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Rational Design of Chelating Phosphine Functionalized Os^(II) Emitters and Fabrication of Orange Polymer Light-Emitting Diodes Using Solution Process**

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A new series of charge neutral Os^(II) pyridyl azolate complexes with either bis(diphenylphosphino)methane (dppm) or *cis*-1,2-bis(diphenylphosphino)ethane (dppee) chelates were synthesized, and their structural, electrochemical, photophysical properties and thermodynamic relationship were established. For the dppm derivatives **3a** and **4a**, the pyridyl azolate chromophores adopt an eclipse orientation with both azolate segments aligned *trans* to each other, and with the pyridyl groups resided the sites that are opposite to the phosphorus atoms. In sharp contrast, the reactions with dppee ligand gave rise to the formation of two structural isomers for all three kind of azole chromophores, with both azolate or neutral heterocycles (i.e., pyridyl or isoquinoliny fragments) located at the mutual *trans*-disposition around the Os metal (denoted as series of **a** and **b** complexes). These chelating phosphines Os^(II) complexes show remarkably high thermal stability, among which and several exhibit nearly unitary phosphorescence yield in deaerated solution at RT. A polymer light-emitting device (PLED) prepared using 0.4 mol % of **5a** as dopant in a blend of poly(vinylcarbazole) (PVK) and 30 wt % of 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) exhibits yellow emission with brightness of 7208 cd m⁻², an external quantum efficiency of 10.4 % and luminous efficiency of 36.1 cd A⁻¹ at current density of 20 mA cm⁻². Upon changing to 1.6 mol % of **6a**, the result showed even better brightness of 9212 cd m⁻², external quantum efficiency of 12.5 % and luminous efficiency of 46.1 cd A⁻¹ at 20 mA cm⁻², while the max. external quantum efficiency of both devices reaches as high as 11.7 % and 13.3 %, respectively. The high PL quantum efficiency, non-ionic nature, and short radiative lifetime are believed to be the determining factors for this unprecedented achievement.

1. Introduction

The transition-metal complexes showing strong phosphorescent emission at RT have received a great deal of attention in recent years due to their rich photophysical properties^[1] and potentials for fabricating the organic light emitting diodes (OLEDs) suited for full color displays, white-emitting devices for general lighting applications and backlight panels of future liquid crystal displays.^[2] This flourishing demand for high efficiency phosphors has inspired the investigation of the Ir^(III) and

Pt^(II) complexes with various cyclometalated chromophores,^[3,4] for which the strong metal-ligand bonding governed by the chelating chromophores renders the enhanced chemical stability, while the spin-orbit interaction imposed by the central heavy metal atom would effectively promote singlet-to-triplet intersystem crossing as well as subsequent radiation decay that yields phosphorescence. Thus, the resulting phosphorescent OLEDs would give efficiencies far beyond the 25 % theoretical limit predicted for those using fluorescent emitting materials.^[5]

Parallel to the study involving the luminescent Ir^(III) complexes, our research team has been focusing on the design, preparation and evaluation of less accessible Os^(II) emitting materials.^[6] Due to the lower positive charge at the central Os^(II) metal cation, the Os^{2+/3+} oxidation is shifted to a lower potential in comparison with the Ir^{3+/4+} couple of its isoelectronic Ir^(III) complexes. Likewise, the lowest energy excited state of Os^(II) complexes should contain an increased proportion of the metal-to-ligand charge transfer (MLCT) character. This property is important in light of their enticing photophysical behavior. On one hand, the increase of the MLCT participation may render a significant reduction of its radiative lifetime compared with respective Ir^(III) system where its phosphorescence may be more subject to the contribution from the relatively long-lived ligand-centered $\pi\pi^*$ transition.^[7] On the other hand, with regard to the basic performances in OLEDs, the ca-

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thodic shifted oxidation potential pushes up the energy level of HOMO and makes suitable the neutral Os(II) complexes to serve as the sites for direct charge trapping. In addition, the shortened radiative lifetime should reduce the triplet-triplet annihilation in devices under higher dopant concentration or at the higher driving voltage. As a consequence, the highly emissive Os(II) complex offer its prospect to be among the best emitting dopants for the phosphorescent OLEDs.^[8]

In our previous studies, several prototypical Os(II) dopants displayed good OLED performance; c.f. (1) and (2), which possess two monodentate PPh₂Me ligands located at the *trans*-disposition (**Chart 1**), despite of the fact that they are all prepared from their precursors [Os(CO)₂(fppz)₂] or [Os(CO)₂(fptz)₂], in

which the carbonyl ligands adopted a distinctive *cis*-orientation.^[9] Obviously, the thermal and physical properties of these Os(II) complexes 1 and 2, and consequently the device performance can be further improved from the viewpoint of chemistry and molecular design. Among several key steps for the improvement, one focus is to optimize phosphine ligands in view of their variety and configuration, such that a much robust configuration can be achieved. This leads us to intuitively select the chelating phosphines as the replacement for monodentate phosphines.

The respective synthetic pathways render new series of charge neutral, pyridyl azolate Os(II) complexes bearing either bis(diphenylphosphino)methylene or *cis*-1,2-bis-(diphenylphosphino)ethene chelate in high yields. It should be noted that although the design of some titled Os(II) emitting materials seems somewhat similar to our previously reported Ru(II) congeners,^[10] their basic structural, electrochemical, photophysical and thermodynamic characteristics are much superior; for example, the chelating phosphine Os(II) metal complexes discussed in this manuscript, for which they are significantly more stable versus the *trans* phosphine Os(II) complexes 1 and 2 as well as the *cis* substituted Ru(II) complexes.^[6b] This is mainly due to the improved bonding interaction between the third-

row metal element and chelating phosphines. Furthermore, several of these newly synthesized Os(II) complexes have also achieved nearly unitary phosphorescence yield in deaerated solution at RT, which are in sharp contrast to their second-row, *cis*-Ru(II) congeners discussed earlier.^[10] As a result, they would exhibit better EL efficiencies and improved device lifetime versus our previous design, rendering better suitability for future commercial OLED design. Detailed experimental data and respective discussion are elaborated in the following sections.

2. Results and Discussion

2.1. Synthesis and Characterization

As mentioned earlier, treatment of dicarbonyl complexes [Os(CO)₂(fppz)₂] or [Os(CO)₂(fptz)₂] with freshly sublimed Me₃NO, followed by addition of PPh₂Me gave isolation of phosphine substitution products [Os(fppz)₂(PPh₂Me)₂] (1) or [Os(fptz)₂(PPh₂Me)₂] (2), on which the phosphine ligands are resided at the *trans*-disposition.^[11] Moreover, the preparation was further optimized using a one-pot concept that involves the *in-situ* generation of [Os(CO)₂(fppz)₂] or [Os(CO)₂(fptz)₂] from treatment with Os₃(CO)₁₂ in diethylene glycol monomethyl ether (DGME), followed by sequential addition of Me₃NO and then phosphines such as PPh₂Me.^[12] This modified approach afforded the final products 1 and 2 in much improved yields (≥ 70 %); hence this procedure, so far, was considered to be the most efficient method for preparation of related complexes. Unfortunately, although complexes 1 and 2 are stable in solid state for an extended period of months at RT, these samples are somewhat sensitive to the dried, activated silica gel, causing notable changes of color over a period of hours.

We were then interested in the similar reaction using Os₃(CO)₁₂, (fppz)H and bis(diphenylphosphino)ethane (dppe) in hoping to obtain the related fppz complex with a chelating dppe ligand. Interestingly, this reaction gave only a bright, red-emitting powdery material which is essentially insoluble in all common organic solvents. Based on the established structure for 1 and 2, this unknown material may possess a one dimensional, long chain structure (**Chart 2**) that would inevitably reduce its solubility in common organic solvents. No further attempt was made to identify this material due to its intractable nature. On the other hand, upon switching to the chelating bis(diphenylphosphino)methane (dppm), due to the reduction of spatial separation between the diphenylphosphino units that favors the formation of chelating interaction, discrete orange

complexes $[\text{Os}(\text{fppz})_2(\text{dppm})]$ (**3a**) and $[\text{Os}(\text{fptz})_2(\text{dppm})]$ (**4a**) were successfully isolated in moderate yields (**Chart 3**). Accordingly, their structure and photophysical characteristics would reveal the effects anticipated by the coordination isomerism.

After then, the syntheses were extended to systems involving another chelating phosphine; i.e., *cis*-1,2-bis(diphenylphosphino)ethene (dppee). A total of three azolate chromophores, namely: 3-(trifluoromethyl)-5-(2-pyridyl)pyrazole (fppz)H, 2-pyridyl-3-trifluoromethyl-1,2,4-triazole (fptz)H and 3-(trifluoromethyl)-5-(1-isoquinolyl)pyrazole (ifpz)H, each of which shows distinctive optoelectronic properties, were selected for this investigation. In sharp contrast to the previous examples employing either dppe or dppm ligand, the reactions with dppee all gave two isomeric products denoted as isomers **a** and **b**, for which the azolate fragments are resided at the mutual *trans* and *cis*-disposition, respectively (see **Chart 4**). These Os^{II} complexes exhibit good solubility in all organic solvents as well as significantly improved stability upon adsorbing on the surface of activated silica gel. This viewpoint is supported by negligible degradation, as monitored by ^1H NMR and UV-vis spectroscopy, over a long period of several days. Moreover, in addition to their structural relationship established using ^1H NMR, complexes **4a**, **6b** and **7b** were identified using single

crystal X-ray diffraction studies. Selected ^1H NMR spectra of complexes **5a** and **5b** are depicted in Figure 1. It is notable that the olefinic protons of dppee ligand of isomer **b**, which belonged to a second-order AA'XX' spin system, for which the signals occurred at the much downfield position compared with those of isomer **a**. Such a spectral feature was also observed between the pair of complexes **6a/6b** and **7a/7b**, and can be used as a quick reference for differentiating their molecular structure.

Figure 1. ^1H NMR spectra of complexes **5a** and **5b**; the olefinic protons of dppee ligand, showing a unique AA'XX' spectral pattern, are identified and marked with asterisk.

Amid isolation and characterization of both isomers, one intriguing question is regarding their reactivity relationship as well as how to conduct the possible interconversion. Accordingly, we have made an attempt to address this issue by heating of **6b** in refluxing DGME solution. The ^1H NMR analysis confirmed the formation of an approx. 1:1 mixture of **6a** and **6b** in 48 hours, while heating of **6a** failed to show any formation of **6b** under identical condition, indicating an irreversible process. In sharp contrast, neither isomers of pyrazolate complexes **5** and **7** have revealed the anticipated isomerization under the identical reaction conditions. Clearly, this rearrangement is strongly influenced by the nature of azolate chelates, i.e., the complex with *cis*-arranged triazolate fragments tend to be less stable, while those with the *trans*-triazolate fragments or even pyrazolate fragments give a negligible rate of conversion in a qualitative manner.

2.2. X-Ray Crystallography

Figure 2 depicts the molecular structure of complex **4a**, showing a mandated *cis*-P,P arrangement and an acute P–Os–P bite angle of $71.14(3)^\circ$ for the dpmm chelate. The fptz chromophores adopt an eclipse orientation with both triazolate nitrogen atoms N(2) and N(6) aligned *trans* to each other, and with the pyridyl nitrogen atoms N(1) and N(5) located *trans* to the chelating phosphorus atoms. The adoption of *cis*-P,P arrangement in **4a** has notably improved the Os–P bond strength. This is confirmed by a reduction of averaged Os–P distance from 2.362 Å in the *trans*-P,P complex $[\text{Os}(\text{fppz})_2(\text{PPh}_2\text{Me})_2]$ to ~ 2.275 Å in **4a**, alone with an increase of the Os–N_(py) bonding from 2.090 Å in $[\text{Os}(\text{fppz})_2(\text{PPh}_2\text{Me})_2]$ to a greater value 2.133 Å in **4a**, while leaving the *trans* Os–N_(tz) distances unaltered; 2.073 Å in $[\text{Os}(\text{fppz})_2(\text{PPh}_2\text{Me})_2]$ vs. 2.060 Å in **4a**.^[11] This variation of bonding is presumably caused by the much greater *trans*-effect of the π -accepting phosphine, compared

Figure 2. ORTEP diagram of complex **4a** with thermal ellipsoids shown at 30 % probability level; all four phenyl groups on the dpmm ligand were removed for clarity. Selected bond distance and angles: Os–N(1) = 2.127(3), Os–N(2) = 2.061(3), Os–N(5) = 2.140(3), Os–N(6) = 2.058(3), Os–P(1) = 2.280(1), Os–P(2) = 2.275(1) Å, and $\angle\text{P}(1)\text{–Os–P}(2) = 71.14(3)^\circ$.

with the pyridyl N-donor atoms. The increase of Os–P bonding in **4a** may also reduced the electron density on Os^(II) center, giving an increase of its HOMO/LUMO gap and the relative emission energy for this type of *cis* complexes. The overall molecular structure and the relatively orientation is identical to the analogous Ru^(II) isoquinolyl complex that reported earlier in literature.^[10]

An X-ray structural characterization of **6b** was then conducted to unravel its differences with the dpmm complex **4a**. As shown in Figure 3, the pyridyl nitrogen atoms N(1) and N(5) are now located at the positions *trans* to one another, rather than being *trans* to the phosphine ligands. This distinctive structural configuration has results in strengthening of Os–N_(py) bonding, c.f. Os–N(1) = 2.093(5) and Os–N(5) = 2.099(5) Å.

Figure 3. ORTEP diagram of complex **6b** with thermal ellipsoids shown at 30 % probability level; all four phenyl groups on the dppe ligand were removed for clarity. Selected bond distance and angles: Os–N(1) = 2.093(5), Os–N(2) = 2.082(5), Os–N(5) = 2.099(5), Os–N(6) = 2.085(5), Os–P(1) = 2.2825(17), Os–P(2) = 2.2800(18) Å, and $\angle\text{P}(1)\text{–Os–P}(2) = 83.02(6)^\circ$.

Moreover, the triazolate ligands in **6b** are *trans* to the phosphine ligand and show bond distances (Os–N(2) = 2.082(5) Å and Os–N(6) = 2.085(2) Å) being comparatively longer than those in **4a** where they are *trans* to each other. These differences can be rationalized in terms of the poor competition of bonding to phosphine, which is known to be the stronger π -acceptor.^[13] Negligible variation on Os–P distances is observed, except that the P–Os–P bite angle is now increased to $83.02(6)^\circ$ in **6b**. This enlarged angle is consistent with the formation of a five-membered chelate that showed a less degree of internal ring strain. Moreover, the crystal structure of the related isoquinoline complex **7b** is also determined (Fig. 4), which also shows very similar Os–N and Os–P coordination distances. Most importantly, its key geometrical feature, i.e., with two *trans*-oriented isoquinoline donors, is different from that of its Ru^(II) isoquinolyl analogue^[10] as well as to the previously discussed fptz coordinated Os^(II) complex **6b**, confirming the formation of structural isomerism.

Figure 4. ORTEP diagram of complex **7b** with thermal ellipsoids shown at 30 % probability level; all four phenyl groups on the dppe ligand were removed for clarity. Selected bond distance and angles: Os–N(1) = 2.097(4), Os–N(2) = 2.081(4), Os–N(4) = 2.107(4), Os–N(5) = 2.079(4), Os–P(1) = 2.2792(14), Os–P(2) = 2.2894(13) Å, and $\angle$ P(1)–Os–P(2) = 83.49(5)°.

2.3. Photophysical and Electrochemical Properties

Photophysical and electrochemical properties of these osmium complexes can be systematically tuned by modification of the azolate chromophores and the ancillary phosphine ligands; the respective data are listed in Table 1. For the UV/vis spectrum of dppe incorporated complexes **3a** and **4a**, the high energy absorption bands at ~ 353 nm are dominated by the azolate $\rightarrow$ pyridine intraligand $\pi\pi^*$ transition (Fig. 5), which is identified by their large extinction coefficients of ~ 11000 $\text{M}^{-1}\text{cm}^{-1}$ as well as their spectral similarity with respect to the free ligand in the anionic form (not shown here). The next lower energy band with peak wavelength at ~ 460 nm, is assigned to the spin allowed MLCT transition due to its relatively lower extinction coefficient of ~ 2500 $\text{M}^{-1}\text{cm}^{-1}$. In good

Figure 5. The UV-vis absorption spectra of **3a** (—○—) and **4a** (—▲—) in CH_2Cl_2 at RT and their normalized emission spectra (λ_{ex} : 450 nm).

agreement with the MLCT absorption peak position, the emission signals for **3a** and **4a** occur at 586 and 580 nm, respectively. Both emissions show featureless line shape, an essential character for the MLCT transition, and exhibit a near unitary quantum efficiency in degassed fluid solution at RT. The emission lifetime of **4a** is slightly longer, which could be tentatively attributed to the reduction of the MLCT character, a direct result of the incorporation of more electron withdrawing triazolate units that lowered the electron density at the $\text{Os}(\text{II})$ metal center. Further support of this viewpoint is given in the section of theoretical approaches.

For further comparison, the UV/vis spectra of complexes **5**, **6** and **7** are depicted in Figure 6. Adopting the same interpretation principle, both the lowest energy with great MLCT contribution and the next higher energy absorption (< 360 nm) with $\pi\pi^*$ absorption of **5a** and **6a** can be assigned. For complexes bearing same chromophoric ligands, the results show hypsochromic shift by changing the chelate from dppe (**3a** and **4a**)

Table 1. Photophysical and electrochemical properties for complexes **3–7**. [a] Samples were degassed and recorded in CH_2Cl_2 at RT, while data in square brackets [] are measured as vacuum deposited solid film at RT. [b] All electrochemical potentials were measured in a 0.1 M TBAPF₆/ CH_2Cl_2 and THF solution for oxidation and reduction reaction, and reported in volts using Fc/Fc^+ as reference; ΔE_p is defined as E_{ap} (anodic peak potential) – E_{cp} (cathodic peak potential) and these data are quoted in mV. The Pt electrode and Au(Hg) alloy were selected as the working electrode of oxidation and reduction processes, respectively.

	Photophysical Properties [a]					$E_{1/2}(\text{V})$ [ΔE_p (mV)] [b]	
	abs. λ_{max} ($\epsilon \times 10^{-3}$) $\text{M}^{-1}\text{cm}^{-1}$	PL λ_{max} (nm)	Φ (%)	τ (ns)	$k_r \times 10^6$	Oxidation $E_{1/2}$	Reduction $E_{1/2}$
3a	266(19), 294(26), 353(11), 460(2.0)	586 [557]	95 [95]	890 [1350]	1.10 [0.70]	0.06 [100]	–2.87 [120], –3.17 [160]
4a	280(22), 354(11), 460(1.8)	580 [590]	95 [41]	1600 [775]	0.59 [0.53]	0.34 [80]	–2.63 [100], –2.97 [130]
5a	286(24), 315(15), 345(10), 456(1.5)	584 [538]	80 [48]	1950 [420]	0.41 [1.10]	0.12 [80]	–2.88 [150], –3.20 [200]
5b	288(27), 350(11), 430(2.7)	544 [577]	2 [–]	100 [–]	0.2	0.26 [80]	–2.88 [150], –3.30 [190]
6a	275(25), 337(12), 450(1.9)	572 [536]	90 [65]	563 [780]	1.60 [0.83]	0.42 [100]	–2.63 [140], –2.99 [170]
6b	276(23), 350(10), 427(2.5)	547 [566]	1 [57]	7 [900]	1.38 [0.63]	0.53 [80]	–2.64 [120], –3.04 [210]
7a	306(23), 348(13), 362(14), 400(7.7), 494(2.1)	690 [675]	30 [6]	5230 [330]	0.57 [0.18]	0.09 [90]	–2.27 [150], –2.50 [140]
7b	308(28), 340(20), 354(19), 396(13), 460(5.8)	620 [650]	63 [9]	2670 [620]	0.24 [0.15]	0.24 [100]	–2.31 [130], –2.58 [140]

Figure 6. UV-vis absorption spectra and the normalized emission of complexes **5–7** in CH_2Cl_2 solution at RT.

to dppee (**5a** and **5b**). This could be due to the fact that dppee possesses a more electron withdrawing *cis*-ethene group relative to the methylene linker in dpbm; the latter is generally considered to possess stronger electron donating strength. In comparison to **5a** and **6a**, the lowest lying absorption peaks of their geometrical isomers **5b** and **6b** both shift notably to the higher energy region with weaker absorptivity centered at around 430 and 427 nm, respectively. As shown in Figure 6, similar behaviors are also observed in their emission spectra recorded in solution; i.e., despite of their emission profiles being featureless as well, the emission of isomers **a** appears at longer wavelength region and reveals significantly higher quantum yields (**5a**: $\lambda_{\text{max}} = 584$ nm, $\Phi = 0.80$; **6a**: $\lambda_{\text{max}} = 572$ nm, $\Phi = 0.90$) versus those observed for the second geometrical isomers **b** (**5b**: $\lambda_{\text{max}} = 544$ nm, $\Phi = 0.02$; **6b**: $\lambda_{\text{max}} = 547$ nm, $\Phi = 0.01$). The results cannot be simply rationalized by the widely-accepted energy gap law,^[14] which predicts more facile radiationless deactivation and hence lower emission efficiency in isomers **a**, a result which is opposite to the tendency observed experimentally. Alternatively, the results can plausibly be explained by the stronger electron donating effect of the *trans* located azolate moieties in isomers **a**.^[15] A consequence is to elevate the osmium d_{π} orbitals energy in series **a**, resulting in an increase of the MLCT character and hence a decrease of the energy gap. The increase of MLCT character should then lead to a larger radiative decay constant that is in favor to compete with the radiationless decay rates, giving rise to a relatively larger quantum yield. Support of these conclusions also can be obtained via the observation of shorter Os-azolate bond distances of isomers **a** in the X-ray crystallographic study. Supplementary support is also rendered via the frontier orbital analyses of the lower lying transitions (vide infra).

As for the isoquinoline derivatives **7a** and **7b**, a much intense absorption in their lower lying singlet transitions (> 400 nm) manifests the increase of ligand (ifpz) $\pi\pi^*$ contribution compared with that of fppz (see **5a** and **5b**). This may be rationalized by the raise of HOMO (π orbital) energy in the pyrazolate moiety of the ifpz ligand in the proximate isoquinoline (ifpz) versus pyridine moiety (in fppz). This, in combination with the decrease of LUMO in isoquinoline due to the elongation of the

π -conjugation, significantly decreases the S_0 – S_1 energy gap for **7a** and **7b**. Furthermore, the emission of **7a** occurred at 690 nm with $\Phi = 0.30$, showing both lower energy gap and lower quantum efficiency than that of isomer **7b** (620 nm; $\Phi = 0.63$). The lower emission quantum efficiency for **7a**, which is opposite to the trend observed in the pair of complexes **5a/5b** and **6a/6b**, may be understood with the operation of energy gap law. It is noteworthy that the energy gap law should operate more efficiently once the emission gap is decreased to the red, simply due to the increase of the high-frequency vibrational overlap between T_1 and S_0 , inducing the radiationless deactivation.

2.4. Theoretical Approaches

Supplementary supports of the above mentioned results and rationalization are rendered via the computational approaches. Theoretical confirmation of the underlying basis for the photophysical properties of the studied complexes was provided by the density functional theory (DFT) MO calculations. With the use of the TD-B3LYP method incorporating the B3LYP/LANL2DZ and 6-31G* optimized geometry, the vertical (i.e., Franck–Condon) excitation energy from the ground-state to low lying excited states was calculated. Figure 7 depicts the features of the lowest unoccupied (LUMO) and the highest occupied (HOMO) frontier orbitals for two prototypical complexes **6a**, **6b**, **7a**, and **7b**, which are mainly involved in the lower-lying transitions. The descriptions and the energy gaps of all complexes are listed in Table 2. Obviously, the calculated S_1 and T_1 energy levels for the titled complexes are qualitatively consistent with those 0-0 onset of the absorption (S_1) and phosphorescence (T_1) spectra. An equally important result is that the calculation also correctly predicts that the S_0 – S_1 (or S_0 – T_1) gap is in the order of **6b** > **6a** (and **7b** > **7a**), giving a firm support for the experimental results and the corresponding rationalization (vide supra). Thus, the theoretical level adopted here should be suitable for studying the photophysical properties of these complexes in a qualitative manner.

Based on the frontier orbital analyses, the lowest singlet and triplet excited states for complexes **6** and **7** are dominated by MLCT (Os $d_{\pi} \rightarrow$ pyridyl for **6a** and **6b**, Os $d_{\pi} \rightarrow$ isoquinoline for **7a** and **7b**) and ILCT ($\pi\pi^*$, triazolate $\rightarrow$ pyridyl for **6a** and **6b**, pyrazolate $\rightarrow$ isoquinoline for **7a** and **7b**). In other words, one can also envisage that the involved occupied orbitals are apparently much located at the central Os(II) atom, leading to appreciable MLCT contribution. For example, results of the calculation show ~ 68 % (58 %) and 53 % (49 %) $^3\text{MLCT}$ contribution for **6a** (**7a**) and **6b** (**7b**), respectively. Similar tendency, i.e., greater $^3\text{MLCT}$ contribution for **5a** (cf. **5b**) was also resolved (not shown here). The results firmly support the aforementioned *trans* alignment of the azolate fragments in series **a** (**5**, **6**, and **7**) as revealed by structural analysis of **4a** and the recently reported Ir(III) azolate deriva-

Figure 7. The representative frontier orbitals (HOMO and LUMO) involved in the lowest transitions of **6a**, **6b**, **7a**, and **7b**.

Table 2. The calculated energy levels of the first singlet and triplet excited states of **6a**, **6b**, **7a**, and **7b**.

Entry	State	Cal. $\lambda_{\max}$	f	Assignment	Character
6a	T ₁	472.7	0	H → L (+86%) H-1 → L+1 (+10%)	MLCT: 67.6%
	S ₁	450.1	0.0029	H → L (+97%)	MLCT: 69.6%
6b	T ₁	444.3	0	H → L (+74%) H-2 → L (9%) H-1 → L (8%) H-3 → L (+5%)	MLCT: 52.9%
	S ₁	411.8	0.0043	H → L (+95%)	MLCT: 52.6%
7a	T ₁	569.5	0	H → L (+60%) H-1 → L+1 (16%) H-2 → L (12%) H-3 → L+1 (+9%)	MLCT: 57.5%
	S ₁	528	0.0028	H → L (+96%)	MLCT: 66.7%
7b	T ₁	554.7	0	H → L (+38%) H-1 → L (+27%) H-2 → L+1 (+25%) H-4 → L (10%) H-3 → L+1 (7%)	MLCT: 48.8%
	S ₁	482.4	0.0067	H → L (+96%)	MLCT: 48.7%

tives.^[15] The larger extent of the MLCT character in series **a** complexes is responsible for the greater transition moment

due to the direct involvement of MLCT in spin-orbit coupling, consistent with the larger radiative decay rate constant resolved experimentally.

2.5. Electrochemistry

The redox potentials of all Os(II) complexes were determined from cyclic voltammetry, and the data are summarized in Table 1. It is believed that the oxidation occurred mainly at the Os(II) metal center, concomitant with contributions from the azolate and phosphine chelates. Accordingly, complex **3a** gives the oxidation potential at 0.06 V, while fptz complex **4a** exhibits a higher oxidation potential at 0.34 V due to the presence of an extra nitrogen atom, which further lowered the electron density at the metal atom. Similarly, the oxidation potentials of complexes **5a** (0.12 V) and **6a** (0.42 V) revealed that the dppee ligand would produce a greater anodic shift compared with those of dpmm ligand, which is due to the fact that dppee ligand is a better π -acceptor compared with dpmm ligand, a property that was stated during discussing their photophysical properties. Moreover, complex **7a/7b** exhibits a cathodic shift versus **5a/5b**, attributed to their greater π -conjugation at the isoquinolinyl fragments, while the variation of the oxidation potentials between the pair of isomers **5a/5b**, **6a/6b** and **7a/7b** indicates that all isomers **b** possess a greater amount of anodic shift versus their isomers **a**, showing that the configuration isomerism has exerted a significant influence to the electron density at metal center, consistent with the conclusion drawn from both photophysical data and theoretical frontier orbital analyses (vide supra).

As for the reduction behavior, except for the isoquinoline complexes **7a** and **7b**, the rest of them exhibit one fully reversible reduction couple at the lower potential, and another reversible or semi-reversible peak at the higher potential depending on their relative value. This finding and their similarity led us to propose that the observed reduction was mainly associated with the pyridyl groups, while the azolate unit (fppz vs. fptz) and phosphine chelate (dpmm vs. dppee) may still influence the observed electrochemical data in a way similar to their oxidation couples. The reduction potentials shown in Table 1 are fully consistent with this delineation; however, the variation is far less significant than that imposed on the oxidative potentials. Finally, the exceedingly low reduction potentials (−2.27/−2.50 V and −2.31/−2.58 V) were observed for complexes **7a** and **7b**, concluding that the replacement of pyridine with isoquinoline group would notably reduce the HOMO/LUMO energy gap and concurrently decrease their reduction potentials.

2.6. Electroluminescence Properties of PLED Devices

To evaluate their potential for the fabrication of PLEDs, complexes **5a** and **6a** were employed as the representative dopants for the typical devices ITO/PEDOT(35 nm)/doped emitting layer (50–70 nm)/TPBI (30 nm)/Mg:Ag (100 nm)/Ag(100 nm). As for the host material, a blend of poly(vinylcarbazole) (PVK) and 30 wt % of 2-*tert*-butylphenyl-5-biphenyl-

1,3,4-oxadiazole (PBD) was selected,^[16] among which PVK is a blue-emitting material with good hole transporting properties and is blended with PBD to enable a balance between electron and hole transporting properties. The PEDOT layer was used as a hole injection layer to facilitate hole conduction, as well as to smoothen the relatively rough surface of the ITO layer.^[17] In addition, a layer of 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)-benzene (TPBI) was deposited at the cathode, which served as both electron-transporting and hole-blocking layer. Figure 8a depicts the PL and EL spectra of 0.4 mol % of **5a** (relative to PVK monomer units). The PL profile contains two emission

Figure 8. PL and EL spectra of a) 0.4 mol % of **5a**, b) 0.4 mol % of **6a**, and c) 1.6 mol % of **6a** doped in the PVK/PBD host.

signals: the one at ca. 415 nm is a characteristic emission of the PVK/PBD host, while the other at ca. 548 nm is attributed to the triplet emission of **5a**. In contrast, the corresponding EL spectrum exhibits only the orange emission deriving from **5a**. The dramatic difference between the PL and EL spectra reveals that the Förster energy transfer from the host to the dopant sites cannot account solely for the observed EL. Thus, a second mechanism involving the direct charge trapping must be invoked.^[18,19]

Figure 8b displays the PL and EL spectra of device using dopant **6a** at the same concentration. The PL spectrum also exhibits two emissions originating from the host and dopant, respectively. From their relative intensity, we conclude that the degree of Förster energy transfer occurred in this **6a**-based device is comparable to the previously discussed device using **5a** as dopant. However, in sharp contrast to the **5a**-based device where the host emission is totally suppressed, the EL spectrum of **6a**-based devices still presents a substantial amount of the PVK host emission. This phenomenon implies the occurrence

of a reduced charge trapping effect in **6a** than **5a**-based device does. According to the energy level diagram illustrated in Figure 9, the HOMO of **6a** occurs at -5.2 eV, versus that of **5a** (-4.9 eV); this subtle change in the HOMO level then produced a major impact to their emission properties. For complex **5a**, its ionization potential is 0.9 eV below the HOMO level of

Figure 9. Energy level diagram (in eV) for materials utilized for the preparation of PLEDs having the device configuration ITO/PEDOT/PVK-PBD blend/TPBI/Mg:Ag.

PVK/PBD; therefore, holes can be trapped efficiently at the dopant sites and then recombined with electrons to form excitons. Upon switching to **6a**, the charge trapping becomes less effective because of the shallow potential (depth: 0.6 eV) exerted by **6a** within the PVK/PBD host. Even the holes can be trapped at the sites of **6a**, there is still possible for them to hop back to the HOMOs of the PVK upon overcoming this smaller barrier.^[8g,20] As a result, a number of the excitons may eventually reform at the host site. Nevertheless, the saturated-orange phosphorescence can be realized using a higher concentration of **6a** at 1.6 mol %. As shown in Figure 8c, the EL spectrum is again dominated by the triplet emission from the dopant with peak maxima centered at 560 nm.

Figure 10 displays the current density vs. voltage (I - V) characteristics of the **5a** and **6a**-doped devices. It is apparent that the driving voltage of the **5a**-based device is higher than that of the respective **6a**-based devices. This result is consistent with the charge trapping mechanism proposed in previous section. Furthermore, the driving voltage of the device using 1.6 mol % of **6a** was only slightly increased; this fact is also coincident with the weaker charge trapping effect between **6a** and PVK/PBD host. Table 3 summarizes the EL performances of these PLED devices. The maximum external quantum efficiency (max. η_{ext}) of the devices with 0.4 mol % of **5a** and **6a** are 11.7 % (40.4 cd A^{-1} at 2.1 mA cm^{-2}) and 11.7 % (38.5 cd A^{-1} at 2.2 mA cm^{-2}); whereas, the CIE coordinates are located at (0.45, 0.53) and (0.42, 0.52), respectively, and do not show variation upon changing the applied voltage. Furthermore, the performance of **6a**-doped device is improved upon increasing the doping concentration to 1.6 mol %, for which the peak external quantum efficiency reaches 13.3 % (48.9 cd A^{-1} at 6.3 mA cm^{-2}) with a maximum luminance of 28816 cd m^{-2} at 16 V (96 mA cm^{-2}). Figure 10 displays the external quantum efficiency and power efficiency plotted against the current den-

Figure 10. a) Plots of current density as function of the applied voltage for **5a** and **6a**-doped PLEDs at various doping concentrations; b) plots of the external quantum efficiency and power efficiency vs. the current density.

Table 3. Performance of PLED devices doped with **5a** and **6a**. [a] Measured at current density of 20 mA/cm². [b] With applied driving voltage at 9 V.

Device	Os-5a	Os-6a	Os-6a
Dopant concentration	0.4 mol%	0.4 mol%	1.6 mol%
Voltage (V)[a]	15.7	11.9	12.8
Brightness (cd/m ²)[a]	7208	6238	9212
E.Q.E. (%) [a]	10.4	9.5	12.5
L.E. (cd/A)[a]	36.1	31.2	46.1
Max Brightness	23073 @ 20V	16855 @ 17V	28816 @ 16V
Max E.Q.E. (%)	11.7	11.7	13.3
Max L.E. (cd/A)	40.4	38.5	48.9
Max P.E. (lm/W)	10.5	15.4	16.8
EL λ_{max} (nm) [b]	566	562	562
CIE, x and y [b]	0.45 and 0.53	0.42 and 0.52	0.42 and 0.56

sity of these orange-emitting devices. The **6a**-based devices exhibit the prominent performance on power efficiency, which reaches as high as 16.8 lm W⁻¹ and is 1.7 times higher than that of the **5a**-based device due to the significantly lowered driving voltage.

3. Conclusion

This article presents a rational design for a new series of luminescent charge-neutral osmium complexes, which involves

the usage of two pyridyl azolate chromophores and a phosphine chelate around the Os(II) metal cation in giving the corresponding complexes with all *cis*-coordinated chelating geometries. The syntheses using dppm ligand afforded only one product with its anionic azolate fragments adopting the *trans*-N,N configuration, while the reactions with dppe chelate afforded two isomers; one showing the aforementioned configuration (**a** series), while the other exhibiting another configuration (i.e., **b** series) with *trans*-N,N-arranged, neutral pyridine (or isoquinoline) fragments. Complexes **5a** and **6a** showed bright yellow and orange emission in solid state and were selected as a prototype for fabrication of phosphorescent PLEDs using PVK/PBD as the host, showing the max. external quantum efficiency as high as 11.7 % and 13.3 %, respectively. The non-ionic nature, high emission quantum efficiency, and short radiative lifetime of these Os(II) emitting materials are believed to be the determining factors that gave this unprecedented achievement.

4. Experimental

General Information and Materials: Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) mode or fast atom bombardment (FAB) mode. ¹H and ¹³C NMR spectra were recorded on Varian Mercury-400 or INOVA-500 instruments; chemical shifts are quoted with respect to the internal standard tetramethylsilane for ¹H and ¹³C NMR data. Elemental analyses were carried out at the NSC Regional Instrumentation Center at National Chao Tung University, Hsinchu, Taiwan. The pyridyl azolate chelates, namely: 3-trifluoromethyl-5-(2-pyridyl) pyrazole (fppz)H, 3-trifluoromethyl-5-(2-pyridyl)-1,2,4-triazole (fptz)H [21], and its isoquinolyl derivative, 3-trifluoromethyl-5-(1-isoquinolyl) pyrazole (ifpz)H [22] were prepared according to the literature procedures. All reactions were conducted under N₂ atmosphere using anhydrous solvents or solvents treated with an appropriate drying reagent.

Preparation of [Os(fppz)₂(dppm)]: A solution of [Os(fppz)₂(CO)₂] (150 mg, 0.22 mmol) in 20 mL of diethylene glycol monomethyl ether (DGME) was first treated with freshly sublimed Me₃NO (59 mg, 0.78 mmol) at room temperature. After then, the phosphine ligand dppm (176 mg, 0.45 mmol) was added and the solution was heated at 180 °C for 24 h. After removing the solvent under vacuum, the oily residue was separated by silica gel column chromatography eluting with a 1:1 mixture of ethyl acetate and hexane. The resulting orange component was further recrystallized from acetone/methanol at room temperature, giving 105 mg of [Os(fppz)₂(dppm)] (**3a**, 0.11 mmol, 48 %).

Spectral data of **3a**: ¹H NMR (500 MHz, d₆-acetone, 298 K, δ): 7.88–7.84 (m, 4H), 7.70 (d, 2H, J_{HH} = 8.0 Hz), 7.64 (dt, 2H, J_{HH} = 6.5, 1.0 Hz), 7.44 (d, 2H, J_{HH} = 5.5 Hz), 7.32 (t, 2H, J_{HH} = 7.5 Hz), 7.25 (t, 4H, J_{HH} = 7.5 Hz), 7.06 (t, 2H, J_{HH} = 7.5 Hz), 6.93 (dt, 2H, J_{HH} = 6.0, 1.6 Hz), 6.89–6.86 (m, 4H, J_{HH} = 6.0 Hz), 6.87 (s, 2H), 6.78–6.74 (m, 4H), 5.37 (t, 2H, J_{HP} = 11.0 Hz). ³¹P NMR (202 MHz, d₆-acetone, 298 K, δ): –43.9 (s). ¹⁹F NMR (470 MHz, d₆-acetone, 298 K, δ): –60.4 (s). MS (FAB, ¹⁹²Os): m/z 1000 (M^+). Anal. calcd for C₄₃H₃₂F₆N₆O₅P₂: C 51.70, N 8.41, H 3.23; found: C 51.75, N 8.41, H 3.31.

Preparation of [Os(fptz)₂(dppm)]: A solution of Os₃(CO)₁₂ (100 mg, 0.11 mmol) and fptzH (146 mg, 0.68 mmol) in 30 mL of DGME was heated at ~ 180 °C for 24 h. The temperature was then lowered to ~ 120 °C, freshly sublimed Me₃NO (70 mg, 0.93 mmol) dissolved in 12 mL of DGME was gradually added, followed by addition of dppm (203 mg, 0.53 mmol). This mixture was then heated at 180 °C for another 24 h. After stopping the reaction, the solvent was removed under vacuum, and the oily residue was separated by silica gel column chromatography eluting with a 2:1 mixture of ethyl acetate and hexane. The

resulting orange product was further recrystallized from acetone/methanol at room temperature, giving 102 mg of $[\text{Os}(\text{fptz})_2(\text{dppe})]$ (**4a**, 0.10 mmol, 31 %).

Spectral data of **4a**: ^1H NMR (500 MHz, d_6 -acetone, 298 K, δ): 7.91–7.82 (m, 8H), 7.65 (d, 2H, $J_{\text{HH}} = 5.5$ Hz), 7.40 (t, 2H, $J_{\text{HH}} = 7.0$ Hz), 7.33 (t, 4H, $J_{\text{HH}} = 7.5$ Hz), 7.24 (dt, 2H, $J_{\text{HH}} = 6.5$, 1.5 Hz), 7.08 (t, 2H, $J_{\text{HH}} = 7.5$ Hz), 6.90 (t, 4H, $J_{\text{HH}} = 8.0$ Hz), 6.71–6.67 (m, 4H), 5.42 (t, 2H, $J_{\text{HP}} = 11.0$ Hz). ^{31}P NMR (202 MHz, d_6 -acetone, 298 K, δ): –44.7 (s). ^{19}F NMR (470 MHz, d_6 -acetone, 298 K, δ): –64.0 (s). MS (FAB, ^{192}Os): m/z 1002 (M^+). Anal. calcd for $\text{C}_{41}\text{H}_{30}\text{F}_6\text{N}_8\text{OsP}_2$: C 49.20, N 11.20, H 3.02; found: C 48.90, N 11.11, H 3.31.

Preparation of $[\text{Os}(\text{fppz})_2(\text{dppee})]$: Similar to the procedure described above for **3a**, this reaction was conducted using $\text{Os}_3(\text{CO})_{12}$ (100 mg, 0.11 mmol), fppzH (146 mg, 0.68 mmol), Me_3NO (70 mg, 0.93 mmol) and dppee (210 mg, 0.53 mmol). Two isomeric products, denoted as **5a** and **5b**, were obtained in 34 % and 16 %, respectively.

Spectral data of **5a**: ^1H NMR (500 MHz, d_6 -acetone, δ): 7.91–7.89 (m, 4H), 7.88–7.77 (m, 2H), 7.60 (dt, 2H, $J_{\text{HH}} = 8.0$, 1.0 Hz), 7.54 (d, 2H, $J_{\text{HH}} = 8.0$ Hz), 7.34 (t, 2H, $J_{\text{HH}} = 7.0$ Hz), 7.25 (t, 4H, $J_{\text{HH}} = 7.0$ Hz), 7.05–7.01 (m, 4H), 6.84–6.79 (m, 6H), 6.71 (s, 2H), 6.69 (t, 4H, $J_{\text{HH}} = 8.5$ Hz). ^{31}P NMR (202 MHz, d_6 -acetone, δ): 31.45 (s). ^{19}F NMR (470 MHz, d_6 -acetone, δ): –59.59 (s). MS (FAB, ^{192}Os): m/z 1012 (M^+). Anal. calcd for $\text{C}_{44}\text{H}_{32}\text{F}_6\text{N}_6\text{OsP}_2$: C 52.28, N 8.31, H 3.19; found: C 52.39, N 8.45, H 3.27.

Spectral data of **5b**: ^1H NMR (500 MHz, d_6 -acetone, 298 K, δ): 8.76–8.65 (m, 2H), 8.30(t, 4H, $J_{\text{HH}} = 8.0$ Hz), 7.58 (d, 2H, $J_{\text{HH}} = 6.0$ Hz), 7.45 (t, 4H, $J_{\text{HH}} = 7.0$ Hz), 7.38 (t, 2H, $J_{\text{HH}} = 7.0$ Hz), 7.32 (d, 2H, $J_{\text{HH}} = 7.5$ Hz), 7.27 (ddd, 2H, $J_{\text{HH}} = 7.8$, 7.2, 1.6 Hz), 6.89 (t, 2H, $J_{\text{HH}} = 7.0$ Hz), 6.81 (s, 2H), 6.76 (t, 4H, $J_{\text{HH}} = 7.5$ Hz), 6.41 (t, 4H, $J_{\text{HH}} = 8.5$ Hz), 6.11 (ddd, 2H, $J_{\text{HH}} = 7.7$, 7.2, 1.6 Hz). ^{31}P NMR (202 MHz, d_6 -acetone, 298 K, δ): 31.74 (s). ^{19}F NMR (470 MHz, d_6 -acetone, 298 K, δ): –60.00 (s). MS (FAB, ^{192}Os): m/z 1012 (M^+). Anal. calcd for $\text{C}_{44}\text{H}_{32}\text{F}_6\text{N}_6\text{OsP}_2$: C 52.28, N 8.31, H, 3.19; found: C 52.22, N 7.75, H 3.67.

Preparation of $[\text{Os}(\text{fptz})_2(\text{dppee})]$: Similar to the procedure described above for **4a**, this reaction was conducted using $\text{Os}_3(\text{CO})_{12}$ (100 mg, 0.11 mmol), fptzH (146 mg, 0.68 mmol), Me_3NO (70 mg, 0.93 mmol) and dppee (203 mg, 0.53 mmol). The reaction mixture was separated using silica gel column chromatography. Two isomeric products, denoted as **6a** (114 mg, 0.11 mmol) and **6b** (73 mg, 0.07 mmol), according to the order of their elution, were isolated in 34 % and 22 % yields, respectively. Single crystals of **6a** and **6b** were obtained from a mixed solution of acetone/methanol and THF/hexane, respectively.

Spectral data of **6a**: ^1H NMR (500 MHz, d_6 -acetone, 298 K, δ): 8.03–7.91 (m, 2H), 7.88–7.82 (m, 6H), 7.76 (d, 2H, $J_{\text{HH}} = 7.5$ Hz), 7.41 (t, 2H, $J_{\text{HH}} = 7.0$ Hz), 7.32 (t, 4H, $J_{\text{HH}} = 8.0$ Hz), 7.27 (d, 2H, $J_{\text{HH}} = 5.5$ Hz), 7.15 (t, 2H, $J_{\text{HH}} = 6.0$ Hz), 7.06 (t, 2H, $J_{\text{HH}} = 8.0$ Hz), 6.86 (dt, 4H, $J_{\text{HH}} = 7.5$, 1.0 Hz), 6.59 (t, 4H, $J_{\text{HH}} = 8.0$ Hz). ^{31}P NMR (202 MHz, d_6 -acetone, 298 K, δ): 30.58 (s). ^{19}F NMR (470 MHz, d_6 -acetone, 298 K, δ): –63.95 (s). Anal. calcd for $\text{C}_{42}\text{H}_{30}\text{F}_6\text{N}_8\text{OsP}_2$: C 49.80, N 11.06, H 2.99; found: C 49.84, N 10.94, H 3.16.

Spectral data of **6b**: ^1H NMR (500 MHz, d_6 -acetone, 298 K, δ): 8.86–8.71 (m, 2H), 8.25–8.21 (m, 4H), 7.60–7.56 (m, 4H), 7.50 (dt, 4H, $J_{\text{HH}} = 7.6$, 1.6 Hz), 7.43 (t, 4H, $J_{\text{HH}} = 7.6$ Hz), 6.92 (t, 2H, $J_{\text{HH}} = 7.2$ Hz), 6.82 (t, 4H, $J_{\text{HH}} = 7.6$ Hz), 6.41–6.37 (m, 6H). ^{31}P NMR (202 MHz, d_6 -acetone, 298 K, δ): 33.42 (s). ^{19}F NMR (470 MHz, d_6 -acetone, 298 K, δ): –63.59 (s). MS (FAB, ^{192}Os): m/z 1014 (M^+). Anal. calcd for $\text{C}_{42}\text{H}_{30}\text{F}_6\text{N}_8\text{OsP}_2$: C 49.80, N 11.06, H 2.99; found: C 49.87, N 11.09, H 3.25.

Preparation of $[\text{Os}(\text{ifpz})_2(\text{dppee})]$: Similar to the procedure described above for **3a**, this reaction was conducted using $\text{Os}_3(\text{CO})_{12}$ (100 mg, 0.11 mmol), ifpzH (180 mg, 0.68 mmol), Me_3NO (70 mg, 0.93 mmol) and dppee (230 mg, 0.58 mmol). Two isomeric products, denoted as **7a** (52 mg, 0.047 mmol, 14 %) and **7b** (67 mg, 0.06 mmol, 18 %), were separated using column chromatography eluting with a 1:2 mixture of EA and hexane. Single crystals of **7a** and **7b** were obtained from a mixture of EA/hexane and CH_2Cl_2 /hexane, respectively.

Spectral data of **7a**: ^1H NMR (400 MHz, d_6 -acetone, 298 K, δ): 8.60–8.57 (m, 2H), 8.02–7.98 (m, 1H), 7.92–7.86 (m, 5H), 7.78–7.73 (m, 2H), 7.70–7.65 (m, 4H), 7.34 (t, 2H, $J_{\text{HH}} = 7.6$ Hz), 7.26 (s, 2H), 7.25–

7.18 (m, 6H), 7.06 (dd, 2H, $J_{\text{HH}} = 6.4$, 1.6 Hz), 6.95 (dt, 2H, $J_{\text{HH}} = 7.6$, 1.6 Hz), 6.70–6.66 (m, 4H), 6.63–6.59 (m, 4H). ^{31}P NMR (242 MHz, d_6 -acetone, 298 K, δ): 30.9 (s). ^{19}F NMR (470 MHz, d_6 -acetone, 298 K, δ): –59.6 (s). MS (FAB, ^{192}Os): m/z 1112 (M^+). Anal. calcd for $\text{C}_{52}\text{H}_{36}\text{F}_6\text{N}_6\text{OsP}_2$: C 56.21, N 7.56, H 3.27; found: C 56.18, N 7.83, H 3.68.

Spectral data of **7b**: ^1H NMR (400 MHz, d_6 -acetone, 298 K, δ): 8.88–8.74 (m, 2H), 8.52 (d, 2H, $J_{\text{HH}} = 8.0$ Hz), 8.37–8.31 (m, 4H), 7.68–7.58 (m, 6H), 7.45 (t, 2H, $J_{\text{HH}} = 6.8$ Hz), 7.39–7.35 (m, 6H), 6.53–6.47 (m, 8H), 6.42–6.37 (m, 6H). ^{31}P NMR (242 MHz, d_6 -acetone, 298 K, δ): 31.04 (s). ^{19}F NMR (470 MHz, d_6 -acetone, 298 K, δ): –60.22 (s). MS (FAB, ^{192}Os): m/z 1112 (M^+). Anal. calcd for $\text{C}_{52}\text{H}_{36}\text{F}_6\text{N}_6\text{OsP}_2$: C 56.21, N 7.56, H 3.27; found: C 55.83, N 7.53, H 3.44.

X-Ray Diffraction Studies: Single crystal X-ray diffraction data were measured on a Bruker SMART Apex CCD diffractometer using (Mo K α) radiation ($\lambda = 0.71073$ Å). The data collection was executed using the SMART program. Cell refinement and data reduction were performed with the SAINT program. The structure was determined using the SHELXTL/PC program and refined using full-matrix least squares. Crystallographic refinement parameters of complexes **4a**, **6b**, and **7b** are summarized in Table 4, while corresponding CIF data (excluding structure factors) were deposited in the Cambridge Crystallographic Data Centre with the deposition numbers from CCDC-651017 to 651019, respectively. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Electrochemical Measurement: Cyclic voltammetry (CV) measurements were performed using a BAS 100 B/W electrochemical analyzer. The oxidation and reduction measurements were recorded using Pt wire and Au disks coated with Hg as working electrodes, respectively, in anhydrous CH_2Cl_2 and THF solution containing 0.1 M TBAPF₆ as the supporting electrolyte, at the typical scan rate of 100 mV s^{–1}. The potentials were measured against an Ag/Ag⁺ (0.01 M AgNO₃) reference electrode with ferrocene as the internal standard.

Photophysical Data Measurement and PLED Fabrication: Steady-state absorption, emission, and phosphorescence lifetime measurements both in solution and in the solid state have been described in our previous reports [23]. For measuring quantum yields in the solid state, an integrating sphere (Labsphere) was used. The solid film was prepared via a vapor deposition method and was excited by a 514-nm Ar⁺ laser line. The emission was then acquired by an intensified charge-coupled detector for subsequent analyses [24]. The fabrication procedures for the PLED devices including those for patterning and cleaning of ITO substrates followed those described in the literature [25].

Computational Methodology: Calculations on the electronic ground state of complexes **7a** and **7b** were carried out using B3LYP density functional theory [26]. A “double- ζ ” quality basis set consisting of Hay and Wadt’s effective core potentials (LANL2DZ) [27] was employed for Os atom, and a 6-31G* basis [28], for H, C, N, and F atoms. A relativistic effective core potential (ECP) replaced the inner core electrons of Os(II), leaving the outer core ($5s^25p^6$) electrons and the $5d^6$ valence electrons. Time-dependent DFT (TDDFT) calculations using the B3LYP functional were then performed on the basis of the structural optimized geometries [29]. Typically, the lowest triplet and singlet roots of the nonhermitian eigenvalue equations were obtained to determine the vertical excitation energies. Oscillator strengths were deduced from the dipole transition matrix elements (for singlet states only). The ground-state B3LYP and excited-state TDDFT calculations were carried out using Gaussian03 [30].

Compositions of molecular orbitals in terms of the constituent chemical fragments were calculated using the AOMix program [31]. For the characterization of the HOMO–x $\rightarrow$ LUMO+y transitions as partial charge transfer (CT) transitions, the following definition of the CT character has been used:

$$\text{CT(M)} = \%(\text{M})\text{HOMO}-x - \%(\text{M})\text{LUMO}+y \quad (1)$$

where $\%(\text{M})\text{HOMO}-x$ and $\%(\text{M})\text{LUMO}+y$ are electronic densities on the metal in HOMO–x and LUMO+y. If the excited state, e.g., S₁ or

Table 4. Crystal data and structure refinement parameters for complexes **4a**, **6b**, and **7b**.

Complex	4a	6b	7b
Empirical formula	C ₄₄ H ₃₆ F ₆ N ₈ O ₈ P ₂	C ₄₂ H ₃₀ F ₆ N ₈ O ₈ P ₂	C ₅₇ H ₄₇ Cl ₄ F ₆ N ₈ O ₈ P ₂
Formula weight	1058.95	1012.88	1323.95
Temperature	150(2) K	230(2) K	200(2) K
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	P2 ₁ /c	P2 ₁ /n
a	11.4719(9) Å	11.5975(5) Å	11.3096(3) Å
b	12.4745(10) Å	17.9503(8) Å	24.3065(7) Å
c	17.5581(14) Å	19.6808(9) Å	20.3206(6) Å
α	75.234(2)°		
β	86.246(2)°	92.283(2)°	99.721(1)°
γ	62.994(2)°		
Volume, Z	2161.1(3) Å ³ , 2	4093.9(3) Å ³ , 4	5505.9(3) Å ³ , 4
Density (calculated)	1.627 Mg/m ³	1.643 Mg/m ³	1.597 Mg/m ³
Absorption coefficient	3.095 mm ⁻¹	3.262 mm ⁻¹	2.633 mm ⁻¹
F(000)	1048	1992	2636
Crystal size (mm ³)	0.22 × 0.15 × 0.15	0.10 × 0.10 × 0.10	0.25 × 0.25 × 0.07
Reflections collected	23506	31302	42277
Independent reflections	9894 [R(int) = 0.0335]	9400 [R(int) = 0.0813]	12634 [R(int) = 0.0600]
Max. and min. transmission	0.6539 and 0.5492	0.7362 and 0.7362	0.8371 and 0.5590
Data/restraints/parameters	9894 / 3 / 553	9400 / 0 / 524	12634 / 3 / 671
Goodness-of-fit on F ²	1.004	1.066	1.084
Final R indices [I > 2σ(I)]	R ₁ = 0.0326, wR ₂ = 0.0741	R ₁ = 0.0533, wR ₂ = 0.1026	R ₁ = 0.0470, wR ₂ = 0.1074
R indices (all data)	R ₁ = 0.0372, wR ₂ = 0.0792	R ₁ = 0.0778, wR ₂ = 0.1178	R ₁ = 0.0633, wR ₂ = 0.1172
Largest diff. peak and hole	1.202 and -1.187 eÅ ⁻³	1.353 and -1.460 eÅ ⁻³	1.851 and -1.167 eÅ ⁻³

T₁, is formed by more than one one-electron excitation, then the metal CT character of this excited state is expressed as a sum of CT characters of each participating excitation, i → j:

$$CT_I(M) = \sum_{i,a} [C_I(i \rightarrow j)]^2 (\% (M)_i - \% (M)_j) \quad (2)$$

where C_I (i → j) are the appropriate coefficients of the I-th eigenvector of the CI matrix. Accordingly, one can very effectively use the MO compositions in terms of fragment orbital contributions to probe the nature of electronic transitions.

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