

Synthesis of a novel photoelectrical material: (R)-2,2', 2'', 2''''-(2,2'-bis(heptyloxy)-[1,1'-binaphthalene]-4,4',6,6'-tetrayl)tetra -thiophene

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Abstract: Novel organic molecules composed of central 1,1'-binaphthalene-2,2'-diol have been designed and constructed via the Vilsmeier-Haack reaction, which offers a much milder and more efficient route over three steps. Optical properties of the resulting molecule were examined by UV-vis and fluorescence spectroscopies and show strong emission peaks in the blue light regions. Thus, the molecules are expected to be promising light-emitting materials for organic light-emitting diodes applications.

Introduction

During the past decade, extensive research has been carried out on conjugated organic molecules and polymers, due to their potential electronics and optoelectronics applications such as photovoltaic cells, electrochromic cells and organic light-emitting diodes.¹⁻² 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.⁴ Moreover, the donor-acceptor materials broadly provide large π -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 significance, which have highly capable of accepting both electrons and holes while exhibiting high luminescence quantum yield. However, 1,1'-binaphthalene-2, 2'-diol, which has biphenyl structure with rigid plane, as well as large π -conjugated system, will show the satisfactory property of electrical and optical.

In this article, we design and synthesize new compounds (R)-2,2', 2'', 2''''-(2,2'-bis(heptyloxy)-[1,1'-binaphthalene]-4,4',6,6'-tetrayl)tetra -thiophene, based on 1,1'-binaphthalene-2,2'-diol units at the center and introduced an alkyl group and thiophene to improve electronic and optical properties of organic conjugated molecules. The optical properties were characterized by UV-vis and fluorescence spectroscopies in solution, which exhibit that the target compounds would be promising candidates for organic light-emitting diodes.

Experimental section

Characterization:¹H NMR and ¹³C NMR spectra were collected on a Bruker AM-400WB spectrometer in chloroform-d or DMSO as solvent and tetramethylsilane (TMS) as the internal standard. Ultraviolet absorption spectra were measured using a Shimadzu UV-1800 UV spectrometer. Emission spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. The specific rotation were obtained by using a Automatic Polarimeter IV.

Synthesis of (R)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene

To a solution of (s)-1,1'-bi-2naphthol (5 g, 17 mmol) and 1-bromoheptane (5.3 mL, 34 mmol) in ethanol (100 mL) was heated to 70°C, then potassium carbonate was added in portions and refluxed for 24 h. After it was cooled to room temperature, the reaction mixture was filtered then evaporation of the filter liquor followed by flash chromatography on silica gel (eluted with hexanes) gave an oily compound **1** (7.8 g) in 98% yield. $[\alpha]^{20D} = +56.17$ (c = 0.10, THF); $^1\text{H NMR}$ (400 MHz, DMSO) δ 7.93 (d, J = 9.0 Hz, 2H), 7.85 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 9.0 Hz, 2H), 7.29 (dd, J = 8.1, 1.5 Hz, 2H), 7.24 – 7.12 (m, 4H), 3.95 (m, 4H), 1.45 – 1.36 (m, 5H), 1.14 (dd, J = 13.7, 6.5 Hz, 4H), 1.05 – 0.96 (m, 8H), 0.91 (m, 4H), 0.83 (t, J = 7.2 Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 154.59, 134.27, 129.30, 128.97, 127.73, 125.96, 125.51, 123.34, 120.82, 115.93, 77.30, 76.99, 76.67, 69.81, 31.61, 29.41, 28.76, 25.53, 22.42, 14.01.

Synthesis of (R)-4,4',6,6'-tetrabromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene

The oily compound **1** (6 g, 13 mmol) was dissolved in AcOH (100 mL), and Br₂ (6.6 mL, 130 mmol) was added over 30 min at room temperature. The reaction mixture was stirred at this temperature for another 12 h. Saturated sodium bisulfite was added to quench the excess Br₂ and the mixture was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over anhydrous Na₂SO₄, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: petroleum ether (b.p. 60-90 °C)/ethyl acetate, 20:1, v/v) to give a yellow oily compound **2** (9.4 g) in 92% yield. $[\alpha]^{20D} = +56.64$ (c = 0.10, THF); $^1\text{H NMR}$ (400 MHz, CDCl₃) δ 8.39 (d, J = 1.8 Hz, 2H), 7.71 (s, 2H), 7.30 (dd, J = 9.0, 1.9 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 4.11 – 3.70 (m, 4H), 1.46 – 1.36 (m, 4H), 1.13 (dd, J = 13.4, 6.7 Hz, 4H), 1.08 – 0.97 (m, 8H), 0.96 – 0.87 (m, 4H), 0.84 (t, J = 7.2 Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl₃) δ 154.39, 133.07, 130.56, 129.38, 128.82, 127.32, 122.38, 120.34, 119.21, 119.18, 69.79, 31.69, 29.14, 28.74, 25.59, 22.48, 14.13.

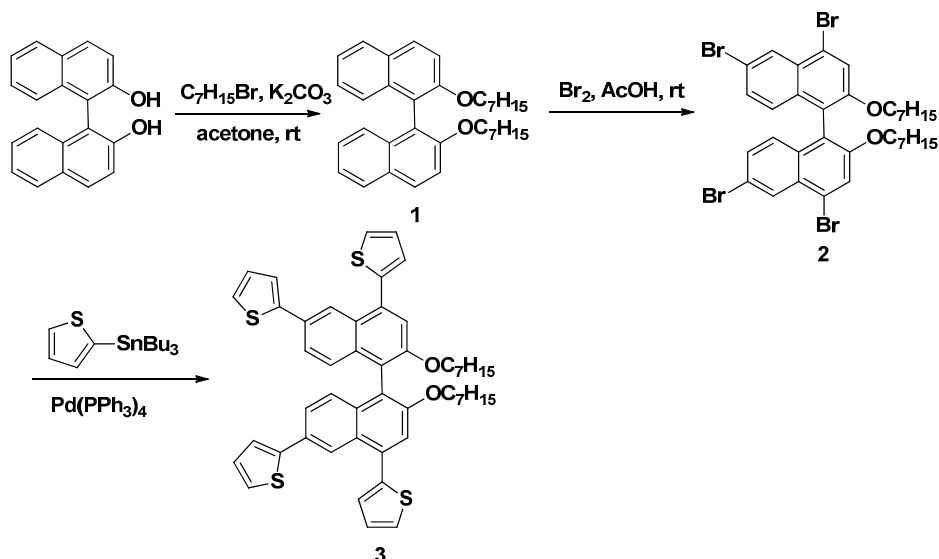
Synthesis of (R)-2,2',2'',2'''-(2,2'-bis(heptyloxy)-[1,1'-binaphthalene]-4,4',6,6'-tetrayl) tetra-thiophene

A suspension of the compound **2** (8 g, 10 mmol), 2-tributylstannylthiophene (22.4 g, 60 mmol) was added in 100 mL THF, and the resulting mixture was purged with N₂ for 30 min. Tetrakis (triphenylphosphine)palladium (5 g, 4.3 mmol) was then added, and the reaction mixture was heated to 110 °C for 48 h. After it was cooled to room temperature, excess solvent was removed under vacuum and the crude product was purified with column chromatography using petroleum ether/ethyl acetate (10 : 1) to give a compound **3** (6.5 g) in 81% yield. $[\alpha]^{20D} = +56.81$ (c = 0.10, THF); $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.49 (s, 2H), 7.90 (d, J = 4.5 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 7.68 (s, 2H), 7.64 – 7.53 (m, 4H), 7.47 (s, 2H), 7.42 (s, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.17 (s, 2H), 4.11 (dd, J = 9.8, 6.5 Hz, 4H), 1.53 – 1.30 (m, 4H), 1.12 – 0.80 (m, 16H), 0.80 – 0.60 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 153.53, 143.39, 140.38, 133.18, 129.45, 128.37, 127.84, 127.01, 126.71, 126.03, 125.49, 124.56, 123.49, 121.26, 119.45, 117.64, 68.68, 30.99, 28.63, 28.06, 24.98, 21.68, 13.62.

Results and Discussion

Synthetic design

As illustrated in Scheme 1, the target compound **4** was synthesized via the Vilsmeier-Haack reaction. First, the reaction of (s)-1,1'-bi-2naphthol with 1-bromoheptane and potassium carbonate in acetone give **1** in 98 % yield. Then (R)-4,4',6,6'-tetrabromo-2,2'-bis (methoxymethoxy) -1,1'-binaphthalene and Bromine in acetic acid at the roomtemperature to give **2** in 92 % yield. The target compound **3** was reacted using (R)-4,4',6,6'-tetrabromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene and 2-tributylstannylthiophene to give a yield of 81 %.



Scheme 1. The synthesis route of the compound **3**

Optical properties

The photophysical characteristics of Stock and Compound **3** have been investigated by UV-vis absorption and fluorescence emission in THF solutions. The maximum absorption wavelength of Stock and Compound **3** is 232 nm and 294 nm, the large bathochromic shift (62 nm) of the absorbance maximum is attributed to the electron-withdrawing groups. As shown in Fig.1 Stock and Compound **3** exhibit an emission maximum at 388 nm and 459 nm, which also bring a large bathochromic shift (62 nm). Meanwhile, the intensity of fluorescence emission of Compound **3** (969) is much larger than Stock (263), the satisfactory property of electrical and optical of Compound **3** would be promising candidates for organic light-emitting diodes.

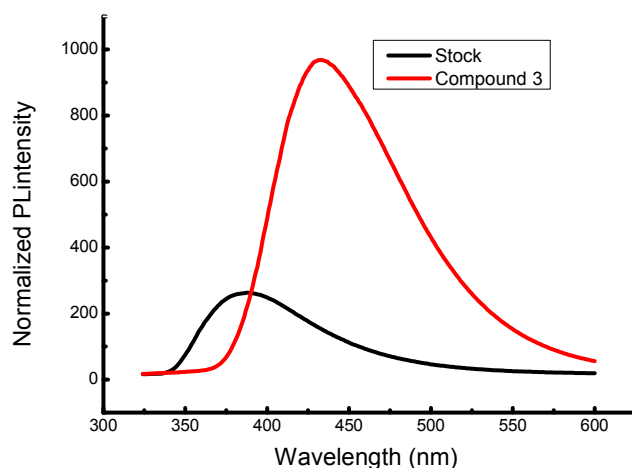


Fig 1 Fluorescence spectra of Stock and Compound **3** in THF (2.0×10^{-5} Mol/L)

Conclusion

In summary, the target Compound **3** is designed and synthesized via the Vilsmeier-Haack reaction with a much milder and more efficient route. Further work about optical, electrochemical, thermal properties and selfassembly behaviors is underway. Optical properties were characterized by the mean of UV-vis and fluorescence spectroscopies in solution. Compound **3** exhibit a large bathochromic shift of the absorbance maximum and emission maximum relative to Stock in solution. Meanwhile, the intensity of fluorescence emission of Stock had been improved by introducing an alkyl group and thiophene. So Compound **3** is more promising candidates for light-emitting materials applications. Furthermore, studies on experiments on optical and electrical

properties are ongoing in our group, which will be reported in due course.

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