Phosphorescent Tetradentate Platinum(II) Complexes Containing Fused 6/5/5 or 6/5/6 Metallocycles

Guijie Li,* Gang Shen, Xiaoli Fang, Yun-Fang Yang,* Feng Zhan, Jianbing Zheng, Weiwei Lou, Qisheng Zhang, and Yuanbin She*



Pt(*bp*-8) have dominant ligand-centered (³LC) mixed with small metal-to-ligand charge-transfer (³MLCT) characters in T₁ states, resulting in relatively low quantum efficiencies (Φ_{PL}) of 5–33% and 12–32% in dichloromethane solution and PMMA film, respectively. By contrast, Pt(*ppy*-1) possesses much more ³MLCT character in the T₁ state, enabling a high Φ_{PL} of 95% in dichloromethane and 90% in DPEPO film, and large radiative decay rates. The strength of the Pt–N¹ coordination bond plays a critical role in the photostability. Pt(*ppy*-1)- and Pt(*bp*-6)-doped polystyrene films demonstrate long photostability lifetimes of 150 min for LT₉₇ and LT_{98.5}, respectively. A Pt(*ppy*-1)-based green OLED using 26mCPy as host realized a peak EQE of 18.5%, which still maintained an EQE of 10.4% at 1000 cd/m², and an L_{max} of over 40 000 cd/m² was achieved. This study should provide a valuable reference for the further development of efficient and stable phosphorescent Pt(II) complexes.

INTRODUCTION

An organic light-emitting device (OLED) is a key technology for full-color display application in high-end electronics.^{1,2} The design and development of light-emitting materials play a critical role in this field and have been attracting great attention in both academia and industry.³⁻⁹ Heavy metal complexesbased phosphorescent materials have a potential ability to harvest both electrogenerated singlet and triplet excitons to achieve unity internal quantum efficiency (IQE) and act as an important kind of light-emitting material in OLED fabrications.^{3,4} With the efforts of the past three decades, many phosphorescent transition metal complexes, such as Ir(III), Pt(II), Au(III), Pd(II), Rh(III), and Ru(II) complexes,¹⁰⁻¹⁸ have been developed, and OLEDs using the phosphorescent metal complexes as emitters have demonstrated good device performances with high external quantum efficiencies (EQEs),^{19–25} high color purities,^{14,15,26–30} or long operational lifetimes,^{9,27,29,31–50} indicating the potential applications of the phosphorescent metal complexes in full-color display and solid-state lighting. However, the phosphorescent OLEDs that can meet the commercial application for electronics are scarce. In general, red, green, and blue are three essential components

transition orbital analyses reveal that Pt(bp-6), Pt(bp-7), and

in the full-color display; thus, all stable and efficient RGB lightemitting materials are highly desired.

The structure-property relationship, especially the effect of molecular structure on the excited-state property, is an essential research topic. Typically, the lowest triplet excited state (T₁) of the phosphorescent metal complexes originates from a mixed interligand charge-transfer (³ILCT) state with a metal-to-ligand charge-transfer (¹MLCT/³MLCT) character.⁵¹⁻⁶¹ The degree of the spin-orbital coupling (SOC) depends on the nature of the excited state. The phosphorescent metal complexes with more MLCT character enhance both the intersystem crossing (ISC) rates of S₁ \rightarrow T₁ and radiative decay rate of T₁ \rightarrow S₀, and usually realize a short triplet state lifetime (τ) and high quantum efficiency (Φ_{PL}).²⁸ Meanwhile, the complexes typically show broad unstructured emission spectra, resulting in low color purity. By contrast,

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Figure 1. (a) Chemical structures of previously reported tetradentate 6/5/6 Pt(II) complexes with *bp*-containing ligands. (b) Chemical structures of newly developed tetradentate 6/5/5 and 6/5/6 Pt(II) complexes with *ppy*- or *bp*-containing ligands. The bond length of the Pt–N¹ from DFT calculation based on optimized S₀ geometry for each Pt(II) complex is marked. The *ppy* and *bp* represent conjugated phenylpyridine and biphenyl group, respectively. Py, pyridyl group; Ac, acridinyl group; Ph, phenyl group; AAc, aza acridinyl group; ACz, aza carbazolyl group; Cz, carbazolyl group.

through rational design, the ligand-centered (${}^{3}LC$) dominant phosphorescent complexes 30,62 can exhibit narrow emission spectra and achieve ultra high color purity with a full-width at half-maximum (fwhm) of about 20 nm, ${}^{26-28,30,62}$ but their decay lifetimes are relatively long, which make the devices have a large efficiency roll-off. Thus, the tuning of the excited-state property of metal complexes showing both a short decay lifetime and narrow emission spectrum remains a great challenge, and the structure-property relationship research provides an in-depth understanding of the complexes and facilitates to solve this issue.

It has been well documented that a rigid structural scaffold can minimize the excited-state structural deformations of Pt(II) complexes and reduce nonradiative decays, enabling improved emission quantum efficiencies.^{47,63} Hence, compared to OLEDs doped with bidentate and tridentate cyclometalated Pt(II) complexes, tetradentate Pt(II) complexes-based OLEDs typically demonstrated better device performances in efficiencies^{17,18,20,26–30} and stabilities.^{29,30,32,34–37,41–44} Recently, we reported a new series of biphenyl (*bp*)-based Pt(II) complexes with fused 6/5/6 metallocycles employing tetradentate ligands with only a nitrogen atom as bridging group (Figure 1a).⁶¹ The Pt(II) complexes exhibited high Φ_{PL} in both dichloromethane solution and doped PMMA film and also showed excellent photostability in doped polystyrene film, which were attributed to their rigid molecular structures and chemically stable biphenyl- and pyridine-based ligands.⁶¹ In this work, another series of phenylpyridine (ppy)-based 6/5/5 and biphenyl (bp)based 6/5/6 Pt(II) complexes with new tetradentate ligands using nitrogen or oxygen atoms as bridging groups are designed and synthesized (Figure 1b). The bridging nitrogen atoms are designed as an acridinyl group (Ac) for Pt(ppy-1)and Pt(bp-6), and as a more rigid carbazolyl group (Cz) and aza carbazolyl group (ACz) for Pt(bp-7) and Pt(bp-8). The two Pt-N coordination bonds are incorporated at the paraposition of the Pt(II) ion in Pt(ppy-1), and at the orthoposition in the other three Pt(II) complexes. Their electrochemical, photophysical, and excited-state properties are systematically investigated through experimental and theoretical studies. Our study reveals that the ligand structures significantly affect the excited-state properties, and the bond length of the $Pt-N^1$ coordination bonds have a great influence on their photostabilities.

EXPERIMENTAL SECTION

The synthesis and structural characterization of the 6/5/5 and 6/5/6 Pt(II) complexes are provided in the Supporting Information. The theoretical calculations were performed using Gaussian 09 according to a previous report.⁶¹ Electrochemical measurements were performed on a CH1760E electrochemical analyzer. The absorption spectra were measured on an Agilent 8453 UV–vis spectrometer. Steady-state emission experiments and decay lifetime measurements were performed on a Horiba Jobin Yvon FluoroLog-3 spectrometer.

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Scheme 1. Synthesis of Pt(ppy-1)



Scheme 2. Synthesis of Ligand L(bp-6)



Scheme 3. Synthesis of Ligands L(bp-7) and L(bp-8)



Low-temperature (77 K) emission spectra and decay lifetimes were measured in 2-MeTHF cooled with liquid nitrogen. See the Supporting Information for details.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic routes of the Pt(II) complexes are shown in Schemes 1–4. The ligand

| Scheme 4. S | ynthesis of Pt(<i>l</i> | p-6), Pt(bp-7 |), and L(<i>bp</i> -8) |
|------------------|---|-------------------------|-------------------------------|
| 1 (bp-6) | 1.05 equiv PtCl ₂ | 20 equiv t-BuOK | D (() D) 000(|
| L(<i>bp</i> -0) | benzonitrile 180 °C, 2.5 d | THF 76 °C, 5 h | (two steps) |
| 1 (6 - 7) | 1.05 equiv PtCl ₂ | 20 equiv t-BuOK | Dt (h = 7) 00(|
| L(<i>bp-1</i>) | benzonitrile 180 °C, 3 d | THF 76 °C, 5 h | (two steps) |
| l (bp-8) | 1.1 equiv K ₂ PtCl ₂ 0.1 equiv <i>n</i> -Bu ₄ NBr | 20 equiv <i>t</i> -BuOk | Bt/bp 9) 0% |
| L(<i>DP</i> -0) | AcOH, rt, 12 h, then 120 °C, 2 d | THF 76 °C, 5 h | (two steps) |

L(ppy-1) could be facilely synthesized through boronation of 1-Br⁶¹ using 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (OMBDB) catalyzed by Pd(dppf)Cl₂, Suzuki coupling reaction of 1-B with methyl 6-bromopicolinate

Scheme 5. Improved Synthesis of Pt(bp-7)

| l (bm 7) | 1.05 equiv PtCl ₂ | 3.0 equiv SnCl ₂ | Bt(bp 7) 72% |
|------------------|-------------------------------|--|---------------------|
| L(<i>bp-1</i>) | benzonitrile 180 °C, 1.5 d | CH ₂ Cl ₂ rt, 2 d | (two steps) |

(MBP) catalyzed by Pd(PPh₃)₄, and hydrolysis reaction of 1-OCH₃. Then metalation of the L(ppy-1) with K_2PtCl_4 in acetic acid and chloroform under nitrogen gave Pt(ppy-1) in 70% yield⁶⁶ (Scheme 1). CuI-catalyzed C-O bond coupling of 3bromophenol with 2-bromopyridine afforded 2-Br, which was borated to afford 2-B, and then 2-B coupled with 1-Br to give L(bp-6) (Scheme 2). L(bp-7) could be easily made through direct Suzuki coupling of 3-Br⁶⁷ with 2-B, and L(bp-8) was obtained through boronation of 3-Br and then a Suzuki coupling reaction (Scheme 3). Pt(bp-6), Pt(bp-7), and Pt(bp-8) were synthesized by metalation with PtCl₂ in benzonitrile at 180 °C or K₂PtCl₄ in acetic acid to give a mixture of Pt(II) and Pt(IV) complexes,^{68,69} and the Pt(IV) complex in the mixture was reduced by t-BuOK to form the desired Pt(II) complex with 29%, 8%, and 9% isolated yield, respectively (Scheme 4).^{61,69} The low yields of Pt(bp-7) and Pt(bp-8) were attributed the long distance between the Py and Py or ACz in L(bp-7) and L(bp-8), resulting in weak coordinations with the Pt(II) ion and easy decomposition in harsh reaction conditions. Notably, direct metalation of L(ppy-7) or L(ppy-8)



Figure 2. ORTEP drawings of X-ray single crystal diffraction structures and crystal packing views of (a) Pt(bp-6) (CCDC 2036928) and (b) Pt(bp-7) (CCDC 2036927). Solvent molecules were omitted for clarity. Ellipsoids are shown at the 50% probability level.

| Table 1. Electrochemical | l Properties an | d Energy Leve | els of Tetra | dentate Pt(II | i) Complexes |
|--------------------------|-----------------|---------------|--------------|---------------|--------------|
|--------------------------|-----------------|---------------|--------------|---------------|--------------|

| complex | $E_{\rm ox}$ [V] | $E_{\rm red}$ [V] | $HOMO^a / LUMO^b [eV]$ | ΔE_{g}^{c} [eV] | $E_{\mathrm{T1}}^{d} [\mathrm{eV}]$ | calcd HOMO/LUMO e [eV] |
|--------------------|------------------|-------------------|------------------------|-------------------------|-------------------------------------|-----------------------------|
| Pt(<i>ppy</i> -1) | 0.51 | -2.10 | -5.31/-2.70 | 2.61 | 2.44 | -5.40/-1.89 |
| Pt(<i>bp</i> -6) | 0.27 | -2.61 | -5.07/-2.19 | 2.88 | 2.48 | -4.67/-1.28 |
| Pt(<i>bp</i> -7) | 0.24 | -2.51 | -5.04/-2.29 | 2.75 | 2.24 | -4.65/-1.42 |
| Pt(<i>bp</i> -8) | 0.20 | -2.34 | -5.00/-2.46 | 2.54 | 2.23 | -4.61/-1.61 |
| a | , | ь , | N | | | |

^{*a*}HOMO = $-(E_{ox} + 4.8)$ eV. ^{*b*}LUMO = $-(E_{red} + 4.8)$ eV. ^{*c*} ΔE_g = LUMO – HOMO. ^{*d*}Triplet energies estimated from the peak of the phosphorescent emission spectrum at 77 K in 2-MeTHF. ^{*e*}From DFT calculations at the B3LYP/6-31G(d)/LANL2DZ level based on optimized S₀.



Figure 3. Absorption spectra of the Pt(II) complexes in dichloromethane at room temperature. Their T_1 absorption transitions are shown in the inset.

with K_2PtCl_4 in acetic acid afforded very little desired Pt(II) complexes, which were difficult to purify by column chromatography to get pure products. However, the isolated yield of Pt(*bp*-7) could be significantly improved by shortening

the reaction time of the metalation, and employing $SnCl_2$ as reductant (Scheme 5). The synthetic details are provided in the Supporting Information. All the new intermediates and newly developed 6/5/5 and 6/5/6 Pt(II) complexes were characterized by ¹H and ¹³C NMR spectroscopy, high resolution mass spectrum (HRMS), and elemental analysis.

Theoretical Investigation, X-ray Structure, and Electrochemistry. Density functional theory (DFT) calculations^{47,61} reveal that Pt(ppy-1) has a significantly planar molecular geometry with small distortion and a very small dihedral angle of only 16.6° between the terminal pyridine and carboxyl planes in the S₀ state (Tables S1 and S2). By contrast, the molecular geometries of Pt(bp-6), Pt(bp-7), and Pt(bp-8)are profoundly twisted in S₀ states with large dihedral angles of 48.9–52.6° between the two terminal aryl planes in S_0 states (Tables S1 and S2). ¹H NMR spectra of the two methyl groups on the 9-position of the acridinyl moiety show two single peaks of 1.34 and 1.88 ppm for Pt(ppy-1) and 1.37 and 1.84 ppm for Pt(bp-6), respectively; similar results are also observed in their ¹³C NMR spectra, which reveal their unsymmetric chemical environments and twisted molecular geometries (see Supporting Information). All the Pt(II) complexes exhibit smaller dihedral angles in T1 states compared to S₀ states, and the structural deformation in Pt(ppy-1) (0.1°) is much smaller than those of the other three

| Table 2. Calculated Excitation Energy (E), Wavelength (λ) | Oscillator Strength (f) , Main | Orbital Contribution, and Cl | narge |
|--|----------------------------------|------------------------------|-------|
| Characters of the T_1 and S_1 States of $Pt(II)$ Complexes ^{<i>a</i>} | | | |

| complex | state | E [eV] | λ [nm] | f | orbital contribution (>10%) | assignment |
|--------------------|----------|------------|---------------|----------------|---------------------------------|---|
| Pt(<i>ppy</i> -1) | T_1 | 2.472 | 502 | 0 | HOMO \rightarrow LUMO (87%) | ${}^{3}\text{MLCT}(\pi_{ppyCOO}d_{\text{Pt}} \rightarrow \pi_{\text{Py}}^{*})$ |
| | S_1 | 2.716 | 457 | 0.0196 | HOMO \rightarrow LUMO (96%) | $^{1}\text{LC}(\pi_{ppy} \rightarrow \pi_{ppy}^{*}), \ ^{1}\text{MLCT}(\pi_{ppyCOO} d_{\text{Pt}} \rightarrow \pi_{\text{Py}}^{*})$ |
| Pt(<i>bp</i> -6) | T_1 | 2.472 | 502 | 0 | HOMO \rightarrow LUMO (80%) | 3 MLCT $(\pi_{bp}$ d _{Pt} $\rightarrow \pi_{Py}^{*})$ |
| | S_1 | 2.669 | 465 | 0.0212 | HOMO \rightarrow LUMO (97%) | $^{1}\text{LC}(\pi_{bp} \rightarrow \pi_{bp}^{*}), \ ^{1}\text{MLCT}(\pi_{bp}\text{d}_{\text{Pt}} \rightarrow \pi_{\text{Py}}^{*})$ |
| Pt(<i>bp</i> -7) | T_1 | 2.249 | 551 | 0 | HOMO \rightarrow LUMO (72%) | ³ MLCT (π_{bp} d _{Pt} $\rightarrow \pi_{Py}^{*}$) |
| | S_1 | 2.519 | 492 | 0.0073 | HOMO \rightarrow LUMO (97%) | $^{1}\text{LC}(\pi_{\text{CzPh}} \rightarrow \pi_{\text{CzPh}}^{*}), \ ^{1}\text{MLCT}(\pi_{bp}\text{d}_{\text{Pt}} \rightarrow \pi_{\text{Py}}^{*})$ |
| Pt(<i>bp</i> -8) | T_1 | 2.196 | 565 | 0 | HOMO \rightarrow LUMO (57%) | 3 MLCT $(\pi_{bp}$ d _{Pt} $\rightarrow \pi_{ACz}^{*})$ |
| | | | | | HOMO \rightarrow LUMO+1 (21%) | |
| | S_1 | 2.407 | 515 | 0.0338 | HOMO \rightarrow LUMO (94%) | $^{1}\text{LC}(\pi_{\text{CzPh}} \rightarrow \pi_{\text{CzPh}}^{*}), \ ^{1}\text{MLCT}(\pi_{bp}d_{\text{Pt}} \rightarrow \pi_{\text{ACz}}^{*})$ |
| Calculated by | the TD B | I VD mothe | d with a basi | s sat of SV fo | r H SVP for C E and N atoms a | nd a daf? TZVP basis sat for the Pt atom based on |

^aCalculated by the TD-B3LYP method with a basis set of SV for H, SVP for C, F, and N atoms, and a def2-TZVP basis set for the Pt atom based on optimized S_0 geometries.

complexes $(1.6-2.6^{\circ})$ (Table S2). Notably, the coordination bonds Pt-N¹ in Pt(*bp*-7) (2.232 Å) and Pt(*bp*-8) (2.237 Å) are significantly longer than those in Pt(ppy-1) (2.047 Å), Pt(bp-6) (2.187 Å), and the previously reported Pt(bp-1), Pt(*bp*-2), and Pt(*bp*-3) (2.182–2.186 Å)⁶¹ (Figure 1); this is attributed to that the rigid Cz segment in Pt(bp-7) and Pt(bp-7)8) makes its 9-position pyridine away from the central Pt(II) ion. This is also supported by the X-ray analyses that the bond length of Pt-N¹ in Pt(*bp*-7) (2.1460(19) Å) is significantly longer than that of Pt(bp-6) (2.115(2) Å), and the Ac moiety in Pt(bp-6) is a seriously twisted chair configuration. In contrast, the Cz moiety in Pt(bp-7) is a planar configuration (Figure 2a,b Tables S2-S4). Additionally, intermolecular C-H… π interactions are observed in Pt(*bp*-6) between the methyl group and the pyridine ring (Figure 2a), and intermolecular $\pi - \pi$ interactions are observed in Pt(*bp*-7) between the two pyridine rings with a distance of 3.396 Å (Figure 2b).

Pt(bp-6), Pt(bp-7), and Pt(bp-8) show similar highest occupied molecular orbital (HOMO) distributions predominantly on the π_{AcPh} , π_{CzPh} orbitals and the d_{Pt} centers, and the lowest unoccupied molecular orbital (LUMO) distributions dominantly occupy on the two π_{Py} for Pt(*bp*-6) and Pt(*bp*-7), and exclusively on π_{ACz} for Pt(*bp-8*) (Figure S1), indicative of a stronger electron-withdrawing ability of the ACz compared to Py. Pt(ppy-1) has significantly different HOMO and LUMO distributions. The HOMO is mainly on the π_{Ac} -p_{Pt-O}- π_{OC} orbitals, and the LOMO is dominantly on the electrondeficient two π_{Py} moieties (Figure S1). Additionally, Pt(*ppy*-1) exhibits stabilized HOMO and LUMO levels (-5.40 and -1.89 eV, respectively) compared to the *bp*-based Pt(II) complexes, which are -4.67, -4.65, and -4.61 eV for HOMO levels, and -1.28, -1.42, and -1.61 eV for HOMO levels of Pt(bp-6), Pt(bp-7), and Pt(bp-8), respectively (Figure S1), because the electron-withdrawing ability of the ppy is much stronger than that of the bp moiety. This result can be also supported by the electrochemical study that Pt(ppy-1) has a greatly larger oxidation potential of 0.51 eV than those of the bp-based Pt(II) complexes of 0.20-0.27 eV, and less negative reduction potential of -2.10 eV compared to the other Pt(II) complexes of -2.61 to -2.34 eV (Table 1). These significant differences reveal that the redox processes in *ppy*-based Pt(*ppy*-1) are different with those in the bp-based Pt(II) complexes. The oxidation process of Pt(ppy-1) is mainly on the Ac-Pt moiety, and the reduction process is dominantly on the electron-deficient two Py rings. Pt(bp-6) has the oxidation process on the bp-Pt moiety, and reduction process on the Py ring. Pt(bp-7) and Pt(bp-8) have the oxidation processes on

the CzPh-Pt moieties; however, the reduction processes are much different, mainly on the Py ring and ACz moiety, respectively. Moreover, the HOMO and LUMO levels calculated from the redox values are in good agreement with the trend from the DFT calculations (Table 1). All the Pt(II) complexes exhibit irreversible redox processes except the reduction process of Pt(ppy-1) (Figure S2). These results demonstrated that the distribution and energy levels of the frontier orbitals can be effectively regulated through rational ligand design.

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Photophysical and Excited-State Properties. The UVvis absorption spectra of the Pt(II) complexes and their corresponding ligand in dichloromethane (DCM) solutions at room temperature (RT) are illustrated in Figures 3 and S3. For all the Pt(II) complexes, the intense absorption bands below 325 nm are assigned as spin-allowed ligand-centered (¹LC) π $\rightarrow \pi^*$ transitions from localized ppy in Pt(ppy-1), localized bp in Pt(bp-6), and from localized CzPh in Pt(bp-7) and Pt(bp-8)on the basis of the time-dependent density functional theory (TD-DFT) calculations^{47,61} (Tables 2, S5-S8) and natural transition orbital (NTO) analyses^{61,64} (Figure S4). Notably, Pt(*ppy*-1) exhibits much weaker $\pi \rightarrow \pi^*$ transitions than those of the other Pt(II) complexes because of less aryl groups in Pt(ppy-1) (Figure 3). The absorptions at the region of 340-475 nm are attributed to spin-allowed metal-to-ligand chargetransfer (¹MLCT) transitions, which are involved with both the center Pt(II) ion and the cyclometalating ligand (Figure 3). Pt(ppy-1) has a very weak unstructured ³MLCT transition involving $\pi_{ppyCOO}d_{Pt} \rightarrow \pi_{Py}^*$ (Figure S4). However, Pt(*bp*-6), Pt(*bp*-7), and Pt(*bp*-8) show well-resolved ${}^{3}MLCT$ transitions at about 498, 550, and 555 nm, respectively, involving $\pi_{bp} d_{Pt} \rightarrow$ π_{Pv}^* for Pt(*bp*-6) and Pt(*bp*-7), and $\pi_{bp}d_{Pt} \rightarrow \pi_{ACz}^*$ for Pt(*bp*-8)' (Figure S4); these ³MLCT transitions are in good agreement with the T₁ absorptions by the TD-DFT calculations of 502, 551, and 565 nm, respectively (Table 2).

The emission spectra of the Pt(II) complexes in various conditions are illustrated in Figures 4 and S5, and the data are recorded in Table 3. Ligand modifications have a great influence on the photophysical properties. At 77 K in 2-methyltetrahydrofuran (2-MeTHF), all the Pt(II) complexes show well-resolved vibronic emission spectra, indicating the dominant ³LC characters in their T₁ states.^{30,62} Pt(*ppy*-1) and Pt(*bp*-6), both of which have PyAc-containing ligands, show a dominant emission peak in high energy region at 508 and 500 nm, respectively (Figure 4). By contrast, PyCz-based Pt(*bp*-7) and Pt(*bp*-8) have a dramatic red shift of about 50 nm and show a dominant emission peak at 553 and 557 nm,



Figure 4. Photoluminescence spectra of the tetradentate Pt(II) complexes (a) at 77 K in 2-MeTHF (dash-dotted lines), (b) at room temperature in dichloromethane solution (solid lines), and (c) at room temperature in PMMA film (solid-ball lines).



Figure 5. Photoluminescence spectra of (a) Pt(*ppy*-1) and (b) Pt(*bp*-7) in various thin films.

respectively (Figure 4). Especially, Pt(bp-7) has a red shift of about 53 nm compared to Pt(bp-6), although they have similar ligands; this is attributed to the extended conjugation of Cz compared to Ac, resulting in a significantly stabilized LUMO for Pt(*bp-7*) and a small energy gap ($\Delta E_{\rm g}$) between the HOMO and LUMO (Figure S1). Additionally, the Pt(II) complexes have excited lifetimes (τ) of 5.3–11.9 μ s. PyAcbased Pt(*bp*-6) (τ = 11.9 μ s) has a similar excited lifetime with PyAc-based Pt(*bp*-1), Pt(*bp*-2), and Pt(*bp*-3) (τ = 11.9, 11.4, and 12.2 μ s, respectively)⁶¹ and exhibits very little blue-shift emission spectrum, 500 nm for Pt(bp-6) and 504, 512, and 505 nm for Pt(bp-1), Pt(bp-2), and Pt(bp-3), respectively⁶¹ (Figure 1). This indicates that the bridging atoms of nitrogen or oxygen have a small influence on their excited photophysical properties. However, PyCz-based Pt(bp-7) and Pt(bp-8) have significantly shortened τ of 5.7 and 5.3 μ s, respectively, which are only half that of the PyAc-based Pt(bp-1), Pt(bp-2), Pt(bp-3), and Pt(bp-6), indicating the great influence of the Cz

| Table 3. | Photoph | vsical Propertie | s of Tetrad | entate Pt(II |) Complexes |
|----------|---------|------------------|-------------|--------------|-------------|
|----------|---------|------------------|-------------|--------------|-------------|

| | emission at 2-MeT | 277 K in emission at RT in 5 wt % CHF emission at RT in DCM | | | | | | | | | | |
|-------------------|-----------------------|---|-----------------------|--------|-----------------------|---------------------------------------|--|-----------------------|--------|-----------------------|---------------------------------------|--|
| complex | λ_{\max} [nm] | τ [µs] | λ_{\max} [nm] | τ [µs] | $\Phi_{	ext{PL}}$ [%] | $k_{\rm r} \; [10^4 \; {\rm s}^{-1}]$ | $k_{\rm nr} \; [10^4 \; {\rm s}^{-1}]$ | λ_{\max} [nm] | τ [μs] | $\Phi_{	ext{PL}}$ [%] | $k_{\rm r} \; [10^4 \; {\rm s}^{-1}]$ | $k_{\rm nr} \; [10^4 \; {\rm s}^{-1}]$ |
| Pt(ppy-1) | 508 | 7.8 | 516 | 6.4 | 95 | 14.8 | 0.8 | 516 | 5.3 | 68 | 12.8 | 6.0 |
| Pt(<i>bp</i> -6) | 500 | 11.9 | 506 | 8.2 | 33 | 4.0 | 8.2 | 506 | 9.1 | 32 | 3.5 | 7.4 |
| Pt(bp-7) | 553 | 5.7 | 557 | 4.0 | 10 | 2.5 | 22.5 | 558 | 4.2 | 12 | 2.9 | 21.0 |
| Pt(bp-8) | 557 | 5.3 | 563 | 3.5 | 5 | 1.4 | 28.6 | 564 | 3.8 | 14 | 3.7 | 22.6 |

^aDCM, dichloromethane; 2-MeTHF, 2-methyltetrahydrofuran; PMMA, poly(methyl methacrylate).

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Table 4. Photophysical Properties of Tetradentate Pt(II)Complexes in Various Thin Films^{*a*}

| thin film | λ_{\max} [nm] | $\tau \ [\mu s]$ | Φ_{PL} [%] | $k_{\rm r} \; [10^4 \; {\rm s}^{-1}]$ | $k_{\rm nr} \; [10^4 \; {\rm s}^{-1}]$ |
|--------------------------------------|-----------------------|------------------|------------------------|---------------------------------------|--|
| 5 wt % Pt(<i>ppy</i> -1) in PMMA | 516 | 5.3 | 68 | 12.8 | 6.0 |
| 5 wt % Pt(<i>ppy</i> -1) in mCBP | 516 | 6.2 | 62 | 10.0 | 6.1 |
| 10 wt % Pt(ppy-1) in mCBP | 519 | | | | |
| 5 wt % Pt(<i>ppy</i> -1) in DPEPO | 518 | 5.0 | 90 | 18.0 | 2.0 |
| 5 wt % Pt(bp-7) in PMMA | 558 | 4.2 | 12 | 2.9 | 21.0 |
| 5 wt % Pt(bp-7) in mCBP | 562 | 5.0 | 7 | 1.4 | 18.6 |
| 10 wt % Pt(<i>bp-</i> 7) in mCBP | 562 | | | | |
| 5 wt % Pt(<i>bp-</i> 7) in DPEPO | 558 | 4.6 | 17 | 3.7 | 18.0 |

^aDPEPO, bis[2-(diphenylphosphino)phenyl]ether oxide; mCBP, 3,3di(9H-carbazol-9-yl)biphenyl.



Figure 6. Photostability comparison of the previously reported Pt(bp-2) and the newly developed Pt(ppy-1), Pt(bp-6), Pt(bp-7), and Pt(bp-8). The photostabilities of the Pt(II) complexes were assessed using the complex-doped polystyrene film (5 wt %) excited by UV light of 375 nm at 500 W/m².

moiety of the ligands on the excited lifetimes of the Pt(II) complexes.

At RT in dichloromethane solution and PMMA film, all four Pt(II) complexes show broadened emission spectra with a little red shift compared to the cryogenic emission spectra, where Pt(ppy-1) exhibits an extremely broad featureless spectrum merged from the vibrational peaks of v_{0-0} and v_{0-1} (Figures 4 and S5). The four Pt(II) complexes show a quantum efficiency $(\Phi_{\rm PL})$ of 5–95% and 12–68%, and τ of 3.5–8.2 μ s and 3.8– 9.1 μ s in dichloromethane solution and PMMA film, respectively (Table 3). Pt(ppy-1) exhibits broad structureless spectra, high $\Phi_{\rm PL}$ of 95% and 68%, and large radiative rate $(k_{\rm r})$ of 14.8×10^4 and 12.8×10^4 s⁻¹ in dichloromethane and PMMA, respectively, revealing more ${}^{3}MLCT(\pi_{ppyCOO}d_{Pt} \rightarrow \pi_{Py}^{*})$ character in T₁ states (Table 3). By contrast, Pt(*bp*-6), Pt(bp-7), and Pt(bp-8) still show well-resolved vibronic emission spectra, indicative of dominant ${}^{3}LC(\pi_{bp} \rightarrow \pi_{bp}^{*})$ mixed with small ³MLCT($\pi_{bp}d_{Pt} \rightarrow \pi_{Py}^*$) characters for Pt(bp-6), ³LC($\pi_{CzPh} \rightarrow \pi_{CzPh}^*$) mixed with small ³MLCT($\pi_{bp}d_{Pt} \rightarrow \pi_{Py}^*$) characters for Pt(bp-7), and ³LC($\pi_{CzPh} \rightarrow \pi_{CzPh}^*$) mixed with small ³MLCT($\pi_{bn}d_{Pt} \rightarrow \pi_{ACz}^*$) for Pt(*bp*-8) in their T₁

states by NTO analyses (Figure S4). These analyses also can be supported by the fact that Pt(bp-6), Pt(bp-7), and Pt(bp-8)exhibit much lower Φ_{PL} and smaller k_r compared to Pt(ppy-1)(Table 3). Another reason for the low Φ_{PL} of Pt(bp-6), Pt(bp-7), and Pt(bp-8) is their large structural deformations in T_1 states, especially the long and weak $Pt-N^1$ coordination bonds in Pt(bp-7) and Pt(bp-8) (Figure 1), which are revealed by the TD-DFT calculations discussed above. Additionally, Pt(bp-6), Pt(bp-7), and Pt(bp-8) exhibit nearly identical emission spectra in both dichloromethane solution and PMMA film (Figure S5), also revealing the dominant ³LC mixed with small ³MLCT characters in their T_1 states.

Notably, the intensity of the vibronic v_{0-1} sideband of Pt(ppy-1) with a N*C^N^O-coordinated ligand is extremely high and merges with the v_{0-1} vibrational peak to form a broad emission spectrum (Figure 4), because the strong δ -donating ability of the O⁻ enhances the ³MLCT character in T₁ states. However, N^*C^*N -coordinated Pt(bp-6) with smaller ³MLCT character shows a much vibronically featured spectrum and lower v_{0-1} vibrational peak (Figure 4). Increasing the molecular rigidity through employing Cz to replace Ac of Pt(*bp*-6), Pt(*bp*-7) exhibited a further smaller v_{0-1} vibrational peak (Figure 4). Pt(bp-8), which adopts ACz as nitrogen brigding atom in the ligand design (Figure 1), possesses the most rigid molecular skeleton and shows a significantly decreased v_{0-1} sideband in various conditions (Figure 4), also indicative of dominant ³LC mixed with small ³MLCT characters in the T1 state. The decreased intensities of the vibronic sidebands increase the color purity of the Pt(II) complexes-based phosphorescent emitters and facilitate their applications in the OLED field. Additionally, the spectrometer also shows influence on the spectrum. The v_{0-1} vibrational peaks of Pt(bp-7) and Pt(bp-8) measured by the HITACHI F-7000 spectrometer are much smaller than those by the Horiba Jobin Yvon FluoroLog-3 spectrometer (Figure S6). This is attributed to the different gratings, as well as the detectors have different sensitivities to the light with the same wavelength.

The photophysical properties of Pt(ppy-1) and Pt(bp-7) in various thin films were also investigated (Figure 5 and Table 4). Compared to the doped PMMA film, 5 wt % Pt(ppy-1) doped CBP film shows similar τ_i and a $\Phi_{\rm PL}$ PL spectrum with a smaller sideband at about 550 nm. Increasing the concentration to 10 wt %, and no excimer emission can be observed, although Pt(ppy-1) has a planar molecular geometry with a very small dihedral angle of only 16.6° between the terminal pyridine and carboxyl planes in the S₀ state (Tables S1 and S2), indicating no $Pt \cdots Pt$ interaction in the excited states. The $\Phi_{\rm PL}$ of 5 wt % Pt(ppy-1) doped DPEPO film is significantly enhanced to 90%, which is attributed to the high $E_{\rm T}$ of DPEPO (3.0 eV) to result in efficient energy transfer from the host to Pt(bp-1). Similar results are also found for the Pt(bp-1) in various thin films. No significant solvatochromic behavior is observed for Pt(bp-7), which is in agreement with its excitedstate property of a dominant ${}^{3}LC(\pi_{CzPh} \rightarrow \pi_{CzPh}^{*})$ character discussed above.

Photostability Studies. High photostability of the Pt(II) complexes is essential to be used as emitters for device fabrication, and also critical to device operational lifetime improvement. However, the photostability study of Pt(II) complexes is scarce.^{61,65} The photostability of the newly developed Pt(II) complexes was assessed according the previously reported method using UV irradiation, which was the 5 wt % Pt(II) complexes-doped polystyrene film excited by



Figure 7. (a) Energy level diagram and chemical structures of the materials used for the Pt(ppy-1)-doped OLEDs. (b) EL spectra, (c) current density-voltage (*J*-*V*) characteristics, (d) external quantum efficiency (EQE) versus luminance plots, and (e) power efficiency-luminance (*P*-*L*) characteristics of the Pt(ppy-1)-doped OLEDs. HTL: hole-transporting layer; EML: emissive layer; ETL: electron-transporting layer.

UV light of 375 nm at 500 W/m² (Figure 6).⁶¹ Pt(*ppy*-1) demonstrated a photostability lifetime of 150 min, LT₉₇, at 97% of initial luminance, which was significantly superior to that of our previously reported Pt(*bp*-2) with LT₈₅, at 85% of initial luminance, of 125 min under identical conditions (Figure 6).⁶¹ The photostability can be further improved by using an oxygen-bridged ligand; Pt(*bp*-6) achieved an estimated photostability lifetime of 150 min, about LT_{98.5}, at 98.5% of initial luminance (Figure 6). However, the PyCz-

based Pt(*bp*-7) and Pt(*bp*-8) exhibited relatively poor photostabilities, which decreased to LT_{95} and LT_{86} for a lifetime of 150 min, respectively (Figure 6). This is attributed to the long and weak coordination bonds Pt–N¹ in Pt(*bp*-7) (2.232 Å) and Pt(*bp*-8) (2.237 Å) (Figure 1), resulting in rapid decomposition under the excitation of the UV light. This photostability study reveals the importance of the integrated design of the ligand to well coordinate with the center Pt(II) ion. pubs.acs.org/IC

| Ta | ble | 5. | EL | Per | tormance | ot | Pt(ppy-1 | l)-L |)oped | OLEDs" |
|----|-----|----|----|-----|----------|----|----------|------|-------|--------|
|----|-----|----|----|-----|----------|----|----------|------|-------|--------|

| | | | | | EQE (%) | | | |
|-----------------------------|------------------------|-------------------------------|-----------|------|----------------------|-----------------------|---------------|----------------|
| EML | $V_{\rm on}~({\rm V})$ | $\lambda_{\rm EL}~({\rm nm})$ | fwhm (nm) | peak | 100 cd/m^2 | 1000 cd/m^2 | $L_{\rm max}$ | CIE (x, y) |
| 10% Pt(ppy-1):DPEPO | 6.4 | 518 | 80 | 3.9 | 1.9 | 0.8 | 1165 | (0.358, 0.560) |
| 10% Pt(<i>ppy</i> -1):mCBP | 3.9 | 518 | 66 | 7.2 | 6.7 | 7.2 | 43709 | (0.349, 0.602) |
| 10% Pt(ppy-1):26mCPy | 2.4 | 516 | 58 | 18.5 | 12.3 | 10.4 | 40979 | (0.298, 0.634) |

 ${}^{a}V_{on}$: turn-on voltage at 1 cd/m². fwhm: full width at half-maximum. EQE: external quantum efficiency. L_{max} : maximum brightness. CIE: Commission Internationale de l'Eclairage. 26mCPy: 2,6-di(9H-carbazol-9-yl)pyridine.

Electroluminescence (EL) Properties. On the basis of the high of the Φ_{PI} (90%) of 5 wt % Pt(*ppy*-1) doped DPEPO film, Pt(ppy-1)-based OLED was fabricated using DPEPO as host material with the device structure of ITO/HATCN (10 nm)/TAPC (30 nm)/Pt(ppy-1):DPEPO (10%, 35 nm)/ TmPyPB (55 nm)/LiF (1 nm)/Al (100 nm) (structure I). HATCN was used as hole injection material, and TAPC and TmPyPB were employed as hole- and electron-transporting materials, respectively (Figure 7). The device performance is shown in Table 5. It was unexpected that the device exhibited a large turn-on voltage of 6.4 V and an extremely low peak EQE of only 3.9% with a CIE coordinates of (0.358, 0.560) (Figure 7, Table 5). This could be attributed to the poor chargetransfer ability of the DPEPO, which also resulted in low current density and small luminance (Figure 7c). The device performance could be significantly improved employing mCBP as host material (structure II), which showed a decreased turnon voltage of 3.9 V and a peak EQE of 7.2% with very small roll-off (Figure 7d, Table 5). Notably, a L_{max} of 43 709 cd/m² could be achieved because of the improved balance of charge carriers (Figure 7c). Moreover, OLED using 26mCPy as host material realized a peak EQE of 18.5% (structure III), which still maintained an EQE of 10.4% at 1000 cd/m², and an L_{max} of over 40 000 cd/m^2 was achieved. The EL spectrum was much narrower than those using mCBP or DPEPO as host materials. It is believed that the device performance can be further improved by optimizing the device structure with charge blocking materials.

DISCUSSION

In 2013, Che and co-workers first reported a series of highly robust phosphorescent tetradentate Pt(II) complexes with N^C^N^O ligands containing 5/5/6 metallocycles, Pt-2-F₂, Et-Pt-2-F₂, and their analogues (Figure 8).^{70,71} The extremely planar molecular geometries of the Pt-2-F2 and Et-Pt-2-F2 enabled both monomer and excimer emissions in high concentrations, making them ideal emitters for single-doped white OLEDs. Our previous study demonstrated the dihedral angle of only 0.6° between the terminal pyridine and phenyl planes for Et-Pt-2- F_2 in the S₀ state by DFT calculation,⁴ which is much smaller than that of Pt(ppy-1) (16.6°). Pt-2-F₂doped white OLED achieved an EQE of 16.5% with CIE (0.33, 0.42) and CRI (Color Rendering Index) of 77. Further studies demonstrated that incorporating an electron-donating large steric group (3,5-di-tert-bulylphenyl) into the ligands, or breaking the conjugation with a N- or C-linker could further enhance the Φ_{PL} tune the emission color of the N^C^NO Pt(II) complexes, and meanwhile avoid the excimer emission (Figure 8).^{72–74} Compared to Pt-2-F₂ (λ = 482 nm) and Et-Pt-2-F₂ (λ = 480 nm), Y-Pt (λ = 553 nm), Pt-1-Pt-5 (λ = 517-551 nm) and the newly developed Pt(ppy-1) (λ = 516 nm) show a significant red shift in dichloromethane solution at RT, making them good emitters for high performance green and



Figure 8. Chemical structures of selected *ppy*-based tetradentate Pt(II) complexes with N^C^N^O ligands and their photophysical properties in dichloromethane solution at room temperature reported by Che's group.⁷⁰⁻⁷⁴

yellow OLEDs.^{72–74} The Pt-1-based green OLED demonstrated a peak EQE of 18.2% with efficiency stability (2.4% roll-off at 1000 cd/m²), and CIE coordinates of (0.282, 0.657) using a similar device structure of the Pt(*ppy*-1)-based OLED.⁷² Pt-4- and Pt-5-based OLEDs demonstrated peak EQEs over 20% and realized maximum power efficiencies of 118 and 126 lm/W.⁷⁴ All the N^C^N^O Pt(II) complexes show broad and less featured or Gaussian-type emission spectra, revealing a large percent of ³MLCT character in their exciter states, which is also supported by the fact of the high Φ_{PL} and short τ . Moreover, the HOMO distributions of Pt-4 and Pt-5 are mainly on the π_{Ph} - p_{Pt-O} - π_{OC} orbitals discussed above. These studies suggested that the N^C^N^O Pt(II) complexes for OLED fabrications.

CONCLUSIONS

In summary, we developed a series of ppy-based 6/5/5 and bp-based 6/5/6 Pt(II) complexes employing tetradentate ligands

with nitrogen or oxygen atoms as bridging groups. Experimental and theoretical studies reveal that ligand structural modifications have great influences on the electrochemical, photophysical, and excited-state properties and photostabilities of the Pt(II) complexes. All the Pt(II) complexes strongly emit in various conditions and show Φ_{PL} and au of 5–95% and 3.5– 8.2 μ s in dichloromethane solution at RT, and 12-68% and 3.8–9.1 μ s in PMMA film at RT. The TD-DFT calculations and NTO analyses reveal that Pt(bp-6), Pt(bp-7), and Pt(bp-8)have dominant ³LC mixed with small ³MLCT characters in T₁ states, resulting in relatively low $\Phi_{ ext{PL}}$ but emission spectra with decreased vibronic sidebands and high color purities. By contrast, Pt(ppy-1) possesses much more ³MLCT character in the T₁ state, enabling high Φ_{PL} and large k_r . All the Pt(II) complexes show high photostabilities in 5 wt % doped polystyrene films; especially, PyAc-based Pt(ppy-1) and Pt(bp-6) demonstrate long photostability lifetimes of 150 min for LT_{97} and $LT_{98.5}$, respectively. The strength of Pt-N¹ coordination bonds has a great influence on their photostabilities. This work suggests that rational and integrated design of the ligand should be taken into account to well coordinate with the center Pt(II) ion. Host materials significantly affected the Pt(ppy-1)-based green OLEDs. Using 26mCPy as host, the OLED demonstrated a peak EQE of 18.5% with CIE coordinates of (0.298, 0.634), which still maintained an EQE of 10.4% at 1000 cd/m², and an L_{max} of over 40 000 cd/m^2 was achieved. This study should provide a valuable reference for the further development of efficient and stable phosphorescent Pt(II) complexes for display and lighting applications.

EXPERIMENTAL SECTION

The detailed synthesis and structural characterization of all the tetradentate Pt(II) complexes are provided in the Supporting Information. Diffraction data of Pt(*bp*-6) and Pt(*bp*-7) were collected on a Bruker SMART APEX diffractometer with Mo KR radiation (λ) 0.71073 Å at 170 K. Cyclic voltammetry and different pulsed voltammetry were carried out using a CH1760E electrochemical analyzer. The theoretical calculations were performed using Gaussian 09. The absorption spectra of the Pt(II) complexes were performed on an Agilent 8453 UV–vis spectrometer, and steady-state emission and decay lifetime experiments were measured on a Horiba Jobin Yvon FluoroLog-3 spectrometer. All devices were fabricated by vacuum thermal evaporation and then were tested outside the glovebox after encapsulation. Please see the Supporting Information for details.

ASSOCIATED CONTENT

G Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02569.

DFT calculations of Pt(II) complexes (Tables S1, S2, S5–S8, Figure S1); crystal data and structure refinement for Pt(*bp*-6) and Pt(*bp*-7) (Tables S3, S4); cyclic voltammograms of the Pt(II) complexes (Figure S2); comparisons of absorption spectra of the Pt(II) complexes and their ligands (Figure S3); NTO analyses (Figure S4); comparisons of luminescence spectra of the Pt(II) complexes at 77 K in 2-MeTHF, at RT in DCM solution, and at RT in PMMA film (Figure S5); luminescence spectra comparison measured by different spectrometers (Figure S6); detailed synthetic procedures; ¹H, ¹³C NMR, and HRMS spectra of the Pt(II) complexes (PDF)

Accession Codes

CCDC 2036927 and 2036928 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

- Guijie Li College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, People's Republic of China; Occid.org/0000-0002-0740-2235; Email: guijieli@zjut.edu.cn
- Yun-Fang Yang College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, People's Republic of China; Email: yangyf@zjut.edu.cn
- Yuanbin She College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, People's Republic of China; ⊙ orcid.org/0000-0002-1007-1852; Email: sheyb@zjut.edu.cn

Authors

- Gang Shen College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, People's Republic of China
- Xiaoli Fang College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, People's Republic of China
- Feng Zhan College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, People's Republic of China
- Jianbing Zheng College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, People's Republic of China
- Weiwei Lou College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, People's Republic of China
- Qisheng Zhang MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China; orcid.org/0000-0002-0899-6856

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c02569

Notes

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