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Electronic, optical and charge transfer properties of α,α′-bis(dithieno-[3,2-*b*:2′,3′-*d*]thiophene) (BDT) and its heteroatom-substituted analogues

Ahmad Irfan [a,*], Muhammad Nadeem [b,1], Makshoof Athar [a], Farah Kanwal [a], Jingping Zhang [c,*]

[a] *Institute of Chemistry, University of the Punjab, Lahore 54590, Pakistan*
[b] *Department of Chemistry, University of Agriculture, Faisalabad-38040, Punjab, Pakistan*
[c] *Faculty of Chemistry, Northeast Normal University, Changchun 130024, China*

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ABSTRACT

The ground state geometry of α,α′-bis(dithieno[3,2-*b*:2′,3′-*d*]thiophene) (BDT) and its heteroatom-substituted analogues have been optimized using B3LYP/6-31G** and PBE0/6-31G** level of theories. The absorption spectra have been computed in the presence and absence of solvent at PCM and CPCM models. The designed analogues where sulfur was substituted by NH (NHBDT), oxygen (OBDT) are blue shifted while BH substituted one (BHBDT) is red shifted. The vertical ionization potentials of NHBDT and OBDT are comparatively smaller than BDT revealing that injection barrier for hole would be small. The calculated vertical electronic affinity of BHBDT is 3.32 eV while its vertical ionization potential is 6.53 eV. Balanced hole and electron reorganization energies predicted that it would be good ambipolar material.

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1. Introduction

The investigation and studies of charge-carrier in organic molecular crystals has continued for more than 4 decades [1,2]. Development of new organic semiconductors with improved performance in specific devices (i.e., thin film transistors (TFT), light-emitting diodes, and photovoltaic cells) is an important aspiration for materials chemists [3]. In organic materials, both the electronic couplings between molecules and the electron vibration interactions due to *intramolecular* and *intermolecular* relaxations are responsible to impact the carrier mobilities [4]. The theoretical methods used to study and design new conjugated charge-carrier materials should be able to accurately determine those parameters that are relevant for the required technological applications. Realizing the importance of π-stacking, Katz and co-workers [5] have successfully synthesized high mobility (0.04 $\mathrm{cm^2/V\,s}$) OTFT material, bis-(benzodithiophene). Li et al. synthesized OTFT α,α′-bis(dithieno[3,2-*b*:2′,3′-*d*]thiophene) (BDT) having the mobility up to 0.05 $\mathrm{cm^2/Vs}$ [6].

The charge transport in OTFT is also known as a Brownian motion process, described by a particle diffusion process [7,8], coupled with the Marcus theory of the electron transfer rate for a self-exchange reaction process [9].

$$K = V^2/h(\pi/\lambda k_B T)^{1/2}\exp(-\lambda/4k_B T) \tag{1}$$

There are two major parameters that determine the self-exchange electron-transfer (ET) rate: the intermolecular transfer integral (V) and the reorganization energy (λ). To improve and enhance the performance immense progress has been made to develop new molecular semiconductors and device fabrication techniques [10]. More recently, ambipolar OTFTs have become the focus of research due to their potential multifarious practical applications in organic integrated circuits [11]. Due to the high injection barrier for single charge carrier, either hole or in particular electron, relative to the work function, and potential gold source–drain electrode only few single-component organic semiconductors have been found to exhibit ambipolar transfer property in practical devices [12]. Generally, small bandgaps are found to display high conductivities intrinsically [13].

With the aim of finding the rational approaches to enhance the charge transfer properties and explain structure–property relationship; model compound BDT and its analogues have been investigated where the S in BDT has been substituted by N (NHBDT), O (OBDT) and B (BHBDT), as shown in Fig. 1.

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* Corresponding authors. Tel.: +86 431 85098652; fax: +86 431 85099521 (J. Zhang), tel.: +92 42 99230463; fax: +92 42 99230998 (A. Irfan).

E-mail addresses: irfaahmad@gmail.com (A. Irfan), zhangjingping66@yahoo.com.cn (J. Zhang).

[1] Present address: Subsurface Technology, Petronas Research Sdn Bhd. (PRSB), Bangi-43300, Selangor, Malaysia.

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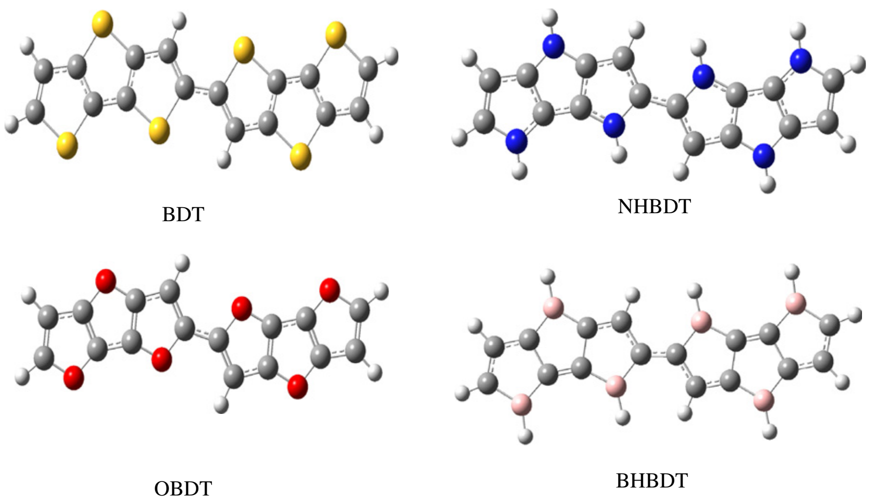

BDT NHBDT

OBDT BHBDT

Fig. 1. The structures of BDT, its analogues, NHBDT, OBDT and BHBDT.

2. Methodology

The neutral, anion and cation structures of BDT have been optimized at the B3LYP [14] and PBE0 [15] functionals with 6-31G** basis set. The absorption spectra have been calculated by time dependent density functional theory (TD-DFT) using PBE0 and B3LYP by adopting 6-31G** basis set [16]. The absorption spectra have also been computed by considering the solvent (chloroform) in Polarizable Continuum Model (PCM) [17] and conductor-like polarizable continuum model (CPCM) [18]. The PBE0/6-31G** level overestimate the spectra thus B3LYP/6-31G** level has been applied to investigate all the properties of the BDT and its analogues. The reorganization energies at the density functional theory (DFT) level have been calculated using the B3LYP functional and 6-31G** basis set [19].

The reorganization energy is further divided into two parts: $\lambda_{\text{rel}}^{(1)}$ and $\lambda_{\text{rel}}^{(2)}$, where $\lambda_{\text{rel}}^{(1)}$ corresponds to the geometry relaxation energy of one molecule from neutral state to charged state, and $\lambda_{\text{rel}}^{(2)}$ corresponds to the geometry relaxation energy from charged state to neutral one [20].

$$\lambda = \lambda_{\text{rel}}^{(1)} + \lambda_{\text{rel}}^{(2)} \tag{2}$$

In the evaluation of λ, the two terms were computed directly from the adiabatic potential energy surfaces [16,21].

$$\lambda = \lambda_{\text{rel}}^{(1)} + \lambda_{\text{rel}}^{(2)} = [E^{(1)}(X^+) - E^{(0)}(X^+)] + [E^{(1)}(X) - E^{(0)}(X)] \tag{3}$$

Here, $E^{(0)}(X)$, $E^{(0)}(X^+)$ are the ground-state energies of the neutral and charged states, $E^{(1)}(X)$ is the energy of the neutral molecule at the optimized charged geometry and $E^{(1)}(X^+)$ is the energy of the charged state at the geometry of the optimized neutral molecule. These calculations have been performed with the Gaussian03 package [22].

3. Results and discussion

3.1. Electronic structures and optical properties

The HOMO is distributed on all the edge-tip carbon atoms with no contribution from the S and O atoms in BDT and OBDT, respectively while in NHBDT there is small contribution from the N atoms of the two terminal units. The LUMO is distributed on all the C and S atoms in BDT, C and N atoms in NHBDT while C and O atoms in OBDT. BHBDT, HOMO and LUMO are more delocalized than the BDT, NHBDT and OBDT see Fig. 2. The BDT was optimized in the presence and absence of solvent (chloroform) to investigate the effect of solvent on the energies of HOMO (E_{HOMO}), LUMO (E_{LUMO}) and HOMO–LUMO gap (E_{gap}) at the B3LYP/6-31G** and PBE0/6-31G** level of theories. It was observed that solvent has no effect on the E_{HOMO}, E_{LUMO} and E_{gap}, as reported in Table 1. But it was noticed that PBE0 overestimate the E_{gap}, i.e., 3.56 eV compared to experimental value 2.8 eV [6]. The calculated E_{gap} at B3LYP functional (3.18 eV) is in agreement with the experimentally calculated values [6]. HOMO and LUMO energies in the investigated systems follow the trend as: NHBDT > OBDT > BDT > BHBDT which is coupled with the same tendency in E_g too. Furthermore, the absorption wavelength of BDT was also computed in the presence and absence of solvent (PCM and CPCM in chloroform) at the B3LYP/6-31G**and PBE0/6-31G** level of theories. The calculated absorption is in good agreement with the experimental data when solvent has been incorporated. The computed wavelengths, in the absence of solvent, underestimate generally in BDT. To further investigate the effect of solvent, BDT was optimized in the presence of solvent to compute the absorption. It was noticed that optimization in solvent has no effect on the absorption spectra; only TD calculations in solvent are profound and giving reasonable results, whereas PBE0 underestimate the absorption. The calculated wavelengths 434 nm in PCM and 435 nm in CPCM at the B3LYP/6-31G** level are in good agreement with experimental value (440 nm) [6]. Thus the modeled systems were investigated at the B3LYP/6-31G** level of theory.

The computed absorption wavelength for NHBDT has been observed 370 nm in both the models PCM and CPCM which is 64 nm and 65 nm blue shifted, respectively compared to the calculated absorption wavelengths of BDT. The OBDT is 29 nm blue shifted in both the models. The absorption wavelengths for BHBDT are 646 nm and 648 nm in PCM and CPCM, respectively. The absorption spectra in NHBDT and OBDT are blue shifted whereas BHBDT is red shifted compared to BDT. In general these observations are associated with the trends of energy difference as reported in Table 1.

3.2. Charge transfer properties

The vertical and adiabatic ionization potentials, electronic affinities and reorganization energies are tabulated in Table 2. It is well known that injection barrier for hole and electron of the semiconducting material and work function of the electrode corresponds to the energy difference between the ionization potential or electron

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