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Recent advances in white organic light-emitting diodes employing a single-emissive material

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Abstract. Recent progress in the development of materials and devices for single-doped white devices is presented with a particular focus on the development of platinum complexes exhibiting excimer emission. White organic light emitting diodes (WOLEDs) are strong candidates for the next generation of solid-state lighting, yet many of the best devices generate white light using multiple emitters embedded in a comparably complex device structure, raising the difficulty of consistently manufacturing these devices at a low cost and leading to challenges in color stability. These problems can be overcome by fabricating excimer-based WOLEDs, which construct a broad spectrum from a single emitter using blue monomer emission and red excimer emission. Through rational emitter design, the color quality and device efficiencies have steadily improved with recent achievements of external quantum efficiencies over 20% and a color rendering index greater than 80. Furthermore, recent applications of tetradentate platinum complexes for single-doped WOLEDs have yielded devices with a performance superior to many state-of-the-art multilayer WOLEDs as well as promising device operational stability. [DOI: 10.1117/1.JPE.4.040991]

Keywords: organic light emitting diode; electrophosphorescence; Pt-based emitters; solid-state lighting; excimer.

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1 Introduction

Organic electronic devices have seen considerable investigation across a wide range of fields over the past several decades. Organic light-emitting diodes (OLEDs) in particular have been widely celebrated for their potential as energy efficient and low-cost devices for next generation display and solid-state lighting applications. This is due, in part, to the ability of organic electronic devices to be fabricated in high-throughput solution processing or thermal evaporation techniques on a wide range of substrates including metal foils, plastics, or glass.[1] Such versatility affords the development of flexible, shatter-resistant, light weight devices and opens up an avenue for near limitless design possibilities for creative form factors and new applications. Through rapid development in material design and novel device architectures, OLEDs emitting across the visible spectrum have been demonstrated.[2–9] In particular, the development of phosphorescent transition metal complexes has yielded impressive efficiencies due to their ability to harvest 100% of electrogenerated excitons, i.e., both singlet and triplet excitons.[10,11] In fact, devices employing both Ir and Pt complexes have essentially demonstrated 100% electron to photon conversion efficiencies.[12,13] Commercialization of small OLED displays for handheld electronics and initial production of large area screens employing these complexes have already begun. Nevertheless, further improvements in device efficiencies, operational stability, and materials' variability are needed to achieve widespread commercial acceptance.

One of the primary remaining frontiers in optoelectronic devices is the development of a cost effective and energy efficient replacement for existing white lighting technologies.[14]

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White lighting is estimated to consume nearly 20% of the electricity produced in the United States and two billion light bulbs are purchased annually in the United States.[14,15] This incredibly large market provides not only a large economic opportunity, but also an opportunity to significantly reduce electricity consumption. The worldwide lighting market is currently dominated by inefficient incandescent bulbs which waste a sizeable portion of worldwide electricity generation due to large heat losses. A growing portion of the world's lighting needs is being met by fluorescent bulbs which are more efficient, but their disposal is significantly complicated by toxic materials in their composition, such as Hg, and they tend to have nonideal emission color. Solid-state lighting, through either organic or inorganic LEDs, solves many of the issues of low efficiencies and lifetimes through their ability to directly convert electrical charges to light rather than secondary emission from different primary excitation sources such as heat (incandescent lighting) or plasmas (fluorescent lighting).[16] The development of highly efficient, environmentally benign solid-state lighting with long-operational lifetimes could have an incredible impact on energy consumption and waste generation. The approach to achieve this target has been most successful in the development of white inorganic LEDs, which have achieved laboratory efficiencies exceeding 250 lm/W and are already commercially available.[17] Nevertheless, the high fabrication cost of this technology could inhibit widespread worldwide adoption. OLEDs, on the other hand, are made from easily synthesized organic materials on low-cost substrate materials, are compatible with large-scale roll to roll processing, and efficiencies exceeding 100 lm/W for white OLEDs (WOLEDs) have recently been reported.[18] Nevertheless, commercialization has not yet been realized due in part to lower efficiencies than that of their inorganic counterparts, the challenge in developing a stable and efficient blue emitter, and the dramatic limitation in the emission brightness.[19] The drop off in efficiency at high brightness is especially challenging and will likely require large area panels in order to provide sufficient luminance in contrast to inorganic LEDs, which are point sources typically composed of one or several individual diodes.[20] The major consequence of this design constraint is that the large area devices have to be fabricated easily and cheaply in order to compete with commercial lighting sources, which are compared in Table 1.

Since most organic emitters exhibit relatively narrow emission spectra, white light is typically produced from the combination of multiple emissive species spanning the visible spectrum.[21] Device architectures for WOLEDs can be constructed in a number of unique ways including: tandem or striped devices,[22] blue devices with down-conversion phosphors,[23] multiple emissive layers within a single device,[24] multiple emissive dopants within a single layer,[25] or even the combination of phosphorescent dopants in a fluorescent host.[26] The use of red, green, and blue emissive materials in separate layers has been widely successful in separately tuning the emissive layers to achieve an appropriate balance of colors and also to achieve very high efficiencies.[27] Such a strategy necessarily increases the complexity of the device to accommodate the additional layers and to maintain the balance of color. Employing a single-emissive layer doped with multiple emissive materials is conceptually simpler to fabricate than multiple emissive layers; however, rapid energy transfer (ET) from high-energy blue emitters to lower-energy red emitters significantly complicates the color balance and optimization of efficiency.[28,29] Furthermore, in all the aforementioned strategies, issues of color variation with increasing

Table 1 Comparison of different illumination sources.

Source	Advantages	Disadvantages
Incandescent	Low cost; blackbody source with CRI: 100	Low operational lifetime: 1000 h; low efficiency: 10 to 20 lm/W
Fluorescent	Low cost; efficiencies of 40 to 80 lm/W; operational lifetimes of 10,000 h	Contains hazardous materials like Hg; CRI < 80
Inorganic LED	Operational lifetime of >50,000 h; efficiencies >100 lm/W; CRI: 80 to 90	High manufacturing cost; point source
Organic LED	Efficiencies >100 lm/W; operational lifetime >10,000 h; CRI > 90	Low brightness; low cost manufacturing of large area panels remains challenging

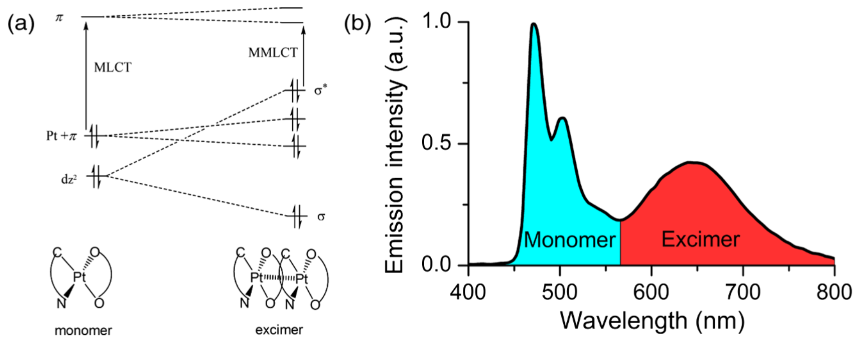

Fig. 1 (a) Example of formation of phosphorescent excimer and (b) example of a typical emission spectrum observed for excimer based WOLEDs.

driving current or color aging due to different degradation rates of the various emissive materials have been observed and can pose a significant challenge to the development of a commercial product.[30] Thus, in order to reduce the complexity of the device structure for more economically feasible large area white lighting sources, a WOLED containing a single emitter is greatly desired.

One of the most significant developments in single-doped WOLED is the exploitation of the excimer emission properties of square planar metal complexes, typically cyclometalated Pt(II)

Table 2 Summary of device performances of previously reported single-doped WOLEDs.

Emitter	CIE	CRI	η_{EQE} (peak)	η_{EQE} (500 cd/m^2)	η_{PE} (peak)	η_{PE} (500 cd/m^2)	References
3	(0.36, 0.44)	67	3.3	2.3	7.3	5.2	31
2	(0.36, 0.44)	67	6.4	4.3	12.2	8.1	31
2	(0.40, 0.43)	81	—	5.7	—	5.2	37
2	(0.46, 0.47)	69	18	15.9	29	12.6	37
6	(0.45, 0.53)	—	5.33	—	5.9	—	38
12	(0.31, 0.44)	—	>15.6	6.5[b]	33.9	—	39
13	(0.32, 0.42)	—	5	—	10.9	—	39
15	(0.43, 0.43)	<60	15.5	13.5[b]	—	9.5[b]	40
19	(0.33, 0.36)	—	9.3	—	7.3	—	41
20	(0.33, 0.38)	65	—	18.1	—	11.8	42
21	(0.34, 0.35)	74	—	11.5	—	6.8	43
23	(0.36, 0.37)	87	—	3.7	—	—	44
25	(0.33, 0.33)	80	20.1	17.9	51	34	35
26	(0.37, 0.40)	80	15.9	15.6	37.8	25.2	35
29	(0.50, 0.46)	—	3.3	—	—	—	45
37	(0.41, 0.44)	75	9.5	6.2[b]	11.6	5.5[b]	46
38	(0.41, 0.45)	74	12.7	11.5[b]	17.0	12.4[b]	46
39	(0.33, 0.42)	77	16.5	—	55.8	—	47
40	(0.37, 0.42)	70	24.5	17.7[b]	55.7	24[b]	36

[a] η_{EQE} is external quantum efficiency and η_{PE} is power efficiency.
[b] Performance is reported at 1000 cd/m^2 rather than 500 cd/m^2.

complexes.[31] Excimers, or excited state dimers, are the excited states shared between two emitter molecules which interact through a combination of ligand-centered $\pi - \pi$ interactions and Pt–Pt bimetallic interactions, the latter of which is illustrated in Fig. 1(a).[32] Emission from the excimer species, observed in both concentrated solutions and solid state, is a broad structureless emission band that is red-shifted from that of the monomer, as illustrated in Fig. 1(b). Through the combination of a blue monomer emission and a red excimer emission, a broad white spectrum spanning the visible spectrum can be achieved. In contrast to ground-state dimers, excimers have no bound ground state (i.e., no excimer absorption is observed) and hence the cascade of energy from the monomer to low-energy excimers can be avoided and a balanced white light can be achieved.[33] This distinction is supported by excitation spectra which are identical for the monomer and excimer emissions, indicating the formation of an intermediate excited monomer prior to excimer formation in photoluminescent (PL) emission.[34] Through careful theoretical work on phosphorescent excimers, the design of new device structures, and the development of new emissive materials, a greater understanding of the factors controlling the excimer emission has been achieved and a white device exceeding 20% has now been demonstrated.[35,36] The device performance of selected reports that demonstrate this progress is given in Table 2. In this article, we will review the recent progress in the development of single-doped WOLEDs employing Pt-based excimer emitters. We will start with a discussion of color tuning strategies for achieving an ideal white color, followed by a discussion on the efficiency of excimer-based white emission, and finish with a discussion of recent developments in excimer emitting materials.

2 Color Tuning

To achieve an ideal white light, the emission source needs to have both an emission color close to that of natural sunlight and must exhibit significant emission spanning the entire visible spectrum. The Commission Internationale de l'Eclairage (CIE) coordinates define the color of the emission source as perceived by the human eye and are controlled through the balance of red, green, and blue emissions, but provide no information on how well the emission spectrum matches that of natural light in rendering the colors of objects. Thus, another parameter, the color rendering index (CRI) is needed to describe the ability of colors to be reproduced with the illumination source in comparison with natural light sources. Excimers-based WOLEDs have a strong advantage due to the typically broad emission of the excimer species that is complimentary to the high-energy monomer emission. Nevertheless, the selection of materials with appropriate monomer and excimer energies and appropriate balance can be challenging.

To achieve an optimal white light, a number of color tuning parameters must be precisely controlled: the monomer and excimer emissions must be appropriately balanced to achieve desirable CIE coordinates, the monomer emission must be sufficiently blue to span the visible spectrum for high CRI, and the excimer emission much be sufficiently red but must not leave a gap

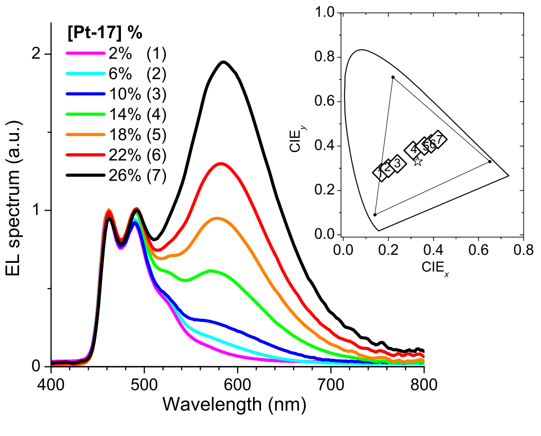

Fig. 2 Color variation as a function of dopant concentration for an excimer-based white device in the structure: ITO/PEDOT/NPD (30 nm)/TAPC (10 nm)/x% Pt-17:26 mCPy (25 nm)/PO15 (20 nm)/LiF/Al (from Ref. 54).

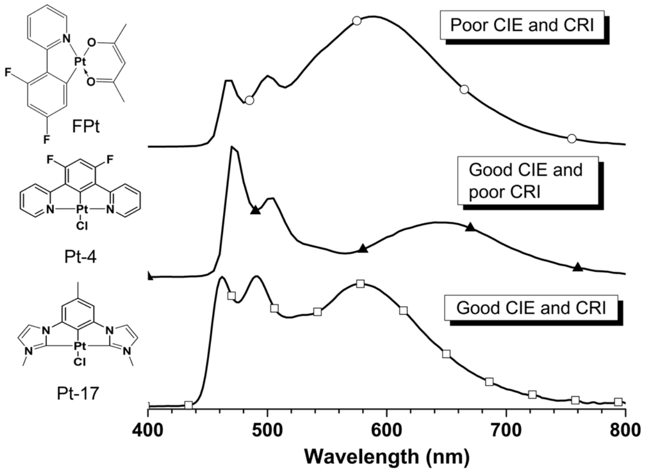

Fig. 3 Electroluminescent spectra of devices using FPt, Pt-4, and Pt-17 with their corresponding chemical structures on the left (from Ref. 54).

between the monomer and excimer emissions. The balance between monomers and excimers can typically be controlled by varying the dopant concentration, as shown in Fig. 2, since at a higher concentration there is a higher probability of two dopants being nearest neighbors. However this dependence can often depend on the molecular structure.[48] Modification of the monomer emission energy can be done through the rational design of a cyclometalating ligand. In particular, the design of cyclometalating ligands with high triplet energy or the application of electron-withdrawing ancillary ligands have both shown wide success in color tuning.[49–51] The tuning of the excimer emission, on the other hand, is much more complicated and depends on a combination of a number of parameters including: monomer triplet energy, Pt-Pt separation, relative monomer orientations in the aggregate, and the distribution of the molecular orbitals.[52,53] Consequently, concrete design rules for tuning the excimer emission have yet to be developed, but can generally be described by a decrease in emission energy with an increasing degree of $\pi - \pi$ stacking or decreasing the Pt-Pt separation. However, the relative contribution of these factors may vary among the different classes of cyclometalated Pt complexes.[32]

The importance of meeting the color tuning requirement can be illustrated with the emission spectra of three different optimized excimer white devices given in Fig. 3. For FPt, the monomer emission is insufficient to contain all deep blue photons and the overwhelming dominance of the excimer emission yields both poor CIE and CRI. If an optimized device can achieve color balance at moderate concentrations, as in Pt-4–based white devices, then good CIE coordinates can be achieved, but large gaps in the yellow-green color region and the lack of significant deep blue emission will still lower its CRI. If the monomer emission is blue-shifted and the excimer peak has appropriate energy and intensity, then good CRI and CIE can both be achieved, as in the case for Pt-17.[54]

3 Efficiency of Excimer-Based WOLEDs

In addition to achieving a balanced broad white emission, it is also crucial to optimize the efficiency of the OLEDs. The efficiency of the electron to photon conversion process, known as the external quantum efficiency (EQE), can be described by the equation: $\eta_{\text{ext}} = \chi \cdot \eta_r \cdot \eta_t \cdot \eta_{\text{out}} \cdot \Phi_{\text{PL}}$, where η_r is the efficiency of exciton formation from injected charges, η_t is the efficiency of the energetic transfer of excitons to the dopant molecules, χ is the fraction of excitons which can contribute to emission (0.25 for fluorescent emitters and 1 for phosphorescent emitters), Φ_{PL} is the PL quantum yield of the emitter, and η_{out} is the efficiency of outcoupling of the emitted light to air. η_r and η_t can both be close to unity for devices with well-balanced charges, minimal charge traps (CTs) and recombination centers, and an appropriate design of transporting layers to prevent the exciton quenching.[55] η_{out} is typically between 25% and 30% due to the waveguiding effects, substrate losses, plasmon quenching, and other optical losses.[56] Thus, for optimized devices employing a phosphorescent emitter with Φ_{PL} approaching unity, EQEs of 20% to 30% are possible without any advanced outcoupling techniques. Another commonly used metric is power efficiency (PE), which is the ratio of the power of the emitted light as perceived by the human eye, to the electrical power input, in units of lumens per watt (lm/W). Such a metric takes into account the driving voltage as a component of the power input, as well as the color of the emitted light and the responsivity of the human eye. Both of these, in addition to other more specific values, such as the maximum achieved luminance (measured in cd/m^2), turn-on voltage (i.e., the voltage at $1\ \text{cd}/\text{m}^2$), or EQE and PE at practical luminances for white lighting of 500 to $1000\ \text{cd}/\text{m}^2$, are important parameters for the evaluation of OLED devices.[57]

The efficiencies of monochromatic devices depend on the emission properties of individual molecules, which can be maximized through the design of a molecular emitter with a high Φ_{PL}. Efficient monochromatic devices have been achieved for a large number of Ir and Pt emitters which demonstrate a Φ_{PL} approaching unity.[12,13] Typically, to achieve such efficient emission, conjugated cyclometalating ligands bound to Ir or Pt metal centers have been utilized. This is due to the strong ligand field of the metal–carbon bonds which typically raise the nonradiative metal centered excited states, allowing an efficient radiative decay process from the low-lying ligand centered triplet states with varying degrees of metal-to-ligand charge transfer admixing.[58] Similarly, the design of various ancillary ligands which enhance the ligand field and facilitate efficient radiative pathways has also been explored.[59] Second, the design of emissive materials with rigid structures is important to ensure that the geometry of the excited and ground states is similar, resulting in an efficient radiative decay process.[60]

The efficiency of bimolecular excimer emission on the other hand is much less understood. Two distinct mechanisms have been proposed for excimer formation in OLED devices, namely ET and direct CT generated excimers.[34] The former mechanism involves the formation of an intermediate excited triplet monomer which is in direct contact with a neighboring ground-state monomer followed by the formation of the bimolecular excimer state. The generation of the initial excited monomer can occur via ET from the host, ET from another monomer, or CT directly on the monomer. The excimer emission then proceeds as

$$M + {}^3M^* \rightarrow {}^3(M\text{-}M)^* \rightarrow h\nu_{\text{ex}} + 2M.$$

In the latter mechanism, a radical anionic form of the monomer and a radical cationic form of the second neighboring monomer can directly form a coulombically bound exciton localized over both the involved monomers, which is described as

$$M^- + M^+ \rightarrow {}^3(M\text{-}M)^* \rightarrow h\nu_{\text{ex}} + 2M.$$

Since the formation of the radical anions and cations is predominantly possible through either oxidation or reduction of the monomers from the injected charges, the CT mechanism can only occur in electroluminescent devices where charged species exist. In fact, such a mechanism may be favored in selected cases where the CT character of highly doped emissive layers may significantly facilitate such a process. Conversely, the ET mechanism can contribute to either photolumiesence or electroluminescence due to the neutral nature of the species involved in such a process. The exact nature and relative contribution of these two mechanisms remain a topic of debate, but it is widely suggested that in electroluminescent devices both processes exist.[34]

Regardless of the formation mechanism, the final step in the emission process is the decay of the triplet excimer to form two singlet ground-state monomers either radiatively or nonradiatively. Overall, at least four decay rates must be considered for optimization of efficiency, that is: k_{r}^{M}, k_{nr}^{M},k_{r}^{EX}, and $k_{\text{nr}}^{\text{EX}}$, where the superscripts EX and M indicate excimer or monomer decay rates, respectively. While the radiative and nonradiative decay rates for the monomer species can be probed through transient photoluminescence measurements, the decay rates of excimer species cannot be easily decoupled from those of the monomer since both species exist in concentrated solutions as well as thin films.

The efficiency of the excimer species, relative to their monomer species, can be inferred from the quantum yield of thin films which have a dominant excimer character. Such a study was carried out for two related molecules to compare the relative monomer and excimer efficiencies of the two materials in doped films, as shown in Fig. 4.[35] This study demonstrated that for films with low-dopant concentration of a primarily monomer character, the Φ_{PL} of Pt-16 (0.42 ± 0.05)

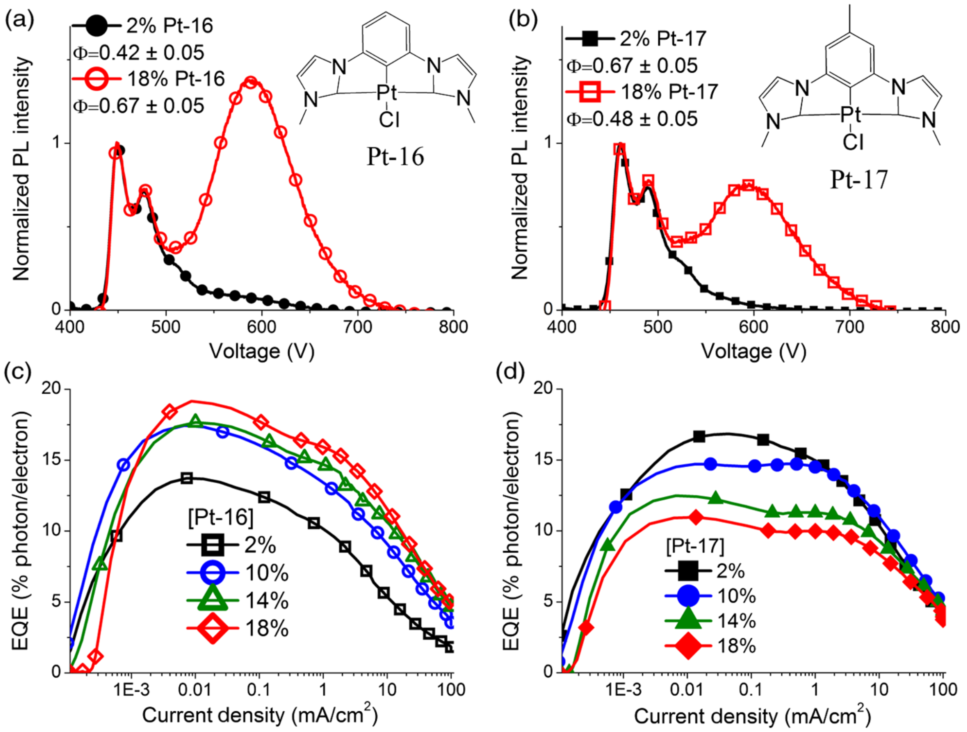

Fig. 4 Thin film photoluminescent (PL) spectra for (a) Pt-16 and (b) Pt-17 for 2% and 18% dopant concentrations with the respective quantum yields inset in the figure and the external quantum efficiency (EQE) as a function of concentration for (c) Pt-16 and (d) Pt-17 for devices in the structure: ITO/PEDOT:PSS/NPD (30 nm)/TAPC (10 nm)/x% emitter:26mCPy (25 nm)/PO15 (40 nm)/LiF/Al. Data from Ref 35.

was much lower than that of Pt-17 (0.67 ± 0.05). Yet at high concentrations of 18% doping concentrations in which a substantial excimer emission exists, Φ_{PL} of Pt-16 (0.67 ± 0.05) was much higher than that of Pt-17 (0.48 ± 0.05). This indicates that the monomer species of Pt-17 is very efficient while the excimer emission is less efficient, whereas for Pt-16 the opposite is true with more efficient excimer than monomer emission. The major consequence of this is that as the doping concentration is increased, the peak EQE decreased for Pt-17 and increased for Pt-16. This dependence of efficiency on dopant concentration complicates the simultaneous optimization of efficiency and color. Thus, in order for the highest efficiencies to be achieved for a balanced white device, both the excimer and monomer species should be efficient.

4 Emissive Materials for Excimer-Based WOLEDs

In order to develop efficient single-doped white devices, the development of emissive materials with efficient monomer and excimer emission bands of appropriate energy are crucial. Excimer emissions from small molecular platinum complexes are by far the most common due to their square planar coordination geometry and high emission efficiency.[61] Such complexes can be categorized into three general classes, namely bidentate complexes, tridentate complexes, and tetradentate Pt complexes.

4.1 *Bidentate Pt(II) Complexes*

Bidentate cyclometalated Pt complexes are the most widely studied due to the similarity of their ligands to the well-developed Ir complexes. In the paramount report by Brooks et al.,[50] the functionalization and degree of conjugation of cyclometalating ligands for bidentate Pt(II) complexes were thoroughly studied. It was uncovered that a sufficiently deep blue emission could be obtained by fluorinating a phenyl pyridine ligand to form FPt (**2** in Fig. 5) which is structurally

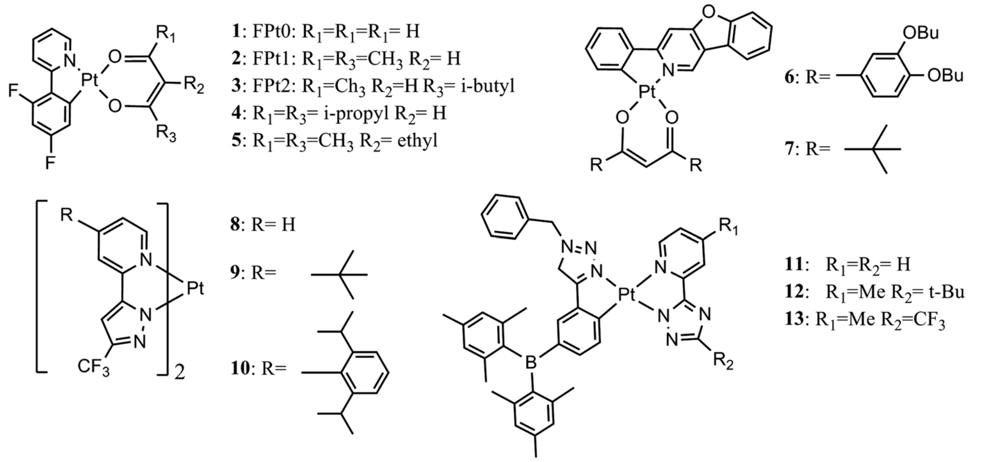

Fig. 5 Selected bidentate Pt complexes used for excimer emitting white organic light emitting diodes (WOLEDs).

similar to the commonly used deep blue Ir emitters, FIrpic and FIr6.[62,63] Excimer-based white devices were initially fabricated by doping **2** in 4,4'-bis(N-carbazolyl) biphenyl (CBP), which showed a monomer emission at 470 nm and an excimer emission peak at 570 to 580 nm.[31,33] Unfortunately, a balanced white for this complex could only be achieved for low-doping concentrations of ~4% which is too low for efficient devices and the emission of the CBP host could not be totally quenched at these concentrations.[33] Thus, initial color tuning strategies for FPt-based emitters focused on inhibiting excimer formation so that excimers would only form at higher concentrations. By increasing the degree of steric bulk on the diketonate ancillary ligand of **2**, the excimer emission at low concentrations could be significantly suppressed. In the case of adding a single isobutyl group, **3**, balanced white emission could be achieved at around 10% doping in CBP and the addition of two isopropyl groups, **4**, resulted in balanced emission at even higher concentrations of 20% in CBP. Devices of **3** doped in a CBP host resulted in white emission of CIE of (0.36, 0.44), CRI of 67, and a peak EQE of 3.3%.[31] The decrease in excimer emission intensity with increased steric bulk can be explained by the combination of increasing the intermolecular spacing between dopants, reducing the intermolecular interaction, and potentially increasing the "solubility" of the dopant within the host matrix to form a more dispersed layer. The latter of these effects was further exploited by simply changing the host materials for devices of **2** from CBP to 1,3-Bis(N-carbazolyl)benzene (mCP) to achieve a balanced emission at a concentration of approximately 16% in mCP, which resulted in a peak EQE of 6.4%. Further enhancement of this efficiency was demonstrated by again changing the host material to 2,6-bis (N-carbazolyl) pyridine (26mCPy) which had a minimal effect on the emission spectrum but improved the charge balance. Ultimately, a peak EQE of nearly 18% could be achieved for a warm white with color coordinates of (0.46, 0.47) and a CRI of 69.[37] Nevertheless, the still poor CRI values due to the lack of deep blue and red emissions require a new molecular design motif to achieve better color.

Complexes of [(dibenzo[b,d]furan-4-yl)-pyridinato-N,C^3]Pt(II) 1,3-diketonates were also recently explored as dopants for single-doped WOLEDs.[38] Both complexes **6** and **7** were shown through x-ray diffraction of single crystals to stack in an antiparallel way (i.e., $\hat{\mathrm{C}}\mathrm{N}$ on $\hat{\mathrm{O}}\mathrm{O}$) with close molecular stacking between adjacent molecules with a distance ranging from 3.39 to 3.51 Å which is short enough for strong $\pi - \pi$ interaction, while neither complex showed bimetallic Pt–Pt interactions. Only **6** showed a strong excimer character at high concentrations, since the increased conjugation on the aromatic ancillary ligand led to significant π–π stacking interactions between adjacent dopant molecules when stacked in an antiparallel way. Single-doped polymer LEDs (PLEDs) employing **6** were tuned to give balanced monomer and excimer emissions at 516 and 631 nm, respectively. Thus, the excimer was appropriately red to cover more of the deep red spectrum, yet the emission of the monomer was missing all the spectra below 500 nm, and only CIE coordinates between (0.40, 0.57) and (0.56, 0.43) could be achieved. PLEDs employing these emitters demonstrated a peak EQE of 5.33% for a primarily green monomer emission, but decreased with increasing concentration to 1.22% for an orange-red emission. This drop in efficiency is possibly due to a less efficient emission process from the excimer species. Nevertheless, this report provided some clear evidence on the importance of aromatic groups with intimate intermolecular π–π contact on the formation of excimer emission.

One example class of deep blue emissive materials exhibiting excimer emission is those employing dimesitylboryl functionalized phenyl-1,2,3-triazole C^N-type cyclometalating ligands. Wang et al.[39] reported a series of these complexes systematically functionalizing the C^N ligand as well as varying the ancillary ligand. In particular, complexes with pyridyl-1,2,4-triazole ancillary ligands, i.e., complexes **11** to **13**, are promising candidates as emitters for blue and single-doped WOLEDs due to their blue monomer emission between 460 and 475 nm and high PL quantum yields. Blue emission was achieved for these complexes due to the much higher lowest unoccupied molecular orbital (LUMO) level for the broken conjugation of the 5-membered triazole ring. All three of these complexes also exhibited excimer emission at ~555 nm. The addition of functional groups of methyl and *t*-butyl for **12** resulted in reduced excimer formation compared with that of **11**, whereas replacing the *t*-butyl with CF_3 for **13** showed increased excimer formation compared with that of **11**. As a consequence, at even a 2% dopant concentration, **13** showed strong excimer emission whereas for **12**, a balanced white could be achieved at moderate doping concentrations. As a result, a WOLED of 10% complex **12** doped in 26 mCPy resulted in an EQE of 15.6% at 100 $\mathrm{cd/m^2}$ and a peak PE of 33.9 lm/W for a white emission color of (0.31, 0.44). Although the CRI was not reported, the excimer emission peak at 550 nm is expected to keep the CRI below the desired value of over 80. While this result is one of the best reported for bidentate Pt complexes, the device efficiency is reduced since the Φ_{PL} of **12** decreases from 0.96 at a doping concentration of 5% to 0.65 at a doping concentration of 10%, indicating that the excimer species is likely inefficient. This further demonstrates the importance of achieving both efficient monomer and excimer emissions in order to simultaneously optimize the color and efficiency.

4.2 *Tridentate Pt(II) Complexes*

Despite the success of Pt complexes with bidentate ligands, more improvements can be expected with tridentate cyclometalating ligands since improved molecular rigidity is conducive to efficient emission.[60] Furthermore, the possibility of the two bidentate cyclometalating ligands distorting out of plane may lead to nonradiative pathways for recombination from the monomer excitons and excimers, which lower the efficiencies.[64] Tridentate ligands can complex to the Pt metal ions in a number of ways through either Pt-C or Pt-N bonds. Pt complexes employing N̂N̂N- and ĈĈC-type ligands are typically not neutral, so are rarely used in devices. Additionally, Pt complexes employing N̂N̂C and ĈN̂C ligands tend to have low PL quantum yields due to the low-radiative decay rates or low-lying *d-d* states, resulting in high nonradiative decay rates.[65] Furthermore, the formation of molecular aggregates tends to quench the emission and excimer emission is rarely observed in these classes of complexes.[66] Pt complexes employing N̂ĈN cyclometalating ligands, on the other hand, have shown very high Φ across a wide range of emission energies and can exhibit strong excimer emission. The success of this class can be attributed to the strong ligand field induced by the cyclometalating carbon-Pt bond, leading to an increase of the *d-d* state energy.[67] As such, nearly all recent reports of excimer-based WOLEDs employing tridentate complexes have been based on Pt N̂ĈN-type complexes and their analogs, which will be discussed in more detail here (Fig. 6).

The prototypical N̂ĈN Pt complex, Pt(II) 1,3-di-(2-pyridyl)benzene chloride (**14**), exhibits a bright green emission at 491 nm for low concentrations and a broad excimer peak around 700 nm for higher concentrations.[67] The insufficient blue portion of the monomer emission spectrum and the large gap between the monomer and excimer emissions lead to poor CRI and CIE coordinates. The monomer emission can be tuned through modifying the highest occupied molecular orbital (HOMO), primarily located on the phenyl ring, or the LUMO, primarily localized on the pyridyl ring.[50] To increase the emission energy, the HOMO level can be lowered through the introduction of electron withdrawing groups on the central benzene ring. For example, the introduction of a weakly electron-donating methyl group on the central phenyl ring for **16** leads to a slight red-shift of the maximum emission peak (505 nm), whereas for **15**, the substitution of the

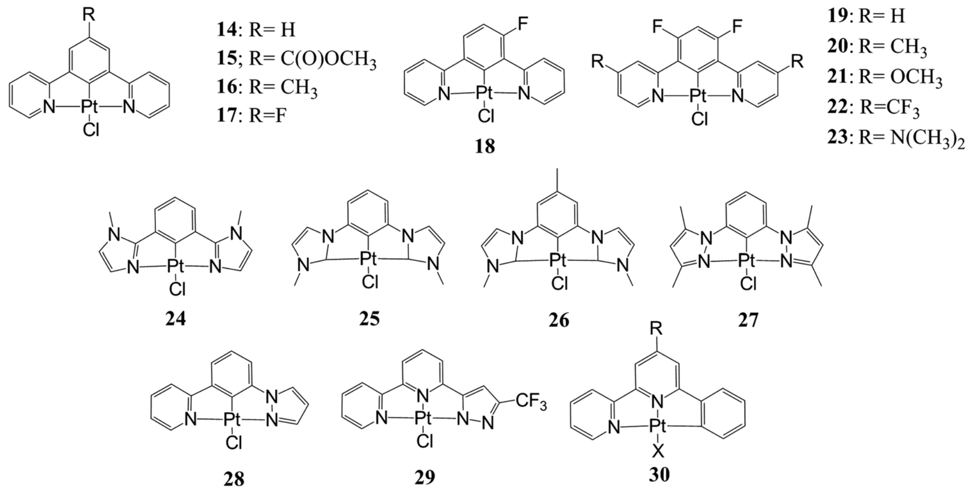

Fig. 6 Selected tridentate Pt complexes used for excimer emitting WOLEDs.

CO_2Me leads to a slight blue-shift of the maximum emission peak (481 nm).[68] The excimer emission peak for **15** is around 700 nm, so single-doped devices employing **15** are color tunable from blue-green to deep red and can achieve warm white light of (0.43, 0.43) but with poor CRI due to the combination of minimal deep blue emission and dominant deep red emission.[40] The efficiency of such a device was very high, peaking at 15.5%, and exhibited a low roll off to 13.5% at 1000 cd/m^2, indicating that, if appropriately color tuned, this class of complexes could be extremely useful for single-doped white devices.

In the attempts to color tune complexes based on **14**, the location of the electron withdrawing and donating groups is extremely important. For example, the addition of an electron withdrawing fluorine atom at the fifth position in the benzene (*para* to the metal ion), **17**, leads to a red shift (504 nm), whereas the addition of fluorine at the fourth position (*meta* to the metal ion), **18**, leads to a blue shift (481 nm).[69] This can be attributed to the fact that adding the fluorine atom has an inductive electron withdrawing effect through the σ-bond to lower the energy level of both the HOMO and LUMO orbitals. However, there is also a mesomeric electron donating effect of the fluorine atom through the π-orbitals when *para* to the metal ion leads to potential destabilization of the HOMO level.[70] Conversely, the location of the fluorine atom in the *ortho* position to the pyridyl group has a similar destabilization effect on the LUMO energy level, resulting in the increase of emission energy. Ultimately, a blue emission peaking at 471 nm can be achieved through the addition of two fluorine groups to form **19**, which is the tridentate analog of FPt (compound **2**).[41] Single-doped white devices employing **19** have been widely explored since both its monomer emission (~470 nm) and excimer emission (~650 nm) are more appropriate than the previously reported materials for yielding a balanced white light with CIE coordinates of (0.33, 0.35). The efficiency of white devices employing **19**, however, is only 9.3% and 8.2 lm/W.

Another complementary approach to tuning the monomer emission has been demonstrated through a number of reports by Williams and coworkers by adding electron donating groups to the pyridyl rings of **19**.[42–44] The addition of electron donating groups to the fourth position of the pyridyl rings where there is a node in the HOMO, will destabilize the LUMO without significantly affecting the HOMO energy level. Consequently, the monomer emission energy is blue-shifted as $H \rightarrow CH_3 \rightarrow OCH_3 \rightarrow N(CH_3)_2$ for **19 to 22,** respectively. Furthermore, this functionalization may significantly modify the emission efficiency of the white devices. The quantum yield for dilute solutions of **19** and **20** is 0.85 and 0.87, respectively, whereas for neat thin films they are 0.35 and 0.65, respectively.[42] This indicates that the excimer of **19** may be less efficient than the monomer, yet the introduction of methyl groups to the pyridyl rings may facilitate a more efficient emission process from this bimolecular species. Consequently, white devices of **20** achieved a peak EQE over 18% for CIE coordinates of (0.33, 0.38) and a CRI of 65. The CRI is further improved by increasing both the monomer and excimer emission energies to cover a wider range of the visible spectrum, while minimizing the gap between monomer and excimer

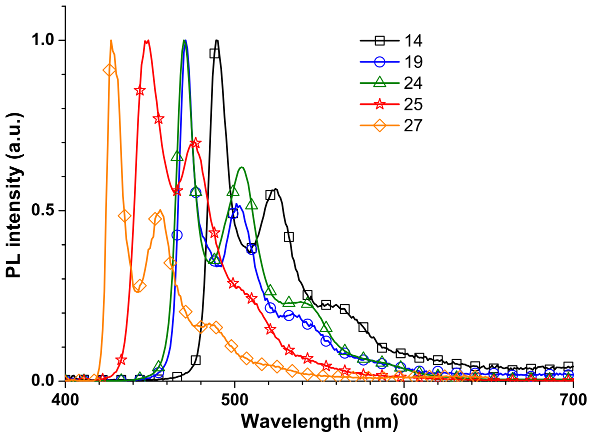

Fig. 7 The PL emission spectra of **14**, **19**, **24**, and **25** in a solution of CH_2Cl_2 at room temperature and of **27** in a 2% PMMA thin film.

emission spectra. Ultimately, a monomer emission peak of 453 nm and a broad excimer emission of 596 nm are achieved for **22** and are color tunable from sky blue to orange-red with a balanced broad white achieved for moderate dopant concentrations of around 20%, yielding a CRI as high as 88 and CIE coordinates of (0.37, 0.39) which are approaching the quality of the best commercial light sources.[44] However, the device only demonstrated a peak EQE of 3.7% despite the high-quantum yield of the emitter (0.6).

An alternative approach to destabilizing the LUMO is to replace the pyridyl ring with a 5-membered ring such as methylimidazole (**24**), methylimidazole carbene (**25–26**), or pyrazole (**27**).[71] Such a color tuning strategy is demonstrated in Fig. 7 as the emission peak of **14** is blue-shifted to 470 nm for **24**, 448 nm for **25**, and 430 nm for **27**, effectively covering the full range of blue colors. The emission of **24** is nearly identical to that of **19**, shown in Fig. 7 as a reference which is missing much of the deep blue, whereas **27** has a high triplet energy exceeding those of many carbazole-based host materials. Complexes **25** and **26**, employing methyl imidazole carbene, on the other hand, will be well suited for excimer-based devices as they cover a sufficient portion of the blue spectrum and are compatible with the state-of-the-art host materials from an energy standpoint. Devices employing complex **26** can be color tuned from blue (0.17, 0.28) to orange-white (0.42, 0.43) through varying the dopant concentration with a warm white of (0.37, 0.40) and a CRI 80 achieved at a concentration of 18%.[54] However, the increase in doping concentration is accompanied by a loss in efficiency, as shown in Fig. 4.[35] Devices of **25**, however, are shown to increase the efficiency with increasing doping concentrations, resulting in a peak EQE approaching 20% at high-dopant concentrations. Ultimately, by doping **25** in a cohost of di-(4-N,N-ditolyl-amino-phenyl) cyclohexane (TAPC) and 2,8-bis (diphenylphosphoryl)-dibenzothiophene (PO15), a peak EQE of 20.1% and a peak PE of 51 lm/W were achieved for a pure white color of (0.33, 0.33) and a CRI 80, as shown in Fig. 8.[35]

The efficiency of over 20% for a high-quality white light demonstrates the achievement of a significant milestone for excimer-based WOLEDs by producing white light that is comparable in emission color and efficiency to the best reported WOLEDs employing multiple emissive materials. Nevertheless, the inefficient monomer of **25** and the potential electrochemical instability of the halogen containing Pt-$\hat{N}\hat{C}$N complexes and other tridentate analogs illustrate the need for an improved materials design motif.

4.3 *Tetradentate Pt(II) Complexes*

In recent years, a number of tetradentate platinum emitters have been demonstrated with efficient emission.[13,72–76] The rigid molecular structure of tetradentate complexes is likely to achieve high efficiencies by suppressing nonradiative pathways through molecular distortion. Furthermore, removing the need for a monoanionic ligand as the fourth coordination to the Pt metal, as in the case in tridentate Pt complexes, may eliminate a potential degradation pathway to achieve

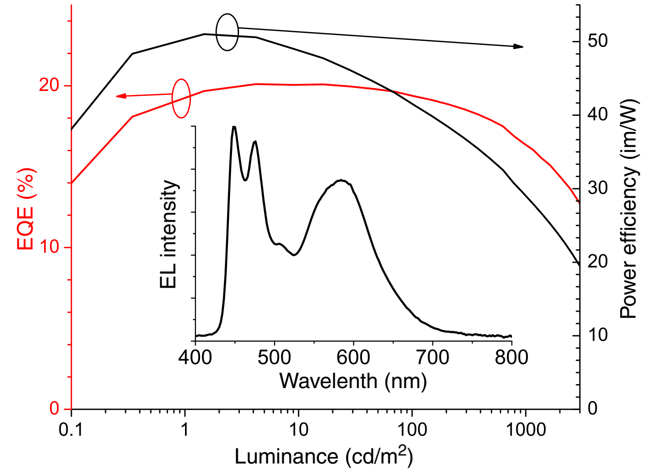

Fig. 8 EQE and power efficiency (PE) versus luminance and electroluminescent (EL) spectrum of a WOLED in the structure: ITO/PEDOT:PSS (20 nm)/TAPC (25 nm)/10% **25** in TAPC:PO15 (1:1) (10 nm)/PO15 (30 nm)/BmPyPB/LiF/Al.

the high-operational stability.[77] In our group, we have recently demonstrated an asymmetric tetradentate molecular design employing phenyl pyridine, phenyl methyl imidazole, phenyl methyl imidazole carbene, and phenyl pyrazole lumophores with phenoxypyridyl ancillary ligands.[13,78] Similar to the color tuning for the tridentate analogs, this class of emitters was tunable from green to deep blue with emission maxima of 512 nm for **31**, 468 nm for **32**, 442 nm for **33**, and 430 nm for **34**. While these complexes were extremely efficient, approaching quantum yields of unity, this class of emitters showed no excimer formation due to their nonplanar molecular geometry (Fig. 9).[13]

By replacing the phenoxypryidyl ancillary ligand with a more planar ligand to form a planar symmetric complex Pt7O7 (**40**), excimer emission can be observed at the higher dopant concentration, as shown in Fig. 10.[36] This cyclometalated Pt complex showed a narrow monomer peak at 472 nm and an excimer peak at 592 nm and is capable of achieving a warm white with color coordinates of (0.37, 0.43) and a CRI of 70. Remarkably, this emitter exhibited efficient emission across all the tested concentrations, achieving a peak EQE of 26.3% for low-dopant concentrations of 2% and 24.1% for dopant concentrations as high as 18%. Furthermore, devices of **40** in a stable structure yielded moderate device operational lifetimes of 36.5 h to 50% of initial luminance at a high brightness of 2775 cd/m^2. This demonstrates that the tetradentate

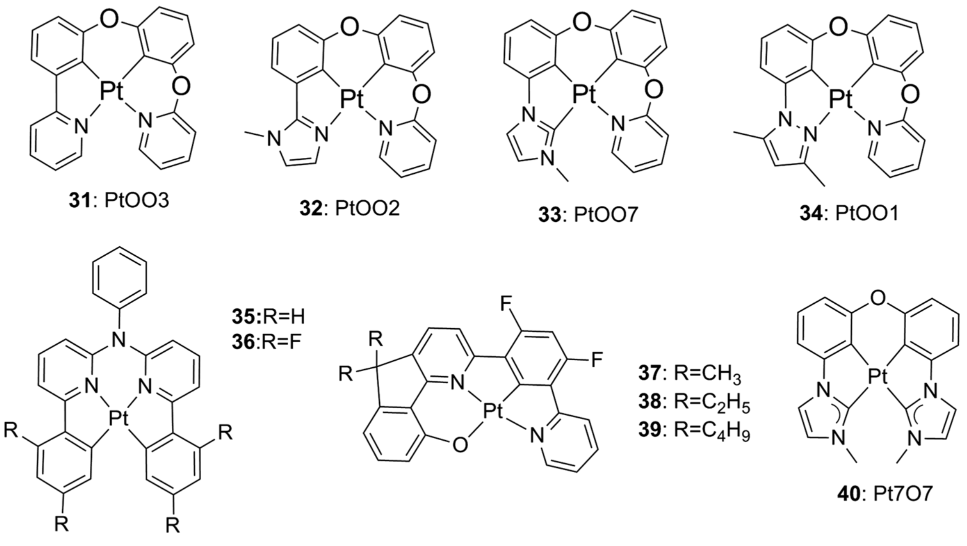
31: PtOO3
32: PtOO2
33: PtOO7
34: PtOO1
35:R=H
36:R=F
37: R=CH_3
38: R=C_2H_5
39: R=C_4H_9
40: Pt7O7

Fig. 9 Selected tetradentate Pt complexes used for excimer emitting WOLEDs.

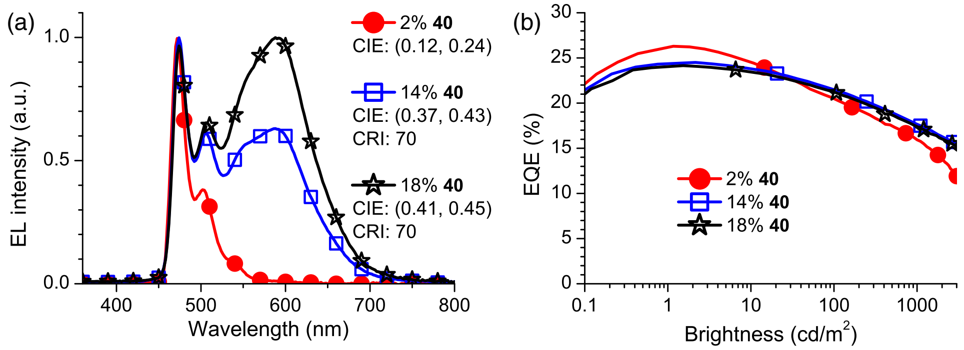

Fig. 10 (a) EL spectra and (b) EQE versus brightness for devices of complex **40** as a function of concentration in the structure: ITO/HATCN (10 nm)/NPD (40 nm)/TAPC (10 nm)/*x*% **40**:mCBP (25 nm)/DPPS (10 nm)/BmPyPB (40 nm)/LiF/Al.

molecular design can be stable, but more work is needed to further improve the performance and operational lifetime of these white devices.

Another molecular design reported by Kui et al.[47] that has showed great promise as an efficient emitter for both blue and white devices is the Pt O^N^C^N-type complexes, **37–39**, which retain the N^C^N portion of the efficient blue tridentate complexes but connect the phenoxyl group to the rest of the ligand and increase the rigidity of the molecules by constructing an additional nonconjugated carbon bridge.[47] These complexes were relatively planar, enabling significant intermolecular π–π interactions and demonstrating an excimer emission peaking at 620 nm. White devices employing these complexes have shown high efficiencies of 16.5% and 55.8 lm/W for a warm white of (0.33, 0.42) and a CRI of 77. Additionally, Cheng et al.[46] demonstrated that the molecular packing, and consequently the susceptibility to excimer formation, could be tuned by modifying the length of alkyl chains on the carbon bridge (**37–39**).[46] As the chain length decreased, the susceptibility to excimer formation increased dramatically. The ethyl-substituted complex, **38**, achieved equivalent monomer and excimer peak heights at 16% dopant concentration compared with 20% for **39**. Furthermore, the methyl-substituted complex, **37**, achieved an equivalent peak height at only 10% dopant concentration. Polymer light emitting diodes employing complex **38** achieved a peak EQE of 12.7% and remained as high as 11.5% at 1000 cd/m^2 for a white device of color coordinates (0.41, 0.45) and a CRI of 74, which is one of the most efficient solution-processed excimer-based WOLEDs.

5 Conclusions and Future Outlook

In summary, excimer-based WOLEDs are good candidates for next generation white lighting due to their tunable broad emission spectra spanning the visible spectrum, their recently reported high efficiencies, and their ability to be fabricated in a simple single-dopant emissive layer. The color tuning of emission through appropriate molecular design requires that the monomer emission spectrum includes a certain portion of the deep blue spectrum, while the excimer emission covers most of the orange and red spectra. An appropriate balance of the two can be achieved for moderate concentrations. Moreover, the development of efficient single-doped WOLEDs requires that the monomer and excimer species emit efficiently in a device setting. The development of bidentate, tridentate, and tetradentate Pt(II) complexes demonstrates a wide variety of possibilities for the molecular design. The general trend of improved emission efficiency with higher molecular rigidity tends to favor the performance of tetradentate Pt complexes, which have only recently been explored for efficient OLED applications. The design principle for such materials is supported by the recent demonstration of nearly 25% EQE for white devices employing a tetradentate platinum complex. Moreover, the possibility of a halogen-free emitter design may facilitate the development of stable single-doped WOLEDs with initial operation lifetime results in the range of hundreds of hours at a typical operational brightness of 1000 cd/m^2. The development of tetradentate Pt complexes with efficient monomer and excimer emissions is necessary to further improve the spectral coverage. Also, improvements in device architecture and emitter design are necessary to further improve the device operational lifetime. Finally, the achievement of nearly 13% peak EQE for solution-processed single-doped white polymer LEDs illustrates the distinct advantage over other solution-processed WOLED designs which are complicated by the ET between separate emitters. Nevertheless, further development of emissive materials and device architectures is still needed to simplify the device structure and to reduce the device fabrication cost.

Acknowledgments

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