

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

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**Abstract:** A novel electron donor unit based on phenothiazine has been designed and constructed. The target compound ( $2E,2'E$ )-3,3'-(5,5'-(10-octyl-10H-phenothiazine-3,7-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) was easily synthesized in high yields with a milder and efficient route via the Knevenagel reaction. Aliphatic chains and cyanoacetic acid could improve the solubility and the optical and electrical properties of small molecules. As expected, the target compound should be a promising donor to construct D-A type materials for applications in organic light-emitting diodes (OLEDs).

### Introduction

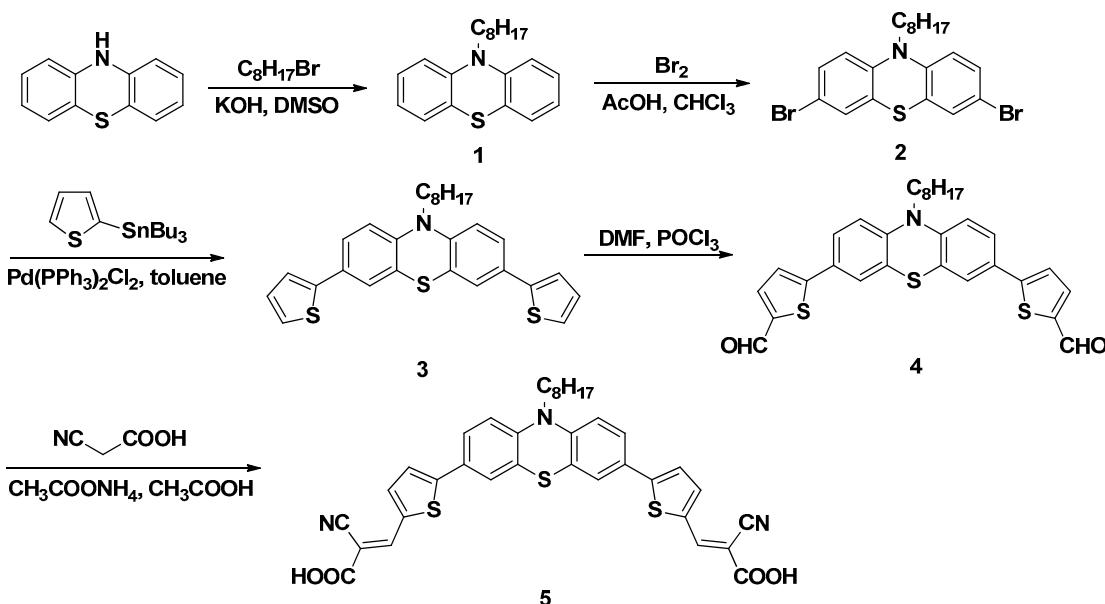
D-A type molecules have great advantages on physical properties easily being tuned over a wide range by appropriate chemical modification to the structures of donors or acceptors, which have received significant interest by researchers, used as light-emitting and electroluminescent multifunctional materials for organic light-emitting diodes<sup>1-2</sup>. When comparing with other materials, donor-acceptor materials broadly provide large  $\pi$ -electron delocalization over the molecules leading to desirable semiconductor properties for electrical and optical applications. The requirement of these materials should be donor-acceptor molecules that combine high fluorescence quantum yields with low ionization potential or high electron affinity. To make a improvement of the property of OLEDs, the feature of emissive materials we desired should be highly capable of accepting both electrons and holes while exhibiting high luminescence quantum yield.<sup>3</sup>

So far, the electron donors such as triarylamine, carbazoles and pyrroles and the electron acceptors such as ketone, nitro, pyridine and benzothiazole have been studied in forming D-A type materials.<sup>4-6</sup> Phenothiazine and its derivatives, are of well-known heterocyclic architectures with electron-rich sulfur and nitrogen heteroatoms, which are stronger, and potentially better electron donors, resulting from their 0.7 eV lower ionization potentials and more stable radical cations.<sup>7</sup>

In this article, we design and synthesize new compounds ( $2E,2'E$ )-3,3'-(5,5'-(10-octyl-10H-phenothiazine-3,7-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid), based on phenothiazine 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:  $^1\text{H}$  NMR and  $^{13}\text{C}$  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.  $\text{CHCl}_3$  and DMF were dried over  $\text{CaH}_2$  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 (2E,2'E)-3,3'-(5,5'-(10-octyl-10H-phenothiazine-3,7-diyl) bis(thiophene-5,2-diyl)) bis(2-cyanoacrylic acid) (**5**)

In our previous report, compounds **3** and **4** have been synthesized via the Susuki coupling reaction and the Vilsmeier-Haack reaction, respectively, as illustrated in Scheme 1. Firstly, the reaction of 10H-phenothiazine and 1-bromooctane in DMSO under a mild condition gave **1** in 92% yield. Secondly, bromine was added to 10-octyl-10H-phenothiazine and acetic acid in CHCl<sub>3</sub> to give **2** in 96% yield. Then, a mixture of 3.0 equiv. of tributyl(thiophen-2-yl)stannane, 3,7-dibromo-10-octyl-10H-phenothiazine and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> used as a catalyst afforded P1 in 66% yield via the Still coupling reaction. In the last step, DMF and POCl<sub>3</sub> were added to **3** to give **4** in a yield of 84 %.

#### Synthesis of 10-octyl-10H-phenothiazine (**1**)

10H-phenothiazine (20.0 g, 100.4 mmol) and 1-bromooctane (25.2 g, 130.5 mmol) were dissolved in DMSO (200 ml) and stirred for 30 min at room temperature. A sodium hydroxide solution (112 ml, v: 50%) was slowly added and then stirred for 24 h at room temperature. The reaction mixture was poured into water, extracted acetic ether and washed with saturated brine. 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-yellow oil. Yield: 28.7 g, (92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.38–7.32 (m, 4H), 7.13–7.09 (m, 2H), 7.04 (d, J = 8.4 Hz, 2H), 4.00 (t, J = 6.8 Hz, 2H), 2.01 (d, J = 12.8 Hz, 2H), 1.63–1.51 (m, 10H), 1.16 (t, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 145.52, 127.45, 125.28, 122.49, 115.63, 47.64, 32.03, 29.48, 27.17, 22.92, 14.39.

#### Synthesis of 3,7-dibromo-10-octyl-10H-phenothiazine (**2**)

Bromine (29.6 g, 185.1 mmol) was added dropwise through a dropping funnel to a solution of 10-octyl-10H-phenothiazine (26.2 g, 84.1 mmol) and acetic acid (30 ml) in CHCl<sub>3</sub> (30 ml) in a ice bath. After the complete addition of bromine, the reaction solution was stirred for 12 h at room temperature. Then the reaction was terminated by adding dilute aqueous sodium sulfite. The mixture was extracted by acetic ether 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/acetic ether (20:1 v/v) as the eluent. The product was obtained as dark brown oil. Yield: 38.0 g, (96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.18 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 1.2 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 3.69 (s, 2H), 1.72 (d, J = 6.6 Hz, 2H), 1.39–1.27 (m, 10H), 0.92 (t, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 143.98, 130.16, 129.65, 126.35, 116.65, 114.80, 47.67, 31.92, 29.35, 26.87, 22.85, 14.42.

#### Synthesis of 10-octyl-3,7-di(thiophen-2-yl)-10H-phenothiazine (**3**)

A mixture of 3,7-dibromo-10-octyl-10H-phenothiazine (10.0 g, 21.3 mmol), tributyl (thiophen-2-

yl)stannane (23.9, 63.9 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>(1.20 g, 1.70 mmol) in dry THF (200 ml) was stirred for 24 h at 80°C under N<sub>2</sub>. 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 yellowpowders. Yield: 6.73 g, (66 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.32 (d, J = 6.0 Hz, 4H), 7.14–7.20 (m, 4H), 6.99 (t, J = 4.2 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 3.78 (s, 2H), 1.79–1.72 (m, 2H), 1.40–1.21 (m, 10H), 0.91–0.80 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 143.46, 127.98, 125.03, 124.70, 124.13, 122.30, 115.43, 47.64, 31.76, 29.23, 26.93, 22.63, 14.09.

#### Synthesis of 5,5'-(10-octyl-10H-phenothiazine-3,7-diyl)bis(thiophene-2-carbaldehyde) (4)

10-octyl-3,7-di(thiophen-2-yl)-10H-phenothiazine (3.4 g, 7.2 mmol) and DMF (20 ml) was dissolved in 1,2-dichloroehane (150 ml) and Phosphorus oxychloride (20 ml) was added dropwise, keeping the reaction temperature below 5 °C. After POCl<sub>3</sub> added completely, the reaction solution was stirred at reflux for 12 h. Then the mixture was poured into a cooled saturated sodium bicarbonate solution, neutralized with odium bicarbonate solution, extracted with dichloromethane and washed with saturated brine. The organic layer separated and dried over anhydrous magnesium sulfite. The crude product was purified using column chromatography with petroleum ether/dichloromethane (10:1, v/v) as the eluent. The product was obtained as orange solids. Yield: 13.2 g, (84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.76 (s, 2H), 7.60 (d, J = 3.9 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 7.26 (s, 2H), 7.18 (d, J = 3.8 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H), 3.74 (t, J = 7.0 Hz, 2H), 1.79 – 1.63 (m, 2H), 1.34-1.16 (m, 10H), 0.77 (t, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 182.06, 152.61, 144.68, 141.25, 137.10, 127.27, 125.29, 124.38, 123.95, 122.73, 115.13, 47.37, 31.22, 28.71, 26.33, 22.12, 13.61.

#### Synthesis of (2E,2'E)-3,3'-(5,5'-(10-octyl-10H-phenothiazine-3,7-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (5)

A mixture of 5,5'-(10-octyl-10H-phenothiazine-3,7-diyl)bis(thiophene-2-carbaldehyde) (4) (1.0 g, 1.9 mmol), 2-cyanoacetic acid ( 0.37 g, 4.3 mmol), ammonium acetate ( 0.43 g, 5.6 mmol) in AcoH (30 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 purple solid. Yield: 1.1 g (88 %). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.43 (s, 2H), 7.94 (s, 2H), 7.64 (s, 2H), 7.56 – 7.45 (m, 4H), 7.01 (d, J = 5.2 Hz, 2H), 3.84 (s, 2H), 1.65 (s, 2H), 1.35-1.18 (m, 10H), 0.78 (d, J = 6.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 163.70, 151.94, 146.53, 144.79, 141.40, 133.96, 127.73, 126.62, 124.52, 123.59, 116.55, 96.86, 54.53, 48.63, 31.11, 28.61, 25.98, 22.04, 13.92.

## 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 phenothiazine 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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