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Synthesis and optoelectronic properties of a novel dinuclear cyclometalated platinum(II) complex containing triphenylamine-substituted indolo[3,2-*b*]carbazole derivative in the single-emissive-layer WPLEDs

Junting Yu, Jian Luo, Qing Chen, Keqi He, Fanyuan Meng, Xianping Deng, Yafei Wang *, Hua Tan, Haigang Jiang, Weiguo Zhu *

College of Chemistry, Key Lab of Environment-Friendly Chemistry and Application in Ministry of Education, Xiangtan University, Xiangtan 411105, China

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A novel bi-picolinic acid derivative of H_2dipic-BTICz containing binary triphenylamine-substituted indolo[3,2-*b*]carbazole (BTICz) unit and its dinuclear platinum(II) complex of (dfppy)$_2$Pt$_2$(dipic-BTICz) were synthesized as a single-component emitter used in the white polymer light-emitting diodes (WPLEDs), where dfppy is 2-(2,4-difluorophenyl)pyridine and dipic-BTICz is an anion of H_2dipic-BTICz. The photophysical and electrochemical properties of (dfppy)$_2$Pt$_2$(dipic-BTICz) were investigated. Compared with the reported mononuclear platinum complex of (dfppy)Pt(pic), (dfppy)$_2$Pt$_2$(dipic-BTICz) exhibited a red-shifted photoluminescent peak at 434 nm in dilute dichloromethane (10^{-5} M), but a weakened and red-shifted aggregation emission peak at 640 nm besides its intrinsic emission at 445 nm in its neat films. Stable pure white emissions with CIE coordinates of (0.325±0.005, 0.345±0.015) and a maximum brightness of 208 cd/m^2 were observed in the (dfppy)$_2$Pt$_2$(dipic-BTICz)-doped single-emissive-layer (SEL) PLEDs using a blend of poly(vinylcarbazole) and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole as a host matrix at 1 wt % dopant concentrations under applied voltages from 9 to 14 V. It indicates that the intrinsic and aggregation emissions of this dinuclear platinum complex were effectively tuned by inserting a new BTICz fluorophore in the dual picolinic acid derivative. Therefore, it is a promising single-component emitter to get white emission in SEL PLEDs.

1. Introduction

Since Kido and his co-workers reported the first white organic light-emitting diode in 1994,[1] white organic and polymer light-emitting diodes (WOLEDs/WPLEDs) have attracted significant 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.[2–4] Up to date, various WOLEDs/WPLEDs have been reported with single-emissive-layer (SEL),[1,5,6] multiple-emissive-layer (MEL),[3,7,8] tandem,[9–11] and microcavity structures.[12,13] Among these white-emitting devices, the SEL-based ones possess a simple process technique and were considered as a class of promising commercial lighting sources. To the best of our knowledge, two approaches are mainly presented to construct the white-emitting SEL devices. On one hand, multi-emitters with various emissive colors are used in the same host matrix as the activity layer.[1,14–18] However, this type of devices displays an inherent problem in color stability as the blue emitter has a shorter lifetime than the green and red emitters. On the other hand, a single-component emitter with a wide spectral band emission is employed in the host matrix as the emitting layer.[19,20] In this case, stable white emission was obtained due to simultaneously mixing the intrinsic emission in short-wave region and the aggregate (excimers or electromers) emission in long-wave region.[21–23] Usually, the single-component emitters in the second devise type are blue-emitting fluorescent[24,25] and phosphorescent materials[22,23,26–28] with a planar molecular structure. Compared to fluorescent materials, phosphorescent materials exhibited higher luminescent efficiency and have more potential in developing high-efficiency white-emitting devices as they can harvest single and triplet excitons leading to 100% internal quantum efficiency in theory. To date, most of the reported phosphors used as single-component emitters in the SEL WOLEDs were bidentate platinum(II) complex of (dfppy)Pt(acac)[22] and N–C–N

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* Corresponding authors. Tel.: +86 731 58298280; fax: +86 731 58292251; e-mail addresses: wangyf_miracle@hotmail.com (Y. Wang), zhuwg18@126.com (W. Zhu).

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coordinated tridentate platinum(II) complex of PtL^{2}Cl.[23,27,28] For example, Jabbour et al. made a (dfppy)Pt(acac)-doped device using 2,6-bis(*N*-carbazolyl) pyridine (26mCPy) as a host matrix, which exhibited near-white emission with a power efficiency of 29.1 lm/W and a Commission Internationale de l' Eclairage (CIE) 1931 chromaticity coordinate of (0.46, 0.47).[22] Cocchi et al. used PtL^{2}Cl and its derivatives as dopant to fabricate the WOLEDs with an external quantum efficiency (EQE) of 18.3%, a power efficiency of 11.8 lm/W and a CIE coordinate of (0.33, 0.38).[23] Recently, we developed some mono-, di- and tri-nuclear platinum(II) complexes as single-component emitters in the SEL WPLEDs, and stable white emission was achieved in these platinum-doped devices.[29–34] However, the EQE and brightness, as well as color stability have not reached satisfactory levels.

In order to further study the relationship between the molecular structure of the dinuclear platinum(II) complex and high-efficiency white-emitting SEL WPLEDs, we here designed and synthesized another novel dual picolinic acid derivative of H$_2$dipic-BTICz with a donor–acceptor (D–A) structure and its hetero-dinuclear cyclometalated platinum(II) complex of (dfppy)$_2$Pt$_2$(dipic-BTICz), in which a triphenylamine-substituted indolo[3,2-*b*] carbazole (BTICz) group as the D unit and two pending picolinic acid as the A units were non-conjugatedly connected by hexyloxy. We expected that the BTICz group should be able to enhance the blue emission component and carrier-transporting ability. The non-conjugated linkage between the D and A units is available to control intra- and inter-molecular energy transfer, as well as improve the film-formation and dispersibility. Furthermore, the aggregation (excimer/exciplex) emission of the resulting dinuclear platinum complex can be efficiently tuned in a host matrix. Therefore, this dinuclear cyclometalated platinum(II) complex is expected to become a promising single-component white-emitting phosphor used in WPLEDs. In this context, the photophysical, electrochemical, and electroluminescent properties of (dfppy)$_2$Pt$_2$(dipic-BTICz) were studied. As expected, this A–D–A-type dinuclear platinum complex presented controllable aggregation (excimer/exciplex) emission in a blend of poly(*N*-vinylcarbazole) (PVK) and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) under electric field. Stable white emissions with CIE coordinates of (0.315±0.015, 0.375±0.045) were observed in the SEL PLEDs using (dfppy)$_2$Pt$_2$(dipic-BTICz) as a single-component emitter and PVK–PBD as a host matrix from 1 to 2 wt % dopant concentrations. Compared to the previous (dfppy-mhb-dfppy)Pt$_2$(acac)$_2$ and (dfppy)$_2$Pt$_2$(dipic)$_2$,[31,32] this novel dinuclear cyclometalated platinum(II) complex exhibited more stable white emission with a maximum brightness of 208 cd/m^2 in the device at the doped concentration of 1 wt % due to the additional effect of the inserting BTICz fluorophore. To our best knowledge, this is a new example on stable white emission from the dinuclear cyclometalated platinum(II) complexes-doped SEL PLEDs at the dopant concentrations from 1 to 2 wt %. Therefore, this dinuclear cyclometalated platinum(II) complex with a blue-emitting fluorophore inserted into the dual piconilic acid derivative should become a novel promising single-component emitter used in the SEL WPLEDs with stable white emission.

2. Synthesis and characterization

As shown in Scheme 1, compounds of **2** and **3** were prepared following the literature procedures.[35–37] Compound **4** was synthesized according to the general alkylation procedure.[37,38] Methyl picolinate derivative (**5**) was synthesized via an etherification reaction using cesium carbonate as base and acetone as solvent. Intermediate **6** was obtained by hydrolyzation of compound **5** in the present of sodium hydroxide aqueous solution and THF. (dfppy)$_2$Pt$_2$(dipic-BTICz) was achieved according to our previous procedures by a chloride cleavage of the (dfppy)$_2$Pt$_2$Cl$_2$ dimer with the di-picolinic acid derivative.[39] ^{1}H NMR, ^{13}C NMR spectra, MALDI-TOF mass spectrometry, and elemental analysis confirmed that (dfppy)$_2$Pt$_2$(dipic-BTICz) were successfully obtained.

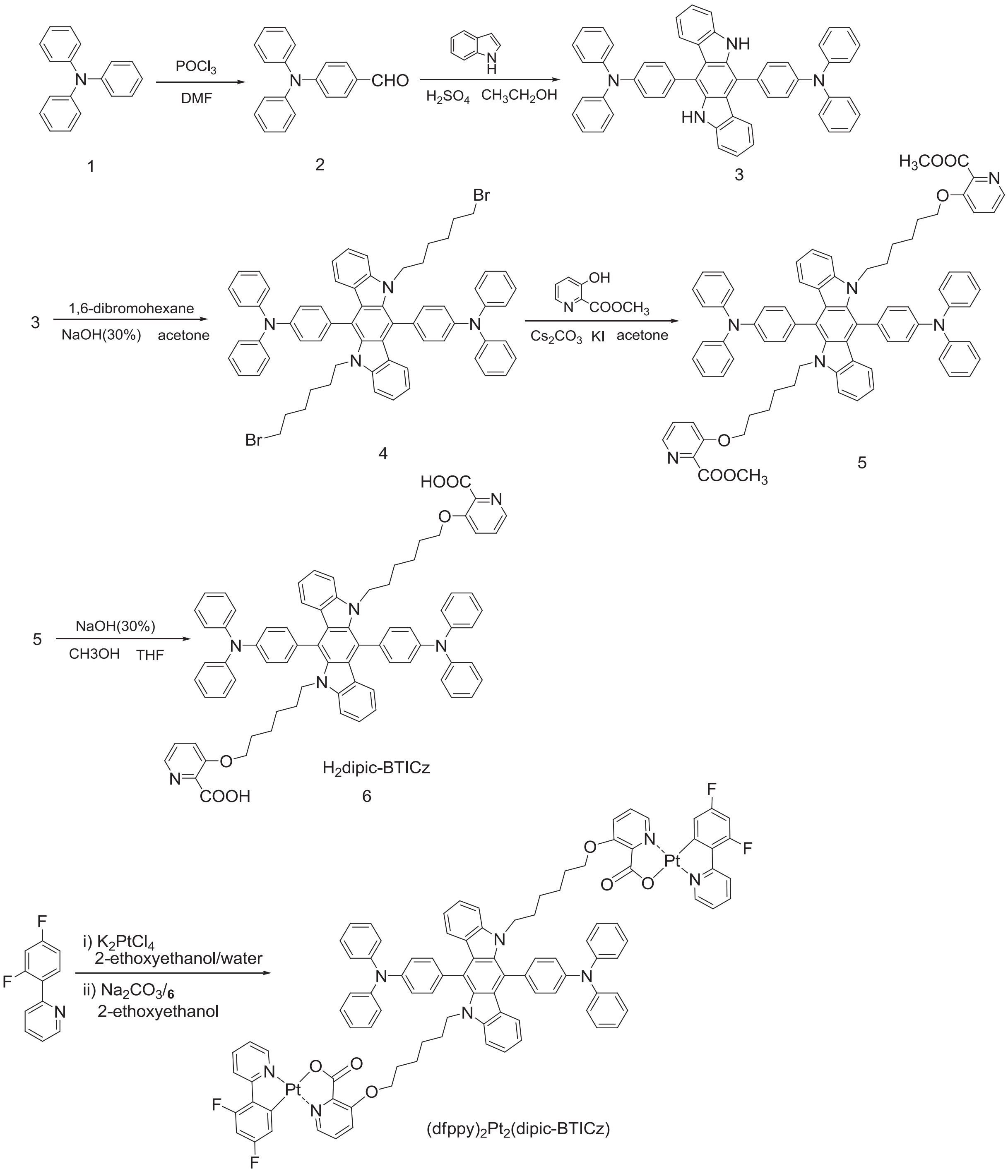
3. Photophysical properties

The UV–vis absorption spectra of (dfppy)$_2$Pt$_2$(dipic-BTICz) in dichloromethane (CH$_2$Cl$_2$) and its neat film are shown in Fig. 1. For comparison, the optophysical data of (dfppy)$_2$Pt$_2$(dipic-BTICz) and the mononuclear platinum complex of (dfppy)Pt(pic)[31–33] are listed in Table 1. Three distinct absorption bands were observed for the absorption spectrum of (dfppy)$_2$Pt$_2$(dipic-BTICz) in CH$_2$Cl$_2$ solution. Intense absorption in high-lying region about 287–309 nm is assigned to the ligand-centered (LC) spin-allowed π–π* electron transition of the BTICz unit. The absorption band about 321–338 nm is attributed to the singlet intraligand (IL) π–π* electron transition and/or the ligand to ligand charge transfer (LLCT) transition.[40] The weak absorption in the low-lying region at 393–420 nm is originated from the spin-allowed and spin-forbidden singlet metal-to-ligand charge transfer (^{1}MLCT and ^{3}MLCT) transitions, to a certain extent, together with the contribution of the triplet ^{3}IL π–π* transition and ^{3}LLCT transition. Compared to the mononuclear counterpart of (dfppy)Pt(pic), (dfppy)$_2$Pt$_2$(dipic-BTICz) exhibited an additional intense absorption band from the BTICz unit, which should be available to improve the energy-transfer efficiency from the host matrix to the dinuclear platinum complex in PLEDs. In addition, we noted that (dfppy)$_2$Pt$_2$(dipic-BTICz) displayed 10 nm red-shift and enhanced absorption spectrum in its neat film instead of its solution. This implies the increasing intermolecular interaction existed in the solid state.

The photoluminescence (PL) spectra of (dfppy)$_2$Pt$_2$(dipic-BTICz) in CH$_2$Cl$_2$ and its neat film at RT are also shown in Fig. 1. Similar PL profiles were observed for both mono- and di-nuclear platinum(II) complexes in dilute CH$_2$Cl$_2$ (10^{-5} M). The typical emission peak located at 435 nm, which is assigned to the electronic transition from MLCT to ground state.[41] Compared to the PL of (dfppy)Pt(pic), the PL spectrum of (dfppy)$_2$Pt$_2$(dipic-BTICz) displayed a bathochromic shift by 16 nm due to more intramolecular interaction resulting from the D–A system.[42] Interestingly, the PL spectra in Fig. S1 exhibited varieties with increasing (dfppy)$_2$Pt$_2$(dipic-BTICz) concentrations from 10^{-6} M to 10^{-2} M in CH$_2$Cl$_2$ (see Supplementary data). In this situation, the above typical emission peak was gradually red-shifted with increasing concentrations. This phenomenon is attributed to the different aggregation states at various concentrations in CH$_2$Cl$_2$. However, (dfppy)$_2$Pt$_2$(dipic-BTICz) displayed two resolved emission peaks at around 445 nm and 640 nm in the neat film. The emission intensity from the high-lying is much stronger than that from the low-lying one. It is obvious that (dfppy)$_2$Pt$_2$(dipic-BTICz) exhibited weaker aggregation emission than (dfppy)Pt(pic), which indicates that the non-conjugated linkage among the BTICz unit and two terminal (dfppy)Pt(pic) chromophores is available to make the dinuclear platinum(II) complex exhibit tunable aggregation emission.

4. Thermal property

The thermal stability of (dfppy)$_2$Pt$_2$(dipic-BTICz) was characterized by Thermogravimetric Analysis (TGA) under nitrogen atmosphere. The recorded TGA curve is shown in Fig. S2 (see Supplementary data). The decomposition temperature (T_d) value with a 5% weight loss is 284 °C, which is comparable to that of (dfppy)Pt(pic). It implies that (dfppy)$_2$Pt$_2$(dipic-BTICz) has a good thermal stability. The non-conjugatedly inserted BTICz unit between the dual picolinic acid has only a minor effect on the thermal stability of its dinuclear cyclometalated platinum(II) complex.



Scheme 1. Synthesis of dinuclear platinum(II) complex of $(dfppy)_2Pt_2$(dipic-BTICz).

5. Electrochemical property

The electrochemical property of the $(dfppy)_2Pt_2$(dipic-BTICz)-based neat film was examined by cyclic voltammetry, and its corresponding data are listed in Table 1. A reversible oxidation potential (E_{ox}) was observed at 1.1 eV. The E_{red} value was estimated by the energy band gap (E_g) and E_{ox} according to the following formula: $E_{red}=E_{ox}-E_g$, in which E_g was generally evaluated from the onset of the low-lying absorption. As a result, the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energy levels (E_{HOMO} and E_{LUMO}) were calculated to be −5.54 eV and −2.68 eV according to the empirical formula: $E_{LUMO}=-(E_{red}+4.34)$ and $E_{HOMO}=-(E_{ox}+4.34)$, respectively.[43] Obviously, $(dfppy)_2Pt_2$(dipic- BTICz) exhibited increasing E_{HOMO} and E_{LUMO} values compared to the (dfppy)Pt(pic). The BTICz unit is favor to improve the hole injection and transportation for its resultant dinuclear platinum(II) complex.

6. Electroluminescent property

To illustrate electrophosphorescent performance of $(dfppy)_2Pt_2$(dipic-BTICz), the SEL devices with a configuration of

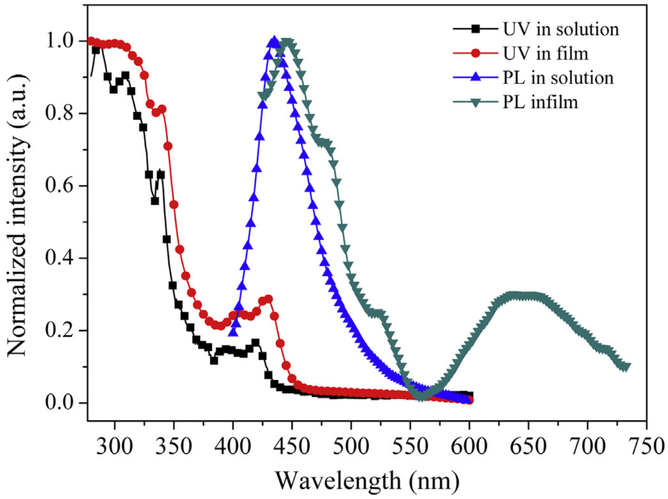


Fig. 1. UV–vis absorption spectra and PL spectra of $(dfppy)_2Pt_2$(dipic-BTICz) in dilute CH_2Cl_2 solution (10^{-5} M) and its neat film at 298 K.

Table 1
UV–vis absorption, PL, and electrochemistry properties of $(dfppy)_2Pt_2$(dipic-BTICz) and (dfppy)Pt(pic)

Compound	UV–vis[a] (λ_{ab}/nm)	Emission[b] (λ_{em}/nm)	Emission[c] (λ_{em}/nm)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
$(dfppy)_2Pt_2$ (dipic-BTICz)	287,309,321, 338,393,420	434	445, 478, 520, 640	−5.42	−2.68	2.74
(dfppy)Pt(pic)	264, 325, 348	418	427, 601	−6.63	−3.46	3.17

[a] Measured in CH_2Cl_2 at RT at a concentration of 10^{-5} mol/L.
[b] Measured in CH_2Cl_2 at RT (λ_{ex}=400 nm).
[c] Evaluated in the neat film.

ITO/PEDOT:PSS (50 nm)/Pt(II) complex (x wt %)+PVK:PBD (70 nm)/LiF (0.5 nm)/Al (150 nm) were fabricated by a spin-coating process. The electroluminescent (EL) spectra and their corresponding CIE chromaticity diagrams of the $(dfppy)_2Pt_2$(dipic-BTICz)-doped devices at dopant concentrations from 1 to 8 wt % at 13 V are shown in Fig. 2.

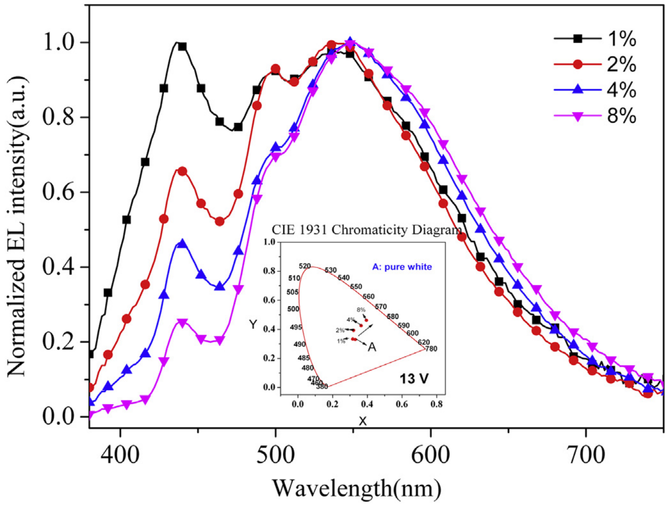


Fig. 2. The EL spectra and CIE chromaticity diagram of the $(dfppy)_2Pt_2$(dipic-BTICz)-doped devices at dopant concentrations from 1 to 8 wt % under an applied voltage of 13 V.

Three distinct peaks at about 437, 500, and 548 nm were observed in the EL spectra, respectively. Their CIE coordinates varied from (0.32, 0.33) to (0.39, 0.46) with increasing dopant concentration from 1 to 8 wt %. White emissions were achieved from these devices at 1 and 2 wt % dopant concentrations under different applied voltages from 9 to 14 V. Fig. 3a and b shows the EL spectra and CIE chromaticity diagrams of the devices at 1 and 2 wt % dopant concentrations under different applied voltages from 9 to 14 V. In this situation, the CIE coordinates were very stable at (0.325±0.005, 0.345±0.015) at 1 wt % dopant concentration, and had a minor change from (0.31, 0.35) to (0.33, 0.42) at 2 wt % dopant concentration. When the dopant concentrations increased to 4 and 8 wt %, the $(dfppy)_2Pt_2$(dipic-BTICz)-doped devices presented near-white emission and orange-yellow emission with stable CIE coordinates, respectively (see Supplementary data, Figs. S3 and S4).

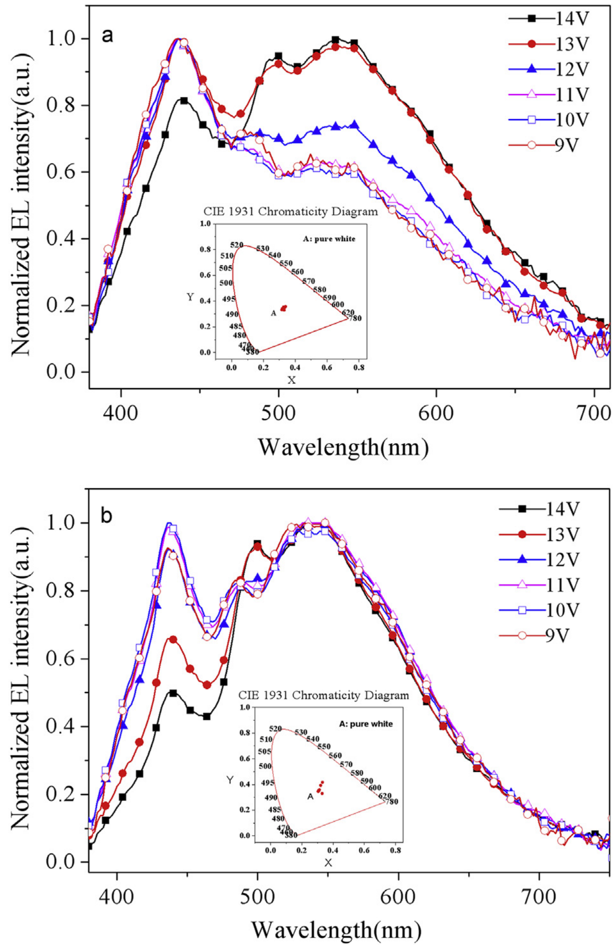


Fig. 3. The EL spectra and CIE chromaticity diagram of the $(dfppy)_2Pt_2$(dipic-BTICz)-doped devices at dopant concentrations of 1 wt % (a) and 2 wt % (b) under different applied voltages.

Fig. 4a and b exhibits the luminance–voltage (L–V) and the current density–voltage (J–V) curves of the $(dfppy)_2Pt_2$(dipic-BTICz)-doped devices at dopant concentrations from 1 to 8 wt %, respectively. The EL performances of these devices are summarized in Table S1 (see Supplementary data). The pure white emission was observed in the device with the maximum brightness of 208 cd/cm^2 and a maximum current efficiency of 0.16 cd/A at 1 wt % dopant concentration at different applied voltages from 9 to 14 V. Although these EL performances could not reach an ideal level, the $(dfppy)_2Pt_2$(dipic-BTICz)-doped devices exhibited stable white emission from 1 to 2 wt % dopant concentrations at various applied voltages. Therefore, this dinuclear platinum(II) complex could be a promising phosphorescent

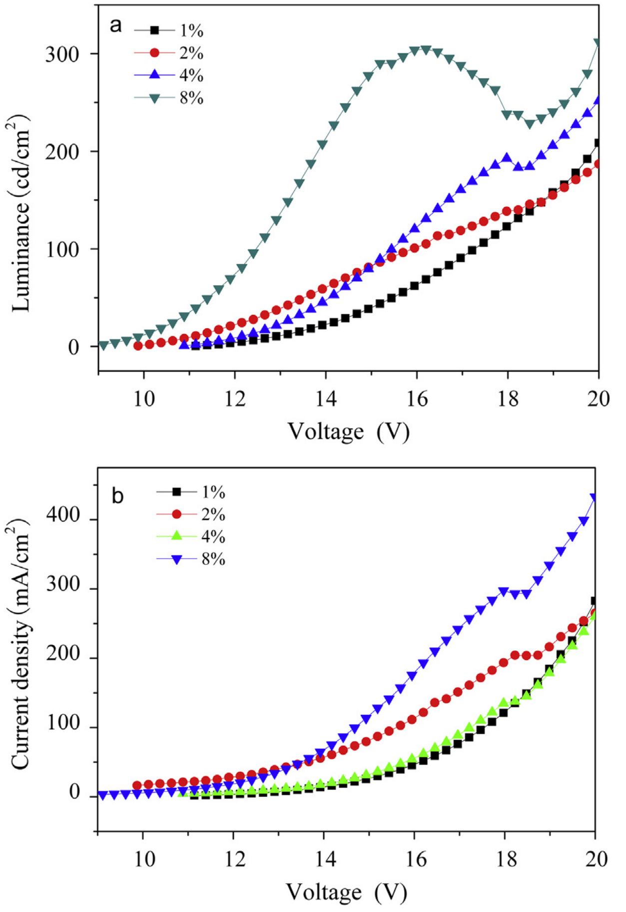


Fig. 4. The *L*–*V* (a) and *J*–*V* (b) curves of the (dfppy)$_2$Pt$_2$(dipic-BTICz)-doped devices at dopant concentrations from 1 to 8 wt %.

material in application of SEL WPLEDs. To our best knowledge, this is a new example on the stable white emission from the dinuclear platinum(II) complex-doped SEL PLEDs. Compared to the (dfppy)Pt(pic), the (dfppy)$_2$Pt$_2$(dipic-BTICz) with a BTICz fluorescent unit exhibited more controllable aggregation (excimer/exciplex) emission and is available to get stable white emission in the SEL PLEDs as a single-component dopant. It implies that the dinuclear rather than mononuclear cyclometalated platinum(II) complex has a more potential application in the SEL WPLEDs.

7. Conclusions

In summary, a novel dinuclear cyclometalated platinum(II) complex of (dfppy)$_2$Pt$_2$(dipic-BTICz) containing a dual picolinic acid and an blue-emitting BTICz fluorophore was synthesized. Inserting the blue-emitting BTICz fluorophore into the dual picolinic acid by non-conjugated linkage was proved to effectively tune the aggregation emission for its dinuclear cyclometalated platinum(II) complex. Stable pure white emissions with the CIE coordinates of (0.325±0.005, 0.345±0.015) and a maximum brightness of 208 cd/m^2 were achieved in the (dfppy)$_2$Pt$_2$(dipic-BTICz)-doped SEL PLEDs at 1 wt % dopant concentration under different applied voltages. This work provides another way to obtain stable white emission in the SEL PLEDs employing a novel dinuclear cyclometalated Pt(II) complex of (dfppy)$_2$Pt$_2$(dipic-BTICz) as a single-component phosphorescent emitter. In order to further improve the device performance, device optimization is being studied in our laboratory.

8. Experimental

8.1. Methods

All ^{1}H NMR spectra were acquired using a Bruker Dex-400 NMR instrument using $CDCl_3$ as a solvent. Mass spectra (MS) were recorded on a Bruker Autoflex TOF/TOF (MALDI-TOF) instrument using dithranol as a matrix. The UV–vis absorption and photoluminescence spectra were measured on a Varian Cray 50 and Perkin–Elmer LS50B luminescence spectrometer, respectively. Cyclic voltammetry was carried out on a CHI660A electrochemical workstation in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution at a 100 mV/s scan rate under nitrogen protection. A micro-platinum spar (ø=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 to 600 °C at a 20 °C/min heating rate under a nitrogen atmosphere.

8.2. 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 spectra scan spectrophotometer (Photo Research). The SEL devices were fabricated by a spin-coating process with a configuration of ITO/PEDOT:PSS (50 nm)/(dfppy)$_2$-Pt$_2$(dipicBTICz)+PVK–PBD (70 nm)/LiF (0.5 nm)/Al (150 nm), where indium tin oxide (ITO) acted as the anode, poly(ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) acted as the hole-injection layer, LiF and Al were employed as electron injection layer and cathode layer, respectively. The emitting layer consisted of the (dfppy)$_2$Pt$_2$(dipic-BTICz) dopant and a blend of PVK and PBD (PVK–PBD) used as the host matrix. The weight ratio of PBD was 30 wt % in PVK–PBD blend. Dopant concentrations varied from 1, 2, 4 to 8 wt %.

8.3. 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). 6,12-Bis(4-diphenylaminophenyl)-5,11-dihydroindolo[3,2-*b*]carbazoles (**3**)[36,37] and (dfppy)Pt(pic) were synthesized according to the described procedures before.

8.4. 6,12-Bis(4-diphenylaminophenyl)-5,11-di(6-bromohexyl) indolo[3,2-*b*]carbazole (4)

A mixture of compound **3** (3.2 g, 4.3 mmol), 1,6-dibromohexane (14.7 g, 60.3 mmol), aqueous sodium hydroxide (33%; 20 mL), and tetrabutylammonium bromide (TBAB, 0.1 g) in DMF was stirred vigorously at 80 °C under the nitrogen for 24 h. The mixture was cooled to RT and extracted with DCM (3×50 mL). The combined extracts were dried over magnesium sulfate and evaporated under reduced pressure. The excess 1,6-dibromohexane was recovered from the mixture by Kugelrohr distillation. The crude product was purified by dry flash chromatography using hexane/DCM (1:1, v/v) as eluent to give as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ (ppm): 7.55 (d, *J*=8.15 Hz, 4H), 7.40–7.33 (m, 16H), 7.29 (d, *J*=7.2 Hz, 4H), 7.20 (d, *J*=7.6 Hz, 2H), 7.10 (t, *J*=7.05 Hz, 4H), 6.99–6.96 (m, 4H), 6.82 (d, *J*=7.88 Hz, 2H), 4.04 (t, *J*=5.72 Hz, 4H), 3.38 (t, J=6.72 Hz, 4H), 1.85–1.78 (m, 4H), 1.62–1.60 (m, 4H), 1.44–1.38 (m, 4H), 1.30–1.12 (m, 4H).

8.5. Compound 5

A mixture of compound **4** (1.61 g, 1.50 mmol), methyl 3-hydroxypicolinate (0.46 g, 3.00 mmol), potassium iodide (100 mg, 0.60 mmol), cesium carbonate (4.89 g, 15 mmol), and 18-crown-6 (80 mg, 0.30 mmol) in 80 mL acetone was heated to reflux under stirring for 48 h. After cooled to RT, the mixture was filtered. The collected solid was washed by DCM three times. The combined organic solution was distilled successively under ordinary and reduced pressure. The residue was purified by silica gel column chromatography using EA/PE (3:2, v/v) as eluent to provide a yellow solid in a yield of 44.08%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS), δ (ppm): 8.25 (d, J=3.6 Hz, 2H), 7.55 (d, J=7.96 Hz, 4H), 7.38–7.32 (m, 16H), 7.27 (d, J=5.44 Hz, 8H), 7.07 (m, 8H), 6.96 (t, J=7.7 Hz, 2H), 6.81 (d, J=7.84 Hz, 2H), 4.04–3.98 (m, 8H), 3.89 (s, 6H), 1.81–1.78 (m, 4H), 1.47–1.44 (m, 4H), 1.20–1.18 (m, 4H), 0.87–0.86 (m, 4H). TOF-MS: 1212.741.

8.6. Compound 6

A mixture of compound **5** (0.46 g, 0.4 mmol), NaOH (20%, 5 mL), anhydrous ethanol (5 mL), and THF (20 mL) was stirred vigorously for 2 h at 65 °C, then for another 20 h at RT. 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** as a green solid in a yield of 91.8%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS), δ (ppm): 13.1 (s, 2H), 8.18 (d, J=4.2 Hz, 2H), 7.54 (d, J=7.6 Hz, 4H), 7.34–7.32 (m, 16H), 7.27 (d, J=5.44 Hz, 8H), 7.09–7.07 (m, 8H), 6.98 (t, J=6.8 Hz, 2H), 6.81 (d, J=7.84 Hz, 2H), 4.06 (t, J=0.48 Hz, 8H), 1.85–1.82 (m, 4H), 1.63–1.60 (m, 4H), 1.48–1.45 (m, 4H), 0.88–0.86 (m, 4H).

8.7. (dfppy)$_2$Pt$_2$(dipic-BTICz)

To a mixture of [(dfppy)PtCl]$_2$ dimer (0.4 g, 0.48 mmol), compound **6** (0.26 g, 0.24 mmol) and sodium carbonate (0.26 g, 2.4 mmol) were stirred in 2-ethoxyethanol (20 mL) under inert gas 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 MgSO$_4$ and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE/EA (2:5, v/v) as eluent to gain (dfppy)$_2$Pt$_2$(dipic-BTICz) as a dark yellow solid in a yield 38.6%. ^{1}H NMR (400 MHz, CDCl$_3$, TMS), δ (ppm): 9.13 (d, J=5.6 Hz, 2H), 8.61 (d, J=4.8 Hz, 2H), 7.97 (d, J=8.0 Hz, 2H), 7.87 (t, J=7.4 Hz, 2H), 7.55 (t, J=7.6 Hz, 6H), 7.36–7.32 (m, 20H), 7.13–7.05 (m, 8H), 6.95 (t, J=7.2 Hz, 6H), 6.84–6.78 (m, 4H), 6.63 (t, J=8.6 Hz, 2H), 4.10 (t, J=6.2 Hz, 4H), 4.05 (t, J=8.6 Hz, 4H), 1.86–1.84 (m, 4H), 1.49–1.46 (m, 4H), 1.18–1.15 (m, 4H), 0.87–0.86 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$, TMS), δ (ppm): 170.50, 163.56, 158.00, 149.86, 147.79, 147.76, 142.59, 142.53, 141.35, 139.52, 132.93, 132.62, 132.56, 131.50, 129.65, 129.50, 129.40, 128.10, 125.40, 125.11, 124.91, 124.39, 123.16, 123.05, 122.51, 121.61, 117.88, 117.61, 115.66, 114.45, 108.48, 99.50, 99.23, 70.33, 70.20, 44.28, 29.73, 28.66, 26.49, 25.58. TOF-MS: 1953.637.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.12.069.

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