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High-Efficiency Red-Light Emission from Polyfluorenes Grafted with Cyclometalated Iridium Complexes and Charge Transport Moiety

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We report a new route for the design of electroluminescent polymers by grafting high-efficiency phosphorescent organometallic complexes as dopants and charge transport moieties onto alky side chains of fully conjugated polymers for polymer light-emitting diodes (PLED) with single layer/single polymers. The polymer system studied involves polyfluorene (PF) as the base conjugated polymer, carbazole (Cz) as the charge transport moiety and a source for green emission by forming an electroplex with the PF main chain, and cyclometalated iridium complexes as phosphorescent dopants. The devices prepared therewith can emit red light with the high efficiency 2.8 cd/A at 7 V and 65 cd/m², comparable to that of the same Ir complex-based OLED, and can emit the light with broad band containing blue, green, and red peaks (2.16 cd/A at 9 V). Phosphorescent OLEDs have attracted great attention^{1–3} for the high efficiency resulting from efficient energy transfer to the phosphorescent dopant having short lifetime by strong spin–orbit coupling; however the fabrication procedure is complicated due to the required large number of layers. An incorporation of the Ir complex in poly(vinyl carbazole) (PVK) or poly(dioctylfluorene) (PFO) through blending^{4,5} has been reported, but the devices give low efficiency (although an enhanced performance can be obtained by multilayer structure) and may be subject to potential phase separation.

The chemical structures of the polymers prepared in this study are shown in Figure 1. The monomers with green or red Ir complexes were prepared from the monosubstituted diketone, 9-hexyl-9-(11,13-dioxo-tetradecyl)-2,7-dibromofluorene, and the corresponding Ir chloride-bridged dimers. The PFs with various contents of Cz moiety and Ir complexes were obtained by the Suzuki- or Yamamoto-type polymerization method.

UV–vis spectra of the PFs with or without the modification exhibit absorptions that are almost contributed from the main chains as demonstrated by the overlapping of the spectra of PFO and PFOR12 in Figure 1a. Photoluminescence (PL) spectra of the red Ir complex-modified PFs without the Cz moiety show typical blue emission from the main chains and additional red emission typical for the red Ir complexes PFOR1 and PFOR12, but not for PFOR01. However, if additional 0.5 mol % green Ir complex in the feed is incorporated for the latter (PFOG05R01), a weak red emission appears. The photoluminescence excitation (PLE) spectrum of PFOR12 (Figure 1a) collected at 619 nm is similar to the absorption spectrum but with an appreciable intensity at the longer wavelength 490 nm (at which PFOR12 even has no appreciable absorption). Obviously these indicate an incomplete energy transfer from the main chain to the red Ir complex even at the red Ir content as high as 7 mol % (the actual composition for PFOR12). Since the green Ir complex (Ir(ppy)₃) can transfer energy^{4c} to the red Ir complex

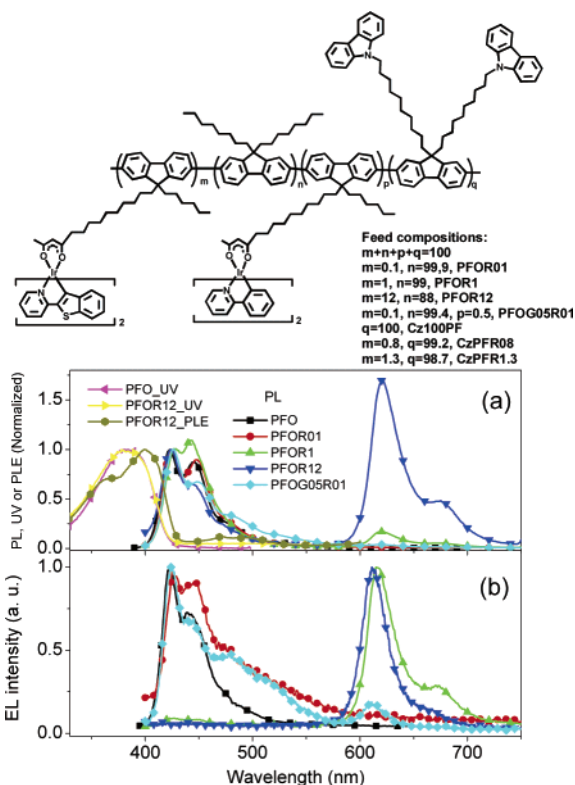


Figure 1. PL (a) and EL (b) spectra of the polymers without carbazole and UV–vis spectra of PFO and PFOR12 and PLE (a) spectrum of PFOR12. The chemical structures of the polymers are summarized (see SI for individual structures); the feed ratios are used for the compositions in the copolymers, which may be somewhat different from the actual compositions.

(btp₂Ir(acac)), the green Ir complex in the copolymer may also behave as a bridge to provide a more efficient energy transfer from the main chain to the red Ir complex through a sequential energy-transfer process (see Supporting Information (SI) for further discussion).^{1b,6} For the PFs with Cz group (CzPFR08, CzPFR1.3), similar blue and red emissions are also found in the PL spectra (Figure 2). The incorporation of the Cz group to PF is originally for reducing the barrier height for hole injection (but unexpected effects are observed as to be revealed later); this is different from the case of poly(phenylene vinylene)s, in which only an incorporation of an electron transport moiety is required,⁷ since both barriers for electron and hole injections are not high. The electroluminescent (EL) spectra are shown in Figures 1b and 2. The intensities for the red emission in the EL spectra are dramatically higher than that in the PL spectra, indicating an occurrence of charge trapping as to be revealed later. As Cz100PF has a PL spectrum similar to that of PFO in the blue region 400–475 nm, the additional green emission in the EL should be contributed from a possible cross recombination between the main-chain fluorene units and the side-

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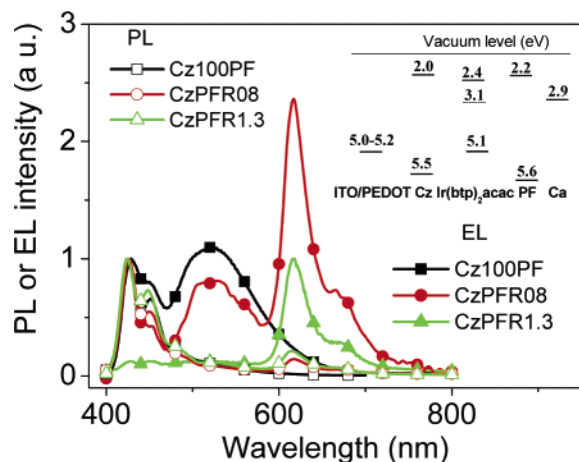


Figure 2. PL and EL spectra from the polymers with Cz. (Inset) Band diagram, in which the LUMO for $\text{btp}_2\text{Ir}(\text{acac})$ has the energy level for singlet state at 2.4 and triplet state at 3.1 eV.

chain Cz, that is, an electrophile.⁸ For the CzPFR with high red Ir complex content 1.3 mol % in the feed, there is only red emission from the Ir complex and almost no blue emission from the main chain in the EL. For that with lower Ir complex content 0.8 mol % in the feed, all the components of blue, green, and red light emissions appear, indicating CzPFR is a potential candidate polymer to provide a high-quality white light for use in full color display with color filters. The decreased intensity of green light emission relative to the blue and its disappearance would indicate an occurrence of energy transfer from the green electrophile to the red Ir complex.⁹

The occurrence of charge trapping can be inferred from the J - V results of the hole-dominating device, hole mobility measurement, and cyclic voltammetry (CV) study of the red Ir complex, $\text{btp}_2\text{Ir}(\text{acac})$. Hole-dominating devices provide a decrease of hole currents with the increase of the red Ir complex content, and the hole mobility measurement by time-of-flight (TOF) indicate that with only 1 mol % of Ir complex the polymer PFOR1 has a hole mobility ($3.1 \times 10^{-7} \text{ cm}^2/\text{V s}$ at $5 \times 10^5 \text{ V/cm}$) 2 orders of magnitude lower than PFO ($7.7 \times 10^{-5} \text{ cm}^2/\text{V s}$ at $5 \times 10^5 \text{ V/cm}$) and PFOR12 has even lower hole mobility ($8.4 \times 10^{-8} \text{ cm}^2/\text{V s}$ at $8 \times 10^5 \text{ V/cm}$). These indicate the occurrence of hole trapping on the side chain Ir complex. The CV study of PFO, Cz moiety, and the red Ir complex gives the band diagram as shown in the inset in Figure 2 (see SI). As can be seen, the HOMO and LUMO (the triplet state) energy levels of the red Ir complex lay between those of the main chain, which permits both hole and electron trapping during the electric field excitation.

The performances of the bipolar devices are listed in Table 1. The device with Cz100PF has a maximum external quantum efficiency (η_{max}) higher than that with PFO by a factor of 15. The device with CzPFR1.3 has the highest efficiency 2.8 cd/A at 7 V and 65 cd/m^2 for red PLED and remains high (1.6 cd/A at 15 V and 4321 cd/m^2). It is the highest in PLED and comparable to that from the same Ir complex-based OLED (0.98 cd/A at 6800 cd/m^2

Table 1. Performance of the Devices with the Polymers

polymer	turn-on voltage ^a (V/100 nm)	max efficiency (cd/A) (η_{max} , %) (V)	max brightness (cd/m^2) (V)
PFO	5.7	0.049 (0.05) (9 V)	258 (11 V)
PFOR01	6.9	0.037 (0.017) (8 V)	57 (11 V)
PFOR1	6.9	0.88 (0.57) (10 V)	1479 (13 V)
PFOR12	8.0	1.0 (0.43) (17.5 V)	508 (23 V)
PFOG05R01	6.7	0.23 (0.16) (15 V)	335 (18 V)
Cz100PF	3.3	1.28 (0.74) (5 V)	5029 (7 V)
CzPFR08	4.3	2.16 (1.32) (9 V)	3735 (10 V)
CzPFR1.3	4.9	2.8 (1.59) (7 V)	4321 (15 V)

^a Brightness over 0.2 cd/m^2

and 690 mA/cm^2).^{3a} The incorporation of Cz can significantly increase the efficiency and lower the turn-on voltage.

In summary, efficient red emission electrophosphorescent PLEDs are obtained by simultaneous incorporation of Ir complexes and charge transport moieties on the side chains of polyfluorene. Energy transfer from an electrophile formed between fluorene main chain and side-chain carbazole moieties, in addition to that from the PF main chain, to the red Ir complex can significantly enhance the device performance. By choosing proper conjugated polymers and other organometallic complexes, high-efficiency devices for various emission colors with single polymer/single layer can be expected.

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Supporting Information Available: Instrumental, device fabrication details, TOF measurement, GPC results, and the synthesis details of the monomers and polymers (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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