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White light-emitting devices based on star-shape like polymers with diarylmaleimde fluorophores on the side chain of polyfluorene arms

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ABSTRACT

A series of novel star-shape like white polymers were synthesized by employing the benzene as the core, and incorporating different amount of bis (4-methoxyphenyl) maleimide guest onto the side-chain of the polyfluorene (PF) arm host. Due to the large feed ratio of core, such a construction strategy could efficiently avoid or suppress the formation of linear PF which always existed in the previous star-like polymers employing guest as core. When applied to the single emitting layer devices fabricated by solution spin-coating method, the efficiency of the devices enhanced gradually with the amount of guest increasing from 0.01% to 2%. The device performance was further improved substantially by annealing at 140 °C. A typical device base on P1 containing 1% dopant exhibited maximal luminous efficiency of 6.13 cd/A. Interestingly, the increase of efficiency is not originated from the self-dopant effect of α or β crystalline phase, which was always produced by thermal treatment at 120 °C in linear or previous star-like polyfluorenes. Morphology analysis disclosed that annealing made the polymeric molecules stack become closer, consequently resulting in a more effectively charge transfer and energy transfer from host to guest. As a result, the compact molecular stacking of the star-shape like polymers should be responsive for the high efficiency of annealed devices. The results would be conducive to design new star-shape like polymers with more arms, and improve the performance of white devices.

1. Introduction

White organic light-emitting diodes (WOLEDs) have attracted considerable attention in recent decades due to their potential applications in the field of lighting and flat panel display [1–7]. By choosing suitable fluorescent [5,8,9] or phosphorescent [10,11] chromophores as emitting materials, various kinds of WOLEDs have been fabricated [2,3,11–15]. Thereinto, white polymeric light-emitting diodes (WPLEDs) using polymer materials as the active layer, show great potential in the future applications for facile solution processing at low cost. WPLEDs could be mainly fabricated by either blending several polymers with different emission together to form a single/multi layer or incorporating several different colored fluorophores into a single polymer molecule [3,5,16,17]. Especially for the latter strategy, when the hosts and guests were linked together by a covalent bond to form a single molecule [8,10,18,19], the intrinsic phase separation resulting in low efficiency and color instability of devices would be effectively suppressed. For example, Wang and co-workers covalently attached the orange chromophore with high quantum yield into the main chain and side chain of the blue linear polyfluorene. The single layer WPLED exhibited a maximum luminous efficiency (LE) of 3.8 cd/A and 9.3 cd/A, respectively [20,21]. The optimal device performance of these systems was comparable to that of small molecules.

Recently, single white star-shape like polymers were employed to fabricate highly efficient WPLEDs, because their branched and globular features would efficiently inhibit the intermolecular interactions. Star-like white polymers with four arms were firstly designed by choosing an orange chromophore 2, 1, 3-benzothiadiazole as the guest core, and polyfluorene as the blue emissive arms. When the content of orange core reaching 0.03%,

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white electroluminescence including simultaneous blue and orange emission was observed with a maximum LE of 7.06 cd/A [22]. Further expanding the star-shape like polymer from four arms to six arms by using star-shaped orange cores, higher efficiency of WPLEDs based on the star-shape like polymers as active materials were achieved [23]. We also chosed an orange chromophore (bisindolylmaleimide) as the core and polyfluorene and/or polycarbazole as the arms to get a series of three arms star-shape like polymers, applied in the WPLEDs to give a maximum LE of 7.2 cd/A [24]. Just recently, Lai and co-workers synthesized a four-armed star-shaped single-Polymer system with red benzothiadiazole derivative chromophore as the core, blue PF as arms and green chromophore as dopant on the arms, realizing a pure and stable white emission with a LE of 1.57 cd/A, and CIE coordinate of (0.31, 0.34) [25].

The above results indicate that the host-guest partly energy transfer strategy in the star-shape like polymers is an efficient way to realize highly efficient white electroluminescence. Nevertheless, due to the very low feed ratio of guest core monomer, the linear polyfluorene would be unavoidably formed and mixed with the star-shape like polymers, which is not beneficial for the luminescent efficiency [22,24]. In this paper, a new strategy was adopted to construct single white three-arm star-shape like polymers by introducing a yellow chromophore, diphenylmaleimide derivative, into the side-chain of the polyfluorene arms, and employing a non-fluorophore benzene unit as the core. In the case, highly pure host-guest star-like polymers were obtained by using relatively large feed ratio of benzene core. Additionally, the non-emissive and relatively simple core used in the new construction strategy, replacing the emissive guest core used in the traditional method, avoids the complex synthetic procedure of emissive core.

2. Experiments

NMR spectra were measured in $CDCl_3$ on a Bruker Ascend 400 FT-NMR spectrometer, ^1H and ^{13}C chemical shifts were quoted relative to the internal standard tetramethylsilane. UV–vis absorption spectra were obtained on a Shimadzu UV-2600 spectrophotometer. The PL spectra were probed on a Shimadzu RF-5301 PC spectrophotometer. Cyclic voltammetry measurements were carried out on a CHI600D electro-chemical analyzer using a three-electrode configuration under nitrogen atmosphere. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration with a Waters 1515 instrument. Thermal analyses were performed with a Mettler 851e analysis system. Differential scanning calorimetry was done on a Mettler DSC822e instrument. The nanoscale morphology of the films was observed with tapping mode-AFM by Agilent 5500. Grazing incidence X-ray diffraction (GIXRD) data were collected using an X'Pert 3 Powder diffractometer (Philips, USA) with Cu $K\alpha$ radiation. The films thickness test were conducted on the Profilometer (Dektak XT, Bruker).

In the process of devices fabrication, Indium-tin oxide (ITO) with a sheet resistance < 50Ω was used as the substrate, and washed with detergent, deionized water, acetone and isopropyl alcohol in sequence. The ITO glass substrates were dried with nitrogen flow, and followed by oxygen plasma cleaning for 4 min. A 25 nm thick poly-(ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT: PSS) was spin-coated onto the ITO substrate, followed by baking at 150 °C for 15 min, the polymer layer was then spin-coated on top of the PEDOT: PSS layer from a chlorobenzene solution (10 mg/mL) through a Teflon filter (0.2 μm). An electron-transporting layer 2,2′,2″-(1,3,5-benzeneriyl)tris(1-phenyl-1H-benzimidazole) (TPBI) was grown through thermal evaporation using at a chamber under pressure of 3×10^{-4} Pa. And then a thin layer of LiF (1 nm) was deposited onto the TPBI layer, followed by aluminum layer (120 nm). Lastly, the device was encapsulated with UV-curing glue in glove box. The current–voltage and light-intensity measurements were done on Keithly 2400 source meter and a PR-655 Spectra Scan Spectrophotometers.

All the reagents and solvents used in the experiments were obtained from commercial suppliers and used as received or purified according to standard procedures. Compound C1, C2 and C5 were synthesized by the reported procedure [22,26–28]. Thin layer chromatography was performed on MERKY silica Gel 60 thick layer plates. Column chromatography was performed on Sorbent Technologies brand silica gel (230–400 mesh).

2.1. Synthesis of 1-(6-(3,6-dibromo-9H-carbazol-9-yl)hexyl)-3,4-bis(4-methoxyphenyl) pyrrolidine-2,5-dione (C3)

A mixture of C1 (311 mg, 1.0 mmol) and potassium tertbutanolate (224 mg, 2 mmol) in DMF (20 mL) was stirred under nitrogen atmosphere for 2 h at 45 °C before the solution of C2 (585 mg, 1.2 mmol) in DMF (5 mL) was added. Then, the reaction was stirred overnight and quenched with water. The resulted mixture was extracted with CH_2Cl_2, washed with brine. The organic layer was separated and dried over $MgSO_4$. After the solvent was removed, the residue was purified by column chromatography with PE: DCM (3:1) as eluent, to get C3 as yellow solid with a yield of 50%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, $J = 1.8$ Hz, 2H), 7.54–7.49 (m, 2H), 7.45 (d, $J = 8.3$ Hz, 4H), 7.28–7.21 (m, 3H), 6.86 (d, $J = 8.5$ Hz, 4H), 4.22 (t, $J = 7.2$ Hz, 2H), 3.82 (s, 6H), 3.58 (t, $J = 7.0$ Hz, 2H), 1.81 (d, $J = 6.8$ Hz, 2H), 1.39–1.34 (m, 4H), 1.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.36, 160.70, 139.28, 133.96, 131.42, 129.06, 123.47, 123.27, 121.33, 114.11, 111.99, 110.40, 55.32, 43.22, 37.95, 28.69, 28.42, 26.69, 26.49. HRMS (ESI) m/z $[M+Na]^+$ calcd 737.0627, found 737.0621.

2.2. Synthesis of 1-(6-(3-bromo-6-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazol -9-yl)hexyl)-3,4-bis(4-methoxyphenyl)pyrrolidine-2,5-dione (C4)

A mixture of C3 (144 mg, 0.2 mmol), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36 mg, 0.14 mmol), [1,1,-Bis(diphenylphosphino)ferrocene]-dichloropalladium (II) (7 mg, 0.01 mmol), potassium acetate (6 mg, 0.06 mmol) and 1.4-dioxane (10 mL) was stirred at 80 °C overnight under nitrogen atmosphere. After cooling to room temperature, the reaction was quenched with water and then extracted with ethyl acetate, washed with brine, dried over magnesium sulfate ($MgSO_4$). After the solvent was removed, the obtained residue was isolated by column chromatography with PE: DCM (15:1) as eluent to give C4 as a light yellow solid with a yield of 30%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.23 (s, 1H), 7.91 (d, $J = 8.3$ Hz, 1H), 7.51 (d, $J = 9.0$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 4H), 7.38 (d, $J = 8.3$ Hz, 1H), 6.87 (d, $J = 8.3$ Hz, 4H), 4.27 (t, $J = 9.7$ Hz, 2H), 3.83 (s, 6H), 3.58 (d, $J = 14.4$ Hz, 2H), 1.90–1.78 (m, 4H), 1.25 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ171.36, 160.68, 139.13, 133.97, 131.43, 128.31, 124.84, 123.33, 121.36, 114.09, 112.08, 110.20, 55.31, 43.12, 38.01, 28.76, 28.48, 26.76, 26.56. HRMS (ESI) m/z $[M+Na]^+$ calcd 785.2373, found 785.2368.

2.3. General suzuki cross-coupling polymerization procedure

To a mixture of 1,3,5-tribromobenzene (3.8 mg, 0.012 mmol), tetrabutylammonium iodide (TBAI 30 mg, 0.081 mmol), tetrakis(-triphenylphosphine) palladium(0) (20 mg,0.018 mmol), C5 (213.7 mg, 0.36 mmol), and C4, toluene (5 mL), potassium carbonate (2 M, 2 mL) solution was added. The mixture was refluxed for 48 h under nitrogen atmosphere. Then the polymer was end-