PREPARATION OF DITHIENO [3,2-C: 2`,3`-E]OXEPINE-4,6-DIONE BASED POLYMERS FOR SOLAR CELLS APPLICATIONS

SULAIMAN Y ALFAIFI

Chemistry Department , King Abdulaziz University
E-mail: salfaifi@kau.edu.sa

Abstract - Conjugated polymers have attracted much attention and academic research as a result of their potential use in the area of organic photovoltaic. In this project, series of copolymers will be prepared and successfully via Stille cross-coupling. Furthermore, these copolymers are designed designed taking in account some parameters that affect poto-electronic properties of polymers.This project will report the synthesis copolymers with small band gapbased on benzodithiopheneunit (BDT) andBenzodiselenophene (BDSe) asdonor units compined with bithiophene imide (BTI) andquaterthiophene imide (QTI) as electron – deficient unit. In the same time , this paper will focus on the polymer blends with fullerene derivatives (PCBM) and examine their performances in solar cells devices.

Keywords - Solar Cells, Band Gap, Efficiency, Copolymers , Fullerene.

I. INTRODUCTION

At the moment , there is a great effort of research interest in the developments of new sources of renewable energy . Photovoltaic solar cells (PV) based on silicon cells offer a promising alternative sources of energy in this area. However, their high cost of production is the limiting factor of this technology. Conversely , solar cell technology based on dye-sensitized nano- porous TIO2 photoelectrochemical cells (Gratzel cells) have also revealed great promise and considerable research efforts are targeted in that direction [1] .

Organic photovoltaics (OPVs) based on conjugated polymers are attracting attention because of their unique advantages, such as low price, low toxicity , simplicity of processing, , flexibility, etc.[2-5] . Device architectures based on a bulk heterojunction (BHJ) system is the best among all kinds of OPV's device architectures . This system is a mixture of donor (D) and acceptor (A) units existing as bicontinuous and interpenetrating network.. A typical solar cell works in three steps(1) absorption the light and generate excitons (2) dissociation of excitons into free charge carriers and (3) charge transporting and collection in electrodes [6- 13]. The performance of OPV devices mainly based on these processes and have to be improved to attain a high power efficiency. In recent years, there are there are much improvements in PCEs particularly for polymer solar cells. So far , power efficiency (PCEs) have increased to 12 % in bulk heterojunction (BHJ) OPVs using polymer semiconductor [14]. However, organic solar cells (OPV) performance is still in the early stages of development and competition comparing to their inorganic counterparts , and to enhance the device performance more intensive research will be required. The power efficiency PCE in the organic solar devices, can be dominated and characterized intricately by some important parameters with respect to electron processing. These parameters are short-circuit current (Jsc), fill factor (FF) and circuit voltage (Voc), [15]. Consequently, improving the performance of device requires three steps: (i) reducing the energy gap separating the(HOMO) and (LUMO) or bitals of the donor molecule in order to absorb more sun radiation , to achieve high J_{sc} value. (ii) decreasing the HOMO energy of the donor unit to maximize V_{oc} value (iii) increase Jsc value and increase FF upon maximize the charge mobility of the donor unit [16] .Moreover, the gab between LUMOs of D and A (the binding energy)should be higher than 0.3 eV to enhance separation of the charge and prevent charge recombination [17] .In addition , to increase PCE of devices, other considerations should be take into account , the absorption spectral range of the materials , their absorption coefficients , the exciton dissociation rates and the charge carrier mobilities.

II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. Anhydrous diethyl ether and THF were distilled from Na/benzophenone, and toluene

was distilled from Na. CO2 gas was obtained by warming dry ice and drying over P2O5 before use. The Stille reagent 5,5-bis(tributylstannyl)-2,2-bithiophene was synthesized according according to a published procedure.40 Conventional Schlenk techniques were used, and reactions were carried out under N2 unless otherwise noted. Microwave-assisted reactions were run in sealed vessels using a CEM Discover microwave reactor in the temperature controlled mode. UV-vis spectra were recorded on a Cary Model 1 UV-visible spectrophotometer. NMR spectra were recorded on a Varian Unity Plus 500 spectrometer (1H, 500 MHz).

2.2. Experimental Section

2.2.1. Synthesis of 3,3′,5,5′-Tetrabromo-2,2′-bithiophene (1).

Bromine (144 g) , 0.9 mol) was added over I h to a stirred solution of 2,2′-bithiophene (60.0 g, 0.361 mol) in 280 mL of chloroform containing 120 ml of glacial acetic acid in a 1 L round-bottom flask fitted with a reflux condenser (CAUTION: addition of the first two equivalents of bromine produces a stronglyexothermic reaction). The mixture was then stirred at reflux for12 h. Upon cooling to room temperature, acolorless precipitatewas isolated by filtration and washed with methanol. The filtrate was then concentrated, and a second crop of tan precipitate was collected and washed with methanol. The combined solids were dissolved in methylene chloride (150 mL), washed four times with 100 mL of water and once with 100 mL of brine, and dried over anhydrous MgSO4. The organic solution was then filtered, and the solvent was removed by evaporation to give 79 g (90% yield) of a colorless powder. 1H NMR (CDCl3): δ 7.06 (s, 2H) ppm.

2.2.2. Synthesis of 3,3′-Dibromo-2,2′-bithiophene (2).

Zn powder (25 g, 0.485 mol) was added in portions to a vigorously stirred refluxing mixture of bithiophene 1 (77.9 g, 0.162 mol) in 400 mL of ethanol containing 40 mL of water, 100 mL of glacial acetic acid, and 8 mL of 3 M HCl (aq). After refluxing for 2 h, the mixture was filtered hot, and upon cooling to 0 °C, yellow crystals were collected by filtration. The crystals were dissolved in diethyl ether, washed three times with 200 mL of water and once with 100 mL of brine, and dried over anhydrous MgSO4. The organic solution was filtered, and the solvent was removed by evaporation to give 20 g (89% yield) of a light yellow powder. Anal. Calcd for C8H4Br2S2: C, 29.65; H, 1.24. Found: C, 29.59; H, 1.14. 1H NMR (CDCl3): 7.41 (d, J) 5.3 Hz, 2H), 7.09 (d, J) 5.3 Hz, 2H) ppm.

2.2.3. Synthesis of 2,2′-Bithiophene-3,3′-dicarboxylic Acid (3).

Bithiophene 2 (19.44 g, 60.0 mmol) in 150 mL of diethyl ether was added dropwise over 1 h to a stirring solution of n-BuLi (82.5 mL, 1.6 M in hexanes) in 900 mL of ethyl ether at -78 °C. The reaction mixture was then allowed to stir for 1 h at -78 °C before dry CO2 was bubbled into the reaction mixture for 30 min. The reaction mixture was then allowed to stir for an additional 30 min before 1 mL of methanol was added, and the reaction was filtered cold to afford a colorless solid. The solid was dried overnight in vacuo at 100 °C, dissolved in 200 mL of water, acidified with 6 M HCl (aq), and the resulting colorless precipitate isolated by filtration. This diacid was dried overnight in vacuo at 100 °C to yield 14.1 g (92% yield) of a colorless powder. Anal. Calcd for C10H6O4S2: C, 47.23; H, 2.38. Found: C, 47.19; H, 2.45. 1H NMR (CDCl3): 7.45 (d, J) 4.0 Hz, 2H), 7.10 (d, J) 4.5 Hz, 2H). Mp 194-198 °C. MS (EI): m/z (%) 253.79 (100) [M+]

2.2.4. Synthesis of 2,2′-Bithiophene-3,3′-dicarboxylic Anhydride (4).

Diacid 3 (12.6 g, 49.4 mmol) was stirred in 100 mL of acetic anhydride at reflux for 6 h. Upon cooling to 0 °C, the solid was collected by filtration, washed with 20 mL of cold acetic anhydride, and dried in vacuo at 120 °C overnight. The resulting light yellow crystals (11.4 g, 98% yield) were used without further purification. Anal. Calcd for C10H4O3S2: C, 50.84; H, 1.71. Found: C, 50.78; H, 1.66. 1H NMR (CDCl3): 7.68 (d, J) 4.0 Hz, 2H), 7.40 (d, J) 5.0 Hz, 2H). Mp 260-263 °C. MS (EI): m/z (%) 235.96 (100) [M+].

2.2.5. Synthesis of N-(2-Octyldodecyl)-2,2′-bithiophene-3,3′-dicarboximide (M3).

A dry 8 mL microwave reaction tube was charged with amicrostirbar, anhydride 4 (354 mg, 1.50 mmol), 4 (dimethylamino)pyridine (61 mg, 0.50 mmol), and 5 mL of toluene. Next, 2-octyldodecylamine (446 mg, 1.5 mmol) was added dropwise to the suspension over 15 min, and the reaction was allowed to stir for an additional 15 min until no solid remained. The reaction tube was then irradiated with microwaves (PMAX) 300 W) for 2 h at a constant temperature of 220 °C. This procedure was repeated four more times, and the five reaction mixtures were combined in 250 mL of diethyl ether, washed six times with 150 mL of water and one time with 100 mL of brine, and

the organics dried over Mg2SO4. After filtration, the solvent was removed by evaporation to afford a yellow oil (90% pure by 1H NMR) that was purified by column chromatography on silica gel with a mixture of diethyl ether (10%) and hexane (90%) as the eluent. A light yellow oil (1.45 g, 37% yield) was obtained upon concentration of the main fractions. Anal.Calcd for C30H45NO2S2: C, 69.85. H, 8.79; Found: C, 69.79; H, 8.71. 1H NMR (CDCl3): 7.76 (d, J) 5.5 Hz, 2H), 7.24 (d, J) 5.5 Hz, 2H), 4.20 (t, J) 7.5 Hz, 2H), 1.71 (m, 1H), 1.37 (m, 4H), 1.26 (b, 28H), 0.89 (t, J) 7.0 Hz, 6H). MS (EI): m/z (%) 515.29 (100) [M+].

2.2.6. Synthesis of N-(2-Ethylhexyl)-2,2′:5′,2″:5″,2‴-quaterthiophene-4′,3″-dicarboximide (M4).

A dry 8 mL microwave reaction tube was charged with a microstirbar, imide 18 (0.445 g, 0.871 mmol), 2 (tributylstannyl)thiophene (0.650 g. 1.74 mmol), Pd- (PPh3)4 (0.041 g, 0.045 mmol), and DMF (6 mL) before being irradiated with microwaves (PMAX) 300 W) for 5 min at a constant temperature of 120 °C. Upon cooling, an orange precipitate was collected by filtration, washed with methanol (10 mL), and dried in vacuo at 120 °C. The solid was purified by column chromatography on silica gel with a mixture of diethyl ether (30%) and hexane (70%) as the eluent to yield 0.153 g of orange needle-like crystals upon concentration of the main fractions. The crystals were further purified by sublimation under vacuum to give orange needle-like crystals (0.136 g, 22% yield). Anal. Calcd for C26H25NO2S4: C, 61.02; H, 4.92. Found: C, 60.89; H, 4.78. 1H NMR (CDCl3): 7.82 (s, 2H), 7.35 (d, 4.5 Hz, 2H), 7.26 (b, 2H), 4.27 (m, 2H), 1.87 (m, 1H), 1.38-1.26 (m, 8H), 0.92 (m, 6H). Mp 181-184 °C. MS (EI): m/z (%) 511.2 (100) [M+]

III. RESULTS AND DISCUSSION

The monomers M3 , M4 have been prepared according to the scheme in Figure 1 :

The compounds from 1 to 4 have been successfully prepared in good yields over 90 % and their structures were confirmed using , FT-IR, NMR , MS and El. While the yields of M3 and M4 were obtained in low yields ranging from 22 % to 37 % which is attributable to form side products and some difficulty purifying. Themonomerbithiophene imide (BTI) M3 andquaterthiophene imide (QTI) M4 havebeen polymerized with benzodithiopheneunit (BDT) andBenzodiselenophene (BDSe) asdonor units using stille coupling and their performance in the solar cells devices are still under procedure . It will expected that these polymers will introduce optimistic results due to the introduced planarity . Moreover , it is expected that the quinonoid character is dominant as result of the introduce selenophene ringwhich have low aromaticity than thiophene.

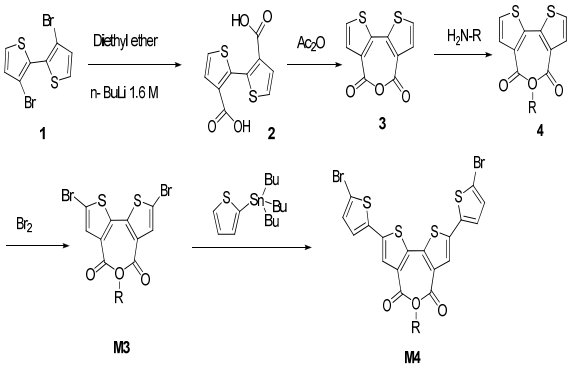


Figure 1: Synthetic route co-monomers.

IV. CONCLUSIONS

In this paper , The monomer M3,M4 have been prepared in a low yield . The structure of these monomers have been successfully confirmed. The work will continue to prepare (PBDTS-BTI , PBDTS-4TI , PBDTT-BTI , PBDTT – 4TI) using stille coupling and the structures of the resulting polymers will be confirmed and investigate their performance in solar cell devices .

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REFERENCES

[1] M. A. Green, K. Emery, D. L. King, S. Igari and W. Warta, Progress in Photovoltaics 2003, 11, 39-45.

[2] S. C. Jain, M. Willander and V. Kumar in Conducting Organic Materials and Devices, Vol. Volume 81 Eds.: M. W. S.C. Jain and V. Kumar), Elsevier, 2007, pp. 188.

[3] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, Science, (1992), 258, 1474.

[4] Ding, P.; Chu, C.-C.; Zou, Y.; Xiao, D.; Pan, C.; Hsu, C.-S. Journal of Applied Polymer Science 2012, 123, 99.

[5] Zhou, E.; Yamakawa, S.; Zhang, Y.; Tajima, K.; Yang, C.; Hashimoto, K. Journal of Materials Chemistry 2009, 19, 7730.

[6] Zou, Y.; Gendron, D.; Badrou-Aich, R. d.; Najari, A.; Tao, Y.; Leclerc, M. Macromolecules 2009, 42, 2891.

[7] P. B. Miranda; D. Moses; Heeger, A. J. Physical Review A 2001, 64.
[8] Blouin, N.; Michaud, A.; Leclerc, M. Adv. Mater. (Weinheim, Ger.) 2007, 19, 2295.
[9] Qin, R.; Li, W.; Li, C.; Du, C.; Veit, C.; Schleiermacher, H.-F.; Andersson, M.; Bo,Z.; Liu, Z.; Inganas, O.; Wuerfel, U.; Zhang, F. Journal of the American Chemical Society 2009, 131, 14612.
[10] Roncali, J. Macromol. Rapid Commun 2007, 28, 1761.
[11] Hoppe, H.; Sariciftci, N. S. Journal of Materials Research 2004, 19, 1924.
[12] de Cuendias, A.; Hiorns, R. C.; Cloutet, E.; Vignau, L.; Cramail, H. 2010, - 59.
[13] Anne, D. C.; Roger, C. H.; Eric, C.; Laurence, V.; Henri, C. Polymer International 2010, 59 1452.
[14] M. Sommer, H. Komber, S. Huettner, R. Mulherin, P. Kohn, N. C. Greenham and W. T. S. Huck, Macromolecules 2012, 45, 4142-4151.
[15] Zhou, H.; Yang, L.; Stoneking, S.; You, W. ACS Applied Materials & Interfaces2010, 2, 1377.
[16] H. Zhou, L. Yang, S. Stoneking, W. You, ACS Appl. Mater. Interfaces 2 (2010) 1377–1383. [13] .
[17] H. Zhou, L. Yang, S.C. Price, K.J. Knight, W. You, Angew. Chem. Int. Ed.122 (2010) 8164–8167.
[18] [14] H. Zhou, L. Yang, W. You, Macromolecules 45 (2012) 607–632.
[19] M. Zhang, Y. Gu, X. Guo, F. Liu, S. Zhang, L. Huo, T.P. Rusell, J. Hou, Adv. Mater. 25 (2013) 4944–4949.
[20] L. Dou, J. Gao, E. Richard, J. You, C.-C. Chen, K.C. Cha, Y. He, G. Li, Y. Yang, J. Am. Chem. Soc. 134 (2012) 10071–10079.
[21] Cartwright, L.; Iraqi, A.; Zhang, Y.; Wang, T.; Lidzey, D. G. RSC Advances2015, 5, 46386.
[22] Umeyama, T.; Watanabe, Y.; Douvogianni, E.; Imahori, H. The Journal of Physical Chemistry C2013, 117, 21148.
[23] Li, Z.; Feng, K.; Liu, J.; Mei, J.; Li, Y.; Peng, Q. Journal of Materials Chemistry A2016, 4, 7372.
[24] Roncali, J. Macromol. Rapid Commun 2007, 28, 1761.
[25] X.Wang, E. Perzon, J. L. Delgado, P. de la Cruz, F. Zhang, F. Langa,M. Andersson, O. Inganäs, Appl. Phys. Lett. (2004), 85, 5081.
[26] Y. J. Kim, H. N. Kim, M.-C. Hwang, Y.-H. Kim and C. E. Park, Synthetic Metals 2014, 198, 93-100.

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