



Modelling and synthesis of solution processable dibenzothiophene derivative for organic electronics

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ABSTRACT

Increasing global demand for new, clean, nontoxic alternative energy resources has lead to a rapid swift in exploring new materials for the production of renewable energy. Thiophene based molecules attracted much attention for the fabrication of various organic electronic devices because of its excellent properties, synthetic flexibility and stability. In this context, we designed and synthesized dibenzothiophene based molecule namely 2,8-di-(4-formylphenyl)dibenzothiophene. Time-Dependent Density Functional Theory (TD-DFT) methods with PBEPBE functional using 6-311G++2d,2p basis set was used for theoretical calculations. The oligomer was synthesized by selective bromination followed by Suzuki coupling. The photophysical and electrochemical properties of this molecule were studied in detail and compared with the theoretical results.

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1. Introduction

Organic electronics is a branch of electronics which utilize organic molecules such as oligomers and polymers for electronic application. Research on π -conjugated material is of enormous interest because of its versatile optical and electronic properties. Semiconducting organic materials become promising candidates for future applications in electronic devices because of its synthetic flexibility, ease of processing and ability to tune the electronic and mechanical properties. So there is a growing interest to develop new conjugated oligomers/polymers for a variety of electronic applications such as organic field effect transistors [1–4], organic photovoltaics [5–7] and organic light emitting diodes [8–11]. The oligomers have gained special attention than polymer molecules due to their high purity and synthetic reproducibility [12–17].

Thiophene based molecules are one of the potential molecule for electronic devices due to high polarisability of sulphur atoms and ease in derivatizing thiophene ring through substitution at different positions [18]. Dibenzothiophene is one of the cheap and

commercially available chalcogenophene compound found in gas oil. It has a low lying HOMO compared with anthracene, flourene and carbazole [19]. So dibenzothiophene is highly stable compared to other oligomeric systems. Its planar structure which makes it favourable for inter molecular interaction and also facilitate excellent charge migration. Eventhough a variety of oligothiophenes and polythiophenes have been reported, dibenzothiophene derivatives which can be used in organic electronics is not much explored. Therefore, it is of great importance to study the photophysical and electrochemical properties of dibenzothiophene based molecules. So with this aim, we modeled and synthesized dibenzothiophene based oligomer, namely 2,8-di-(4-formylphenyl)dibenzothiophene and studied its optical and electrochemical properties.

2. Experimental

2.1. Materials

Dibenzothiophene, 4-formyl phenyl boronic acid and bis(triphenylphosphine)palladium(II) were purchased from Sigma Aldrich and used without further purification. All reagents and solvents were purchased from commercial suppliers and used without

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further purification unless otherwise stated. All reactions were carried out under an inert nitrogen atmosphere.

2.2. Spectroscopic characterization

Conventional thin film chromatography (TLC) plates (silica gel 60 F254,) were used to monitor the progress of the reaction, with spots observed under UV light at 254 and 365 nm. Column chromatography was performed with silica gel (particle size 100–200 mm). NMR spectra were recorded on a Bruker 300 MHz spectrometer. Absorption spectra were measured on Shimadzu UV-2600 and the fluorescence spectra were measured in Perkin Elmer LS 55 spectrofluorimeter. Solution state photoluminescence quantum yield was calculated using quinine sulphate (0.1 M H₂SO₄) as to standard [20]. Spectroscopic grade solvent was used for preparing sample solutions and five different solution of the sample and reference with different concentrations were made and their absorption and emission wavelength were analyzed. The quantum yield was calculated from the gradient obtained by plotting absorbance versus integrated fluorescence intensity using the equation $\phi_x = \phi_{ST} [\text{Grad}_x / \text{Grad}_{ST}] [\eta_x / \eta_{ST}]$, where subscript ST and X denotes standard and test respectively, ϕ is the fluorescence quantum yield and Grad is the gradient from the plot of absorbance and integrated fluorescence intensity and η , the refractive index of the solvent.

2.3. Electrochemical studies

The electrochemical behaviour of the compound was analyzed using cyclic voltammetry. The cyclic voltammograms were recorded with Metrohm Autolab (PGSTAT 204) electrochemical workstation at a constant scan rate of 100 mV/s. Measurements were done using electrochemical cell with three electrodes in tetrabutyl ammonium hexafluorophosphate dissolved in dichloromethane as supporting electrolyte, glassy carbon as working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode. Ferrocene was used as an internal standard for calibrating the potential. Scanning was repeated several times and no change was observed in the cyclic voltammogram obtained.

2.4. Computational studies

All the calculations in the present study have been carried out with Density Functional Theory (DFT) Method with PBEPBE [21] functional using 6-311G++(2d,2p) basis set. The geometry optimization was done without any symmetry constraints. The vibrational frequency analysis on the optimized geometry shows no imaginary frequency. This ensures that the optimized structure corresponds to a minima on the Potential Energy Surface (PES). The Time Dependent Density Functional Theory (TD-DFT) [22–24] calculation was carried out on the geometry optimized structure to determine the vertical excitation energy and electronic absorption spectra for singlet-singlet transitions of DBT-PHF

molecule using the PBEPBE functional with 6-311 g++(2d,2p) basis set. The CPCM (Conductor like Polarizable Continuum Model) model of solvation using chloroform as the solvent was adopted for calculating the solvent effects for both ground and excited states. All the calculations were carried out using the Gaussian 09 [25] program.

2.5. Synthesis

Dibenzothiophene derivative, 2,8-di-(4-formylphenyl)dibenzothiophene (DBT-PHF) was synthesized in a two step reaction as shown in Fig. 1. In the first step, dibenzothiophene was brominated to get 2,8-dibromo compound and in the next step 2,8-dibromodibenzothiophene was coupled with 4-formyl phenyl boronic acid (Suzuki Coupling) to get the final product.

Bromination of dibenzothiophene: About 5 g dibenzothiophene was dissolved in 3 ml chloroform. Using pressure equalizing funnel 3 ml bromine was added drop wise to the above mixture at 0 °C. The reaction mixture was stirred for 24 hrs under nitrogen atmosphere at room temperature. The crude product was filtered off and washed with methanol. It was then dried at room temperature. The product was obtained as white powder.

Synthesis of 2,8-di-(4-formylphenyl)dibenzothiophene (DBT-PHF): 2,8-Dibromo-dibenzothiophene (0.58 mmol), 4-formyl phenyl boronic acid (1.26 mmol), Pd(PPh₃)₄ (0.026 mmol) and K₂CO₃ (1 M) were stirred under inert atmosphere and refluxed at 75 °C for approximately 24 hrs. After cooling the reaction mixture to room temperature, ethyl acetate was added and organic layer was separated from aqueous layer. The solvent was evaporated to get the crude product and pure compound was separated using column chromatography (silica gel, n-hexane as eluent). Yield 69%. ¹H NMR (CDCl₃, ppm): δ 10.03 (s, 1H), 8.40 (s, 1H), 7.96–7.91 (m, 2H), 7.83 (d, J = 8 Hz, 1H), 7.72 (m, 2H), 7.70 (m, 1H). ¹³C NMR (CDCl₃, ppm): 190.8, 145.9, 139.3, 135.6, 135, 134.3, 129.4, 126.9, 125.5, 122.5, 119.4. HRMS [M + Na]⁺ : 415.37

3. Result and discussion

3.1. Computational studies

In order to get preliminary insight into the electronic structure of the dibenzothiophene oligomer, theoretical modelling was performed using density functional theory. HOMO and LUMO energy levels obtained by theoretical calculations were –5.44 eV and –2.97 eV respectively. The band gap of the designed molecule is calculated from these energy levels and it was found to be 2.98 eV. Fig. 2 represents the optimized geometry and molecular orbital distribution of the designed dibenzothiophene derivative. The optimized structure subjected to vibrational frequency calculations shows no imaginary frequency. This ensures the optimized geometry is the minima on the Potential Energy Surface (PES). The computed HOMO, LUMO energy and band gap are summarized in Table 1.

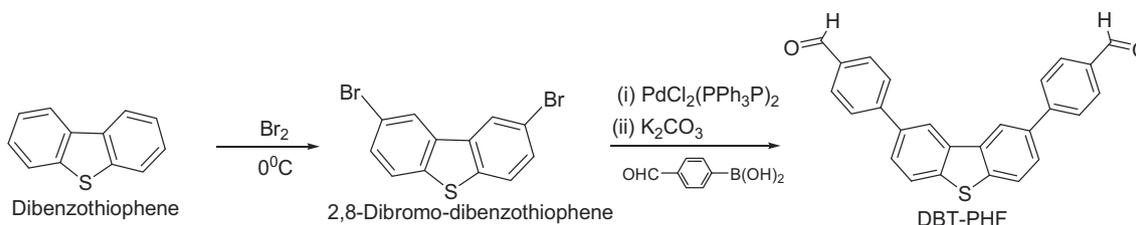


Fig. 1. Synthesis of 2,8-Di-(4-formylphenyl)dibenzothiophene.

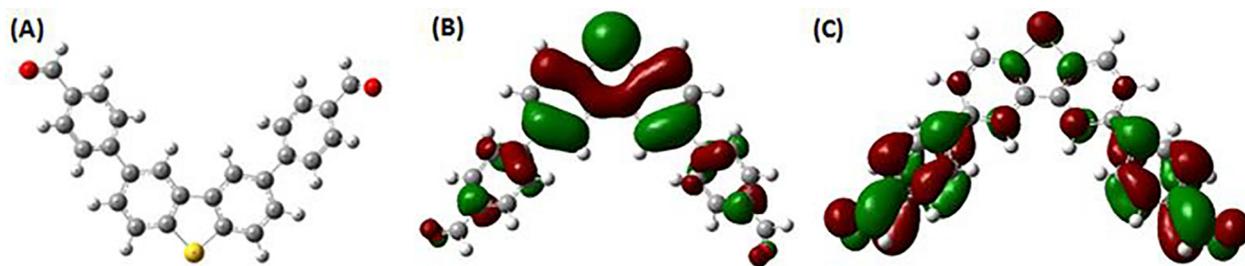


Fig. 2. (A) Optimized structure (B)HOMO of DBT-PHF (C)LUMO of DBT-PHF.

Table 1

Computed Optical gap, HOMO, LUMO energies of the DBT-PHF molecule.

Oligomer	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
DBT-PHF	-5.44	-2.97	2.98

3.2. Synthesis and characterization

2,8-Dibromodibenzothiophene was prepared by bromination of dibenzothiophene according to the reported procedure [26]. DBT-PHF was synthesized from 2,8-dibromodibenzothiophene using Suzuki coupling with 4-formyl phenyl boronic acid and the product

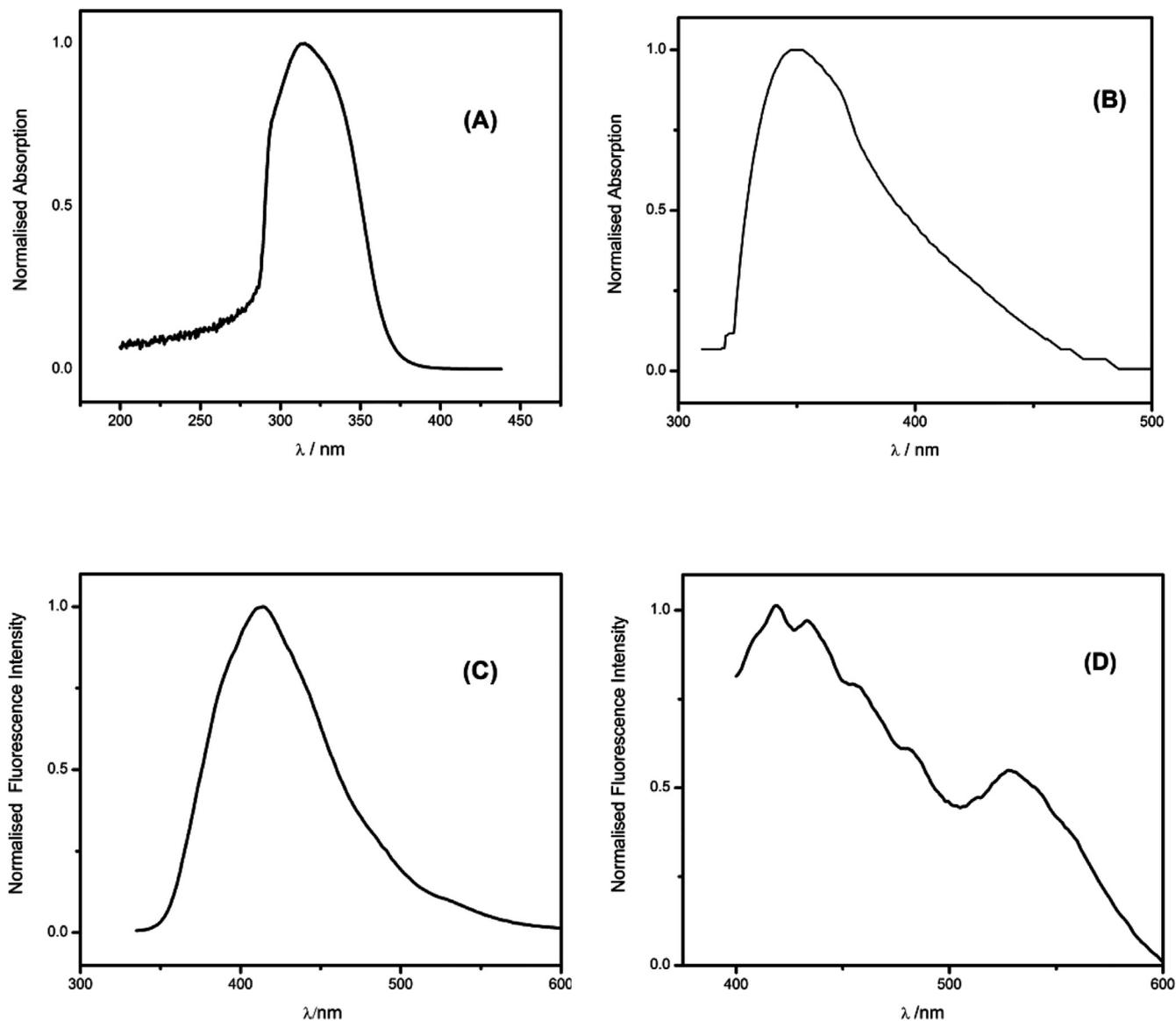


Fig. 3. Absorption spectra of DBT-PHF (A) in chloroform (B) in thin film. Emission Spectra of DBT-PHF (C) in chloroform (D) in thin film.

Table 2
Optical properties of DBT-PHF in solution and solid state.

Compound	Absorption λ max (nm)		Emission λ max (nm)	
	Solution	Thin film	Solution	Thin film
DBT- PHF	315	350	414	418, 433, 530

was obtained with 69% yield. The molecule 2,8-di-(4-formylphenyl)dibenzothiophene shows good solubility in organic solvents like chloroform and dichlorobenzene. Solid and solution samples were stable at room temperature for several months. The structure of the synthesized molecule was confirmed by ^1H NMR, ^{13}C NMR and mass spectrometry.

Absorption and emission spectra of the molecule were recorded both in solution (chloroform) and solid state (dip coated thin film). Fig. 3 shows the normalized UV-Vis absorption and emission spectra of the molecule. In solution state, absorption spans in the range of 295 to 360 with maxima centered at 315 nm. This is due to the π - π^* transition of the conjugated compound. It is observed that the absorption spectra of DBT-PHF are bathochromically shifted compared to parent DBT which shows absorption maximum in the range 280–290 nm. This can be explained by the extended π conjugation of dibenzothiophene ring. In solid state the absorption is broader and red shifted. Absorption spans in the region of 300 to 400 nm and maximum absorbance is observed at 350 nm. This is due to the molecular aggregations occurring in solid state which leads to strong intermolecular interactions. Existences of such interactions between molecules are favourable for the fabrication of various organic electronic devices [27]. In solution state the molecule shows bluish violet emission with emission maxima centered at 414 nm. In solid state emission occurs at higher wavelength compared to solution state. The spectra in solid state are broadened compared to solution state as in absorption spectra. The optical data of the synthesized oligomer is summarized in Table 2.

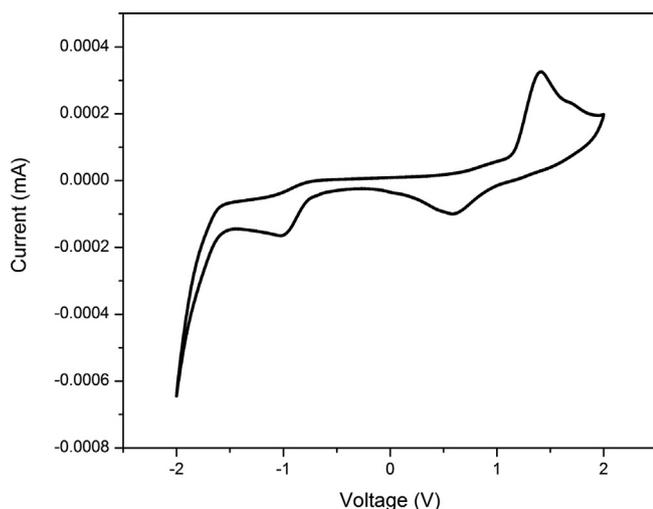


Fig. 4. Cyclic Voltammogram of DBT-PHF in dichloromethane containing 0.1 M n-Bu₄NPF₆ at the scan rate of 100 mV/s.

Table 3
Electrochemical properties of DBT-PHF.

Oligomer	E _{oxd} (V)	E _{onset} (V)	E _{HOMO} (eV)	λ _{onset} (nm)	E _g (eV)	E _{LUMO} (eV)
DBT-PHF	1.40	1.14	-5.52	426	2.91	-2.61

The band gap of the molecule was calculated from the solution state absorption spectra by using the equation, Band gap (eV) = 1240/cut off wavelength in nm. The band gap of the molecule was calculated as 2.91 eV which matches with the value obtained from theoretical calculation.

The solution state quantum yield of the molecule was determined using quinine sulphate (0.1 M H₂SO₄) as standard and was found to be 11%.

Energy levels of molecule were analyzed using cyclic voltammetry as shown in Fig. 4. HOMO and LUMO energy levels were calculated from oxidation and reduction potentials. A reversible oxidation reduction couple was observed and oxidation potential for DBT-PHF was found to be 1.40 V. The HOMO energy levels of molecules were calculated according to the equation $E_{\text{HOMO}} = -(E_{\text{oxd}} + 4.38 \text{ eV})$. LUMO levels are estimated using optical band gap and E_{HOMO} (Energy of HOMO). The HOMO level of the compound determined by using the onset oxidation potential was found to be 5.52 eV and this low lying HOMO level indicates the high oxidation stability of the compound. The electrochemical data of the molecule is tabulated in Table 3.

4. Conclusion

In summary, a dibenzothiophene based oligomeric molecule was modeled, synthesized and characterized. The HOMO, LUMO energy levels and band gap of the oligomer were calculated using time-dependent density functional theory (TD-DFT) methods with PBEPBE functional using 6-311G++2d,2p basis set. The calculated band gap was found to be 2.98 eV. The optical properties of 2, 8-di-(4-formylphenyl)dibenzothiophene were studied by using steady state absorption and emission spectroscopy. The optical absorption spectrum of this compound was characterized with a peak at 315 nm in solution state and 350 nm in thin film. The optical band gap of the DBT derivative was found to be 2.91 eV which is in a good agreement with the theoretical calculation. The fluorescence spectrum was characterized with an emission maximum at 414 nm in solution state and in solid state it was shifted to higher wavelength. E_{HOMO} level was measured using cyclic voltammetry and it was found to be -5.52 eV. In order to get more insight into the application of this molecule in organic electronics, a detailed understanding of charge transport property is essential. A study in this direction is presently under progress in our laboratory.

Declaration of Competing Interest

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