



Synthesis and characterization of red-emitting diketopyrrolopyrrole-*alt*-phenylenevinylene polymers

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ABSTRACT

Two novel diketopyrrolopyrrole (DPP) and p-phenylenevinylene alternating copolymers, poly(1,4-(2,5-dicyano)-phenylenevinylene-*alt*-2,5-dioctyl-3,6-bis(4-vinylphenyl)pyrrolo[3,4-c]pyrrole-1,4-dione) (P1) and poly(1,4-(2,5-diethoxy)-phenylenevinylene-*alt*-2,5-dioctyl-3,6-bis(4-vinylphenyl)pyrrolo[3,4-c]pyrrole-1,4-dione) (P2), were synthesized through Wittig reaction in good yields, and were characterized by FTIR, NMR. Two polymers possessed moderate molecular weights and polydispersities, well-defined structures, and were readily soluble in common organic solvents. In particular, P1 and P2 exhibited excellent thermal stability with $T_d = 393$ and 398 °C at 5% weight loss, respectively. Both P1 and P2 in solution and in thin films exhibited strong red photoluminescence. Both electroluminescence devices using ITO/PEDOT/polymer/Ba/Al configuration with P1 and P2 as the emitting layer showed nearly pure red emission with the emission peaks at 646 nm for P1 and 648 nm for P2, and exhibited low turn-on voltages of 4.5 and 3.4 V, respectively. The results show that P1 and P2 are promising candidates for red emissive materials in polymer light-emitting diodes.

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1. Introduction

Since their electroluminescence (EL) properties were reported firstly by Burroughes in 1990 [1], the light-emitting conjugated polymers have been attracting intensely because of the flexibility available for fine-tuning their luminescence properties through the manipulation of their chemical structures and the feasibility of combining spin-coating or printing processes for preparing large area flat-panel displays [2–6].

Over all the past decade, polymer light-emitting diodes (PLEDs) have been made considerable progress in the possible applications such as flat-panel or flexible display devices [7–9], due to their numerous advantages over cathode ray tubes (CRTs) and liquid crystal displays (LCDs) [10], such as good processability, fast response time, self-emitting property, wide view angle, high contrast, low power consumption, low weight, and facile color tunability over the full visible range, particularly large area color displays and flexibility [11–13]. However, only green PLEDs meet the requirements of commercial use at present [6,13,14]. New red PLEDs still remain among the most wanted performance to be

improved in full-color displays, and further improvements are necessary [15,16].

In most π -conjugated polymers, the injection and transport of holes are more efficient than transport of electrons due to their inherent richness of π -electrons [12,17,18]. As a result, an essential issue for PLEDs with conjugated polymers as the emissive layers reported so far lies in the charge imbalance. Therefore, the electron injection is believed to limit the quantum efficiency of PLEDs devices based on p-dope type polymers. In order to improve the device performance of light-emitting diodes (LEDs), realization of n-dope type polymeric emissive materials, while keeping the high emission property, is both interesting and challenging for researchers [19,20].

In order to synthesize new red-emitting polymeric materials with high electron-transporting ability, we take advantage of the electron-accepting property of diketopyrrolopyrrole (DPP) derivatives. Due to their excellent photostability and high quantum yield of fluorescence, DPP derivatives are potential materials for opto-electrical devices [21–33]. In this paper, we designed two novel red-emitting polymers P1 and P2. P1 contained DPP and 1,4-(2,5-dicyano)-phenylenevinylene units, both of which were electron-acceptor. P2 contained DPP as electron-acceptor and 1,4-(2,5-diethoxy)-phenylenevinylene as electron-donor, resulting in donor-acceptor charge structure. P1 and P2 were successfully synthesized by Wittig reaction. Preliminary electroluminescent results

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showed that P1 and P2 are promising candidates for red emissive materials in PLEDs.

2. Experimental

2.1. Measurement and characterization

^1H NMR spectra were collected on a Bruker DRX 400 spectrometer in CDCl_3 with tetramethylsilane as inner reference. FTIR spectra were recorded on a Tensor 27 spectrometer with KBr pellets. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC 515-410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. Elemental analysis was performed using a Vario EL III instrument. The thermogravimetric analysis (TGA) of polymers was performed under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ using STA449C thermal analyzer. Cyclic voltammetry (CV) was carried out on an EG&G model 283 computer-controlled potential/galvanostat (Princeton Applied Research) with platinum electrodes at a scanning rate of $50\text{ mV}/\text{s}$ against a calomel reference electrode with a nitrogen-saturated solution of Bu_4NPF_6 (0.1 M) in spectrum-grade acetonitrile. UV–vis absorption spectra were recorded on a HP 4803 Instrument. PL and EL spectra were recorded on an Instaspec IV CCD spectrophotometer. The absolute PL quantum yields were determined in an Integrating sphere IS080 (Labsphere) with 325 nm excitation of He–Cd laser (Mells Grid), as the percent of the total output photons in all directions vs the total input photons. The luminance–voltage (L – V) was measured using a Keithley 236 source measurement unit and a calibrated silicon photodiode. The luminance was calibrated using a PR-705 SpectraScan spectrophotometer (Photo research). The external quantum efficiency (EQE) was determined as the percent of the total output photons vs the total input electrons from each electrode.

2.2. Materials

4-Cyanobenzaldehyde, *p*-xylene, hydroquinone, 1-bromooctane and potassium tert-butoxide were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and were used without further purification; other chemicals were commercially analytical-grade quality. The solvents such as chloroform, ethanol, *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF), were dehumidified by 3 Å molecular sieve before use. 4-[1,3]Dioxolan-2-yl-benzonitrile [34], 2,5-dicyano-1,4-xylene-bis(triphenylphosphonium bromide) [35] and 2,5-diethoxy-1,4-xylene-bis(triphenylphosphonium bromide) [36] were prepared following the published procedures. 2,5-Dioctyl-3,6-bis[4-(1,3-dioxan-2-yl)phenyl]pyrrolo[3,4-*c*]pyrrole-1,4-dione (**2**) was synthesized with a slight modification according to the literature [23].

2.3. Syntheses of monomers and polymers

2.3.1. 3,6-Bis[4-[1,3]dioxolan-2-yl-phenyl]-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**1**)

After sodium (1.472 g, 64 mmol) was dissolved in 40 mL of *t*-amyl alcohol at about 100°C over 1 h with FeCl_3 (74 mg, 0.46 mmol), 4-[1,3]dioxolan-2-yl-benzonitrile (7.000 g, 40 mmol) was added, then diisopropyl succinate (3.232 g, 16 mmol) in 20 mL of *t*-amyl alcohol was added dropwise over 1 h. The resulting suspension was strongly stirred for 24 h at 100°C . After the mixture was cooled to room temperature, glacial acetic acid (16 mL) and methanol (200 mL) were added. The mixture was stirred for 4 h, then filtered, washed several times with methanol and water, dried in vacuo to give **1** as red solid (3.871 g, 56%); mp: $>300^\circ\text{C}$. Anal. calcd. for

$\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_6$ (432.43): C, 66.66; H, 4.66; N, 6.48. Found: C, 66.52; H, 4.67; N, 6.47. FTIR (KBr, cm^{-1}): 3139, 2983, 2867, 1640, 1601, 1565, 1515 1443, 1401, 1319, 1142, 1093, 1033, 939, 831, 804, 664.

2.3.2. 2,5-Dioctyl-3,6-bis[4-[1,3]dioxolan-2-yl-phenyl]pyrrolo[3,4-*c*]pyrrole-1,4-dione (**2**)

A mixture of **1** (3.456 g, 8 mmol), potassium tert-butoxide (1.975 g, 17.2 mmol) and 80 mL of dried NMP was heated to 60°C , then 1-bromooctane (9.264 g, 48 mmol) in 20 mL of NMP was slowly added, and the mixture was kept for 24 h at 60°C . After being cooled to room temperature, the mixture was filtered, and the solid was washed with 50 mL of ethyl acetate and water (50 mL \times 3). The organic layer was dried over anhydrous MgSO_4 , and then concentrated via rotary evaporation. The raw product was purified by column chromatography (petroleum/ethyl acetate, 1/5, v/v) followed by recrystallization in dichloromethane and methanol to give **2** as bright orange crystals (2.414 g, 46%); mp: 130 – 131°C . ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 7.81(d, 4H, Ar–H), 7.62 (d, 4H, Ar–H), 5.87 (s, 1H, Ar–CH), 4.14–4.04 (m, 8H, $-\text{OCH}_2$), 3.70 (t, 4H, $-\text{NCH}_2-$), 1.54 (br, 4H, $-\text{CH}_2$), 1.21 (br, 20H, $-\text{CH}_2$), 0.82 (t, 6H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 162.6, 148.1, 141.0, 128.8, 128.7, 126.9, 119.9, 103.0, 65.4, 41.9, 31.7, 29.4, 29.1, 29.0, 26.7, 22.6, 14.0. Anal. calcd. for $\text{C}_{40}\text{H}_{52}\text{N}_2\text{O}_6$ (656.85): C, 73.14; H, 7.98; N, 4.26. Found: C, 73.08; H, 7.94; N, 4.23. FTIR (KBr, cm^{-1}): 2924, 2854, 1668, 1603, 1511, 1455, 1427, 1381, 1345, 1307, 970, 944, 856, 834, 772, 655.

2.3.3. 2,5-Dioctyl-3,6-bis(4-formylphenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (**3**)

A mixture of **2** (1.968 g, 3 mmol), THF (30 mL) and HCl (2 M, 15 mL) was stirred for 2 h at 60°C . After being cooled to room temperature, 30 mL of ethyl acetate was added, washed with water and dried over MgSO_4 . After filtration, the solvent was evaporated and the crude product was purified by recrystallization in dichloromethane and methanol to give **3** (1.67 g, 98%); mp: 128 – 130°C . ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 10.08 (s, 2H, $-\text{CHO}$), 8.03–7.94 (m, 8H, Ar–H), 3.74 (t, 4H, $-\text{NCH}_2$), 1.54 (br, 4H, $-\text{CH}_2-$), 1.18 (br, 20H, $-\text{CH}_2$), 0.82 (t, 6H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 191.1, 162.2, 147.6, 137.6, 133.3, 129.9, 129.2, 111.0, 42.0, 31.6, 29.4, 29.0, 28.9, 26.6, 22.5, 14.0. Anal. calcd. for $\text{C}_{36}\text{H}_{44}\text{N}_2\text{O}_4$ (568.75): C, 76.02; H, 7.80; N, 4.93. Found: C, 76.10; H, 7.85; N, 4.97. FTIR (KBr, cm^{-1}): 2918, 2852, 2817, 2732, 1700, 1676, 1597, 1574, 1547, 1503, 1467, 1415, 1396, 1359, 1317, 1296, 1217, 965, 811, 763.

2.3.4. Poly(1,4-(2,5-dicyano)-phenylenevinylene-alt-2,5-dioctyl-3,6-bis(4-vinylphenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione) (P1)

A solution of sodium ethoxide (0.085 g, 1.25 mmol) in 5 mL of anhydrous ethanol was added to a stirred solution of **3** (0.284 g, 0.5 mmol) and 2,5-dicyano-1,4-xylene-bis(triphenylphosphonium bromide) (0.419 g, 0.5 mmol) in 5 mL of ethanol and 5 mL of chloroform at room temperature. The mixture was stirred for 24 h. The product was precipitated from methanol, filtered and then dissolved in chloroform, precipitated in methanol again. The crude product was purified by a Soxhlet extraction with methanol for 24 h to give P1 as red solid (286 mg, 83%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 7.92–6.59 (m, 14H, Ar–H, $-\text{CH}=\text{CH}-$), 3.72 (br, 4H, $-\text{N}-\text{CH}_2$), 1.54 (br, 4H, $-\text{CH}_2-$), 1.17 (br, 20H, $-\text{CH}_2-$), 0.82 (br, 6H, $-\text{CH}_3$). Anal. calcd. for $(\text{C}_{46}\text{H}_{48}\text{N}_4\text{O}_2)_n$: C, 80.20; H, 7.02; N, 8.13. Found: C, 80.29; H, 7.09; N, 8.13. FTIR (KBr, cm^{-1}): 2922, 2852, 2335, 1672, 1505, 1460, 1390, 1361, 1090, 1053, 960, 722.

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