



Modeling of efficient charge transfer materials of 4,6-di(thiophen-2-yl)pyrimidine derivatives: Quantum chemical investigations



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ABSTRACT

The 4,6-di(thiophen-2-yl)pyrimidine has alternate pi-rich and pi-poor units. To reduce the HOMO–LUMO energy gap and improve the intra-molecular charge transfer pi-backbone has been elongated along with push–pull strategy. The ground state geometries have been optimized by using density functional theory. The frontier molecular orbitals, i.e., highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) have been conferred. The absorption spectra have been computed by using time dependent density functional theory. On the basis of ionization potentials, electron affinities and reorganization energies charge transfer properties have been discussed. We tuned the electronic, photo-physical and charge transfer properties of 4,6-di(thiophen-2-yl)pyrimidine derivatives. It is expected that new designed derivatives might be better/comparable to commonly used hole transfer material (pentacene). The smaller reorganization energies revealing that the electron transfer properties of new designed derivatives might be better/comparable to commonly used electron transfer materials (tris(8-hydroxyquinolino)aluminum). The structure–property relationship has been discussed.

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1. Introduction

The organic compounds with π -conjugation are highly multi-purpose materials for the development of proficient electronic devices e.g. organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), organic thin film transistors (OTFTs), Organic Solar Cells (OSCs), organic light-emitting field-effect transistors (OLFETs), sensors and photovoltaic cells [1–12]. Hepp and coworkers reported the first OLFET in 2003 [13]. This is emerging technology for the electronic devices which address the light emission [14], high brightness and efficiency simultaneously [15,16].

The organic pi-conjugated materials offer certain advantages over the standard/existing inorganic materials like versatility of chemical synthesis, low cost, ease of fabrication, molding into thin films, and the tuning of properties through suitable substitution [17,18]. In particular, a great variety of S-containing π -conjugated derivatives based on the thiophene scaffold have proven to be very efficient semiconducting materials [19–22].

Thiophene containing hetero acenes have attracted the most attention, such as aceno[2,3-b]thiophene [23], 2,2'-binaphtho [2,3-b]thiophene [24], thieno[3,2-b]thiophene [25] derivatives, and benzo-, naphtho- and anthra[2,3-b:6,7-b']dithiophene, [26] for their applications in OFETs. Anthracene and its derivatives are

good and efficient contenders of OFET materials which have been using intensively to enhance the mobility [27].

The 4,6-di(thiophen-2-yl)pyrimidine (**1**) has alternate pi-rich and pi-poor units, i.e., thiophene and pyrimidine [28]. We have designed new derivatives by elongating the pi-backbone (by substituting anthracene at both ends of **1** to reduce the HOMO–LUMO energy gap. The intra-molecular charge transfer has been augmented by substituting the electron activating groups (CH_3) at one end while electron deactivating groups (F, Cl, COOH, CN, NO_2) at other end. It is expected that these techniques would tune the electronic, photophysical and charge transfer properties, see Fig. 1. The effect of electron activating groups, deactivating groups and bridge has been studied on electronic properties, absorption spectra, and charge transfer properties (ionization potentials, electron affinities, reorganization energies). The structure–property relationship has been discussed. The paper is structured as follows: Section 2 presents an outline of the Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TDDFT) methodology used, including the rationale for choosing the hybrid functional and the basis set; Section 3 gives the frontier molecular orbitals, electronic, optical and charge transfer properties with detailed comparisons with experimental and theoretical studies; in Section 4 the major conclusions of the present investigation are presented.

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2. Computational details

Coropceanu and co-workers showed that line shape of the lowest gas-phase ultraviolet photoelectron spectroscopy band is directly related to the geometry relaxation energy [29]. Moreover, among Density Functional Theory (DFT) functionals [30] B3LYP provides the best description of the geometry modifications upon ionization [31]. In the present study, ground state (S_0) geometries have been optimized using DFT. We applied the B3LYP functional [32–34] and 6-31G** basis set [35]. The absorption spectra have been computed using time dependent density functional theory (TDDFT) as this has been proved an efficient and reliable approach [36,37].

The Marcus theory is good to explain the charge transfer rate via the following equation [38]:

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

here transfer integral (V) which needs to be maximized and the reorganization energy (λ) which needs to be small for significant transport.

The λ 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 to charged state, and $\lambda_{\text{rel}}^{(2)}$ corresponds to the geometry relaxation energy from charged to neutral state [39].

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

In the evaluation of λ , the two terms were computed directly from the adiabatic potential energy surfaces [40,41].

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

here $E^{(0)}(M)$, $E^{(0)}(M^+)$ are the ground-state energies of the neutral and charged states, $E^{(1)}(M)$ is the energy of the neutral molecule at the optimized charged geometry and $E^{(1)}(M^+)$ is the energy of the charged state at the geometry of the optimized neutral molecule. It should be noted that the polarization effects from the surrounding molecules, as well as the charge reorientation, have been neglected to minimize the complications involved in the theoretical calculations [42,43]. The adiabatic ionization potential (IPa) and vertical ionization potential (IPv) have been calculated as:

$$\text{IPa} = E^0(M^+) - E^0(M) \quad \text{and} \quad \text{IPv} = E^1(M^+) - E^0(M).$$

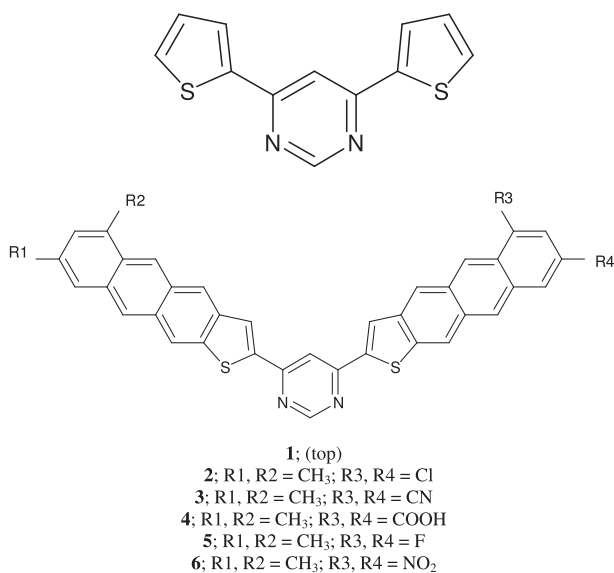


Fig. 1. The investigated compounds in present study 1 (top) and its derivatives.

The ground state energies of the neutral and cation states represented by $E^0(M)$ and $E^0(M)^+$ respectively, and $E^1(M)^+$ is the energy of cation state at the optimized geometry of the neutral molecule. The adiabatic/vertical electron affinity (EAa)/(EAv) of all molecules have been calculated as under;

$$\text{EAa} = E^0(M) - E^0(M)^- \quad \text{and} \quad \text{EAv} = E^0(M)^- - E^1(M)^-$$

here $E^0(M)$ corresponds to the ground state energies of the neutral and $E^0(M)^-$ is the energy of anion states. The term $E^1(M)^-$ represents the energy of anion state at the optimized geometry of the neutral molecule. All the calculations have been performed by using Gaussian09 package [44].

3. Results and discussion

3.1. Electronic structures

The distribution patterns of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for the ground states have been shown in Fig. 2. In 4,6-di(thiophen-2-yl)pyrimidine, the HOMO and LUMO are distributed throughout the backbone. In designed derivatives HOMOs are delocalized towards the electron activating groups, i.e., left side of the systems. In the formation of HOMOs pyrimidine and thiophene rings are also taking part. The LUMOs are localized towards the electron deactivating groups, i.e., pyrimide, thiophene and benzene rings at right side. The HOMOs and LUMOs are also spread over the electron activating as well as electron deactivating groups, respectively. In the formation of HOMOs strong deactivate group has more participation than the LUMO. In ground state comprehensible intra-molecular charge transfer has been observed from push to pull moieties. Moreover, we have noticed that at ground states, the LUMOs are also localized on that moiety which is towards the acceptor group, i.e., strong deactivating group. The thiophene and benzene towards the activating group have no participation in the formation of LUMOs.

The HOMO energies of new designed derivatives are higher while LUMO energies lower than the parent molecule at ground states. The HOMO–LUMO energy gap in new designed systems is smaller than the parent molecule. Generally, electron donating group release the electron towards the pi bond raising the energy of frontier molecular orbitals. While electron withdrawing group attract the electron resulting lowers the HOMOs and LUMOs energies [45].

In the present study, the trend to lower the HOMO and LUMO energies on the base of strength of deactivating group is as $F < \text{COOH} < \text{Cl} < \text{CN} < \text{NO}_2$. The more electron deactivating group lowered the HOMO and LUMO energies more significantly which is in good agreement with the previous study [45]. The smallest HOMO–LUMO energy gaps have been observed for those systems which have NO₂ or CN substituted groups. Such derivatives are affected more which have the strong deactivating groups resulting smaller HOMO–LUMO energy gaps.

In Fig. 3, we illustrated the calculated energies for the HOMOs (E_{HOMO}), LUMOs (E_{LUMO}) and HOMO–LUMO energy gaps (E_{gap}) for the 4,6-di(thiophen-2-yl)pyrimidine and its derivatives at ground states. We found that the computed E_{HOMO} , E_{LUMO} and E_{gap} are in good agreement with the experimental data [28]. The trend of HOMO energies (E_{HOMO}) in new designed derivatives is as follows: $5 > 4 > 2 > 3 > 6$ while in LUMOs energies (E_{LUMO}) is as: $5 > 2 > 4 > 3 > 6$. The –F and Cl– substituted derivatives have higher HOMOs and LUMOs energies than –CN and –NO₂ substituted ones. The stronger electron deactivating groups –CN and –NO₂ are lowering energies of frontier molecular orbitals more significantly. The effect of electron deactivating groups on the LUMO energies has

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