

Progress and perspective of polymer white light-emitting devices and materials

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Within organic optoelectronics, polymer light-emitting devices (PLEDs) are regarded as an important class of devices which can convert electricity into light as a result of radiative decay taking place in semiconducting polymers. Recently, much effort has been devoted to developing efficient white emitting PLEDs for their potential applications in next-generation flat-panel displays and solid-state lighting sources. In this *tutorial review*, we will summarize the advances in white emitting polymers and devices published up till April 2009 by major prestigious institutions in this field. Special attention is paid to the recent progress in highly efficient devices realized by doping an electrophosphorescent guest into a polymer host and other approaches. Also we will summarize the new strategies to realize white emission with simultaneous fluorescent and/or phosphorescent emission from a single polymer in which singlet and/or triplet chromophores are incorporated into the polymer side or main chain through a covalent bond.

Introduction

White light-emitting devices based on small organic molecules or polymers (WOLEDs/WPLEDs) have attracted intense attention in both the scientific and the industrial communities due to their potential applications in areas such as full-colour flat-panel electroluminescent (EL) displays, back-lighting sources for liquid-crystal displays and next-generation solid-state lighting sources.^{1,2} Among various applications, solid-state lighting is of special interest since about 20% of the electricity generated on the planet is consumed by lighting. So far, incandescent lighting bulbs (with a typical

power efficiency of 12–17 lm W⁻¹) and fluorescent lamps (~40–70 lm W⁻¹) have been the most widely used lighting sources. However, an incandescent lighting bulb converts 90% of consumed power into heat while a fluorescent lamp contains small but significant amounts of toxic mercury in the tube, which may complicate the disposal of fluorescent lamps. Therefore, light sources providing energy savings and environmental benefits are needed in many applications. Recently, the efficiencies of WOLEDs have been shown to approach or surpass those of fluorescent lamps due to advances in novel materials synthesis and optimization of device structure in the past few years.^{3,4} Especially, recent developments in using phosphorescent materials have led to significant improvements in device performance up to 100 lm W⁻¹,⁵ thus providing organic semiconducting lighting with a very bright future.

When compared with WOLEDs, the relatively poorer performance of WPLEDs, especially efficiencies in terms of

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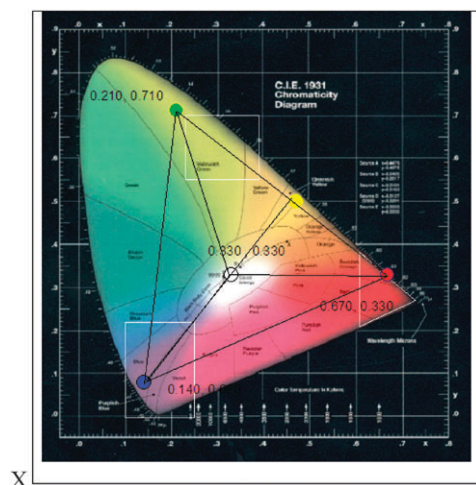


Fig. 1 CIE coordinates of ideal white emission and the NTSC RGB primary colours shown in the CIE 1931 chromaticity diagram.

power efficiency (PE), luminous efficiency (LE) and external quantum efficiency (EQE), hinders their commercialization. Despite this, devices based on polymer materials or solution-process technology have attractive advantages over their vacuum-deposited counterparts, such as low cost of manufacturing, easy processibility over large area size using spin-coating, ink-jet printing and screen-printing technology, compatibility with flexible substrates, relatively small amount of wasted materials and better control of doping level. As a matter of fact, several laboratories have achieved PE of WPLEDs exceeding 20 lm W^{-1} ^{6,7} which outperforms incandescent light bulbs in efficiency, suggesting WPLEDs can find practical applications as large area lighting sources in the near future.

White emission can be obtained based on the principle of additive colour mixing. In practice this is done by mixing the three primary colours (red, green and blue, RGB, denoted as trichromatic WPLEDs) or two complementary colours (for example, blue and orange, denoted as dichromatic WPLEDs). There is a trade off between the luminous efficiency and colour quality for white emission. This means the trichromatic WPLEDs tend to have a better colour quality but lower luminous efficiency while the dichromatic WPLEDs usually have a higher luminous efficiency but poorer colour quality.

Table 1 Best performance characteristics of reported WPLEDs from various fabrication approaches

WPLEDs from various approaches	CIE (x, y)	LE/cd A ⁻¹	EQE (%)	PE/lm W ⁻¹	CRI ^a	Ref.
Polymer host–fluorescent dopants	0.33, 0.43	17.9	—	16.3	—	14
	0.33, 0.34	7.5	2.5	—	—	15
Polymer host–phosphorescent dopants	0.34, 0.47	24.3	14.4	9.5	77	16
	0.40, 0.45	42.9	19.1	20.3	54	6
Polymer blends	0.34, 0.35	14.0	6.9	7.6	79	10
Multiple charge injection/transport layer	0.36, 0.40	11.2	6	16	—	17
Multilayer structures	0.38, 0.38	36.1	—	23.4	—	7
Exciplexes or excimers	0.33, 0.32	4.4	3.0	—	—	11
	0.31, 0.32	3.0	—	—	—	13
Single polymer	0.31, 0.36	12.8	5.4	8.5	—	18
	0.37, 0.30	10.7	5.4	—	—	19
	0.34, 0.36	5.3	2.7	—	88	20

^a The colour rendering index (CRI) is a quantitative measurement (on a 0–100 scale) of the ability of a light source to reproduce the colours of various objects faithfully in comparison with a reference source (*i.e.* daylight), with 100 representing perfect colour reproduction.

Fig. 1 shows the Commission Internationale de L'Eclairage (CIE) coordinates of the RGB primary colours system adopted by the National Television System Committee (NTSC) for colour TV, which are (0.67,0.33) (R), (0.21,0.71) (G) and (0.14,0.08) (B), respectively. Generally, an ideal pure white colour can be realized by additive colour mixing so long as the equi-energy point (with CIE coordinates of (0.33,0.33)) is within the triangle with the RGB emitters' CIE coordinates as vertexes, or if the line joining CIE coordinates of a blue/yellow emitter used passes through the white emission region. Various approaches towards realizing white polymer light-emitting devices from simultaneous, properly balanced emission covering the entire visible light spectrum (400–700 nm) have been reported, including multiple component emissive layers containing an appropriate ratio of RGB phosphorescent or fluorescent dopants,^{8,9} polymer blends containing RGB emitting species,¹⁰ stacked RGB multilayer structures,¹¹ a single polymer with RGB chromophores incorporated into the polymer backbone or side chains¹² and charge transfer



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The purpose of this review is to summarize the recent progress on white polymer light-emitting devices and the white emitting polymers synthesized recently, and to discuss the prospects for a breakthrough in WPLEDs efficiency in the next few years and the possibility of the use of WPLEDs as solid-state lighting sources with a large area size.

Efficient WPLEDs based on polymer host–dopant system

Depending on whether the guest molecules are fluorescent or phosphorescent, excited states (excitons) formed in the polymer can be transferred to the dopant *via* Förster energy transfer²¹ or a combination of Förster energy transfer and Dexter energy transfer.²² Förster energy transfer involves dipole-dipole coupling, is operative for a long range process with a separation of up to 30–100 Å, and only permits singlet-singlet transition. On the other hand, Dexter energy transfer is an intermolecular electron exchange process occurring at an order of a few angstroms in nature, which allows singlet-singlet transition as well as triplet-triplet transition. As a result, for a RGB emitting device in which complete energy transfer is preferred, the optimal dye concentration is found to be ~1% for fluorescent dyes and ~10% for phosphorescent dyes. These numbers actually set an upper limit for the doping concentration of WPLEDs based on a polymer host-dopant system.

molecules was observed. Consistent with the above-mentioned low doping concentration for a polymer host–fluorescent dopant system, it was found that when rubrene was fixed at 0.35 wt%, white emission with CIE coordinates of (0.35,0.40) was obtained. The resulting WPLEDs exhibited a maximal LE of 9.0 cd A⁻¹ and a maximal luminance of 56 000 cd m⁻², respectively. Besides its high charge carrier mobility and ambipolar-transporting properties, the triphenylamine group on the side chain of the polyspirofluorenes can facilitate hole injection, thus significantly improving efficiencies and maximal luminance. Similarly, Huang *et al.* also reported highly efficient fluorescent WPLEDs based on polyfluorenes and rubrene dopant (also with a low doping concentration of 0.2 wt%).¹⁴ It was found that by adding an electron transport material, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), into the PF–rubrene system, a more balanced charge transport was achieved, resulting in a doubled efficiency. Furthermore, these devices can easily reach high luminance at low driving voltages, thus achieving high power efficiency at high luminance (14.8, 13.5, and 12.0 lm W⁻¹ at the luminances of 1000, 2000, and 4000 cd m⁻², respectively). By optimizing the blend concentration of PBD, a peak LE of 17.9 cd A⁻¹ and a peak PE of 16.3 lm W⁻¹ were realized, with CIE coordinates of (0.33,0.43) obtained at 25 mA cm⁻².

Fan *et al.* demonstrated fabrication of efficient fluorescent WPLEDs from PF-dopant systems in which small molecules 4,7-di-2-thienyl-2,1,3-benzothiadiazole (DBT), 4,7-(2'-diselenophenyl)-2,1,3-benzothiadiazole (SeBT), and 4,7-bis(*N*-methylpyrrol-2-yl)-2,1,3-benzothiadiazole (PBT) were incorporated as orange-red emitting chromophores.¹⁵ At an optimal doping concentration around 0.2 wt%, a nearly pure white emission with CIE coordinates of (0.33,0.34) was obtained, and a LE of 7.5 cd A⁻¹ was recorded at luminance over 1000 cd m⁻². EL spectra of the obtained devices were very stable over a wide range of operating voltage. As revealed by atomic force microscopy, the film of resulting PF-dopant shows homogeneous surface morphology which indicates that these dyes have good compatibility with the polymer host with no dye aggregation being shown in the blend films.

Considering that heavy metal-containing phosphorescent materials can utilize singlet as well as triplet excitons *via* Dexter energy transfer owing to strong spin-orbit coupling and this can lead to a tremendous increase in the efficiency of the device to a nearly 100% internal quantum efficiency,²⁴ the generation of white emission by employing phosphorescent complexes is of special interest. Among the reported phosphorescent complexes, iridium based complexes have attracted particular attention because of their high phosphorescence quantum efficiency.²⁵

Kim *et al.* demonstrated highly efficient WPLEDs using blue emitting PFs doped with a green phosphorescent emitter, *fac*-tris[2-(2-pyridinyl)-5-(3,4-di-*sec*-butoxyphenyl)phenyl]iridium(III) [Ir(PBPP)₃] and a red phosphorescent emitter, tris(1-phenylisoquinoline)iridium(III) [Ir(piq)₃].²⁶ In this PF-iridium system, it is very important to blend with poly(*N*-vinylcarbazole) (PVK) as co-host to improve the overall miscibility, as well as to facilitate hole transport. Besides, incorporation of PVK is believed to raise triplet energy levels of the the polymer blend at the PVK/PF

interface, therefore phosphorescence quenching can be avoided owing to the relatively low triplet energy levels of the PFs. By controlling the concentration of dyes and the phase morphology of the blended film, nearly pure white light with CIE coordinates varying slightly between (0.34,0.34) and (0.32,0.32) was obtained, with a peak LE of 12.5 cd A⁻¹. As a result of simultaneous red, green, and blue emission covering the entire visible spectrum, a high CRI between 83–86 was obtained, representing good colour quality which is appropriate for lighting applications.

Our group reported efficient WPLEDs based on a highly efficient blue emitter, polyhedral oligomeric silsesquioxane-terminated poly(9,9-dioctylfluorene) (PFO-poss), doubly doped with two phosphorescent dyes, of which *fac*-tris-[2-(4'-*tert*-butyl)phenylpyridine]iridium(III) [Ir(Bu-ppy)₃] and bis-(1-phenylisoquinolyl)iridium(III) (1-trifluoroacetylacetonate) [(Piq)₂Ir(acaF)] were used as green and red emitters, respectively.⁹ It was found that when the doping concentrations of the red, green triple emitters were fixed at a small value of 0.14 wt%, a pure white light emission with CIE coordinates of (0.33,0.33) was obtained. The peak LE and PE of the obtained devices reached 9.0 cd A⁻¹ and 5.5 lm W⁻¹, respectively. Very low doping concentration in this system seems to suggest that Dexter energy transfer is unlikely to be the dominant mechanism in the EL process.

Besides PFs, PVK is another widely used polymer host for RGB emissions and white emission because of its higher-lying triplet states (2.5–3.0 eV), excellent film-forming properties, high glass transition temperature ($T_g \sim 160^\circ\text{C}$) and hole transport characteristics. Also, apart from the extensively investigated iridium complexes used as highly efficient triplet emitters, osmium complexes are of special interest due to their short radiative lifetime and lower oxidation potential relative to iridium complex systems.¹⁹ Shih *et al.* reported fabrication of WPLEDs by doping of a blue fluorescent dye, 4,4'-bis[2-{4-(*N,N*-diphenylamino)phenyl}vinyl]biphenyl (DPAVB), and a phosphorescent orange emitting osmium complex into a PVK host blended with 30 wt% of electron-transporting PBD.²⁷ This doubly doped device exhibited an intense white emission having CIE coordinates of (0.33,0.34) with a high LE of 13.2 cd A⁻¹. At a high luminance of 1×10^4 cd m⁻², only a minor colour shift was observed, representing a very stable white emission.

Aiming at further improving the overall performance of WPLEDs, the most effective approach at present should be an all phosphorescent RGB dopant blended into a fluorescent host,^{16,28–31} since such WPLEDs can theoretically allow for a conversion of up to 100% of injected charges, leading to an internal quantum efficiency of unity. Given these considerations, our group reported efficient single layer WPLEDs with an emission layer containing a blend of two or three phosphorescent iridium complexes within a PVK/1,3-bis[(4-*tert*-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7) host matrix.¹⁶ We employed iridium bis(1-phenylisoquinoline) (acetylacetonate) (Ir(piq)), iridium tris(2-(4-tolyl)pyridinato-*N,C*^{2'}) (Ir(mppy)₃) and iridium bis(2-(4,6-difluorophenyl)pyridinato-*N,C*^{2'}) picolinate (FIrpic) as RGB emitter, respectively. A series of devices with various dopant concentrations and ratios were fabricated and evaluated, and the results are summarized in Table 2. It was found that the turn-on voltage (defined as the voltage where a luminance of 1 cd m⁻² is measured) of the obtained WPLEDs is as low as 3.9 V, which is quite low among PVK-based PLEDs and very helpful for reducing power consumption. Given the low operating voltage for these devices in combination with the high quantum efficiency of the emitters, white emission (CIE coordinates of (0.34,0.47)) with a high forwarding viewing PE of 10.0 lm W⁻¹ (corresponding to a total PE of 20.0 lm W⁻¹) and a LE of 24.3 cd A⁻¹ was achieved for the triple-doped devices. In other words, if they are used as a lighting source, the total power efficiency of these devices can exceed that of the incandescent light bulb. To provide further insight into the origin of the efficient white emission from the devices, the electrical excitation mechanism of the WPLEDs was investigated. Comparison of PL spectra from the emitting layers with the EL spectra of the devices reveals that the EL spectra have a much higher contribution from the narrow band gap red/green emitters, indicating that charge trapping is the dominant process. On the other hand, energy transfer from wide band gap FIrpic to narrow band gap Ir(mppy)₃ or Ir(piq) *via* Dexter type short-range electron exchange cannot be ruled out. More importantly, the emission colour and the CIE coordinates of the obtained devices remain stable upon variation of the applied current, which is very important for illumination. For instance, as shown in Fig. 2, for a typical device in which the blend ratio between FIrpic and Ir(piq) is 20 : 1, as the current density increases from

Table 2 Device performance of the WPLEDs based on PVK host–RGB iridium complexes dopants¹⁶ (reproduced with permission from ref. 16, copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.)

Composition	CIE		LE/cd A ⁻¹	EQE (%)	PE/lm W ⁻¹	CRI	CCT ^c /K
	<i>x</i>	<i>y</i>					
40 : 1 ^a	0.26	0.36	16.0	12.9	7.6	65	9083
30 : 1 ^a	0.32	0.35	14.6	11.4	5.6	46	6131
20 : 1 ^a	0.33	0.36	16.1	10.0	6.3	52	5896
10 : 1 ^a	0.47	0.34	4.9	5.0	2.2	28	2061
50 : 1 : 1 ^b	0.30	0.47	21.9	13.8	10.0	62	6297
20 : 1 : 1 ^b	0.34	0.47	24.3	14.4	9.5	77	5010
30 : 0.1 : 1 ^b	0.38	0.47	18.9	12.9	8.2	75	3891
50 : 0.1 : 1 ^b	0.26	0.40	16.3	12.1	5.4	62	8267

^a FIrpic : Ir(piq) ratio. ^b FIrpic : Ir(mppy)₃ : Ir(piq) ratio; FIrpic is fixed at 10 wt% of the active layer blend. ^c Correlated colour temperature (CCT) refers to the temperature at which the heated black-body radiator matches the colour of the light source.

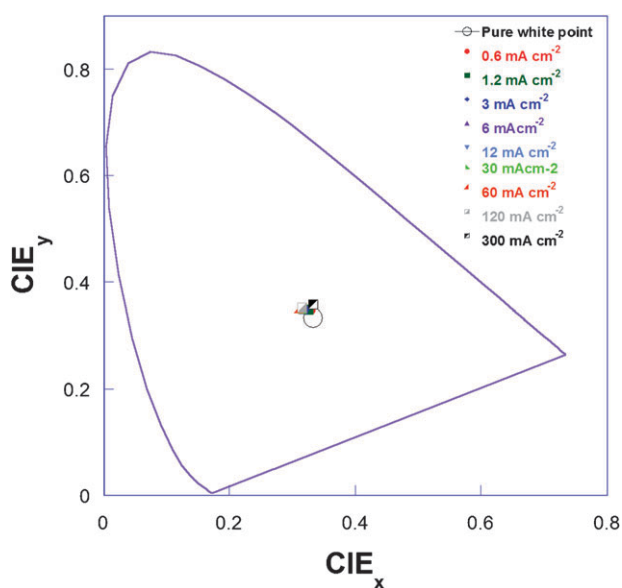
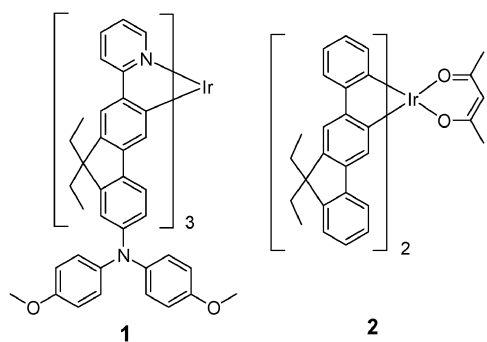


Fig. 2 The CIE coordinates of a typical device (with a blend ratio between FIrpic : Ir(piq) = 20 : 1) upon variation of applied current density over four orders of magnitude from 0.6 mA cm^{-2} to 300 mA cm^{-2} ¹⁶ (reproduced with permission from ref. 16, copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.).

1.2 mA cm^{-2} to 300 mA cm^{-2} , the CIE coordinates shift slightly from (0.34,0.36) to (0.33,0.36).

The efficiencies of white emitting devices can be significantly enhanced if the radiation of their spectra is designed to have a high luminous efficacy, which is associated with the spectral power distribution of a white light source. It has been demonstrated that the optimized luminous efficacy of all radiation can be obtained if a blue–yellow two-colour system is used.³² Therefore, WPLEDs using a combination of efficient electrophosphorescent blue and yellow emitters should lead to optimized efficiencies. Very recently, we reported a series of single emission layer WPLEDs obtained by double doping of blue emitting FIrpic and newly laboratory-made efficient yellow iridium complexes **1** and **2** (see Scheme 1 for the chemical structures) with an appropriate ratio into a PVK host in the presence of electron transporting OXD-7.⁶ The resulting WPLEDs have a peak PE of 20.3 lm W^{-1} (can be up to 40 lm W^{-1} if used as a lighting source) and a peak LE of 42.9 cd A^{-1} with CIE coordinates of (0.395,0.452). More importantly, at a practical luminance of 1000 cd m^{-2} , the



Scheme 1 Chemical structures of yellow phosphors **1** and **2**.⁶

PE is still retained at 16.8 lm W^{-1} (corresponding to a total PE of 30 lm W^{-1}) while the LE is as high as 41.7 cd A^{-1} . The reported efficiencies exceed those of incandescent light bulbs, and approach those of fluorescent lamps, thus paving the way to low-cost and large-area size WPLEDs for solid-state lighting.

Efficient WPLEDs based on all-polymer blends

Besides a polymer host–small molecule dopant system, white emission can be realized from polymer blends in which appropriate ratios of red, green and blue emitting polymers are mixed. Very recently, we reported efficient and colour-stable WPLEDs based on a newly synthesized efficient blue emitting polymer, poly[(9,9-bis(4-(2-ethylhexyloxy)phenyl)fluorene)-co-(3,7-dibenzothiophene-*S,S*-dioxide10)] (PPF-3,7SO10), in an appropriate blending ratio with green emitting poly[2-(4-(3',7'-dimethyloctyloxy)phenyl)-*p*-phenylenevinylene] (P-PPV) and orange–red emitting poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV). In a single active layer WPLED with a blending ratio of 100 : 0.8 : 0.5 (B : G : R) by weight, white light emission with CIE coordinates of (0.34,0.35) was observed, with a LE of 14 cd A^{-1} (corresponding to an EQE of 6.9%) and a PE of 7.6 lm W^{-1} .¹⁰ The devices had an appropriate colour temperature of 2500–6500 K and a high CRI value of 72–79, and were characterized with stable electroluminescent spectra upon change of current density, stress and annealing at high temperature.

Tokito *et al.* reported fabrication of highly efficient WPLEDs by using blue-phosphorescent and red-phosphorescent polymer blends.³³ In these phosphorescent polymers, red emitting and blue emitting iridium complexes were chemically connected with a vinyl polymer backbone, respectively, while the carbazole unit was directly bonded to the backbone as the charge transport unit. White emission with CIE coordinates of (0.34,0.36) was achieved when the blend ratio between the blue-phosphorescent and red-phosphorescent polymer was 10 : 1. The authors noted that the triplet energy of the electron transport material has a strong influence on the performance of the device based on the blue-phosphorescent polymer. In order to avoid quenching of electrophosphorescence by an electron transport material, it is a prerequisite that the electron transport material has a triplet energy higher than or at least comparable to that of the blue Ir-complex molecule. As a result, WPLEDs with OXD-7, whose triplet energy is about 2.7 eV, as electron transport material had an EQE of 4.5%, much higher than those using 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), whose triplet energy is about 2.6 eV, as electron transport material.

Shih *et al.* reported WPLEDs formed from polymer blends consisting of blue and orange polyfluorene copolymers.³⁴ Among these, poly[9,9-bis(4-(5-(4-*tert*-butylphenyl)-[1,3,4]-oxadiazol-2-yl)phenyl)-9',9'-di-*n*-octyl-[2,2']-bifluorene-7,7'-diyl]-*stat*-[9,9-bis(4-(*N,N*-di(4-*n*-butylphenyl)amino)phenyl)-9',9'-di-*n*-octyl-[2,2']-bifluorene-7,7'-diyl] (PFTO) was used as an efficient blue emitter while PFTO-BSeD5, a new orange emitting polymer that incorporates 5 mol% of narrow-band gap benzoselenadiazole (BSeD) units into the polyfluorene backbone, was the orange emitter. Since both the host and

dopant polymers possess hole-transporting triphenylamine moieties (TPA units) and electron-transporting oxadiazole moieties (OXD units) in their side chain, it is expected that balanced charge transport can be obtained in the resulting devices. The obtained device displayed CIE coordinates of (0.32,0.33), with a high LE up to 4.1 cd A^{-1} . In addition, phase separation between the host and dopant can be suppressed effectively because of the very similar chemical structures of these two polymers, leading to very stable emission colour over a relatively wide range of bias (from 11 to 21 V).

Efficient WPLEDs with stacked RGB multilayer structures

Similarly to most of the WOLEDs, WPLEDs can be constructed in a stacked configuration, in which each layer is capable of sequential energy transfer and is fabricated by consecutive deposition of RGB emitting species from orthogonal solvents. Xu *et al.* reported WPLEDs with two emissive layers,¹¹ in which the first active layer containing PVK doped with red emitting copolymer from 9,9-dioctylfluorene and 4,7-di(4-hexylthien-2-yl)-2,1,3-benzothiadiazole (PFO-DHTBT) was cast from chlorobenzene solution, while the subsequent layer consisting of blue emitting PFO-poss and green emitting P-PPV was spin coated from nonpolar *p*-xylene solution. By adjusting the blend ratio and layer thickness of each active layer, pure white emission with CIE coordinates of (0.32,0.33) and a LE of 4.4 cd A^{-1} were achieved. Similarly, Li *et al.* reported that a blend of PVK and hole transporting material poly-(*N,N'*-bis(4-butylphenyl)-*N,N'*-bis(phenyl)-benzidine (poly-TPD) can resist nonpolar organic solvent, and thus can be employed to fabricate efficient WPLEDs with a doubly stacked structure in which PVK and PFO are used as host in each emissive layer, respectively.³⁵ The obtained WPLEDs showed stable white light emission with a LE of 4.4 cd A^{-1} and CIE coordinates of (0.32,0.34) (at a current density of 55 mA cm^{-2}).

Very recently, Joo *et al.* developed a new approach to fabricate stacked multilayer WPLEDs in which the top emissive layer was formed atop of the bottom layer by using a stamp transfer printing technology.³⁶ Stamp transfer printing is a dry patterning process and no intermixing with the layer underneath could happen. Thus stamp transfer printing is considered to be a very effective way to fabricate multilayer WPLEDs. A LE of 4.0 cd A^{-1} was achieved with CIE coordinates of (0.33,0.41). On the basis of this work, the same group reported that the colour of stacked multilayer WPLEDs can be tuned by incorporation of CdSe quantum dots endcapped with ZnS as an interlayer between the two emissive layers.³⁷ The authors noted that, as a result of electron trapping on the quantum dots, more balanced charge transport was achieved and the exciton recombination zone shifted, leading to an improved efficiency and controllable emission colour.

Efficient WPLEDs with multiple charge injection/transport layer

A multilayer structure with a functional charge injection/transport layer has been demonstrated to be an effective approach for developing efficient RGB PLEDs,³⁸ in which

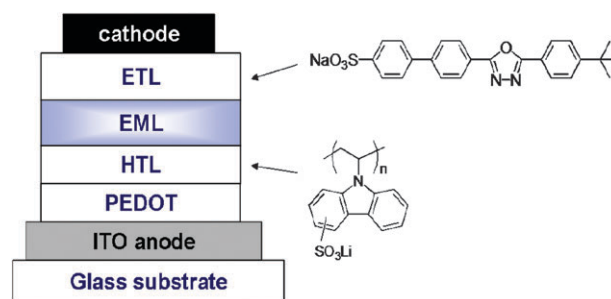


Fig. 3 Device structure of the multilayer WPLEDs and the molecular structure of the materials used.³⁹

each layer has a specific function involving charge transporting, exciton blocking and confinement of recombination zone. Naturally, this strategy can also be applied in the fabrication of highly efficient WPLEDs.

On the basis of previously reported WPLEDs, in which poly(9,9-dioctylfluorene) (PFO) was used as both blue emitter and polymer host,⁸ Gong *et al.* further reported the fabrication of efficient, multilayer WPLEDs by spin-coating, using alcohol/water-soluble polyelectrolyte (chemical structures together with device structure are shown in Fig. 3) as the hole-transporting layer (HTL) and electron-transporting layer (ETL).³⁹ The selection of the HTL/ETL is based on the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy level and their alignment with the Fermi level of each electrode. In the case of Ohmic contact with the electrodes, in which injection barrier height can be neglected, efficient and balanced charge carrier injection and transport can be achieved. Therefore, as compared with control devices, forward view LE was improved from 4.3 cd A^{-1} to 10.4 cd A^{-1} (corresponding to a total LE of 20 cd A^{-1}). Since the HTL/ETL was coated from ethanol solution and the emissive layer (EML) from toluene, it was possible to avoid mixing between the EL layer and the HTL/ETL.

Since the electronic properties of most semiconducting polymers are typically hole-dominant, and characterized by much lower electron mobility, achieving efficient electron injection from the cathode is essential for the optimization of PLEDs. Besides relying on the electronic properties of HTL/ETL,³⁹ introduction of an interlayer with a dipole moment has been demonstrated to be an effective way to facilitate electron injection, even from high work-function metals.³⁸ Recently Zhang *et al.* reported highly efficient all-phosphor WPLEDs with a thin layer of poly[9,9-bis-(6'-(diethanolamino)hexyl)fluorene] (PFN-OH) spin-coated from water-ethanol mixed solvent as ETL.²⁹ It was found that the device performance was strongly dependent on the morphology of the ETL and the processing solvents, which was attributed to varied hole-blocking ability (and subsequent excitons recombination zone confinement) upon a change of PFN-OH chain aggregation induced by the solvents. Optimized devices from water-ethanol (1 : 4 v/v) mixed solution showed a high LE of 20.4 cd A^{-1} and a PE of 14.5 lm W^{-1} with CIE coordinates of (0.312,0.355), while a moderate LE of $5\text{--}6 \text{ cd A}^{-1}$ was observed for the control device. Taking into consideration that this kind of

alcohol/water-soluble copolymer can be doped with water-soluble alkali or alkaline earth-metal salts to further enhance electron injection and electrical conductivity, Huang *et al.*⁷ reported highly efficient all-phosphor WPLEDs with a forward viewing LE over 36 cd A^{-1} , a PE of 23.4 lm W^{-1} and CIE coordinates of (0.38,0.38), in which a Li_2CO_3 -doped poly[9,9-bis(2-(2-(2-diethanolamino-ethoxy)ethoxy)ethyl)fluorene] (PF-OH) was used as ETL. Also, this Li_2CO_3 -doped ETL plays the role of hole-blocking, leading to a more balanced bipolar charge transport. Indeed, the reported power efficiency is among the highest values reported for WPLEDs. Actually, if all emitted photons are taken into account for illumination, the total PE of the devices can reach 40 lm W^{-1} , approaching that of a fluorescent lamp.

Niu *et al.* reported a highly efficient multilayer WPLEDs obtained by using water-soluble poly[9,9-bis(6'-diethoxyphosphorylhexyl)fluorene] (PF-EP) as blue emitting layer and electron transport layer.⁴⁰ Keeping in mind that the red emitting layer was spin coated from toluene, this allows for realization of a multilayer polymer structure. The authors noted that with efficient electron injection from a bilayer PF-EP/Al cathode, a LE of 16.9 cd A^{-1} and a PE of 11.1 lm W^{-1} were achieved for the device with CIE coordinates of (0.38,0.37) at a drive voltage of 7 V.

Compared with their polymeric analogues,^{29,38,39} the oligo-electrolyte counterparts may offer some advantages in that their molecular structures are precisely defined and their synthesis yields no batch-to-batch variations. Xu *et al.*³⁰ demonstrated realization of efficient WPLEDs using conjugated oligoelectrolyte hexacationic fluorene trimer with (*N,N,N*-trimethylammonium)hexyl substituents and tetrakis-(1-imidazolyl)borate counterions (FFF-BIm4) as ETL to lower the electron injection barrier height at the EML/cathode interface. Note that addition of water to methanol (1 : 3, v/v) is required to obtain optimized device performance, which had been shown to avoid selective extraction of electron-transporting small molecules from the EML. Similarly to previous work,^{29,30} An *et al.*³¹ also reported that highly efficient WPLEDs with a LE up to 18 cd A^{-1} can be obtained from a multilayer structure formed by a solution processed technique, in which an alcohol/water-soluble copolymer, poly[(9,9-bis-(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) was incorporated as ETL and Al as cathode. It was suggested that reduction of the barrier height for electron injection from the high work-function cathode is due to the formation of an interface dipole as a result of a strong interaction of an amino group in the side chain of PFN with metal, as revealed by photovoltaic (PV) and electro-absorption (EA) measurements and the X-ray diffraction pattern.³⁸

In addition to the abovementioned alcohol/water-soluble copolymers/polyelectrolytes/oligoelectrolytes, alkali metal salts like Cs_2CO_3 can be dissolved in alcohol and employed as a very good electron-injection (and hole-blocking) layer through solution processing for efficient WPLEDs.¹⁷ For devices with a structure of ITO/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/PFO:MEH-PPV/ Cs_2CO_3 /Al, incomplete transfer of energy from PFO to MEH-PPV occurred, and by changing the concentration of MEH-PPV, the emission colour

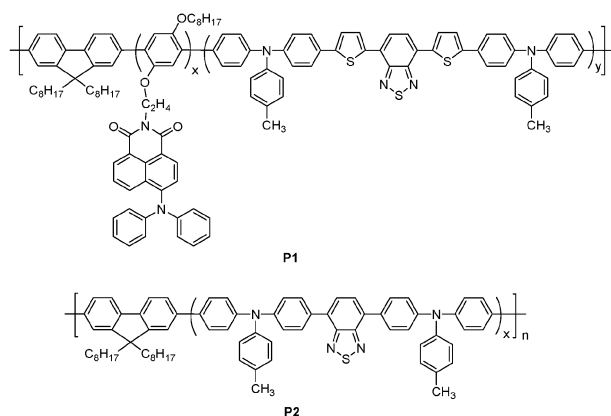
can be readily tuned from orange to white (with CIE coordinates of (0.36,0.40)). Furthermore, a combination of efficient electron injection (from the interface modification aspect) and effective charge confinement (charge-trapping) on the low-band gap MEH-PPV sites (from the materials engineering aspect) led to a remarkable PE of 16 lm W^{-1} . It is important to note that the turn-on voltage of the resulting WPLEDs is only 2.3 V, and at a low applied voltage of 5.4 V, the luminance of the devices reach 10000 cd m^{-2} , which indicates excellent balance of electrons and holes, as well as effective charge confinement in the EL layer.

Single white emitting polymer chemically doped with chromophores

Single white emitting polymer utilizing singlet exciton

In recent years, there has been an emphasis on the design and synthesis of the so-called "single white emitting polymer" capable of white emission from simultaneous blue, green and red emission^{41,42} or complementary blue, orange emission (see Scheme 2).^{12,43,44} The basic strategies to obtain such a polymer are covalently binding chromophores with RGB or complementary colours in the molecular chain of polymer hosts. In this system, one can expect a molecular dispersion of chromophores in a polymer matrix. By decreasing the doping content of the incorporated chromophores at a certain level, incomplete energy transfer will take place, resulting in a simultaneous emission from the host and the chromophores. Thus the spectral range of each individual colour overlaps with each other, creating a continuous spectrum very close to standard white light.

Tu *et al.*⁴³ demonstrated that white electroluminescence can be achieved from a single polymer in which certain amounts of yellow emitting 1,8-naphthalimide derivatives are chemically incorporated into a polyfluorene main chain. Despite the best efficiencies being far away from those required for practical applications (3.8 cd A^{-1} , 2.0 lm W^{-1}), it is clearly revealed that both the matchup of emission wavelengths between the blue and orange emitting species and their relative intensity are critical to obtain white emission with high colour purity. Aiming at a new white emitting polymer with improved



Scheme 2 Molecular structure of single white emitting polymers with fluorescent RGB (P1⁴¹) and complementary (P2⁴⁴) chromophores.

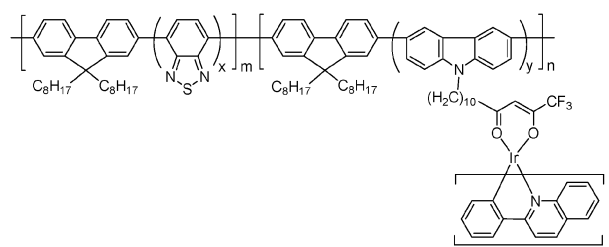
efficiencies, Liu *et al.*⁴⁴ reported the synthesis of a new polymer (P2) in which an orange chromophore (1,8-naphthalimide derivative, with a PL quantum efficiency, $\Phi_{\text{PL}} = 0.25$)⁴³ was replaced by a more efficient chromophore, 4,7-bis(4-(*N*-phenyl-*N*-(4-methylphenyl)amino)phenyl)-2,1,3-benzothiadiazole unit (TPABT, $\Phi_{\text{PL}} = 0.76$). The WPLED based on the obtained polymer gives a pure white emission with CIE coordinates of (0.35,0.32), a LE of 8.99 cd A⁻¹ and a PE of 5.75 lm W⁻¹, which is a dramatic improvement over the device based on a less efficient yellow chromophore (3.8 cd A⁻¹ and 2.0 lm W⁻¹).⁴³ On the other hand, when the blue emitting polymer host PF ($\Phi_{\text{PL}} = 0.55$) was replaced by the less efficient poly-(9,9-dioctyl-2,7-fluorene-*alt*-2,5-bis(hexyloxy)-1,4-phenylene) (PFB, $\Phi_{\text{PL}} = 0.30$), the device exhibited a much lower LE of 2.53 cd A⁻¹ and a PE of 0.73 lm W⁻¹ even when highly efficient orange chromophore TPABT was incorporated in this system. These observations indicate that both efficient blue and orange emissive species are important to obtain efficient white emission.

In consideration of the fact that the PL quantum efficiency of polyfluorene in solid films is not satisfactorily high ($\Phi_{\text{PL}} = 0.55$) and its emission spectrum lies in the deep-blue region ($\lambda_{\text{max}} = 420$ nm), to which the response of the human eye is very weak, it is desirable to explore a substitution of polyfluorene by a more efficient blue emitter with longer emission wavelength. Given these guidelines, polyfluorene derivatives simultaneously incorporating suitable contents of a highly efficient sky-blue emitting unit ($\lambda_{\text{max}} = 470$ nm, $\Phi_{\text{PL}} = 0.84$) and an orange emitting unit (peaked at 568 nm) in a side chain were prepared, and white emission was achieved from balanced emission of the red-shifted sky-blue dopant and the orange chromophores.¹⁸ As a result of enhanced PL efficiency and successful red-shifting of the spectrum of the blue emitting species, a single-layer device based on the designed copolymer exhibited a LE as high as 12.8 cd A⁻¹, a PE of 8.5 lm W⁻¹ and CIE coordinates of (0.31,0.36), among the highest efficiencies ever reported for single polymer based WPLEDs.

In pursuit of a white emitting polymer with high efficiency, very broad emission and superior colour quality, Liu *et al.* examined attaching highly efficient blue, green and red emitting units covalently to the side chain of PFs simultaneously.⁴⁵ The full width at half-maximum (FWHM) of the EL spectra of the obtained copolymer was found to be more than 210 nm, and was characterized by four individual peaks (peaked at 421, 475, 508 and 593 nm, which are attributed to PFs and the blue, green and red units, respectively). As a result of this broad emission (covering the entire visible range from 400 nm to 700 nm), high colour quality white emission with CRI as high as 88–93 was obtained. Indeed, these values are among the highest for WPLEDs ever reported. Besides this, white emission with CIE coordinates of (0.33,0.36), a LE up to 8.6 cd A⁻¹ and a PE of 5.3 lm W⁻¹ was realized in a simple device structure.

Single white emitting polymer utilizing both singlet and triplet excitons

The aforementioned single white polymers are focused on incorporating narrow band gap fluorescent chromophores



Scheme 3 Molecular structure of single white emitting polymer containing both fluorescent and phosphorescent chromophores.⁴⁶

into a polymer molecular chain, thus only singlet excitons were utilized during the electroluminescent processes. In aiming at developing a white emitting polymer capable of utilizing both singlet and triplet excitons, our group has reported a novel strategy to realize white emission from a single polymer by simultaneously introducing fluorescent and phosphorescent species into the polymer molecular chain (see Scheme 3).⁴⁶ In such a system, blue emitting PF was employed as host, the 2,1,3-benzothiadiazole (BT) unit was incorporated into the polymer backbone for green emission, and a triplet iridium complex, iridium(III) bis(2-phenylquinolyl-*N,C*^{2'}) acetylacetonate (IrPhq) was grafted to the polymer side chain as a red emitter. The incorporated BT unit acts as an exciton confinement unit and allows efficient singlet energy transfer from the fluorene segment to the BT unit. It was found that the white emission based on the copolymers was stable at all of the applied voltages, and the optimized device shows a LE of 6.1 cd A⁻¹ with CIE coordinates of (0.32,0.44). The results indicated that this polymer system paves a new way for white emitting polymers by utilizing both singlet and triplet excitons.

Another strategy to generate white emission from a single copolymer by mixing fluorescent and phosphorescent emission is to incorporate both singlet and triplet emitters conjugatively into a polymer backbone. Given this guideline, green emitting BT and red emitting iridium complex [(btp)₂Ir(tmd)] were incorporated into the polyfluorene backbone by Suzuki polycondensation, respectively.⁴⁷ The obtained device exhibited a peak EQE of 3.7%, a peak LE of 3.9 cd A⁻¹ and CIE coordinates of (0.33,0.34), which is very close to the ideal white emission. The EL spectra from these copolymers are stable upon change of applied voltages, representing a promising approach to prepare a white emitting single polymer. Keeping in mind that the emission from the triplet emitter iridium(III) bis(2-(2'-benzo[*b*]thienyl)pyridinato-*N,C*^{3'})-2,2,6,6-tetramethyl-3,5-heptanedione [(btp)₂Ir(tmd)] is too red (peaked at 660 nm) to obtain high LE and good colour purity, Chen *et al.* reported white emitting polymers in which fluorescent BT units and phosphorescent species iridium(III) bis(2-(1-naphthalene)pyridine-*N,C*^{2'})-2,2,6,6-tetramethyl-3,5-heptanedione [(1-npy)₂Ir(tmd)] (peaked at 625 nm) were introduced into the polyfluorene backbone as green and red chromophores, respectively.²⁰ The optimized device showed a LE of 5.3 cd A⁻¹ and a PE of 2.4 lm W⁻¹, with stable CIE coordinates around (0.33,0.34) from 10–14 V (see Fig. 4), corresponding to a one order of magnitude variation of current densities. More importantly, as a result of broad EL spectra (with an FWHM of 240 nm), a

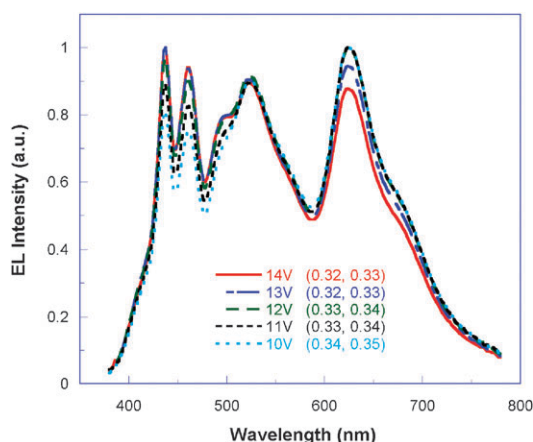


Fig. 4 EL spectra of the resulting device at voltages varying from 10 to 14 V, which corresponds to a variation of current density from 20 to 280 mA m⁻².²⁰ (Reproduced with permission from ref. 20, copyright 2009 Elsevier.)

high CRI value of 88 was obtained, representing very good colour quality for lighting sources.

Parallel to the employment of iridium complexes as phosphorescent emitters for white emission as shown above, the less accessible heavy metal osmium complexes whose radiative lifetime is short relative to the corresponding Ir systems can provide an alternative choice. By covalently incorporating fluorescent green emitting BT units and a phosphorescent red emitting osmium complex (Os(bpftz)) into the backbone of a blue emitting PF, Chien *et al.*¹⁹ prepared a white electrophosphorescent copolymer with CIE coordinates of (0.37,0.30). The white device based on the resulting polymer showed a luminous efficiency of 10.7 cd A⁻¹, ranked as one of the highest values reported so far for single white emitting polymers by simultaneously utilizing both singlet and triplet excitons.

So far, the efficiencies of white emitting polymers utilizing both singlet and triplet excitons are lower than those of the fluorescent counterparts. Nevertheless, this system bears a promising potential for further improvement; since the phosphorescent dye dispersed polymer systems have shown even higher efficiencies, this can be fulfilled by incorporation of more efficient phosphorescent chromophores or by more rational molecular design.

Conclusions and outlook

In the past decade, many approaches toward white polymer light-emitting devices have been proposed, and their emission colours are very close to ideal white emission, with high colour quality. In terms of efficiencies, to date, the best power efficiencies of white polymer light-emitting devices have reached 20 lm W⁻¹ for forwarding or 40 lm W⁻¹ (for total photons emitted in all directions), 20% of the theoretical maximum for white emission,³² close to that of the best WOLEDs. In view of practical applications, at a luminance of 1000 cd m⁻², a total power efficiency 30 lm W⁻¹ has been obtained. We note that all devices with these power efficiency data in this article are not optimized by improving outcoupling

efficiency like in the case of some record WOLEDs.¹ At the current rate, we anticipate the total power efficiency of WPLEDs can reach 60–100 lm W⁻¹ as more novel materials synthesis, optimized device structure and optical design efforts are carried out in the coming few years. Nevertheless, the emission colour of the most efficient WPLEDs is not perfect white, making the devices more suitable for lighting applications than displays. This problem can be overcome by replacing the present sky-blue emitter with a more deep blue one, though this still remains a big challenge for the organic electronics community.

Stable operational lifetime of the devices is necessary in order to find practical applications. In contrast to WOLEDs, so far there are not many reports on shelf and stress lifetime of various types of WPLEDs. Since the most efficient WPLEDs rely on unstable PVK host and blue emitter FIrpic, which are degraded significantly during operation, the design and synthesis of more stable polymer host materials and blue emitters has become one of the most urgent tasks in the field.

To fully exploit the potential of low-cost fabrication of polymer optoelectronic devices with large area size, it is desirable to fabricate the device exclusively by printing techniques without the need for vacuum deposition technology. Recently we demonstrated a novel method to simplify the PLEDs fabrication process by printing a conducting Ag-paste cathode on the top of a water/alcohol soluble PFN thin layer.⁴⁸ An investigation on using this technology to fabricate all-printed WPLEDs is ongoing; it is expected that this method will open the way for the realization of all-printable roll-to-roll WPLEDs for displays and illumination sources.

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