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Blue-emitting copolymers of isoquinoline and fluorene

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ABSTRACT

5,8-Linked copolymers of isoquinoline with fluorene were synthesized by Pd(0)-catalyzed Suzuki polycondensation reaction. The polymers showed good solubility in common organic solvents and the number average molecular weights determined from GPC analysis fall in the range of 7.03–8.08 $\times 10^3$ g/mol. The photoluminescence spectra of these neutral materials in solution exhibit emission maxima in the range 408–426 nm. An X-ray diffraction study on a single crystal of a 5,8-di(9,9-dimethylfluoren-2-yl) isoquinoline model compound shows it to have a non-planar conformation and sheds light on the factors that drive the solid-state packing. The alkylation of the imine nitrogen was achieved by treatment with methyl iodide and the alkylated products were characterized by ^{1}H NMR, ^{13}C NMR and UV–vis spectroscopy. The absorption maxima of model compounds and polymers were red shifted by 46–70 nm upon *N*-alkylation.

1. Introduction

The optical and electronic properties of polymers containing *N*-heterocyclic moieties have been studied extensively for their potential use in organic light emitting diodes (OLEDs), organic solar cells and chemical sensors [1–4]. Quinoline, quinoxaline, oxadiazole and pyridine derivatives have been widely used as electron transporting/hole blocking materials in LED devices and LED blends because these types of units have excellent properties such as high electron affinity, high thermal and oxidation stability, and good charge injection [5–8]. Within the class of conjugated polymers, materials containing *N*-heterocyclic moieties have attracted considerable attention not only because of their electron-accepting abilities but also for the possibility of metal complexation, *N*-oxidation, *N*-protonation, and *N*-alkylation, leading to polymers with unique properties that are different from neutral polymers [4,9–14]. Recently, Swager and Izuhara have reported on a new class of nitrogen-containing polyheterocycles with high electron affinity [15,16]. Polyquinolines have been widely studied as *n*-type semiconductors and emissive materials in electronic devices [17–22]. Compared to quinoline based materials, there have been limited reports on materials derived on isoquinoline for electronic applications [23–26]. Recently, isoquinoline based metal complexes have been studied for their potential application in phosphorescence-based organic and polymeric light-emitting devices [27–29]. Apart from a few reports on polyisoquinolines, synthesis and opto-electronic properties of oligomers or polymers bearing isoquinoline moieties with a 5,8-linkage in the conjugated backbone have not yet been explored. In this contribution, the synthesis, characterization and optical studies of model compounds and copolymers derived from isoquinoline and dialkylfluorene have been investigated. Oligo- and polyfluorenes have emerged as the most attractive blue-emitting materials due to their high efficiency and good thermal stability of polymers [30–37]. Combining the electron affinity of isoquinoline and blue light-emitting nature of highly soluble polyfluorenes, the copolymers are expected to possess good solubility, thermal stability and blue light-emitting properties. The absorption maxima of neutral polymers can be extended by introduction of cations into the polymer backbone. In a previous study, we reported on the synthesis of conjugated polyfluorenyl cations and the control of cation density and solubility by copolymerization [38]. In the case of isoquinoline based materials, the presence of an electron deficient nitrogen atom offers the possibility to tune the optical properties by *N*-alkylation. *N*-alkylation is widely investigated as a means to tailor the optical properties of polyquinoline and polypyridine derivatives. The *N*-alkylated polymers bearing cations in the backbone have exhibited a red shift in absorption maxima as compared to their neutral polymers [13,34,39]. Isoquinoline with different linkage positions offers the possibility to synthesize novel organic materials with tunable optical properties. In this study, copolymers and model compounds of 5,8-linked isoquinoline with fluorene have been prepared, their optical and thermal properties investigated, and the solid-state structure of a model compound

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determined. In addition, conjugated polycations formed by *N*-alkylation of the isoquinoline unit are discussed.

2. Experimental

2.1. Materials

Dry solvents, stored in a glove box, were used for specified reactions. 5,8-dibromoisoquinoline (**2**) and 5-bromoisoquinoline (**3**) were synthesized according to literature procedures [40]. 9,9-Dimethylfluorene-2-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane) (**4**), 2,7-bis(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane)-9,9-dimethylfluorene (**5**), 2,7-bis(4,4,5,5-tetramethyl-[1,3,2]-dioxaboralan-2-yl)-9,9-dioctylfluorene (**8a**) and 2,7-bis(4,4,5,5-tetramethy-[1,3,2]-dioxaboralan-2-yl)-9,9-bis(2-ethylhexyl)fluorene **(8b)** were also synthesized in accordance with literature procedures [41–44].

2.2. Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer operating respectively at 300 MHz for ^{1}H and 75 MHz for ^{13}C NMR using deuterated solvents with tetramethylsilane (TMS) as a reference. UV–vis absorption spectra were recorded in THF solution on a Perkin-Elmer Lambda 25 Spectrophotometer. Photoluminescence measurements were carried out with a Fluorolog HORIBAJOBIN YVON spectrophotometer using a xenon-arc lamp as a source, in THF solution. Thermal degradation was studied by TGA on a Perkin Elmer Pyris 7 thermal analysis system under a dynamic atmosphere of nitrogen at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) data were recorded using a TA DSC Q200 calibrated with indium at heating/cooling rates of 10 °C min^{-1} under nitrogen. The molecular weights of the polymers were determined by Gel Permeation Chromatography against polystyrene standard in THF at 30 °C. The cyclic voltammetric studies were conducted on an Autolab 30, Potentiostat/Galvanostat at a constant scan rate of 20 mV s^{-1}. Platinum wires were used as both the counter and working electrodes, and Ag/AgCl electrode was used as the reference electrode. Thin films of copolymers **9a** and **9b** on platinum electrodes were prepared by dipping the electrode into a 0.5–1.0 wt.% copolymer solution in toluene. The resulting films were dried in a vacuum oven at 80 °C. Cyclic voltammogram of **12a** and **12b** were taken from a solution of corresponding compounds in 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in acetonitrile, which was used as the electrolyte.

2.3. Synthesis of model compounds

2.3.1. Synthesis of 5,8-di(9,9-dimethylfluoren-2-yl) isoquinoline (*6*)

5,8-dibromoisoquinoline **2** (0.25 g, 0.87 mmol), 9,9-dimethyl fluorene-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **4** (0.84 g, 2.63 mmol), 2 M K_2CO_3 (2.6 mL, 5.22 mmol) were added to 5 mL of 1,4-dioxane in a Schlenk flask. The solution was purged with N_2 for 15 min, and then $Pd(PPh_3)_4$ (0.06 g, 2 mol%) was added. The reaction mixture was heated with stirring at 100 °C. The reaction was followed by TLC and after 20 h was worked up. The cooled reaction mixture was extracted into chloroform and the organic layer was washed with brine and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with 0–10% ethyl acetate in hexane as the eluent, to give **6** as a white solid (0.32 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.47 (s, 1H), 8.45 (d, 1H, J = 6 Hz), 7.88 (m, 3H), 7.83–7.79 (m, 3H), 7.70 (d, 1H, J = 7.2 Hz), 7.64 (s, 1H), 7.59–7.49 (m, 5H), 7.39–7.35 (m, 4H). ^{13}C NMR (75 MHz): δ = 154.03, 153.96, 153.85, 151.61, 143.04, 140.78, 139.06, 138.91, 138.66, 138.01, 137.64, 134.73, 130.50, 129.10, 128.89, 127.87, 127.53, 127.10, 124.46, 124.25, 122.66, 120.19, 120.03, 118.71, 47.01, 27.19.

2.3.2. Synthesis of 2,7-di(isoquinol-5-yl)-9,9-dimethylfluorene (*7*)

In a Schlenk flask, 5-bromoisoquinoline **3** (0.28 g, 0.63 mmol), 2,7-bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)-9,9-dimethylfluorene **5** (0.46 g, 2.20 mmol), 2 M K_2CO_3 (4.6 mL, 9.19 mmol) and 6 mL of 1,4-dioxane were taken and purged with N_2 for 15 min. Then, $Pd(PPh_3)_4$ (0.06 g, 2 mol%) was added and the reaction mixture was heated with stirring at 100 °C for 20 h. The cooled reaction mixture was extracted into chloroform and the organic layer was washed with brine and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with 0–20% ethyl acetate in hexane as the eluent, to give **7** as a yellow solid (0.15 g, 53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.34 (s, 2H), 8.54 (d, 2H, J = 5.7 Hz), 8.04 (d, 2H, J = 8.1 Hz), 7.94 (d, 2H, J = 7.8 Hz), 7.85 (d, 2H, J = 5.7 Hz), 7.79 (d, 2H, J = 6.9 Hz), 7.73 (t, 2H, J = 7.35 Hz), 7.59 (s, 2H), 7.53 (d, 2H, J = 7.5 Hz). ^{13}C NMR (75 MHz): δ = 154.24, 152.92, 143.42, 139.49, 138.35, 138.26, 134.18, 130.96, 129.02, 127.11, 126.82, 124.26, 120.19, 118.54, 47.16, 27.21.

2.4. Synthesis of polymers

2.4.1. Synthesis of *9a*

A mixture of 5,8-dibromoisoquinoline **2** (0.25 g, 0.87 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-9,9-dioctylfluorene **8a** (0.56 g, 0.87 mmol) and $Pd(PPh_3)_4$ (0.020 mg, 2 mol%) were added to a degassed mixture of toluene (3 mL), Aliquat 336 (3 drops) and 1.7 mL of 2 M Na_2CO_3. The mixture was vigorously stirred at 85 °C for 48 h under a nitrogen atmosphere. Then, bromobenzene (45 μL, 0.43 mmol) was added as an end capping agent to the mixture and heated for an additional 12 h. After cooling to room temperature, the viscous solution was poured into 300 mL of methanol. The precipitated polymer was isolated by filtration. It was further purified by Soxhlet extraction with acetone followed by reprecipitation from methanol. The polymer was dried under reduced pressure to yield **9a** as a pale yellow solid (0.36 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.51 (s, 1H), 8.57 (d, 1H), 7.99–7.89 (4H, br), 7.74 (s, 1H), 7.62–7.59 (5H, br), 2.11 (4H, br), 1.17–0.82 (m, 30H, br). UV–vis (THF) λ_{max}: 358 nm, GPC: M_n = 8.08 × 10^3 g/mol, PDI = 2.85.

2.4.2. Synthesis of *9b*

A mixture of 5,8-dibromoisoqunoline **2** (0.26 g, 0.90 mmol), 2,7-bis(4,4,5,5-tetramethy-1,3,2-dioxaboralan-2-yl)-9,9-bis(2-ethylhexyl) fluorene **8b** (0.58 g, 0.90 mmol) and $Pd(PPh_3)_4$ (0.021 mg, 2 mol%) were added to a degassed solution of toluene (3 mL), Aliquat 336 (three drops) and 1.8 mL of 2 M Na_2CO_3. The mixture was stirred vigorously at 85 °C for 48 h. Bromobenzene (47 μL, 0.45 mmol) was then added as end capping agent to the mixture and further heated for 12 h with stirring. The reaction mixture was cooled to room temperature and the viscous solution poured into 300 mL of methanol. The precipitated polymer was isolated by filtration and purified by Soxhlet extraction with acetone followed by reprecipitation from methanol. The polymer was dried under reduced pressure to give **9b** in 78% yield (0.36 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.53 (s, 1H), 8.55 (d, 1H), 7.97–7.60 (m, 9H), 2.13 (t br, 4H), 1.00–0.66 (m br, 30H). UV–vis (THF) λ_{max}: 354 nm, GPC: M_n = 7.03 × 10^3 g/mol, PDI = 3.04.