



Organic materials based on MPEP for photovoltaic devices. Correlation structure/electronic properties

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Abstract

The research of new π -conjugated molecules with specific applications has become one of the most interesting topics in the fields of chemical physics and materials science. Thanks to their specific properties, these compounds have become the most promising materials for the optoelectronic device technology such as solar cells. The use of low band gap materials is a viable method for a better harvesting of the solar spectrum and an improved raise of its efficiency. The control of this parameter of these materials is a research issue of ongoing interest. In this work a quantum chemical investigation has been performed to explore the optical and electronic properties of a series of different compounds based on pyridine (MPEP). Different electron side groups were introduced to investigate their effects on the electronic structure. 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 energy E_{gap} of the studied compounds have been calculated and reported. These properties suggest these materials as good candidates for organic solar cells.

Keywords: π -conjugated molecules, pyridine, organic solar cells, DFT, low band-gap, electronic properties.

1. Introduction

Compounds based on 2-methyl-6-phenylethynylpyridine (MPEP) and these derivatives are used in various fields of science and technology and have numerous applications in biology and medicine. The molecule 2-methyl -6 -phenylethynylpyridine (MPEP), is an investigational drug that has been one of the first compounds found to act as a selective antagonist of subtype of metabotropic glutamate receptor mGluR5 [1]. After being used as liquid crystals for LCD screens, was developed by the pharmaceutical company Novartis in the 1990s and has also been shown to produce antidepressant and anxiolytic effects in animals [2] and reduce the effects of morphine withdrawal. Despite the large number and range of applications that offer this type of compounds, the complete analysis of the electronic properties of these compounds has not yet been performed. These compounds have recently been studied by R. Hmamouchi et al. [3]. These studies have shown that the molecules contain aromatic π systems - spelling electrons with a very high absorption maximum (λ_{max}) which can easily trap. For this reason, and as part of a program on the synthesis of new organic materials useful electronic properties and to further elucidate the effect of a substitution at the ring nitrogen atom, and the variation of substituents cycle on the photoconductivity with respect, a number of different pyrazines based on 2-methyl-6-phenylethynylpyridine (MPEP).

Heterojunctions between organic semiconductors are the heart of the operation of light-emitting diodes and photovoltaic cell [4]. A common strategy to improve the power conversion efficiency of the photovoltaic device, by improving the charge transfer exciting and transportation is the development of low-band gap conjugated as a donor of alternative materials (D) - acceptor (A) in the backbone structure of the main polymer. Compounds based on 2-methyl-6-phenylethynylpyridine (MPEP) and its derivatives continue to receive considerable attention for their outstanding optoelectronic properties especially those photoconductors [5]. Modelling studies can provide insight to find relationships between the structure and electronic properties of these compounds. FTD is a very attractive method for calculating finite systems because even the lowest level of DFT. This is extremely important in the design of conjugate molecules. Computer simulation is useful in this area of research, for example, the determination of the stability and electronic structures. This research approach

has been examined in a number of theoretical analyses have also been published [6]. The spectra of geometries, electronic properties, absorption and emission of these compounds are studied using density functional theory (DFT) and the density versus time functional theory (TD / DFT) in order to find potential sensitizers for use in organic solar cells. This paper presents the results of the study of several compounds based on 2-methyl-6-phenylethynylpyridine (MPEP) (PRZ₁, PRZ₂, PRZ₃, PRZ₄, PRZ₅, PRZ₆ PRZ₂₇) (Figure 1).

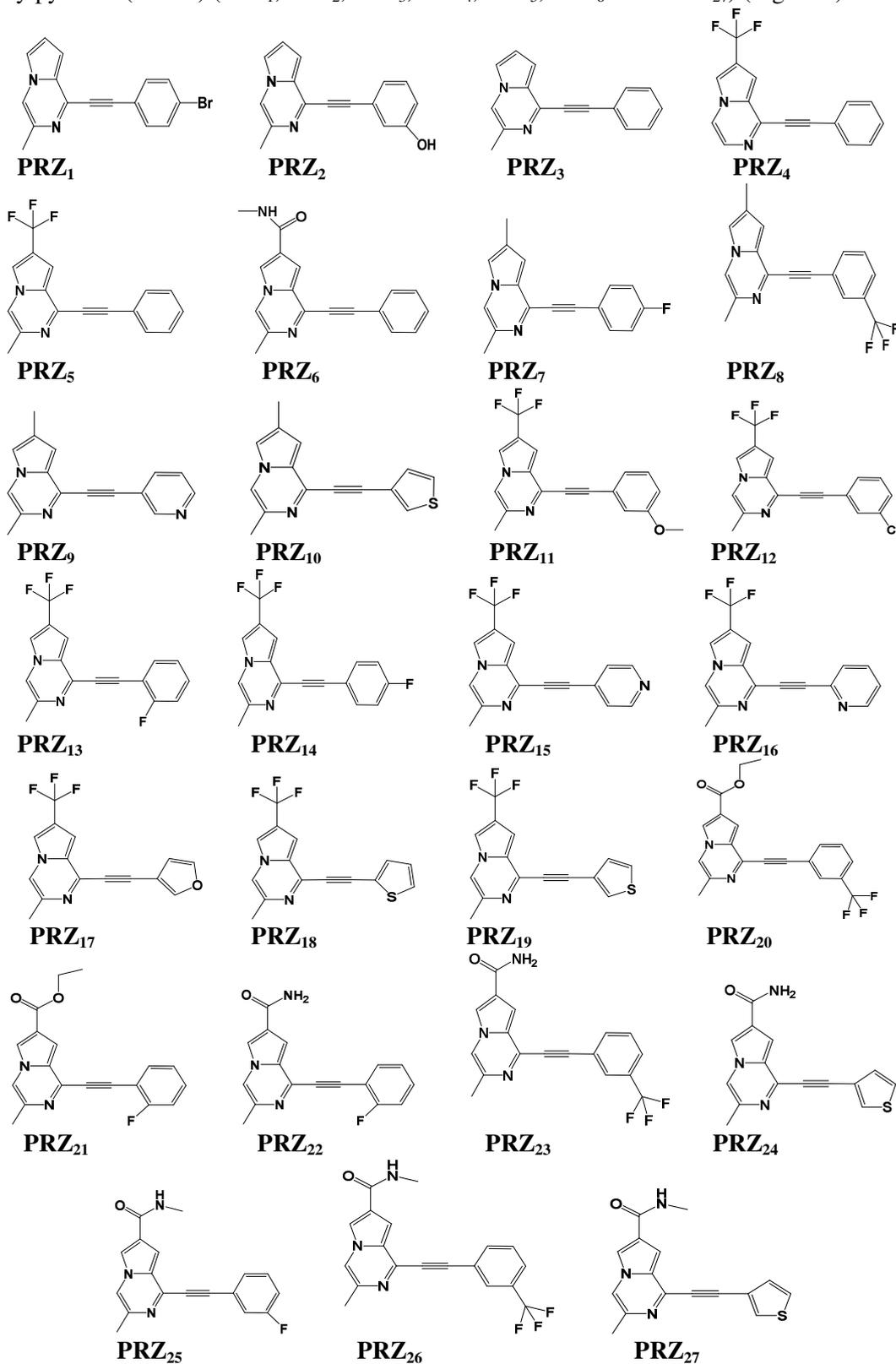


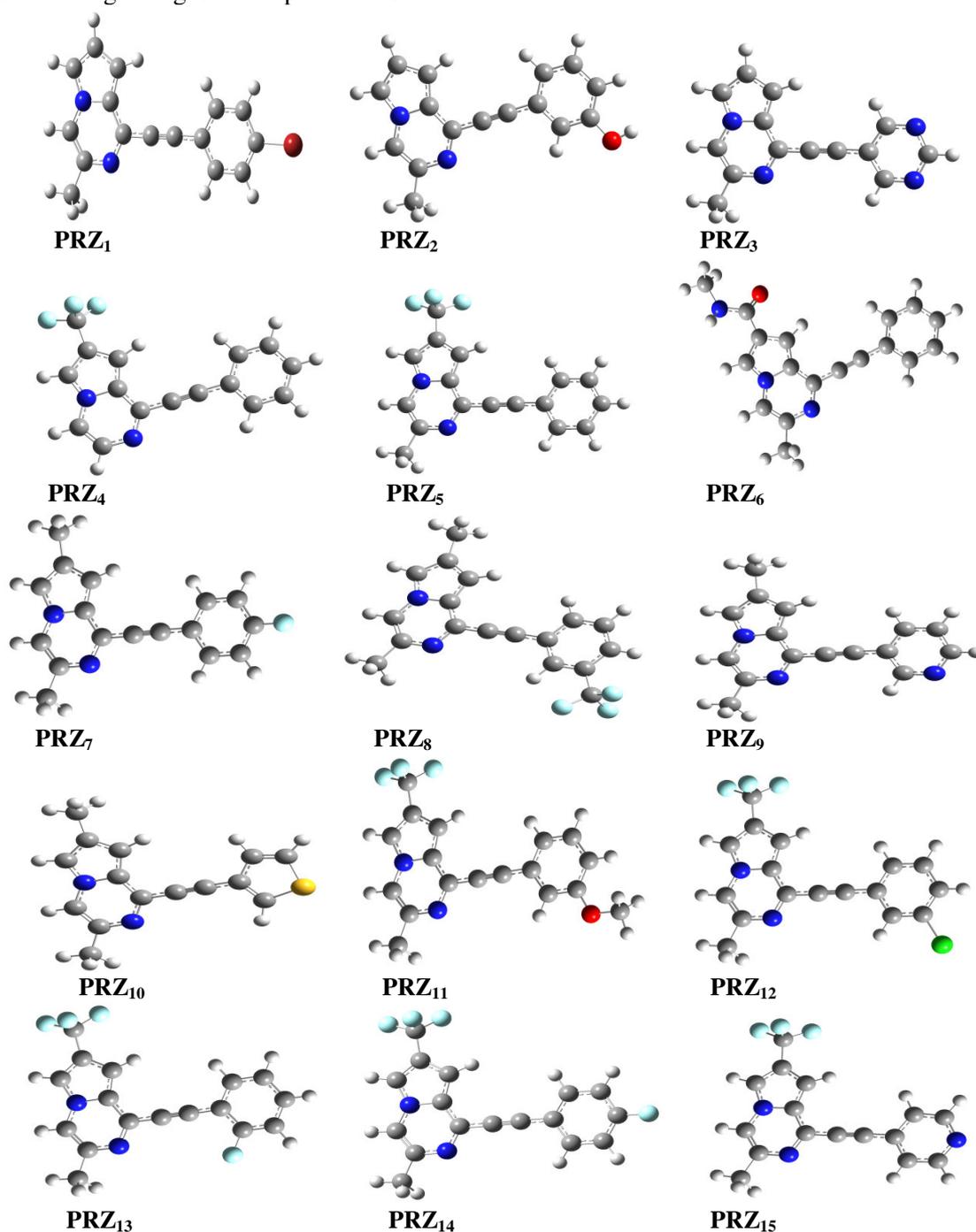
Figure 1: Chemical structure of studied compounds PRZ_i (i= 1-27).

2. Theoretical methodology

DFT method of three-parameter compound of Becke (B3LYP) [7] was used in all the study of the neutral and polaronic compounds. The 6-31G (d) basis set was used for all calculations [8]. To obtain the charged structures, we start from the optimized structures of the neutral form. The calculations were carried out using the GAUSSIAN 03 program [9]. The geometry structures of neutral and doped molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy E_{gap} is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the TD/DFT calculations on the fully optimized geometries [10].

3. Results and discussion

The results of the optimized structures (figure.2) for all studied compounds so that they have similar conformations (quasi planar conformation). We found that the modification of several groups attached to the ring does not change the geometric parameters.



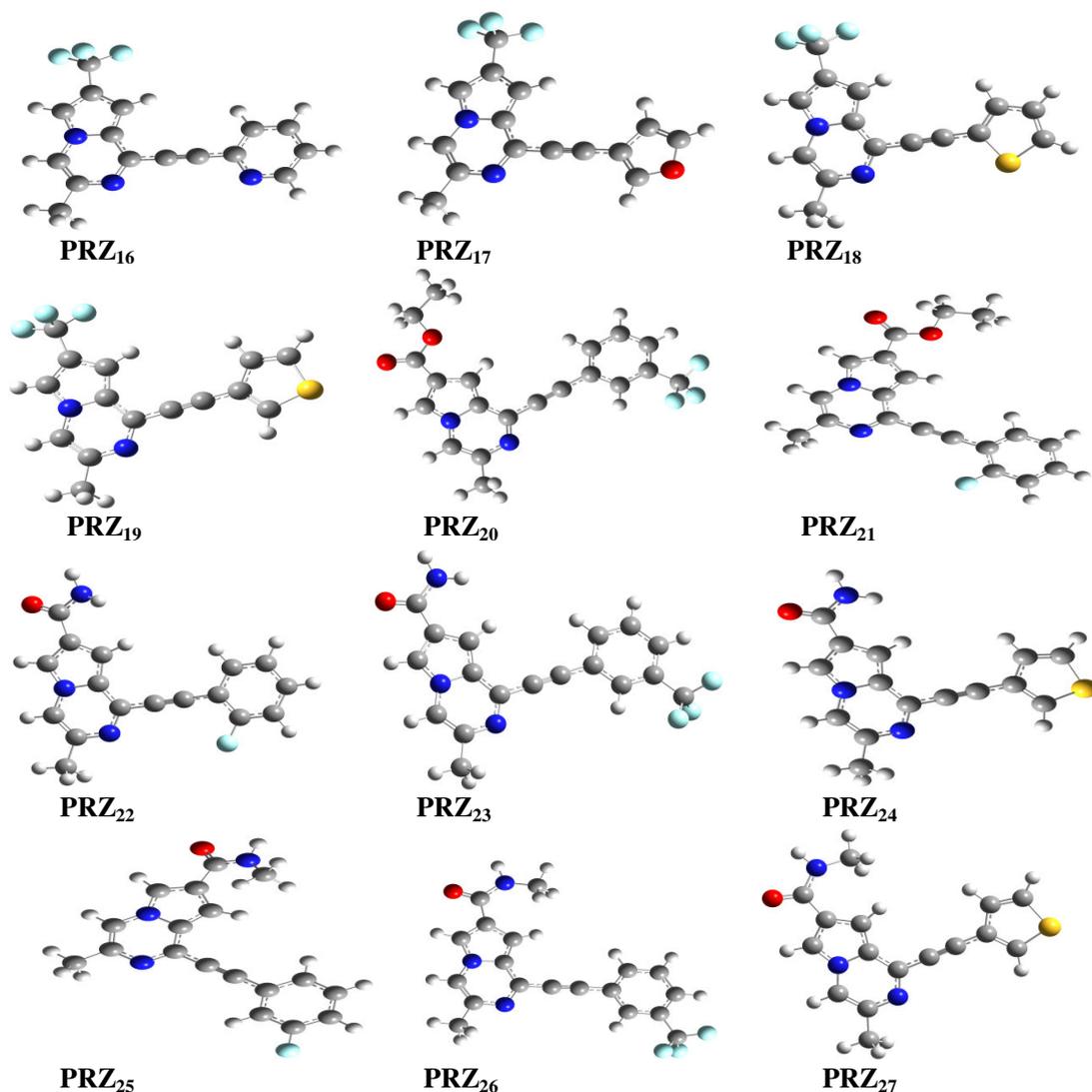


Figure 2: Optimized geometries obtained by B3LYP/6-31G (d) of the studied molecules.

Table 1 lists the calculated frontier orbital energies and energy E_{gap} between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the energy E_{gap} (done) of the studied molecules, also the open circuit voltage V_{oc} (eV) and $\alpha = E_{\text{LUMO}}$ (Donor) $-E_{\text{LUMO}}$ (Acceptor). These parameters will be discussed in the photovoltaic part

Table 1: Energy values of E_{LUMO} (eV), E_{HOMO} (eV), E_{gap} (eV), α (eV) and the open circuit voltage V_{oc} (eV) of the studied molecules obtained by B3LYP/6-31G (d).

MOLECULE	E_{HOMO} (ev)	E_{LUMO} (ev)	E_{gap} (ev)	V_{oc}	α
PRZ₁	-5.424	-1.861	3.562	1.424	1.839
PRZ₂	-5.303	-1.664	3.639	1.303	2.036
PRZ₃	-5.594	-2.117	3.477	1.594	1.583
PRZ₄	-5.787	-2.051	3.736	1.787	1.649
PRZ₅	-5.695	-1.988	3.707	1.695	1.712
PRZ₆	-5.516	-1.857	3.658	1.516	1.843
PRZ₇	-5.290	-1.673	3.618	1.290	2.027
PRZ₈	-5.408	-1.888	3.520	1.408	1.812
PRZ₉	-5.385	-1.845	3.541	1.385	1.855

PRZ₁₀	-5.244	-1.572	3.672	1.244	2.128
PRZ₁₁	-5.653	-1.933	3.720	1.653	1.767
PRZ₁₂	-5.831	-2.173	3.658	1.831	1.527
PRZ₁₃	-5.732	-2.058	3.674	1.732	1.642
PRZ₁₄	-5.731	-2.027	3.704	1.731	1.673
PRZ₁₅	-5.941	-2.337	3.604	1.941	1.363
PRZ₁₆	-5.796	-2.155	3.641	1.796	1.545
PRZ₁₇	-5.684	-1.874	3.810	1.684	1.826
PRZ₁₈	-5.653	-2.077	3.576	1.653	1.623
PRZ₁₉	-5.686	-1.939	3.747	1.686	1.761
PRZ₂₀	-5.728	-2.164	3.564	1.728	1.536
PRZ₂₁	-5.603	-2.005	3.598	1.603	1.695
PRZ₂₂	-5.627	-2.020	3.607	1.627	1.680
PRZ₂₃	-5.752	-2.182	3.570	1.752	1.518
PRZ₂₄	-5.573	-1.891	3.683	1.573	1.809
PRZ₂₅	-5.629	-2.036	3.593	1.629	1.664
PRZ₂₆	-5.694	-2.139	3.555	1.694	1.561
PRZ₂₇	-5.531	-1.848	3.683	1.531	1.852
PCBM C₆₀ (A)	-6.100	-3.700	-	-	-

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. As shown in Table 1, The HOMO and LUMO energies of PRZ₁ to PRZ₂₇ change significantly, the LUMOs for PRZ₁, PRZ₂, PRZ₃, PRZ₄, PRZ₅, PRZ₆, PRZ₇, PRZ₈, PRZ₉, PRZ₁₀, PRZ₁₁, PRZ₁₂, PRZ₁₃, PRZ₁₄, PRZ₁₅, PRZ₁₆, PRZ₁₇, PRZ₁₈, PRZ₁₉, PRZ₂₀, PRZ₂₁, PRZ₂₂, PRZ₂₃, PRZ₂₄, PRZ₂₅, PRZ₂₆, and PRZ₂₇ are located at -1.861; -1.664; -2.117; -2.051; -1.988; -1.857; -1.673; -1.888; -1.845; -1.572; -1.933; -2.173; -2.058; -2.027; -2.337; -2.155; -1.874; -2.077; -1.939; -2.164; -2.005; -2.020; -2.182; -1.891; -2.036; -2.139 and -1.848 eV, respectively. The HOMOs for PRZ₁, PRZ₂, PRZ₃, PRZ₄, PRZ₅, PRZ₆, PRZ₇, PRZ₈, PRZ₉, PRZ₁₀, PRZ₁₁, PRZ₁₂, PRZ₁₃, PRZ₁₄, PRZ₁₅, PRZ₁₆, PRZ₁₇, PRZ₁₈, PRZ₁₉, PRZ₂₀, PRZ₂₁, PRZ₂₂, PRZ₂₃, PRZ₂₄, PRZ₂₅, PRZ₂₆, and PRZ₂₇ are located at -5.424; -5.303; -5.594; -5.787; -5.695; -5.516; -5.290; -5.408; -5.385; -5.244; -5.653; -5.831; -5.732; -5.731; -5.941; -5.796; -5.684; -5.653; -5.686; -5.728; -5.603; -5.627; -5.752; -5.573; -5.629; -5.694 and -5.531 eV, respectively.

It can also be found that, the HOMO and LUMO energies of the studied compounds are slightly different. This implies that different structures play key roles on electronic properties and the effect of slight structural variations, especially the effect of the motifs branched to the pyrazine ring on the HOMO and LUMO energies is clearly seen. In addition, energy (E_{gap}) of the studied molecules differs slightly from 3.477 eV to 3.810 eV depending on the different structures. They are studied in the following order:



On the other hand and from the above analysis, we know that the LUMO energy levels of the molecules studied is much higher than that of the ITO conduction band edge (-4.7 eV). Thus, molecules in excited states of PRZ₁, PRZ₂, PRZ₃, PRZ₄, PRZ₅, PRZ₆, PRZ₇, PRZ₈, PRZ₉, PRZ₁₀, PRZ₁₁, PRZ₁₂, PRZ₁₃, PRZ₁₄, PRZ₁₅, PRZ₁₆, PRZ₁₇, PRZ₁₈, PRZ₁₉, PRZ₂₀, PRZ₂₁, PRZ₂₂, PRZ₂₃, PRZ₂₄, PRZ₂₅, PRZ₂₆, and PRZ₂₇ have a strong ability to inject electrons into ITO electrodes. The experiment phenomenon is quite consistent with previous literature [11], this latter reported that the increase of the HOMO levels may suggest a negative effect on organic solar cell performance due to the broader gap between the HOMO level of the organic molecules and the HOMO level of PCBM. As shown in table 1, both HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosensitizer. One side, the HOMO levels of the studied compounds PRZ_i (i=1 to

27) are lower than that of PCBM. Else next, the LUMO levels of the studied compounds PRZ_i (i=1 to 27) are lower than that of PCBM [12]. To evaluate the possibilities of electron transfer from the studied molecules to the conductive band of PCBM, the HOMO and LUMO levels are compared. In addition, to effectively inject the electron into the CB of PCBM (-3.7 eV); the value of LUMO Donor must be greater than that of PCBM and accordingly $\alpha > 0$ [13]. Knowing that in organic solar cells, the open circuit voltage is found to be linearly dependent on the HOMO level of the donor and the LUMO level of the acceptor. The maximum open circuit voltage (V_{oc}) of the BHJ solar cell is related to the difference between the highest occupied molecular orbital (HOMO) of the donor (our studied molecules) and the LUMO of the electron acceptor, taking into account the energy lost during the photo-charge generation [14]. The theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression:

$$V_{oc} = | E_{HOMO} (\text{Donor}) | - | E_{LUMO} (\text{Acceptor}) | - 0.3 \quad (1)$$

The obtained values of V_{oc} of the studied molecules calculated according to the equation (1) range from 1.24 eV to 1.94 eV (see Table 1), these values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as BHJ solar cell because the electron injection process from the studied molecule to the conduction band of PCBM and the subsequent regeneration is possible in an organic solar cell (Table 1, Fig. 3).

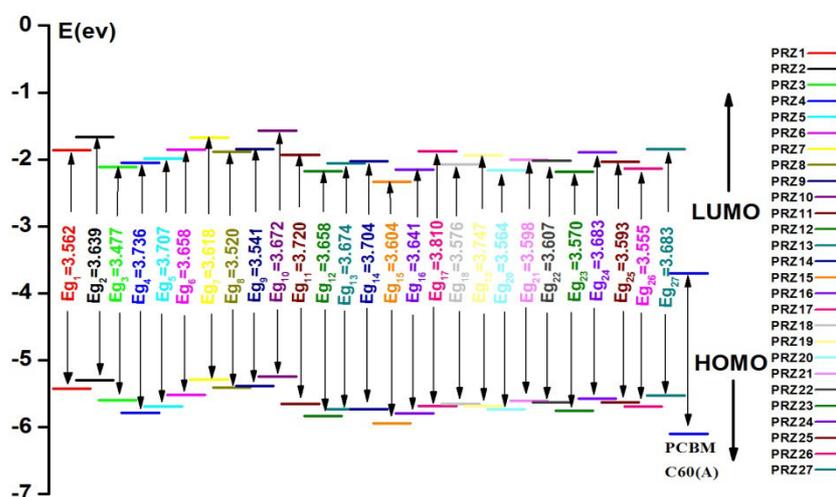
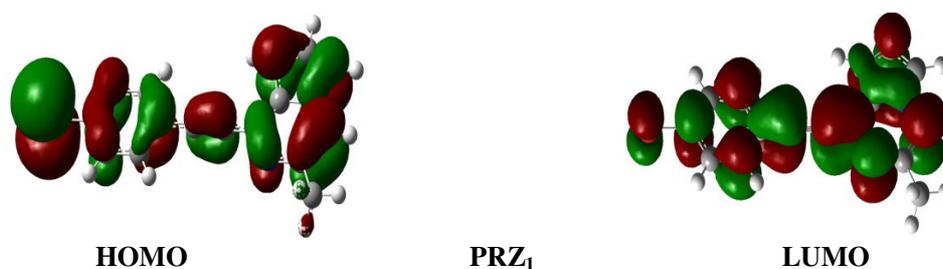
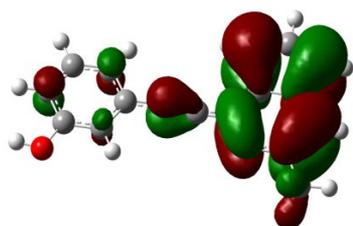


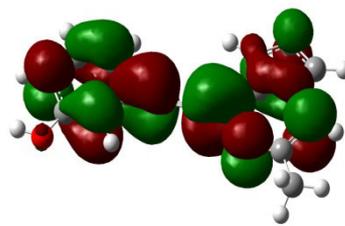
Figure 3: Sketch of DFT/B3LYP/6-31G (d) calculated energy of the HOMO, LUMO levels of studied molecules.

The frontier molecular orbital (MO) 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 excitations properties [15]. In general, as shown in figure 4 (LUMO, HOMO), the HOMOs of these oligomers in the neutral form possess a π -bonding character within subunit and a π -antibonding character between the consecutive subunits while the LUMOs possess a π -antibonding character within subunit and a π -bonding character between the subunits whereas it is the opposite in the case of doped forms.



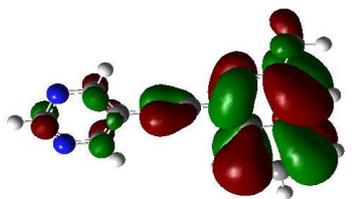


HOMO

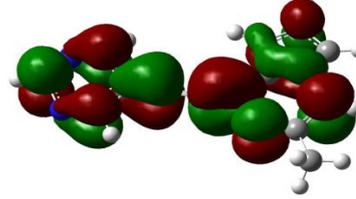


LUMO

PRZ₂

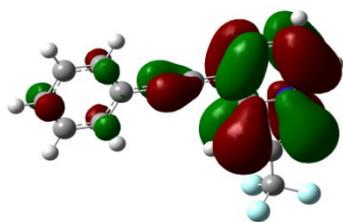


HOMO

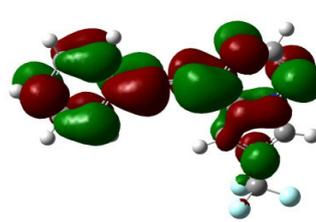


LUMO

PRZ₃

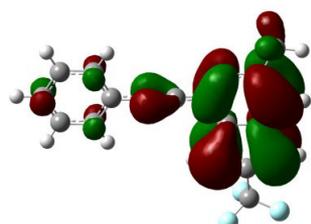


HOMO

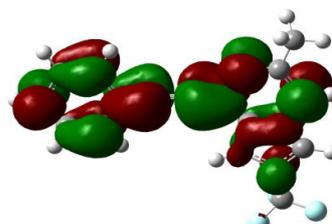


LUMO

PRZ₄

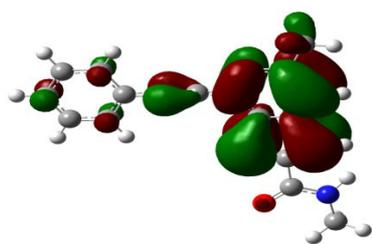


HOMO

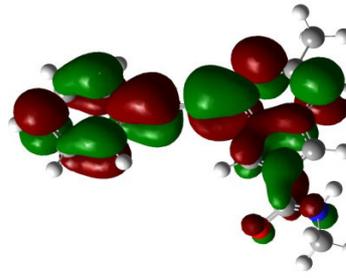


LUMO

PRZ₅

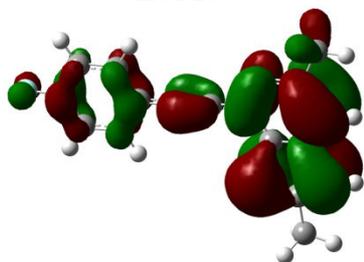


HOMO

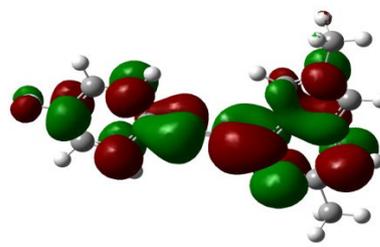


LUMO

PRZ₆

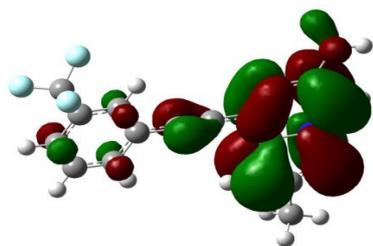


HOMO



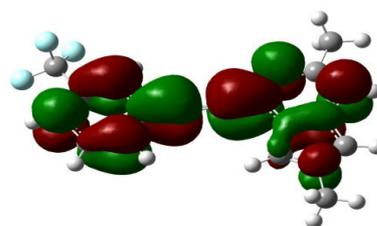
LUMO

PRZ₇

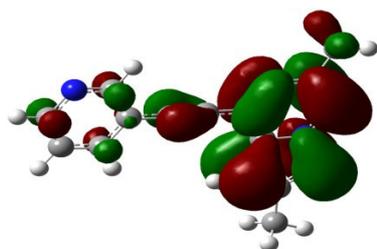


HOMO

PRZ₈

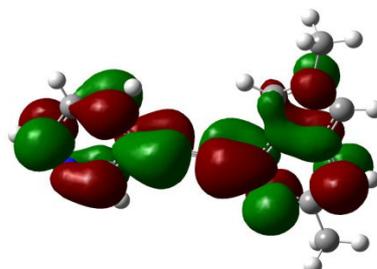


LUMO

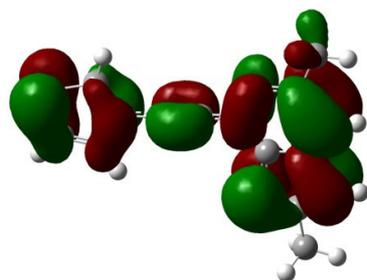


HOMO

PRZ₉

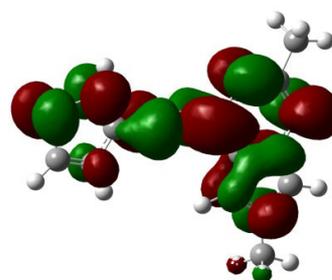


LUMO

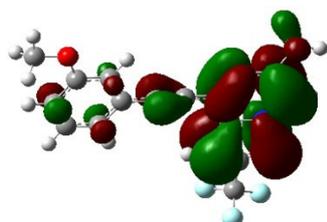


HOMO

PRZ₁₀

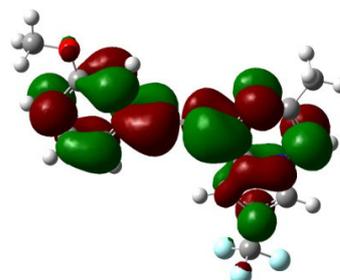


LUMO

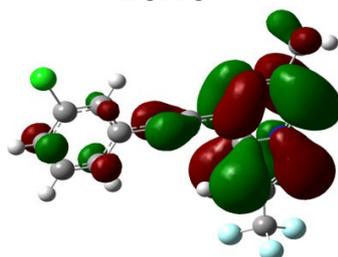


HOMO

PRZ₁₁

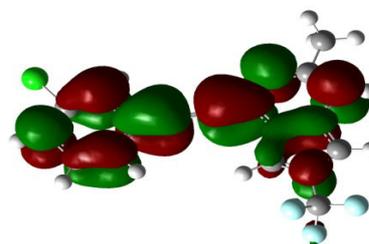


LUMO

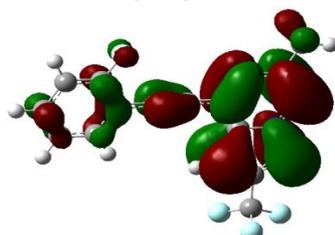


HOMO

PRZ₁₂

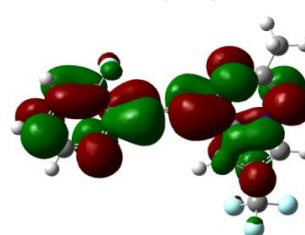


LUMO

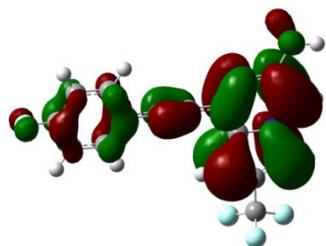


HOMO

PRZ₁₃

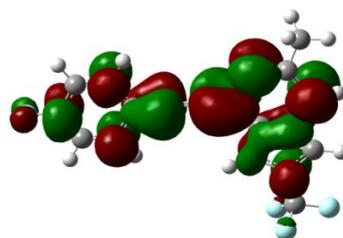


LUMO

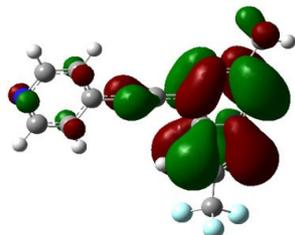


HOMO

PRZ₁₄

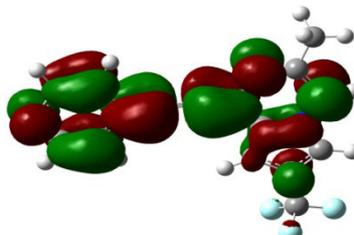


LUMO

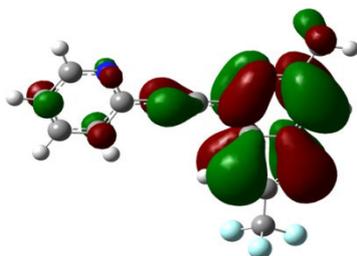


HOMO

PRZ₁₅

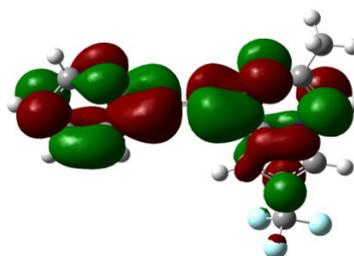


LUMO

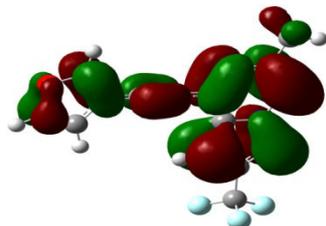


HOMO

PRZ₁₆

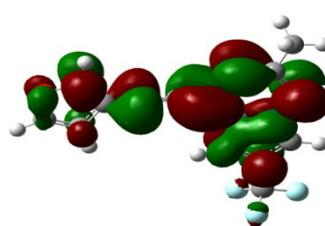


LUMO

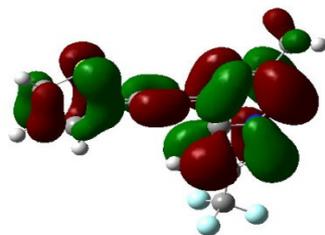


HOMO

PRZ₁₇

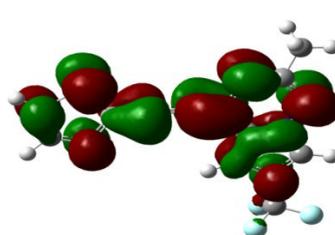


LUMO

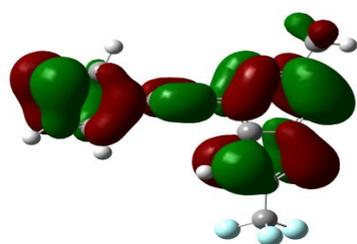


HOMO

PRZ₁₈

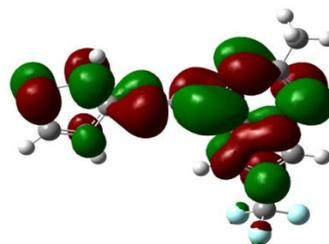


LUMO

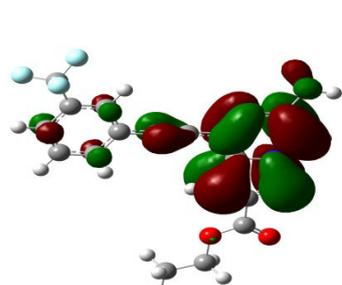


HOMO

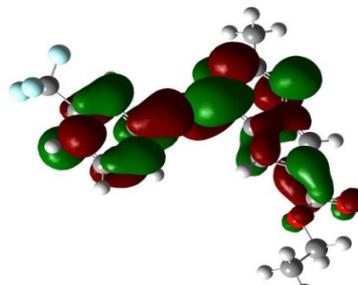
PRZ₁₉



LUMO

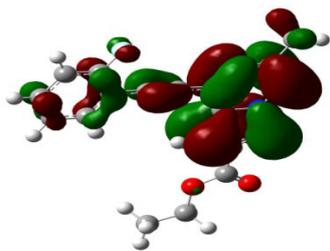


HOMO

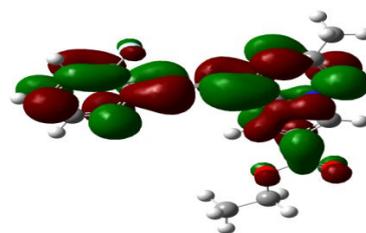


LUMO

PRZ₂₀

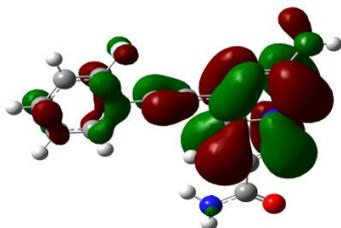


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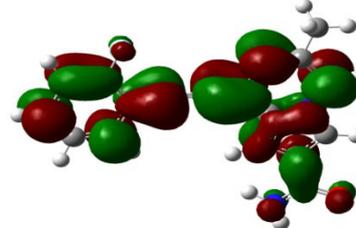


LUMO

PRZ₂₁

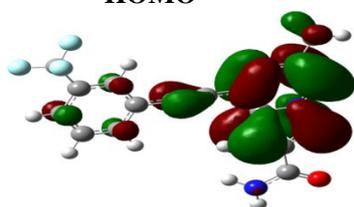


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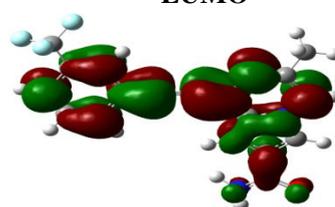


LUMO

PRZ₂₂

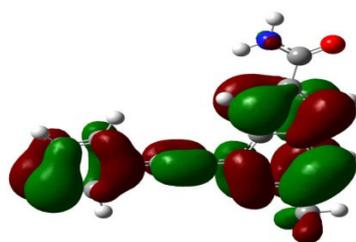


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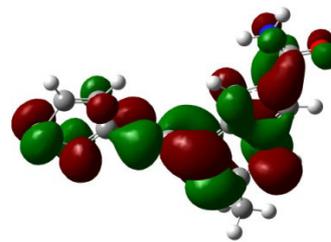


LUMO

PRZ₂₃

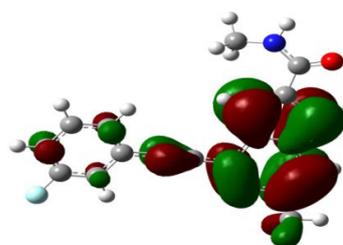


HOMO

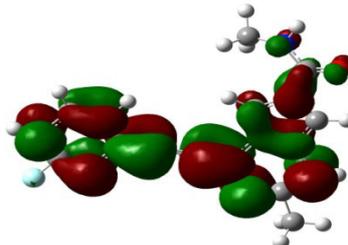


LUMO

PRZ₂₄



HOMO



LUMO

PRZ₂₅

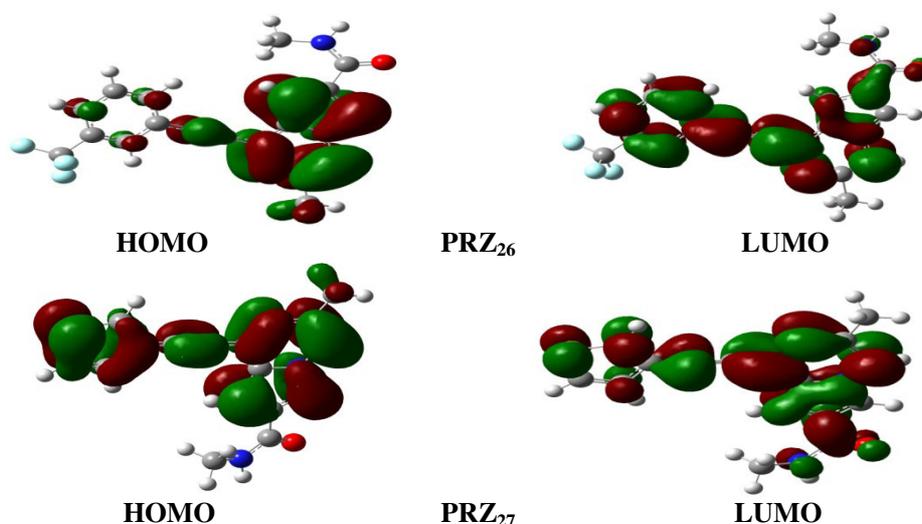


Figure 4: Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level.

On the other hand and 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. In fact, we have calculated the UV-Visible spectra of the studied compounds PRZ_i (i=1 to 27) using TD-DFT starting with optimized geometry obtained at B3LYP/6-31(d) level. As illustrated in table 2, we can find the values of calculated wavelength λ_{\max} and oscillator strengths O.S. Recall that excitation to the S₁ state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbital. The absorption wavelengths arising from S₀→S₁ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in S₀→S₁ electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy.

Data in table 2 shows that there is a bathochromic shift when passing from PRZ₂₇ (304 nm) to PRZ₁₈ (333 nm). This effect is obviously due to the aromaticity in the studied compounds. Those interesting points are seen both in the studying the electronic and absorption properties.

Table 2: Absorption spectra data obtained by TD-DFT methods for the PRZ_i (i=1 to 27) compounds at B3LYP/6-31G (d) optimized geometries.

MOLECULE	$\lambda_{\text{abs}}(\text{nm})$	$E_{\text{activation}}(\text{eV})$	O.S
PRZ ₁	324.69	3.819	0.711
PRZ ₂	320.58	3.867	0.524
PRZ ₃	321.05	3.862	0.427
PRZ ₄	317.81	3.901	0.618
PRZ ₅	317.33	3.907	0.591
PRZ ₆	323.59	3.832	0.574
PRZ ₇	325.29	3.811	0.503
PRZ ₈	328.72	3.772	0.433
PRZ ₉	327.41	3.787	0.418
PRZ ₁₀	321.35	3.858	0.472
PRZ ₁₁	310.77	3.990	0.387
PRZ ₁₂	316.97	3.912	0.588
PRZ ₁₃	318.57	3.892	0.582

PRZ ₁₄	318.94	3.887	0.605
PRZ ₁₅	313.53	3.954	0.487
PRZ ₁₆	315.03	3.936	0.549
PRZ ₁₇	312.95	3.962	0.439
PRZ ₁₈	333.19	3.721	0.554
PRZ ₁₉	316.40	3.919	0.548
PRZ ₂₀	323.94	3.827	0.554
PRZ ₂₁	325.55	3.808	0.574
PRZ ₂₂	325.82	3.805	0.561
PRZ ₂₃	325.06	3.814	0.529
PRZ ₂₄	321.99	3.851	0.561
PRZ ₂₅	328.83	3.77	0.459
PRZ ₂₆	330.49	3.751	0.422
PRZ ₂₇	304.01	3.821	0.510

The corresponding simulated UV–Vis absorption spectra of PRZ_i, presented as oscillator strength against wavelength, are shown in Figure 5. As illustrated in table 2, we can find the values of calculated absorption λ_{max} (nm) and oscillator strength (O.S) of the studied compounds PRZ_i.

The calculated wavelength λ_{abs} of the studied compounds decreases in the following order PRZ₁₈>PRZ₂₆>PRZ₂₅>PRZ₈>PRZ₉>PRZ₂₂>PRZ₂₁>PRZ₇>PRZ₂₃>PRZ₁>PRZ₂₀>PRZ₆>PRZ₂₄>PRZ₁₀>PRZ₃>PRZ₂>PRZ₁₄>PRZ₁₃>PRZ₄>PRZ₅>PRZ₁₂>PRZ₁₉>PRZ₁₆>PRZ₁₅>PRZ₁₇>PRZ₁₁>PRZ₂₇ which is the same order of the reduction of the acceptor strength. This bathochromic effect from PRZ_i 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 S₀-S₁ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO-LUMO transition is predominant in S₀-S₁ electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy.

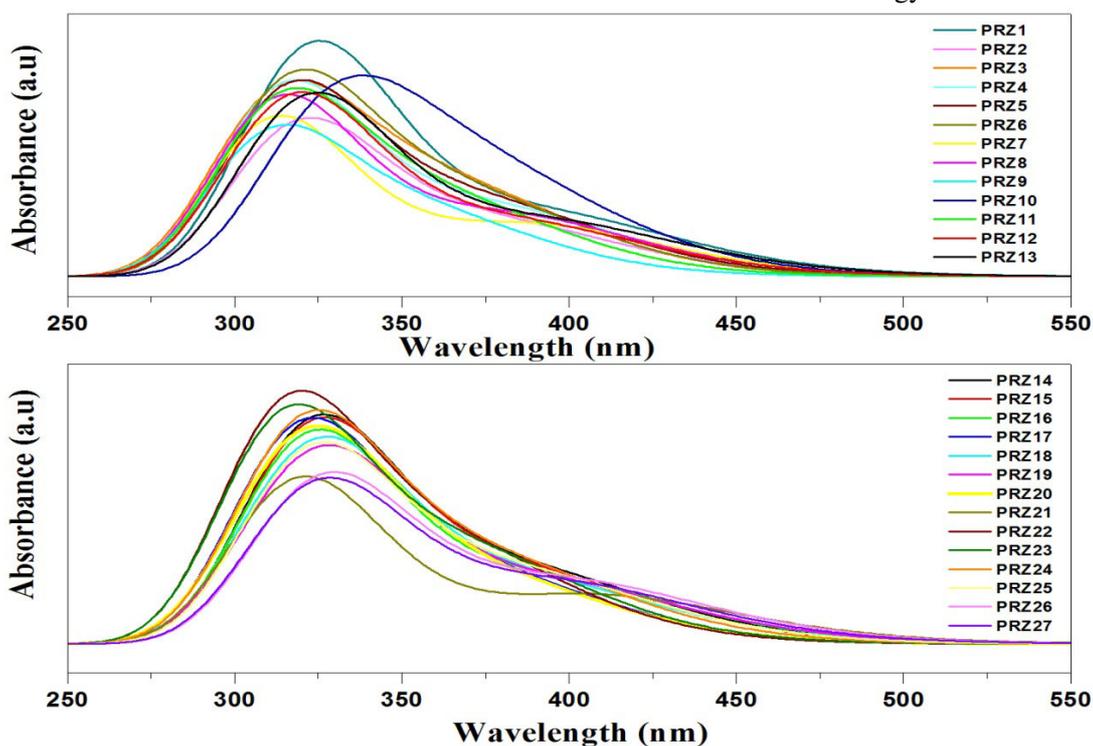


Figure 5: Simulated UV–visible optical absorption spectra of title compounds with

calculated data at the TD-DFT/B3LYP/6-31G(d).

Conclusion

This study is a theoretical analysis of the geometries and electronic properties of three various compounds based on the MPEP which displays the effect of substituted groups on the structural and opto-electronic properties of these materials and leads to the possibility to suggest these materials for organic solar cells application. The concluding remarks are:

- * The results of the optimized structures for all studied compounds so that they have similar conformations (quasi planar conformation). We found that the modification of several groups does not change the geometric parameters.
- * The calculated frontier orbital energies HOMO and LUMO and energy E_{gap} showed that the energy E_{gap} of the studied molecules differ slightly from 3.81 eV to 3.47 eV depending on the different structures. Also we can remark that the energy E_{gap} decreases, This is probably due to the effect of the conjugated system and aromaticity in the compounds studied.
- * The energy E_{gap} of PRZ₃ is much smaller than that of the other compounds.
- * The Molecule PRZ₁₈ witch have a relatively high value of λ_{max} (absorption), is expected to have the most outstanding photophysical properties.
- * All the studied molecules can be used as BHJ solar cell because the electron injection process from the studied molecule to the conduction band of PCBM and the subsequent regeneration are possible
- * This calculation procedure can be used as a model system for understanding the relationships between electronic properties and molecular structure and also can be employed to explore their suitability in electroluminescent devices and in related applications. Presumably, the procedures of theoretical calculations can be employed to predict and assume the electronic properties on yet prepared and efficiency proved the other materials, and further to design new materials for organic solar cells.

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