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Efficient White-Electrophosphorescent Devices Based on a Single Polyfluorene Copolymer**

By *Fang-Iy Wu*, *Xiao-Hui Yang*, *Dieter Neher*,* *Rajasekhar Dodda*, *Ya-Hsien Tseng*, and *Ching-Fong Shu**

An efficient white-light-emitting polymer (**W3**) is realized by covalently attaching a green fluorophore and a red phosphor into the backbone and the side chains, respectively, of polyfluorene at a concentration of 0.04 mol %. In addition, charge-transporting pendant units are included to improve carrier injection and transport. White-electrophosphorescent devices with the structure ITO/PEDOT:PSS/**W3**/CsF/Al (ITO: indium tin oxide; PEDOT:PSS: poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene)) exhibit a low turn-on voltage of 2.8 V and a luminance of ca. 10^3 cd m^{-2} at below 6 V. The peak luminance and power-conversion efficiencies are 8.2 cd A^{-1} and 7.2 lm W^{-1}, respectively. Furthermore, the device shows relatively stable white emission: the Commission Internationale d'Éclairage (CIE) chromaticity coordinates of the devices change only slightly from (0.35,0.38) at 10 mA cm^{-2} to (0.33,0.36) at 100 mA cm^{-2}, with an almost constant color render index (CRI) value of 82 at all measured current densities.

1. Introduction

Polymer light-emitting diodes (PLEDs) have attracted considerable interest because of their easy processability in solution, which allows the utilization of spin-coating and printing methods for the preparation of large-area display devices.[1] In principle, the emission colors of polymers can be easily tuned through covalently binding a guest chromophore to an emissive polymeric host at appropriate doping levels, which typically results in the partial or complete quenching of the host emission and the emergence of dye emission. By tuning the dye concentration to realize complete energy transfer, devices with improved efficiencies and saturated red, green, and blue (RGB) colors have been realized.[2] Several authors also reported white-light emission from dye-functionalized polymers.[3] For instance, Tu et al.[3a] have demonstrated that dichromatic white light can be achieved from polyfluorene (PF) chemically doped with 1,8-naphthalimide segments at a very low concentration. The devices based on the copolymer exhibited a maximum luminance efficiency (*LE*) of 5.3 cd A^{-1} and a power conversion efficiency (*PCE*) of 2.8 lm W^{-1} at 6 V. A maximum brightness of 11 100 cd m^{-2} was reached at 13.2 V. By incorporating a highly fluorescent 4,7-bis(4-(*N*-phenyl-*N*-(4-methylphenyl)amino)phenyl)-2,1,3-benzothiadiazole unit instead of the 1,8-naphthalimide unit as the orange species in the PF chain, the same group reported white-emitting PLEDs with a peak *LE* and *PCE* of 8.99 cd A^{-1} and 5.75 lm W^{-1}, respectively.[3b] The combination of blue emission from fluorene segments and orange emission from the dyes created the perception of white light in the human vision system. Liu et al.[3c] successfully realized white-light electroluminescence (EL) composed of the contributions from the three primary colors by using a simple polymer emitter. The diode was based on a PF copolymer prepared by Suzuki copolymerization with small amounts of a green fluorescent chromophore attached to the side chains and a red fluorescent chromophore covalently bound to the polymer backbone. This device exhibited a maximum brightness of 3786 cd m^{-2} at 19.4 V and a maximum *LE* of 1.59 cd A^{-1}. By using Yamamoto copolymerization, Lee et al.[3d] prepared a PF derivative having broadband emission covering the whole visible region. A white-light-emitting device based on this polymer showed a maximum brightness and a peak *LE* of 820 cd m^{-2} and 0.1 cd A^{-1}, respectively.

As demonstrated by the above mentioned examples, generating whitish light from a single polymer emitter may provide a promising way to realize large-area lighting sources from simple solution processing. However, significant improvements in device performances are needed with regard to the potential application of these devices. One approach to raise the EL efficiency is to incorporate phosphorescent dopants to harvest lu-

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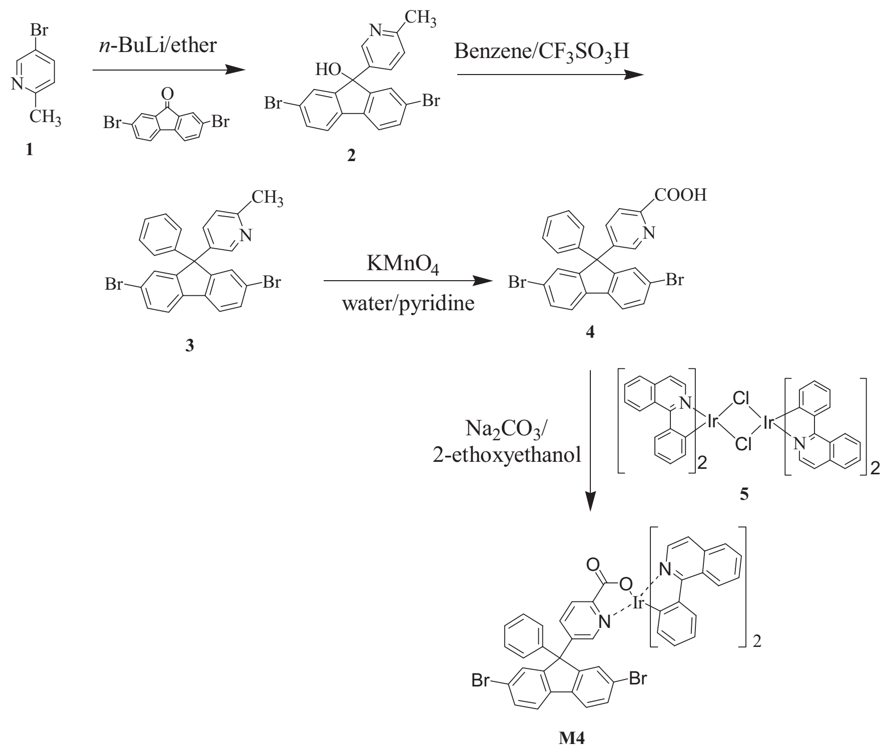
minescence from both singlet and triplet excited states.[4]

Apart from being polymeric hosts for fluorescent dyes,[5] PFs have been shown to being suited for hosting red phosphorescent dyes to realize highly efficient red-light-emitting PLEDs.[6] We reported white-emitting PLEDs using the blend of a PF host doped with a green-emitting PF derivative and a red-emitting Os phosphor as the emissive layer in the EL device with a configuration of indium tin oxide (ITO)/poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS)/blend layer/1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI)/Mg:Ag. This white-emitting device showed a relatively high *LE* of 8.3 cd A^{-1}, but an unsatisfactory *PCE* of 2.1 lm W^{-1} due to a relatively high driving voltage.[7] Also, although the device exhibited efficient and color-stable white electrophosphorescence, the risk of phase-separation could not be completely avoided in such a blended device. Therefore, in this study we chemically incorporated red phosphorescent and green fluorescent components into PF copolymers with the aim to develop a single white-light-emitting polymer. The green- and red-emitting parts in these copolymers were formed by employing small amounts of 4,7-dibromo-2,1,3-benzothiadiazole and a new iridium-containing monomer, respectively, during copolymerization. A large amount of triphenylamine (TPA) and oxadiazole (OXD) moieties were introduced as the pendant groups of the dye-attached PFs.[8] The incorporation of TPAs and OXDs was reported to significantly lower the energy-barrier height for carrier injection from the electrodes and improve the carrier-transporting properties in phosphor-doped PLEDs, leading to the improvement of EL performances.[6b,9] By carefully controlling the concentrations of the low-energy emitting species in the resulting polymers and by utilizating an efficient electron-injection cathode, white electrophosphorescence was achieved by the balanced emission of the three primary colors, with a full width at half-maximum (FWHM) of 205 nm and a peak *LE* of 8.2 cd A^{-1}.



Scheme 1. Synthetic pathway for the synthesis of **M4**.

2. Results and Discussion

2.1. Synthesis and Characterization of M4 and Dye-Attached Copolymers W1–3

The synthetic route for the preparation of the dibromofluorene monomer, **M4**, is shown in Scheme 1. 5-Bromo-2-methylpyridine (**1**)[10] was treated with *n*-BuLi at –78 °C in dry ether and the resulting lithiated species was quenched with 2,7-dibromo-9-fluorenone and as such gave 2,7-dibromo-9-(2-methylpyridine-5-yl)fluoren-9-ol (**2**). The acid-promoted (CF_3SO_3H) Friedel–Crafts reaction of **2** with benzene yielded **3**, which in turn was oxidized using $KMnO_4$ in H_2O/pyridine to afford carboxylic acid (**4**). Subsequent reaction of **4** with the cyclometalated chloride-bridged dimer (**5**)[11] in refluxing ethoxyethanol in the presence of Na_2CO_3 gave the desired monomer. As shown in Scheme 1, **M4** contains a bis[1-phenylisoquinolinato-C^2,*N*]iridium(III) picolinate [Ir(piq)] substituent at the sp^3 carbon (C-9) of fluorene, which serves as a spacer[8] to effectively block the conjugation between the Ir(piq) substituent and fluorene. Scheme 2 shows the synthesis of the dye-attached copolymers **W1**, **W2**, and **W3** and the chemical structure of the green-light-emitting model compound 4,7-bis(9,9-dihexyl-fluoren-2-yl)-2,1,3-benzothiadiazole (DFBT). The OXD monomer **M1**, TPA monomer **M2**, 4,7-dibromo-2,1,3-benzothiadiazole (**M3**), and diboronate **M5** were prepared according to reported procedures.[8,12,13] The **W1** copolymer was prepared by performing a Suzuki coupling reaction between the diboronate **M5** and the dibromides **M1**, **M2**, **M3**, and **M4** (in a mole ratio of 50:24.7:24.7:0.2:0.4), in which **M3** and **M4** were added quickly to the reaction flask from diluted $CHCl_3$ solutions (in concentrations of $1–3 \times 10^{-3}$ M), and the other reactants and solvents were added after the $CHCl_3$ solvent evaporated completely. This copolymerization was undertaken using $Pd(PPh_3)_4$ as the catalyst in a mixture of toluene and 2.0 M aqueous K_2CO_3 in the presence of methyltrioctylammonium chloride (Aliquat 336) as a phase-transfer reagent. When polymerization was complete, the end groups of the polymer chains were capped by heating under reflux sequentially with phenylboronic acid and

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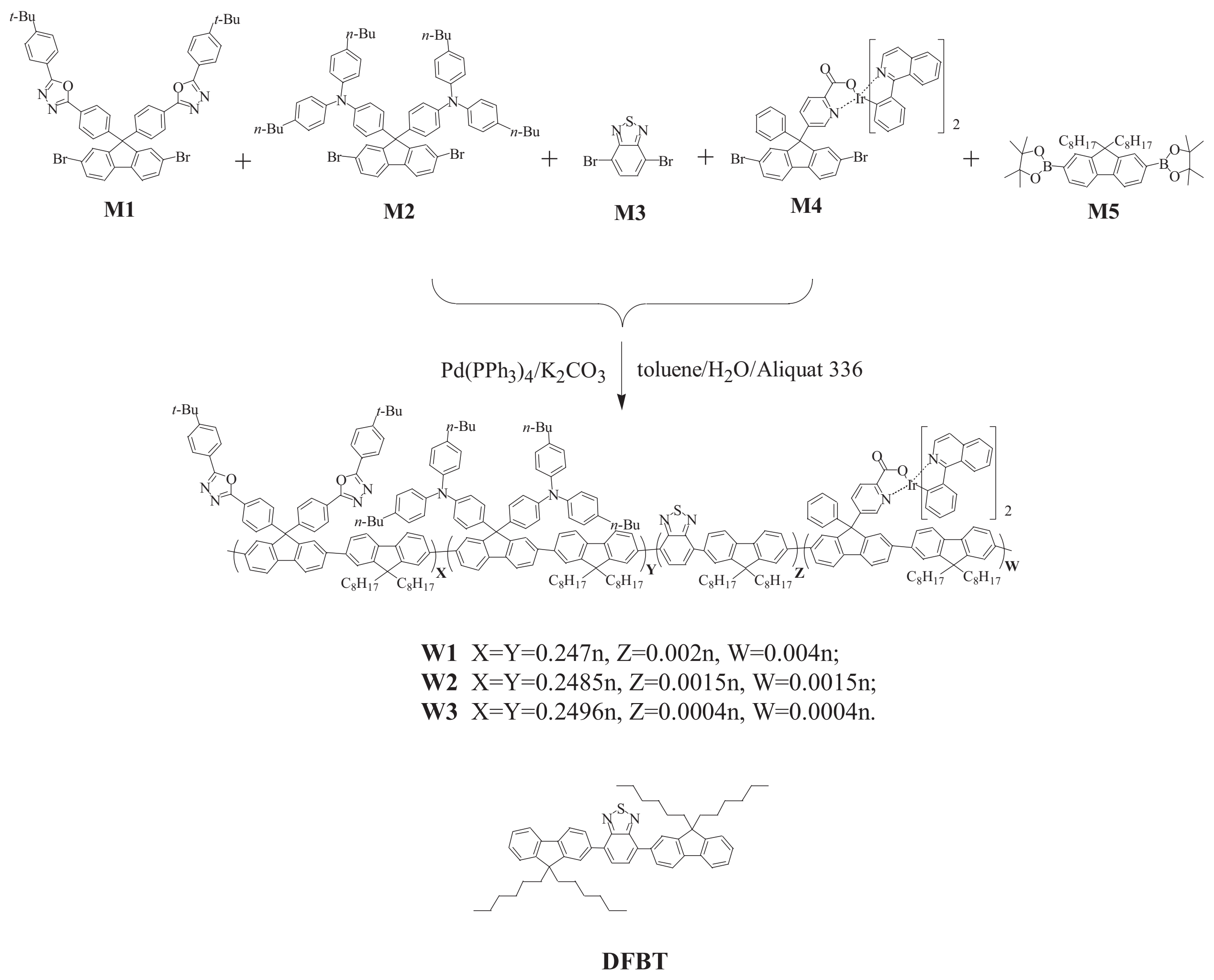

W1 X=Y=0.247n, Z=0.002n, W=0.004n;
W2 X=Y=0.2485n, Z=0.0015n, W=0.0015n;
W3 X=Y=0.2496n, Z=0.0004n, W=0.0004n.

Scheme 2. Synthetic pathways for the dye-attached copolymers and the chemical structure of DFBT.

bromobenzene. **W2** and **W3** copolymers were prepared following the same procedure as described for the synthesis of **W1**, by Suzuki copolymerization of the diboronate **M5** and the dibromides **M1**, **M2**, **M3**, and **M4** in mole ratios of 50:24.85:24.85:0.15:0.15 and 50:24.96:24.96:0.04:0.04, respectively. The resultant PF copolymers are readily soluble in common organic solvents, such as toluene, chlorobenzene, chloroform, and tetrahydrofuran (THF). The number-average molecular weights (M_n) were determined to be 4.6×10^4, 4.3×10^4, and 4.7×10^4 g mol^{-1} for **W1**, **W2**, and **W3**, respectively, with polydispersities of 1.72–1.77. The glass-transition temperatures (T_g) of **W1**–**W3** determined by differential scanning calorimetry (DSC) were ca. 170 °C, almost identical to that of PF-TPA-OXD.[8b] This implies that the attachment of the dyes in such small amounts does not significantly alter the rigidity of the resulting copolymers.

2.2. Optical Properties

The absorption spectra of **W1**, **W2**, and **W3** are similar to that of PF-TPA-OXD (not shown here) in both solution and the solid state, and the absorption contributions from the 2,1,3-benzothiadiazole (BT)-containing and iridium-containing moieties are not observable in the absorption spectra, due to the very small concentrations of these moieties in the copolymers. For the same reason, the photoluminescence (PL) spectra of **W1**, **W2**, and **W3** in diluted THF solution (Fig. 1a) are similar to that of PF-TPA-OXD. However, the incorporation of BT- and iridium-containing moieties leads to a significant change in the luminescence properties of thin films. As indicated in Figure 1b, the PL spectra of **W1**, **W2**, and **W3** films spin-coated on quartz substrates contain, in addition to the backbone emission, a strong emission band centered at 520 nm, which is the characteristic emission of the BT-containing segments, and a minor contribution from the triplet emission of the Ir(piq) substituent at ca. 600 nm. As displayed in Figure 2, the PL spectrum of PF-TPA-OXD overlaps with the absorption spectra of both **M4** and DFBT, which may imply that there is efficient energy transfer from the fluorene segments to the low-energy emitting segments in the dye-attached polymers. The enhanced green and red emission intensities in the PL spectra of the thin-film samples indicate that energy transfer from fluorene seg-

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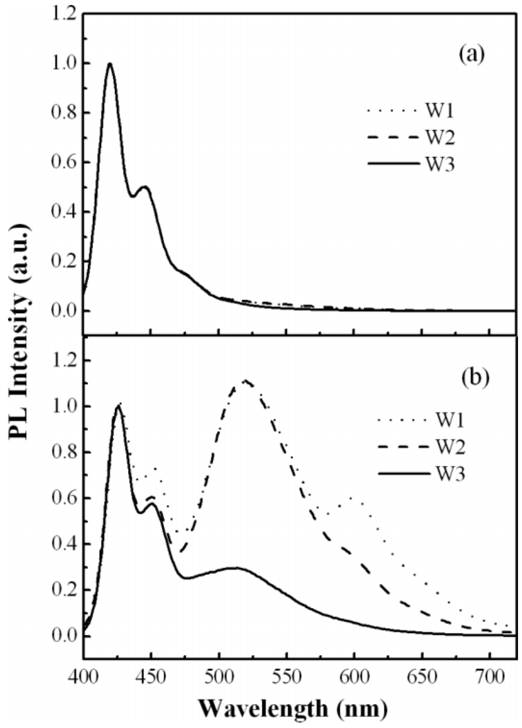

Figure 1. PL spectra of **W1**, **W2**, and **W3** in a) dilute THF solutions and b) in the solid state. The excitation wavelength was 380 nm.

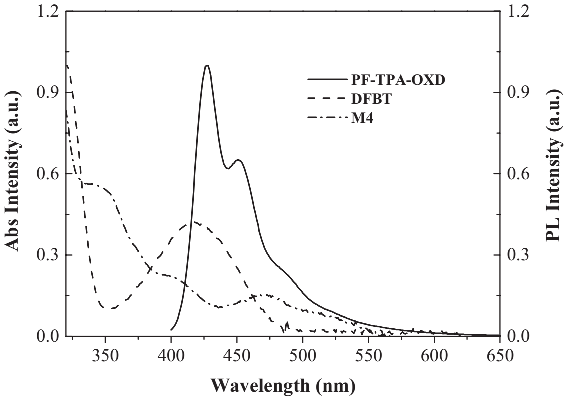

Figure 2. PL spectrum of PF-TPA-OXD in the solid state (excited at 380 nm) and the absorption spectra of DFBT and **M4** in $CHCl_3$ solution.

ments to the low-energy emitting segments is facilitated through both intra- and interchain channels. As expected, the green or red emission intensities decrease as the loading concentration decreases. In comparison with the intensity in the PL spectrum of **W2**, the green emission of **W3** is approximately decreased by a factor of 4, which is consistent with the reduction of the feeding ratios of **M3** and **M4**.

2.3. Cyclic Voltammetry Measurements

Cyclic voltammetry (CV) measurements of the model compound DFBT and monomer **M4** were carried out to obtain information about the energy levels of the green-light and red-light-emitting parts of the PF copolymers, which then allows to draw some general conclusions about the charge-transporting mechanisms in EL devices. For DFBT, the first reduction at –1.91 V occurs predominately at the electron-deficient benzothiadiazole core;[14] while the second reduction at –2.48 V and the first oxidation at 0.92 V takes place along the conjugated 1,4-bis(9,9-dihexyl-fluoren-2-yl)-benzene, as the redox potentials are close to those of terfluorenes.[15] The reduction and oxidation onset potentials of DFBT are –1.84 V and 0.82 V, respectively. For **M4**, an irreversible reduction, which occurs primarily on the electron-accepting heterocyclic portion of the cyclometalated piq ligands, was observed with the onset potential at –2.04 V, and a reversible oxidation, which mainly occurred at the Ir metal site, was found at 0.53 V with an onset potential of 0.45 V.[16] On the basis of the onset potentials of the oxidations and reductions, we estimated the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of DFBT and **M4** with regard to the energy level of ferrocene (4.8 eV below vacuum).[17] The HOMO/LUMO levels of DFBT and **M4** are calculated to be –5.62/–2.96 eV and –5.25/–2.76 eV, respectively. The inset of Figure 3 shows the energy level diagram for the complete devices based on the CV measurements of **M4**, DFBT, and PF-TPA-OXD.[6b,8b] According to this diagram, both the BT-containing fluorophore and iridium-containing phosphor function as electron traps in the PF-TPA-OXD host; in addition, the phosphor may act as a weak trap for holes.

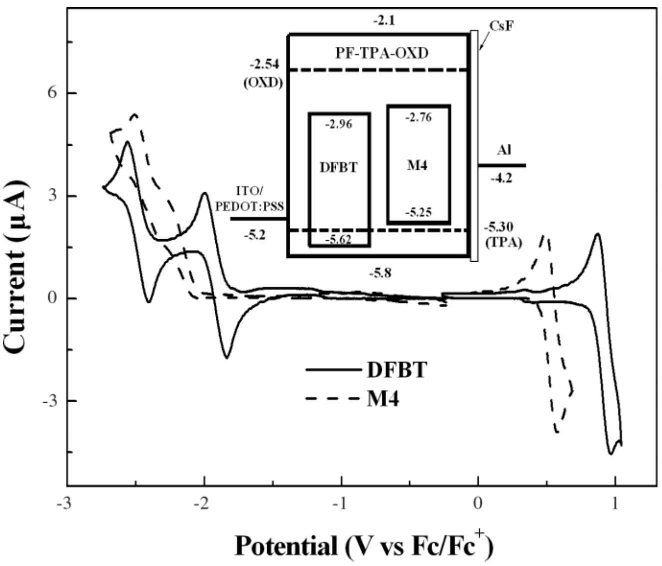

Figure 3. Cyclic voltammograms of DFBT and **M4**. The inset displays the proposed energy-level scheme for the devices having the configuration ITO/PEDOT:PSS/polymer/CsF/Al.

2.4. EL Properties

EL spectra of **W1**-, **W2**-, and **W3**-based devices are shown in Figure 4. Compared with the PL spectra in the solid state, the contributions from both of the green- and red-light-emitting moieties are dramatically enhanced in the EL spectra. The

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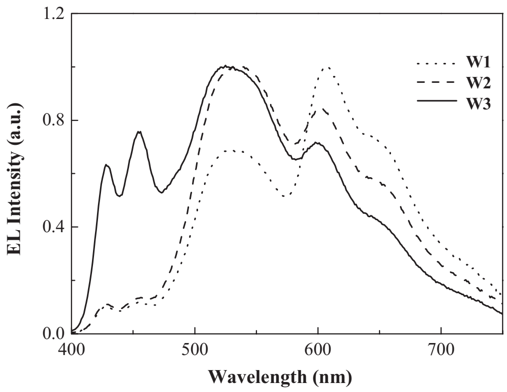

Figure 4. EL spectra of **W1**-, **W2**-, and **W3**-based devices at an operating current density of 20 mA cm^{-2}.

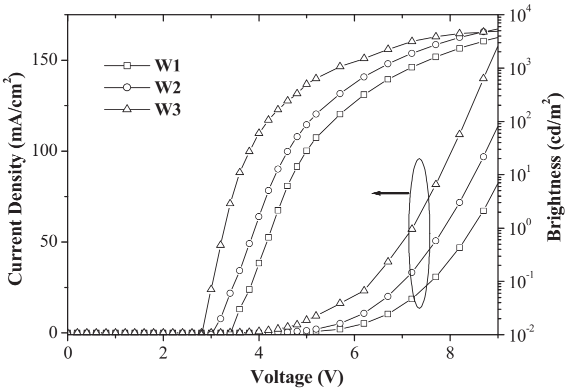

Figure 5. Plots of the current density and luminance as a function of the applied voltage for **W1**-, **W2**-, and **W3**-based devices.

large difference between the EL and PL spectra indicates that the low-energy emitting segments act as charge-trapping sites, which is commonly observed in organic host–guest systems.[18]

In a previous study, however, we noted that low-energy emitting species doped into a PF-TPA-OXD host, with similar trapping depths (ca. 0.1–0.3 eV), were not preferentially populated in EL (compared to PL).[6b] These devices utilized a Mg:Ag alloy cathode and a TPBI electron-transporting/hole-blocking layer. The density and distribution of carriers in the emission layer are probably rather different in the devices with a CsF/Al cathode from those in previous studies. Further experiments are required to understand the working mechanism of the devices.

The EL spectrum of the **W3**-based device possesses well-balanced contributions from all three primary colors and thus covers the whole visible region with a FWHM of 205 nm. Commission Internationale d'Éclairage (CIE) chromaticity coordinates (x,y) for the **W3**-based device are (0.34,0.38) for an operating current density of 20 mA cm^{-2}, which is located very close to the white point (0.33,0.33). At this current density, the devices show a color temperature of ca. 6000 K and a color render index (CRI) value of 82. As expected, the relative blue emission intensity in the EL spectrum is rather sensitive to the concentrations of the low-energy emitting segments.

The current-density–voltage–luminance (J–V–L) characteristics of the devices are shown in Figure 5. The J–V curves are clearly shifted to higher voltages as the proportions of the low-energy emitting moieties increase. This is consistent with the charge-trapping mechanism proposed above on the basis of CV measurements and the observation of a significant difference between the EL and PL spectra.

The turn-on voltages (the voltage required for 0.01 cd m^{-2}) for **W1-**, **W2-**, and **W3**-based devices are around 3 V. The peak LEs for the devices are between 7 and 8.5 cd A^{-1}, corresponding to external quantum efficiencies of 3–4 %, depending on the EL spectrum of the respective device. The operating voltages acquired to achieve a brightness of 10^3 cd m^{-2} are relatively low, typically at around 6–7 V. In particular, as shown in Figure 6a, the maximum LE and PCE of the white-light-emitting device based on **W3** is 8.2 cd A^{-1} (corresponding to an external quantum efficiency of 3.7 %) and 7.2 lm W^{-1} at a voltage of 3.6 V, a current density of 0.13 mA cm^{-2} and a brightness of 11 cd m^{-2}. We believe that the decrease of the luminance efficiency with increasing current density can partially be attributed to the triplet–triplet annihilation process. However, at the moment we can not exclude contributions by other processes such as the dissociation of excitons by the electric field or effects related to the width and location of the recombination zone as a function of bias.

At a bias of 6.0 V, this device reaches a brightness of 1330 cd m^{-2} while a LE of more than 6 cd A^{-1} is still retained. This is higher than the LEs of most white-light EL devices prepared from a single fluorescent polymeric emitter at comparable brightness levels.[3] Moreover, the EL spectra of our white-light PLEDs are almost independent of driven current density from 10 to 100 mA cm^{-2} (see Fig. 6b). As shown in the inset of Figure 6a, there is only a minor shift of the CIE coordinates from (0.35,0.38) at a brightness of 670 cd m^{-2} (10 mA cm^{-2}) to (0.33,0.36) at a brightness of 4200 cd m^{-2} (100 mA cm^{-2}). Thus, the color point remains in the white-light-region and is close to the equal-energy white point (0.33,0.33). In addition, the CRI values of the device were nearly unchanged from 10 mA cm^{-2} to 100 mA cm^{-2}.

3. Conclusions

We have demonstrated efficient white-light electrophosphorescence from a copolymer containing both hole-transporting and electron-transporting groups, with a small concentration of BT-containing segments and iridium complexes covalently linked to the bipolar polyfluorene. In a single emissive layer device configuration, white light was emitted at voltages as low as 2.8 V. The maximum LE and PCE were 8.2 cd A^{-1} and 7.2 lm W^{-1}, respectively. The resulting white-light electroluminescence showed contributions from all three primary colors,

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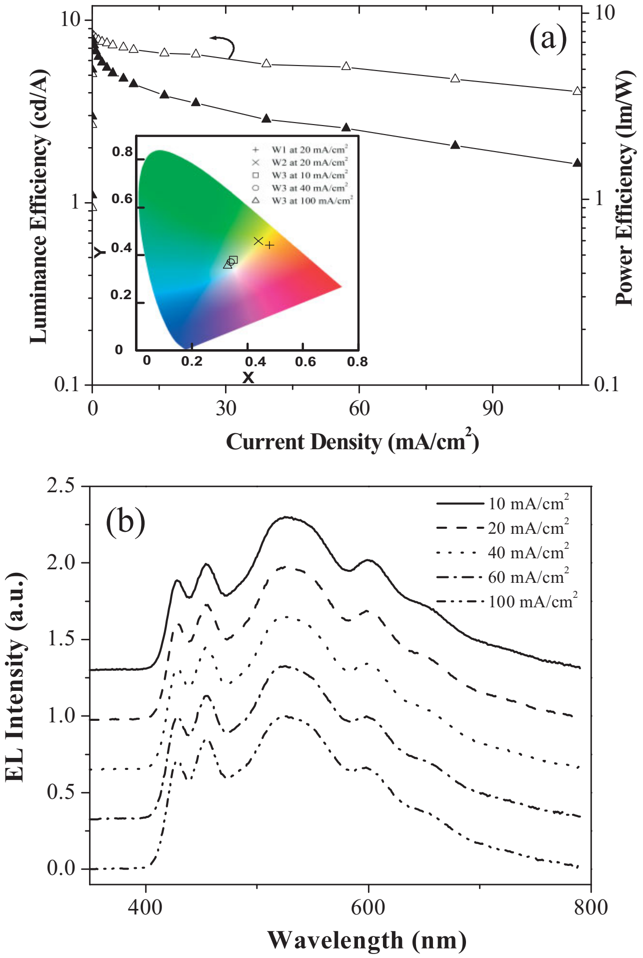

Figure 6. a) *LE* and power conversion efficiency as a function of current density for a **W3**-based device. The inset shows the CIE coordinates (*x*,*y*) of a **W1**- and **W2**-based device at 20 mA cm^{-2} and a **W3**-based device at a current density of 10, 40, and 100 mA cm^{-2}. b) EL spectra of a **W3**-based device at different current densities.

with the CIE coordinates close to the equal-energy white point and with CRI values above 80. The CIE and CRI values remained stable when the brightness increased from 670 cd m^{-2} to 4200 cd m^{-2}. We note that the external quantum efficiency of our devices is still lower than that of white-light-emitting devices using a Pt-complex-grafted non-conjugated polymer.[19] We expect that the EL efficiency can be improved further if phosphors with higher triplet energies (green or blue phosphors) are covalently linked to a host polymer having a wide bandgap.[20]

After the completion of this Full Paper, we noted that similar white-light-emitting polymers containing red phosphor and green fluorophore units were reported by Cao and co-workers.[21]

4. Experimental

4.1. Materials and Characterization

5-Bromo-2-methylpyridine (**1**) [10], and monomers **M1** [8a], **M2** [8b], **M3** [12], and **M5** [13] were prepared according to reported procedures. The solvents were dried using standard procedures. All other reagents were used as received from commercial sources, unless otherwise stated.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker-DRX 300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) spectrometers. Size-exclusion chromatography (SEC) was performed using a Waters chromatography unit interfaced with a Waters 410 differential refractometer; three 5 µm Waters styragel columns (300 mm × 7.8 mm) were connected in series in order to decrease the pore size (10^4, 10^3, and 10^2 Å); THF was the eluent. Standard polystyrene samples were used for calibration. Differential scanning calorimetry (DSC) was performed using a Seiko Exstar 6000DSC unit at a heating rate of 20 °C min^{-1} and a cooling rate of 40 °C min^{-1}. Samples were scanned from 30 to 330 °C, cooled to 0 °C, and then scanned again from 30 to 330 °C. The glass-transition temperatures (T_g) were determined from the second heating scan. UV-vis spectra were measured using a HP 8453 diode-array spectrophotometer. PL spectra were obtained from a Hitachi F-4500 luminescence spectrometer. Cyclic voltammetry measurements were performed using a BAS 100B/W electrochemical analyzer. The oxidation and reduction potentials were measured, respectively, in anhydrous CH_2Cl_2 and THF, containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte, at a scan rate of 50 mV s^{-1}. The potentials were measured against a Ag/Ag^+ (0.01 M $AgNO_3$) reference electrode using ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram.

4.2. Syntheses

2,7-Dibromo-9-(2-methylpyridin-5-yl)fluoren-9-ol (**2**): To a stirred solution of 5-bromo-2-methylpyridine (**1**) (2.00 g, 11.7 mmol) in dry ether (80 mL) was added dropwise *n*-BuLi (5.3 mL, 13.3 mmol, 2.5 M in hexanes) at –78 °C over 20 min. The resulting mixture was stirred at –78 °C for 10 min and at 0 °C for 30 min. The mixture was again cooled to –78 °C, and solid 2,7-dibromo-9-fluorenone (3.89 g, 11.5 mmol) was added in three portions over a period of 20 min. The solution was then allowed to warm to room temperature and stirring was continued overnight. The reaction contents were then quenched with water and diluted with ethyl acetate. The organic phase was washed with excess water and dried over $MgSO_4$. Concentration of the ethyl acetate solution followed by recrystallization with hexane/ethyl acetate afforded **2** (4.10 g, 82.7 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 2.37 (s, 3H), 5.16 (s, 1H), 7.01 (d, 1H, $J = 8.1$ Hz), 7.31 (d, 2H, $J = 1.7$ Hz), 7.38 (d, 2H, $J = 8.0$), 7.44 (dd, 2H, $J = 8.0$, 1.7 Hz), 7.53 (dd, 1H, $J = 8.1$, 2.3 Hz), 7.90 (d, 1H, $J = 2.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 23.3, 81.5, 121.6, 122.6, 123.3, 128.3, 132.5, 134.3, 135.4, 137.4, 145.3, 151.8, 157.1. HRMS (*m*/*z*): [M$^+$] calcd. for $C_{19}H_{13}{}^{79}Br_2NO$, 428.9364; found 428.9362.

2,7-Dibromo-9-(2-methylpyridin-5-yl)-9-phenylfluorene (**3**): To a solution of **2** (2.00 g, 4.64 mmol) in dry benzene (15 mL) at 50 °C, trifluoromethanesulfonic acid (0.82 mL, 9.28 mmol) was added dropwise under nitrogen. The mixture was then refluxed for 4 h. After this period, the reaction mixture was poured into a saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and water and dried over $MgSO_4$. The solvent was evaporated and purified by column chromatography using CH_2Cl_2 for elution to provide **3** (1.63 g, 71.5 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 2.52 (s, 3H), 7.04 (d, 1H, $J = 8.2$ Hz), 7.10–7.13 (m, 2H), 7.25–7.28 (m, 3H), 7.34 (dd, 1H, $J = 8.2$, 2.3 Hz), 7.46 (d, 2H, $J = 1.7$ Hz), 7.49 (dd, 2H, $J = 8.1$, 1.7 Hz), 7.59 (d, 2H, $J = 8.1$ Hz), 8.30 (d, 1H, $J = 2.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 24.1, 63.5, 121.9, 122.1, 123.1, 127.6, 127.8, 128.9, 129.3, 131.4, 135.9, 137.3, 138.1, 143.4, 148.5, 152.2, 157.3. HRMS (*m*/*z*): [M$^+$] calcd. for $C_{25}H_{17}{}^{79}Br_2N$, 488.9727; found 488.9766.

9-(2-Carboxypyridin-5-yl)-2,7-dibromo-9-phenylfluorene (**4**): To a refluxed solution of **3** (1.00 g, 2.04 mmol), pyridine (15 mL), and water (3.0 mL), solid $KMnO_4$ (4.80 g, 30.6 mmol) was added in ten portions over 4 days. After this period, the reaction mixture was filtered and the filtrate was acidified with conc. HCl to pH 3.0; the precipitated solid was then filtered and washed with excess water. The dried solid was

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subjected to column chromatography (hexane/ethyl acetate, 8:2; hexane/acetone, 8:2) to afford **4** (0.30 g, 28.2 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 7.06–7.18 (m, 2H), 7.29–7.40 (m, 3H), 7.47 (s, 2H), 7.56 (d, 2H, $J = 8.1$ Hz), 7.66 (d, 2H, $J = 8.1$ Hz), 7.74 (d, 1H, $J = 7.9$ Hz), 8.13 (d, 1H, $J = 7.9$ Hz), 8.44 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 63.8, 122.2, 122.5, 123.7, 127.7, 128.1, 129.2, 129.3, 132.0, 137.7, 138.1, 142.4, 144.9, 145.9, 147.7, 151.0, 163.9. HRMS (*m*/*z*): [M^+] calcd. for $C_{25}H_{15}{}^{79}Br_2NO_2$, 518.9470; found 518.9526.

Synthesis of Monomer M4: A mixture of the phenylisoquinoline-based iridium dimer [11] **5** (147 mg, 115 μmol), **4** (146 mg, 280 μmol), Na_2CO_3 (122 mg, 1.15 mmol), and 2-ethoxyethanol (3.0 mL) was heated at 100 °C for 24 h under a nitrogen atmosphere. After cooling to room temperature, the precipitate was filtered off and washed with hexane and ethanol, and purified by recrystallization from a mixture of CH_2Cl_2 and ethanol to yield **M4** (201 mg, 78.9 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 6.20 (dd, 1H, $J = 7.8$, 0.9 Hz), 6.31 (dd, 1H, $J = 7.8$, 1.2 Hz), 6.53 (td, 1H, $J = 7.4$, 1.2 Hz), 6.63 (td, 1H, $J = 7.6$, 1.2 Hz), 6.65–6.73 (m, 3H), 6.90 (td, 1H, $J = 7.7$, 1.2 Hz), 6.98 (d, 1H, $J = 1.8$ Hz), 6.99–7.04 (m, 2H), 7.16–7.19 (m, 2H), 7.21 (s, 1H), 7.27 (d, 1H, $J = 1.5$ Hz), 7.39 (dd, 1H, $J = 8.4$, 2.1 Hz), 7.41 (dd, 1H, $J = 8.4$, 1.8 Hz), 7.48 (td, 2H, $J = 8.1$, 1.8 Hz), 7.51 (d, 1H, $J = 8.4$ Hz), 7.52 (d, 1H, $J = 8.1$ Hz), 7.66–7.78 (m, 5H), 7.83–7.95 (m, 3H), 8.09 (dd, 1H, $J = 8.1$, 0.6 Hz), 8.15 (d, 1H, $J = 8.1$ Hz), 8.72 (d, 1H, $J = 6.3$ Hz), 8.84–8.94 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 63.3, 120.6, 120.7, 120.8, 121.2, 121.97, 121.98, 122.1, 122.3, 126.0, 126.3, 126.8, 127.0, 127.2, 127.3, 127.5, 127.6, 127.9, 128.0, 128.68, 128.74, 128.8, 130.1, 130.2, 130.99, 131.03, 131.70, 131.74, 132.5, 133.1, 135.0, 136.8, 137.0, 137.8, 137.9, 139.7, 140.9, 142.3, 145.4, 146.0, 146.2, 149.2, 150.1, 150.3, 150.5, 151.2, 152.5, 168.2, 170.3, 172.4. HRMS (*m*/*z*): [M^++H] calcd. for $C_{55}H_{35}{}^{79}Br_2N_3O_2Ir$, 1120.0725; found 1120.0721. Anal. calcd. for $C_{55}H_{34}Br_2N_3O_2Ir$: C, 58.98; H, 3.06; N, 3.75. Found: C, 58.59; H, 3.60; N, 3.71.

4,7-bis(9,9-dihexyl-fluoren-2-yl)-2,1,3-benzothiadiazole (DFBT): A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (90 mg, 306 μmol), 2-(9,9-dihexyl-fluoren-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [22] (330 mg, 513 μmol), Aliquat 336 (ca. 9 mg), aqueous K_2CO_3 (2.0 M, 2.0 mL), and toluene (10 mL) was degassed; then tetrakis(triphenylphosphine)palladium (ca. 8 mg) was added under vigorous nitrogen flushing. After heating at 105 °C for 12 h, the reaction mixture was poured into water (10 mL) and extracted with EtOAc (10 mL ×2). The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (dichloromethane/hexane, 1:4) to afford DFBT (156 mg, 63.6 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 0.69 (m, 20H), 0.95–1.09 (m, 24H), 1.88–2.03 (m, 8H), 7.22–7.32 (m, 6H), 7.70 (dd, 2H, $J = 5.9$, 1.7 Hz), 7.79 (d, 2H, $J = 8.4$ Hz), 7.81 (s, 2H), 7.88 (d, 2H, $J = 0.9$ Hz), 7.94 (dd, 2H, $J = 8.0$, 1.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 14.0, 22.6, 23.8, 29.7, 31.5, 40.3, 55.2, 119.7, 120.0, 122.9, 123.9, 126.8, 127.2, 127.9, 128.1, 133.6, 136.2, 140.7, 141.3, 151.1, 151.3, 154.4. HRMS (*m*/*z*): [M^+] calcd. for $C_{56}H_{68}N_2S$, 800.5103; found 800.5109.

4.3. General Procedures of Polymerization

W1 is taken as an example. To a solution of **M1** (50.0 mg, 57.0 μmol), **M2** (59.1 mg, 57.0 μmol), **M3** (173 μL, 2.54×10^{-3} M in $CHCl_3$, 0.44 μmol), **M4** (690 μL, 1.33×10^{-3} M in $CHCl_3$, 0.92 μmol), and **M5** (74.1 mg, 115.3 μmol) in toluene (2.0 mL) were added aqueous potassium carbonate (2.0 M, 1.0 mL) and Aliquat 336 (30 mg). The above solution was degassed, and tetrakis(triphenylphosphine)palladium (ca. 3 mg) was added in one portion under a nitrogen atmosphere. The solution was stirred at 90–95 °C for 36 h. The end groups were capped by refluxing for 12 h each with phenylboronic acid (17 mg, 140 μmol) and bromobenzene (22 mg, 140 μmol). After this period, the mixture was cooled and poured into a mixture of methanol and water (50 mL, 2:1 v/v). The crude polymer was filtered, washed with excess methanol, and dried. The polymer was dissolved in $CHCl_3$ and precipitated twice in methanol. The precipitate was collected, washed with acetone for 24 h using a Soxhlet apparatus, and dried under vacuum. The yield was 77.8 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 0.63–0.80 (20H, m), 0.81–0.95 (12H, m), 0.96–1.20 (40H, m), 1.24–1.40 (26H, m), 1.54 (8H, m), 2.02 (8H, m), 2.51 (8H, m), 6.80–7.11 (24H, m), 7.45–7.89 (30H, m), 7.92–8.16 (10H, m).

W2 (84.5 % yield) and **W3** (83.0 % yield) were prepared following the same procedure as described for the synthesis of **W1** using Suzuki coupling reactions between the diboronate **M5** and the dibromides **M1**, **M2**, **M3**, and **M4** in mole ratios of 50:24.85:24.85:0.15:0.15 and 50:24.96:24.96:0.04:0.04, respectively. Because the contents of benzothiadiazole (BT)- and Ir-containing moieties in the PF copolymers are too low for NMR detection, the **W1**–**W3** copolymer exhibited the same ^{1}H spectra as that obtained for the parent PF-TPA-OXD.

4.4. Fabrication of Light-Emitting Devices

The EL devices were fabricated on pre-cleaned and O_2-plasma treated indium tin oxide (ITO) substrates. A layer of 70 nm-thick poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) was first spin-coated from its aqueous solution and baked at 80 °C for 30 min to remove the residual water. Then a layer of copolymer was deposited on top of the PEDOT:PSS layer from chlorobenzene solution. The resulting layer thickness was 70 nm as measured with a Dektak profilometer. The samples were annealed at 80 °C for 30 min [23]. The devices were completed by thermal deposition of a CsF (1 nm)/Al (100 nm) cathode. Current–voltage characteristics were measured with a Keithley 2400 SourceMeter. The brightness of the devices was recorded with a Minolta CS-100 A ChromaMeter. EL spectra were measured using a charge-coupled device fiber spectrometer (Ocean Optics HR2000). With exception of the deposition of the PEDOT:PSS layer, all processes were carried out in a dry nitrogen atmosphere.

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