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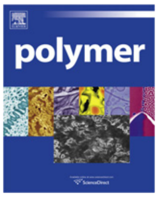

D-A-based polyfluorene derivatives end-capped with cyclometalated iridium complexes by unconjugated linkage: Structure–property relationships

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ABSTRACT

A series of donor(D)-acceptor(A)-based polyfluorene derivatives, which contain carrier-transporting units of carbazole and oxadiazole as the substitutes of the C-9 position of fluorene and are end-capped with the red-emitting iridium bi(phenylisoquilonato)(picolinato) unit by unconjugated linkage, were synthesized and characterized. The molar ratios between the donor of carbazole and the acceptor of oxadiazole moieties were found to significantly influence photoluminescent efficiency, electrochemical and electroluminescent properties of these D-A-based polyfluorene derivatives. While the ratio increased to 3:7, the PFCz3OXD7Ir showed the best device performance in the polymer light-emitting device with a configuration of ITO/PEDOT/polymers/LiF/Al. A turn-on voltage of 6.0 V, a maximum current efficiency of 0.59 cd/A and the highest luminance of 917 cd/m^2 were presented.

1. Introduction

Recently, electrophosphorescent polymers containing cyclometalated complex units have attracted a great deal of attention in polymer light-emitting devices (PLEDs), because this class of polymers can make full use of both singlet and triplet excitons leading to 100% internal quantum efficiency theoretically owing to the strong spin-orbital coupling of these heavy-metal ion [1–5]. Due to relatively short excited-state lifetimes, high luminescent efficiency and excellent color tuning from the blue to the near-infrared region [6–10], Ir^{III} complexes are considered to be a class of important phosphorescent dyes. Additionally, 2,7-polyfluorenes (PFs) are a type of good host materials with high fluorescent quantum yields, excellent thermal and chemical stability, as well as solution processability [11–14]. Therefore, great efforts have been devoted to design and synthesize 2,7-polyfluorene derivatives containing Ir^{III} complexes in order to obtain high-efficiency electrophosphorescent polymers containing Ir^{III} complex units. For example, Cao reported a type of 2,7-polyfluorene derivatives end-capped with orange-emitting Ir^{III} complexes, their single active-layer devices show a maximum external quantum efficiency of 0.34% at a current density of 45.3 mA/cm^2 and a maximum luminance of 604 cd/m^2 at 12 V [15]. Wang presented a white-emitting 2,7-polyfluorene derivatives containing a small number of orange-emitting Ir^{III} complexes in the C-9 position of fluorene unit, and obtained a white-emiting device with a maximum current efficiency of 0.81 cd/A and a maximum brightness of 989 cd/m^2 [16].

In general, 2,7-polyfluorene derivatives have high ionization potential, there is a high-energy barrier in these 2,7-polyfluorene derivatives and electron-blocking layer of poly-(3,4-ethylenedioxy-thiophene) (PEDOT), which results in higher driving voltages and an unbalanced charge injection and transportation. Accordingly, there were increasing research activities on new bipolar-transporting electrophosphorescent polymers with donor (D)-acceptor (A) structure and the relationship between structures and properties, aiming to further improve their efficiencies in PLEDs [17]. Yang reported a series of 2,7-polyfluorene derivatives containing a red-emitting iridium complex and carrier-transporting units as substitutes of the C-9 position of fluorene [18]. A red-emitting device with a maximum current efficiency of 4.2 cd/A and a maximum power efficiency of 3.1 lm/W, and a maximum brightness of 880 cd/m^2 was obtained.

It is noted that the octamethylene-tethered phosphorescent copolymers containing an even dispersion of the pendant red-emitting iridium complexes exhibited higher efficiencies than the spaceless phosphorescent copolymers due to suppression of the back transfer of triplets from the iridium complex unit to the polyfluorene backbone [19]. With this mind, in this paper, a series of D-A-based 2,7-polyfluorene derivatives were designed and synthesized, in which the carrier-transporting units of carbazole

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and oxadiazole as the substitutes were incorporated into the C-9 positions of two fluorene units, and the red-emitting iridium bi(phenylisoquilonato)(picolinato) unit was end-capped into the terminal of polyfluorene backbone, respectively. The incorporation of a hexyloxy or hexyl chain between the polymer backbone and the carrier-transporting pendants is expected to promote the energy transfer from the pendants to polymer backbone and improve the luminescent efficiency of its polyfluorene derivative. The end-capping of the red-emitting iridium complex units by unconjugated linkage of hexyloxy chains is possibly available to block the direct contact between the polyfluorene backbone and the phosphorescent unit, and induce Dexter energy transfer between them. As expected, significant influence of the feed ratios between the donor of carbazole and the acceptor of oxadiazole moieties, as well as the effect of the end-capped iridium complexes on electroluminescent properties of these D-A-based polyfluorene derivatives were observed in the PLEDs. The D-A-based 2,7-polyfluorene derivative (PFCz3OXD7Ir) with a feed ratio of 3:7 as emitter exhibited best electroluminescent properties in the device with a configuration of ITO/PEDOT/polymers/LiF/Al. A turn-on voltage (V_{on}) of 6.0 V, a maximum current efficiency of 0.59 cd/A and the highest luminance of 917 cd/m^2 were obtained in this device.

2. Experimental Section

2.1. Materials and Measurements

All manipulations were performed under dry nitrogen flow. All reagents were obtained from Aldrich and directly used without further purification. Scheme 1 illustrates the synthetic route of the D-A-based polyfluorene derivatives. The molar feed ratios of the M**1**–M**2** monomers were 7:3, 5:5 and 3:7. The corresponding D-A-based polyfluorene derivatives containing phosphorescent iridium complex units were abbreviated as PFCz7OXD3Ir, PFCz5OXD5Ir, PFCz3OXD7Ir. For comparison, the PFCz5OXD5 without iridium complex pendant was synthesized at the same time. The M**1**–M**3** monomers were synthesized by the published procedures [20–21].

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer using tetramethylsilane as a reference in deuterated chloroform solution at 298 K. Molecular weight was determined using a Waters GPC 2410 in tetrahydrofuran via a calibration curve of polystyrene as standard. UV–vis absorption spectra were recorded on a HP-8453 UV visible system. PL spectra were recorded on a Perkin–Elmer LS50B fluorescence spectrophotometer. Cyclic voltammetry was carried out on a CHI660A electrochemical work station in a three-electrode cell dipped in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution in acetonitrile under nitrogen protection at a scan rate of 100 mV/s and room temperature. In this three-electrode cell, a platinum rod, platinum wire and calomel electrode were used as a working electrode, counter electrode and reference electrode, respectively. Devices with a structure of ITO/PEDOT (40 nm)/polymers (80 nm)/LiF (4 nm)/Al (120 nm) were fabricated by following the standard procedure in a controlled dry-box (Vacuum Atmosphere Co.) under N_2 circulation. A 40 nm thick layer of poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) was spun onto pre-cleaned ITO-glass substrates. Then, a 80 nm thick emitting layer of the polymer was spun on the PEDOT:PSS top. The film thickness was determined by a profilometer. Current density (*J*)–voltage (*V*) data were collected using a Keithley 236 source measurement unit. External quantum efficiencies (*EQE*) were obtained by measuring the total light output in all directions in an integrating sphere (IS-080, Labsphere). Luminance was measured by a Si photodiode and calibrated by a PR-705 spectrascan spectrophotometer (Photo Research). EL spectra were recorded using a CCD spectrophotometer (Instaspec 4, Oriel).

*2.2. Synthesis of M**1***

Yield: 79%. mp: 80.0–80.4 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 0.53 (br, 4H), 1.06–1.25 (m, 8H), 1.67–1.70 (m, 4H), 1.79–1.82 (m, 4H), 4.17 (t, $J = 7.4$ Hz, 4H), 7.18 (t, $J = 7.8$ Hz, 4H), 7.30–7.35 (m, 6H), 7.41–7.49 (m, 8H), 8.08 (d, $J = 7.6$ Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 152.2, 140.4, 139.0, 130.3, 126.1, 125.6, 122.8, 121.6, 121.2, 120.3, 118.7, 108.6, 55.5, 42.9, 40.0, 29.5, 28.7, 26.8, 23.5.

*2.3. Synthesis of M**2***

Yield: 77.8%. mp: 121.1–121.7 °C ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 0.64 (br, 4H), 1.14–1.37 (m, 30H), 1.60–1.66 (m, 4H), 1.94–1.98 (m, 4H), 3.91 (t, $J = 7.4$ Hz, 4H), 6.96 (d, $J = 7.8$ Hz, 4H), 7.46 (d, $J = 8.0$ Hz, 4H), 7.48–7.48 (m, 2H), 7.52–7.55 (m, 4H), 8.00 (d, $J = 7.0$ Hz, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 164.4, 164.2, 161.9, 155.2, 152.3, 139.1, 130.4, 128.6, 126.7, 126.1, 126.0, 121.6, 121.2, 116.2, 115.0, 68.1, 55.6, 40.1, 35.1, 31.1, 29.5, 28.9, 25.6, 23.6.

2.4. Synthesis of $[(piq)_2IrCl]_2$

To a mixture of $IrCl_3 \cdot 3H_2O$ (0.3 g, 0.85 mmol) and water (5 mL) was added 1-phenylisoquinoline (0.5 g, 2.44 mmol) and 2-ethoxyethanol (15 mL). The mixture was refluxed under the protection of nitrogen for 20 h. After cooled to room temperature, the colored precipitate was filtered off and washed with water, followed by hexane. Then a red solid was gained (0.42 g, 78.0%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 9.05 (d, $J = 6.4$ Hz, 2H), 8.97 (d, $J = 7.8$ Hz, 2H), 8.13 (d, $J = 8.0$ Hz, 2H), 7.86–7.80 (m, 4H), 7.77 (t, $J = 7.0$ Hz, 2H), 6.83 (d, $J = 8.1$ Hz, 2H), 6.57 (d, $J = 7.6$ Hz, 2H), 6.52 (t, $J = 7.4$ Hz, 2H), 6.04 (d, $J = 8.0$ Hz, 2H).

*2.5. Synthesis of M**4***

A mixture of the $[(piq)_2IrCl]_2$ (0.2 g, 0.16 mmol), 6-(6-(4-bromophenoxy)hexyloxy)-picolinic acid (0.16 g, 0.4 mmol), sodium carbonate (90 mg, 0.85 mmol) and 2-ethoxyethanol (25 mL) was refluxed under nitrogen protection for 12 h. After cooling to room temperature, the mixture was extracted with DCM, and the combined organic layer was dried over anhydrous magnesium sulfate and distillated to DCM. The residue was purified by dry flash silica gel column using petrol ether (PE)-ethyl acetate (EA) (V/V, 1:1) as eluent to gain M**4** (0.18 g, 56.0%) as a red solid. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.98(d, $J = 6.4$ Hz, 2H), 8.68 (d, $J = 6.0$ Hz, 1H), 8.24 (d, $J = 8.0$ Hz, 2H), 8.02 (d, $J = 7.6$ Hz, 1H), 7.99–7.85 (m, 3H), 7.71–7.70 (m, 6H), 7.42–7.34 (m, 2H), 6.93–6.62 (m, 8H), 6.42 (d, $J = 2.0$ Hz, 1H), 6.21 (d, $J = 2.0$ Hz, 1H), 3.88–3.35 (m, 6H), 1.29–1.28 (m, 2H), 1.01–0.91 (m, 4H).

2.6. General procedures of Suzuki polycondensation

Taking the preparation of PFCz5OXD5 as an example: A mixture of monomers M**1** (82.2 mg, 0.1 mmol), M**2** (107.7 mg, 0.1 mmol), M**3** (128.5 mg, 0.2 mmol), K_2CO_3 aqueous solution (2.0 M, 2.0 mL), $Pd(PPh_3)_4$ (10 mg), and Aliquat 336 (2 drops) in toluene (4 mL) was degassed with nitrogen flow and stirred at 90 °C for 48 h under nitrogen atmosphere. After cooled to room temperature (RT), benzeneboronic acid (31.4 mg, 0.2 mmol) was added and the mixture was refluxed for 12 h. Then bromobenzene (34 mg, 0.2 mmol) was injected and the mixture was refluxed for another