



## A Novel Synthesis of 2,5-Dibromo-3-[2-(2-methoxyethoxy)ethoxy]Methylthiophene

Yu-Quan Zhang\*, Yan-Chun Li, Ji-Hua Zhu and Guo-Zhe Guo

College of Chemistry and Chemical Engineering, Longdong University, Xifeng, China

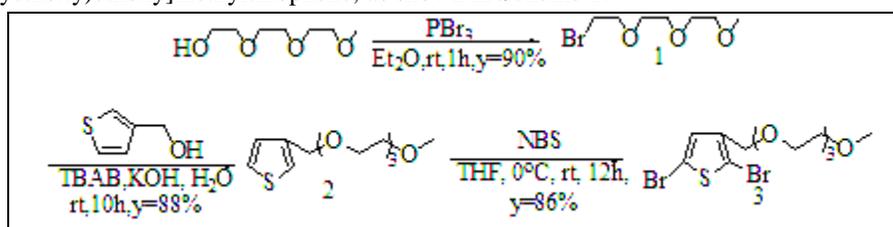
### ABSTRACT

A new synthesis of 2, 5-dibromo-3-[2-(2-methoxyethoxy) ethoxy]methylthiophene, which was prepared in good to high yield in three steps from glycol monomethyl ether glycol as starting material under mild conditions, is reported. Synthesis of intermediates 3-[2-(2-methoxyethoxy)- ethoxy]methylthiophene is reported for the first time.

**Keywords:** 2,5-dibromo-3[2-(2-methoxy)ethoxy]methylthiophene; Etherification; Synthesis; Characterization

### INTRODUCTION

Polymers have been developed into useful materials for a variety of applications, including light-emitting diodes [1,2], photovoltaic cells (PVs) [3-5] and thin-film transistors (TFTs) [6-8]. In the past few years, photovoltaic devices based on conjugated polymers have been extensively studied [3-5]. Regioregular poly (3-alkylthiophene) has been found to be among the most promising conjugated polymers. They can be used as photosensitizers and hole transporters in bulk heterojunction polymer solar cells [9-14]. Power conversion efficiencies (PCE) exceeding 3% under AM1.5 G illumination and between 4 and 5% under white light illumination from a solar simulator have recently been reported [9-14], further improvement on the PCE entails new conjugated polymers with higher carrier mobility and broader, absorption of the solar spectrum, especially in the red and infrared range. Polythiophenes with substituents other than alkyl groups have also been investigated, among which those with electron-donating alkoxy groups have displayed promising electronic and optical properties [15,16], the incorporation of an alkoxy group to the 3-position of the thiophene ring yields poly (3-alkoxythiophenes) with optical absorption maxima at longer wavelength. This may be attributed to both the electron-donating effect of the alkoxy group and the more coplanar conformation [17,18]. Therefore, polymers and copolymers based on 3-alkoxythiophene may also have smaller band gaps [19-21]; consequently, they can more efficiently absorb the red and near infrared portion of the solar emission spectrum. In order to expand the scope of polythiophenes with alkoxy groups to the 3-position of the thiophene, the preparation of monomer is very important, in this paper we describe the synthesis of monomer 2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxy]methylthiophene, as shown in Scheme 1.



Scheme 1: The synthesis of monomer 2,5-dibromo- 3-[2-(2-methoxyethoxy)ethoxy]methylthiophene

## EXPERIMENTAL SECTION

3-thiophene methanol (95%) was purchased from Aladdin (Shanghai), glycol monomethyl ether glycol, phosphorus tribromide, tetrabutyl ammonium bromide, potassium hydroxide, ethyl ether, chloroform were purchased from national medicine group chemical reagent co.LTD. FT-IR spectra were recorded on a Thermo Nicolet Nicolet 560 spectrophotometer using KBr pellets. All NMR analyses were performed on a Bruker Advance spectrometer (600 MHz) in CDCl<sub>3</sub>, TMS (<sup>1</sup>H NMR) was used as internal standards ( $\delta=7.26$ ). Elemental analysis was performed on PE-2400 CHN instrument.

### Synthesis of 2-[(Methoxyethoxy)Ethoxy]Ethyl Bromide 1 [22]

A dry nitrogen-purged flask was charged with ether (10 mL) and tris(ethyleneglycol) mono- methyl ether (0.80 mL, 5.00 mmol), and the mixture was cooled. To this solution was added dropwise phosphorous tribromide (0.24 mL, 2.5 mmol). After the addition was complete, the reaction was allowed to stir for 10 min. To this reaction mixture was then added methanol (0.7 mL), and the reaction mixture was allowed to warm at room temperature and stir for 30 min. The reaction mixture was poured into water (1.0 mL), and the organic phase was washed with 5% sodium bicarbonate and brine. The combined aqueous phase was extracted with ethyl acetate, and the combined organic phases were dried over sodium sulfate. The solvent was removed in vacuo to afford 0.84 g (75%) of the title compound as a colorless clear liquid.

### Synthesis of 3-[2-(2-Methoxyethoxy)Ethoxy]Methylthio-Phene 2

A mixture of 3-thiophenemethanol (9.23 g, 80.8 mmol), **1** (23.2 g, 84.6 mmol), tetrabutyl- ammonium bromide (2.88 g, 8.08 mmol), water (4.32 g), and KOH (10.1 g, 164 mmol) was stirred at room temperature for 10 h. Then water was added, and the mixture was extracted with Et<sub>2</sub>O. The organic layer was washed with water, and dried over anhydrous MgSO<sub>4</sub>. The solution was concentrated to yield crude product, which was separated by column chromatography on silica gel (eluent: petroleum/ethyl acetate=2:1) and The solvent was removed to afford the product as a light yellow oil (15.3 g, 88%), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 3.30 (s, 3H), 3.8-3.6 (m, 12H), 4.60 (s, 2H), 7.08-7.06 (m, 1H), 7.30-7.26 (m, 1H), 7.22 (s, 1H); IR (KBr):  $\nu=3059, 2963, 1630, 1450, 1351, 1278(\text{C-O}), 1112(\text{C-O}) \text{ cm}^{-1}$ . Anal. Calcd. for C<sub>12</sub>H<sub>20</sub>O<sub>4</sub>S: C, 55.36; H, 7.74; S, 12.32. Found: C, 55.28; H, 7.79; S, 12.37.

### Synthesis of Target Product 3

A dry three flask was charged with 200 mL THF and **2** (10.0 g, 36.4 mmol) and the mixture was cooled, the NBS (12.8 g, 72.8 mmol) dissolved in 100 mL of THF solution was added dropwise the bottle under 0°C. After the addition was complete, the reaction was allowed to stir for 12 h. vacuum distillation to remove THF, Then water was added, and the mixture was extracted with Et<sub>2</sub>O. The organic layer was washed with water, and dried over anhydrous NaSO<sub>4</sub>. The solution was concen- trated to yield crude product, which was separated by column chromatography on silica gel (petroleum ether: ethyl acetate=3:2) and the solvent was removed to afford the product as a light yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 3.30 (s, 3H), 3.45-3.6 (m, 12H), 6.60 (s, 1H), 7.08-7.06 (m, 1H), 7.24 (m, 7.30-7.25, 1H); IR (KBr)  $\nu=3059, 2963, 1630, 1450, 1351, 1276(\text{C-O}), 1112(\text{C-O}) \text{ cm}^{-1}$ . Anal. Calcd. for C<sub>12</sub>H<sub>18</sub> Br<sub>2</sub>O<sub>4</sub>S: C, 34.47; H, 4.34; Br, 38.22; S, 7.67. Found: C, 34.42; H, 4.37; Br, 38.18; S, 7.72.

## RESULTS AND DISCUSSION

2,5-Dibromo-3-[2-(2-methoxyethoxy)ethoxy]methyl-thiophene was obtained in three steps from glycol monomethyl ether glycol as starting material under mild conditions. The reaction with Phosphorus tribromide in ether afforded 2-[(methoxyethoxy)ethoxy]ethyl bromide **1**, which were etherified with 3-thiophenemethanol in the presence of tetrabutyl ammonium bromide (TBAB) to give 3-[2-(2-methoxyethoxy)ethoxy]methylthiophene **2** in excellent yields. The reaction with N-bromosuccinimide(NBS) in tetrahydrofuran(THF) was performed to give 3,5-Dibromo-3-[2-(2-methoxyethoxy)ethoxy]methylthiophene in 86% yields. The **2** and **3** compounds were character- ized by elemental analysis, <sup>1</sup>H NMR and IR spectra. The combination analysis of elemental, IR and <sup>1</sup>H NMR showed the target product is obtained.

The **2** compounds, which is not reported, was prepared from 3-thiophenemethanol and 2-[(methoxyethoxy)ethoxy]ethyl bromide. Etherification of 3-thiophenemethanol was carried out with 2-[(methoxyethoxy)ethoxy]ethyl bromide in the presence of KOH and a catalytic amount of tetrabutyl ammonium bromide as a phase transfer catalyst in water at room temperature to afford 3-[2-(2-methoxyethoxy)ethoxy]methyl thiophene **2** in 88% yield, Synthesis of similar compounds was prepared in organic solvent of tetrahydrofuran, organic alkali NaH, and in the absence of water and anaerobic [23]. This paper reported the reaction catalyzed by

inorganic alkali and phase transfer catalyst is carried out in water as a solvent and in the present of anaerobic, the yield was 88%. Water has clear advantages as an environmentally friendly solvent alternative in organic synthesis due to its low cost, non-flammability, non-toxicity.

Synthesis of similar compounds was prepared in organic solvent of tetrahydrofuran, organic alkali NaH, and in the absence of water and anaerobic, the yield was 75% [23]. The **3** compounds in 88% yield was prepared from 3-[2-(2-methoxyethoxy)ethoxy] methyl thiophene **2** and N-bromosuccinimide (NBS) in tetrahydrofuran (THF) under 0°C. Ryan *et al.* [23] reported the **3** compounds was prepared in three steps from 3-thiophenemethanol as starting material in organic solvent of THF, dichloromethane, organic alkali NaH, and in the absence of water and anaerobic under ice water bath, the yield was 75%.

## CONCLUSION

In conclusion, We have developed a reliable, highly efficient method for the synthesis of thiophene with a hydrophilic oxyethylene side chain in excellent yields. The etherification of 3-thiophenemethanol with water, inorganic base and PTC conditions constitutes a new and especially efficient and attractive method. Particularly valuable features of this methodology are its superiority from the point of view of yields, as well as an environmentally more friendly synthesis than the reported methods. From a synthetic perspective, these results open new possibilities for exploiting the synthesis of thiophene monomer with a hydrophilic oxyethylene side chain, which provides a kind of new functional materials for photoelectric devices.

## ACKNOWLEDGEMENT

Financial Support by Natural Science Foundation of China (No.21463023) is acknowledged.

## REFERENCES

- [1] A Heeger. *Angew Chem Int Ed.* **2001**, 40, 2591.
- [2] R Friend; RGymer; A Holmes. *Nature.* **1999**, 397, 121.
- [3] G Yu; J Gao; JC Hummelen. *Science.* **1995**, 270,1789.
- [4] WU Huynh; JJ Dittmer; AP Alivisatos. *Science.* **2002**, 295, 2425.
- [5] KM Coakley; MD Mcgehee. *Chem Mater.* **2004**, 16, 4533.
- [6] C Dimitrakopoulos; P Malenfant. *Adv Mater.* **2002**, 14, 99.
- [7] H Katz; ZJ Bao. *Phys Chem B.* **2000**, 104, 671.
- [8] G Horowitz. *J Mater Res.* **2004**, 19, 1946.
- [9] F Padinger; RS Rittberger; NS Sariciftci. *Adv Funct Mater.* **2003**, 13, 1.
- [10] C Waldauf; P Schilinsky; J Hauch. *Thin Solid Films.* **2004**, 503, 451.
- [11] M Al-Ibrahim; O Ambacher; S Sensfuss. *Appl Phys Lett.* **2005**, 86, 201120.
- [12] M Reyes; K Kim; DL Carrola. *Appl Phys Lett.* **2005**, 87, 1083506.
- [13] W Ma; C Yang; X Gong. *Adv Funct Mater.* **2005**, 15, 1617.
- [14] G Li; V Shrotriya; J Huang. *Nat Mater.* **2005**, 4, 864.
- [15] CJ Brabec; NS Sariciftci; JC Hummelen. *Adv Funct Mater.* **2001**, 11, 15.
- [16] M Leclerc; G Daoust. *Synth Met.* **1991**, 41, 529.
- [17] M Dietrich; J Heinze. *Synth Met.* **1991**, 41, 503.
- [18] X Hu; L Xu. *Polymer.* **2000**, 4, 9147.
- [19] G Daouet; M Leclerc. *Macromolecules.* **1991**, 24, 455.
- [20] RD McCullough; RD Lowe; M Jayaraman. *J Org Chem.* **1993**, 58, 904.
- [21] TA Chen; X Wu; RD Rieke. *J Am Chem Soc.* **1995**, 117, 233.
- [22] WB Thorsten; MT James. *J Am Chem Soc.* **1995**, 117, 4437.
- [23] L Eunji; H Brenton; J Kim; P Zachariah; E Todd; CH Ryan. *J Am Chem Soc.* **2011**, 133, 10390.