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DFT and TD-DFT investigations of new thienopyrazine-based dyes for solar cells: Effects of electron donor groups

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ABSTRACT

Novel five organic donor- π -acceptor molecules ($D-\pi-A$) used for dye sensitized solar cells (DSSCs) and for organic solar cells (OSC), based on thienopyrazine and thiophene were studied by density functional theory (DFT) and time-dependent DFT (TD-DFT) approaches to shed light on how the π -conjugation order influence the performance of the solar cells. The electron acceptor (anchoring) group was 2-cyanoacrylic for all compounds whereas the electron donor unit was varied and the influence was investigated. The theoretical results have shown that TD-DFT calculations, with a hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP) in conjunction with polarizable continuum model of solvation (PCM) together with a 6-31G (d,p) basis set, was reasonably capable of predicting the excitation energies, the absorption and the emission spectra of the molecules. The frontier molecular orbitals (HOMO and LUMO) energy levels of these compounds can be ensuring positive effect on the process of electron injection and regeneration. The trend of the calculated HOMO-LUMO gaps nicely compares with the spectral data. In addition, the estimated values of open-circuit photovoltage (V_{oc}) for these compounds were presented in two cases /TiO₂ and /PCBM. The study of structural, electronics and optical properties for these compounds could help to design more efficient functional photovoltaic organic materials.

Keywords: π -conjugated molecules; thienopyrazine derivatives; solar cells; TD-DFT; optoelectronic properties; V_{oc} (open circuit voltage).

INTRODUCTION

Since their discovery, materials based on organic π -conjugated molecules have good properties such as thermal and photochemical stability and high charge mobility, which make them promising candidates for research on optoelectronic device technology [1], such as LEDs [2], Transistors (TFTs) [3] and low-cost solar cells [4]. Conjugated polymers containing thiophene moieties either in the main or side chains have attracted much attention because of their unique electronic properties, their high photoluminescence quantum efficiency, thermal stability and also their facile color tenability [5]. Thanks to its important specific properties, these new compounds became the most promising materials for the optoelectronic device technology [6]. These properties depend on the degree of electronic delocalization in these materials and on the modification of chemical structure through the incorporation of charge carriers into the molecule backbone. One of the most important factors of controlling physical properties is the band gap, which is a current topic of research. In particular, organic materials with a low gap are desired in optoelectronic applications. Many ways have been used to modulate this parameter the best one is the modification

of chemical structure through the incorporation of charges carriers in the polymer backbone. Most of recent papers have focused on the synthesis of short-chain conjugated compounds. These compounds became the most promising materials for the optoelectronic device technology [7]. Recent work in this area has been focused on the synthesis and design of new molecules combining donor and acceptor blocks, or conjugated systems with narrow band gaps. Roquet *et al.* [8] reported the relationships between the nature of acceptor groups in the molecule and the photovoltaic performances. The results show that the introduction of electron-acceptor groups in the donor structure induces an extension of the photo-response in the visible spectral region, an increase of the maximum external quantum efficiency and an increase of the open circuit voltage under white light illumination.

Among the acceptor groups, the carboxylic acid group is by far the most employed group for attachment of the sensitizers to the semiconductor surface. The carboxylic function is normally used as the electron group for the attachment of the dye on the TiO₂ surface [9]. Due to these advantages, we designed a series of non symmetrical branched molecules based on thiophene and thienopyrazine as a central core and cyanoacrylic acid as the end group connected with different π -conjugated donor groups.

In order to obtain materials with more predominant capability, the development of novel structures is now being undertaken following the molecular engineering guidelines, theoretical studies on the electronic structures of these materials have made great contributions to the rationalization of the properties of known ones and the prediction those of unknown ones [10]. We note that theoretical knowledge of the HOMO and LUMO energy levels of the components is crucial in studying organic solar cells. So, we can save time and money in choosing the adequate organic materials to optimize photovoltaic devices properties. The HOMO and LUMO energy levels of the donor and of the acceptor components for photovoltaic devices are very important factors to determine whether effective charge transfer will happen between donor and acceptor. The offset of band edges of the HOMO and LUMO levels will prove responsible for the improvement of all photovoltaic properties of the organic solar cells.

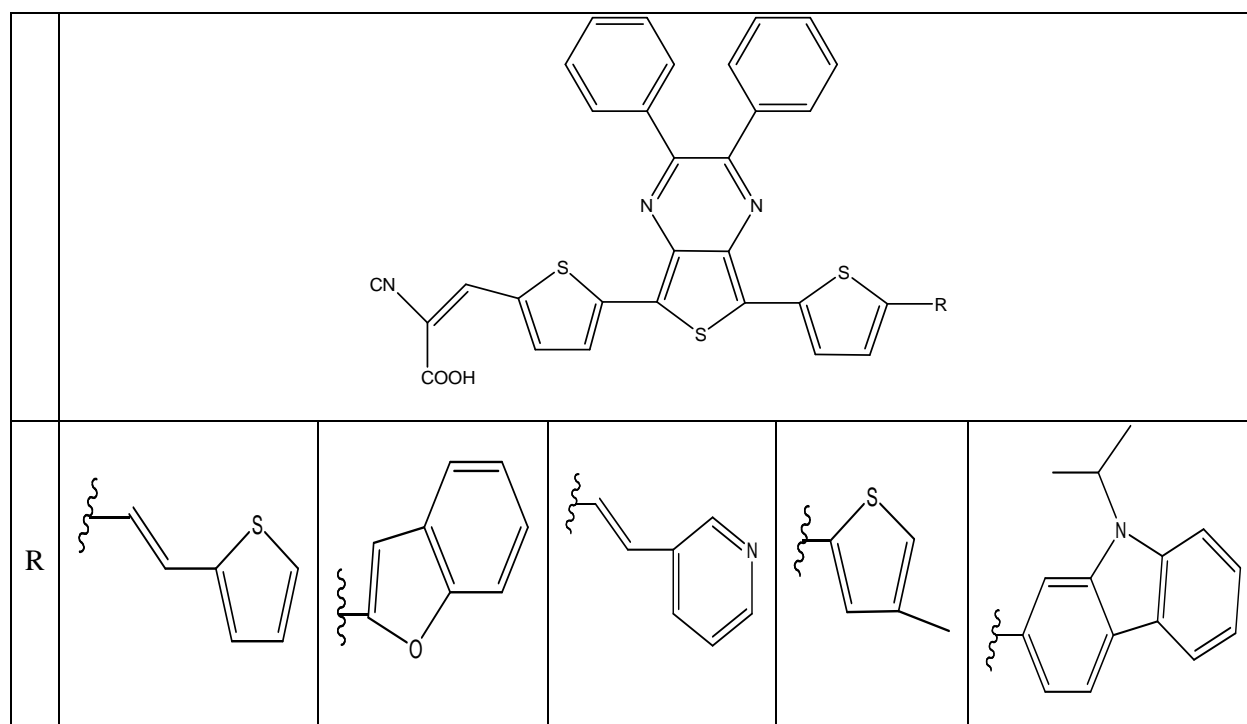


Fig. 1: Chemical structure of studied compounds P_i (i =1 to 5)

In this study, the theoretical analysis on the geometries and electronic properties of conjugated compound based on thienopyrazine (P1, P2, P3, P4 and P5) is reported, as shown in Fig.1. Different electron side groups were introduced to investigate their effects on the electronic structure. The theoretical ground-state geometry and electronic structure of the studied molecules were investigated by the DFT method at B3LYP level with 6-31G(d,p) basis set. The effects of the ring structure and the substituents on the geometries and electronic properties of these materials were discussed with the aim to evidence the relationship between molecular structure and optoelectronic properties. The photovoltaic properties of these compounds P_i (i=1 to 5) as donor blended with PCBM or TiO₂ which are the most acceptors used in OSC and in DSSC devices respectively were studied.

This investigation was used to drive next syntheses towards compounds more useful as active materials in optoelectronic. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells; so the HOMO, LUMO and gap energy and Voc (open circuit voltage) of the studied compounds have been calculated and reported.

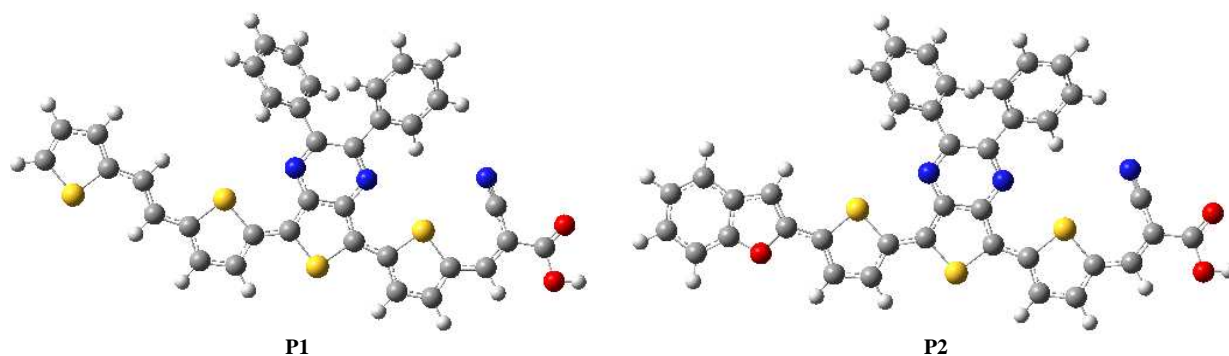
2. Computational methods

All molecular calculations were performed in the gas phase using Density Functional Theory (DFT) using the B3LYP (Becke three-parameter Lee–Yang–Parr) exchange correlation functional [11]. The basis set 6-31G (d, p) was used for all atoms. All the optimizations were done without constraint on dihedral angles. In a recent work, Tretiak and Magyar [12] have demonstrated for a series of D- π -A systems that a good description of the charge transfer states can be achieved when a large fraction of HF exchange is used. A newly designed functional, the long range Coulomb attenuating method (CAM-B3LYP) considered long-range interactions by comprising 19% of HF and 81% of B88 exchange at short-range and 65% of HF plus 35% of B88 at long-range [13]. Furthermore, The CAM-B3LYP has been applied and was reasonably capable of predicting the excitation energies and the absorption spectra of the D- π -A molecules [14-17]. Therefore, the vertical excitation energy and electronic absorption spectra were simulated using TD-CAM-B3LYP method in this work. The inclusion of the solvent effect in theoretical calculations is important when seeking to reproduce or predict the experimental spectra with a reasonable accuracy. Polarizable continuum model (PCM) [18] has emerged in the last two decades as the most effective tools to treat bulk solvent effects for both the ground and excited-states. In this paper, the integral equation formalism polarizable continuum model (IEF-PCM) [19-20] was chosen in excitation energy calculations. The ground state energies and oscillator strengths were investigated using TDDFT calculations on the fully DFT optimized geometries. The calculations were carried out using the Gaussian 09 program [21]. All calculations on the studied compounds of this work were done on cluster machines in the IPREM of Pau in France.

RESULTS AND DISCUSSION

3.1. Ground state geometry

The optimized geometries obtained by B3LYP/6-31G (d, p) of the studied molecules are plotted in Fig. 2. The calculated vibrational spectrum in each molecule has no imaginary frequency, implying that the optimized geometry is located at the minimum point of the potential surface. It was found in other works [17] that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analyses. The main optimized geometry parameters of the studied molecules in all the ground state (S_0) and the excited state (S_1) are compared in Table 1. In the D- π -A molecules, the π -spacer is used as the bridge of intramolecular charge transfer (ICT), therefore, the bridge bonds between A and π -spacer, and D and π -spacer give an account of the interaction among themselves. Herein, the bridge bonds between D and π -spacer and A and π -spacer were marked as L_{B1} and L_{B2} . The shorter length of bridge bonds favored the ICT within the D- π -A molecules. Table 1 shows that L_{B1} of P1, P2, P3, P4 and P5 are 1.437, 1.436, 1.463, 1.445 and 1.464 Å respectively, from the length range of C–C to C=C, of which L_{B1} shows more C=C features. These bond lengths are sorted in the order of P2>P1>P4>P3>P5, which presents the intensity of interaction between thienopyrazine based bridge and donor groups. For all the molecules, L_{B2} does not change significantly. It implies the interaction between A and π -spacer is hardly influenced by D- π interactions.



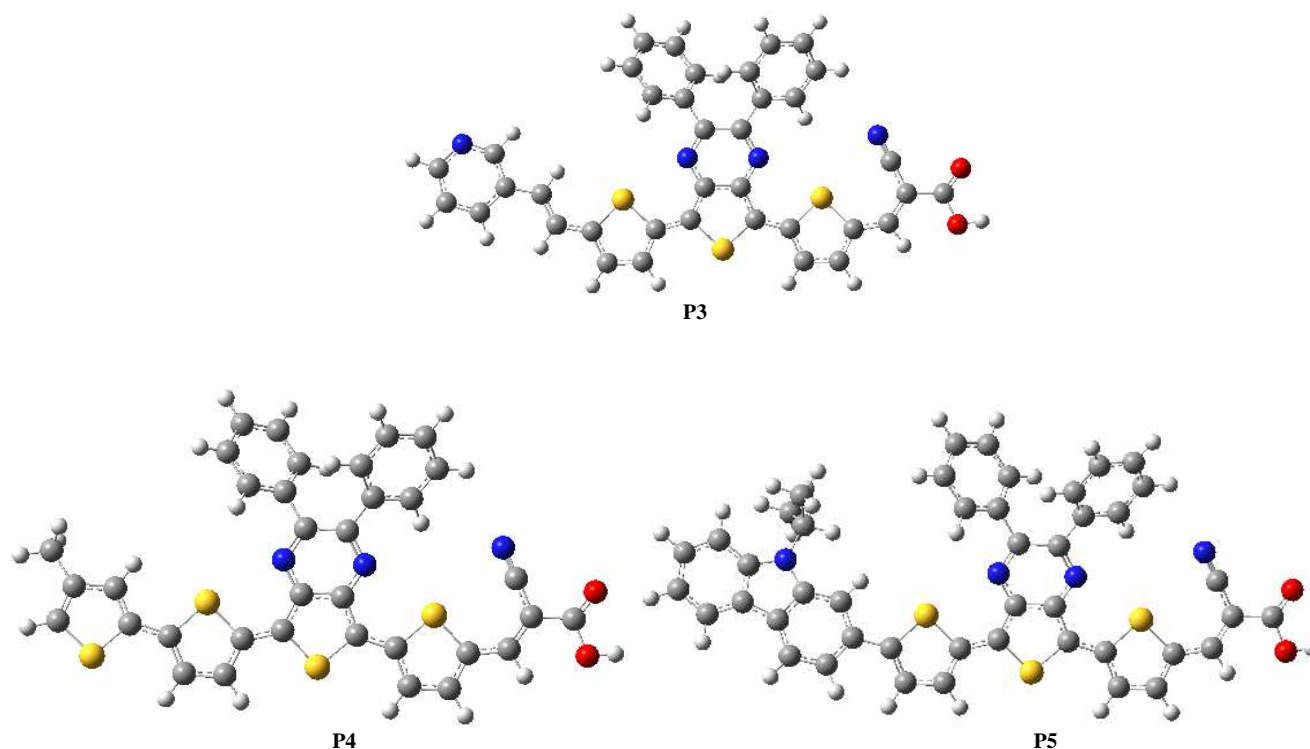


Fig. 2: Optimized geometries obtained by B3LYP/6-31G (d, p) of the studied molecules.

Table 1: Optimized Selected Bond lengths of the studied molecules obtained by B3LYP/6-31G (d, p) level.

Compounds	S0				S1			
	L _{B1}	L _{B2}	Φ_1	Φ_2	L _{B1}	L _{B2}	Φ_1	Φ_2
P1	1.437	1.421	0.7	2.9	1.422	1.411	0.7	3.4
P2	1.436	1.422	1.3	2.9	1.424	1.412	0.3	3.9
P3	1.440	1.422	0.2	2.9	1.429	1.412	0.1	3.2
P4	1.445	1.421	13.7	2.8	1.432	1.411	0.4	3.6
P5	1.464	1.421	26.0	2.7	1.452	1.411	0.9	3.1

In order to state the molecular planarity clearly, two parameters were introduced: Φ_1 , Φ_2 . Here, Φ_1 is the torsional angle between D and π -spacer, Φ_2 is the torsional angle between A and π -spacer. Table 1 shows that Φ_2 is similar for all molecules (2.7°), while Φ_1 for P1, P2, P3, P4 and P5 are tabulated to be 0.7°, 1.2°, 0.2°, 13.8° and 26.0° respectively, which indicates a tendency that close to coplanarity except P4 and P5 due probably to the steric effects of donor groups. On the other hand, upon photoexcitation to the excited state (S_1), the bond lengths for these studied molecules are significantly decreased in comparison with those in the ground state (S_0), especially the linkage between the π -conjugated group and the acceptor moiety (L_{B2}). These results indicate that the connection of acceptor group (2-cyanoacrylic acid) and the π -bridge is crucial for highly enhanced ICT character, which is important for the absorption spectra red-shift.

3.2. Frontier molecular orbitals

The frontier molecular orbital (FMO) contribution is very important in determining the charge-separated states of the studied molecules because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties and provides also the ability of electron hole transport. The energies of the frontier molecular orbitals of studied molecules are given in Table 2. The iso-density plots of the model compounds are shown in Fig. 3. This figure shows that the HOMO and LUMO of all the molecules are spread over the whole π -conjugated backbones with similar character, the HOMO displays anti-bonding character between two adjacent fragments and bonding character within each unit. But the LUMOs exhibit the bonding character between the two adjacent fragments. For all the molecules, the HOMOs are of π nature and are delocalized over the whole carbon double bonds backbone with a small contribution from the C=N bonds of the pyrazine rings and C-S bonds of the thiophene rings in the π -spacer. By contrast, the contribution of pyrazine and thiophene rings is increased in LUMO. Moreover, the HOMO and LUMO topologies show certain overlap, which is a prerequisite to allow for an effective intramolecular charge transfer (ICT). There is a uniform distribution in HOMO for all the molecules to populate the electrons mostly on the electron donor to the π -conjugated spacer, while the LUMOs are essentially localized on

conjugation spacer moiety and the electron acceptor (2- cyanoacrylic acid) fragments. Therefore, the electronic transitions of all D- π -A molecules from HOMO to LUMO could lead to intramolecular charge transfer from the donor units to the acceptor/anchoring groups through the conjugated bridge, so that the HOMO-LUMO transition can be classified as a π - π^* ICT.

Table 2: Energy values in eV of HOMO (E_{HOMO}), LUMO (E_{LUMO}) and gap (E_g) of the studied molecules obtained by B3LYP/6-31G (d, p) level

Compounds	E_{HOMO}	E_{LUMO}	E_g
P1	-4.983	-3.125	1.858
P2	-5.091	-3.157	1.934
P3	-5.127	-3.189	1.938
P4	-5.049	-3.095	1.954
P5	-5.012	-3.052	1.959

It is well known that the HOMO and LUMO energies and energy gaps are weightily relative to optical and electronic properties. Table 2 shows detailed data of absolute energy of the frontier orbital calculated by DFT for the studied molecules P_i ($i=1$ to 5), PCBM and TiO_2 are included for comparison purposes. The calculated parameters (HOMO, LUMO, gap) of P1, P2, P3, P4 and P5 are ((-4.983, -5.091, -5.127, -5.049, -5.012 eV), (-3.125, -3.157, -3.189, -3.095, -3.052 eV), (1.858, 1.934, 1.938, 1.954, 1.959 eV)) respectively. The calculated band gap E_g of the studied compound were in the range 1.858 to 1.959 eV, increases in the following order $P1 < P2 < P3 < P4 < P5$.). As shown in table 2, the change of the electron-donor shows a great effect on the HOMO and LUMO levels. It is deduced that the modification of structure pushes up/down the HOMO/LUMO energies in agreement with their electron donor/acceptor character.

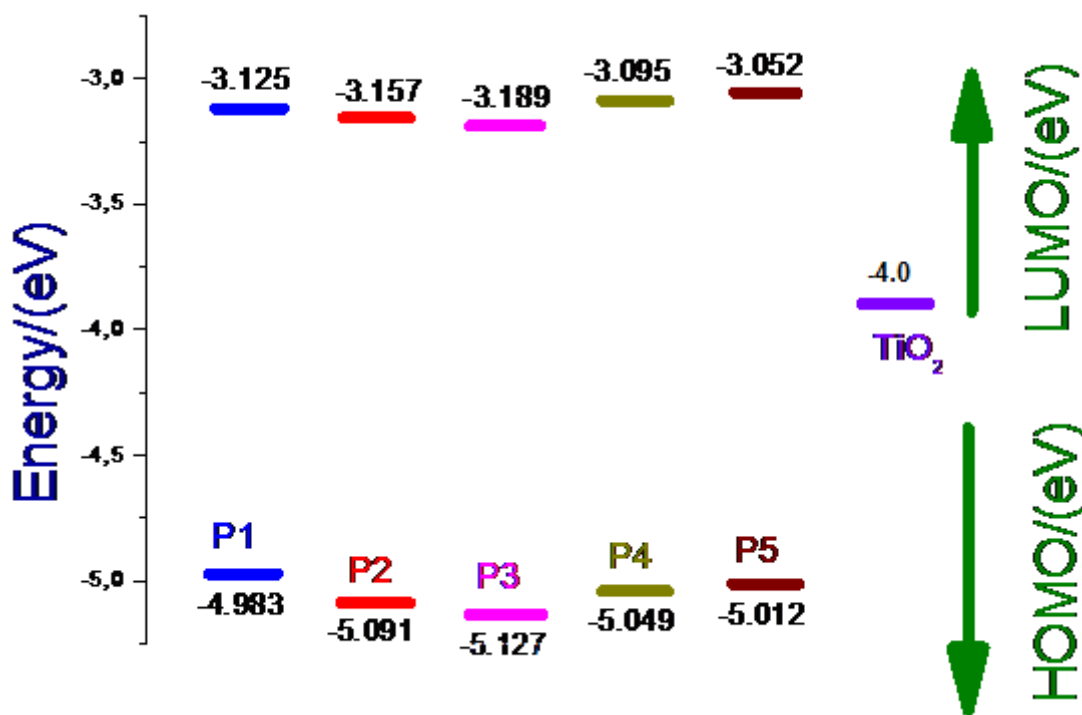


Fig. 3: Sketch of B3LYP/6-31G (d, p) calculated energies of the HOMO, LUMO level of studied molecules

The HOMO and the LUMO energy levels of the donor and acceptor components are very important factors to determine whether effective charge transfer will happen between donor and acceptor. To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of the acceptor TiO_2 or PCBM, the HOMO and LUMO levels were compared (Fig. 3). It is important to note that the LUMO levels of the dyes are higher than that of the conduction band of TiO_2 (-4.0 eV, [23]) and of PCBM (-3.7 eV [24]). The HOMO energy levels of all dyes are much higher than that of TiO_2 conduction band edge and than that of PCBM suggesting that the photoexcited electron transfer from P_i to TiO_2 (or to PCBM) may be sufficiently efficient to be useful in photovoltaic devices.

The power conversion efficiency (η) was calculated according to the following equation (1):

$$\eta = FF \frac{V_{oc} J_{sc}}{P_{inc.}} \quad (1)$$

where $P_{inc.}$ is the incident power density, J_{sc} is the short-circuit current, V_{oc} is the open-circuit voltage, and FF denotes the fill factor.

The maximum open circuit voltage (V_{oc}) of the bulk hetero junction (BHJ) solar cell is related to the energy difference between the highest occupied molecular orbital (E_{HOMO}) of the electron donor and the lower unoccupied molecular orbital (E_{LUMO}) of the electron acceptor, taking into account the energy lost during the photo-charge generation [24]. The theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression (2):

$$V_{oc} = |E_{HOMO}(\text{Donnor})| - |E_{LUMO}(\text{Acceptor})| - 0.3 \quad (2)$$

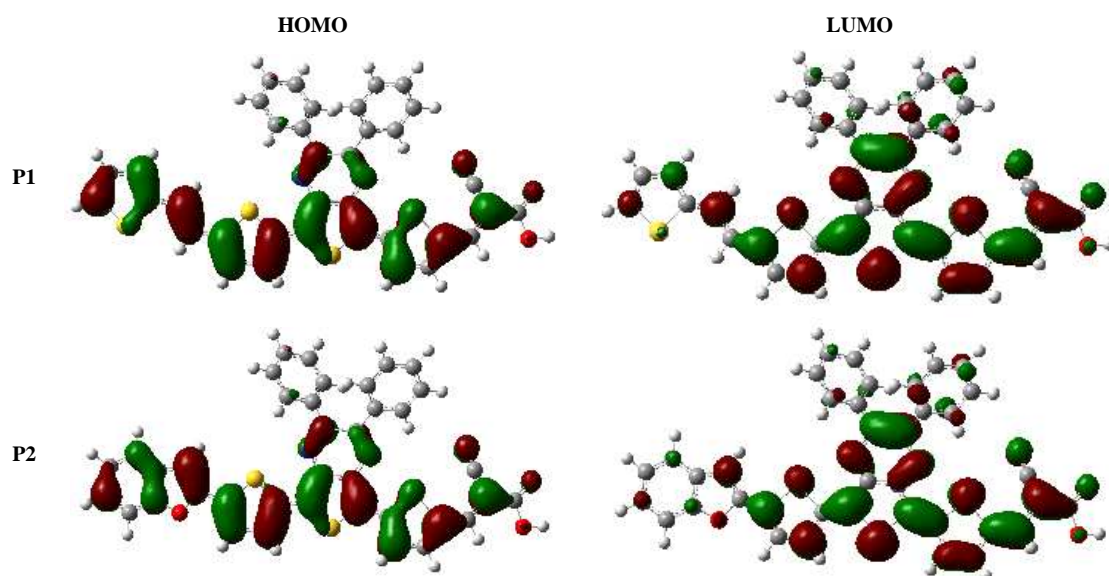
While in DSSCs, the V_{oc} can be approximately estimated by the energy difference between E_{LUMO} of the dye and conduction band (E_{CB}) of the semiconductor TiO_2 :

$$V_{oc} = E_{LUMO} - E_{CB} \quad (3)$$

As shown in table 3, the theoretical values of the open circuit voltage V_{oc} of the studied molecules range from 0.783 eV to 0.927 eV of TiO_2 (0.983 eV to 1.127 eV of PCBM), these values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of the acceptor (TiO_2) is possible and can also be used as organic molecules in organic solar cells with the acceptor (PCBM).

Table 3: Energy values of LUMO(E_{LUMO}), HOMO (E_{HOMO}) and the open circuit voltage V_{oc} of the studied molecules obtained by B3LYP/6-31G (d, p) level

Compou nds	E_{LUMO} (eV)	E_{HOMO} (eV)	V_{oc}/TiO_2 (eV)	$V_{oc}/PCBM$ (eV)
P1	-3.125	-4.983	0.875	0.983
P2	-3.157	-5.091	0.843	1.091
P3	-3.189	-5.127	0.811	1.127
P4	-3.095	-5.049	0.905	1.049
P5	-3.053	-5.012	0.947	1.012
TiO_2	-4.0 [*]			
PCBM	-3.7			



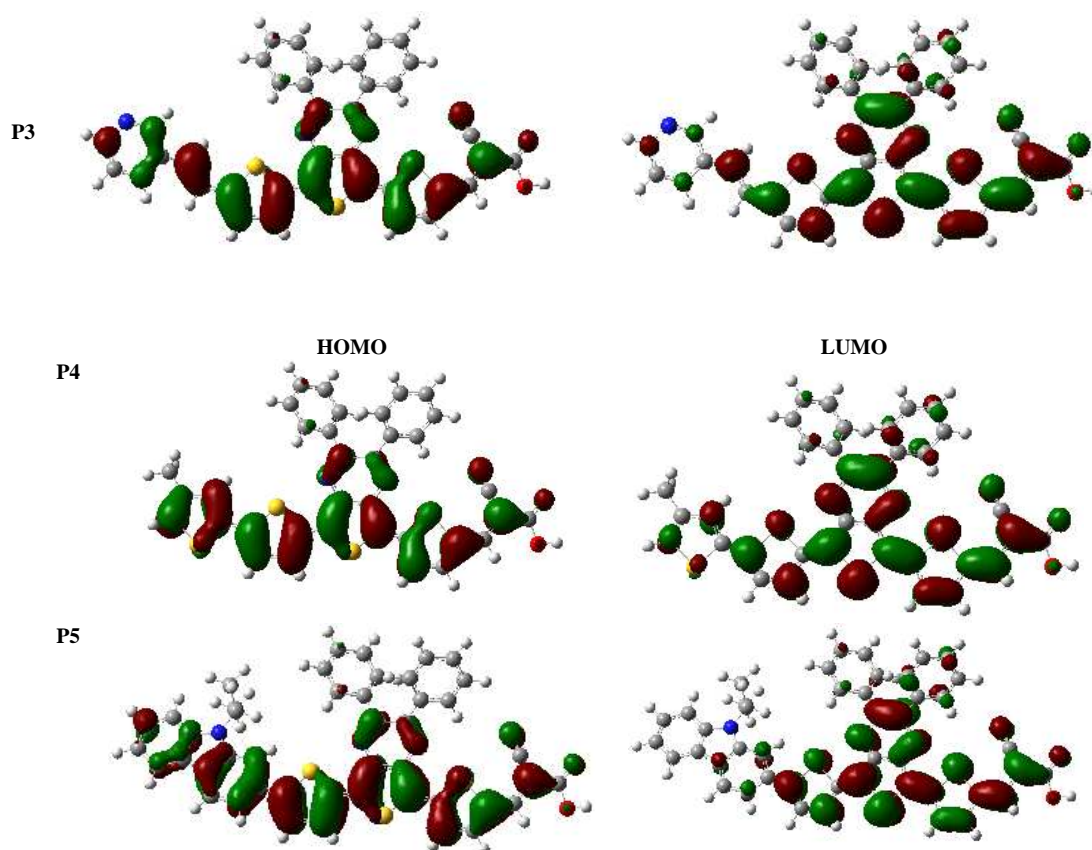


Fig. 4: The contour plots of HOMO and LUMO orbitals of the studied compounds Pi

3.3. Absorption and emission properties

How the absorption of a new material matches with the solar spectrum is an important factor for the application as a photovoltaic material, and a good photovoltaic material should have broad and strong visible absorption characteristics. To gain insight of the optical property and electronic transition, the excitation energy and UV-Vis absorption spectra for the singlet-singlet transition of all compounds were simulated using TD-DFT with CAM-B3LYP functional in chloroform solution [25-26]. Therefore, from the optimized structure obtained with the method B3LYP/6-31G (d, p) of each studied compound, we have calculated the vertical excited singlet states, transitions energies and oscillator strength using TD-DFT method. The corresponding simulated UV-Vis absorption spectra of the studied compounds obtained at the IEF-PCM/TD-CAM-B3LYP/6-31G(d, p) level, presented as oscillator strength against wavelength, is shown in Fig. 5. As illustrated in table 4, we can find the values of calculated absorption λ_{max} (nm) and oscillator strength (O.S) along with main excitation configuration of the studied compounds Pi. As showing in Fig. 5 and Table 4, all compounds exhibit a strong absorption band in the visible region around 626 – 653 nm, which can be assigned to an intramolecular charge transfer (ICT) between the various donating unit and the electron acceptor (2- cyanoacrylic acid) fragments.

The calculated wavelength λ_{abs} of the studied compounds decreases in the following order P1> P3>P2>P4>P5 which is the same order of the band gap. This bathochromic effect from P5 to P1 is obviously due to increased π delocalization. This interesting point is seen both by analyzing electronic and absorption results. Excitation to the S1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. The absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths.

In order to study the emission photoluminescence properties of the studied compounds Pi (i=1 to 5), the adiabatic emission spectra were obtained using the optimized geometry of the first excited singlet state at the TDDFT/CAM-B3LYP/6-31G (d,p) level in chloroform. The emission spectra data of the compounds recorded in chloroform are collected in Table 5. According to the absorption and emission data, the values of Stokes shift (SS) for all compounds were obtained. The emission spectra arising from S1 state is assigned to $\pi^* \rightarrow \pi$ and LUMO \rightarrow HOMO transition character for all molecules. Through analyzing the transition configuration of the fluorescence, we found that the calculated fluorescence is just the reverse process of the lowest lying absorption. Moreover, the observed red-shifted emission of the photoluminescence (PL) spectra in order P1<P3<P4<P2<P5 when passing from P5 to P1

is in reasonable agreement with the obtained results of absorption. Furthermore, the Stokes shift of these compounds is found to be in the range 178.9 and 190.7 nm. These encouraging optical properties suggest that all the compounds will be good candidates in the solar cell devices.

Table 4: Absorption spectra data obtained by TDDFT methods for the title compounds at CAM-B3LYP/6-31G (d, p) optimized geometries in chloroform solvent

Compounds	Electronic transitions	λ_{abs} (nm)	E_{ex} (eV)	O.S	MO/character
P1	$S_0 \rightarrow S_1$	653.1	1.90	1.353	HOMO \rightarrow LUMO
	$S_0 \rightarrow S_2$	421.5	2.94	0.076	HOMO-1 \rightarrow LUMO
	$S_0 \rightarrow S_3$	394.4	3.14	0.076	HOMO \rightarrow LUMO+1
	$S_0 \rightarrow S_4$	366.1	3.39	0.385	HOMO \rightarrow LUMO+2
	$S_0 \rightarrow S_5$	361.0	3.43	0.036	HOMO-7 \rightarrow LUMO
	$S_0 \rightarrow S_6$	353.9	3.50	0.305	HOMO-2 \rightarrow LUMO
P2	$S_0 \rightarrow S_1$	629.2	1.97	1.293	HOMO \rightarrow LUMO
	$S_0 \rightarrow S_2$	411.4	3.01	0.155	HOMO \rightarrow LUMO+1
	$S_0 \rightarrow S_3$	385.7	3.21	0.381	HOMO \rightarrow LUMO+1
	$S_0 \rightarrow S_4$	361.5	3.43	0.025	HOMO-7 \rightarrow LUMO
	$S_0 \rightarrow S_5$	355.2	3.49	0.242	HOMO-2 \rightarrow LUMO
	$S_0 \rightarrow S_6$	341.3	3.63	0.455	HOMO \rightarrow LUMO+2
P3	$S_0 \rightarrow S_1$	634.4	1.95	1.300	HOMO \rightarrow LUMO
	$S_0 \rightarrow S_2$	634.4	3.00	0.112	HOMO \rightarrow LUMO+1
	$S_0 \rightarrow S_3$	385.7	3.22	0.396	HOMO-1 \rightarrow LUMO
	$S_0 \rightarrow S_4$	362.8	3.42	0.094	HOMO-6 \rightarrow LUMO
	$S_0 \rightarrow S_5$	358.7	3.46	0.337	HOMO \rightarrow LUMO+2
	$S_0 \rightarrow S_6$	346.1	3.58	0.255	HOMO -2 \rightarrow LUMO
P4	$S_0 \rightarrow S_1$	628.6	1.97	1.177	HOMO \rightarrow LUMO
	$S_0 \rightarrow S_2$	411.1	3.02	0.200	HOMO \rightarrow LUMO+1
	$S_0 \rightarrow S_3$	383.8	3.23	0.357	HOMO-1 \rightarrow LUMO
	$S_0 \rightarrow S_4$	360.8	3.44	0.010	HOMO-7 \rightarrow LUMO
	$S_0 \rightarrow S_5$	351.5	3.53	0.185	HOMO-2 \rightarrow LUMO
	$S_0 \rightarrow S_6$	336.3	3.69	0.185	HOMO \rightarrow LUMO+2
P5	$S_0 \rightarrow S_1$	625.9	1.98	1.277	HOMO \rightarrow LUMO
	$S_0 \rightarrow S_2$	410.9	3.02	0.154	HOMO \rightarrow LUMO+1
	$S_0 \rightarrow S_3$	384.1	3.23	0.384	HOMO-2 \rightarrow LUMO
	$S_0 \rightarrow S_4$	360.8	3.44	0.009	HOMO -8 \rightarrow LUMO
	$S_0 \rightarrow S_5$	357.8	3.47	0.022	HOMO-1 \rightarrow LUMO
	$S_0 \rightarrow S_6$	352.0	3.52	0.277	HOMO-3 \rightarrow LUMO

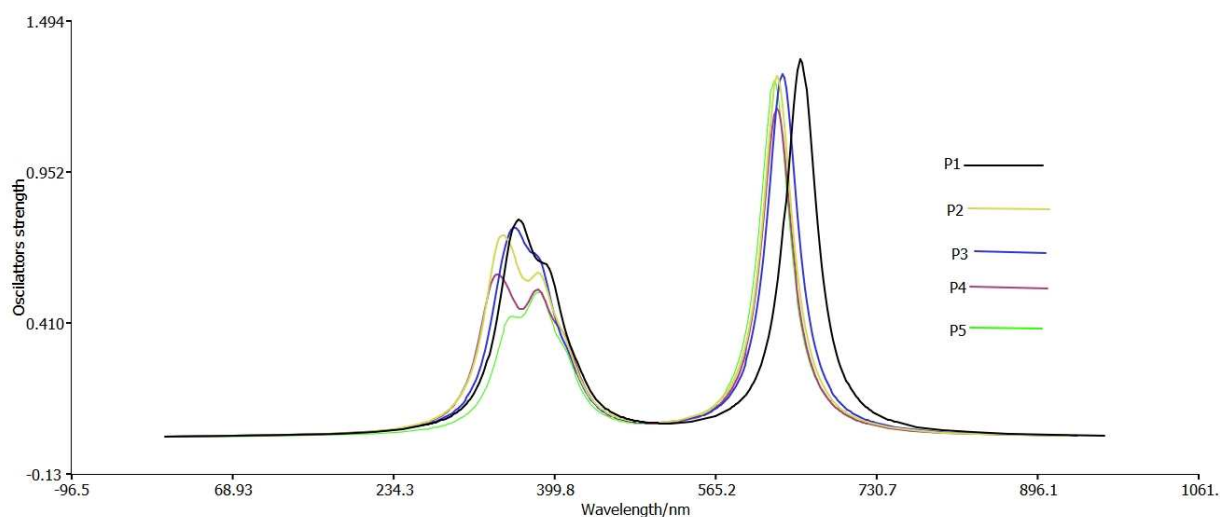


Fig. 5: Simulated UV-visible optical absorption spectra of title compounds with the calculated data at the TDDFT/CAM-B3LYP/6-31G(d, p) level in chloroform solvent

Table 5: Emission spectra data for all dyes obtained with PCM-CAM-B3LYP/6-31G (d,p).

Compounds	Main composition (HOMO=H, LUMO=L)	ΔE (eV)	λ_{\max} (nm)	f	SS (nm)	
P1	L \longrightarrow H	0.69	1.47	843.8	1.422	190.7
P2	L \longrightarrow H	0.69	1.53	808.6	1.343	179.4
P3	L \longrightarrow H	0.70	1.52	814.4	1.342	180.0
P4	L \longrightarrow H	0.70	1.53	812.7	1.244	184.1
P5	L \longrightarrow H	0.69	1.53	804.8	1.345	178.9

CONCLUSION

In this study, we have used the DFT/B3LYP method to investigate theoretical analysis on the geometries and electronic properties of some thienopyrazine-derivatives in alternate donor-acceptor structure. The modification of chemical structures can greatly modulate and improve the electronic and optical properties of pristine studied materials. The electronic properties of new conjugated materials based on thienopyrazine and heterocyclic compounds and different acceptor moieties have been computed using 6-31G (d, p) basis set at density functional B3LYP level, in order to guide the synthesis of novel materials with specific electronic properties. The concluding remarks are:

- The UV-Vis absorption properties have been obtained by using TD/CAM-B3LYP calculations. The obtained absorption maximums are in the range of 713–682 nm.
- The HOMO level, LUMO level, and band gap of the studied compounds were well controlled by the acceptor strength. The calculated band gap (E_{gap}) of the studied molecules was in the range of 1.858-1.959 eV.
- The calculated values of Voc of the studied molecules range from 0.783 to 0.927 eV /TiO₂ 0.983 eV to 1.127 eV/PCBM, these values are sufficient for a possible efficient electron injection.

Therefore, all the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of the acceptor (TiO₂) and the subsequent regeneration is possible in organic sensitized solar cell.

The theoretical results suggest that both the acceptor strength and the stable geometry contribute significantly to the electronic properties of alternating donor-acceptor conjugated copolymers. Finally, the procedures of theoretical calculations can be employed to predict the electronic properties on the other compounds, and further to design novel materials for organic solar cells.

Acknowledgements

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