

Synthesis of 4-Carbazole -7- Thiophen[1,2,5] Thiadiazolo [3,4-c]Pyridine

Y Liu, X H Zhang, W J Ding and X X Sun*

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, China

Corresponding author and e-mail: X X Sun, sunxiaoxia77@126.com

Abstract. A novel A-D-A small organic molecule 4-Carbazole -7- thiophen-[1,2,5]thiadiazolo[3,4-c]pyridine was synthesized by two step with good yield. The compound with good electronic and optical properties may be a candidate for D-A-D type organic light-emitting diodes.

1. Introduction

Designs and synthesis of novel conjugated organic molecules and polymers have drawn widely attention upon the past two decades, owing to develop new synthetic methodology and commercial optoelectronic device which can be put into use, take organic field-effect transistors (OFETs), [1] polymer light-emitting diodes (PLEDs) [2-4] and polymer solar cells (PSCs) [5-6] for example. To carry out the application of full-color advanced flat panel displays, the development of suitable green-, white-, blue- and red-emitting (RGB) organic molecules and polymers [7] will be important. However, the molecular structure, molecular weight, and purity of the polymer are usually uncertain, leading to differences in the properties of different batches of materials, which may lead to batch instability during industrial production in the future. Compared with polymer materials, the molecular structure and molecular weight of organic small-molecule solar cell materials are well-defined, and these materials are relatively easy to separate and purify, have high purity, and have good batch stability in the preparation process. However, the development of organic small molecule solar cell is relatively slow, the types of materials reported in the literature are scarce, and the photoelectric conversion efficiency of the battery is also very low.

2,1,3-benzothiadiazole (BT) has been widely used by researchers to construct D-A conjugated molecules because of its strong coplanarity, strong electron-withdrawing ability, high oxidation-reduction potential and good stability. And D-A type conjugated molecules are widely used in organic photoelectric materials. [8] During the past few years organic small molecules and conjugated polymer materials constructed with BT structural units as acceptor materials have achieved great achievements in organic solar cells, which promoted the development of organic solar cells to a large extent. In the area of solution-processable organic small molecules and conjugated macromolecules constructed by the BT cell, the Li Yongfang Research Group has done massive and systematic research work and has obtained a series of very significant research results. In 2006, the research group constructed a bulk heterojunction solar cell of small molecule Figure 1 using thiophene,

triphenylamine and BT as structural units. The photoelectric conversion efficiency of the compound was 0.26%. In subsequent work, the research group constructed new molecules S2 and S3 by adjusting the chemical bond of S1, the photoelectric conversion efficiency reached 1.23% when the bulk heterojunction solar cell was prepared in which S2 was the donor and [6,6]-phenyl-C71-methyl butyrate (PC71BM) as a receptor material. In 2011, the research group replaced thiophene in the molecule with thiophene which has greater electron-donating capability and coplanarity. The small molecules S4 to S6 are constructed as shown in the figure. It was found that by changing the molecular structure, the absorption wavelength of the material can be effectively broadened and the photoelectric conversion efficiency of this class of compounds can reach 1.44%.

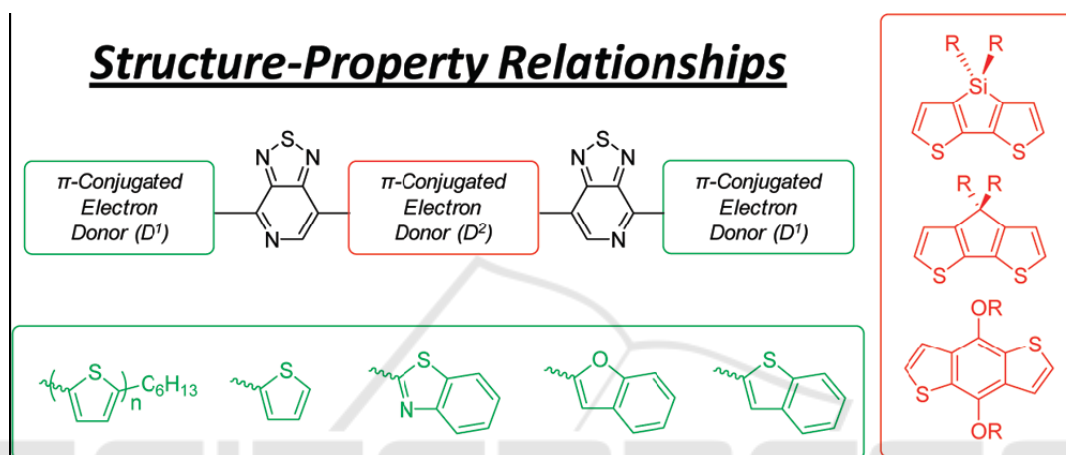


Figure 1. Pyridal-thiadiazole-Based Narrow Band Gap Chromophores.

During solution processing, conjugated molecules including pyridal- [2,1,3]thiadiazole (PT) sections synthesized by Guillermo C. Bazan[9] have recently come up to 6.7% efficiencies of power conversion, molecular bulk-heterojunction (BHJ) organic photovoltaics. Due to the significance of the systems which belong to the novel type of molecule and establishing a more effective pathway to make solid-state performances better, they start to methodically change the structure of the molecule and assess the property–framework relationships. D1-PT-D2-PT-D1 compounds were synthesized by stille coupling reaction where donor meaning a relatively rich electronic ratio compared to PT. Physical properties were measured on a combination of absorption spectroscopy, thermal gravimetric analysis, cyclic voltammetry, solubility and differential scanning calorimetry. Alter to end-capping D1 units due to better control the electronic energy levels both in solution and in steric hindrance.



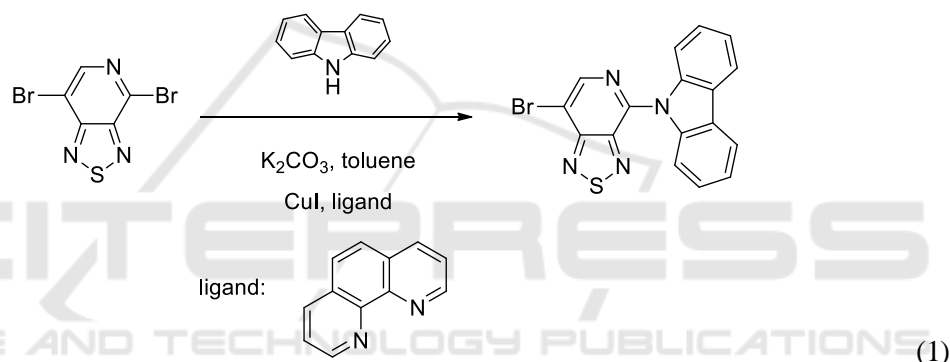
Figure 2. DAA organic molecules.

Ken-Tsung Wong et al.[10] used dicyanovinylene as an electron withdrawing moiety while 2,1,3-benzothiadiazole as another acceptor. Three DAA small-molecule organic solar cells were strategically designed and synthesized through still coupling reaction by changing various electron-donating moieties. At the level of molecules and single compounds, the photophysical and electrochemical properties of the compounds and the energy levels of the molecules were systematically studied. In addition, the connection between the structure of the molecules and their properties was clearly obtained. The UV maximum absorption bands were near 700-800 nm which assigned to the ICT transition. The photoelectric power conversion efficiency (PCE) of solar cell materials was up to 6.6±0.2%, which provides reference data for the design of small molecule compounds used in photovoltaic cell materials.

2. Experimental section

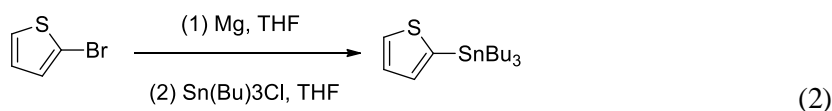
Without being purified, all chemicals and reagents were received from commercial sources. The solvents used in the chemical synthesis is purified by distillation. All chemical reactions are carried out in the atmosphere of argon or nitrogen.

2.1. Synthesis of 7-bromo-4-Carbazole-[1,2,5]thiadiazolo[3,4-c]pyridine



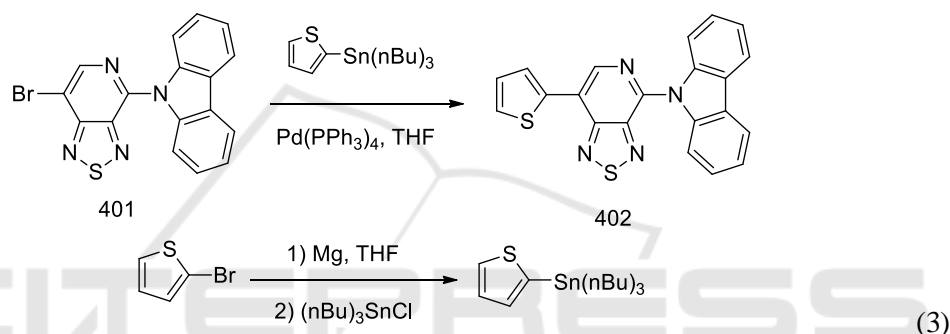
To a 25.0 ml single-mouth flask was added 2,7-dibromopyridothiadiazole (295.0 mg, 1.0 mmol), carbazole (200.6 mg, 1.2 mmol) at room temperature. The cuprous iodide (19.0 mg, 0.1 mmol), sodium carbonate solid (552.0 mg, 4.0 mmol) and 1,10-phenanthroline (36.0 mg, 0.2 mmol), which had been previously dehydrated and dried in a vacuum drying oven were added to the above flask, 15.0 mL of purified toluene was used as the solvent (deoxidation). The reaction system was refluxed overnight under argon protection. TLC showed that the starting material point had disappeared and the reaction was stopped. Then at nature air cooling, Silica gel was directly added to the reaction system, and the solvent was evaporated on a rotary evaporator to obtain a red-brown solid. Column separation was performed using petroleum ether and ethyl acetate as the eluent (V (petroleum ether): V (ethyl acetate) = 15:1) and the second fraction was collected and spin-dried to afford a red solid 125.0 mg in 66.0% yield. ^1H NMR (400 MHz, CDCl_3 , TMS): δ (ppm) 8.72(s, 1H), 8.12-8.10(d, 2H), 7.51-7.59(d, 2H), 7.31-7.41(d, 4H); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 145.34, 133.76, 126.11, 124.45, 123.92, 120.96, 121.16, 115.63, 112.51, 111.57.

2.2. Synthesis of Tributyl(2-thienyl)stannane



In a two neck round bottom flask charged with magnesium (880 mg, 36.8 mmol) in degassed THF (3.0 mL) was slowly added 2-bromothiophene (5.0 g, 30.67 mmol, 1 equiv) in (30 mL degassed THF) to reach reflux temperature. Further stirring at reflux temperature was performed for 1 h. The product was used in the next step without further purification. The solution was transfer to -78 °C. After stirring at the same temperature for 1 h, Tri-n-butyltin chloride (1m in hexane, 10.96 g, 33.74 mmol) was added to the reaction mixture and stirred at the same temperature for 0.5 h. Then the temperature was slowly rise to room temperature while stirring was maintained for 12 h. The aqueous solution of Na₂CO₃ was added into the mixture and the aqueous phase was then extracted with n-hexane three times and washed with 50ml brine. The organic layer was dried over anhydrous magnesium sulfate and filtered. Yellow liquid was obtained after evaporation of the solvent. The residue was purified by column chromatography through Al₂O₃ using n-hexane to give 9.7 g product in 85.0% yield as slight yellow oil.

2.3. Synthesis of 4-Carbazole -7- thiophen-[1,2,5]thiadiazolo[3,4-c]pyridine



To a 10.0 mL single-mouth flask was added 7- bromo-4-Carbazole-[1,2,5]thiadiazolo[3,4-c]pyridine (40.0 mg, 0.11 mmol) and Tributyl(2-thienyl)stannane (156.0 mg, 0.42 mmol) at room temperature. To the flask was added 5.0 ml of purified tetrahydrofuran as a solvent and activated under argon atmosphere at room temperature for 30.0 min. Tetrakis(triphenyl)phosphine palladium (Pd(PPh₃)₄) (20.0 mg, 0.01 mmol) was added to the flask to continue activating for 15 min. Then, the reaction system was transferred to an oil bath at 80 °C and refluxed overnight. The reaction was stopped when TLC test showed that the starting point disappeared and the new point was generated. After cooling this system to room temperature, silica gel was added to the reaction, and the solvent was spin-dried on a rotary evaporator to obtain a bright red solid. Column separation was performed using petroleum ether and ethyl acetate as the eluent (V (petroleum ether): V (ethyl acetate) = 10:1) and the second fraction was collected and spin-dried to collect a red solid 28.0 mg in 70.0% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ(ppm) 8.91(s, 1H), 8.21-8.33(m, 3H), 7.61-7.63(d, 2H), 7.55-7.56(d, 2H), 7.35-7.42(m, 4H), 7.27-7.29(m, 1H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 126.11, 124.45, 123.92, 120.96, 121.16.

3. Result and discussion

A novel A-D-A small organic molecule 4-Carbazole -7- thiophen-[1,2,5]thiadiazolo[3,4-c]pyridine was synthesized by two step with good yield. [1,2,5]thiadiazolo[3,4-c]pyridine was used as an electron withdrawing moiety while carbazole and thiophene as the two different electric donor moiety. The UV-vis absorption spectra of the two molecules in THF are drawn in Figure 3. As shown from Figure 3 that after the incorporation of carbazole on pyridine- thiadiazole, the maximum UV absorption wavelength is significantly red shifted to 458 nm. After the introduction of a thiophene fragment, the UV absorption of the molecule will be followed by a red shift of 20 nm to

478 nm. If we then introduce an electron-donating segment and introduce the above-mentioned fragments into small molecules, the molecules should be applicable to many fields.

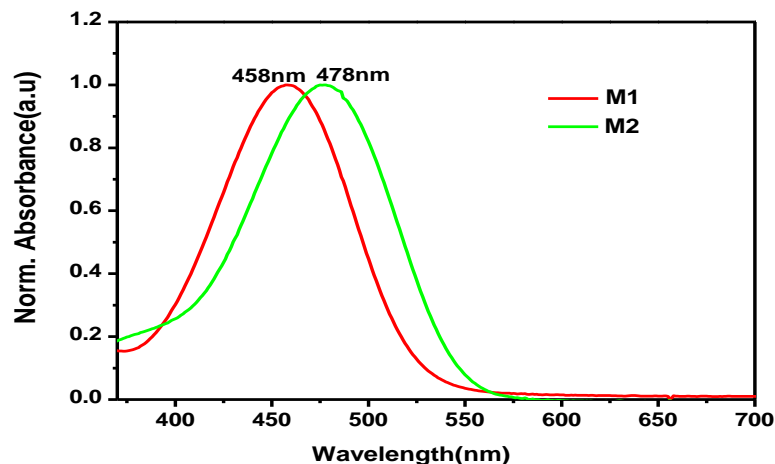


Figure 3. the UV absorption spectra of small molecules M1 and M2.

4. Conclusions

A novel A-D-A small organic molecule 4-Carbazole -7- thiophen-[1,2,5] thiadiazolo[3,4-c]pyridine was synthesized with good yield by two steps. [1,2,5]thiadiazolo[3,4-c]pyridine was served as an electron withdrawing moiety while carbazole and thiophene as the two different electric donor moiety. In order to boost device efficiencies, further engineering of molecular structures and morphology optimization are currently underway.

Acknowledgments

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