

SYNTHESIS OF SOME POTENTIAL SEMI-CONDUCTOR COMPOUNDS VIA ARYLATION OF BENZO[1,2-*b*:4,5-*b'*]DITHIOPHENE

Đến tòa soạn 18-11-2019

Tran Thi Phuong, Nguyen Thi Van Khanh, Nguyen Hien, Duong Quoc Hoan
Department of chemistry, Hanoi National University of Education

TÓM TẮT

Bốn dẫn xuất bán dẫn tiềm năng chứa benzo[1,2-*b*:4,5-*b'*]dithiophene được tổng hợp thành công thông qua phản ứng ghép chéo Heck. Điều kiện phản ứng aryl hóa tối ưu là benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT, 1 equiv.), 1-bromo-4-nitrobenzene (2 equiv.), potassium acetate (5 equiv.), PdCl(C₃H₅)(dppb) (3 mol %) trong dung môi dimethyl acetamide (DMAC) ở 120 °C trong 22 giờ. Sự chọn lọc vị trí của phản ứng aryl hóa thứ nhất và thứ hai lần lượt là vị trí 9 và 10. Sự chọn lọc đó đã được chứng minh trên cơ sở phân tích phổ cộng hưởng từ hạt nhân hai chiều HMBC và phương pháp nhiễu xạ tinh thể X-ray.

Keyword: BDT, dithiophene, benzo dithiophene, Heck coupling reaction, semiconductor

1. INTRODUCTION

In 1956, the Nobel Prize in Physics was awarded jointly to Shockley, Bardeen and Brattain for their contribution to semiconductor research and the development of the transistor. Since then, the semiconductor industry grew rapidly and has played an important role because of advantages it brings to life. Although people have used silicon as a conductor for centuries, this method shows many drawbacks such as high production cost and high energy consuming requirements. In order to overcome this problem, scientists have shifted their focus on the synthesis of other semi-conductor materials. Recently, researchers have discovered that the derivatives of benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) potentially exhibited its ability of becoming semi-conductor materials [1]. It's not until 2011, the combination of BDT units and electron-withdrawing groups (as an end-capped groups) can make the bandgap smaller that plays an important role of semi-conductor materials [2]. For example, octyl cyanoacetate showed a red-shifted absorption spectrum of approximately

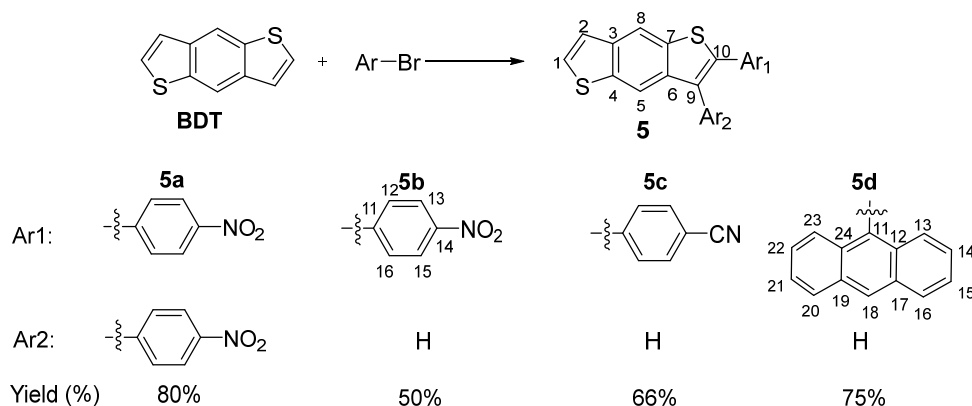
40 nm [3]. Meanwhile, Marks et al. [4] and Nguyen et al. [5] independently synthesized molecule based on BDT and DPP (Diketopyrrolopyrrole) possessed a relatively low optical bandgap of approximately 1.7 eV. Moreover, with the CNR (cyanoacetate) terminal one demonstrated a low bandgap of 1.53 eV [6]. To further explore its application, our research aims to synthesizing some new analogues of BDT with one or two electron-withdrawing groups via the substituent reaction of BDT with different electrophile such as aryl bromide derivatives.

2. RESULTS AND DISCUSSION

BDT was synthesized [7,8]. As BDT in hand, benzo[1,2-*b*:4,5-*b'*]dithiophene based compounds were synthesized following Scheme 1. First of all, reaction of BDT with 1-bromo-4-nitrobenzene was selected to find out the best protocol for the other. Taking advantages of our previous researches [1], dimethyl acetamide (DMAC) and temperature 120 °C were kept in all entries. In comparison, PdCl(C₃H₅)(dppb) appeared to be better catalyst for this transformation than traditional Pd(OAc)₂ (entry 1 and 2). Unfortunately,

Pd(OAc)₂ did not move the reaction forward, in contract, PdCl(C₃H₅)(dppb) promoted the reaction to obtain product. The yields of entries increased according to amount of time of

reactions. After 22h, the reaction kept constantly and gave expected product **5a** in 80%.



Scheme 1. Synthesis benzo[1,2-b:4,5-b']dithiophene based compounds

Through examining different conditions, we have discovered the optimized condition for the substituent reaction of BDT with 1-bromo-4-nitrobenzene is 1 equivalent of BDT, 2 equivalent of bromide substrate, 5 equivalent of potassium acetate and 3 mol % of PdCl(C₃H₅)(dppb) in DMAC, heated at 120 °C

for 22 hours, Table 1. The equivalents of bromo-aromatic reactants were changed for each purpose. Then, when using the optimized condition for our cases, the data of product **5b**, **5c** and **5d** were shown in experimental section. The yields of **5b**, **5c** and **5d** were 50%, 66% and 75% respectively.

Table 1. Optimization arylation of BDT with 1-bromo-4-nitrobenzene

Entry	Catalyst	Time	Yield
1	Pd(OAc) ₂	22 h	No reaction
2	PdCl(C ₃ H ₅)(dppb)	8h	trace
3		12h	16%
4		16 h	20%
5		20 h	65%
6		22 h	80%

Reaction condition: BDT (1 equiv.), 1-bromo-4-nitrobenzene (2 equiv.), potassium acetate (5 equiv.), 3 mol % of PdCl(C₃H₅)(dppb) in DMAC, 120 °C

Structural determination of these compounds is facing two problems: (i) Selectivity of the first arylation (ii) Selectivity of the second arylation. To overcome these barriers, compound **5a** was recorded X-ray, **5b** was recorded HMBC and HSQC spectra. Compound **5d** was recorded all HSQC, HMBC

spectra and X-ray. It was found that the first arylation selectivity was inserted at position α (position 10). Hence, HMBC spectrum of compound **5b** showed a cross peaks of H9 with both C12 and C16. In addition, there was another cross peak of H12 and H16 with C10. Similarly, HSQC and HMBC of compound **5d**

performed a cross peak *a* of C9-H9 (Figure 3); HMBC had cross peaks *b* (Figure 3, HMBC picture) of H9 and C11 and peak *c* showed the

connection of H9 and C10. This connection was determined further by X-ray of compound **5d**, Figure 1, by a new bond C10-C11.

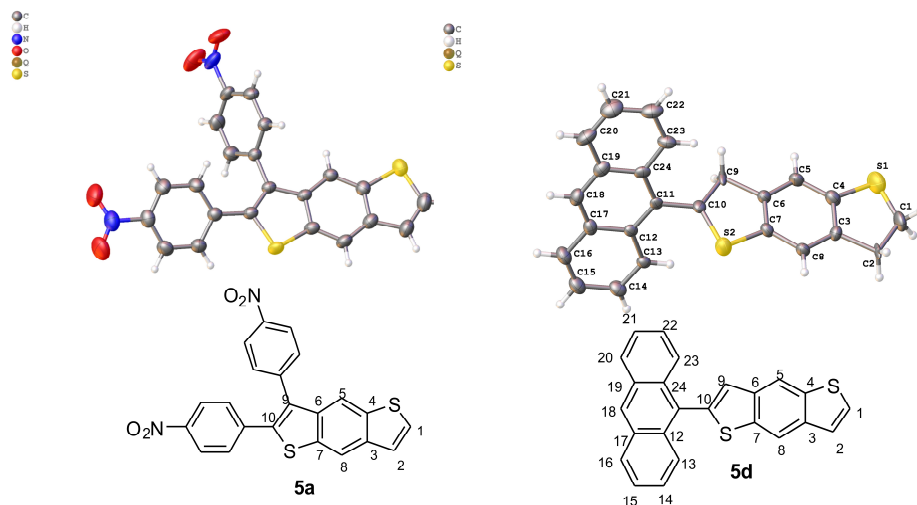


Figure 1. X-ray pictures of compound **5a** and **5d**

Interestingly, the site selectivity of the second direct arylation reaction was at position 9, X-ray of **5a**, Figure 1. To explain the observation, the proposed mechanism shows that migratory insertion is easily happened at C-H bond which has lower electron density, Figure 2. Theoretically, based on the chemical shifts, the

arylation must happen at C9-H9 bond which has the biggest chemical shift value (8.06 ppm) that matched with the prediction of the electron withdrawing group (4-NO₂C₆H₅) which decreased electron density at C9-H9 bond strongly.

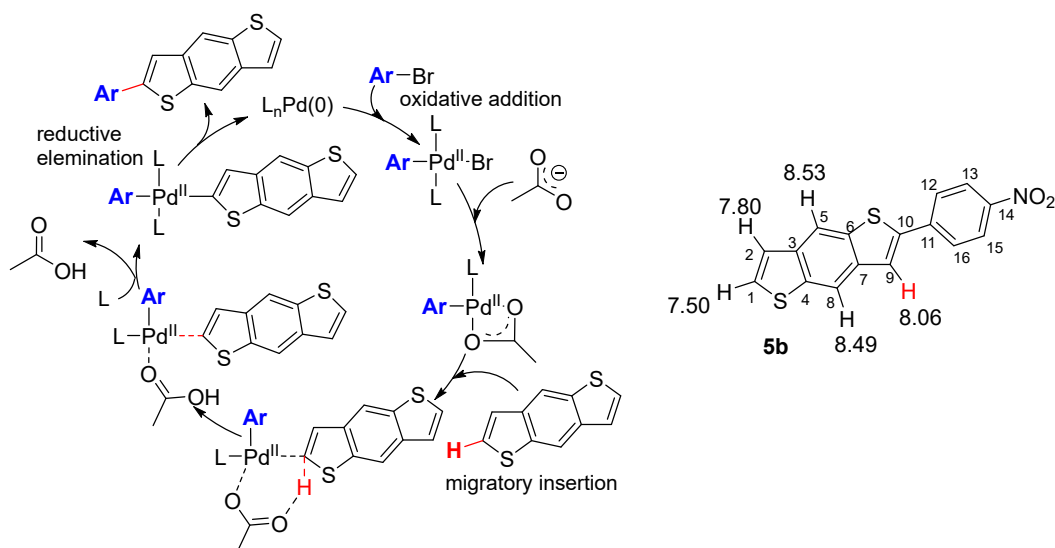


Figure 2. Some information of ¹H NMR of compound **5b**

Besides, assignments of each carbon and hydrogen atom of compound **5b** have been done correctly as showed in Figure 3. For example, cross peak *d* was an evidence for identification of H5 and H8 or C5 and C8 due to 3 bonds from H9 to C5 instead of 4 bonds from H9 to C8. Another example, identification of C1 and C2 or H1 and H2 was

simple because H1, C1 couldn't have any cross peaks with C5/H5 or C8/H8 due to long carbon side chain; meanwhile, C2 and H2 could (see peak *e* and *f*). Furthermore, mass spectra showed right molecular weight of all compounds. MS of compound **5d** was performed in the Figure 3 [9].

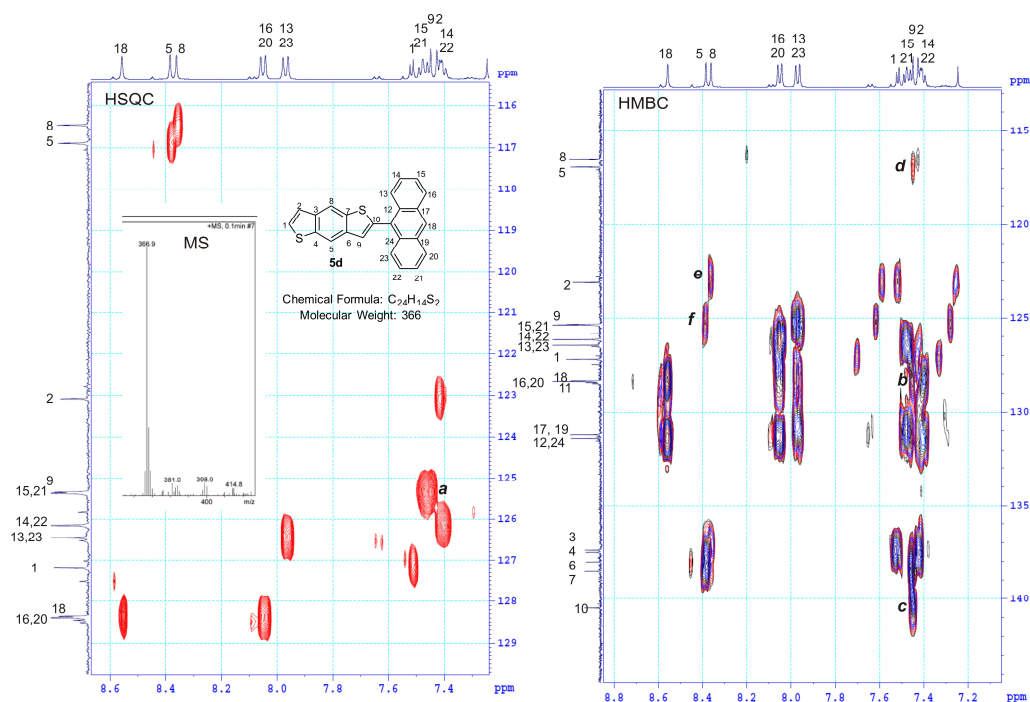


Figure 3. HSQC, HMBC and MS spectra of compound **5d**

3. CONCLUSION

The substituent reactions of BDT with 2 different bromide aryl have been optimized to give corresponding desired BDT derivatives in moderate yield. NMR and X-ray analysis elucidated the selectivity of the first and the second arylations was at positions of 9 and 10 respectively. The reaction is substrate dependent, and potentially have application for semiconductors in organomaterial field.

4. EXPERIMENTAL

ESI mass spectra were recorded using Agilent LC-MSD-Trap-SL series 1100 spectrometer. NMR spectra were recorded on a Bruker AVANCE 500 spectrometer in DMSO- d_6 or $CDCl_3$.

Synthesis of 1,2- di (4-nitrophenyl) benzo (1,2-*b*:4,5-*b'*) dithiophene (**5a**)

To mixture of BDT (30mg, 0.158 mmol, 1 equiv), 1-bromo-4-nitrobenzene (63.8 mg, 0.316 mmol, 2 equiv), potassium acetate (CH_3COOK) (77.4 mg, 0.79 mmol, 5 equiv) and $PdCl_2(C_3H_5)_2(dppb)$ (2.9 mg, 0.005 mmol, 3 mol %) were mixed in 3mL of DMAc and heated at 120°C over the period of 19 hours. After the reaction was completed, the crude mixture was purified by chromatography on silica gel eluted with the mixture of 98% *n*-hexane and 2% ethyl acetate to achieve orange product **5a** (13.65 mg, 80%, mp. = 230-231 °C). 1H NMR ($CDCl_3$, 500 MHz), δ (ppm): 8.36 (s, 1H), 8.35(d, $J = 9.0$ Hz, 2H), 8.15 (d, $J = 9.0$ Hz, 2H), 8.04 (s, 1H), 7.57 (d, $J = 8.5$

Hz, 2H), 7.56 (d, $J = 5.5$ Hz, 1H), 7.46 (d, $J = 8.5$ Hz), 7.42 (d, $J = 5.5$ Hz, 1H); ^{13}C NMR (CDCl_3 , 500 MHz), δ (ppm): 145.2, 145.0, 142.5, 140.7, 139.9, 138.5, 134.2, 128.4, 127.9, 126.2, 125.6, 124.4, 123.5, 122.6, 122.2, 118.6, 118.2, 113.7; ESI-MS, $[\text{M}+\text{H}]^+$, m/z : 432.8.

Synthesis of 2-(4-nitrophenyl)benzo[1,2-b:4,5-b']dithiophene (5b)

Following the synthesis of compound **5a**: from BDT (30mg, 0.158 mmol, 1 equiv), 1-bromo-4-nitrobenzene (31.9 mg, 0.158 mmol, 1 equiv), potassium acetate (CH_3COOK) (77.4 mg, 0.79 mmol, 5 equiv), $\text{PdCl}(\text{C}_3\text{H}_5)(\text{dppb})$ (2.9 mg, 0.005 mmol, 3 mol %), 3mL of DMAc gave **5b** as red crystal (24.6 mg, 50%, mp. = 198-199 °C). ^1H NMR (DMSO-d_6 , 500 MHz), δ (ppm): 8.53 (s, 1H, H5), 8.49 (s, 1H, H8), 8.30 (dd, $J = 6.5$, 2.0 Hz, 2H, H13 and H15), 8.12 (s, 1H, H9), 8.06 (dd, $J = 6.5$, 2.0 Hz, 2H, H12 and H16), 7.80 (d, $J = 5.5$ Hz, 1H, H2), 7.50 (d, $J = 5.5$ Hz, 1H, H1); ^{13}C NMR (DMSO-d_6 , 125 MHz), δ (ppm): 146.6 (C14), 140.3 (C10), 139.5 (C11), 137.9 (C6), 137.4 (3), 136.9 (C4), 136.2 (C7), 128.4 (C2), 126.5 (C12 and C16), 123.8 (C13 and C15), 122.7 (C1), 122.2 (C9), 117.5 (C5), 116.5 (C8); ESI-MS, $[\text{M}+\text{H}]^+$, m/z : 312.8.

Synthesis of 4-(benzo[1,2-b:4,5-b']dithiophen-2-yl)benzonitrile (5c)

Following the synthesis of compound **5a**: from BDT (30mg, 0.158 mmol, 1 equiv), 4-bromobenzonitrile (28.75 mg, 0.158 mmol, 1 equiv), potassium acetate (CH_3COOK) (77.4 mg, 0.79 mmol, 5 equiv), $\text{PdCl}(\text{C}_3\text{H}_5)(\text{dppb})$ (2.9 mg, 0.005 mmol, 3 mol %), 3mL of DMAc gave **5c** as brown crystal (30.3 mg, 66%, mp. = 204-205 °C). ^1H NMR (CDCl_3 , 500 MHz), δ (ppm): 8.29 (s, 1H), 8.26 (s, 1H), 7.81 (dd, $J = 6.5$, 2.0 Hz, 2H), 7.70 ($J = 6.5$, 2.0 Hz, 2H), 7.67 (s, 1H), 7.50 (d, $J = 5.5$ Hz, 1H), 7.36 (d, $J = 5.5$ Hz); ^{13}C NMR (CDCl_3 , 500 MHz), δ (ppm): 142.1, 138.7, 138.1, 137.9, 137.2, 132.7, 127.9, 126.8, 123.0, 120.9, 118.5, 117.5, 116.8, 112.6, 111.7; ESI-MS, $[\text{M}+\text{H}]^+$, m/z : 291.8.

Synthesis of 9-benzo (1,2-b:4,5-b') dithiophenyl anthracene (5d)

Following the synthesis of compound **5a**: from BDT (30mg, 0.158 mmol, 1 equiv), 9-bromoanthracene (20.3 mg, 0.079 mmol, 1 equiv.), potassium acetate (CH_3COOK) (77.4 mg, 0.79 mmol, 5 equiv), $\text{PdCl}(\text{C}_3\text{H}_5)(\text{dppb})$ (2.9 mg, 0.005 mmol, 3 mol %), 3mL of DMAc gave **5d** as white crystal (28.3 mg, 75%, mp. = 210-211 °C). ^1H NMR (CDCl_3 , 500 MHz), δ (ppm): 8.59 (1H, s, H18), 8.42 (s, 1H, H5), 8.40 (s, 1H, H8), 8.09 (d, $J = 8.5$ Hz, 2H, H16 and H20), 8.01 (d, $J = 8.5$ Hz, 2H, H13 and H23), 7.56 (d, $J = 6.0$ Hz, 1H, H2), 7.51 (t, $J = 8.0$ Hz, 2H, H 15 and H21), 7.48 (s, 1H, H9), 7.46 (s, 1H, H1), 7.44 (t, $J = 7.0$ Hz, H14 and H22); ^{13}C NMR (CDCl_3 , 500 MHz), δ (ppm): 140.5 (C10), 138.5 (C7), 138.0 (C6), 137.5 (C4), 137.4 (C3), 131.4 (C12 and C24), 131.2 (C17 and C19), 128.4 (C11), 128.3 (C16 and C20), 128.3 (C18), 127.1 (C1), 126.4 (C13 and C23), 126.1 (C14 and C22), 125.37 (C21 and C25), 125.34 (C9), 123.0 (C2), 116.9 (C5), 116.4 (C8). ESI-MS, $[\text{M}+\text{H}]^+$, m/z : 366.9.

REFERENCES

1. T. M. Ha Vuong, Didier Villemin, Hung-Huy Nguyen, Tin Thanh Le, Tung T. Dang, Hien Nguyen, *Programmed Site-selective Palladium Catalyzed Arylations of Thieno[3,2-b]thiophen*, Chem. Asian J. **12**, 2819 – 2826 (2017).
2. Huo, L.; Li, Z.; Guo, X.; Wu, Y.; Zhang, M.; Ye, L.; Zhang, S.; Hou, J. *Benzodifuran-alt-thienothiophene based low band gap copolymers: substituent effects on their molecular energy levels and photovoltaic properties*. Polym. Chem. **4**, 3047–3056 (2013).
3. Zhou, J.; Wan, X.; Liu, Y.; Zuo, Y.; Li, Z.; He, G.; Long, G.; Ni, W.; Li, C.; Su, X.; Chen, Y. *Small molecules based on benzo[1,2-b:4,5-b']dithiophene unit for high-performance solution-processed organic solar cells*. J. Am. Chem. Soc. **134**, 16345–16351 (2012).

Xem tiếp Tr. 250