Polymeric Alkoxy PBD [2-(4-Biphenyl)-5-Phenyl-1,3,4-Oxadiazole] for Light-Emitting Diodes**

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The syntheses are reported of the title polymeric alkoxyPBD derivative 5 and the dipyridyl analogue 12 using Suzuki coupling reactions of 1,4-dialkoxybenzene-2,5-diboronic acid with 2,5-bis(4-bromophenyl)-1,3,5-oxadiazole, and its dipyridyl analogue, respectively. Thermal gravimetric analysis shows that polymers 5 and 12 are stable up to 370 °C and 334 °C, respectively. Films of polymer 5 spun from chloroform solution show an absorption at $\lambda_{\text{max}} = 367$ nm, and a weaker band at 312 nm, and strong blue photoluminescence at $\lambda_{\text{max}} = 444$ nm. The photoluminescence quantum yield (PLOY) was found to be 27 ± 3 %. For polymer 12, the absorption spectra reveal bands of equal intensity at $\lambda_{\text{max}} = 374$ and 312 nm, with PL at $\lambda_{\text{max}} = 475$ nm. Device studies using polymer 12 were hampered by its instability under illumination and/or electrical excitation. Polymer 5 is stable under these conditions and acts as an efficient electron-transporting/hole-blocking layer. For devices of configuration ITO/PEDOT/MEH-PPV/polymer 5/Al an external quantum efficiency of 0.26 % and brightness of 800 cd/m$^2$ was readily achieved: orange emission was observed, identical to the MEH-PPV electroluminescence.

1. Introduction

2-(4-Biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD) and its tert-butyl derivative (Bu-PBD) have been known as laser dyes for decades due to their high photoluminescence (PL) quantum efficiencies. During the past ten years, a new area of research also requiring highly fluorescent materials, namely polymer light-emitting diodes (LEDs),[1] has attracted extensive attention due to potential applications in display technologies.[2] An optimized LED requires efficient and balanced charge injection from both electrodes, comparable transporting properties of both holes and electrons, and a high quantum efficiency for the radiative decay process. Owing to their electron-deficient nature, molecular and polymeric derivatives of 1,3,4-oxadiazole have been explored in this context as electron-transporting/hole-blocking materials in addition to their potential for light-emission.[3–5] Most importantly, Heeger et al. reported that by blending Bu-PBD with poly(p-phenylenevinylene) (PPV) or poly[2-methoxy-5-(2′-ethyl-hexoxy)-p-phenylene vinylene] (MEH–PPV) electroluminescence efficiencies could be doubled to 50 % of the corresponding photoluminescence.[6] We therefore anticipated that a polymer containing PBD as the repeating unit would exhibit interesting material and photophysical properties. We note that some diaryl-1,3,4-oxadiazole units have been incorporated into polymers either in the main chain or as pendants.[7] Among them, a methacrylate copolymer bearing pendant PBD substituents has been studied,[8] and recently PPV analogues bearing diaryl-1,3,4-oxadiazole[9] and bis(1,3,4-oxadiazole)[10] units normal to the main chain have been reported. We now report the synthesis and photophysical properties of alkoxy-solubilized poly(PBD) (5) and its application as an electron transport/hole blocking layer in LEDs. To the best of our knowledge, conjugated polymeric PBD has not been synthesized previously, so polymer 5 represents a new structural class of oxadiazole polymers. We also describe the pyridine analogue of poly(PBD), namely, polymer 12. The reason for preparing 12 was that we have demonstrated that the introduction of pyridine units into poly(p-phenylene) type polymers improves electron-transporting properties of these materials.[11,12]

2. Results and Discussion

The synthesis of polymers 5 and 12, shown in Schemes 1 and 2, respectively, proceeded via a copolymerization of bis(bromophenyl)oxadiazole (4) or its pyridine analogue (10) with diboronic acid (3) via Suzuki coupling reactions. A model reaction for the polymerization leading to compound 11 was performed and the structures of both the polymers are well established by $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectroscopy, and by CHN analyses. The thermal properties of both polymers 5 and 12 were determined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA traces show that polymers 5 and 12 are stable up to 370 and 334 °C, respectively, to a weight loss of 5 %. Above these temperatures the polymers decomposed significantly to a residual mass of ca. 40 %. Measured by DSC, the
glass-transition temperature \( (T_g) \) of polymers 5 and 12 were 196 and 113 °C, respectively. A melting process was observed for 5 at 260 °C, while polymer 12 did not melt below 300 °C. Low-angle X-ray diffraction (XRD) experiments suggest that films of polymers 5 and 12 are amorphous.

The photophysical properties of both polymers 5 and 12 were studied. The absorption and PL spectra of a film of polymer 5 spun from chloroform solution are shown in Figure 1. The absorption shows a maximum at 367 nm and a second weaker but still well-defined band at 312 nm. The main absorption band is slightly blue-shifted with respect to polypyridine, but red-shifted with respect to the pyridine/phenylene copolymers that we have previously reported.[11] The additional absorption at 312 nm has however, no correspondence in the pyridine/phenylene containing copolymers[11] or in polypyridine. The film shows strong blue PL with a maximum at 444 nm, 0.586 eV lower in energy than the 367 nm absorption profile. PBD in solution absorbs at 300 nm and emits at 380 nm (in cyclohexane with 2 % chloroform).[14] The redder spectra in polymer 5 are due to the extended electron delocalization caused by polymerization, and the substituent effects of the alkoxy groups. The PL quantum yield (PLQY) of a spun film of polymer 5 was measured using an integrating sphere and was found to be 27 ± 3 %.

Figure 2 shows the absorption and PL spectra of a film of polymer 12 spun from chloroform solution. The absorption of the film consists of two equally strong bands at 374 nm and 312 nm. The PL of the film has a maximum at 475 nm, which is significantly red-shifted as compared to the emission of the polymer 5. Furthermore, the PL has a much more pronounced red tail than for polymer 5. Our subsequent studies of this polymer were hampered by problems of stability under illumination and/or electrical excitation. The PLQY of polymer 12 was hard to estimate as the film degraded during the course of the experiment, but we estimate the PLQY to be approximately 6 % with substantial errors. A possible explanation for this degradation could be a cleavage of the polymer chain hence causing instability of the sample and resulting in the low PLQY. Initial studies showed an increased device efficiency compared to single layer MEH–PPV, but the instability of 12 in solution and as a thin film precluded further device studies.

We have investigated polymer 5 as an electron-transporting polymer in bilayer LEDs. Devices were fabricated with MEH–PPV as the light-emitting layer on top of which a layer of the polymer 5 was spun. The electron-deficient nature of the oxadiazole ring makes it an ideal candidate for an electron-transporting/hole-blocking layer. In order to facilitate hole injection, indium tin oxide (ITO) was coated with a layer of poly(3,4-ethylene-
4. Experimental

**General:** 2,5-Bis-(4-bromophenyl)-1,3,5-oxadiazole was prepared as white crystals by dehydration of NO2-bis-(4-bromobenzolic) hydrazide with phosphorous pentoxide under reflux, melting point (m.p.): 258.9–259.2 °C [15]. The latter compound was prepared from a reaction of 4-bromobenzolic hydrazide and 4-bromobenzolic chloride in dry pyridine. 4-Bromobenzolic hydrazide and 4-bromobenzolic chloride were purchased from Aldrich and were used without further purification. 2,5-Dibromohydroquinone and it was prepared from benzoquinone and hydrobromic acid using the procedure as reported [16]. Pd(PPh3)4 was used as the catalyst in polymerizations was prepared as bright yellow crystals as reported [17], while Pd(PPh3)2Cl2 was purchased from Avocado. All the palladium-catalyzed reactions were carried out under argon atmosphere.

The thickness of the MEH–PPV layer was 90 nm and the film of polymer 5 was 20 nm thick. For single-layer polymer devices a 50 nm layer was used. Aluminun cathodes were evaporated through a shadow mask under pressures of typically 10–4 mbar to define an active area of 2 mm². Current–voltage–light output characteristics were measured using a Keithley source-measure unit and multimeter, and the electroluminescence spectrum was measured with a CCD spectrometer. The thickness of the MEH–PPV layer was 90 nm and the film of polymer 5 was 20 nm thick. For single-layer polymer devices a 50 nm layer was used. Aluminum cathodes were evaporated through a shadow mask under pressures of typically 10–4 mbar to define an active area of 2 mm². Current–voltage–light output characteristics were measured using a Keithley source-measure unit and multimeter, and the electroluminescence spectrum was measured with a CCD spectrometer.

**Polymer 5:** To the mixture of compounds 3 [13] (0.6333 g, 1.5 mmol) and 4 (0.5701 g, 1.5 mmol) was added freshly distilled dimethylformamide (DMF) (50 mL) and the mixture was purged with argon for 15 min. Pd(PPh3)4 (100 mg), and 1 M Na2CO3 solution (7.5 mL) was added sequentially. The flask was wrapped in Al foil and the mixture was stirred at 80 °C under argon to obtain a light gray suspension. The mixture was cooled to room temperature, and water (30 mL) was added slowly with stirring. The light gray solid collected by suction filtration was washed with water and methanol. The solid was dissolved in chloroform (10 mL) then filtered through a Celite column. The filtrate was dropped into stirred methanol (250 mL) and the mixture was left standing overnight. Suction filtration followed by drying under high vacuum at 50 °C yielded polymer 5 as a light gray solid (0.65 g, 78 %). Anal. found (calcd. C20H15N3O3S3): C 77.71 (78.23), H 7.95 (8.02), N 5.05 (5.07). Br 0 (1). 1H NMR (CDCl3) δ [ppm]: 0.80–0.90 (m, 6H), 1.20–1.40 (m, 8H), 1.67 (m, 1H), 3.91 (d, J = 4.8 Hz, 2H), 7.08 (s, 1H), 7.28 (d, J = 7.8 Hz, 2H), 8.28 (d, J = 8.1 Hz, 2H). 13C NMR (CDCl3) δ [ppm]: 111.15, 140.23, 23.03, 23.08, 20.09, 39.58, 71.65, 115.44, 122.39, 126.49, 130.16, 130.25, 141.83, 150.45, 164.61. A gel permeation chromatography (GPC) measurement (THF eluent, polystyrene as standard) indicated Mw = 15800 and polydispersity (PD) = 2.0.

**4-(2-Bromo-5-phenyl)-2-methyl-3-butyen-2-ol:** To the solution of 2,5-dibromopyridine (9.48 g, 40 mmol) and 2-methyl-3-butyen-2-ol (3.36 g, 40 mmol) in dry THF (150 mL) was added dropwise a 60% aqueous solution of triethylamine (22.56 %), 240 (4.33 %), 241 (21.71 %), 242 (2.45 %). 1H NMR (CDCl3) δ [ppm]: 1.53 (s, 6H), 4.81 (s, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.64 (d, JAB = 8.4 Hz, JAC = 2.4 Hz, 1H), 8.51 (d, J = 2.4 Hz, 1H). 13C NMR (CDCl3) δ [ppm]: 30.84, 64.63, 73.94, 96.02, 119.66, 127.72, 138.72, 140.93, 150.44.

3. Conclusion

In conclusion we have synthesized conjugated polymeric PBD and demonstrated that it is an efficient electron transporting material for applications in polymer electronics. Replacing phenylene units with pyridylenes in the polymer does not improve the electron transporting properties.
5-Bromopyridine-2-carboxylic Acid 8: Compound 7 (6.83 g, 28.45 mmol) was suspended in water (250 mL) and the mixture was heated to ca. 90 °C. K<sub>2</sub>CO<sub>3</sub> powder (15 g) was added in small portions with vigorous stirring until the purple color persisted. The mixture was then heated and stirred for an additional 1 h at 100 °C, followed by a suction filtration to remove the resulting MnO<sub>2</sub> solids. The colorless filtrate was concentrated by vacuum distillation (yield 11.64 (11.47)). 1H NMR (CDCl<sub>3</sub>, 200 MHz) δ ppm: 7.99 (d, J = 8.7 Hz, 1H), 8.25 (dd, J<sub>1</sub> = 8.4 Hz, J<sub>2</sub> = 4.1 Hz, 1H), 8.83 (dd, J<sub>1</sub> = 2.4 Hz, J<sub>2</sub> = 0.6 Hz, 1H). 13C NMR (DMSO-d<sub>6</sub>) δ ppm: 123.90, 124.77, 140.10, 147.10, 150.36, 156.56.

2,5-Bis(5-bromo-2-pyridyl)-1,3,4-oxadiazole 10: Compound 9 (0.90 g, 2.25 mmol) was mixed with polyphosphoric acid (ca. 10 mL) and P<sub>2</sub>O<sub>5</sub> (1 g) and the mixture was stirred at 20 °C for 2 min then 1 M Na<sub>2</sub>CO<sub>3</sub> (3 mL), after vigorous stirring at 85 °C for 48 h and 100 °C for 12 h. The yield of 12 after purification was 0.52 g (94 %). Anal. found (calcd.) C<sub>12</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub>, M = 216.18, C 72.10, H 2.77, N 25.03, C 72.10, H 2.77, N 25.03. 1H NMR (CDCl<sub>3</sub>, 200 MHz) δ ppm: 3.19, 3.77, 123.32, 126.35, 126.98, 133.69, 134.99, 138.74, 141.55, 148.87, 152.34, 164.57.

Polymer 12: By analogy with the preparation of polymer 5, polymer 12 was synthesized from diboronic acid 3 (0.422 g, 1 mmol) and compound 10 (0.382 g, 1 mmol) in freshly distilled DMF (50 mL), in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (72 mg) and 1 M Na<sub>2</sub>CO<sub>3</sub> (3 mL), after vigorous stirring at 85 °C for 48 h and 100 °C for 12 h. The yield of 12 after purification was 0.52 g (94 %). Anal. found (calcd.) C<sub>12</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub>, M = 216.18, C 72.10, H 2.77, N 25.03, C 72.10, H 2.77, N 25.03. 1H NMR (CDCl<sub>3</sub>, 200 MHz) δ ppm: 0.87 (t, J = 5.2 Hz, 2H), 1.26–1.43 (m, 8H), 1.69 (m, br. 1H), 3.93 (d, J<sub>1</sub> = 4.0 Hz, 2H), 7.09 (s, 1H), 8.17 (d, J<sub>1</sub> = 8.2 Hz, 1H), 8.43 (d, J<sub>1</sub> = 8.0 Hz, 1H), 9.06 (s, 1H). 13C NMR (CDCl<sub>3</sub>, 200 MHz) δ ppm: 11.05, 13.98, 22.93, 29.87, 30.56, 39.36, 74.81, 115.09, 122.53, 127.47, 136.32, 137.19, 141.60, 150.77, 150.87, 164.66. GPC using polystyrene as standard indicated that Mn = 16 000, M<sub>n</sub> = 26 600, M<sub>w</sub> = 51 200, and PD = 1.66.

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