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A feasible approach to obtain near-infrared (NIR) emission from binuclear platinum(II) complexes containing centrosymmetric isoquinoline ligand in PLEDs

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ABSTRACT

Organic light-emitting diodes (OLEDs) of deep-red (DR)/near-infrared (NIR) emission have become an emerging hot topic in applications for medical and night-vision devices. In this article, one novel symmetrical binuclear platinum(II) complexes as well as its mononuclear analogues, namely (DIQB)[Pt(DPM)]₂ and (DIQB)Pt(DPM), involving big rigid planar ligand 1,4-di(isoquinolin-1-yl)benzene (DIOB) and auxiliary ligand dipivaloylmethanato (DPM), were successfully synthesized and characterized. Intrinsic DR emission peaked at 618 nm with a photoluminescence quantum yield (Φ) of 2.42% and lifetime of 0.37 µs was obtained in the (DIQB)Pt(DPM) solution. Wondrously, an outstandingly 112 nm red-shifted emission peaked at 730 nm with a ϕ of 0.77% and lifetime of 0.26 µs was observed in (DIQB)[Pt(DPM)]₂ solution. Density functional theory (DFT/TD-DFT) calculations were carried out to reveal the emission process and a predominant ³ILCT/³MLCT characteristics. As a result, the emission of platinum(II) complexes is tuned from DR to NIR via appending an additional platinum(II) ion. OLEDs based on (DIQB)Pt(DPM) exhibited an efficient DR emission at 666 nm with a maximum external quantum efficiency (EQE) of 2.86% and a brightness of 1632 cd/cm² at dopant concentration of 3 wt %, In contrast, an outstandingly 80 nm red-shifted NIR emission at 746 nm with a EQE of 0.58% and a radiance of up to 10036 mW/Sr/m² was obtained for the (DBIQ)[Pt(DPM)]₂ device at the same dopant concentration. Moreover, the efficiency roll-off was efficiently inhibited in the (DIQB)[Pt(DPM)]2-doped devices. This work demonstrates that binuclear platinum(II) complexes dominated by centrosymmetric type C^N-C^N tetradentate big rigid planar ligand is an effective strategy for obtaining NIR luminescent materials.

1. Introduction

Inspired by the successful advancement of visible organic light emitting devices (OLEDs), the researches on deep-red (DR) to nearinfrared (NIR) OLEDs involved in electromagnetic radiation wavelength range from 650 nm to 2500 nm have been drawn tremendous efforts in the recent years, mainly due to their special applications in photodynamic therapy, night-vision readable displays, optical communication and chemical sensors [1–5]. So far, several kinds of DR-NIR OLEDs focused on organic molecules [6–8], conjugated polymer [9], lanthanide complex [10], and transition metal complexes [11–31], have been employed as DR/NIR emitters. For the iridium(III) complexes, a DR-emitting OLED based on an iridium(III) complex presented an EQE of 11.2% [11]. The highest efficient NIR-emitting OLEDs based on iridium(III) complexes were obtained with EQEs of 3.4% at 702 nm and 3.1% at 714 nm [16]. Among these of the reported platinum(II) complexes [17–28], not only have both singlet and triplet excitons, but also help to harvest unity internal quantum efficiency. Therefore, enormous researches based on platinum(II) complexes have been founded with tunable emission color from DR to NIR in their high-efficiency devices [17–28]. Nevertheless, in terms of the low energy NIR phosphorescent emitting materials, vibrational coupling between the ground and excited

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Scheme 1. Synthetic route of platinum(II) complexes.

electronic states are strong and accompanied with fast nonradiative decay [32]. Therefore, the efficiencies of large amounts NIR emission materials still lag far behind that of visible light emission materials to date.

As transition metal complexes, platinum(II) complexes have demonstrated efficient emission in NIR emitting OLEDs due to its unique d^8 electron structure [17–31]. This structure ensures that the platinum (II) complex molecules exhibit a high degree of planarity, variety of excited states, and strong intermolecular interactions. And have been developed quite high EQEs of 2.0-24% with peak emissions between 650 and 800 nm. For instance, two more efficient NIR OLEDs were fabricated based on cyclometallated platinum(II) complexes with the EQEs of 13.9% and 16.7%, respectively [26]. So far, the most efficient NIR-emitting non-doped OLEDs based on platinum(II) complex exhibited an unusual EQE of up to 24% with peak at 740 nm [27]. Nevertheless, these results suffering from easy aggregation and rather long phosphorescence lifetimes, and all these platinum(II) complexes present serious efficiency roll-off in devices at high current density. Consequently, it is still a challenge to exploit DR and NIR emitting platinum(II) complexes with high efficiency and low roll-off in OLEDs.

As is well known, binuclear platinum(II) complexes can occasionally extending the conjugation length as well as increasing the spin-orbit coupling (SOC) effect induced by its incorporated d orbital, which seems to be an inspiring approach to obtain efficient NIR platinum(II) emitters [18,23-25]. In our previous work, a binuclear platinum(II) complex was incorporated using pyrenyl-dipyridine (BuPyrDPy) as cyclometalating ligand, which is bridged with an ancillary ligand of dipivaloylmethanato (DPM) [28]. The results demonstrated that the DR to NIR emission was realized by appending additional metal ion. Inspired by above mentioned merit. It is expected this types of binuclear platinum(II) complexes could obtain NIR emission by grafting addition metal ion, we dedicated our efforts to devise novel NIR emission materials based on binuclear platinum (II) complexes bearing centrosymmetric big rigid planar ligand 1,4-di(isoquinolin-1-yl)benzene (DIQB) and auxiliary ligand DPM. In this work, one novel symmetrical binuclear platinum(II) complexes as well as its mononuclear homologous, namely (DIQB)[Pt(DPM)]2 and (DIQB)Pt(DPM), are primarily synthesized and characterized. Synthetic routes of the platinum(II) complexes are shown in Scheme 1. We selected DIQB unit as rigid expanded cyclometalated

ligand, mainly due to its highly extended π conjugation and more rigid chelating architectures. Meanwhile, DPM with dendritic structure was chosen as an auxiliary ligand, which is mainly beneficial for its effectively inhibit intermolecular interactions and enhance solubility [26, 28], their photophysical, electrochemical, thermal as well as electroluminescent (EL) properties were systematically investigated. Further density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations are engaged to clarify their luminous behavior. As expected, (DIQB)Pt(DPM) presented DR emission at 618 nm with a photoluminescence quantum yield (ϕ_{PL}) of 2.42% and a lifetime of 0.37 µs in dichloromethane (DCM) solution. Encouragingly, a NIR emission at 730 nm with a $\Phi_{\rm PL}$ of 0.77% and a short lifetime of 0.26 μs was obtained in (DIQB)[Pt(DPM)]₂ solution. Shorter phosphorescent lifetime means fewer triplet-triplet annihilation (TTA) processes and thus lower roll-off efficiency [33,34]. As a result, a DR emission peak at 666 nm with a maximum EQE of 2.86% and a brightness of 1632 cd/m^2 was obtained for the device containing 3 wt % (DIQB)Pt(DPM). Also, the (DIQB)[Pt (DPM)]2-doped devices afford a red-shifted 80 nm NIR isolated dual emissions at about 624 nm and 746 nm with a maximum EOE of 0.58% and a radiance of 10036 mW/Sr/m^2 . Moreover, its efficiency roll-off was efficiently inhibited in the (DIOB)[Pt(DPM)]₂-doped devices. These findings will open a novel avenue to exploit highly efficient NIR-emitting devices via binuclear platinum(II) complexes with centrosymmetric large rigid planar ligand.

2. Experimental section

2.1. Materials and synthesis

Unless otherwise stated, all chemicals and reagents were purchased from commercial sources without further purification. All reactions were implemented under nitrogen protection and monitored by thinlayer chromatography. As shown in Scheme 1, the ligand DIQB was synthesized by a common Suzuki coupling reaction [28,33]. The target platinum(II) complexes of (DIQB)Pt(DPM) and (DIQB)[Pt(DPM)]₂ were synthesized by an one-pot method [24,25]. The chemical structure of ligand DIQB was fully confirmed with ¹H NMR and MALDI-TOF mass spectrometry. Furthermore, the complex (DIQB)Pt(DPM) was confirmed with ¹H NMR and high resolution MS spectrometry. Particularly, the (DIQB)[Pt(DPM)]₂ was determined by ¹H NMR, MALDI-TOF mass spectrometry and single-crystal X-ray diffraction.

2.1.1. Synthesis of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzene (M1)

Under nitrogen atmosphere protection, a mixture of 1,4-dibromobenzene (5.0 g, 21.37 mmol), bipinate borate (13.56 g, 53.42 mmol), KOAc (12.58 g, 128.22 mmol) and Pd(dppf)Cl₂ (781 mg, 1.07 mmol) in 1,4-dioxane(40 mL) were stirred at 80 °C for 24 h. After being cooled to room temperature (RT), then the mixture was washed with saturated brine, extracted with DCM, and the combined organic layer was dried over anhydrous MgSO₄. The organic solvent was removed by rotary evaporation and the residue was passed through a flash silica gel column using petroleum ether (PE)/dichloromethane (DCM) (*V/V*, 3/1) as the eluent to afford white solid, then recrystallized from n-hexane to obtain white needle-like crystals (4.80 g, 68.51%). ¹ H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 7.80 (s, 1H), 1.35 (s, 6H). (MALDI-TOF) MS (*m*/*z*) for C₁₈H₂₈B₂O₄, Calcd: 330.220; Found, 330.012 [M+H]⁺.

2.1.2. Synthesis of 1,4-di(isoquinolin-1-yl) benzene (DIQB)

A mixture of 1-bromoisoquinoline (1.0 g, 4.81 mmol), M1 (722.0 mg, 2.19 mmol) and K₂CO₃ (1.81 g, 13.10 mmol) in 6.5 mL H₂O, 6.5 mL EtOH and 10 mL toluene were stirred at 80 °C for 24 h under nitrogen protection. After cooled to RT and washed with methanol (3 × 30 mL). The organic solvent was removed by rotary evaporation and then recrystallized from methanol to obtain white crystals (680 mg, 93.8%). ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 8.67 (d, *J* = 5.7 Hz, 2H), 8.22 (dd, *J* = 8.5, 0.6 Hz, 2H), 7.95–7.87 (m, 6H), 7.77–7.67 (m, 4H), 7.63–7.54 (m, 2H). MALDI-TOF MS (*m*/*z*) for C₂₄H₁₆N₂, Calcd: 332.410, Found, 333.000 [M+H]⁺.

2.1.3. Synthesis of complex (DIQB)Pt(DPM) and (DIQB)[Pt(DPM)]₂

Under nitrogen protection, a mixture of DIQB (200 mg, 0.60 mmol) and K₂PtCl₄ (550 mg, 1.32 mmol) were dissolved in 2-ethoxyethanol (12 mL) and stirred at reflux for 48 h. After cooling to RT, the mixture was poured into water and filtered, then the precipitate was washed with water and a small amount of methanol, and dried under high vacuum to get a crude dimer (320 mg). Without further purification, a mixture of dimer (320 mg, 0.17 mmol) and DPM (443 mg, 2.41 mmol) with Na₂CO₃ (638 mg, 6.02 mmol) were suspended in 15 mL THF solution and stirred at reflux for 12 h. The reaction was quenched with water and the mixture was extracted with DCM (3 \times 30 mL), and the combined organic layer was dried over anhydrous MgSO₄. The residue was purified by chromatography on a silica gel column using PE/DCM (V/V, 3/1) as the eluent. Finally, an orange solid (DIQB)Pt(DPM) (100 mg, 23.0%) and a dark red solid (DIQB)[Pt(DPM)]₂ (150 mg, 22.9%) were obtained, respectively. (DIQB)Pt(DPM): ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 9.07 (d, J = 6.5 Hz, 1H), 9.01 (d, J = 8.6 Hz, 1H), 8.69 (d, J = 5.6 Hz, 1H), 8.53 (d, J = 8.3 Hz, 1H), 8.33 (d, J = 8.3 Hz, 1H), 8.22 (d, J = 1.8 Hz, 1H), 7.91 (d, J = 8.3 Hz, 2H), 7.82 (t, J = 7.0 Hz, 1H), 7.71 (d, J = 14.4, 10.8, 4.5 Hz, 4H), 7.55 (t, J = 7.1 Hz, 2H), 5.84 (s, 1H), 1.43-0.93 (m, 18H). High resolution MS (m/z) for C₃₅H₃₄N₂O₂Pt, Calcd: 709.230; Found, 710.233 [M+H]⁺. (DIQB) [Pt (**DPM**)]₂: ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 9.26 (d, J = 8.7 Hz, 2H), 9.04 (d, J = 6.5 Hz, 2H), 8.49 (s, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.76 (t, J = 7.5 Hz, 2H), 7.64 (t, J = 7.8 Hz, 2H), 7.48 (d, J = 6.5 Hz, 2H), 5.85 (s, 2H), 1.34 (d, J = 18.3 Hz, 36H). MALDI-TOF MS (m/z) for C₄₆H₅₂N₂O₄Pt₂, Calcd: 1086.320; Found, 1086.633 [M+H]⁺.

2.2. Instrumentation

¹H NMR spectra was recorded on a Bruker DRX-400 spectrometer at 400 Hz using CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard. Mass spectrometry (MS) results were obtained on a Bruker Autoflex MALDI-TOF instrument. High resolution MS was achieved on waters Xevo G2-Xs QTof instrument. Single-crystal X-ray

diffraction studies were performed on a Bruker SMART Apex CCD diffractometer equipped with graphite monochromatized (Mo Ka) radiation, and the structures were solved by direct methods, and refined by a full-matrix least-squares technique using the SHELXL-97 crystallographic software package. The UV-Vis absorption spectra and photoluminescence (PL) spectra were obtained from the DCM solution and recorded with Shimadzu UV-2600 and Perkin-Elmer LS50B fluorescence spectrometers, respectively. Steady-state fluorescence measurements were recorded on a PerkinElmer LS45 instrument, while performing time-resolved fluorescence measurements using a time-dependent single photon counting (TCSPC) spectrometer (DeltaFlex-01-DD/HORIBA) with a Delta diode laser (510 nm) as excitation sources. Thermal analysis (TGA) was conducted on a NETZSCHSTA449 instrument at a heating rate of 20 °C/min. The Cyclic voltammetry (CV) was performed using CHI630E at a scan rate of 50 mV/s in CH₃CN solutions. All experiments were carried out in a three-electrode compartment cell with a Pt-wire counter electrode, a Pt-disk working electrode and Ag/AgCl reference electrode.

2.3. PLED fabrication and measurement

The structure of the doped devices is ITO/PEDOT:PSS(40 nm)/poly-TPD(30 nm)/[PVK:OXD-7(7:3)]:Complexes (x wt %, 50 nm)/TmPyPb (50 nm)/CsF(1.2 nm)/Al (120 nm). The PEDOT:PSS is used as a hole injection layer and poly-TPD is used as a hole transport layer (HTL). PVK:OXD-7 has good hole and electron transport ability as a mixed host. All devices with the emitting layers (EMLs) based on PVK:OXD-7(7:3) doped with platinum(II) complexes, with different doping concentrations of 3 wt%, 6 wt% and 9 wt%, respectively. TmTyPB is used as an electron transport layer (ETL) and a hole blocking layer (HBL), and CsF is used as an electron injection layer. PEDOT:PSS(40 nm) films covered by poly-TPD (30 nm) were spin-coated on precleaned ITO glass substrates and annealed at 120 °C for 20 min then the light emitting layer was spin-coated onto the PEDOT substrate from a mixture of PVK:OXD-7 and phosphors. After that, TmPyPb was evaporated onto the active layer. Finally, the CsF/Al layer was deposited on the top of the emitting layer. In order to prevent degradation and emission quenching caused by oxygen and water, all the above operations are performed in a nitrogen atmosphere or a vacuum state (1 \times 10⁻⁴ Pa), and the PLED is encapsulated before characterization. The EL spectra and current density (J)-voltage (V)-radiance (R) curves were obtained using a PHO-TORESEARCH Spectra Scan PR 735 photometer and a KEITHLEY 2400 Source Meter constant current source at room temperature. The EQE values were calculated by assuming a Lambertian distribution.

3. Result and discussion

3.1. Synthesis, characterization, thermal and single-crystal properties

Synthetic routes for the platinum(II) complexes of (DIQB)Pt(DPM) and (DIQB)[Pt(DPM)]2 are outlined in Scheme 1. DPM was employed as the ancillary ligand to restrain intermolecular interactions and improve solubility of the complexes. 1,4-benzenediboronic acid bis(pinacol) ester (M1) was prepared via 1,4-dibromobenzene and 4,4,4',4',5,5,5',5'octamethyl-2,2'-bi(1,3,2-dioxaborolane). 1,4-di- (isoquinolin-1-yl)benzene (DIQB) was synthesized by Suzuki coupling reaction with M1 and 1-bromoisoquinoline. Subsequently, based on the DIQB two coordination sites, one or two platinum (II) complexes can be prepared by one pot method reported in the literature, ^{[24,25} and the structures of DIQB and corresponding complexes were fully characterized by ¹H NMR, the structures of DIQB and (DIQB)[Pt(DPM)]2 were determined by MALDI-TOF mass spectra and the (DIQB)Pt(DPM) was carried out on high resolution MS, which confirmed their well-defined chemical structures (Fig. S1-S6, see ESI⁺). Particularly, the structure of the (DIQB)[Pt (DPM)]₂ was determined by single-crystal X-ray diffraction.



Fig. 1. a) ORTEP diagram of (DIQB)[Pt(DPM)]₂ with the atom numbering scheme (ellipsoids are drawn at the 50% probability level), b) Crystal structures and C) Intermolecular stacking of (DIQB)[Pt(DPM)]₂, respectively.



Fig. 2. Absorption and photoluminescence spectra of ligand and platinum(II) complexes in $\rm CH_2Cl_2$ solution.

3.2. Thermal stability

Thermal properties of both complexes were employed by thermogravimetric analysis (TGA) (Fig. S7, see ESI†). High thermal decomposition temperatures (T_d) of 306 for (DIQB)Pt(DPM) and 380 °C for (DIQB) [Pt(DPM)]₂ were obtained at 5% weight loss, respectively, demonstrating that the introduction of the additional metal platinum(II) ion is beneficial to enhance the thermal stability of its platinum(II) complex.

3.3. Single-crystal structures

A purplish red flaky single crystal of (DIQB)[Pt(DPM)]₂ was formed by slow diffusion of their methanol/dichloromethane solutions at room temperature. The ORTEP diagram, molecular structures and crystalpacking diagram are shown in Fig. 1. Crystal data and refinement parameters and selected bond lengths and angles are summarized in Table S1 and S2. The corresponding platinum-ligating atom bond lengths in (DIQB)[Pt(DPM)]₂ are similar to many C^N bidentate platinum complexes. And the Pt-C bonds are slightly shorter than the Pt-N bonds, also exhibit obvious trans effect to the corresponding trans Pt-O bonds. As shown in Fig. 1, the whole ligand frameworks execute much planarity that welded by the chelated metal ions in (DIQB)[Pt (DPM)] $_2$ and a torsion angle of 12.60° was observed between benzene and isoquinoline unit and intra-ligand charge transfer character (ILCT) from benzene to isoquinoline can be expected in such a donor-acceptordonor ligand system. A large Pt- Pt separation of 6.43 Å between the adjacent platinum centers also means the absence of metal-metal-toligand charge transfer (MMLCT) in the crystal states in the crystal-

Photophysical and thermal parameters of platinum(II) complexes	Table 1
	Photophysical and thermal parameters of platinum(II) complexes

Complex ^a	$\lambda_{abs}^{\ \ b}$ nm, [$\epsilon \times 10^{-4} M^{-1} cm^{-1}$]	λ _{ΡL} ^b [nm]	Φ _p ^b [%]	τ ^c [μs]	$k_{\rm r}^{\rm d}$ [10 ⁴ s ⁻¹]	k_{nr}^{d} [10 ⁶ s ⁻¹]	T _d [°C]
Pt-1	413(0.97),369 (2.15),352 (1.81), 325(2.22),270 (3.06),280 (2.87)	618	2.42	0.37	6.54	2.64	306
Pt-2	570(6.6),535 (6.1),450 (1.3),424(1.2), 392(2.8),375 (2.0),310 (3.4),286(4.0)	730	0.77	0.26	2.96	3.82	380

^a (DIQB)Pt(DPM) and (DIQB)[Pt(DPM)]₂ replaced with Pt-1 and Pt-2, respectively.

^b Measured in CH₂Cl₂ solution.

^c Measured in degassed CH₂Cl₂ relative to Ir(piq)₂(acac) ($\Phi_p = 0.2$, $\lambda_{ex} = 475$ nm) and calculated according to the equation $\Phi_s = \Phi_r (\eta_s^2 I_s A_r / \eta_r^2 I_r A_s)$. ^c Measured in degassed toluene solution.

^d Radiative decay rate $k_r = \Phi/\tau$ and nonradiative decay rate $k_{nr} = (1-\Phi)/\tau$.

packing plot of (DIQB)[Pt(DPM)]2.

3.4. Photophysical properties

The absorption spectra of ligand DIQB and both platinum(II) complexes in dilute DCM solutions are displayed in Fig. 2, and the elaborated absorption data are listed in Table 1. The absorption spectrum of (DIQB) Pt(DPM) showed a typical profiles of platinum(II) complex, in which an intense high-lying band under 350 nm is corresponding to π - π * electron transition absorption ascribed with the DIQB ligand. While the lowerenergy absorption band range from 350 to 630 nm was ascribed to the mixing spin-allowed and spin-forbidden metal-to-ligand charge-transfer states (¹MLCT and ³MLCT), somewhat with the ligand-centered π - π * transition or ligand-to-ligand charge transfer (LLCT) transition. Furthermore, the (DIQB)[Pt(DPM)]₂ presented a more intense absorption coefficients from the spin-allowed π - π^* and MLCT transitions, which was resulted from the extended conjugate molecular framework introduced by additional metal ion [24-26,28]. Furthermore, the optical energy gaps (E_g^{opt}) are 2.44 eV for (DIQB)Pt(DPM) and 1.99 eV for (DIQB)[Pt(DPM)]2 according to their absorption edges, a narrower band gap is observed for (DIQB)[Pt(DPM)]_2, owing to the enhanced π conjugation system based on extra metal ion [24-26,28]. Their transitions were also evidenced by the time-dependent density functional theory (TD-DFT) calculations at the S₀ geometry structure (Fig. S8 and S9, see ESI[†]). The overlapping absorption bands of 350–500 nm in (DIQB)[Pt(DPM)]2 shows an around 20 nm red-shifted emission in

Table 2

Electrochemical data of the platinum(II) complexes.

Complexes	$\lambda_{oneset} (nm)^{a}$	$E_{\rm ox}$ (V) ^b	$E_{\rm HOMO}~({\rm eV})^{\rm c}$	$E_{\rm LUMO} ({\rm eV})^{\rm d}$	E_g^{opt} (eV) ^e	HOMO/LUMO ^{cal} (eV) ^f	E_g^{cal} (eV) ^f
Pt-1	509	0.78	-5.41	-2.97	2.44	-5.41/-2.14	3.27
Pt-2	623	0.70	-5.33	-3.34	1.99	-4.86/-2.28	2.58

^a Absorption edges of the films.

^b Data are versus Fc/Fc^+ (Fc is ferrocene) estimated from the onset oxidation curve.

^c Deduced from the equation $E_{\text{HOMO}} = -(E_{\text{ox}} - 0.47)-5.1$, where 0.47 V is the potential for ferrocene vs. Ag/AgCl and 5.1 eV is the energy level of ferrocene to the vacuum energy level.

^d $E_{\text{LUMO}} = E_{\text{HOMO}} + \Delta E_g^{opt}$.

^e $\Delta E_{\sigma}^{opt} = 1240/\lambda_{oneset}$.

^f Calculated by DFT.

comparison with those of the (DIQB)Pt(DPM), which is arising from the increased in conjugating length and the enhanced donor-acceptor characteristics of the ligand induced by the introduction to a second metal platinum ion [26,35,36].

As also shown in Fig. 2 and summarized in Table 1, the PL spectra of both complexes in DCM solution presented typical characteristic of platinum(II) species [17–28]. The (DIQB)Pt(DPM) exhibits an intense DR emission peak at 618 nm with a shoulder around 655 nm under photo-excitation at 413 nm in DCM solution. As compared, a remarkably NIR emission at 730 nm with a shoulder around 800 nm was obtained from binuclear (DIQB)[Pt(DPM)]₂ under photo-excitation at 570 nm. Obviously, the (DIQB)[Pt(DPM)]₂ displays an outstandingly 112 nm red-shifted emission compared to its mononuclear complex. And illustrating that grafting an additional metal ion would effectively tune molecular conjugation of its corresponding complex. Meanwhile, the $\Phi_{\rm PL}$ of 2.42% and 0.77% were detected in DCM solution for (DIQB)Pt (DPM) and (DIQB)[Pt(DPM)]₂ at RT, and together with excited-state lifetimes of 0.38 and 0.26 µs (Fig. S10, see ESI†), respectively. The quite decreased k_r value towards to longer emission wavelength in the complexes is chiefly assigned to a fast decay passage in terms of a vibrionic coupling between ground and excited states, which is subjected by "energy gap law" [32]. The shorter phosphorescent lifetimes for the (DIQB)[Pt(DPM)]₂ would decrease its TTA and triplet-polaron annihilation (TPA) [33,34].

3.5. Electrochemical properties

Using ferrocene as the internal standard, the electrochemical characteristics of both platinum(II) complexes were investigated by cyclic voltammetry (CV) in CH₃CN solution (Fig. S11, see ESI[†]), and their detailed parameters are listed in Table 2. The irreversible onset oxidation potentials (Eox) of (DIQB)Pt(DPM) and (DIQB)[Pt(DPM)]2 are observed at 0.78 V and 0.70 V vs Fc/Fc⁺, respectively. According to the following equation: $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.63)$ eV [25–27], their highest occupied molecular orbit (HOMO) energy levels (E_{HOMO}) are -5.41 eVand -5.33 eV for (DIQB)Pt(DPM) and (DIQB)[Pt(DPM)]2, respectively. Based on their corresponding optical energy gaps (E_g^{opt}) and E_{HOMO} levels, the lowest unoccupied molecular orbital (LUMO) energy levels (E_{LUMO}) are estimated to be -2.97 eV for (DIQB)Pt(DPM) and -3.34 eV for (DIQB)[Pt(DPM)]2, respectively. The orderly lowered energy gaps from (DIQB)Pt(DPM) to (DIQB)[Pt(DPM)]2 are associated with the related increased HOMO energy levels, which is mainly triggered by the increased molecular planarity and the additional metallic d orbital of the binuclear complex, agreed much well with the mentioned above red-shifted UV spectra [25].

3.6. Theoretical calculations

Density functional theory (DFT) calculations were carried out to understand the geometry and optical properties on complexes using the Gaussian 09W program at the B3LYP/6-31G(d)/LanL2DZ level [28], and further analyze its optical properties with a conductor-like polarizable



Fig. 3. Calculate S_1 , T_1 , HOMO and LUMO energies, as well as HOMO and LUMO topologies of platinum(II) complexes.

continuum model (PCM) for DCM as the solvent. Representative frontier orbitals of the both platinum(II) complexes as shown in Fig. 3, and more iso-surface contour plots are shown in Fig. S12 and S13, further related data are summarized in Table S3. The calculated HOMO and LUMO energy levels of (DIQB)Pt(DPM) and (DIQB)[Pt(DPM)]2 are -5.41 eV/-2.14 eV and -4.86 eV/-2.28 eV, respectively (Table 2). The trend of energy gaps are perfectly reasonable, and the lowered LUMO level of (DIQB)[Pt(DPM)]2 matches well with most bimetallic species [27, 37-39]. As shown in Fig. 3, the (DIQB)[Pt(DPM)]₂ stacking shows more littler dropped dihedral angles (10.86°) between the centre ring and second isoquinoline unit than that of the (DIQB)Pt(DPM) (43.63°). This implies that appending an additional platinum(II) ion could enhance the intramolecular planarity, which is beneficial to enhancing conjugated degree. Moreover, to further understand the absorption spectra of the both complexes, their computational absorption spectra are shown in Fig. S8 and S9. The transition energy and oscillator strength calculated by TD-DFT of the two complexes in the S₀ geometry are agree well with the profile of the experimental absorption spectra. The S₁ states of the both complexes have almost exclusively HOMO→LUMO characteristics, but (DIQB)[Pt(DPM)]₂ shows a larger delocalized region than (DIQB)Pt (DPM), which demonstrates that the low energy of the lowest-energy absorption bands happened in (DIQB)[Pt(DPM)]2. According to the energy level diagram (Fig. 4), the electron cloud of LUMO are distributed in the DIQB ligand and central platinum(II) ion. Therefore, both the platinum(II) complexes have a similar LUMO energy levels. In contrast, the electron cloud of the HOMO is mainly located on the central platinum(II) ion, ligand and donor benzene unit.

As shown in Fig. S12 and Fig. S13, the lowest triplet state T₁ of the



Fig. 4. Energy level diagrams and chemical structures of related materials in PLED device.



Fig. 5. EL spectra of platinum(II) complexes doped devices at various concentrations from 3 to 9 wt %.

Table 3		
EL parameters of platinum(II) complexes doped devices with diffe	rent	dopant
concentrations.		

Complexes (wt %)	V _{on} ^a (V)	J ^b (mA/ cm ²)	λ _{EL} ^c (nm)	EQE _{max} ^d (%)	EQE ^e (%)	$\frac{L_{max}^{f}/R_{max}^{g}}{(cd/m^{2})/}$ (mW/Sr/m ²)
3 wt% Pt-1	11.6	4.97	666	2.86	1.84	1632 ^f
6 wt% Pt-1	11.2	6.73	622	2.49	1.70	1752 ^f
9 wt% Pt-1	10.1	8.70	622	2.11	1.52	1658 ^f
3 wt% Pt-2	12.8	23.69	746	0.58	0.53	10036 ^g
6 wt% Pt-2	12.0	91.36	745	0.51	0.47	9667 ^g
9 wt% Pt-2	11.2	33.49	745	0.45	0.42	9046 ^g

^a Turn-on voltage at 1 cd/cm².

^b Current density at maximum EQE.

^c The maximum EL emission peak.

^d The maximum external quantum efficiency.

^e EQE value at 100 mA cm⁻².

^f Brightness.

g Radiant intensity.

both complexes was investigated. TD-DFT calculations on T_1 state of (DIQB)Pt(DPM) displays that it has mainly HOMO→LUMO characteristics (62.2%) with a certain influence from HOMO-1→LUMO (23.2%) and HOMO-4→LUMO (5.8%). For (DIQB)[Pt(DPM)]₂, the T_1 state mainly originates from the contribution of HOMO→LUMO (90.2%) and minor from HOMO-1→LUMO (5.6%). The triplet states mixing with an ¹MLCT states that included different *d* orbitals can effectively promote the spin-orbital coupling (SOC) characteristic of metal complexes [23, 40]. It is worth noting that the HOMO, HOMO-1, and HOMO-4 orbitals of the two complexes all involved different *d* orbitals of platinum(II) ion, which may further facilitate SOC between S_1 and T_1 states [40].

3.7. Electroluminescence (EL) properties

The device structures and energy level diagrams of all materials employed in devices are depicted in Fig. 4. The HOMO/LUMO levels of both platinum(II) complexes are well matched between the HOMO level of PVK (-5.8 eV) and the LUMO level of OXD-7 (-3.0 eV), an efficient energy transfer from the host to the guest should happen in the emitting layer. Spin-coated OLEDs were fabricated with a configuration of ITO/ PEDOT:PSS (40 nm)/poly-TPD (30 nm)/[PVK:OXD-7(7:3)]: complexes (x wt %, 50 nm)/TmPyPb(50 nm)/CsF (1.2 nm)/Al (120 nm). The EL spectra of OLEDs based on platinum(II) complexes with different concentrations from 3 wt % to 9 wt %, and all devices as shown by the EL spectra in Fig. 5, further detailed devices data are summarized in Table 3. The maximum EL peaks located at 623 and 666 nm with wide band for the (DIQB)Pt(DPM) doped device, and 746 nm accompanied by a shoulder at around 810 nm for (DIQB)[Pt(DPM)]2 doped device, respectively. With increasing dopant concentration of (DIQB)Pt(DPM), the DR emission at 666 nm is preliminarily decreased, which is caused by the steadily larger LUMO separation of the EML to the ETL and the gradually smaller HOMO separation of that to HTL, and ultimately achieving a more balanced electron/hole transportation in device [41]. While the (DIQB)[Pt(DPM)]2-doped devices presents a NIR emission peak at 746 nm with a shoulder at around 810 nm within the all doping concentrations, which is largely associated with its much suitable HOMO/LUMO levels in devices (Fig. 5b). Upon increasing the dopant concentration from 3 wt % to 9 wt %, a minor high-lying emission peak at around 429 nm from the host blend were decreased in the both devices, which provided an efficient forward energy transfer from host to



Fig. 6. J-V-R profiles of platinum(II) complexes doped devices at various concentrations from 3 to 9 wt %.



Fig. 7. EQE-J characteristics of platinum(II) complexes doped devices at various concentrations from 3 to 9 wt %.

dopant [25]. Meanwhile, the EL spectra exhibit somewhat red-shift in all devices, illustrating the strong polarization influence and intermolecular interactions of these complexes [25,42].

To demonstrate balanced electron/hole transportation, their electronand hole-only devices had been also fabricated. Their electron-only and hole-only devices were fabricated with the structures of ITO/ZnO (30 nm)/PVK:OXD-7(7:3)]:neat film of Pt complexes (40 nm)/Ca (30 nm)/Al and ITO/PEDOT:PSS (30 nm)/PVK:OXD-7(7:3)]:neat film of Pt complexes (40 nm)/MoO₃(10 nm)/Al, respectively. As shown in Fig. S14, the current densities of electron-only and hole-only devices based on (DIQB)Pt(DPM) were much higher than those devices based on (DIQB)[Pt(DPM)]₂, and demonstrating that the higher electron transport ability of (DIQB)Pt(DPM) neat film than that of (DIQB)[Pt(DPM)]₂ neat film. Consequently, the (DIQB)Pt(DPM) device could display more balanced hole and electron transport behavior, and thereby obtain higher EQE [26,43].

The *J*–*V*–*R* and *EQE–J* characteristics of the both platinum(II) complexes for all devices are shown in Figs. 6 and 7, respectively, and summarized the relevant data of all EL in Table 3. The turn-on voltages (V_{on}) of the all devices preliminary dropped in turn with increasing dopant concentrations, which implies that the energy transfer processes of the both platinum(II) complexes-doped devices are mainly dominated by the Dexter transfer mechanism rather than the carrier-trapping mechanism [44]. At dopant concentration of 3 wt%, the maximum EQE and brightness (radiant emittance) were obtained to be 2.86%/1632 cd/m² and 0.58%/10036 mW/Sr/m² for the (DIQB)Pt (DPM) and (DIQB)[Pt(DPM)]₂ doped device, respectively. Furthermore, compared with the (DIQB)Pt(DPM)-doped devices, an efficiency roll-offs are efficiently suppressed in the (DIQB)[Pt(DPM)]₂-based devices. For instance, at 3 wt % dopant concentration of (DIQB)[Pt(DPM)]₂, a slight dropped in its *EQEs* level from 0.58 to 0.53% with increasing current density from 23.69 mA/cm² to 100 mA/cm², which should be triggered by the increased rigidity skeleton and reduced phosphorescence lifetime originated from the introduction of an additional platinum(II) ion [24, 25,42].

4. Conclusion

In summary, based on simply centrosymmetric isoquinoline ligand, a binuclear platinum(II) complex of (DIQB)[Pt(DPM)]₂ and its mononuclear homologous of (DIQB)Pt(DPM) were successfully obtained. The binuclear (DIQB)[Pt(DPM)]₂ presents a red-shifted PL spectrum by 112 nm and higher Φ_{PL} of 2.42% than the mononuclear (DIQB)Pt(DPM). At the 3 wt % dopant concentration, the (DIQB)Pt(DPM)-doped device presented a DR emission with a peak at 666 nm and a maximum EQE of 2.86%. In contrast, an outstandingly 80 nm red-shifted NIR emission at 746 nm with a EQE of 0.58% was obtained in the (DIQB)[Pt(DPM)]₂-doped device. Moreover, an efficiency roll-offs are efficiently suppressed in the (DIQB)[Pt(DPM)]₂-based devices. This work provides that high-efficiency NIR-emitting binuclear platinum(II) complexes can be achieved by grafting centrosymmetric big rigid planar ligand.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.orgel.2020.105902.

References

- [1] V.J. Pansare, S. Hejazi, W.J. Faenza, R.K. Prud'homme, Chem. Mater. 24 (2012) 812–827.
- [2] K.S. Schanze, J.R. Reynolds, J.M. Boncella, B.S. Harrison, T.J. Foley, Synth. Met. 137 (2003) 1013–1014.
- [3] S.J. Zhu, R. Tian, A.L. Antaris, X.Y. Chen, H.J. Dai, Adv. Mater. 31 (2019) 1900321.
 [4] Y.M. Zhang, Y.F. Wang, J. Song, J.L. Qu, B.H. Li, W.G. Zhu, W.Y. Wong, Adv. Opt. Mater. 6 (2018) 1800466.
- [5] E.L. Williams, J. Li, G.E. Jabbour, Appl. Phys. Lett. 89 (2006), 083506.
- [6] Q. Wan, J.L. Tong, B. Zhang, Y. Li, Z.M. Wang, B.Z. Tang, Adv. Opt. Mater. (2019) 1901520.
- [7] J.X. Jiang, Z. Xu, J.D. Zhou, M. Hanif, Q.L. Jiang, D.H. Hu, R.Y. Zhao, C. Wang, L. L. Liu, D.G. Ma, Chem. Mater. 31 (2019) 6499–6505.
- [8] T.X. Liu, G.H. Xie, C. Zhong, S.L. Gong, C.L. Yang, Adv. Funct. Mater. (2018) 1706088.
- [9] P. Murto, A. Minotto, A. Zampetti, X.F. Xu, M.R. Andersson, F. Cacialli, E.G. Wang, Adv. Opt. Mater. 4 (2016) 2068–2076.
- [10] M.I. Kozlov, A.N. Aslandukov, A.A. Vashchenko, A.V. Medvedko, A.E. Aleksandrov, R. Grzibovskis, A.S. Goloveshkin, L.S. Lepnev, A.R. Tameev, A. Vembris, Dalton Trans. 48 (2019) 17298–17309.
- [11] J.H. Jou, Y.T. Su, M.T. Hsiao, H.H. Yu, Z.K. He, S.C. Fu, C.H. Chiang, C.T. Chen, C. H. Chou, J.J. Shyue, J. Phys. Chem. C 120 (2016) 18794–18802.
- [12] J. Xue, L.J. Xin, J.Y. Hou, L. Duan, R.J. Wang, Y. Wei, J. Qiao, Chem. Mater. 29 (2017) 4775–4782.
- [13] X.S. Cao, J.S. Miao, M.R. Zhu, C. Zhong, C.L. Yang, H.B. Wu, J.G. Qin, Yong Cao, Chem. Mater. 27 (2015) 96–104.
- [14] D.X. Ma, T.J. Tsuboi, Y. Qiu, Lian Duan, Adv. Mater. (2016), https://doi.org/ 10.1002/adma.201603253.
- [15] C.F. You, D.H. Liu, M.B. Zhu, J.T. Yu, B. Zhang, Y. Liu, Y.F. Wang, We. Zhu, J. Mater. Chem. C 8 (2020) 7079–7088.
- [16] S. Kesarkar, W. Mróz, M. Penconi, M. Pasini, S. Destri, M. Cazzaniga, D. Ceresoli, P. R. Mussini, C. Baldoli, U. Giovanella, A. Bossi, Angew. Chem. 55 (2016) 2714–2718.
- [17] H.F. Xiang, Z.X. Xu, V.A.L. Roy, B.P. Yan, S.C. Chan, C.M. Che, P.T. Lai, Appl. Phys. Lett. 92 (2008) 163305.

- [18] S. Culham, P.H. Lanoë, V.L. Whittle, M.C. Durrant, J.A.G. Williams, V. N. Kozhevnikov, Inorg. Chem. 52 (2013) 10992–11003.
- [19] Y.M. Zhang, Z. Yin, F.Y. Meng, J.T. Yu, C.F. You, S.Y. Yang, H. Tan, W.G. Zhu, S. J. Su, Org. Electron. 50 (2017) 317–324.
- [20] K.H. Kim, J.L. Liao, S.W. Lee, B. Sim, C.K. Moon, G.H. Lee, H.J. Kim, Y. Chi, J. J. Kim, Adv. Mater. 28 (2016) 2526–2532.
- [21] G. Cheng, Q.Y. Wan, W.H. Ang, C.L. Kwong, W.P. To, P.K. Chow, C.C. Kwok, C. M. Che, Adv. Optical Mater. (2018) 1801452.
- [22] W.C. Chen, C. Sukpattanacharoen, W.H. Chan, C.C. Huang, H.F. Hsu, D. Shen, W. Y. Hung, N. Kungwan, D. Escudero, C.S. Lee, Y. Chi, Adv. Funct. Mater. (2020) 2002494.
- [23] M.Z. Shafikov, R. Daniels, P. Pander, F.B. Dias, J.A.G. Williams, V.N. Kozhevnikov, ACS Appl. Mater. Interfaces 11 (2019) 8182–8193.
- [24] W.J. Xiong, F.Y. Meng, C.F. You, P. Wang, J.T. Yu, X.G. Wu, Y. Pei, W.G. Zhu, Y. F. Wang, S.J. Su, J. Mater. Chem. C 7 (2019) 630–638.
- [25] S.Y. Yang, F.Y. Meng, X.G. Wu, Z. Yin, X.Z. Liu, C.F. You, Y.F. Wang, S.J. Su, W. G. Zhu, J. Mater. Chem. C 6 (2018) 5769–6777.
- [26] X.L. Yang, H.R. Guo, X.B. Xu, Y.H. Sun, G.J. Zhou, W. Ma, Z.X. Wu, Adv. Sci. (2019) 1801930.
- [27] K.T. Ly, R.W.C. Cheng, H.W. Lin, Y.J. Shiau, S.H. Liu, P.T. Chou, C.S. Tsao, Y. C. Huang, Y. Chi, Nat. Photon. 11 (2017) 63–68.
- [28] Z.R. Hao, F.Y. Meng, P. Wang, Y.F. Wang, H. Tan, Y. Pei, S.J. Su, Y. Liu, Dalton Trans. 46 (2017) 16257–16268.
- [29] A. Zampetti, A. Minotto, F. Cacialli, Adv. Funct. Mater. 29 (2019) 1807623.
- [30] C. Cebrián, M. Mauro, J. Org. Chem. 14 (2018) 1459-1481.
- [31] X. Wang, S.N. Wang, Chem. Rec. 19 (2019) 1693-1709.
- [32] R. Englman, J. Jortner, Mol. Phys. 18 (1970) 145-164.
- [33] Q. Wang, I.W. Oswald, M.R. Perez, H.P. Jia, B.E. Gnade, M.A. Omary, Adv. Funct. Mater. 23 (2013) 5420–5428.
- [34] X.Y. Cai, X.L. Li, G.Z. Xie, Z.Z. He, K. Gao, K.K. Liu, D.C. Chen, Y. Cao, S.J. Su, Chem. Sci. 7 (2016) 4264–4275.
- [35] X.L. Yang, B. Jiao, J.S. Dang, Y.H. Sun, Y. Wu, G.J. Zhou, W.Y. Wong, ACS Appl. Mater. Interfaces 10 (2018) 10227–10235.
- [36] N. Su, F.Y. Meng, J.H. Chen, Y.F. Wang, H. Tan, S.Y. Su, W.G. Zhu, Dyes Pigments 128 (2016) 68–74.
- [37] E.V. Puttock, M.T. Walden, J.G. Williams, Coord. Chem. Rev. 367 (2018) 127–162.
 [38] F.Y. Meng, D.C. Chen, W.J. Xiong, H. Tan, Y.F. Wang, W.G. Zhu, S.J. Su, Org.
- Electron. 4 (2016) 18–22.
 [39] Z.R. Hao, Y. Liu, Y. Huang, F.Y. Meng, Y.F. Wang, H. Tan, S.J. Su, W.G. Zhu, J. Organomet. Chem. 835 (2017) 52–59.
- [40] T. Hofbeck, H. Yersin, Inorg. Chem. 49 (2010) 9290–9299.
- [41] J. Lee, J. Lee, Y. Chu, Org. Electron. 10 (2009), 1529-1523.
- [42] Z.R. Hao, K. Zhang, P. Wang, X.M. Lu, Z.Y. Lu, W.G. Zhu, Y. Liu, Inorg. Chem. 59 (2019) 332–342.
- [43] B.Q. Liu, H. Nie, X.B. Zhou, S.B. Hu, D.X. Luo, D.Y. Gao, J.H. Zou, M. Xu, L. Wang, Z.J. Zhao, A.J. Qin, J.B. Peng, H.L. Ning, Y. Cao, B.Z. Tang, Adv. Funct. Mater. 26 (2016) 776–783.
- [44] Z.Y. Hu, Y.F. Wang, D.Y. Shi, H. Tan, X.S. Li, L. Wang, W.G. Zhu, Y. Cao, Dyes Pigments 86 (2010) 166–173.