Pt(II) Complexes with High Color Purity in Blue Organic Light-Emitting Diodes via Ligand Engineering

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Abstract

The planar structure of the Pt(II) complex makes it susceptible to intermolecular interactions. To address this, bulky groups like 3,5-di-tert-butylphenyl in Pt1 and 2,6-diisopropylphenyl in Pt2 were introduced. This modification resulted stable spectra at high doping concentrations, a narrow full-width at half maximum (FWHM) of 18 nm, and a maximum external quantum efficiency (EQE) of 21.4%.

Keywords

Blue device; phosphorescence; platinum (II) complex; organic light-emitting diodes

1. Objective and Background

Currently, in the field of organic light-emitting diode (OLED) research, significant efforts are focused on achieving commercially available blue phosphorescent OLEDs. This interest is motivated by the theoretical potential of phosphorescent OLEDs to achieve up to 100% internal quantum efficiency, compared to traditional fluorescent OLEDs, which are limited to a maximum of 25% efficiency. Achieving this 100% efficiency relies on harnessing triplet excitons for emission.(1-3) However, for effective utilization of triplet states, heavy metals such as iridium (III) and platinum (II) are essential. Through spin-orbit coupling (SOC), induced by the presence of these heavy metals, singlet and triplet states can be mixed, thereby allowing efficient light emission from triplet excitons.(4)

Iridium (III) complexes are known for their strong metal-ligand charge transfer (MLCT) character, attributed to their strong SOC.(5) This pronounced SOC facilitates rapid intersystem crossing (ISC), resulting in a short exciton lifetime. The reduced exciton lifetime is beneficial for device longevity, making Ir (III) complexes highly effective for applications requiring extended device stability. However, the strong MLCT character of Ir (III) complexes also results in a broad emission spectrum, which limits color purity.

In contrast, Pt (II) complexes primarily exhibit ligand-centered (LC) emission, which contributes to their much narrower emission spectra.(6) Despite this advantage, Pt (II) complexes have not yet achieved commercialization, unlike Ir complexes, which are widely used in red and green OLEDs.(7) One reason for this is color purity: Pt complexes adopt a square planar geometry, in contrast to the octahedral structure of Ir complexes. This square planar geometry makes Pt complexes more susceptible to intermolecular interactions, which can compromise color purity.(8)

In this study, bulky blocking groups (3,5-di-tert-butylphenyl and 2,6-diisopropylphenyl groups) were introduced to control intermolecular interactions, achieving a Commission International de l'Eclairage *y* co-ordinate (CIE *y*) value of less than 0.15,(9) thereby meeting the requirements for a commercially viable deep blue OLED. The 2,6-diisopropylphenyl-substituted complex Pt2 exhibited greater rigidity than the 3,5-di-tert-butylphenyl-substituted Pt1, resulting in narrower FWHM and a reduced secondary peak in both photoluminescence (PL) and electroluminescence (EL) data. The photoluminescence quantum yield (PLQY) was also higher for Pt2. Additionally, differences in dihedral angles due to the steric hindrance of these substituents affected the degree of conjugation, causing a red shift in Pt1 compared to Pt2, which exhibited better color coordinates. Under high doping concentrations, Pt2 showed smaller shifts in both FWHM and emission wavelength, indicating improved spectral stability.

2. Results

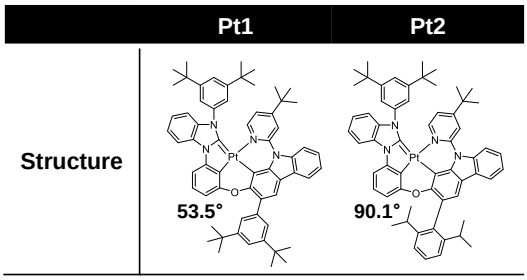

Figure 1. Molecular structures of Pt1 and Pt2.

As shown in **Figure 1**, Pt1 has a 3,5-di-tert-butylphenyl group attached at the 6-position of carbazole, resulting in a structure with a dihedral angle of 53.5° between the pyridine and carbazole planes. In contrast, Pt2 features a 2,6-diisopropylphenyl group at the same position, where the steric hindrance of the isopropyl groups creates a dihedral angle exceeding 90° with the pyridine-carbazole planes. The frontier molecular orbital (FMO) distribution was calculated through density functional theory (DFT) calculations using the B3LYP/genECP basis set. Examination of the highest occupied molecular orbital (HOMO) reveals that, due to the extended conjugation, electron distribution of Pt1 spread to the substituent. However, for Pt2, the large dihedral angle

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effectively disrupts conjugation, preventing the electron distribution from extending to the substituent.

Table 1. Photophysical properties of Pt1 and Pt2.

	UV-Vis (nm)	λ 298 K/77 K (nm)	FWHM 298 K/77 K (nm)	E_{T1} (eV)	E_g (eV)	HOMO/ LUMO (eV)
Pt1	318; 372	455/ 452	36/19	2.74	2.88	-5.66/ 2.78
Pt2	320; 370	455/ 448	28/17	2.77	2.87	-5.64/ 2.77

The ultraviolet-visible (UV-vis) absorption and room-temperature photoluminescence (RTPL) were measured in dichloromethane (DCM) at a concentration of 1.0×10^{-5} M at 298 K. Low-temperature photoluminescence (LTPL) was measured in tetrahydrofuran (THF) at 77 K with a concentration of 1.0×10^{-5} M. The photophysical properties of Pt1 and Pt2 are summarized in **Table 1**. The triplet energy was determined from the peak values of LTPL. Also, the HOMO level was obtained through cyclic voltammetry (CV) oxidation, and the lowest unoccupied molecular orbital (LUMO) level was calculated by subtracting the HOMO value from the energy gap derived from the UV-vis onset. Pt1 exhibited a peak at 452 nm with a narrow FWHM of 19 nm, resulting from extended conjugation at 77 K. In contrast, Pt2 showed a peak at 448 nm with a narrower FWHM of 17 nm due to disruption of conjugation, which prevented a red shift. Notably, the increased rigidity of Pt2, caused by significant steric hindrance, suppressed non-radiative emission, resulting in a PLQY of 99%, which is 4% higher than that of Pt1. Additionally, to assess the orientation value influenced by the blocking group, angle-dependent photoluminescence (ADPL) measurements were conducted. Emission dipole orientation (EDO) ratio showed a 5.2% increase for Pt2 compared to Pt1 (**Table 2**).

Table 2. PLQY and EDO values of Pt1 and Pt2.

	PLQY (%)	EDO ratio (%)
Pt1	95	69.5
Pt2	99	74.7

To evaluate the device properties of the two materials, a single-host blue phosphorescent OLED was fabricated and assessed. As shown in **Figure 2**, the device structure was constructed through vacuum deposition with the following layer sequence: PEDOT (40 nm)/TAPC (10 nm)/TCTA (5 nm)/mCP (5 nm)/3-CzPB:Pt emitter (25 nm:5, 10, 20 wt%)/TSPO1 (25 nm)/LiF (1.5 nm)/Al (200 nm). PEDOT refers to Poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate), TAPC is 4,4′-(cyclohexane-1,1-diyl)bis(N,N-di-p-tolylaniline), TCTA is tris(4-(9H-carbazol-9-yl)phenyl)amine, mCP is 1,3-bis(N-carbazolyl)benzene, 3-CzPB is 2,6-bis(3-(9H-carbazol-9-yl)phenoxy)benzonitrile,(10) and TSPO1 is diphenyl[4-(triphenylsilyl)phenyl]phosphine oxide. The Pt emitter was doped into the 3-CzPB layer at 5, 10, and 20 wt% concentrations for evaluation.

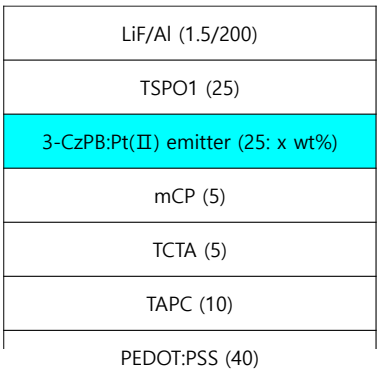

Figure 2. Device structures (nm).

To examine whether the bulky substituents in Pt1 and Pt2 suppress intermolecular interactions, the device performance data at high doping concentration was compared with that of PtON-TBBI.(11) When bulky blocking groups were introduced, significant improvements were observed at high doping concentrations compared to PtON-TBBI, which lacks any blocking groups. As shown in **Figure 3**, even as the doping concentration was increased from 5 wt% to 20 wt%, the difference in FWHM was clearly decreased. Additionally, as presented in **Table 3**, the wavelength shift was also reduced. In the case of Pt2, the structure twisted perpendicular to the pyridine-carbazole plane effectively suppressed intermolecular interactions, resulting in the most stable performance with minimal changes.

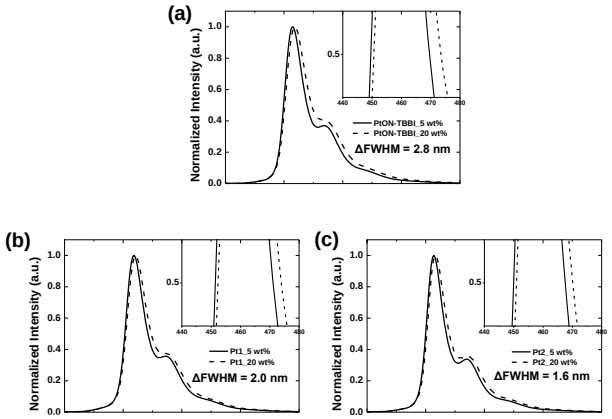

Figure 3. FWHM variation according to doping concentration of (a) PtON-TBBI, (b) Pt1 and (c) Pt2

Table 3. Wavelength and FWHM of PtON-TBBI, Pt1 and Pt2 according to doping concentration.

	PtON-TBBI 5 wt%	PtON-TBBI 20 wt%	Pt1 5 wt%	Pt1 20 wt%	Pt2 5 wt%	Pt2 20 wt%
λ (nm)	457	459	459	461	457	458
FWHM (nm)	20.1	22.9	19.6	21.6	17.6	19.2

The maximum external quantum efficiency for Pt1 and Pt2 at 10 wt% doping are shown in **Figure 4**. Pt1 exhibited a peak at 460 nm with a FWHM of 20.4 nm, while Pt2 showed a narrower peak at 457 nm with an FWHM of 18.0 nm. Pt2 emitted light at shorter wavelengths than Pt1 due to the

disruption of conjugation extension in the HOMO orbital. Additionally, the steric hindrance from the isopropyl groups increased rigidity, suppressing vibrational modes and reducing the second peak, resulting in a 2.4 nm narrower FWHM. This led to a significant improvement in the CIE *y* value, with excellent color purity, maintaining CIE $x < 0.14$ and CIE $y < 0.11$. Both materials achieved their maximum EQE at 10 wt%, with Pt1 reaching 19.6% and Pt2 reaching 21.6%, as summarized in **Table 4**.

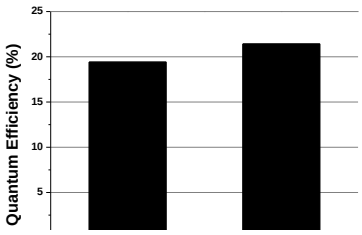

Figure 4. Quantum efficiency with 10 wt% doping concentration of Pt1 and Pt2.

Table 4. Device properties of Pt1 and Pt2 at 10 wt% at a luminance of 1000 cd/m²

	λ (nm)	FWHM (nm)	CIE		EQE $_{max}$ (%)
			x	y	
Pt1 10 wt%	460	20.4	0.135	0.121	19.6
Pt2 10 wt%	457	18.0	0.138	0.109	21.6

3. Impact of Research

In this study, materials were synthesized to improve the color purity, which has been a weak point in conventional blue phosphorescent devices. Bulky blocking groups, namely the 3,5-di-tert-butylphenyl group and 2,6-diisopropylphenyl group, were introduced at the pyridine-carbazole 6-position of PtON-TBBI, increasing the complex's rigidity and suppressing intermolecular interactions through steric hindrance. As a result, narrow FWHM values of 19.6 nm and 17.6 nm were obtained for Pt1 and Pt2 at a 5 wt% doping concentration, respectively. Even at a high doping concentration of 20 wt%, the FWHM difference remained below 2.0 nm, and minimal wavelength shifts were observed, demonstrating a stable blue spectrum. These findings provide design guidelines for blue Pt complexes with narrow FWHM and high color purity in the deep blue region.

4. References

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