An efficient synthesis of 3,4-Dihydrofuro [3,4-B] [1,4] dioxepine-6,8-dicarboxylic Acid

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Abstract. As a class of important conjugated polymers, electroluminescent material of polyfuran possess a lot of merits, including good stability, structure is easy to be modified and controllable electrochemical properties. This study uses ethylene diglycol, diethyl oxalate, 1,3-dibromopropane and so on as raw materials to synthesize 3,4-ethylenedioxy furan monomer and similar derivatives via oxidation, acetylation, hydrolysis and elimination reaction, etc.

1. Introduction
Conjugated polymer materials, as a new type of light-emitting body, has aroused great concern in the material and chemical industry because of its great application prospects in lighting, display device and so on. Compared with the current widely used fluorescent lamp and LCD display device, polymer light-emitting-diode (PLED) has characteristics of low energy consumption, simple manufacturing process, flexible, low-cost, colorful and tremendous market potential [1-3].

One of the most important applications of organic electroluminescence is realization of full-color display device to replace the traditional display. Red, green and blue are the basic colors of full-color display [4]. Among them, green fluorescent polymer materials such as P-PPV has made great progress in brightness and efficiency, but there is still space for improvement in material color purity and efficiency of the device [5-7]. In recent years, organic conjugated small molecule compounds gradually become the focus of study, this kind of material with determination of molecular structure, controllable synthesis, good repeatability, monodisperse, stable glass state and good film-forming properties, these characteristics make it can be applied in organic electro luminescence device and become a potential material [8-9].

As a new generation of information functional materials, organic polymer semiconductor materials have attracted worldwide attention and become the object of research and development that more and more research institutions competing for [10]. The study on organic polymeric semiconductor materials is mainly focused on the small molecules which can be deposited by evaporation or the polymer which can be processed by solution. Due to the expensive equipment and complex process, more and more research is focused on the polymer. Because of its wide range of material selection, solution processing(can use some low-cost processing methods, such as spin coating, inkjet printing, screen printing, static pulling, etc.), easy fabrication of large area devices, and good flexibility, the polymer semiconductor materials have attracted extensive attention [11-13]. By spin coating although can get uniform large area devices, but as solvent volatilizing speed too fast in the film-forming process and the donor material P3HT can not form a sufficient crystallization in the process of
precipitation, cause the P3HT in the mixed film of the photosensitive layer did not form a good hole transport channel, so the efficiency of the device is usually very low [14-15].

Most of the electrochromic materials are printing and spraying in the traditional organic solution, printing and spraying of low steam pressure in water is a big challenge [16]. EDOT of side chain hydroxyl or carboxyl extension is very stable in aqueous phase, with super high conductivity, strong side chain function, can be converted into other groups, strong biological coupling ability and electrochemical polymerization is very easy to occur in conventional electrolytes [17-19]. In 2010, John R. Reynolds reported that after the side chain has been functionalized, the electroluminescent material can be sprayed in the water solution, which can reduce the environmental pollution and cut the cost [20].

Figure 1. The structures of the materials

If we can further optimize the structure of the conjugated polymer and increase the molecular order or reduce the disorder to enhance the mobility of the carrier, the photoelectric conversion efficiency of polymer will be further improved. In view of D-A type polymers can regulate the intensity of intra molecular charge transfer by selecting appropriate donor and receptor, makes the D-A conjugated polymers exhibit properties such as narrow band gap, broad spectrum absorption, high electron affinity and low ionization energy, high migration rate and so on. In order to synthesize new type of optoelectronic materials, project team has synthesized three new compounds, namely, diethyl-3,4-dihydroxyfuran-2,5-dicarboxylate; 3,4-dihydrofuro[3,4-b][1,4]dioxepine-6,8-dicarboxylate; 3,4-dihydrofuro[3,4-B][1,4]dioxepine-6,8-dicarboxylic acid

2. Experimental Section

2.1. Materials and Characterization
Methanol was dried over CaH₂ and then distilled prior to use in synthesis. Ethylene diglycol was purchased from Energy Chemical Co. and were used as received. Other solvents and reagents were analytical grade and purchased from Energy Chemical Co. and used without further purification.¹H and ¹³C NMR spectra were obtained with a mercury-300 spectrometer with tetramethylsilane (TMS) as the internal reference and chloroform-d (CDCl₃) or DMSO as solvent. The mass spectra were determined on a Daltonics Esquire 6000 spectrometer.
2.2. Synthesis

\[ \begin{align*}
\text{(I)} & \quad \overset{a}{\underset{\text{CH}_3\text{OH}}{\text{CH}_2\text{COOH}}} \quad \overset{b}{\underset{\text{CH}_3\text{OOC}}{\text{CH}_2\text{COOH}}} \\
\text{(II)} & \quad \overset{c}{\underset{\text{CH}_2\text{COOCH}_3}{\text{CH}_2\text{COOCH}_3}} \\
\text{(III)} & \quad \overset{d}{\underset{\text{H}_3\text{COOC}}{\text{H}_2\text{COOC}}} \quad \overset{e}{\underset{\text{HOOC}}{\text{HOOC}}} \\
\text{(IV)} & \quad \overset{f}{\underset{\text{EDOF}}{\text{EDOF}}} \\
\end{align*} \]

a) HNO\textsubscript{3}, 90–100°C, 12h.  
b) CH\textsubscript{3}OH, SOCl\textsubscript{2}, RT, 24h.  
c) CH\textsubscript{2}ONa, CH\textsubscript{3}OH, (COOEt)\textsubscript{2}, 70°C, 10h.  
d) BrCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}Br, K\textsubscript{2}CO\textsubscript{3}, DMF 110°C, reflux 5h.  
e) NaOH

**Figure 2.** The synthesis of 3,4-dihydrofuro[3,4-b][1,4]dioxepine-6,8-dicarboxylic acid

2.2.1. Diglycolic acid(I)  
Add 500 ml water and 500 ml concentrated nitric acid to an appropriate three-necked flask, the ethylene diglycol (111.8 g, 1.05 mol) then was slowly added to the mixture, the resulting solution was stirred overnight at 100°C. After reaction, the mixture was concentrated by evaporation under reduced pressure to removal of the excess of nitric acid. Wait until the reaction liquid was evaporated to dryness, the resultant product was further dried by vacuum drying oven, and the yield is 95.3 g (67.7 %).  
1H NMR (400 MHz, DMSO) \( \delta \) 12.79 (s, 2H), 4.09 (s, 4H).

2.2.2. Dimethyl 2,2'-oxydiacetate(II)  
Diglycolic acid (10.0 g, 0.075 mol) was added to a 250 ml three-necked flask, then SOCl\textsubscript{2} (21.6 ml, 0.30 mol) was added dropwise, hydrochloric acid can be produced in the process of dropping. After dropping, the mixture stirred at room temperature for 6h. Add an ice bath outside the reaction system, then the dry methanol (50 ml) was added drop by drop to the resulting mixture, when the system is no longer producing gas the mixture was warmed up to room temperature and stirred overnight. Evaporate the excess of SOCl\textsubscript{2} and methanol, the residual liquid was extracted by ethyl acetate and neutralized by saturated solution of NaHCO\textsubscript{3}, the obtained organic phase was washed with water, dried over anhydrous MgSO\textsubscript{4}. The solvent was then removed by rotary evaporation to give a white solid (yield: 9.27 g, 76.3 %).  
1H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 4.26 (s, 2H), 3.78 (s, 3H).  
13C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 170.11, 68.12, 51.99.

2.2.3. Diethyl-3,4-dihydroxyfuran-2,5-dicarboxylate(III)  
200 ml of dry methanol was added into a 500 ml three-necked flask, and tiny sodium (2.13 g, 0.09 mol) was added, stirred until the sodium was dissolved entirely (the solution was milky white feculent liquid), add the dimethyl 2,2'-oxydiacetate (10.0 g, 0.06 mol), the mixture was heated to 75°C for 30min. Then the diethyl oxalate (6.76 g, 0.05 mol) was added, the solution becomes yellow feculent liquid, after that reflux for 3–4h, a great deal of yellow solid was precipitated. The yellow solid was washed with ethanol (dried over anhydrous MgSO\textsubscript{4}), then added a small amount of water to dissolve, then added slowly hydrochloric acid (which was dilute twice). The yellow solution transformed gradually into achromaticity and considerable white solid deposited from it. Then filtrated and dried the precipitation, the yield is 8.26 g (63.7%).  
1H NMR (400 MHz, d-DMSO, ppm): \( \delta \) 3.76 (s, 6H), 10.26 (s, 2H).  
13C NMR (101 MHz, DMSO): \( \delta \) 51.81, 127.76, 144.14, 158.96.  
LRMS (ESI-) M/z calcd for C\textsubscript{8}H\textsubscript{8}O\textsubscript{7}. [M-H]- 215.1; found 215.2.

2.2.4. 3,4-dihydrofuro[3,4-b][1,4]dioxepine-6,8-dicarboxylate (IV)  
A 50 ml single-necked flask, diethyl-3,4-dihydroxyfuran-2,5-dicarboxylate (1.0 g, 4.6 mmol) was added, DMF (25 ml) was added as solvent and dry potassium carbonate (1.28 g, 9.2 mmol) was added. The mixture was heated to 110°C, after that 1,3-dibromopropane (1.87 g, 9.2 mmol) was added drop wise to reaction system, then
the mixture was refluxed overnight. After completion, the reaction mixture was cooled to room temperature and add proper amount of water to the system, filtered to get a white solid and dried it, the yield is 0.69 g (58.5%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.41 - 4.29 (m, 4H), 3.91 (s, 6H), 2.36 (dt, \(J = 10.4, 5.1\) Hz, 2H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.75, 146.02, 129.87, 71.49, 51.47, 32.18; LRMS (ESI+) M/z calcd for C\(_{11}\)H\(_{12}\)O\(_7\). [M+Na]+ 279.0; found 279.1.

2.2.5. 3,4-dihydrofuro[3,4-b][1,4]dioxepine-6,8-dicarboxylic acid (V) 3,4-dihydrofuro[3,4-b][1,4]dioxepine-6,8-dicarboxylate(0.5g, 2.0mmol) and 10 ml of 10 M sodium hydroxide solution were added into a 50 ml single-necked flask, the mixture was heated to 60°C. After the solid were dissolved entirely, the mixture was stirred for 3h. This mixture was washed three times with dichloromethane, and dilute hydrochloric acid was added drop by drop until no precipitation. The white solid was separated by filtration, and the yield is 0.39 g (85.5%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 13.24 (s, 2H), 4.32 - 4.09 (m, 5H), 2.32 - 2.02 (m, 2H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.14 146.59, 130.98, 72.22, 33.19. LRMS (ESI+): M/z calcd for C\(_9\)H\(_8\)O\(_7\). [M+H]+ 458.1; found 458.3.

3. Results and Discussion

In this study, the main routes of the reaction are: oxidation of the ethylene diglycol, acetylation of the diglycolic acid, synthesis of the furan ring, Williamson reaction, hydrolysis of esters, etc. In the esterification process of diglycolic acid, we adopt the method of first acetylation and then esterification to increase the rate and yield of the reaction. In order to get a better result, we adopt sodium hydroxide solution instead of ethanol solution of sodium hydroxide in the process of ester hydrolysis. The amount of methanol is the key to the synthesis of the furan ring and in further treatment the excess of the methanol must be evaporated.

4. Conclusions

In summary, we have successfully synthesized 3,4-dihydrofuro[3,4-b][1,4]dioxepine-6,8-dicarboxylic acid which can be utilized for synthesis of a new type of organic electroluminescent material by using low-cost and readily available ethylene diglycol as raw material. Compared to existing procedures, the high yield, operational simplicity, easy availability and inexpensive reagents make the procedure more attractive. 3,4-dihydrofuro[3,4-b][1,4]dioxepine-6,8-dicarboxylic acid has a special substituent group which can increase the solubility of the polymer and is conducive to the formation of noncoplanar structure, reduce the fluorescence quenching, improve the quantum efficiency and stability.

Acknowledgments

We are grateful for the financial support of the National Natural Science Foundation of China (No.21462018), the Science Fund of the Technology Office of Jiangxi, China (2009ZDS11100 and 20132BBE50024).

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