SYNTHESIS OF *N*-BENZOYL DITHIENO[2,3-B:2’,3’-] PYRROLE MONOMER AS ACCEPTOR UNIT BUILDING IN DONOR-ACCEPTOR CONJUGATED POLYMER

NGUYEN ANH THU*, NGUYEN QUOC VIET*,
NGUYEN THANH TRUNG*, NGUYEN TRAN HA**

ABSTRACT

A monomer of N-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole (BDP), has been successfully prepared via copper-catalyzed amidation. Then, this monomer was brominated to form 2,6-dibromo-N-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole (DiBDP) monomer. The structures of monomers were confirmed via the nuclear magnetic resonance (^{1}HNMR) and Fourier transform infrared (FT-IR). BDP and DiBDP monomers will be used as monomers for Suzuki polycondensation reaction to synthesize the donor-acceptor (D-A) conjugated polymers.

Keywords: donor-acceptor (D-A) conjugated polymers, Polymeric solar cells, Suzuki polycondensation.

TÓM TẮT

Tổng hợp monomer N-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole như là đơn vị hút điện tử ứng dụng trong polymer dẫn điện cấu dạng cho nhận

Một monomer của họ N-acyl dithieno[2,3-b:2’,3’-d]pyrrole (DTP), N-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole (BDP), đã được tổng hợp thành công bằng phản ứng amide hoá sử dụng hệ xúc tác đồng. Monomer này được thực hiện phản ứng brom hoá để tạo ra monomer 6-dibromo-N-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole (DiBDP). Quy trình tổng hợp và khảo sát tính chất của các monomer này, bao gồm kết quả phân tích đánh giá bằng ^{1}HNMR và FT-IR, sẽ được trình bày trong nghiên cứu này. Monomer BDP và DiBDP sẽ được sử dụng làm nguyên liệu chính cho phản ứng trùng ngưng Suzuki tổng hợp các polymer dẫn có cấu trúc dạng cho – nhận điện tử.

Từ khóa: polymer dẫn điện cấu trúc cho nhận (D-A), pin mặt trời hữu cơ, phản ứng trùng ngưng Suzuki.

1. Introduction

Polymer solar cells (PSCs) have attracted great interests in both academic and industry because of their various distinctive advantages including flexibility, simple manufacturing techniques, ability to incorporate other technologies, low material cost

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[*] M.Sc., HCM City University of Technology, Vietnam National University Ho Chi Minh City; *Email: nguyenanhthu211@gmail.com*

[**] Ph.D., HCM City University of Technology, Vietnam National University Ho Chi Minh City

[4]. At the meantime, despite of their advantages, PSCs have some drawback and other technical limitations that they have low stability, low power conversion efficiency and short lifetime [9]. Consequently, enormous efforts have been devoted to overcome these weaknesses as well as to improve the operated efficiency of PSCs. An effective way to broaden absorption of PSCs is to narrow their band gaps. Recently, one of the most concerned research direction to do so is to alternatively bind an electron-rich unit (D) and an electron-deficient unit (A) into the same polymer backbone [10]. For this kind of polymers, the interactions between the donor segments and the acceptor segments will form a new higher HOMO level and a new lower LUMO level. Through the interaction between push – pull driving forces, the electrons will redistribute from the initial orbitals (before interacting) to the new hybridized orbitals of the polymer. As a result, the magnitude of the band gap will be reduced. The degree of band gap reducing depends much on the strength of the donor, acceptor units imposed in the polymer backbone. Therefore, judicious selection of donor, acceptor segments can allow to adjust the band gap magnitude to the expected value.

Experimentally, it is recognized that the narrower the optical band gap, the stronger the electron-withdrawing ability of acceptor unit in the copolymer [16]. Besides that, the combinations of medium/strong donor units and medium/strong acceptor units usually result in good photovoltaic performances (PCE > 5 %) [2,5,8,11-15]. From that, medium and strong acceptor units are believed to be a good choice for effective D-A conjugated polymer [1,3,12].

Therefore, in recent years, the *N*-acyl dithieno[2,3-b:2’,3’-d]pyrrole (DTP) moieties have been received considerable interest due to their good planar crystal structure, strong electron-withdrawing ability and symmetrical chemical structure with the side chain at the bridging unit [1,3,12]. The foregoing leads to materials with low band gaps and high mobility. These structures can be incorporated into various polymeric, oligomeric and molecular materials with a great desire to construct different low band gap donor – acceptor conjugated polymers which are useful in a large variety of applications such as OLED, FET and photovoltaic cells.

Thus aim of this study is to synthesize the monomer *N*-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole (BDP) which is DTP derivative and brominated BDP in order to prepare 2,6-dibromo-*N*-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole (DiBDP) monomer. These building monomers can be used to copolymerize with other electron-donating building blocks for synthesis of the D-A conjugated copolymers via Suzuki reactions and arylation reactions.

2. Experiment

2.1. Materials

3,3’-dibromo-2,2’-bithiophene (98 %); *N’*,*N*-dimethylethylene diamine (DMEDA, 95 %), copper (I) iodide (CuI, 98 %) were purchased from AK Scientific and used as received. Benzamide (99 %) was purchased from Sigma Aldrich. *N*-

bromosuccinimide (NBS, 99 %) was purchased from Merck. Chloroform ($CHCl_3$, Fisher Scientific, 99 %), toluene (Merck, 99 %), *n*-heptane (Labscan, 99 %) and diethyl ether (Merck, 99 %) were used as received. All reactions were carried out in oven-dried flask under purified nitrogen.

2.2. Characterization

Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra were recorded using BIO-RAD Excalibur spectrometer equipped with an ATR Harrick Split PeaTM.

^{1}HNMR spectra of the compounds were recorded in deuterated chloroform ($CDCl_3$) with a 500 MHz spectrometer – Bruker AMX500 apparatus, and the chemical shift are given relative to tetra methyl silane (TMS).

2.3. Synthesis of N-Benzoyl dithieno[2,3-b:2’,3’-d]pyrrole monomer

To a 50 mL rounded-bottomed flask equipped with a magnetic stirrer was added copper iodide (0.19 g, 1 mmol), DMEDA (1.728 mL, 8 mmol), potassium carbonate (4.15 g, 30 mmol), followed by evacuation and backfilling with nitrogen. Then, toluene and a small amount of distilled water (1 equiv.) were added to the reaction mixture and the solution was stirred for 30 minutes. Benzamide (12 mmol) was added, followed by 3,3’-dibromo-2,2’-bithiophene (3.24 g, 10 mmol). The reaction mixture was stirred for 24 hours at 110 ^oC. The reaction was cooled to the room temperature in the next step, washed with distilled water (3 x 20 mL) and extracted with chloroform (3 x 20 mL). The organic phase was dried by anhydrous K_2CO_3. The solvent was removed by rotary evaporation. The crude product was purified by silica column chromatography (with the eluent as following – 4 *n*-heptane: 1 ethyl acetate) to give the isolated product as a white crystalline solid (3.82g, $R_f = 0.75$, yield: 45.29%).

^{1}HNMR (500 MHz, $CDCl_3$), δ (ppm) 7.73 (d, 2H), 7.65 (t, 1H), 7.55 (t, 2H), 7.1 (d, 2H), 6.85 (br s, 2H)

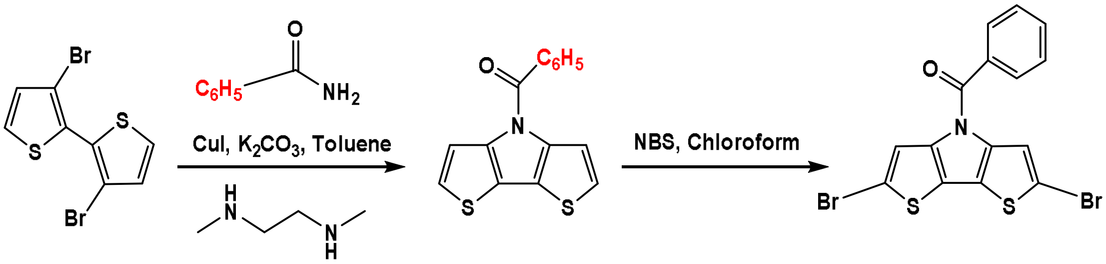
2.3. Synthesis of 2,6-dibromo-N-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole monomer

To a solution of compound *N*-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole (1.014 g, 3.56 mmol) in 30 mL chloroform was added *N*-bromosuccinimide (NBS) (1.25 g, 7 mmol) at 0 ^oC, followed by evacuation and backfilling with nitrogen. The mixture was stirred for about 24 hours. After that, the mixture was washed with distilled water (3 x 20 mL) and extracted with chloroform (3 x 20 mL). The organic phase was dried by anhydrous K_2CO_3. The solvent was removed by rotary evaporation. The crude product was purified by silica column chromatography (the eluent as following – 4 *n*-heptane: 1 ethyl acetate) to give the isolated product as a white crystalline solid (1.172 g, R_f = 0.57, yield: 74.34%).

^{1}HNMR (500 MHz, $CDCl_3$), δ (ppm) 7.72 (m, 2H), 7.69 (m, 1H), 7.57 (t, 2H), 6.87 (br s, 2H)

3. Result and discussion

The synthesis of monomers BDP and DiBDP are shown in Scheme 1. According to the protocol for Ulmann reaction (copper-catalyzed *N*-arylation of amines), monomer BDP was synthesized by using copper-catalyzed amidation 3,3’-dibromo-2,2’-bithiophene at the reflux temperature, in presence of CuI as the catalyst, DMEDA as the ligand for coupling amides with thiophene rings, toluene as solvent and K_2CO_3 as the base. The reaction proceeded with the formation of a dark-blue complex of copper (I) iodide and DMEDA and a subsequent brown mixture after 24 hours. After completion of reaction, the monomer was extracted with chloroform, washed with distilled water and purified via column chromatography using the eluent of *n*-heptane /ethyl acetate (v/v: 4/1). It should be noted that the coupling of 3,3’-dibromo-2,2’-bithiophene and benzamide was affected by increasing of intermediated compound of aryl-Cu(III) complexes. For this reason, the catalyst content of CuI and chelating nitrogen ligand - DMEDA was increased double times comparing with normal catalyst content and the mole ratio of CuI/DMEDA was established about 1:8. Moreover, the arylation of benzamide is dramatically accelerated by addition of distilled water (1 equivalent) to the reaction mixture. This can be explained that the water can increase the solubility of the base K_2CO_3 thus facilitating deprotonation of benzamide. Interestingly, the yield of the coupling of 3,3’-dibromo-2,2’-bithiophene and benzamide was observed (Yield: 45.29%) that is higher than the yield of this reaction performed by Rasmussen group (Yield: 36%) [3]. It is necessary to brominate of BDP monomer as intermediated product for forthcoming reactions such as conjugated oligomerization and conjugated polymerization. So the obtained BDP monomers reacted with 2 equivalent of NBS based on the nucleophilic substitution mechanism to form DiBDP monomers. The reaction was performed in chloroform as media solvent at 0 ^{o}C in 24h. Then, the reaction mixture was extracted with chloroform, washed with distilled water several times and purified by column chromatography to give a pale yellow solid in high yield (74.34%). The advantage of using NBS instead of bromine is that it provides a low-level concentration of bromine and through that the acyl carbonyl group can be protected from nucleophilic attack.



Scheme 1. *Synthesis routes of BDP and DiBDP monomers*

The ATR FT-IR spectra of monomer BDP (Fig 3.1) displayed several peaks between 2921 and 3109 cm^{-1} which contributed to C-H stretching vibrations of the benzyl rings. The peak at 1680 cm^{-1}, which was ascribed to the C=O stretching vibrations clearly proved for the existence of the *N*-acyl group in this monomer structure. The peaks at 1482/1443 cm^{-1} and the bands in range of 656 to 974 cm^{-1} are assigned to the aromatic C-C stretching vibrations and aromatic C-H deformation vibrations respectively. Whereas the bands from 1307 to 1384 cm^{-1} are assigned to the aromatic C-N stretching vibrations of the pyrrole units. In addition, the bands in range of 690 – 721 cm^{-1} and 615 cm^{-1} are ascribed in order to the thiophene C-S-C bending and S-C stretching vibrations.

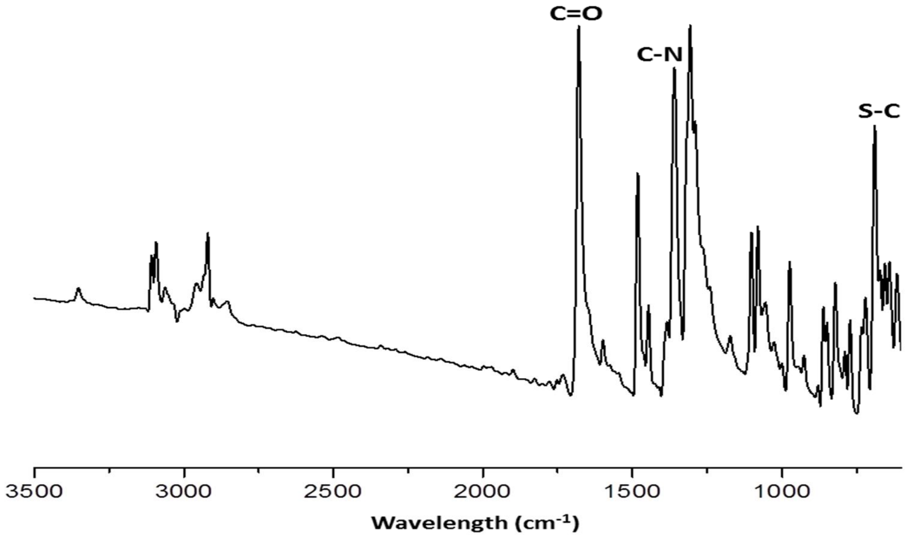


Figure 3.1. *FT-IR spectrum of monomer BDP*

In the ^{1}HNMR spectrum of monomer BDP (Fig. 3.2), the doublet peak at 7.73 ppm, the triplet peak at 7.65 ppm and the triplet peak at 7.55 ppm respectively corresponded to the five protons on the benzene ring, in particular, two at positions ‘d’, one at position ‘f’ and two at positions ‘e’. The doublet peak at 7.1 ppm corresponded to the two protons on the thiophene rings ‘peak b’. The broad singlet peak at 6.85 ppm was assigned to two protons left on the thiophene rings ‘peak a’. The chemical shifts along with the integrals of obtained signals were suitable with the structural formula of this monomer. These results indicated that copper-catalyzed amidation reaction successfully forming the desired monomer.

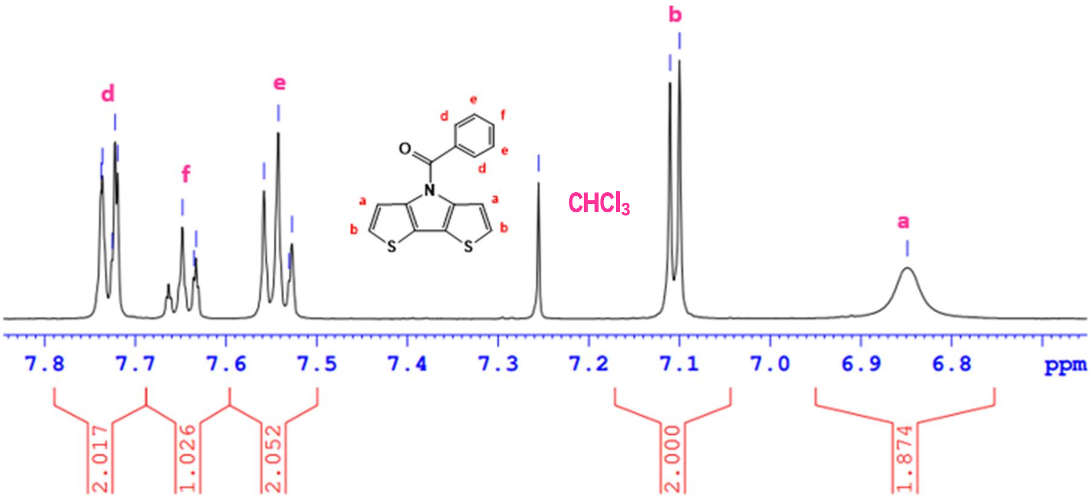


Figure 3.2. *^{1}H NMR spectrum of monomer BDP in CDCl$_3$*

Figure 3.3 shows the ^{1}HNMR spectrum of DiBDP monomer. The signal at 7.72 ppm was assigned to the two protons at position ‘d’ on the benzene ring. The multiple peak at 7.69 ppm of the proton at position ‘f’ was overlapped with the peak coming from protons at position ‘d’. The broad singlet peak at 6.87 ppm corresponded to the two protons at position ‘a’ on the thiophene rings. Besides that, in the ^{1}HNMR spectrum of monomer DiBDP, there is no signal observed at 7.1 ppm. This demonstrated that the two protons at the position ‘b’ of monomer BDP were replaced by two bromine atoms. These results indicated that brominate replacement reaction successfully forming the desired monomer.

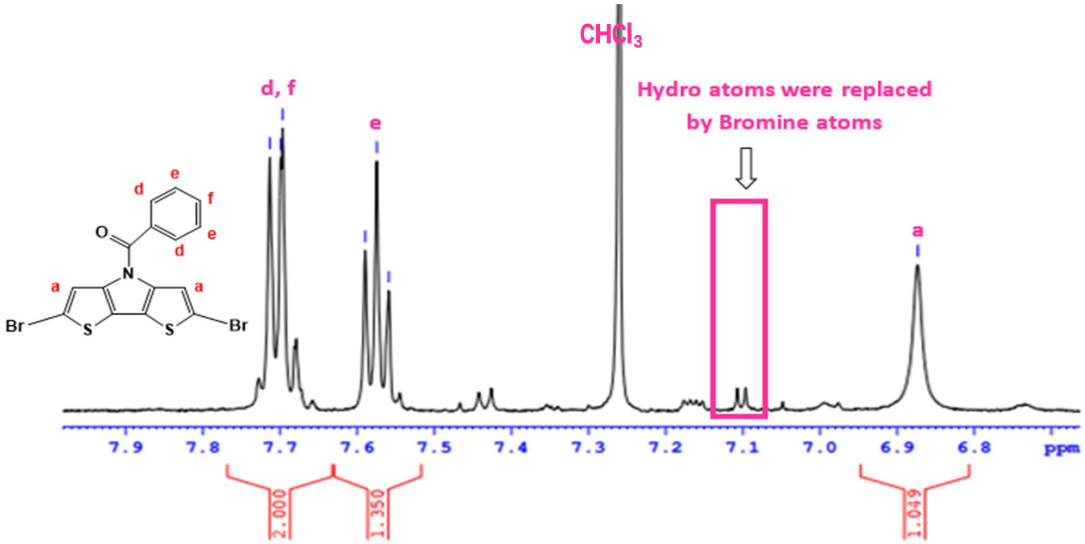


Figure 3.3. *^{1}H NMR spectrum of monomer DiBDP in CDCl$_3$*

However, in the brominating process, side by side the desired monomer – DiBDP, there was still have one side product (MoBDP) which only one proton at position ‘b’ of BDP monomer was replaced by bromine atom. Here the separation of two components (DiBDP and MoBDP) depends upon the extent absorption to stationary phase. The rate of the movement (R_f) of DiBDP is 0.57 while the MoBDP’s R_f is 0.43. DiBDP with lower absorption affinity to the silica moved faster and eluted out first (yield: 74.34%) and vice versa MoBPD with greater absorption to stationary phase was eluted later with a yield around 15%. This side product was also characterized by ^{1}HNMR spectroscopy to clarify its structure. Based on the chemical shifts at 7.1 ppm and the integrals of these signal in the ^{1}HNMR spectra of BDP, DiBDP and MoBDP, the relative ratio of the amount of equivalent protons at the position ‘b’ was displayed clearly (Fig. 3.4).

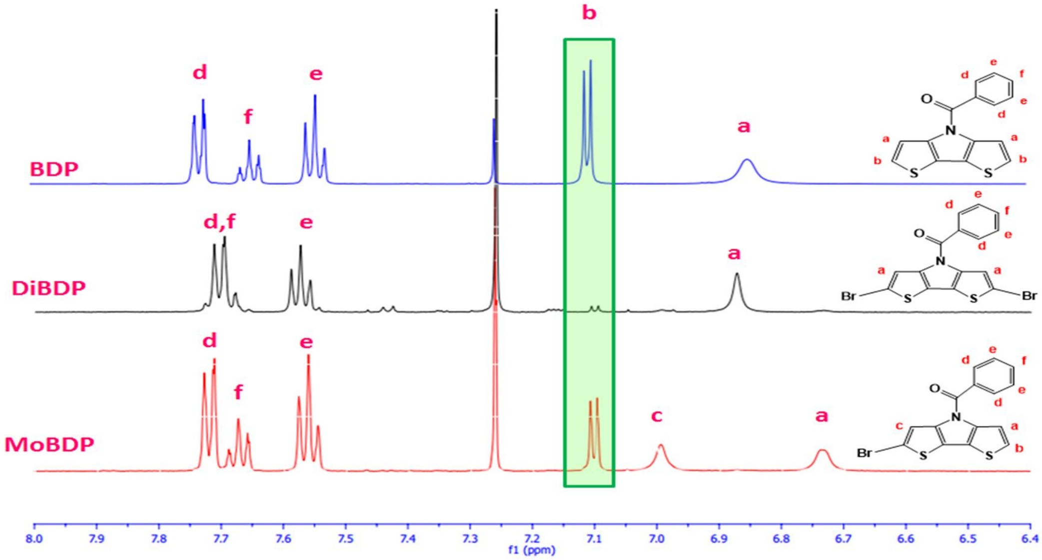


Figure 3.4. *Comparison ^{1}HNMR spectra of the monomers BDP – DiBDP – MoBDP in $CDCl_3$*

4. Conclusion

In conclusion, the derivate of a class of dithieno[2,3-b:2’,3’-d]pyrrole incorporating with *N*-acyl group, particularly *N*-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole monomer, has been achieved via copper-catalyzed amidation reaction. Then monomer BDP was imposed bromine by the brominating replacement reaction to create 2,6-dibromo-*N*-benzoyl dithieno[2,3-b:2’,3’-d]pyrrole monomer. The chemical structures of these monomers were clarified by ^{1}HNMR and FT-IR analyses. Further studies on these monomers are underway in our laboratory for generation of D-A conjugated polymers.

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