

Synthesis and Characterization of Small Functional Molecule Composed of BseDz

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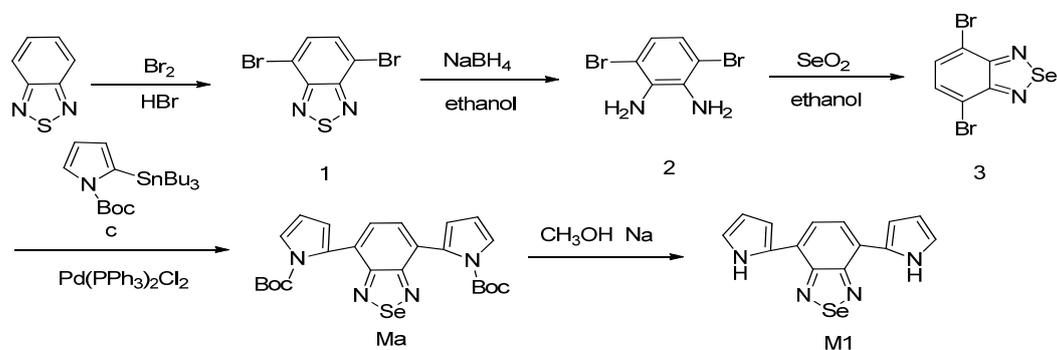
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Abstract. Novel organic conjugated molecule composed of central benzoselenadiazole (BseDZ) units as electron acceptor and two pyrrole groups as electron donors was prepared via the Stille coupling reaction. The molecular structure was verified by ¹HNMR and ¹³CNMR. UV-vis spectroscopy shows that molecule has broad absorption spectrum and a low band gap by theoretical calculation, The fluorescence spectra exhibit strong emission peaks in the organic light regions. Cyclic voltammetry exhibited that molecule have reversible redox curve, property of electrochemical is stable. which suggest that it has potential application value in photovoltaic material.

Introduction

The D-A type molecules have attracted much attention because of their great potential applications as photoactive materials in molecular electronics, Owing to the advantages of π -conjugated molecules, ease of molding, and outstanding physical characteristics, they have found application to organic photovoltaic cells(OPVs)^[1], organic light emitting diodes(OLEDs)^[2-3], organic thin film transistors (OTFTs)^[4-6], and organic transparent conducting electrodes^[7]. One of the most successful approaches to these low band gap polymers is the application of an alternating sequence of donor-acceptor (D-A) units in π -conjugated molecules^[8], since the semiconducting behavior of π -conjugated molecules originates from the dispersion of the HOMO and LUMO levels of the monomer into a valence and a conduction band upon chain elongation, a narrow band gap can indeed be obtained by starting from a monomer that already has a narrow HOMO–LUMO energy separation. Building on rapid developments and tremendous progresses in the field of organic photovoltaic solar cells and organic light-emitting diodes (OLEDs), then BseDZ-based molecules have a good promising in those field.

In this article, we synthesize and characterize a new D-A type molecules composed of central BseDZ and terminal pyrrole groups segments M1. the electron donor efficiency of pyrrole groups is better than other five circular groups because of the N-substituted. The target molecules are synthesized and characterized in details. Their photoelectric properties are also studied by means of UV-vis/fluorescence spectroscopy and cyclic voltammetry.



Scheme1. Synthetic route to monomers

Experimental

General. ^1H NMR and ^{13}C NMR spectra were collected using a Bruker AM-400WB spectrometer in chloroform- d (CDCl_3) and $\text{DMSO}-d_6$ as solvent and tetramethylsilane (TMS) as the internal standard. Ultraviolet absorption spectra were measured using a Shimadzu UV-1800 UV spectrometer. Emission spectra were obtained on a Hitachi F-4500 fluorescence spectrometer.

Materials. DMF was dried over CaH_2 and then distilled under nitrogen atmosphere and deoxygenated by purging with nitrogen for 30 min before use in monomer synthesis. THF was dried over sodium/benzophenone and distilled under argon atmosphere before use. Solid films were easily formed by spin coating from PMMA-THF solution (1 mg ml^{-1} , quartz substrate). Thiophene, methanol, bromobutane, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, Selenium dioxide, Sodium borohydride and other chemicals were obtained commercially and used without further purification.

Synthesis. The synthetic route of small molecules is shown in Scheme 1, The detailed synthetic processes are as following.

4,7-dibromobenzo[*c*][1,2,5]thiadiazole

A mixture of benzo[*c*][1,2,5]thiadiazole (5.00 g, 36.8 mmol) and drops of liquid Br_2 (6 ml) in 80% HBr (50 ml) at room temperature, then heating to reflux at 120°C for 48 h. TLC monitoring the reaction, stopping the reaction when raw materials disappear. The reaction mixture was poured into saturated sodium sulfite (Na_2SO_3) solution and the aqueous layer was extracted with ethyl acetate (EA) three times, the combined organic phase was dried over anhydrous magnesium sulfate (MgSO_4). After filtration, concentration in vacuum gave the yellow solid crude product, which was recrystallized from methanol. Yield: 12.0 g (91%), ^1H NMR (400 MHz, CDCl_3): $\delta=7.42$ (d, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta=145.7, 135.3, 107.2$ ppm.

3,6-dibromobenzene-1,2-diamine

To a three neck round-bottom flask containing ethanol (50 mL), 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (2.9 g, 10.0 mmol) and adding NaBH_4 slowly, the reaction was allowed to warm at room temperature and stirred for 48h. The reaction mixture was poured into the water, then extracting with EA three times, the organic layer washed by saturated salt water, drying with MgSO_4 for 12h. The crude product was concentrated in vacuum, getting yellow solid. (yield: 81%). ^1H NMR (400 MHz, CDCl_3): $\delta=6.87$ (d, 2H), 3.92 (s, 4H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta=133.73, 123.27, 109.70$ ppm.

4,7-dibromobenzo[*c*][1,2,5]selenadiazole

Monomer 2 (0.7g, 2.5mmol) was dissolved completely in anhydrous ethanol (20ml), selenium dioxide (0.3g, 2.5mmol) dissolving in water were added to a 100ml flask, then stirred at 85°C for 12h. The reaction mixture was concentrated in vacuum and recrystallized from ethanol. 0.7 g (yield: 95%). ^1H NMR (400 MHz, CDCl_3): $\delta=7.52$ (d, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta=146.1, 135.5, 107.6$ ppm.

4,7-di(1H-pyrrol-2-yl)benzo[*c*][1,2,5]selenadiazole (M1)

Ma was prepared by monomer 3 and c (tert-butyl 2-(tributylstannyl)-1H-pyrrole-1-carboxylate) with a molar ratio of 1:3, respectively. The reaction was heating for reflux in THF under argon atmosphere for 2d. Then the crude product was purified by column chromatography on neutral alumina (EA/PE, 1:1 v/v) to obtain a yellow fluorescent compound. After the Stille coupling, Ma was dissolved in methanol and Na with a molar ratio of 1:14, then the reaction mixtures were heated under argon atmosphere for 1d. The crude product was evaporated and extracted with dichloromethane. The monomer was purified by column chromatography (PE/EA, 2:1 v/v) to obtain target product M1 in 72% yield. ^1H NMR(400MHz, CDCl_3): $\delta=7.8-7.75$ (s, 2H), 7.65-7.6 (s, 2H), 7.2 (d, 2H), 6.95-6.87 (t, 2H), 6.45-6.4(d, 2H) ^{13}C NMR(100MHz, CDCl_3): $\delta=126.8, 126.8, 126.9, 127.9, 139.4, 157.2$ ppm.

Results and Discussion

Optical properties

Tab.1 Optical data of molecule M1

molecule	solution				film			
	$\lambda_{\text{abs}}^{\text{a}}/\text{nm}$	$\lambda_{\text{lum}}^{\text{b}}/\text{nm}$	Stokes Shift	$\lambda_{\text{onset}}^{\text{a}}/\text{nm}$ ($E_{\text{g}}^{\text{c}}/\text{eV}$)	$\lambda_{\text{abs}}^{\text{a}}/\text{nm}$	$\lambda_{\text{lum}}^{\text{b}}/\text{nm}$	Stokes Shift	$\lambda_{\text{onset}}^{\text{a}}/\text{nm}$ ($E_{\text{g}}^{\text{c}}/\text{eV}$)
M1	257,333,401	600	199	480(2.58)	261,337,405	564	159	483(2.56)

^aMeasured in a dilute ACN solution (1×10^{-5} M). ^bExcited at the absorbance maximum. ^cEstimated from the onset of absorbance ($E_{\text{g}} = 1240/\lambda_{\text{onset}}$).

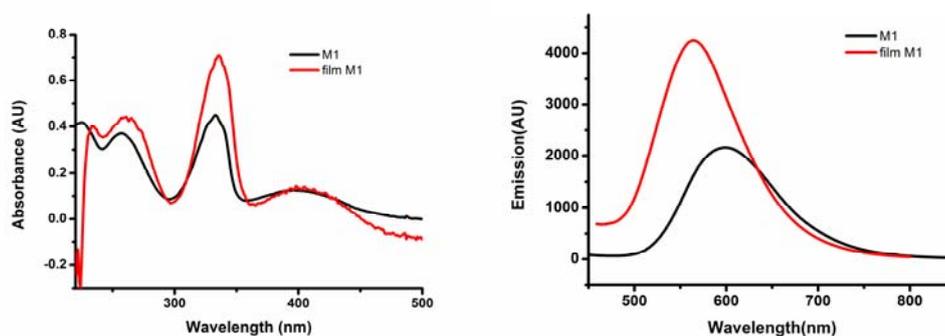


Fig.1 Uv-abs and fluorescence spectrum of molecule M1 in the solution and PMMA films

Table 1 showed that product M1 exhibited three obvious absorption spectra bands in ACN solution(257,333,401nm) and PMMA thin film(261,337,405nm), the scope of absorption spectra range from 257 nm to 337 nm, which were ascribed to the localized π - π^* transition, and the peak absorbing from 401nm to 405nm could be attributed to the intramolecular charge-transfer(ICT) transition between the center benzoselenadiazole unit and the terminal pyrrole[9]. Absorption peak of M1 in PMMA thin film exhibited longer wavelength than that in ACN solution state, which showed that the presence of intermolecular interaction in the thin film. In solution, the fluorescence spectra of M1 exhibit an emission maxima at 600 nm, which brings a relatively large bathochromic shift(36nm), From the PMMA thin film to the ACN solution, the fluorescence spectra of the target molecules were slightly red-shifted, attributing to the presence of stronger interactions between molecules (packing effect). The fluorescence spectra exhibit that the emission maxima of compound M1 from 564 nm to 600 nm in thin film and solution, which belonged to orange light range. Thus, the target compounds is expected to be a promising pure orange light-emitting material for applications in organic light-emitting diodes (OLEDs).

Electrochemical properties

The electrochemical properties of the target molecules M1 was investigated by Cyclic voltammetry (CV) measurements in ACN at room temperature under argon, containing 0.1 M n-Bu4NPF6 as a supporting electrolyte. The data of electrochemical potentials were summarized in Table 2, the onset oxidation and reduction potentials from the cyclic voltammetry correspond to the HOMO and LUMO energy levels, respectively. As Fig.2 shown, the CV of M1 exhibited irreversible oxidative and reduction processes.

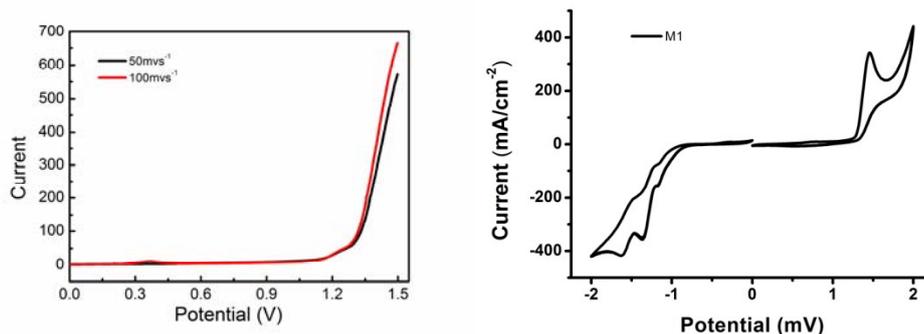


Fig.2 Electrochemical scanning curve of molecule M1

As expected, when growth rate of voltage is 100mVs^{-1} , oxidation curve is smooth, oxidation effect is best. Cyclic voltammetry (CV) reveals that the electron transfer in the process of electrochemical, we can see initial oxidation potential of 1.32 V from the diagram, oxidation curve is very smooth, oxidation process is stable, On the other hand, during cathodic scan, reversible reduction of M1 is -1.20 , ascribed to low electron density, the small molecule M1 has the stable redox curve, the electrochemical property is stable. The range of HOMO is from -5.2 to -5.8 , which show that molecule contains a good electron donor group, optical band gap and electrochemical band gap belong to a narrow band gap range, which can be concluded that small molecule M1 has potential application value in the field of organic photoelectric materials.

Summary

In summary, we have designed and synthesized the target product M1 based on central BseDZ as electron acceptor(A) unit and pyrrole as electron donor(D) unit. it exhibited broad absorption and good solubility in common organic solvents. Optical spectra of the target molecule reveals that the introduction of electronic donor induces an intramolecular charge transfer, leading to a blue-shift of the absorption maximum. Meanwhile, the absorption maximum in the PMMA thin film showed longer wavelength compared with that in the ACN solution, which told us stronger intermolecular interactions in solid state. The molecule has relative low band gap in solution and solid state. These results indicated that the target molecule is expected to be promising candidates for organic solar cells and luminescent material.

Acknowledgements

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