



The effect of donors–acceptors on the charge transfer properties and tuning of emitting color for thiophene, pyrimidine and oligoacene based compounds



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ABSTRACT

We have designed 4,6-di(thiophen-2-yl)pyrimidine (DTP) derivatives with the aim to tune the electronic, optical and charge transport properties then predicted their properties of interests by applying the density functional theory and time dependent density functional theory. The anthracene has been substituted at both ends of the DTP with the aim to enhance the properties. The intra-molecular charge transfer (ICT) has been improved by substituting the electron-donating groups (EDGs) at one end while electron-withdrawing groups (EWDGs) at other end. We have conducted theoretical studies on the effect of EDGs (OH and OCH₃), EWDGs (F, Cl, COOH, CN, NO₂) and π -backbone on electronic, photophysical (absorption and emission), and charge transfer properties (ionization potentials, electron affinities and reorganization energies). The structure–properties relationship has been discussed. The ground (S_0) and excited state (S_1) state geometries have been optimized using DFT/B3LYP/6-31G** and TD-B3LYP/6-31G** level of theories, respectively. The comprehensible ICT has been observed from highest occupied molecular orbitals to lowest unoccupied molecular orbitals in new designed derivatives. The decreased injection barrier is revealing that new designed derivatives would be better charge transport materials than the parent molecule. Moreover, smaller hole reorganization energies of DTPBA_OH_Cl, and DTPBA_OH_F are revealing that these might be better/comparable to pentacene. The computed electron reorganization energies of new designed materials are smaller than that of well known and commonly used electron transport material (*mer*-Alq3) illuminating that the electron mobility of all the new designed derivatives might be better/comparable with *mer*-Alq3.

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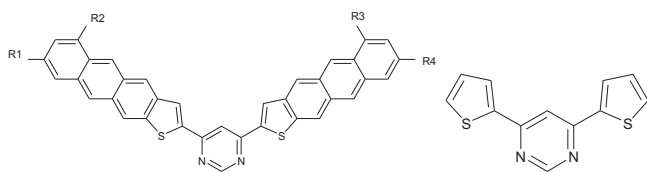
1. Introduction

The electronic industry is developing rapidly which is producing small circuits, portable cell phones, small supercomputers, faster internet communications, etc. Now it is not possible to develop the pharmaceuticals, track climate changes, nanosensors, or image the human brain without computers. The 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) and sensors, etc. have attracted attention during the last decade [1–12]. The OLFETs have gained consideration since 2003 [13–16]. The

π -conjugated organic materials have advantages due to low cost, ease of fabrication, environmental friendliness, molding into thin films, and the tuning of properties through suitable substitution [17,18]. The thiophene based organic compounds have received significant attentions which are being used as efficient semiconducting materials [19–22]. Moreover, thiophene and acenes based materials are promising which have been studied intensively [23–26]. Anthracene and its derivatives are good contenders which have been used in OFETs [27].

The 4,6-di(thiophen-2-yl)pyrimidine (DTP) has alternate π -rich and π -poor units, i.e., thiophene and pyrimidine [28]. To tune the electronic, optical and charge transport properties, we have designed new derivatives by substituting anthracene at both ends of DTP. The intra-molecular charge transfer (ICT) has been augmented by substituting the electron-donating groups (EDGs) at one end while electron-withdrawing groups (EWDGs) at the

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DTPBA_OCH₃_Cl; R1, R2 = OCH₃; R3, R4 = Cl
 DTPBA_OCH₃_CN; R1, R2 = OCH₃; R3, R4 = CN
 DTPBA_OCH₃_COOH; R1, R2 = OCH₃; R3, R4 = COOH
 DTPBA_OCH₃_F; R1, R2 = OCH₃; R3, R4 = F
 DTPBA_OCH₃_NO₂; R1, R2 = OCH₃; R3, R4 = NO₂
 DTPBA_OH_Cl; R1, R2 = OH; R3, R4 = Cl
 DTPBA_OH_CN; R1, R2 = OH; R3, R4 = CN
 DTPBA_OH_COOH; R1, R2 = OH; R3, R4 = COOH
 DTPBA_OH_F; R1, R2 = OH; R3, R4 = F
 DTPBA_OH_NO₂; R1, R2 = OH; R3, R4 = NO₂

Fig. 1. The optimized structures of DTP and its derivatives investigated in the presented study.

other end, see Fig. 1. We have conducted theoretical studies on the effect of EDGs (OH and OCH₃), EWGs (F, Cl, COOH, CN, NO₂) and π -backbone on electronic, photophysical (absorption and emission), and charge transport properties (ionization potentials, electron affinities and reorganization energies). The structure–properties 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 transport; in Section 4 the major conclusions of the present investigations are presented.

2. Results and discussion

2.1. Electronic structures

The distribution patterns of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals

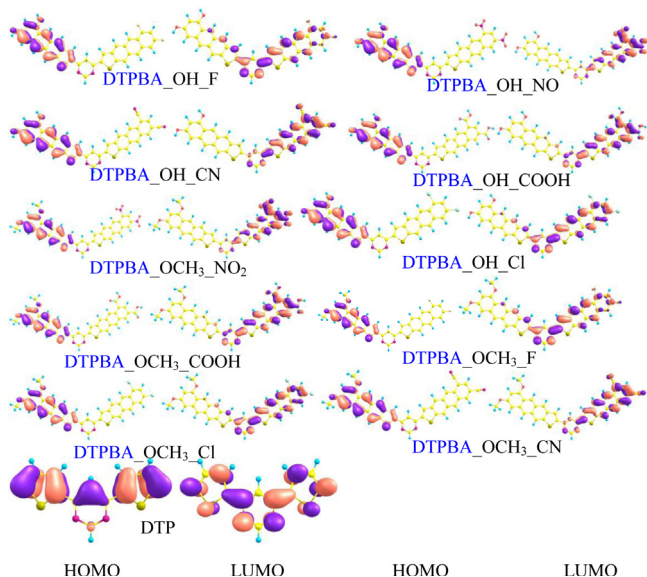


Fig. 2. Distribution pattern of the HOMOs and LUMOs of the ground states.

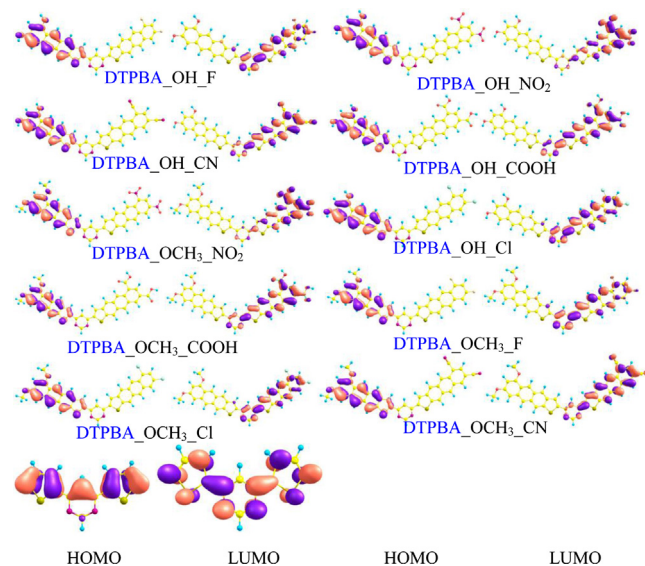


Fig. 3. Distribution pattern of the HOMOs and LUMOs of the first excited states.

(LUMOs) for the ground and excited states have been shown in Figs. 2 and 3, respectively. In DTP, the HOMO and LUMO are distributed throughout the backbone. In designed derivatives HOMOs are delocalized toward the EDGs, i.e., left side of the compounds. The pyrimidine and thiophene rings are also taking part in the formation of HOMOs of DTP. The LUMOs are localized toward the EWGs, i.e., pyrimidine, thiophene and benzene rings at right side. The HOMOs and LUMOs are also spread over the EDGs and EWGs, respectively. The strong EWG has more contribution in the formation of HOMOs rather than LUMOs. In ground state comprehensible ICT has been observed from donor (push) to acceptor (pull) moieties. The thiophene and benzene toward the EDGs have no participation in the formation of LUMOs. The distribution pattern of the HOMOs and LUMOs at the excited states is alike at the ground states.

The HOMO energies (E_{HOMO}) of new designed derivatives are higher while LUMO energies (E_{LUMO}) lower than the parent molecule at both ground and excited states, respectively. The HOMO–LUMO energy gaps (E_{gap}) in new designed compounds are smaller than the parent molecule. By introducing the stronger EDGs augment the E_{HOMO} in the studied derivatives. The trend to higher the E_{HOMO} is as OCH₃ > OH while to lower the E_{LUMO} is as OCH₃ < OH on the base of strength of EDGs both at ground and excited states. The trend to higher the E_{HOMO} on the base of strength of EWGs is as F > COOH > CN > NO₂ whereas tendency to lower the E_{LUMO} is as F < COOH < Cl < CN < NO₂ both at ground and excited states. The smallest E_{gap} have been observed for those compounds which have NO₂ or CN substituted groups. The derivatives which have strong EDGs and EWGs are effected more resulting smaller E_{gap} i.e., DTPBA_OCH₃_NO₂ (1.65 eV) < DTPBA_OH_NO₂ (1.69 eV).

In Table 1, we listed the calculated energies for the E_{HOMO} , E_{LUMO} and E_{gap} for the DTP and its derivatives at ground and first excited states. We found that the computed E_{HOMO} , E_{LUMO} and E_{gap} of DTP are in good agreement with the experimental data [28]. The trend of E_{HOMO} is as follows: DTPBA_OCH₃_F > DTPBA_OCH₃_COOH > DTPBA_OCH₃_Cl > DTPBA_OH_F = DTPBA_OH_COOH > DTPBA_OH_Cl > DTPBA_OCH₃_CN > DTPBA_OCH₃_NO₂ > DTPBA_OH_CN > DTPBA_OH_NO₂ > DTP while in E_{LUMO} is as: DTP > DTPBA_OCH₃_F > DTPBA_OH_F > DTPBA_OCH₃_Cl > DTPBA_OH_Cl > DTPBA_OCH₃_COOH > DTPBA_OH_COOH > DTPBA_OCH₃_CN > DTPBA_OH_CN > DTPBA_OCH₃_NO₂ > DTPBA_OH_NO₂ > The trend of E_{gap} in studied compounds is

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