

First Principles Investigations of Electronic, Photoluminescence and Charge Transfer Properties of the Naphtho[2,1-b:6,5-b']difuran and Its Derivatives for OFET

(Prinsip Pertama Kajian Elektronik, Fotopendarkilau dan Ciri Pemandahan Cas Nafto

[2,1-b :6,5-b '] difuran dan Terbitannya untuk OFET)

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ABSTRACT

We have designed new derivatives of naphtho [2,1-b:6,5-b'] difuran as DPNDF-CN1 and DPNDF-CN2. The molecular structures of DPNDF, its derivatives DPNDF-CN1 and DPNDF-CN2 have been optimized at the ground (S_0) and first excited (S_1) states using density functional theory (DFT) and time-dependent density functional theory (TD-DFT), respectively. Then the highest occupied molecular orbitals (HOMOs), the lowest unoccupied molecular orbitals (LUMOs), photoluminescence properties, electron affinities (EAs), reorganization energies (λ_s) and ionization potentials (IPs) have been investigated. The balanced $\lambda(h)$ and $\lambda(e)$ showed that DPNDF, DPNDF-CN1 and DPNDF-CN2 would be better charge transport materials for both hole and electron. The effect of attached acceptors on the geometrical parameters, electronic, optical and charge transfer properties have also been investigated.

Keywords: Computer modeling and simulation; electronic materials; first principle calculations; organic semiconductors; photoluminescence

ABSTRAK

Kami telah mereka bentuk terbitan baru nafta [2,1-b :6,5-b'] difuran sebagai DPNDF-CN1 dan DPNDF-CN2. Struktur molekul DPNDF, terbitannya DPNDF-CN1 dan DPNDF-CN2 telah dioptimumkan pada keadaan asas (S_0) dan teruja pertama (S_1) masing-masing dinyatakan menggunakan teori ketumpatan berfungsi (DFT) dan teori ketumpatan berfungsi bersandarkan masa (TD-DFT). Maka orbital molekul berisi tertinggi (HOMOs), orbital molekul tak berisi terendah (LUMOs), ciri-ciri fotopendarkilau, kesamaan elektron (EA), tenaga penyusunan semula (λ_s) dan keupayaan pengionan (IP) telah dikaji. $\lambda(h)$ dan $\lambda(e)$ yang seimbang menunjukkan bahawa DPNDF, DPNDF-CN1 dan DPNDF-CN2 merupakan bahan-bahan angkutan cas yang baik untuk kedua-dua lohong dan elektron. Kesan pengepilan penerima ke atas parameter geometri, sifat pemandahan elektronik, optik dan cas juga telah dikaji.

Kata kunci: Bahan-bahan elektronik; fotopendarkilau; pemodelan komputer dan simulasi; pengiraan prinsip pertama; semikonduktor organik

INTRODUCTION

Organic semiconductor materials (OSMs) are of enormous attention for experimental and theoretical researchers due to their mechanical elasticity, affordable prices, low in weight and fabrication on bendable substrates. These properties give OSMs advantages over the formal inorganic semiconductor material based transistors. Since first reported in 1986 (Tsumura et al. 1986) OSMs were intensively investigated for their applications in optoelectronic devices and microelectronics, such as organic field-effect transistors (OFETs) (E. Katz 1997; Horowitz & Hajlaoui 2000; Newman et al. 2004), organic light-emitting diodes (OLEDs) (Ho et al. 2000; Tang & VanSlyke 1987) and organic photo-voltaic devices (OPVs) (Ho et al. 2000; Padinger et al. 2003).

OFETs could be synthesized by including π -conjugated electron system (Hofmann 1856) or aromatic (IUPAC 1997) that help out to delocalize the orbital wave functions (Schleyer 2005) and represent a nice relation between

the geometric and electronic structures as well (Brédas et al. 2004; 1999; Bredas & Street 1985; Cornil et al. 1998; Warshel & Karplus 1974; Yang et al. 2000).

In organic semiconducting materials, many experimental and theoretical researchers focused on thiophene containing materials because of their applications in OFETs and OLEDs (Buonocore & Matteo 2009; Das et al. 2011; Irfan et al. 2011a; Koezuka et al. 1987; Letizia et al. 2010; Pingel et al. 2009; Unni et al. 2006; Wrackmeyer et al. 2011; Wu et al. 2012). However a few studies have been reported in the literature showing investigations about the furan containing material in OFETs and OLEDs (Gidron et al. 2011; Miyata et al. 2007, 2005; Wu et al. 2003). This may be due to the instability shown under oxidation conditions which had been reported earlier (Distefano et al. 1991). Recently Mitsui et al. (2012) had experimentally synthesized naphtho[2,1-b:6,5-b']difuran (DPNDF) and its derivatives for solution-processed single-crystal organic field-effect transistors with high hole

mobility and concluded that NDF might be good organic material for OFET.

In our present work as a starting point the experimental crystal of DPNDF (Mitsui et al. 2012) has been used as parent molecule and two new structures were derived as DPNDF-CN1 and DPNDF-CN2. In DPNDF-CN1 two CN (Cyanide) groups were attached as acceptors at the both ends of DPNDF at position P1 and P2, while two more CN groups had been attached at position P3 and P4 in DPNDF-CN2 (Figure 1). Geometries of these molecules were optimized for ground (S_0) as well as excited (S_1) states and then compared. The properties of these molecules such as electronic, charge transfer and photoluminescence have been evaluated. The computational results of these molecules have been compared with experimental data where available. Furthermore a comparison is made between their properties to predict about the good charge transport OSMs for OFETs.

COMPUTATIONAL DETAILS

The initial structures of these molecules were optimized at the S_0 state by applying DFT with Becke's B3 exchange functional (Becke 1993) and Lee-Yang-Parr correlation functional LYP (Lee et al. 1988) jointly expressed as B3LYP (Stephens et al. 1994) with 6-31G** basis set (Cho et al. 2012; Irfan et al. 2011b, 2010; Sajoto et al. 2012). Whereas the geometries of the molecules were optimized within TD-DFT (Bauernschmitt & Ahlrichs 1996; Chaudhry et al. 2013; Furche & Ahlrichs 2002; Scalmani et al. 2006; Van Caillie & Amos 2000) for S_1 state at the level of hybrid functional TD-B3LYP (Chaudhry et al. 2013; Lee et al. 2004; Li et al. 2007; Zwier et al. 2007) and basis set 6-31G**. The same level of theory have been used to

calculated electronic and photoluminescence properties of the studied systems.

The reorganization energy for hole (λ_h) and electron (λ_e) was evaluated as $\lambda_{h/e} = \lambda_{+/-} + \lambda_{1/2}$ where $\lambda_{+/-}$ is the relaxation energy from neutral to charged (cation/anion) state and $\lambda_{1/2}$ is the energy of geometry relaxation from charged (cation/anion) to neutral state (Gruhn et al. 2002; Reimers 2001). For $\lambda_{h/e}$ the two terms are calculated directly from the adiabatic potential energy surfaces (Chaudhry et al. 2013; Coropceanu et al. 2006; Irfan et al. 2009).

$\lambda_{h/e} = \lambda_{+/-} + \lambda_{1/2} = [E^1(R)^{+/-} - E^0(R)^{+/-}] + [E^1(R) - E^0(R)]$. $E^0(R)$ and $E^0(R)^{+/-}$ are the energies of neutral and charged (cation/anion) species optimized at ground state, $E^1(R)$ is the energy of neutral at the optimized charged (cation/anion) species and $E^1(R)^{+/-}$ is energy of the charge (cation/anion) at the geometry of the optimized neutral species. These reorganization energies were calculated using DFT at the B3LYP/6-31G** level for all the molecules.

The adiabatic / vertical ionization potential (IPa) / (IPv) have been calculated at the same level of theory as follows:

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

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

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

Here, $E^0(R)$ corresponds to the ground state energies of the neutral and $E^0(R)^-$ is the energy of charged (anion)

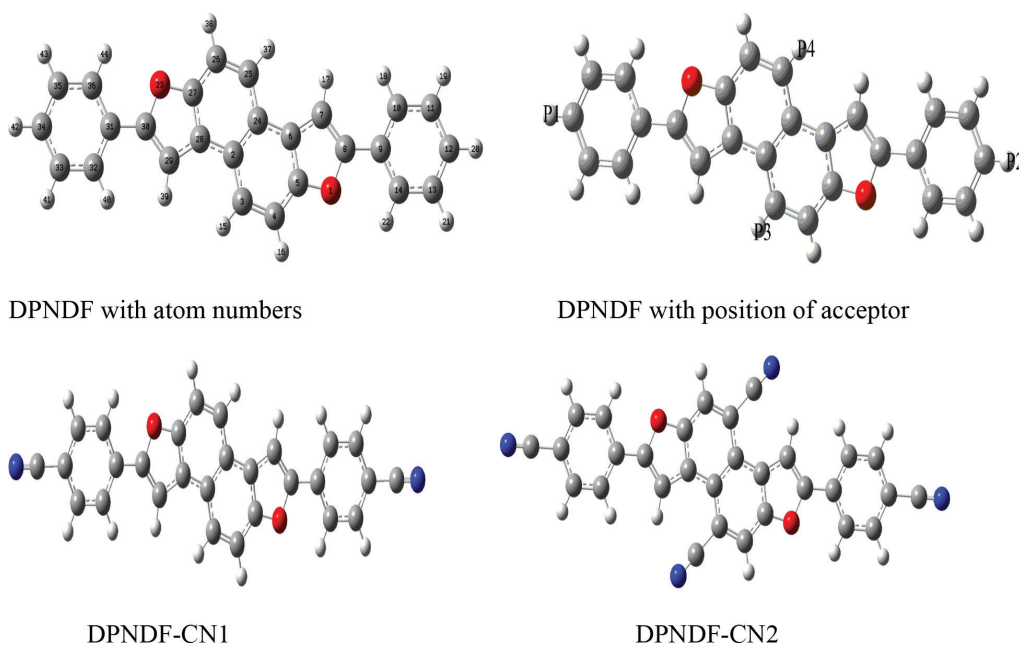


FIGURE 1. Molecules with atom numbers and position of acceptor groups

states. The term $E^I(R)$ represents the energy of charged (anion) state at the optimized geometry of the neutral molecule. All these calculations were carried out using GAUSSIAN 09 package (Frisch et al. 2009).

RESULT AND DISCUSSION

GEOMETRIES

Ground state The bond lengths and bond angles for the studied molecules optimized at S_0 state have been given in Table 1. We have discussed in detail the bond lengths and bond angles with the O atoms and at the positions of P1, P2, P3 and P4 as well as the bond lengths and bond angles between phenyl group and the NDF Rings. All other bond lengths and bond angles have not been changed significantly. As shown in Table 1, it is clear that the bond length O1-C8 decreased by 0.06 Å for DPNDF-CN1 while C2-C3 and C24-C25 increased by 0.015 Å for DPNDF-CN2, the C3-C4 and C25-C26 decreased by 0.001 Å for DPNDF-CN1 and increased by 0.01 Å for DPNDF-CN2 as compared with parent molecule DPNDF. No significant effects towards the lengthening or shortening has been observed for bond angles.

Excited state The optimized geometrical parameters at S_1 state have been presented in Table 2. The bond lengths C11-C12 and C33-C34 has been increased by 0.014 and 0.012 Å, the bond lengths C12-C13 and C34-C35 increased by 0.013 and 0.01 Å, the bond lengths C2-C3 and C24-C25 increased by 0.022 Å for DPNDF-CN2, respectively, whereas in DPNDF-CN2, the bond lengths CN-C12 and CN-C34 were not changed as compared with DPNDF-CN1. In all other bond lengths, the change is very small and has been neglected.

The bond angles for these three molecules have not been increased or decreased significantly at S_1 state.

For DPNDF the bond lengths has been increased as C3-C4 and C25-C26 by 0.033 Å, whereas the decreased bond lengths were C8-C9 and C30-C31 by 0.025 Å, C2-C3 and C24-C25 by 0.023 Å, respectively from ground to excited state. The bond lengths in DPNDF-CN1 and DPNDF-CN2 have been changed slightly while going from S_0 to S_1 states. No significant changes has been observed in the bond angles of DPNDF, DPNDF-CN1 and DPNDF-CN2 from S_0 to S_1 states.

ELECTRONIC PROPERTIES

Ground state The distribution patterns of HOMOs and LUMOs at S_0 state have been given in Figure 3. In DPNDF for HOMO formation, the charge has been delocalized on C7-C8, C5-C6, C3-C4, C25-C26, C27-C28, C29-C30, C10-C9-C14 and C32-C31-C36 while on C12 and C34 charge is localized (lone-pair). Both the O atoms were not taking part in HOMO formation. Similar behavior of charge delocalization was observed for DPNDF-CN1 and DPNDF-CN2 and the lone pair has been formed for all N atoms in the CN groups.

For LUMO formation the delocalization of charge has been found on C10-C11, C13-C14, C8-C9, C6-C7, C4-C5, C2-C3, C24-C25, C26-C27, C28-C29, C30-C31, C35-C36 and C32-C33. The charge is localized (lone-pair) on C12, C34 and on both O atoms. Same kind of LUMO formation has been found for the two derivatives DPNDF-CN1 and DPNDF-CN2 with lone pair on all N atoms.

The energies of HOMO (E_{HOMO}), LUMO (E_{LUMO}) and HOMO-LUMO energy gap (E_g) for all three molecules at S_0 state were tabulated in Table 3. The E_{HOMO} of parent molecule DPNDF is -5.10 eV, which is in a good agreement with the experimental value of DPNDF -5.48 eV (Mitsui et

TABLE 1. Calculated optimized bond lengths in Angstrom (Å) and bond angles in degree (°) at the B3LYP/6-31G** level of theory at S_0 state

Bond Lengths	DPNDF	DPNDF-CN1	DPNDF-CN2
C11-C12, C33-C34	1.397	1.406	1.406
C12-C13, C34-C35	1.396	1.405	1.404
O1-C8, O23-C27	1.385	1.379	1.376
O1-C5, O23-C30	1.365	1.364	1.360
C8-C9, C30-C31	1.457	1.454	1.454
C2-C3, C24-C25	1.425	1.424	1.440
C3-C4, C25-C26	1.380	1.379	1.390
CN-C12, CN-C34	-	1.432	1.432
CN-C25, CN-C3	-	-	1.430
Bond Angle			
C11-C12-C13	119.48	119.45	119.62
C33-C34-C35	119.48	119.45	119.62
C5-O1-C8	106.83	106.76	106.60
C27-O23-C30	106.83	106.76	106.60
C2-C3-C4	121.95	122.01	121.90
C24-C25-C26	121.95	122.01	121.90
O1-C8-C9	116.62	116.59	116.76
O22-C29-C30	116.62	116.59	116.76

TABLE 2. The optimized bond lengths in angstrom (Å) and bond angles in degree (°) at the TD-B3LYP/6-31G** level of theory at S_1 state

Bond Lengths	DPNDF	DPNDF-CN1	DPNDF-CN2
C11-C12, C33-C34	1.400	1.414	1.412
C12-C13, C34-C35	1.400	1.413	1.410
O1-C8, O23-C27	1.385	1.382	1.380
O1-C5, O23-C30	1.368	1.366	1.365
C8-C9, C30-C31	1.432	1.431	1.431
C2-C3, C24-C25	1.402	1.404	1.424
C3-C4, C25-C26	1.413	1.408	1.423
CN-C12, CN-C34	-	1.425	1.427
CN-C25, CN-C3	-	-	1.423
Bond Angle			
C11-C12-C13	119.42	119.15	119.50
C33-C34-C35	119.42	119.15	119.50
C5-O1-C8	107.04	107.02	106.77
C27-O23-C30	107.04	107.02	106.77
C2-C3-C4	122.59	122.38	122.51
C24-C25-C26	122.59	122.38	122.51
O1-C8-C9	117.40	117.35	117.54
O22-C29-C30	117.40	117.35	117.54

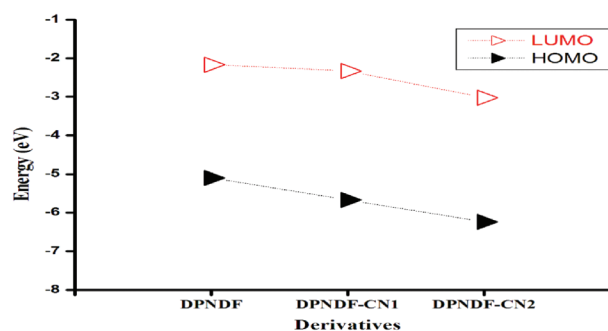
TABLE 3. The E_{HOMO} , E_{LUMO} and E_g in eV for S_0 states at the B3LYP/6-31G** level of theory

Molecule	Exp*(E_{HOMO})	E_{HOMO}	E_{LUMO}	E_g
DPNDF	-5.48	-5.10	-2.17	2.93
DPNDF-CN1	-	-5.67	-2.33	3.34
DPNDF-CN2	-	-6.24	-3.02	3.22

a: Experimental data from ref. (Mitsui et al. 2012)

al. 2012). The trend of E_{HOMO} and the E_{LUMO} is DPNDF-CN2 (-6.24 eV, -3.02 eV) > DPNDF-CN1 (-5.67 eV, -2.33 eV) > DPNDF (-5.10 eV, -2.17 eV), whereas the trend in E_g is DPNDF-CN2 (3.22 eV) > DPNDF-CN1 (3.34 eV) > DPNDF (2.93 eV). This increase in E_{HOMO} and E_{LUMO} may be due to the effect of the attached CN group, which is a strong electron deactivating group resulting significantly affect the energies of frontier molecular orbitals. This comparison for E_{HOMO} , E_{LUMO} and E_g have also been shown in Figure 2 for these molecules in S_0 state at the B3LYP/6-31G** level of theory.

Excited state The HOMOs and LUMOs distribution patterns in S_1 state have been evaluated using TD-DFT at TD-B3LYP/6-31G** level of theory and have been shown in Figure 4. In the formation of HOMO for DPNDF, it was found that the charge has been delocalized on C7-C8, C5-C6, C3-C4, C25-C26, C27-C28, C29-C30, C10-C9-C14 and C32-C31-C36 while charge is localized at C12 and C34. The O and N atoms have no contribution in the formation of HOMOs. The charge delocalization has the same pattern for DPNDF-CN1 and DPNDF-CN2 as of DPNDF. Charge has been delocalized on C10-C11, C13-C14, C8-C9, C6-C7, C4-C5, C2-C3, C24-C25, C26-C27, C28-C29, C30-C31, C35-C36 and C32-C33 in the formation of LUMO for the

FIGURE 2. Comparison of HOMO and LUMO energy levels for S_0 state at the B3LYP/6-31G** level of theory

parent molecule DPNDF while the charge is localized (lone-pair) on C12, C34 and on both O atoms. Similar behavior has been seen in LUMO formation for the molecule of DPNDF-CN1 and DPNDF-CN2 with lone pair on all N atoms where charge has been localized.

The energies of E_{HOMO} , E_{LUMO} and E_g for all three molecules at S_1 state are presented in Table 4. The E_{HOMO} of parent molecule DPNDF is -4.9 eV, which has been decreased as compared to S_0 state value of same molecule -5.10 eV. The trend of E_{HOMO} and the E_{LUMO} is DPNDF-CN2

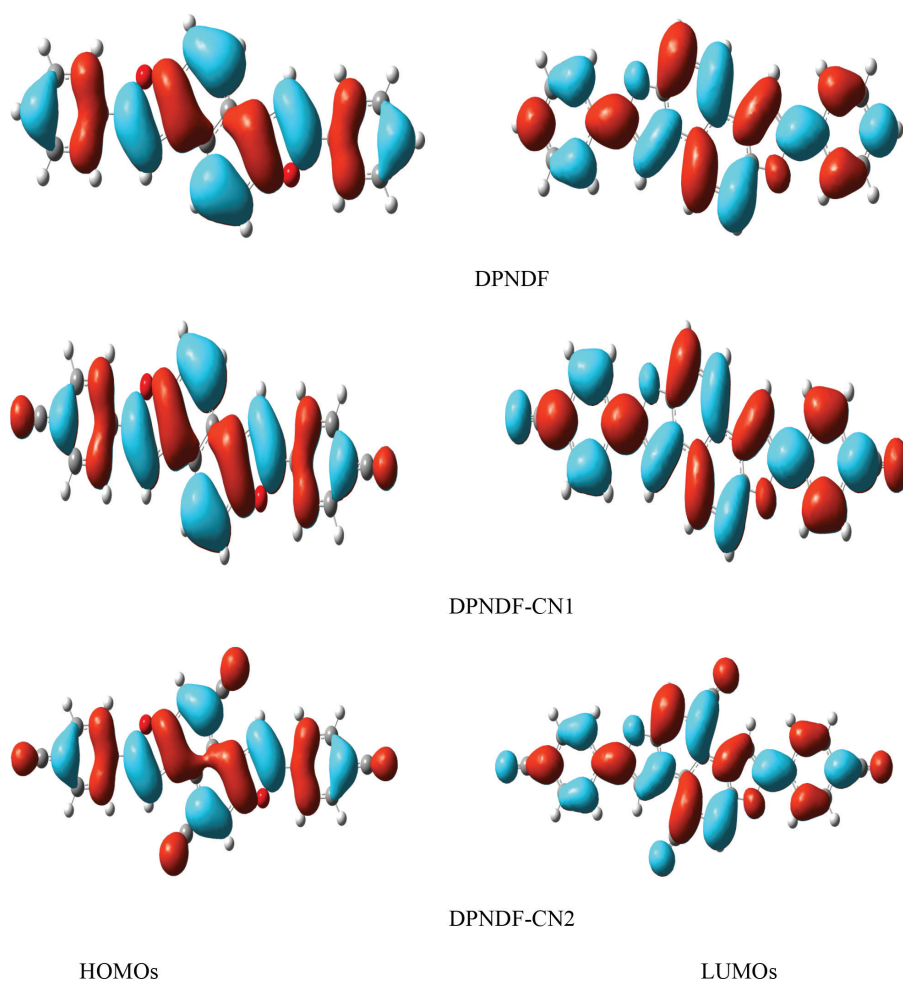


FIGURE 3. Distribution patterns of HOMOs and LUMOs at S_0 state for all molecules (Red color represents negative wave function and blue color represents positive wave function)

TABLE 4. The E_{HOMO} , E_{LUMO} and E_g of HOMO-LUMO (eV) for S_1 states at the TD B3LYP/6-31G** level of theory

Molecule	E_{HOMO}	E_{LUMO}	E_g
DPNDF	-4.9	-1.73	3.17
DPNDF-CN1	-5.51	-2.54	2.97
DPNDF-CN2	-6.08	-3.20	2.88

(-6.08 eV, -3.20 eV) > DPNDF-CN1 (-5.51 eV, -2.54 eV) > DPNDF (-4.9 eV, -1.73 eV), whereas the trend in the E_g is DPNDF (3.17 eV) > DPNDF-CN1 (2.97 eV) > DPNDF-CN2 (2.88 eV). This increase in E_{HOMO} and E_{LUMO} may be due to the effect of the attached CN group, which is a strong electron deactivating group resulting significantly affect the energies of frontier molecular orbitals. The graphical comparison of E_{HOMO} , E_{LUMO} at S_1 state is shown in Figure 5 for clarity.

Photoluminescence properties Wavelengths of absorption/emission ($\lambda_{\text{abs}}/\lambda_{\text{emis}}$), oscillator strength (f) and HOMO to LUMO transition have been calculated and tabulated in Table 5. Table 5 shows the maximum transition at the

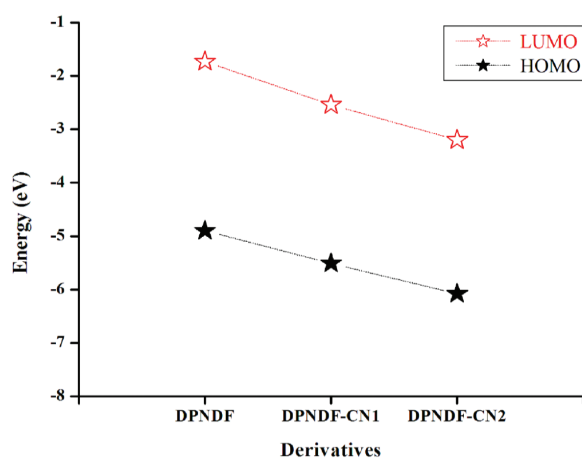


FIGURE 4. Comparison of HOMO and LUMO energy levels for S_1 state at the TD B3LYP/6-31G** level of theory

S_0 state from HOMO to LUMO for the three molecules. For DPNDF is HOMO→LUMO (99%), for DPNDF-CN1 is HOMO→LUMO (100%) and for DPNDF-CN2 is HOMO→LUMO (99%). Similarly the maximum HOMO to LUMO contribution

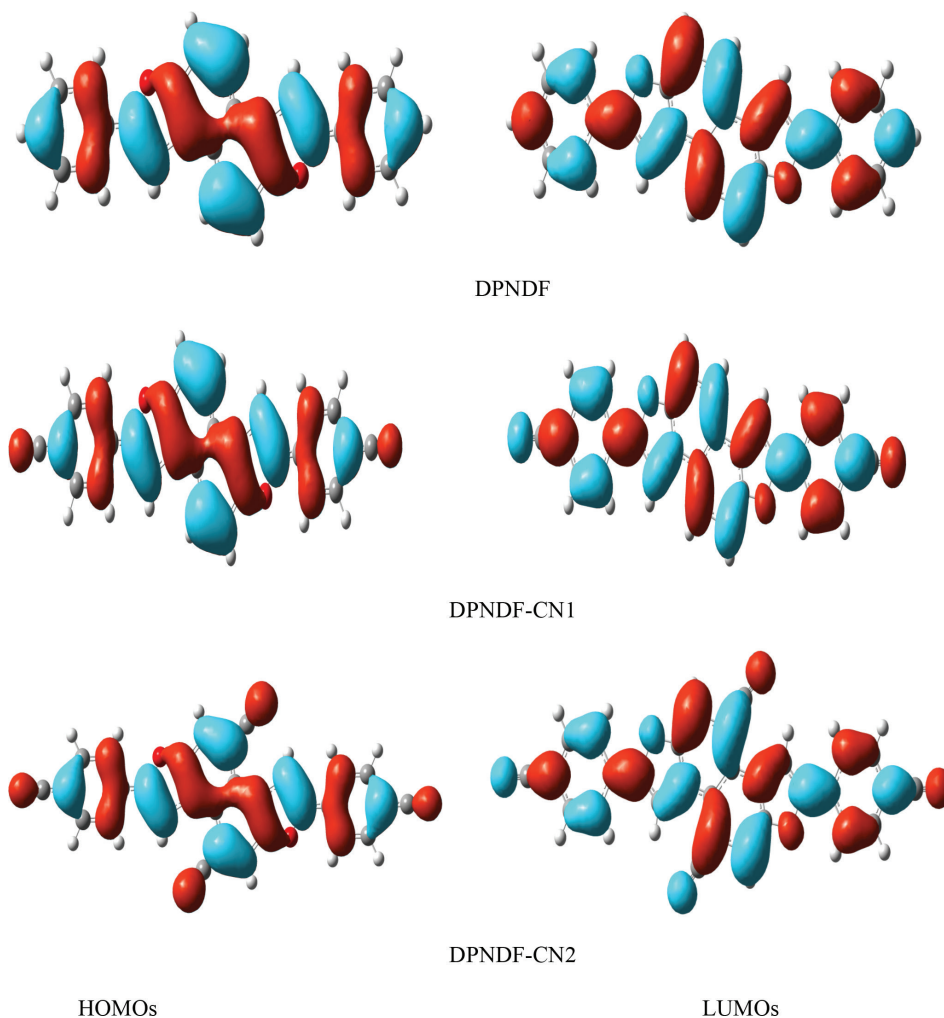


FIGURE 5. Distribution patterns of HOMOs and LUMOs at S_1 state for all molecules

TABLE 5. Calculated wavelengths in nm for absorption (λ_{abs}), emission (λ_{emis}), oscillator strength (f) and HOMO to LUMO transition for S_0 and S_1 States at the B3LYP/6-31G** level

Molecule	λ_{abs}	f	Transition	λ_{emis}	f	Transition
DPNDF	381	1.09	HOMO→LUMO (99%)	427	1.21	HOMO→LUMO (100%)
DPNDF-CN1	411	1.40	HOMO→LUMO (100%)	456	1.53	HOMO→LUMO (100%)
DPNDF-CN2	424	1.16	HOMO→LUMO (99%)	469	1.26	HOMO→LUMO (99%)

for S_1 state is following the same trend as for S_0 state. The λ_{abs} and λ_{emis} have the red shift of 30 and 29 nm for DPNDF-CN1, whereas 43 nm and 42 nm for DPNDF-CN2, respectively as compared to the parent molecule of DPNDF with an absorption wavelength of 381 nm.

Charge transfer properties EAs and IPs are the most imperative properties to calculate the charge injection barriers, which have also been evaluated at the B3LYP/6-31G** level of theory. In organic semiconductor materials higher EA and lesser IP are much crucial to enhance the hole and electron injection capability. The IP_a / IP_v and EAA / EAV of these derivatives have been calculated and tabulated in

Table 6. A graphical comparison of the IP_v and EAV has been shown in Figure 6 to represent the results more clearly. In OFETs the materials having bigger EAV might be better for n-type and materials with smaller IP_v may support p-type charge injection (Zhang et al. 2008). From Table 6 it is clear that DPNDF-CN1 and DPNDF-CN2 have . higher EAV, i.e. 1.23 and 1.90 eV, respectively showing these materials would be better electron transporters compared with parent molecule. It is expected that the introduction of CN enhances the EAS ensuring efficient electron transfer materials.

The reorganization energy is the quantity which is very important for estimation of the ability to carry the charge in solid (Brédas et al. 2002; Marcus 1993). The

TABLE 6. The IPa, IPv, EAa, EAv, $\lambda(h)$ and $\lambda(e)$ at the B3LYP/6-31G** level of theory. All values in eV

	Exp ^a	DPNDF	DPNDF-CN1	DPNDF-CN2
IP (vertical)	-	6.36	6.88	7.38
IP (adiabatic)	-	6.27	6.80	7.31
EA (vertical)	0.17	0.29	1.23	1.90
EA (adiabatic)	-	0.40	1.33	1.98
$\lambda(h)$	-	0.17	0.15	0.14
$\lambda(e)$	-	0.21	0.20	0.17

a: Experimental data from ref. (Mitsui et al. 2012)

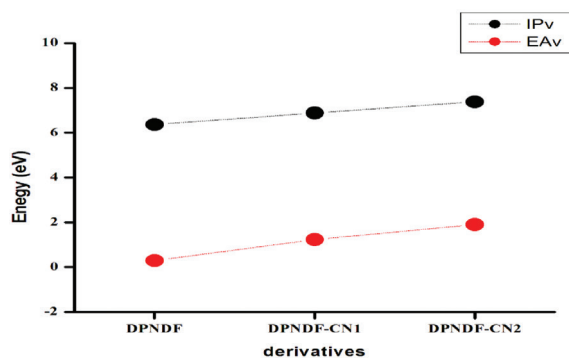


FIGURE 6. Graphical representation of IPv and EAv calculated at the B3LYP/6-31G** level of theory

reorganization energies at the DFT/ B3LYP/6-31G** level of theory for electron $\lambda(e)$ and for hole $\lambda(h)$ have been given in Table 6. A graphical representation of $\lambda(h)$ and $\lambda(e)$ has been given in Figure 7 at the same level of theory to show the tendency more clearly. From Table 6 it is clear that the DPNDF, DPNDF-CN1 and DPNDF-CN2 have almost balanced $\lambda(h)$ and $\lambda(e)$, therefore, they might be good candidates for electron and hole charge transport. The parent molecule of DPNDF has $\lambda(h)$ as 0.17 eV which is in a very good agreement with experimental $\lambda(h)$ for the DPNDF (Mitsui et al. 2012). The $\lambda(h)$ in DPNDF-CN1 and DPNDF-CN2 are 0.15 and 0.14 eV, respectively at the B3LYP/6-31G** level of theory. These values of $\lambda(h)$ for DPNDF-CN1 and DPNDF-CN2 are smaller than that of DPNDF (0.17 eV), sulfur analogue DPNDT (0.19 eV) (Shinamura et al. 2011) and α -oligofurans (0.23 eV) (Mohakud et al. 2010), hence support high hole carrier transport ability in DPNDF-CN1 and DPNDF-CN2.

CONCLUSION

The HOMOs and LUMOs in all the studied compounds are delocalized as well as localized throughout the molecular structure. The acceptor groups have been taking part in the formation of HOMOs and LUMOs and the lone pair has been formed for all N atoms in the CN groups. The HOMO energy of parent molecule DPNDF is in a good agreement with the experimental energy. The CN groups increases the HOMO and LUMO energies. The λ_{abs} and λ_{emis} have the red shift of 30 nm and 29 nm for DPNDF-CN1, whereas 43 and 42 nm for DPNDF-CN2, respectively, as compared to the

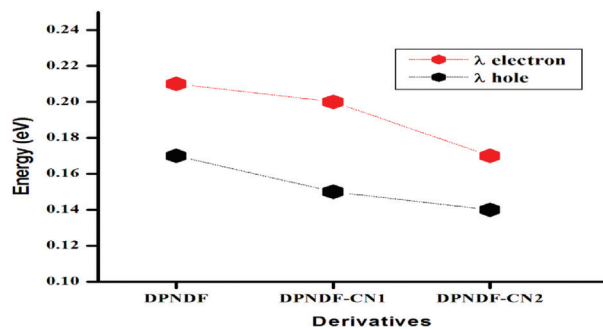


FIGURE 7. Comparison of the reorganization energy for hole $\lambda(h)$ and for electron $\lambda(e)$ calculated at the B3LYP/6-31G** level of theory

parent molecule of DPNDF with an absorption wavelength of 381 nm. The DPNDF-CN1 and DPNDF-CN2 have the higher EAv, so they might be better electron transport material compared to with parent molecule. The DPNDF, DPNDF-CN1 and DPNDF-CN2 have almost balanced $\lambda(h)$ and $\lambda(e)$ showing that these derivatives would also be good hole as well as electron transport materials.

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