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Novel Fluorene-based Conjugated Copolymer Containing Cyclobutenedione Unit for Light Emitting Diodes

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Abstract: A novel fluorene-based conjugated copolymer containing cyclobutenedione unit was synthesized by Suzuki reaction. Its structure and properties were characterized by FTIR, ^{1}HNMR, elemental analysis, PL spectroscopy, DSC, TGA and cyclic voltammetry. The resulting polymer shows strong yellow PL emission (561 nm) and good solubility in polar aprotic solvents, *i.e.* THF, DMF, DMAC, DMSO, *etc.* DSC and TGA studies reveal that the novel polymer possesses excellent thermal stability with high glass transition temperature of 127 ℃ and onset decomposition temperature of 411℃. Cyclic voltammetry measurement demonstrated that the polymer has both hole and electron-transporting property.

Keywords: Fluorene-based copolymer, cyclobutenedione unit, light-emitting diodes.

Since the discovery of polymeric light-emitting diodes (PLEDs) by the Cambridge group[1], great progress has been made in the field of PLEDs due to their potential application in display industry.

Recently, fluorene-based conjugated polymers have emerged as very promising candidates for PLEDs[2] because of their combined desirable properties, such as high fluorescence quantum yield, good film-forming and hole-transporting properties. Moreover, color-tuning and carrier-balance can be achieved by incorporating an electron-deficient monomer into the polymer backbone.

Squaric acid (1, 2-dihydroxycyclobutene-3, 4-dione) has a simple aromatic structure and should be regarded as a novel aromatic compound. As a consequence, the four-membered ring system of squaric acid has been studied widely in many fields, such as electrophotography[3], solar energy conversion[4] and nonlinear optics[5], for its excellent electronic properties.

Herein, we designed a novel fluorene-based conjugated copolymer containing cyclobutenedione unit: poly{(9,9-dehexylfluorene-2,7-diyl)-alt-[3,4-bis(*p*-phenylene)-3-cyclobutene-1,2-dione]} (PFCD) (shown in Figure 1), which was expected to have the following characteristics: (ⅰ) an improved electron-withdrawing characteristic of cyclobutenedione moiety incorporated into polyfluorene backbone to increase the electron affinity of the resulting polymer and (ⅱ) a high delocalized electronic state of

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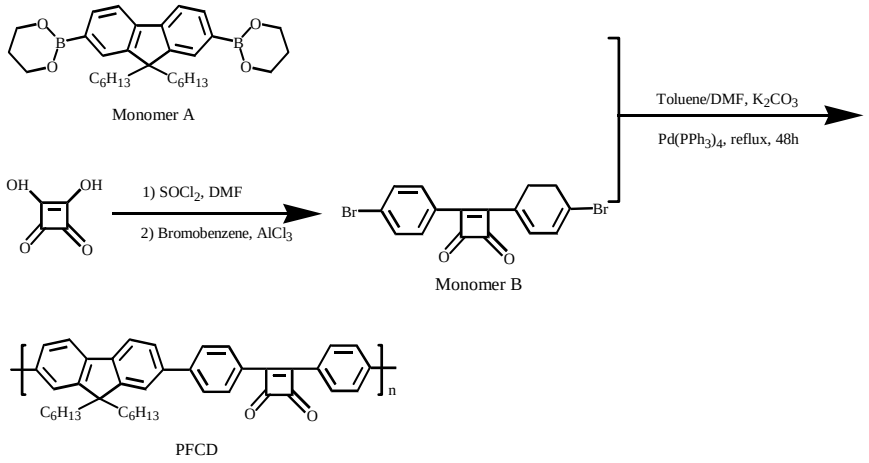
cyclobutenedione to control the π-conjugation length and realize the color-tuning of polyfluorene. PFCD was synthesized by Suzuki coupling reaction, it is expected to be prospective material for PLED application. The synthetic route for novel polymer PFCD are given in **Figure 1.**

Figure 1 Synthetic route for PFCD



Synthesis and Characterization

Monomer A: 9, 9-Dihexylfluorene-2, 7-bis(trimethylene boronate), was synthesized from 2, 7-dibromofluorene as the starting material[6].

Monomer B: 3, 4-Bis(4-bromophenylene)-3-cyclobutene-1, 2-dione), was prepared by Friedel-Crafts reaction of bromobenzene and squaryl dichloride obtained by treatment of squaric acid with $SOCl_2$[7].

Polymer PFCD: The polymerization was carried out through palladium-catalyzed Suzuki condensation between monomer A and B in the presence of K_2CO_3. The polymerization condition is as follows: Under an argon atmosphere, monomer A (0.502 g, 1 mmol), monomer B (0.392 g, 1 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), toluene (2.5 mL), DMF (2.5 mL) and 2 mol/L K_2CO_3 (5 mL) were placed in a three-necked flask and refluxed for 48 hr. After cooling, the mixture was poured into 200 mL of methanol and deionized water (10:1). A fibrous solid was obtained by filtration. The solid was washed with methanol, water and then methanol. After washing for 24 hr in a Soxhlet apparatus with acetone to remove the oligomers and the catalyst residues, the resulting polymer was obtained as greenish-yellow powders (406 mg, 72%). Anal. Calcd for $(C_{41}H_{40}O_2)_n$: C, 87.19%; H, 7.08%. Found: C, 86.74%; H, 7.23%. ^{1}H NMR (400Mz, DMSO, ppm): δ 8.02-7.99 (m, 4H), 7.91-7.64 (m, 6H), 7.42-7.34 (m, 4H), 2.5 (br, 4H), 1.23-0.64 (m, 22H). FT-IR (KBr, ν cm^{-1}): 2928, 2854, 1692, 1649, 1601, 1511, 1465, 1402, 1316, 1248, 1211, 1170, 1088, 1018, 816.

Results and Discussion

PFCD has good solubility in polar aprotic solvents, *e.g.* THF, DMF, DMSO. However, the polymer has very poor solubility in other organic solvents, such as $CHCl_3$, $CHCl_2$, toluene. Thus, PFCD is a promising material to make multi-layer PLEDs. The molecular weights of the polymer determined by gel permeation chromatopraphy (GPC) against the polystyrene standards in THF are M_w=25670 and M_n=23155 (polydispersity, 1.11). The thermal properties of the polymer were determined by TGA and DSC measurements. TGA result (heating at 10℃ min^{-1} in nitrogen) reveals that PFCD has good thermal stability with the onset decomposition temperature (Td) of 411℃. The DSC thermogram of this polymer shows a clear glass transition at 126℃, which is much higher than that of typical polyfluorene (PF) (~55℃) [8].

Figure 2 Cyclic voltammogram of PFCD in CH_3CN

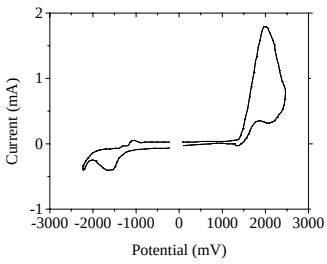
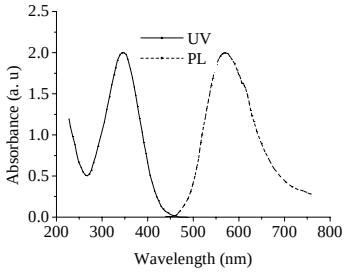


Figure 3 UV-Vis absorption and PL of PFCD in film



The electrochemical behavior of PFCD was investigated by cyclic voltammetry (shown in Figure 2). On sweeping the polymer cathodically, the onset of the n-doping process occurs at the potential of –1.24 V and gives a reduction peak at –1.63 V. In the anodic scan, the p-doping process onsets at 1.40 V, and then gives an oxidation peak at 1.97 V. Thus, the energy band gap of the polymer (E_g) can be estimated to be 2.65 eV. The HOMO and LUMO energy levels can be estimated as –5.80 and –3.16 eV from the p-doping and n-doping onset potentials, respectively. Comparing with PFs, PFCD is more electronegative, which could be attributed to the electron-withdrawing property of cyclobutenedione unit.

The UV-Vis absorption and photoluminescence (PL) spectra of PFCD as film (spun-cast from a solution in THF at the concentration of 30 mg mL^{-1}) on microslides are shown in Figure 3. The absorption onsets at 468 nm and exhibits a maximum peak at 346 nm. From the onset wavelength, the optical band gap of the polymer can be estimated to be 2.65 eV. This result is consistent with that determined by cyclic voltammetry measurement. The film can emit intensive yellow fluorescence under the irritation of UV light. The PL spectrum exhibits a maximum peak at 569 nm.

In conclusion, a novel fluorene-based copolymer containing cyclobutenedione unit, PFCD, was prepared through Suzuki coupling polymerization. This polymer shows good thermal stability and film-forming property. It's strong PL indicated that it could

be used as light emitting material. Intensive studies on the electroluminescent property of this polymer in PLEDs are in progress.

Acknowledgment

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