Journal of King Saud University – Science xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of King Saud University – Science

journal homepage: www.sciencedirect.com

How methoxy groups change nature of the thiophene based heterocyclic chalcones from p-channel to ambipolar transport semiconducting materials

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ARTICLE INFO

Article history:
Received 8 January 2017
Accepted 31 March 2017
Available online xxxx

Keywords:
Semiconductors
Density functional theory
Optoelectronic properties
Charge transport properties
Intrinsic mobility

ABSTRACT

Chalcone derivatives gained significant consideration from scientific community due to their potential applications ranging from better biological activity to the efficient semiconducting properties. Present investigation deals with the in-depth study of three chalcone derivatives (2E)-1-(2,5-Dimethyl-3-thienyl)-3-(2-methoxyphenyl)prop-2-en-1-one (**1**), (2E)-3-(3,4-Dimethoxyphenyl)-1-(2,5-dimethylthiophen-3-yl)prop-2-en-1-one (**2**), and (E)-1-(2,5-Dimethyl-3-thienyl)-3-(2,4,5-trimethoxyphenyl)prop-2-en-1-one (**3**) highlighting their optoelectronic, charge transport (CT) and nonlinear optical (NLO) response. The ground and excited state geometries are optimized by applying density functional theory (DFT) and time dependent DFT, respectively. The effect of electron donating groups on the frontier molecular orbitals, absorption and emission wavelengths are investigated and discussed thoroughly using the quantum chemical calculations. The comprehensive intra-molecular charge transfer (ICT) is perceived from the occupied orbitals to the unoccupied molecular orbitals. A novel structure-property relationship is established on the basis of their calculated electronic structures, frontier orbitals and density of states. The electro-optical and nonlinear optical (NLO) properties are finely tuned in the chalcone derivatives comprising of di- and tri-methoxy groups at peripheral. The nature of the p-type and ambipolar charge transport behavior of the compounds **1**–**3** is limelighted on the basis of their ionization potentials, electron affinities, reorganization energies, transfer integrals and intrinsic mobility. The mono- and di-substituted methoxy chalcone derivatives show the ambipolar performance owing to the better transfer integral and intrinsic mobility values for hole and electron. Whilst tri-methoxy at peripheral would lead the p-channel characteristics due to the balanced reorganization energy (hole and electron) and superior hole transfer integrals leads to higher hole intrinsic mobility.

1. Introduction

Since their discovery, the organic semiconductor materials (OSMs) are immensely studied by experimental and theoretical approaches (Tsumura et al., 1986). The OSMs are cheap, light weight and also easy to fabricate. The OSMs also have larger area flexible displays via solution processing of active inks potentially a cheap production process. These prospective applications make them appropriate for optoelectronic devices (García de Arquer et al., 2017; Oehzelt et al., 2015).

The chalcones have distinctive properties which make them suitable for biological active compounds (Maydt et al., 2013), sensors (Niu et al., 2006) and semiconducting devices such as organic light-emitting diodes (OLEDs) (Makoto Satsuki et al., 2007), displays, thin film field effect transistors (TF-FET) (Itai, 2012), solar cells (Chambon et al., 2013) and photo-reaction agents, which can absorb energy in the form of light to initiate the reaction (Park, 2014). Moreover, thiophene based materials are auspicious because of the semiconducting nature, nonlinear optical response (Torruellas et al., 1990) and efficient electron transport properties (Venkataraman et al., 2006).

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jksus.2017.03.010
1018-3647/

Previously, thiophene based heterocyclic chalcones showed improved electro-optical properties. (Ki-Jun, 2012). Therefore, in the present study, we have selected three chalcone derivatives comprising of thiophene moieties and methoxy groups. We aim to investigate the structural, frontier molecular orbitals, total/partial density of states (TDOS/PDOS)), optical (absorption (λ_{abs}) and fluorescence (λ_{fl}) spectra), nonlinear optical (NLO) and charge transport properties (ionization potentials (IPs), electron affinities (EAs), hole/electron reorganization energies (λ_h/λ_e.), hole/electron transfer integrals (t_h/t_e)) and intrinsic mobility (μ_h/μ_e) by density functional theory (DFT) and time dependent DFT. To the best of our knowledge, there is no such computational study for above selected chalcone derivatives. This is the first time that we are going to investigate in depth study of these chalcone derivatives, i.e., (2E)-1-(2,5-Dimethyl-3-thienyl)-3-(2-methoxyphenyl)prop-2-en-1-one (**1**) (Abdullah et al., 2010a), (2E)-3-(3,4-Dimethoxyphenyl)-1-(2,5-dimethylthiophen-3-yl)prop-2-en-1-one (**2**) (Abdullah et al., 2010b), and (E)-1-(2,5-Dimethyl-3-thienyl)-3-(2,4,5-trimethoxyphenyl)prop-2-en-1-one (**3**) (Abdullah et al., 2010c) (see Fig. 1).

2. Computational details

In some earlier studies, it was found that among the standard DFT (Zhang et al., 2013) functionals, the B3LYP delivered the reasonable results for geometry optimizations of various size molecules (Sánchez-Carrera et al., 2006; Zhu et al., 2016; Cvejn et al., 2016; Irfan et al., 2017). Over the time, the B3LYP was used many times to calculate the optoelectronic and charge transfer properties, that provide good agreement with experimental evidences (Zhang et al., 2008). Earlier studies showed that the B3LYP/6-31G** level of theory is good to reproduce the experimental data (Preat et al., 2010, 2009). Moreover, this level is rational to limelight on the electronic and charge transport properties (Huong et al., 2013). In the present study, B3LYP/6-31G** level of theory was embraced to optimize the ground state (S_0) geometries, however the excited state (S_1) geometries, absorption and emission spectra were calculated at TD-DFT (Matthews et al., 1996) using the TD/B3LYP/6-31G** level (Scalmani et al., 2006). The Marcus theory Eq. (1) was adopted to shed light on the charge transfer rate (Marcus and Sutin, 1985).

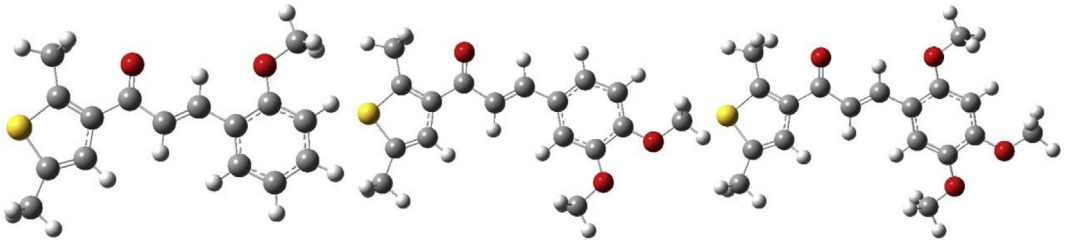
$$W = t^2/h(\pi/\lambda k_B)^{1/2} \exp(-\lambda/4k_BT) \quad (1)$$

The transfer integrals (t) and reorganization energy (λ) are important parameters. For the superior mobility and charge transport t must be maximized while the λ should be smaller. We used the direct method to calculate the t values. In our previous studies, we successfully regenerate the experimentally reported mobilities using this approach. For instant, the hole mobility of α-α′-bis(dithieno[3,2-*b*:2′,3′-*d*]thiophene) (BDT) was experimentally reported as 0.05 $cm^2 V^{-1} s^{-1}$ (Li et al., 1998) and it was successfully reproduced as 0.05 $cm^2 V^{-1} s^{-1}$ (Irfan et al., 2011) by the direct method that has been explained in the computational details. In our recent studies (Chaudhry et al., 2014, 2015), the hole intrinsic mobilities of the parent crystals DPNDF and C8-DPNDF were reproduced as 1.1 and 4.69 $cm^2 V^{-1} s^{-1}$ (Chaudhry et al., 2014, 2015), which are comparable to the experimentally reported hole mobilities, i.e. 1.3 and 3.6 $cm^2 V^{-1} s^{-1}$ (Mitsui et al., 2012), respectively. Similarly, the electron mobility of *mer*-tris(8-hydroxyquinolinato)-aluminum (III) (*mer*-Alq3) has been reproduced (Lin et al., 2004) which is consistent with the experimental electron mobility 3×10^{-6} $cm^2 V^{-1} s^{-1}$ (Naka et al., 2000). All above-mentioned results indicate that our adopted approach is very reliable to reproduce the comparable results and are in good agreement with the experimentally reported values of mobilities. In current investigation, we use the same direct method to compute the charge transport parameters. Computational details about the *t and* λ and intrinsic mobility can be found in Supporting information). All these quantum chemical calculations were performed by using Gaussian09 package (Frisch et al., 2009). The total/partial density of states (TDOS/PDOS) have been computed by GGA (generalized gradient approximation) at PW91 functional (Perdew et al., 1992) and DNP basis set (Nadykto, 2008) via DMol3 code (Delley, 2000) employed in Accelrys Materials Studio package (Materials Studio Modeling, 2004).

3. Results and discussion

3.1. Geometries

The S_0 and S_1 significant geometrical parameters, i.e., bond lengths (Å) and bond angles (degrees, °) of three chalcone derivatives **1**–**3** at B3LYP/6-31G** and TD-B3LYP/6-31G** levels of theory are tabulated in Table S1. The computed S_0 bond lengths and bond angles were found in reasonable agreement with the experimental crystal structural parameters The S_1-C_{12} (S_1-C_{14}) bond lengths are being overestimated, i.e., 0.029 (0.024), 0.035 (0.033) and 0.036 (0.026) Å in **1**–**3**, respectively. This overestimation in the bond lengths is due to the experimental geometrical data is in the solid phase whilst the computed parameters are in gas phase. No significant effect on the geometries was observed by varying the number of methoxy groups. Here, the lengthening or shortening in the bond lengths, as well as variation in the bond angles from S_0 to S_1 was also discussed. In compounds **1**–**3**, the lengthening from the S_0 to S_1 was 0.027, 0.027 and 0.026 Å for S_1-C_{12} bond length, respectively. For S_1-C_{14} bond length, the shortening was discerned 0.016, 0.016 and 0.017 Å in **1**–**3** from S_0 to S_1, respectively. Whilst for C_9-O_2 bond length, the lengthening was noticed from S_0 to S_1, i.e., 0.042, 0.051 and 0.053 Å in compounds **1**–**3**, respectively. The C_{10}-C_9-O_2 bond angle decreases 20.58°, 20.64° and 20.89° while C_{10}-C_9-C_8 increases 8.65°, 8.88° and 9.28° from S_0 to S_1 in **1**–**3**, respectively.



1 **2** **3**

Fig. 1. The optimized structures of the chalcone derivatives investigated in the presented study (yellow = S; red = O).