



DFT based modeling of asymmetric non-fullerene acceptors for high-performance organic solar cell

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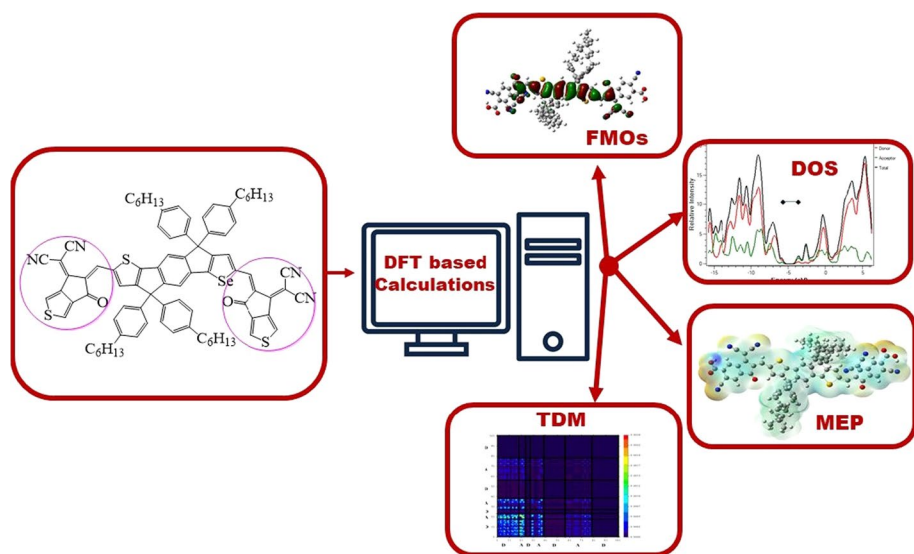
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Abstract

In this study, five new asymmetrical fullerene-free acceptor molecules (**N1** to **N5**) have been designed for organic solar cell applications. Density functional theory and time dependent density functional theory has been employed for exploring the opto-electronic, photovoltaic and geometric properties of the designed molecules. A narrow energy band gap with high red-shifting in the absorption spectrum has been noted. High open circuit voltage with good values of reorganizational energy of electron suggested that designed molecules are effective contributor for solar cell applications. Transition density matrix and frontier molecular orbitals analysis also expressed the presence of charge density within a molecule with different types of transitions. Finally, blend study also performed for exploring the charge transfer between donor polymer and acceptor molecule.

Graphical abstract



Keywords Asymmetrical NFAs · DFT · PCE · End-capped modifications · MEP

1 Introduction

In recent years, organic solar cells (OSCs) using non-fullerene acceptors (NFAs) received tremendous interest and progressed rapidly (Granqvist 2003; Crabtree and Lewis 2007). OSCs have increased their power conversion efficiency (PCEs) due to donor and NFA innovations, as well as device optimization (Hoppe and Sariciftci 2004; Servaites et al. 2011). Aromatic rings having asymmetrical structure, in particular, are used in the development of NFAs, which have benefits such as effective intramolecular charge transfer, broad absorption, and molecular face-to-face arrangement, are extensively utilized as donor parts of low molecular weight NFAs (Jadhav et al. 2019; Kajiyama et al. 2012; Pounraj et al. 2018; Kim et al. 2020).

Currently, much effort has been dedicated to modifying its chemical structure, and optimization of associated devices, resulting in maximum PCE in NFAs-OSCs (Gao et al. 2020a, b; Li et al. 2020a; Tan et al. 2019). The limit of future commercialization of OSCs is because the synthesis of these complex aromatic rings is generally costly and tedious, having a low yield (Mahmood et al. 2015a, b, 2021, 2022; Mahmood and Irfan 2020a). Due to the large variety of small molecules, there is an urgent need to develop novel materials with both high yield and low cost (Yan et al. 2018; Geng et al. 2019; Meng et al. 2018). NFAs cost can be considered as part of the synthetic complexity. In this aspect, conformational locking can provide a novel approach for constructing NFAs containing unfused core units, providing a simplified synthetic pathway, and reducing the cost (Segev et al. 2018; Wilson et al. 1993; Hummelen et al. 1995). In valuable literature, different reports are present which explore the photovoltaic and opto-electronic properties of unique molecules (Adeel et al. 2021; Shehzad et al. 2021).

NFAs containing Indacenodiselenophene (IDSe) have shown improved optical properties in OSCs (Chang et al. 2013; Wang et al. 2022). Replacement of one of thiophene with selenophene in IDT gave asymmetric core SePT (Li et al. 2020b). Recently, Liu and his co-workers used selenophene in IDT asymmetric core flanked with 2-(3-oxo-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-ylidene) malononitrile (IN) terminal groups, this molecule provided improved flexibility in molecular orbitals and better absorption properties (Li et al. 2020b).

Motivated from above results, we take synthesized T–Se–Th based asymmetric NFA molecule as reference molecule (Li et al. 2020b). By end-capped modifications of reference molecule, we have designed five new asymmetrical fullerene free acceptor molecules (**N1** to **N5**) for solar cell applications. After end-capped modifications, different geometric and photovoltaic parameters have been computed through density functional theory and time dependent-density functional theory. Frontier molecular orbital analysis, transition density matrix, open circuit voltage, binding and excitation energies of the designed molecules have been studied through DFT. Results of the above-mentioned analysis recommended that designed molecules are effective contributors for the active layer of organic solar cells.

2 Computational methodology

The systematical analysis was done using Gaussian 09W (Frisch et al. 2009) and the outcomes were anticipated through Gauss View 5.0 (Dennington et al. 2009). Absorption maximum wavelength of reference molecule was obtained after its optimization using

level DFT and 6-31G(d,p) on four chosen functionals i.e. B3LYP, CAM-B3LYP, ω B97XD, and MPW1PW91. The $\lambda_{\max}$ values obtained on B3LYP, CAM-B3LYP, ω B97XD, and MPW1PW91 were 682, 532, 514 and 646 nm, respectively. The computationally obtained $\lambda_{\max}$ of reference on B3LYP functional matched precisely to the experimental value of 682 nm (Li et al. 2020b). UV/Visible calculations of reference molecule and all newly fabricated molecules was done by using Chloroform as a solvent.

Frontier molecular orbital approach, the partial density of states (PDOS), transition density matrices (TDM), dipole moment analysis, and molecular electrostatic potential (MEP) analysis were done using B3LYP and 6-31G (d,p) along with DFT level. Along with these analyses, reorganization energy calculations of holes and electrons were also done. It has two classes, one is internal reorganization energy (λ_{int}) and the other is external reorganization energy (λ_{ext}) demonstrating modifications in internal geometry and impact of external stimuli, respectively. As the impact of external stimuli is very little, thus it was neglected. To calculate the reorganization energy of electrons (λ_e) and holes (λ_h), the equations given below were useful (Alwadai et al. 2022; Asif Iqbal et al. 2022; Mehboob et al. 2022).

$$\lambda_e = [E_0^- - E_-] + [E_-^0 - E_0] \quad (1)$$

$$\lambda_h = [E_0^+ - E_+] + [E_+^0 - E_0] \quad (2)$$

E_0^- and E_+^0 represent neutral molecule's energies through the optimized structures of anions and cations respectively while E_- and E_+ are energies of optimized anions and cations using the neutral molecule. E_0^- and E_+^0 represent single point energies of anions and cations while E_0 is neutral molecule's single point energy in lowest energy state (Yasir Mehboob et al. 2022; Mehboob et al. 2021a, b, c).

3 Results and discussion

3.1 Selection of basis set

In current study, the reference molecule was modified with different end-capped groups and five freshly fabricated molecules **N1–N5** were obtained. Absorption maximum wavelength of reference molecule was obtained after its optimization using level DFT and 6-31G(d,p) on four chosen functionals i.e. B3LYP, CAM-B3LYP, ω B97XD, and MPW1PW91. The $\lambda_{\max}$ values obtained on B3LYP, CAM-B3LYP, ω B97XD, and MPW1PW91 were 682, 532, 514 and 646 nm, respectively. The computationally obtained $\lambda_{\max}$ of reference on B3LYP functional matched precisely to the experimental value of 682 nm (Li et al. 2020b). It can also be seen in Fig. 1 showing the comparison between the maximum absorption wavelengths obtained computationally and experimentally. This also justifies the use of B3LYP functional for further computational analysis done on the newly designed molecules **N1–N5**.

3.2 Frontier molecular orbital analysis

The two-dimensional structure of the reference molecule and newly modified acceptor groups are shown in Fig. 2. FMO analysis demonstrated the MOs of reference and newly tailored molecules which is an important factor in manufacturing NFA based solar cells

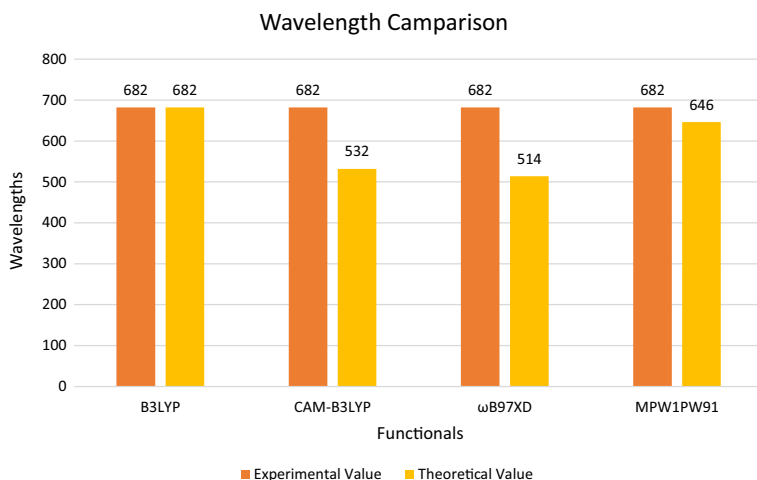
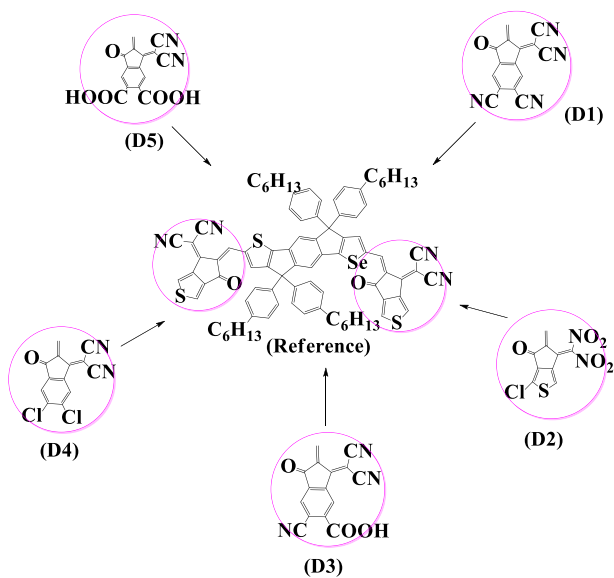


Fig. 1 Column Chart showing comparison of $\lambda_{\max}$ obtained experimentally and at four Functional level B3LYP, CAM-B3LYP, ω B97XD, and MPW1PW91 using DFT with 6-31G (d,p) basis set

(Khan et al. 2019; Khalid et al. 2020). It relates the energies of both HOMO and LUMO. HOMO and LUMO of **R** and newly fabricated molecules obtained through FMO analysis are shown in Fig. 3. HOMO influences the bonding properties while LUMO influences the anti-bonding properties of NFA molecules in ground state and excited state. A stronger electron-withdrawing group within the acceptor part of the molecule helps to increase the $\lambda_{\max}$ value causing red shift in NFA. A molecular orbital having higher or lower energy also determines its stability. The more stable a molecular orbital is the

Fig. 2 2D structure of Reference and newly fabricated terminal groups **D1–D5**



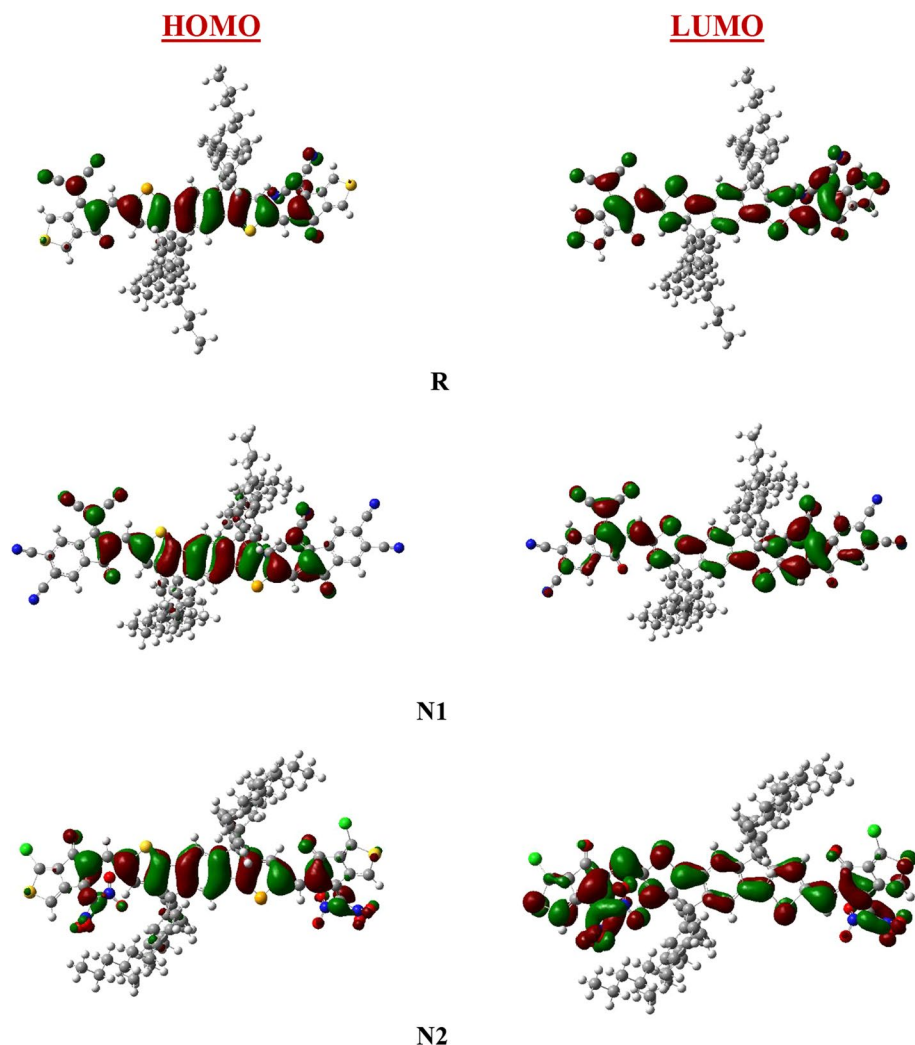


Fig. 3 HOMO LUMO graphs of **R** and **N1–N5** applying DFT and 6-31G(d,p) level of DFT

easier will be electronic transportations throughout the excitation process which makes an NFA efficient to be used in OSCs.

A less stable-completely filled HOMO plays a more effective role in electronic excitation than a more stable HOMO (Mahmood and Irfan 2020b; Mahmood et al. 2014, 2018, 2019a, b; Mahmood 2019). The LUMO should also be stable enough to hold the transported electrons during the excitation process for more time and competently. The acceptor region is the LUMO in NFAs which if perfectly tuned can be useful in capturing more photons and effectively converting those into electric signals to make NFA based SCs more proficient. The electronic transportation rate between HOMO and LUMO is directly related to the percentage of electronic transitions in an excited molecule.

The graphical representation of molecular orbitals of **R** and newly fabricated molecules are shown in Fig. 3.

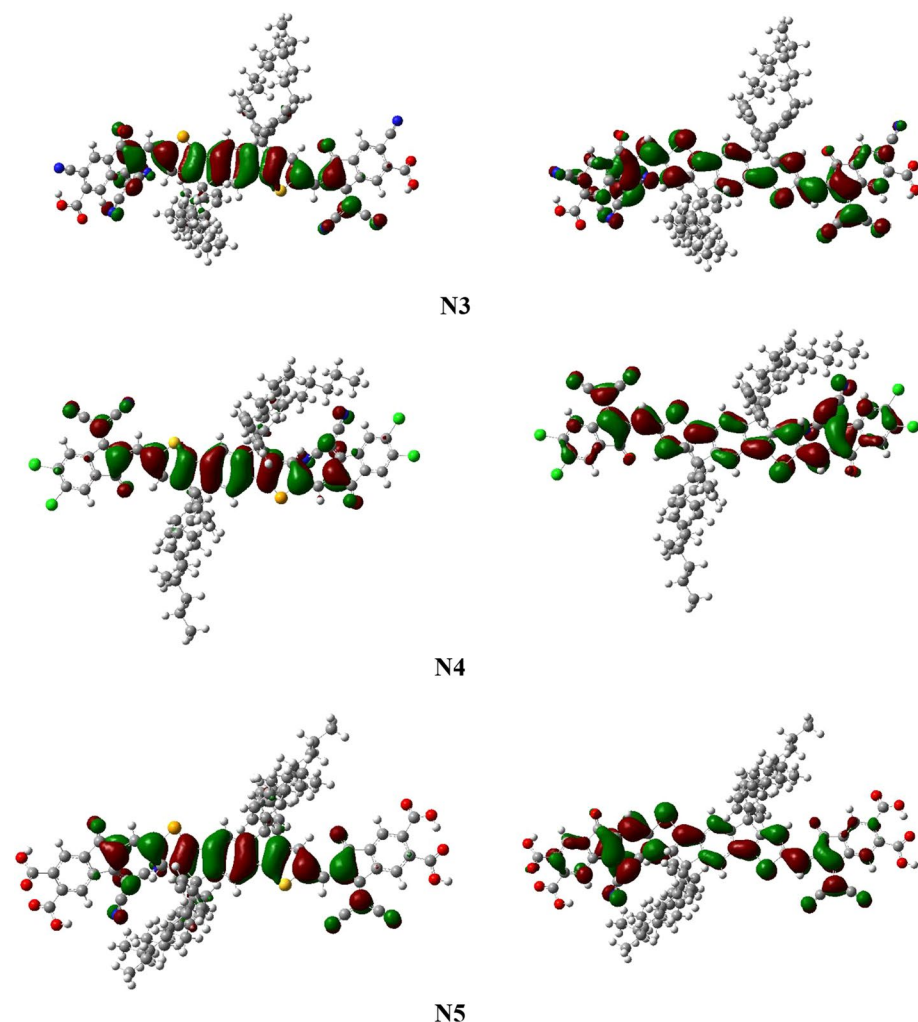


Fig. 3 (continued)

The more electron capturing ability the acceptor part has, the more efficiently electrons are transported from donor part toward the acceptor part. In current study, the HOMO of the reference molecule and all newly designed molecules were identical, showing the presence of an electronic population on the donor region of the molecules. However, the LUMO graphs showed that the electronic density was distributed all over the molecule but was denser on the acceptor groups. In **N1**, the LUMO graph showed that the electronic population was spread all over but was richer on one side of the molecule. **N2** LUMO showed electron density was present all over the molecule but most of this density was accumulated on both acceptor sides of the molecule. In **N3**, **N4**, and **N5** the electron population was present all over the molecules but denser on the acceptor regions.

Thus, these outcomes proved the electron-deficient nature of the acceptor groups. The best electronic flow from the donor part towards the acceptor part is shown by **N2** because of the stronger electron capturing effect of its end capped groups i.e., dinitro and thiochloro

groups. The computationally calculated data of E_{HOMO} , E_{LUMO} and band-gap of **R** and newly fabricated molecules **N1–N5** is displayed in Fig. 4.

These calculations revealed that the energies of HOMO and LUMO of newly fabricated molecules were lower than that of **R**. The change in energy was due to the increase in conjugation in acceptor sides connected to an asymmetric central unit. This also caused an increase in absorption maxima.

The energies of HOMO of the reference and five newly fabricated molecules are shown in an increasing order **N1** < **N3** < **N5** < **N2** < **N4** < **R**. While the increasing order of LUMO energy of reference and newly fabricated molecules is **N1** < **N3** < **N2** < **N5** < **N4** < **R**. It is clear that **N1** showed MOs of least energy because it possessed stronger electron capturing end-capped groups i.e., two dicyano groups and improved conjugation. It was followed by **N3** containing one acid and three cyano groups on terminal parts which made it more electron-deficient and stronger electron-withdrawing acceptor moiety than **N2** (one thiochloro and dinitro end-capped groups), **N5** (two acid and dicyano end-capped groups), and **N4** (dicyano and dichloro groups). The highest values of E_{HOMO} and E_{LUMO} were displayed by **N4** as compared to other newly fabricated molecules which was because of relatively less strong electron capturing end-capped groups.

R > **N4** > **N5** > **N3** > **N1** > **N2** is the decreasing order of **R** and newly designed molecules' energy band gaps. The difference between E_{LUMO} and E_{HOMO} is the energy bandgap. We determined that the energy band gaps of all **N1–N5** molecules were smaller than the **R** molecule due to the greater electron-withdrawing action affected by the terminal groups by comparing the energy band gaps of all freshly synthesized molecules and **R** molecules. The **N2** molecule, which featured a dichloro and thiochloro functional group in its acceptor region, had the lowest energy band gap. **N1** displayed a greater bandgap than **N2** but lesser than **N3**, **N5**, and **N4** because of its two dicyano groups. **N3** containing one acid and three cyano groups in acceptor moiety exhibited a greater energy band gap than **N2** and **N1**. **N3** bandgap energy was followed by **N5** (two acid and dicyano electron-withdrawing groups), and **N4** (dicyano and dichloro

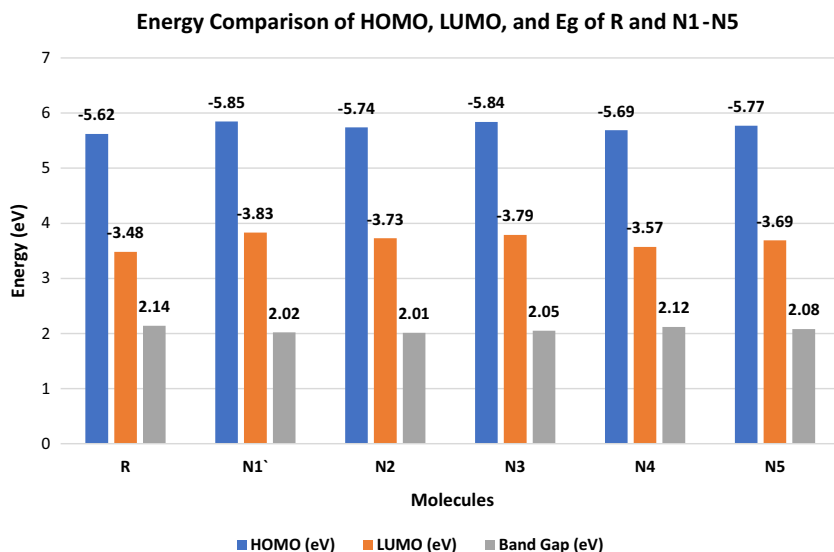


Fig. 4 E_{HOMO} , E_{LUMO} , and energy band gap (E_g) of reference and newly designed molecules **N1–N5**

terminal groups). The bar chart representation of E_{LUMO} and E_{HOMO} , and their difference (E_g) is shown in Fig. 4.

The FMO studies gave conclusion that all the newly fabricated molecules **N1–N5** showed better electron capturing nature than **R**. And among all the newly fabricated molecules, most appropriate results were displayed by **N2** making it a good choice to give a proficient NFA based SCs.

3.3 Partial density of states

The partial density of states (PDOS) technique relates the bonding, anti-bonding atoms, and molecular orbitals (Mehboob et al. 2021d, e, f). The PDOS graphs of reference and newly fabricated molecules **N1–N5** are displayed in Fig. 5. From the graphs, it is clear that the modification in terminal groups of acceptor parts shifted the electronic density towards itself. The overall study of the electronic distribution revealed that all the new NFAs showed proficient electronic distribution along with improved charge transportation from the donor to the acceptor part relative to the **R** molecule.

This technique was used for further clarifying the results obtained from FMO analysis. The density of states calculations of reference and all newly fabricated molecules were done on the same functional level B3LYP using a basis set 6-31G(d,p). The left side of the PDOS plots symbolized the HOMO region while the right side is symbolizing the LUMO region of **R** and **N1–N5** molecules. The red lines characterize the comparative intensity of the donor part while the green lines are of the acceptor part. The HOMO of all the fabricated molecules showed that the electronic population was mainly on the core unit while in the LUMO, this electronic population was shifted on the acceptor region more than the reference molecule. The proficient electronic intensity transition of reference and all the newly designed molecules are shown in decreasing order **N2 > N3 > N5 > N1 > N4 > R**. This proved the application of these NFA molecules in making efficient SCs.

3.4 Molecular electrostatic potential (MEP)

Molecular electrostatic potential indicates the electron-deficient and electron-rich regions for analyzing the electron's distribution in the molecule. MEP plots of reference and newly fabricated molecules **N1–N5** are shown in Fig. 6. The molecules are colored showing different regions (electrophilic and nucleophilic) according to electronic distribution and the scale indicates how electronic distribution relates to the colors.

Three major colors are present in the plots as well as in scales i.e., red, blue, and green which indicates an abundance of positive charge, an abundance of a negative charge, and a neutral region respectively. The reference and all newly fabricated molecules **N1–N5** showed a similar trend in MEP plots indicating the donor part in blue color showing its electron-rich and electron-donating nature while the acceptor end-capped groups were in red proving their electron-deficient and electron-withdrawing nature. This different electronic distribution in the different regions of molecules indicated an improved charge transfer which would make efficient NFA based polymer solar cells.

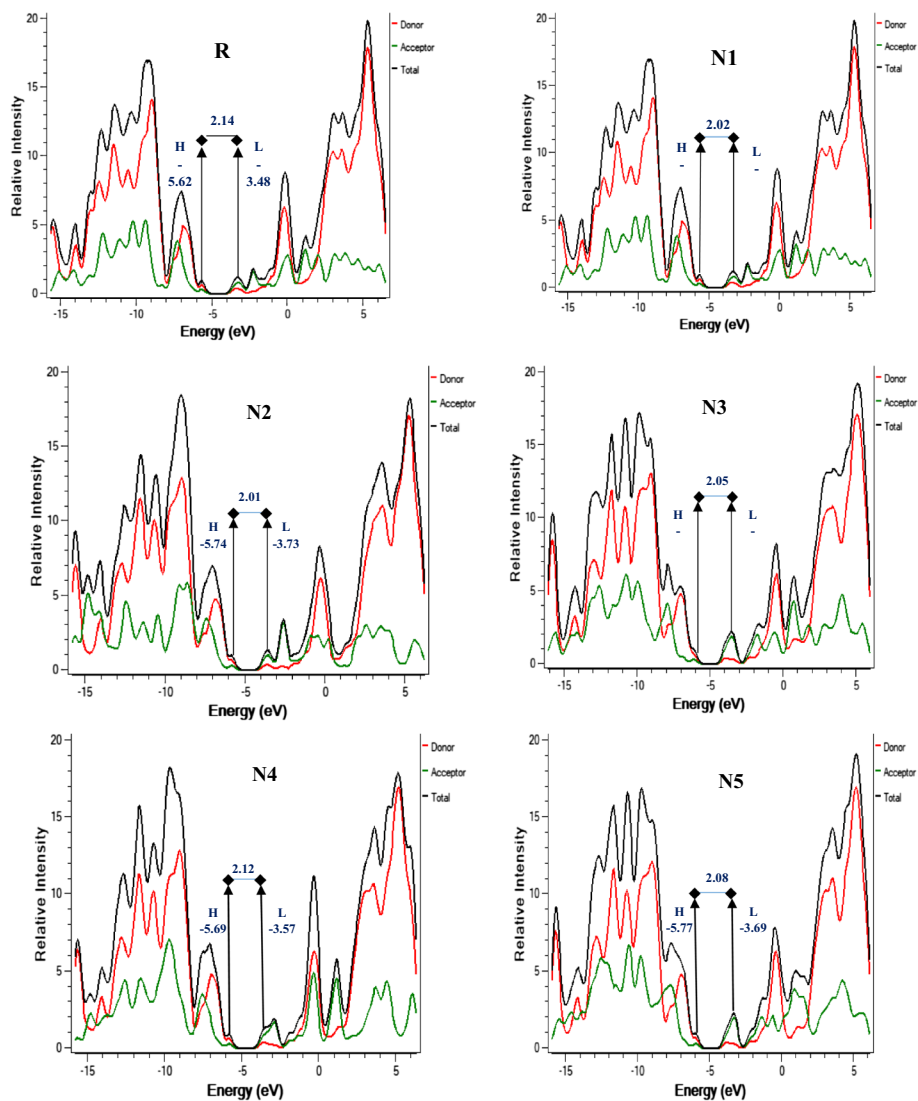


Fig. 5 PDOS graphs of **R** and **N1–N5** calculated at B3LYP, 6-31G(d,p) level of DFT

3.5 Optical properties

Optical properties of **R** and newly fabricated molecules **N1–N5** were analyzed using TD-SCF with basis set 6-31G(d,p) and solvent chloroform along with model CPCM. This analysis gave information about the absorption maximum in the electromagnetic spectrum (Iqbal et al. 2021; Mehboob et al. 2020, 2021g). Optical properties included maximum absorption wavelength (nm), transition energy (eV), oscillation strength (f), and major contributing orbitals.

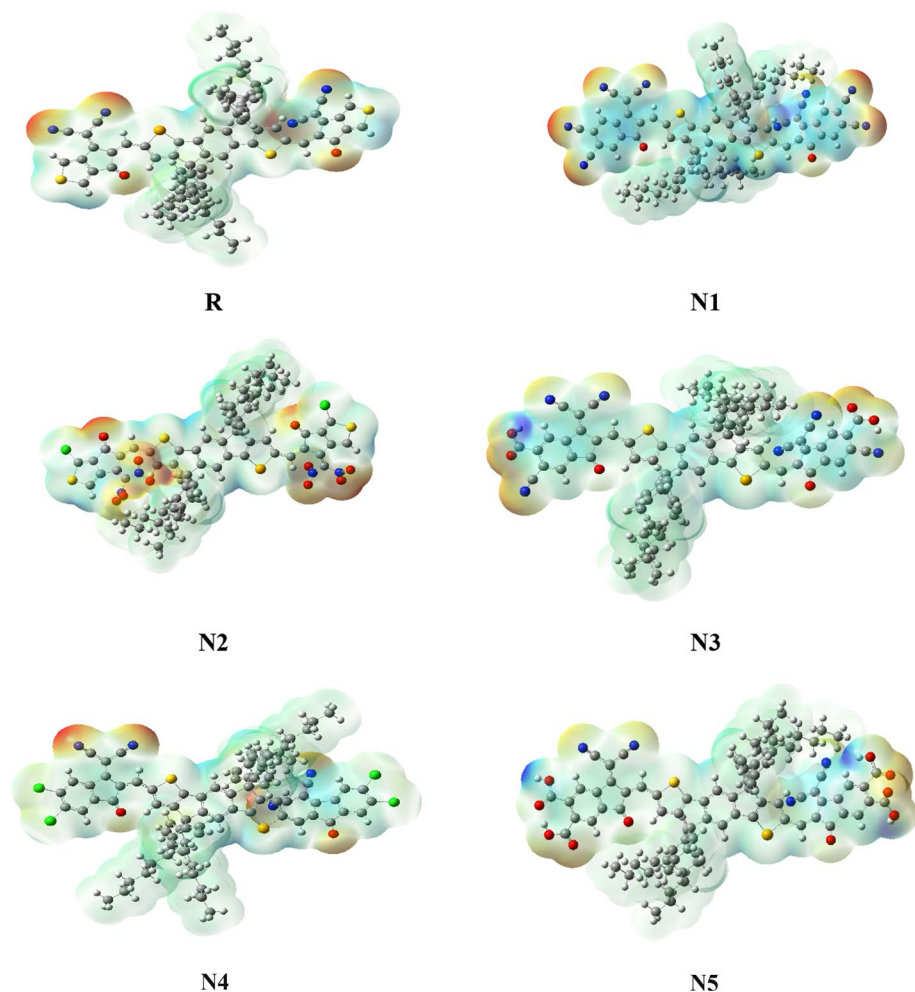


Fig. 6 MEP plots of **R** and **N1–N5** applying DFT and basis set 6-31G(d,p)

The wavelength of maximum absorption ($\lambda_{\max}$) of **R** and new fabricated molecules **N1–N5** are 682, 729, 735, 714, 696, and 708 nm respectively. All newly tailored molecules have greater $\lambda_{\max}$ as compared to **R** while all the values were within visible spectral range with **N2** having the highest $\lambda_{\max}$ value due to electron-withdrawing effect caused by thioclouro group along with dinitro group present in its acceptor moiety. It was followed by **N1**, **N3**, **N5**, and **N4** respectively. **N1** showed higher $\lambda_{\max}$ than **N3**, **N5**, and **N4** due to the presence of two dicyano groups in its acceptor part. The difference in acceptor groups of **N1** and other molecules with lower $\lambda_{\max}$ was that in **N3** one cyano group was replaced by an acid group, in **N5** two cyano groups were replaced by two acid groups while in **N4** two cyano groups were replaced by two chloro groups. The increase in absorption maximum is known as redshift. The difference between $\lambda_{\max}$ of newly fabricated molecules from the reference molecules gave us the value of the red shift shown by our designed molecules. The redshift shown by **N1–N5** compared to **R** is 47, 53, 32, 14, and 26 nm respectively.

It is clear from this difference that acceptor groups **D1–D5** present on molecules **N1–N5** showed more electron-withdrawing properties and among all these newly fabricated molecules, **N2** is showing maximum redshift.

Excitation energy is also known as transition energy. It is also an important optical property that defines the charge transportation trend in the desired molecules. Smaller excitation energy promotes the electronic transition from HOMO to LUMO making the molecules efficient NFAs. In our study, all the tailored molecules have smaller transition energy than **R** which made them have higher charge mobilities than that of the **R** molecule (Frisch et al. 2009). **N2** has the lowest excitation energy value than the other tailored molecules i.e., 1.69 eV followed by **N1** (1.70 eV), **N3** (1.73 eV), **N5** (1.75 eV), and **N4** (1.78 eV), respectively as shown in Table 1. Thus, it was concluded that **N2** molecule having **D2** terminal group was proved to be the best choice among the newly fabricated molecules while all the **N1–N5** NFAs showed better results than the reference molecule.

3.6 Dipole moment

The values of dipole moment considered as capable characteristics for calculating the improved performance of the organic solar cells (OSCs) as the solubility of the organic solar cells largely depends upon the values of dipole moment (*D*). Generally, the fabrication mechanism of solar cells is greatly affected by the dipole moment and directly proportional to the solubility. Stability of the organic solvents is higher due to the higher value of dipole moment. Higher the dipole moment means it is greatly soluble in organic solvent and solubility of OSCs materials increases as the dipole moment increases (Khan et al. 2019). Systematically calculated dipole moment values of **R** and **N1–N5** molecules have been shown in Table 1.

It gave information about the solubility of the investigated molecule in an organic solvent i.e., chloroform in our case. A higher dipole moment indicated greater solubility in the solvent making the solution processing of NFAs feasible. Greater dipole moment assists in efficient charge separation in the molecule. **N3** molecule showed the highest dipole moment of 7.40 D followed by **N4**, **N1**, **R**, **N5**, and **N2** respectively. Greater dipole moment helps molecules to be self-arranged for better charge mobilities.

Table 1 The computationally calculated and experimentally recorded λ_{max} (nm), Excitation energy (eV), oscillator strength, major contribution of molecular orbitals

Molecules	Calculated λ_{max} (nm)	Experimental λ_{max} (nm)	Energy (eV)	Osc. Strength (<i>f</i>)	Assignment	Dipole moment
R	682	682	1.82	2.1932	HOMO → LUMO (99%)	6.71
N1	729	–	1.70	1.8572	HOMO → LUMO (98%)	6.87
N2	735	–	1.69	1.8184	HOMO → LUMO (98%)	3.60
N3	714	–	1.73	2.0238	HOMO → LUMO (98%)	7.40
N4	696	–	1.78	2.0189	HOMO → LUMO (98%)	7.07
N5	708	–	1.75	1.9664	HOMO → LUMO (98%)	5.44

3.7 Reorganization energy

Reorganization energy is used for the systematic calculation of electrons and holes mobilities. The holes and charge mobilities calculated systematically help in elaborating the working of SCs. This depends on many aspects including structural properties of anions and cations.

The geometry of anion defines the transportation of electrons from a donor while the geometry of cation describes the hole accumulation in the acceptor part of a molecule. So, reorganization energy is used to study the electron transportation between the donor and acceptor. It is categorized into two classes i.e., external, and internal reorganization energy. We considered only the latter type and neglected the external reorganization energy because there is no external environmental effect on the investigated molecules (Yasir Mehboob et al. 2021).

Reorganization energy calculations were done with the help of Eqs. 1 and 2 and the outcomes were shown in Table 2. The results revealed that **N1** and **N3** showed the lowest energy values which assigned highest electron mobilities to these two molecules. All the other molecules showed comparable results with reference molecule.

3.8 Transition density matrix and binding energy

The transition density matrix technique was utilized for assessing the electronic transitions within the reference and newly fabricated molecules (**N1–N5**). It was done using same functional i.e. B3LYP with basis set 6-31G(d,p). As hydrogen atoms have little effect on transition, so they were neglected. The TDM graphs of R and new molecules **N1–N5** were plotted using Multiwfn and are displayed in Fig. 7.

TDM analysis is used to study the excitations, electron–hole localization, and relation between the donor and acceptor part within the molecule. In the TDM graphs, x-axis and y-axis indicates the number of atoms 1-n where n is total number of atoms in the respective molecule. For this study, we differentiated the reference and newly designed molecules into two main parts i.e., donor and acceptor region. The TDM provides an in-depth understanding of the electronic transitions occurring in a photovoltaic material. The uniqueness of this approach involves the fact that it depicts the electron–hole pair of molecules as a 3D (three-dimensional) map. The TDM also depicts the delocalization process and the interrelationship of the designed substance lengths. To clearly understand the process, we divided the molecule into two groups: (1) the acceptor unit, and (2) the donor unit. Moreover, now the respected acceptor, and donor area are drawn on the Heat Maps. It could be seen through the plots that the holes and electrons of exciton were accumulated in the donor and

Table 2 Reorganization energy of electrons and holes of **R** and **N1–N5** calculated at B3LYP, 6-31G(d,p) level of DFT

Molecules	λ_e (eV)	λ_h (eV)
R	0.0087	0.0069
N1	0.0073	0.0074
N2	0.0119	0.0076
N3	0.0075	0.0091
N4	0.0091	0.0076
N5	0.0094	0.0084

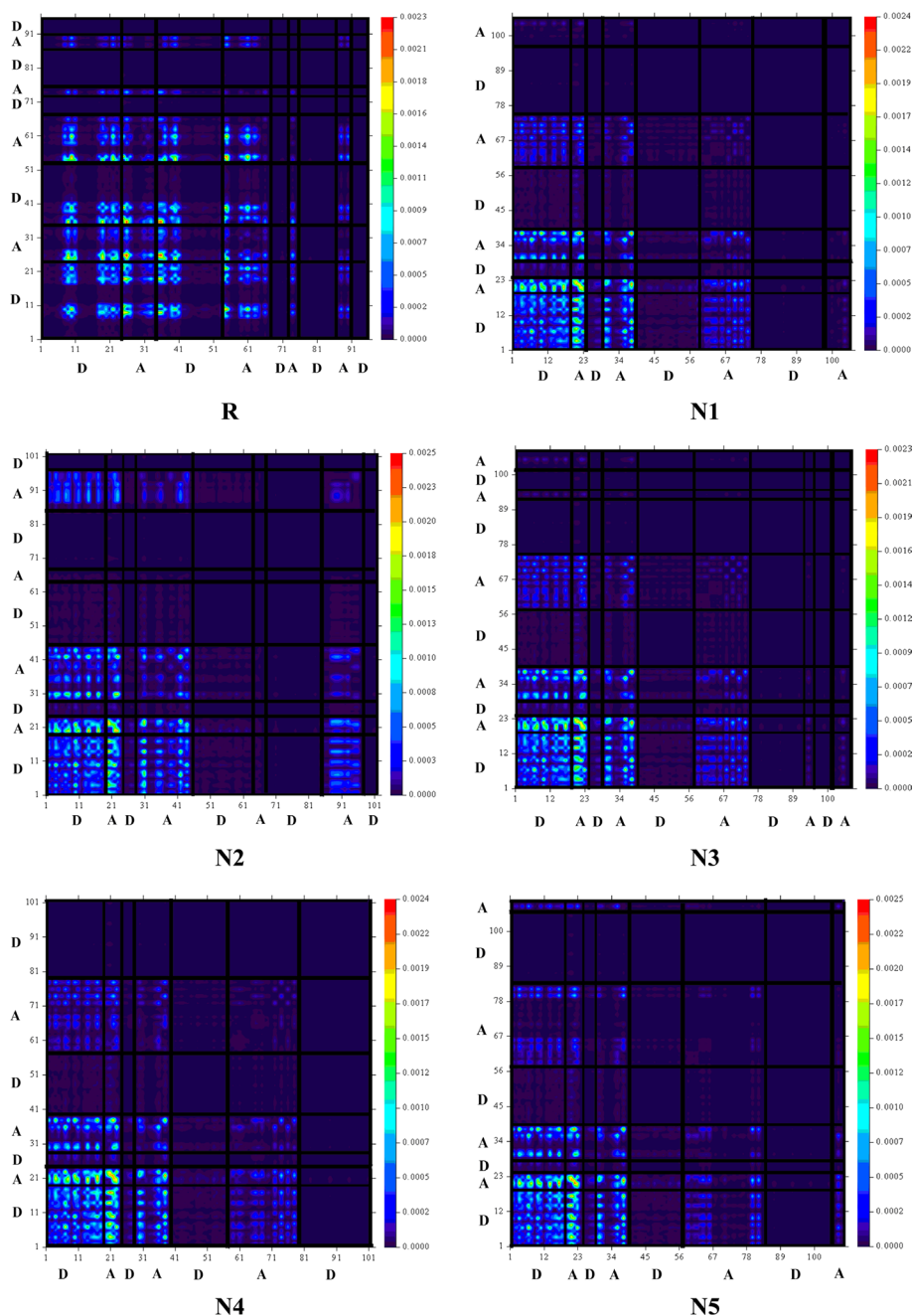


Fig. 7 TDM graphs of **R** and **N1–N5** calculated at B3LYP and DFT level and plotted by MultiWFN

acceptor region respectively. As compared to **R**, most of the electron density was accumulated in the acceptor region with a little density on the donor part in **N1–N5** molecules. This proved that the electronic transportation from the donor region to the acceptor region

was improved efficiently by fabricating the end-capped groups within the NFAs. These NFAs will give efficient non-fullerene based solar cells.

Binding energy (E_b) is an important factor influencing dissociation potential thus affecting the performance of a solar cell. Binding energy has an inverse relation with charge mobilities. Molecules having greater binding energies have lower charge mobilities and lower current densities. This analysis was used to relate the Columbic force among the holes and electrons in a molecule. This interaction between holes and electrons is directly dependent upon the binding energy and binding energy is inversely dependent upon exciton breakdown in an excited state. Low binding energy of a molecule allows easy disassociation of exciton in the active layer of solar cell. Therefore, a molecule with low binding energy will show high performance in the active layer of organic solar cell. The below-mentioned equation was used to calculate the binding energies of R and newly fabricated molecules **N1–N5**.

$$E_b = E_{H-L} - E_{opt} \quad (3)$$

E_{H-L} is band gap between the bonding and anti-bonding molecular orbital, E_{opt} is minimum first excitation energy. The binding energies of R and all the newly fabricated molecules are tabulated in Table 3. All newly designed molecules showed comparable values of binding energy as R because of the electron withdrawing nature of the terminal groups. Thus, proving these molecules to be an effective NFAs.

3.9 Open circuit voltage

Open circuit voltage is significant for evaluating the SC's efficiency. When light falls on SCs, the electron gets excited from the donor's HOMO to the donor's LUMO. Then, this electron moves from the donor's LUMO to the acceptor's LUMO. Open circuit voltage (V_{oc}) is highest value of voltage when the circuit's current falls to zero. It is the difference between E_{HOMO}^D of the donor and E_{LUMO}^A of the acceptor subtracting 0.3 (an empirical factor). It is also shown below in equation form.

$$V_{OC} = (E_{HOMO}^D - E_{LUMO}^A) - 0.3 \quad (4)$$

All the new molecules **N1–N5** are NFA based acceptors, so we calculated the V_{OC} using a common polymer donor i.e., PTB7-Th. The outcomes can be visualized in Fig. 8. For more charge transportation from donor to an acceptor molecule, the energies of HOMO and LUMO play a significant role. HOMO with higher energy and LUMO with lower energy facilitate more charge transportation. The open circuit

Table 3 Band gap(eV), excitation energy (eV), and Binding energy values of **R** and **N1–N5**

Molecules	E_{H-L}	E_x	E_b
R	2.14	1.82	0.32
N1	2.02	1.70	0.32
N2	2.01	1.69	0.32
N3	2.05	1.73	0.32
N4	2.12	1.78	0.34
N5	2.08	1.75	0.33

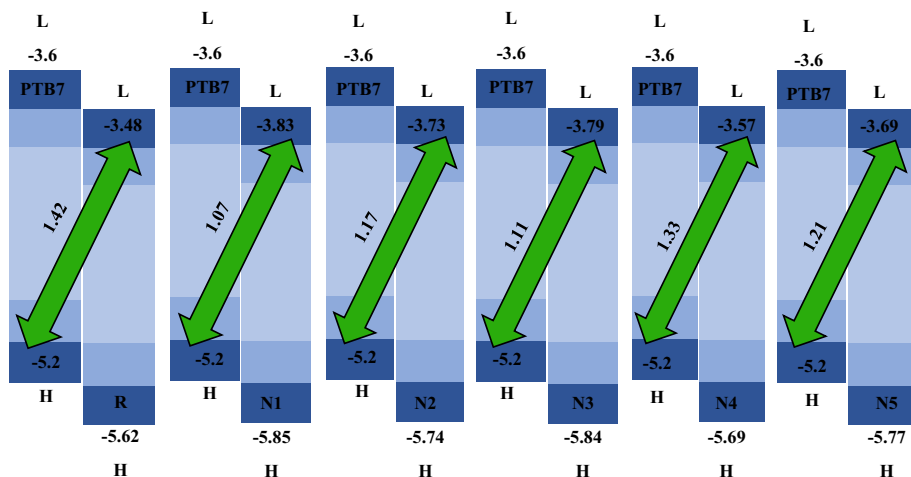


Fig. 8 Systematically calculated open circuit values of reference and newly fabricated molecules **N1–N5**

voltage is in inverse relation with short circuit current. The lower V_{oc} values of these molecules were due to the smaller energy gap which will enhance their short circuit current. And J_{sc} as an important factor will contribute in increasing the PCE values in acceptor based SCs.

3.9.1 Charge transfer (CT) analysis through N2/PTB7-Th complex

All newly fabricated molecules are acceptor type thus for the charge transfer analysis, we used PTB7-Th polymer donor. As the **N2** acceptor molecule was proved to be the best choice among all newly fabricated molecules. It had lowest bandgap along with higher λ_{max} , therefore we used **N2** molecule for CT analysis. The optimization of PTB7-Th and **N2** complex was done on DFT and B3LYP with basis set 6-31G(d,p). The interface interaction suggested that the electron population is on the boundary of acceptor and donor maximizing the charge transfer within the complex. The optimized structure is displayed in Fig. 9 (Khalid et al. 2020).

The charge distribution in the molecular orbitals was also studied at function B3LYP with basis set 6-31G(d,p). The outcomes displayed in Fig. 10 concluded that in HOMO, the donor had most of the electron population but in LUMO most of the electronic density resided on the acceptor molecule. This proved the electronic shifting from the donor part towards the acceptor part (Alwadai et al. 2022; Asif Iqbal et al. 2022; Mehboob et al. 2021a, b, c, 2022; Yasir Mehboob et al. 2021; Khan et al. 2019; Khalid et al. 2020; Mahmood and Irfan 2020b; Mahmood et al. 2014, 2018, 2019a). It also confirmed the acceptor-type nature of our designed molecule **N2**. Similar molecules are reported in valuable literature. Recently, end-capped modifications of Y6 molecule have been reported. The designed molecules expressed effective energy band gap values with good light harvesting ability. In present report, designed molecules expressed more narrow energy band gap as compared to Y6A1–Y6A5 molecules. Moreover, the designed molecules also expressed high light absorption ability as compared to reported molecules (Mehboob et al. 2021h).

Fig. 9 Optimized complex of N2 with PTB7-Th

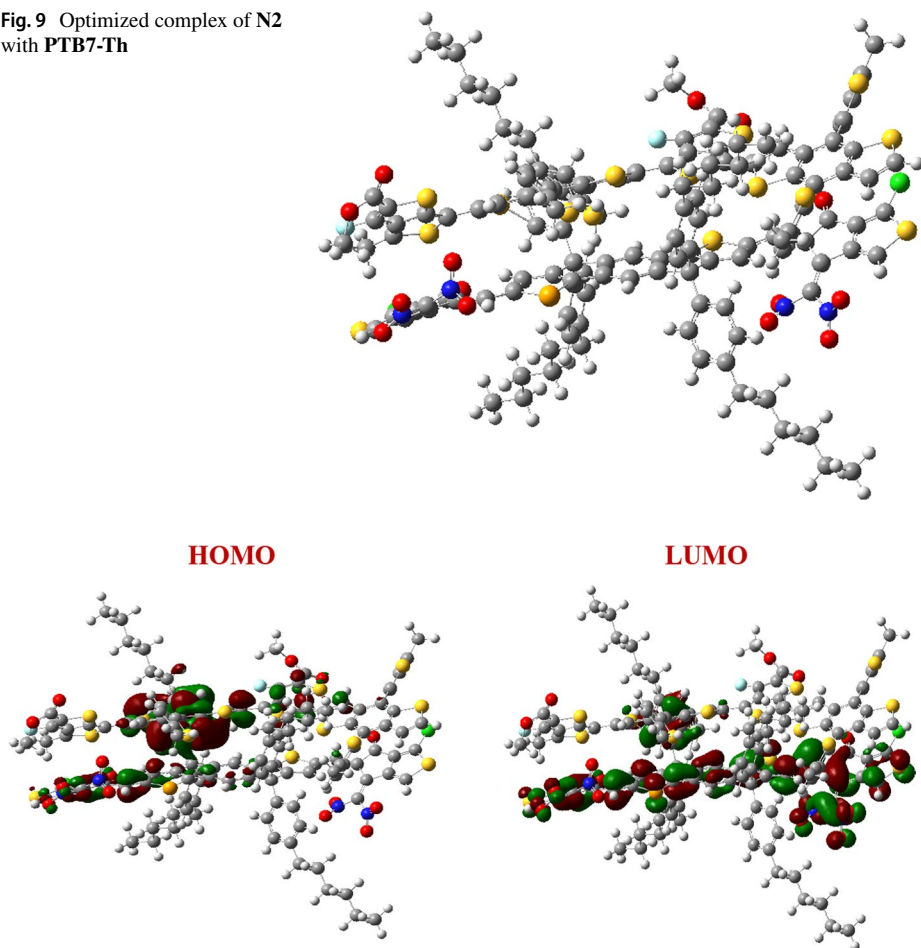


Fig. 10 HOMO, LUMO graphs N2 complex with PTB7-Th

4 Conclusion

Five novels NFAs **N1–N5** were designed by the method of modifying the terminal groups of acceptor parts to enhance the optoelectronic and photovoltaic properties of non-fullerene acceptors based SCs. We used an asymmetric electron-donating core SePT with acceptor groups **D1–D5**, respectively. We systematically calculated optical, and structural properties of these molecules on DFT level with B3LYP/6-31G(d,p) and compared these with reference molecule. We used FMO approach for the investigation of MOs which concluded that all the tailored molecules showed better properties compared to **R**. All molecules showed lower excitation energies and binding energies attributing to improved charge mobilities. **N2** molecule displayed the highest maximum absorption wavelength, lowest excitation energy and least energy bandgap in chloroform solvent. TDM, MEP, FMO analyses confirmed acceptor nature of all these molecules. Designed molecules will be good electron-transporting materials in NFA based OSCs. A complex of **N2** with PTB7-Th donor polymer proved its acceptor type property. Thus, it is concluded that all these new molecules

N1–N5 especially **N2** have improved photovoltaic properties and are promising NFAs to be used in polymer solar cells.

5 Associated content

Optimized Cartesian coordinates of all studied molecules (**R** and **N1–N5**) are available in supporting information file.

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Declaration

Conflict of interest All authors declared no conflicts of interest.

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