₂ Pt ₂ (dipic)	-5.864	-5.864	-2.247	-2.247	-1.754

Table 2. Just as most of cyclometalated complexes,²⁷ the electronic cloud is distributed among the Pt center and the cyclometalated ligand of dfppy for HOMO, while the electronic cloud is localized principally on the dfppy, the Pt center, and the pic ancillary ligand for LUMO. The distribution of electronic cloud for the dinuclear platinum(II) complex of (dfppy)₂Pt₂(dipic) is similar to that for the mononuclear platinum(II) complex of (dfppy)Pt(pic). However, the bridged biphenyl unit provides a little contribution to the HOMO and LUMO. It should be related to that the conjugate degree between two (dfppy)Pt(pic) chromophores is destroyed by the aliphatic ether chain in (dfppy)₂Pt₂(dipic). As shown in Table 2, the average energies of HOMO and LUMO are -5.86 and -2.25 eV for (dfppy)₂Pt₂(dipic) and -6.22 and -2.16 eV for (dfppy)Pt(pic), respectively, which is calculated by its near-degenerate pairs of HOMO, HOMO-1 and LUMO, LUMO+1. Therefore, the energy gap of (dfppy)₂Pt₂(dipic) is narrower than that of (dfppy)Pt(pic). The A-D-A-based dinuclear platinum(II) complex exhibits bathochromic emission compared to its mononuclear platinum(II) complex.

2.4. Thermal and dispersible properties

The thermal stability of platinum(II) complexes was evaluated by thermogravimetric analysis (TGA) under N₂ stream with a scanning rate of 20 °C/min and their TGA curves are shown in Fig. S3. The decomposition temperature (T_d) values are 236 °C for (dfppy)₂Pt₂(dipic) and 294 °C for (dfppy)Pt(pic), which correspond to a 5% weight loss. Both platinum(II) complexes exhibit high thermal stability.

In order to make clear their dispersibility in polymer matrix, the films of $(dfppy)_2Pt_2(dipic)$ and (dfppy)Pt(pic) doped into a blend of PVK+PBD at 10 wt% doping concentration were made. Their surface morphologies were recorded by atomic force microscopy (AFM) and are shown in Fig. 3. The $(dfppy)_2Pt_2(dipic)$ and (dfppy)Pt(pic)-doped films exhibit a roughness with R_a =0.603 nm and R_a =0.537 nm, respectively. It indicates that both platinum(II) complexes have a good dispersibility in the PVK–PBD matrix.

2.5. Electrochemical property

The electrochemical property of the (dfppy)₂Pt₂(dipic) complex was examined by cyclic voltammetry. The electrochemical curve is shown in Fig. S4 and its corresponding data are listed in Table 1. The (dfppy)₂Pt₂(dipic) complex presents an irreversible oxidation potential (E_{ox}) at about 1.49 V and a reversible reduction potential (E_{red}) at about -1.75 V. The HOMO and LUMO energy levels are calculated to be -5.46 eV and -2.89 eV according to an empirical formula: E_{LUMO} =-(E_{red} +4.34) and E_{HOMO} =-(E_{ox} +4.34), respectively.²⁸ Compared to our reported (dfppy)Pt(pic) (Table 1),²⁹ (dfppy)₂Pt₂(dipic) has a narrow energy gap leading to a minor red-shift emission, which is consistent with the theoretical calculation.

2.6. Electroluminescent property

The electroluminescent (EL) spectra and their CIE chromaticity diagrams of the (dfppy)₂Pt₂(dipic)-doped PVK–PBD devices in the



Fig. 3. Atomic force microscope images for the platinum(II) complexes-doped PVK–PBD films at 10% doping concentration: (a) (dfppy)₂Pt₂(dipic); (b) (dfppy)Pt(pic). (The film thickness was ~70 nm.).

dopant concentrations from 1 wt % to 10 wt % at 10 V are shown in Fig. 4. Three distinct peaks at about 430 nm, 484 nm, and 546 nm are observed in these EL spectra, respectively. Their CIE coordinates vary from (0.25, 0.28) to (0.31, 0.41) with increasing dopant concentrations from 1 wt % to 10 wt % at 10 V. White emission from



Fig. 4. The EL spectra and CIE 1931 chromaticity diagram of the $(dfppy)_2Pt_2(dipic)$ -doped PVK–PBD PLEDs with different concentrations from 1 wt % to 10 wt %.

these devices are exhibited at the given dopant concentrations. Fig. 5 shows the EL spectra and the CIE 1931 chromaticity of the PLED at 2 wt % dopant concentration under different applied voltages from 7 V to 12 V. Obviously, the CIE coordinates at white-region have minor change from (0.30, 0.38) to (0.32, 0.37). For comparison, the EL spectra and their corresponding CIE coordinates of the other PLEDs at 1 wt%, 4 wt%, and 10 wt% dopant concentrations with increasing applied voltages are shown in Fig. S5. Minor change for these EL spectra and their corresponding CIE coordinates are also observed at the given dopant concentrations and applied voltages. Therefore, the dinuclear platinum(II) complex is a promising class of single dopant to construct stable white-emitting SEL-based PLEDs. In these fabricated devices, the device exhibited pure white emission with a maximum brightness of 277 cd/cm² and a maximum current efficiency 0.1 cd/A at 4 wt% dopant concentration.



Fig. 5. The EL spectra and CIE 1931 chromaticity diagram of (dfppy)₂Pt₂(dipic)-doped PVK–PBD PLEDs with dopant concentration 2 wt % under different applied voltages.

For comparison, the EL spectra and CIE chromaticity diagrams of the (dfppy)Pt(pic)-doped PVK—PBD devices in the dopant concentrations from 1 wt% to 10 wt% at 10 V are shown in Fig. 6. The intense orange-red emission rather than white emission is observed and their maximum emission peaks vary from 558 nm to 612 nm with increasing dopant concentrations from 1 wt% to 10 wt%. In addition, a weak emission peak at about 430 nm is also



Fig. 6. The EL spectra and CIE 1931 chromaticity diagram of the (dfppy)Pt(pic)-doped PVK–PBD PLEDs with different concentrations from 1 wt % to 10 wt %.

observed at the dopant concentrations from 1 wt % to 4 wt % and gradually decreases with increasing the dopant concentrations. This weak emission peak does not disappear until the dopant concentration increases to 8 wt %. The corresponding CIE coordinates vary from (0.39, 0.47) to (0.52, 0.44) with increasing dopant concentrations from 1 wt % to 10 wt % at 10 V. The best performance is obtained in the device with a maximum brightness of 560 cd/cm² and a maximum current efficiency of 0.30 cd/A at 4% dopant concentration.

Therefore, constructing an A–D–A-based dinuclear platinum(II) complex is available to control its formation excimers and get whiteemitting PLEDs with single dopant. Mononuclear platinum(II) complex presents greater tendency to form excimers than dinuclear platinum(II) complex. As a result, the SEL-based WPLEDs are more available to obtain using the dinuclear platinum(II) complex rather than mononuclear platinum(II) complex as single dopant.

3. Conclusion

A dinuclear platinum(II) complex of (dfppy)₂Pt₂(dipic) and a mononuclear platinum(II) complex of (dfppy)Pt(pic) were obtained. Distinct difference in PL and EL properties were observed for both platinum(II) complexes in their neat films and PLEDs. Stable white emissions from the (dfppy)₂Pt₂(dipic)-doped devices were exhibited, while the (dfppy)Pt(pic)-doped devices gave orange-red emissions. Therefore, the A–D–A-based dinuclear platinum(II) complex is a promising class of single dopant to construct stable white-emitting SEL-based PLEDs. In order to obtain high-efficiency SEL-based WPLEDs, optimization of the (dfppy)₂Pt₂(dipic)-doped devices need be further carried out.

4. Experimental section

4.1. General

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 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). All ¹H NMR spectra were acquired at a Bruker Dex-400NMR instrument using CDCl₃ as a solvent. Mass spectra (MS) were recorded on a Bruker Autoflex TOF (MALDI-TOF) instrument using dithranol as a matrix. The UV absorption and photoluminescence spectra were measured with a Varian Cray50 and Perkin-Elmer LS50B Luminescence Spectrometer, respectively. Electrochemical measurements were made using a CHI660A electrochemical work station with a scan rate of 100 mV s^{-1} at room temperature under N₂ atmosphere. A conventional three-electrode configuration consisting of a Pt working electrode, a Pt-wire counter electrode, and a calomel electrode reference electrode was used. The solvent in all measurements was CHCN and the supporting electrolyte was 0.1 M tetra (n-butyl)ammonium hexafluorophosphate. EL spectra were recorded with an Insta-Spec IV CCD system (Oriel). Luminance was measured with a Si photodiode and calibrated by using a PR-705 spectrascan spectrophotometer (Photo Research).

The single-emissive-layer devices were fabricated with a structure of ITO/PEDOT/PSS (50 nm)/dopant+PVK-PBD (70 nm)/Ca (10 nm)/Al (150 nm), in which ITO is used as an anode, PEDOT/PSS is used as a hole-injection layer, and Ca/Al is employed as a cathode. The emitting layer consists of the dopants of platinum(II) complexes and host matrix of the PVK-PBD blend. Doping weight concentrations of platinum(II) complexes are 1 wt %, 2 wt %, 4 wt %, 8 wt %, and 10 wt %, respectively. PBD weight ratio is 30 wt % in the PVK-PBD blend. 4.1.1. *Methyl* 3-hydroxypicolinate (2). To a stirred mixture of 3-thydroxypicolinic acid (10 g, 71.9 mmol) in 350 mL CH₃OH and 5 mL H₂SO₄ was added several drops benzene as dehydrate; the resulting mixture was refluxed for another 24 h under the protection of nitrogen. After cooled to room temperature (rt), the mixture was poured into brine and extracted with ethyl acetate (EA). The organic layer was washed with brine for three times and then dried over anhydrous Na₂SO₄. After removal of the solvent, the intermediate (2) was gained as a white solid (11.0 g, 93.1%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.68–7.62 (m, 2H), 7.52–7.50 (d, *J*=7.92 Hz, 2H), 7.45–7.43 (d, *J*=7.92 Hz, 2H), 4.28–4.25 (t, *J*=12.4 Hz, 2H), 3.94 (s, 3H), 1.94–1.89 (m, 4H), 1.62–1.57 (m, 2H), 1.25–1.04 (m, 14H), 0.84–0.81 (t, *J*=11.8 Hz, 3H), 0.59–0.58 (m, 4H).

4.1.2. Methyl 3-(6-bromohexyloxy)picolinate (**3**). A mixture of methyl 3-hydroxypicolinate (4.0 g, 26.1 mmol), 1,6-dibromohexane (19.0 g, 78.3 mmol), K_2CO_3 (18.0 g, 130.5 mmol), and DMF (60 mL) was stirred at 80 °C for 24 h under nitrogen atmosphere. The resulting mixture was cooled to rt, poured into water (200 mL), and then extracted with DCM (3×30 mL). The combined organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using DCM as eluent to give the compound **3** as a reddish brown oil (6.3 g, 76.5%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.28–8.27(d, J=3.8 Hz, 1H), 7.43–7.40 (t, J=11.8 Hz, 1H), 7.37–7.35 (d, J=8.4 Hz, 1H), 4.09–4.06 (t, J=11.9 Hz, 2H), 3.97 (s, 3H), 3.45–3.42 (t, J=13.2 Hz, 2H), 1.92–1.87 (m, 8H).

4.1.3. Compound **4**. A mixture of compound **3** (2.0 g, 6.3 mmol), 4,4'-dihydroxybiphenyl (0.5 g, 2.7 mmol), potassium acetate (2.8 g, 20.8 mmol), and DMF (60 mL) was stirred at 80 °C for 24 h under nitrogen atmosphere. The resulting mixture was cooled to rt, poured into water (100 mL), and then extracted with DCM (3×30 mL). The combined organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE/EA (10:1) as the eluent to give the compound **4** as a white solid (1.3 g, 38.6%). ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 8.31 (s, 2H), 7.46–7.39 (m, 8H), 6.95–6.93 (d, *J*=7.7 Hz, 4H), 4.11–4.08 (t, *J*=12.4 Hz, 4H), 4.03–4.00 (t, *J*=12.6 Hz, 4H), 3.97 (s, 6H), 1.90–1.84 (m, 16H). Anal. Calcd for C₃₈H₄₄N₂O₈: C 69.49, H 6.75, N 4.27. Found: C 69.35, H 6.64, N 4.32%.

4.1.4. *Compound* **5**. A mixture of compound **4** (1.0 g, 1.5 mmol), NaOH (50%, 5 mL), anhydrous ethanol (5 mL), and THF (10 mL) was stirred vigorously for 2 h at 60 °C, then for another 24 h at room temperature. The mixture was poured into water and extracted with DCM (3×30 mL). The combined organic layer was dried over anhydrous magnesium sulfate, distilled, and then the solvent was removed by rotary evaporation to gain compound **6** (0.82 g, 87.0%) as a white solid. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 13.1 (s, 2H), 8.13–8.12 (d, *J*=4.2 Hz, 2H), 7.60–7.58 (d, *J*=8.4 Hz, 2H), 7.51–7.44 (m, 6H), 6.98–6.96 (d, *J*=8.3 Hz, 2H), 4.09–4.06 (t, *J*=12.2 Hz, 4H), 4.00–3.98 (t, *J*=9.9 Hz, 4H), 1.74 (m, 16H). Anal. Calcd for C₃₆H₄₀N₂O₈: C 68.77, H 6.41, N 4.46. Found: C 68.40, H 6.21, N 4.61%.

4.1.5. Complex $(dfppy)_2Pt_2(dipic)$. To a mixture of K₂PtCl₄ (0.2 g, 0.5 mmol) and water (4 mL) was added a solution of 2-(2,4-difluoro)phenylpyridine (50 mg, 0.26 mmol) and 2-ethoxyethanol (12 mL). The mixture was stirred under N₂ atmosphere at 80 °C for 24 h. After cooled to rt, the colored precipitate was filtered off and was washed with water and hexane to gain a [(dfppy)PtCl]₂ dimmer as a yellow solid (0.32 g) and directly used in the following process.

A mixture of **[(dfppy)PtCl]**₂ (0.32 g, 0.38 mmol), compound **5** (0.6 g, 0.95 mmol), and sodium carbonate (0.1 g, 0.95 mmol) were

stirred in 2-ethoxyethanol (15 mL) under N₂ atmosphere at 100 °C for 24 h. After cooled to rt, the mixture was extracted with DCM and the mixed organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE/DCM (1:2) as eluent to gain (dfppy)₂Pt₂(dipic) as a yellow solid (0.32 g, 41.6%). ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 9.23–9.22 (d, *J*=5.3 Hz, 2H), 8.69–8.67 (d, *J*=5.2 Hz, 2H), 8.05–8.03 (d, *J*=8.0 Hz, 2H), 7.93–7.91 (t, 2H), 7.72–7.70 (d, *J*=8.6 Hz, 2H), 7.58–7.54 (m, 2H), 7.46–7.44 (d, *J*=8.4 Hz, 6H), 7.21–7.17 (t, 2H), 6.94–6.92 (d, *J*=8.6 Hz, 4H), 6.68–6.66 (t, 2H), 4.25–4.22 (t, *J*=12.8 Hz, 4H), 4.04–4.01 (t, *J*=12.5 Hz, 4H), 2.02–2.0 (t, *J*=13.9 Hz, 4H), 1.89–1.85 (t, *J*=13.3 Hz, 4H), 1.67–1.58 (m, 4H), 0.90–0.86 (t, *J*=16.8 Hz, 4H). TOF-MS: 1419.3. Anal. Calcd for C₅₉H₅₃F₄N₄O₈Pt₂: C 50.18, H 3.78, N 3.97. Found: C 50.24, H 3.91, N 4.08%.

4.1.6. *Complexes (dfppy)Pt(pic).* It was prepared according to the synthetic procedure of complex (dfppy)₂Pt₂(dipic) except the ratio between the **[(dfppy)PtCl]**₂ dimmer and picolinic acid, which is 1:2.5 according to the reported procedure.²⁴ ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 9.23–9.22 (d, *J*=5.5 Hz, 1H), 9.10–9.09 (d, *J*=5.5 Hz, 1H), 8.24 (s, 2H), 8.08–8.06 (d, *J*=8.1 Hz, 1H), 7.95–7.91 (t, *J*=15.1 Hz, 1H), 7.74–7.72 (t, *J*=10.6 Hz, 1H), 7.23–7.20 (t, *J*=12.6 Hz, 1H), 6.95–6.93 (d, *J*=7.6 Hz, 1H), 6.71–6.66 (t, *J*=19.1 Hz, 1H). TOF-MS: 508.12. Anal. Calcd for C₁₇H₁₀F₂N₂O₂Pt: C 40.24, H 1.99, N 5.52. Found: C 40.41, H 1.91, N 5.38%.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.01.042.

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