

## Synthesis of a novel D-A type photoelectrical material based on fluorene

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**Abstract:** Novel D-A type conjugated organic molecules composed of central fluorene units and cyanoacetic acid terminal groups have been designed and constructed. The article was aimed at improving the solubility of small molecules by introducing aliphatic chains, and improving the optical and electrical properties of small molecules by introducing cyanoacetic acid. The target compounds would be promising candidates for organic light-emitting diodes.

### Introduction

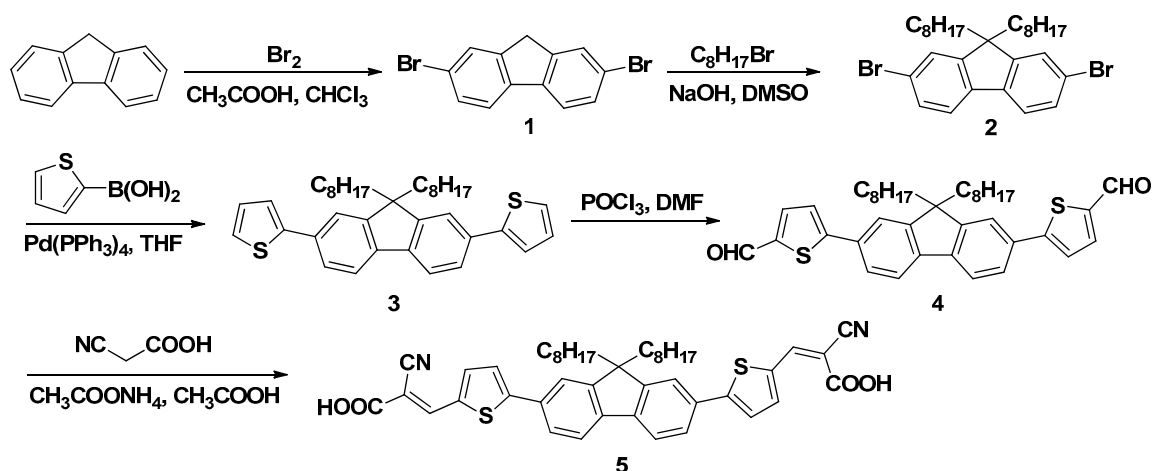
During the past decade, organic conjugated molecules with donor-acceptor architectures have attracted much academic and technological research attention, due to their potential electronics and optoelectronics applications such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs).<sup>1-3</sup> Conjugated organic molecules have great advantages on higher purity, fixed molecular weight and their clear molecular structure compared with organic polymers, which will receive a significant amount of interest by researchers in the coming years.<sup>4</sup> Moreover, the donor-acceptor materials broadly provide large  $\pi$ -electron delocalization over the molecules, leading to desirable semiconductor properties for electrical and optical applications.

In order to improve the property of these materials, exploring new synthesis and investigation of conjugated molecules is significant, which have highly capable of accepting both electrons and holes while exhibiting high luminescence quantum yield. As an electron donor, fluorene has biphenyl structure with rigid plane and large  $\pi$ -conjugated system, plays an important role in the donor-acceptor organic molecules. Fluorene and its derivatives were extensively investigated and have become active highlight in recent years, because of their special structures, various functional groups and being easily modified endowing their wide potential application in photoelectrical materials.<sup>5</sup>

In this article, we design and synthesize new compounds (2Z,2'E)-3,3'-(5,5'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid), based on fluorene units at the center and introduced cyanoacetic acid group and thiophene to improve electronic and optical properties of organic conjugated molecules. The target compounds would be promising candidates for organic light-emitting diodes. Optical properties, electrical Properties and thermodynamic properties will be studied in future work.

### Experimental Section

Characterization: <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were collected on a Bruker AM-400WB spectrometer in chloroform-d or DMSO as solvent and tetramethylsilane (TMS) as the internal standard. Materials: Diethyl ether and tetrahydrofuran (THF) were dried over sodium benzophenone and distilled under argon atmosphere before use. CHCl<sub>3</sub> and DMF were dried over CaH<sub>2</sub> and then distilled under nitrogen atmosphere and deoxygenated by purging with nitrogen for 30 min before use in monomer synthesis. Other chemicals were purchased from Acros and used without further purification.



Scheme 1. The synthesis route of (2Z,2'E)-3,3'-(5,5'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (**5**)

In our previous report, the compound **4** was synthesized via the Vilsmeier-Haack reaction as illustrated in Scheme 1. First, the reaction of 9H-fluorene with Bromine and acetic acid in  $\text{CHCl}_3$  give **1** in 89 % yield. Then 2,7-dibromo-9H-fluorene and 1-bromooctane in DMSO with a moderate condition to give **2** in 96 % yield. In the next step, 2,7-dibromo-9,9-dioctyl-9H-fluorene reacted with 2.5 equiv. of thiophen-2-ylboronic acid to afford **3** in 86 % yield. The target compound **4** was reacted using DMF and  $\text{POCl}_3$  to give a yield of 80 %.

#### Synthesis of 2,7-dibromo-9H-fluorene (**1**)

Bromine (4.03 g, 25.2 mmol) was slowly added using a syringe to the solution of 9H-fluorene (2.00 g, 12.0 mmol) and acetic acid (1 ml) in  $\text{CHCl}_3$  (30 ml). After stirring the mixture at room temperature for 12 h, a precipitate was obtained and filtered, washed with distilled water and methanol. The product was obtained as white crystals. Yield: 3.46 g (89 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.66 (s, 2H), 7.58 (d,  $J$ =7.6 Hz, 2H), 7.50 (d,  $J$ =8.0 Hz, 2H), 3.84 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  44.79, 139.82, 130.03, 128.29, 121.21, 36.56.

#### Synthesis of 2,7-dibromo-9,9-dioctyl-9H-fluorene (**2**)

2,7-dibromo-9H-fluorene (2.80 g, 8.64 mmol) and 1-bromooctane (3.67 g, 19.0 mmol) were dissolved in DMSO (40 ml) and stirred for 30 min at room temperature. A sodium hydroxide solution (10 ml, v: 50 %) was slowly added and then stirred for 24 h at room temperature. The reaction mixture was poured into water and extracted by acetic ether. The organic layer separated and dried over anhydrous magnesium sulfite. The crude product was purified using column chromatography with petroleum ether as the eluent. The product was obtained as off-white solid. Yield: 4.55 g (96 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.53–7.51 (m, 2H), 7.47–7.45 (m, 4H), 1.95–1.91 (m, 4H), 1.25–1.05 (m, 20H), 0.84 (t,  $J$ =7.0 Hz, 6H), 0.59 (s, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.57, 139.21, 130.17, 126.78, 121.61, 121.15, 55.60, 40.19, 31.80, 29.90, 29.21, 28.51, 23.65, 22.70, 14.27.

#### Synthesis of 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)dithiophene (**3**)

A mixture of 2,7-dibromo-9,9-dioctyl-9H-fluorene (4.00 g, 7.30 mmol), thiophen-2-ylboronic acid (2.34 g, 18.5 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.92 g, 0.80 mmol) in dry THF (150 ml) and a 2.0 M  $\text{K}_2\text{CO}_3$  aqueous solution (20 ml) was stirred for 24 h at 80 °C under  $\text{N}_2$ . After cooling the mixture to the room temperature, the solvent was removed, and the product was purified using column chromatography on a silica gel with petroleum ether. The product was obtained as green oil. Yield: 3.51 g (86 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.61 (s, 2H), 7.58 (s, 2H), 7.39 (d,  $J$ =3.6 Hz, 2H), 7.29 (d,  $J$ =5.2 Hz, 2H), 2.04–2.01 (m, 4H), 1.25–1.05 (m, 20H), 0.89 (t,  $J$ =7.0 Hz, 6H), 0.71 (s, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.04, 145.37, 140.54, 133.69, 128.37, 125.34, 124.73, 123.18, 120.57, 120.33, 55.62, 40.78, 32.18, 30.38, 29.58, 24.19, 23.00, 14.51.

#### Synthesis of 5,5'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(thiophene-2-carbaldehyde) (**4**)

2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)dithiophene (0.5 g, 0.9 mmol) and DMF (1.39 ml) was dissolved in 1,2-dichloroethane (20 ml) and  $\text{POCl}_3$  (1.66 ml) was carefully added through a dropping funnel, keeping the reaction temperature below 5 °C. After the complete addition of  $\text{POCl}_3$ , the

reaction solution was stirred for 12 h at reflux. Then the mixture was poured into a cooled saturated sodium bicarbonate solution, neutralized with Na<sub>2</sub>CO<sub>3</sub> solution, extracted with dichloromethane and washed with brine. The organic layer separated and dried over anhydrous magnesium sulfite. The crude product was purified using column chromatography with petroleum ether/dichloromethane (2:1, v/v) as the eluent. The product was obtained as yellow solid. Yield: 0.44 g, (80 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ= 9.91 (s, 2H), 7.77 (d, J=4.3, 4H), 7.71 (d, J=8.0 Hz, 2H), 7.64 (s, 2H), 7.50 (s, 2H), 2.05–2.02 (m, 4H), 1.13–1.05 (m, 20H), 0.78 (t, J=6.6 Hz, 6H), 0.66 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 182.72, 154.79, 152.26, 142.25, 141.64, 137.44, 132.42, 125.73, 124.06, 120.78, 120.71, 55.56, 40.21, 31.74, 29.87, 29.14, 23.76, 22.58, 14.03.

### Synthesis of (2Z,2'E)-3,3'-(5,5'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (5)

A mixture of 5,5'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(thiophene-2-carbaldehyde) (4) (0.5 g, 0.82 mmol), 2-cyanoacetic acid (0.28 g, 3.27 mmol), ammonium acetate (0.25 g, 3.27 mmol) in AcOH (50 mL) was stirred for 12 h at 120 °C under N<sub>2</sub>. After it was cooled to room temperature, the reaction mixture was poured into ice water then filtered. The product was obtained as red solid. Yield: 0.52 g (85 %). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.52 (s, 2H), 8.05 (d, J = 3.6 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.89 (s, 4H), 7.79 (d, J = 7.8 Hz, 2H), 2.05 (s, 4H), 1.06–0.88 (m, 20H), 0.67 (t, J = 6.9 Hz, 6H), 0.48 (s, 4H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 163.61, 153.32, 151.87, 146.53, 141.29, 134.47, 131.76, 125.35, 121.28, 120.38, 116.43, 98.14, 55.25, 40.15, 31.06, 28.89, 28.34, 23.15, 21.95, 13.75.

### Conclusions

In conclusion, the target compound **5** has been successfully prepared via the Knevenagel reaction in acceptable yields with a much milder and more efficient route, were designed to construct novel donor-acceptor conjugated organic molecules based on central fluorene units as electronic donors and cyanoacetic acid terminal groups as electronic acceptors. Optical properties, electrical Properties and thermodynamic properties will be studied in future work.

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