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

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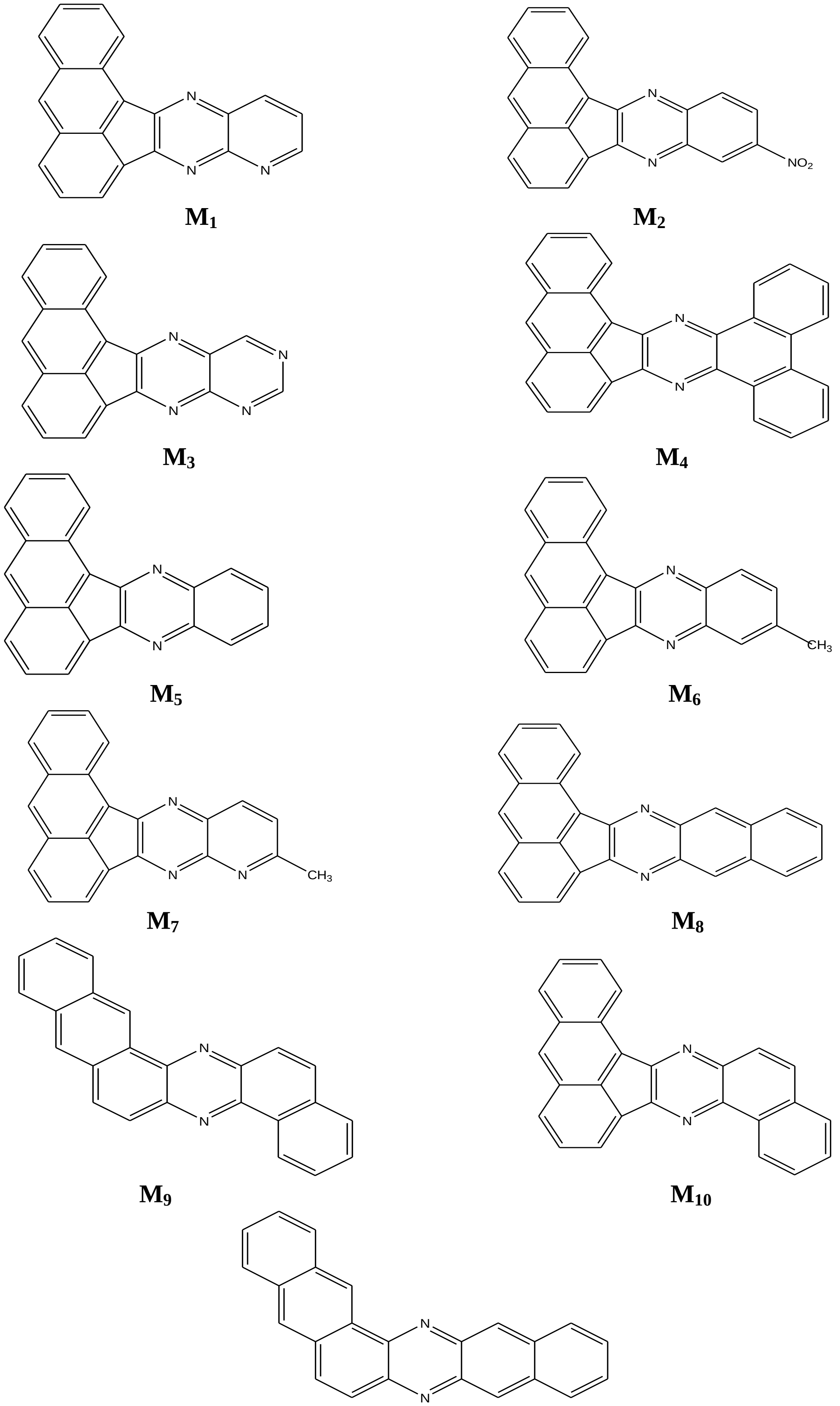
Abstract

The research in new pi-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 antracene and pyrazine. 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 Egap 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, anthracene, pyrazine, organic solar cells, DFT, low band-gap, electronic properties.

1. Introduction

Hetero-junctions between organic semiconductors are central to the operation of light-emitting and photovoltaic diodes [1]. A common strategy to enhance the power conversion of the photovoltaic device efficiency, by improving the exciton charge transfer and transport, is the development of low band gap conjugated materials as an alternating donor (D)-acceptor (A) structure in the main polymer backbone [2]. The pyrazines based on aceanthraquinoxaline and its derivatives still receive considerable attention for their exceptional optoelectronic properties especially photoconductive ones [3]. In the course of a program on the synthesis of new organic materials with useful electronic properties and in order to elucidate further the effect of nitrogen atom ring substitution as well as variation of ring substituents on the relative photoconductivity, a number of various pyrazines based on aceanthraquinoxaline (Figure 1) were prepared by Aleksandar Golubovic and al. [4]. These materials offer many advantages in terms of easy synthesis and purification, and generally exhibit high relative photoconductivity. Therefore designing and synthesizing molecules with interesting properties play a crucial role in technology. At the same time it is important to understand the nature of the relationship between the molecular structure and the electronic properties to provide guidelines for the development of new materials. Recent work in this area has been focused on the synthesis and design of new molecules combining several conjugated systems with narrow band gaps [5]. A fundamental understanding of the ultimate relations between structure and properties of these materials is necessary to benefit from their adaptative properties to photovoltaic cells. In parallel with this experimental work on these new materials, theoretical efforts have indeed begun to constitute an important source of valuable information which complements the experimental studies, thereby contributing to the understanding of the molecular electronic structure as well as the nature of absorption and photoluminescence [6]. In this paper, eleven compounds based on aceanthraquinoxaline (M_1, M_2, M_3, M_4, M_5, M_6, M_7, M_8, M_9, M_{10}, and M_{11} (shown in Figure 1), are designed. The geometries, electronic properties, absorption and emission spectra of these studied compounds are studied by using density functional theory (DFT) and time-dependent density functional theory (TD/DFT) with the goal to find potential sensitizers for use in organic solar cells.



M$_1$ **M$_2$** **M$_3$** **M$_4$** **M$_5$** **M$_6$** **M$_7$** **M$_8$** **M$_9$** **M$_{10}$** **M$_{11}$**

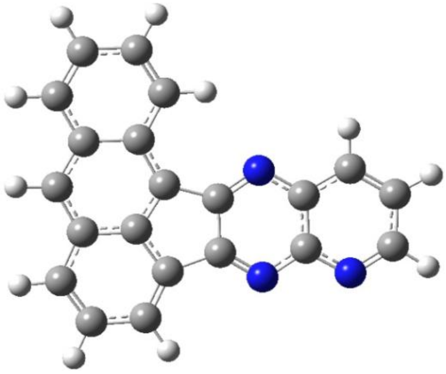
Figure 1: Structures of the studied molecules

2. Theoretical methodology

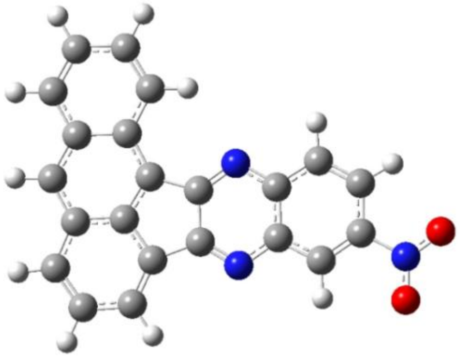
DFT method of three-parameter compound of Becke (B3LYP) [7] was used in all the study of the neutral and polaronic compounds. The 6-31G (d) basis set was used for all calculations [8]. To obtain the charged structures, we start from the optimized structures of the neutral form. The calculations were 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 ZINDO/s, calculations on the fully optimized geometries. In fact, these calculation methods have been successfully applied to other conjugated polymers [10].

3. Results and discussion

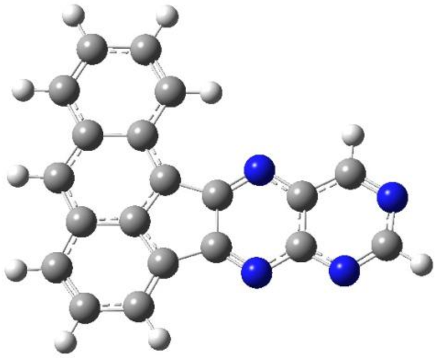
The results of the optimized structures (Figure.2) for all studied compounds so that they have similar conformations (quasi planar conformation). We found that the modification of several groups attached to the pyrazine ring does not change the geometric parameters.



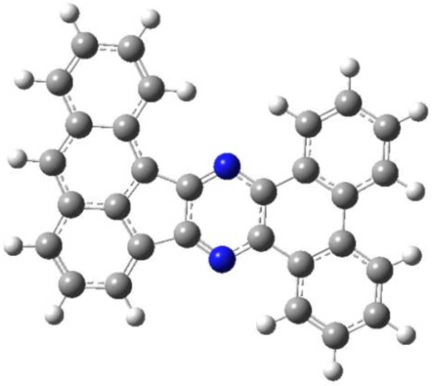
M_1



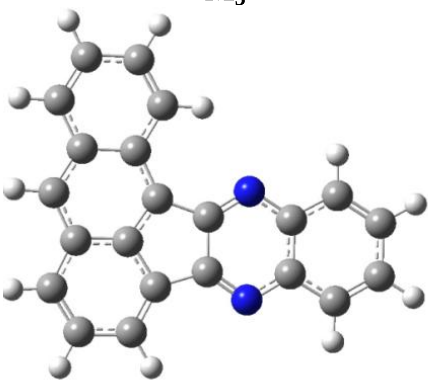
M_2



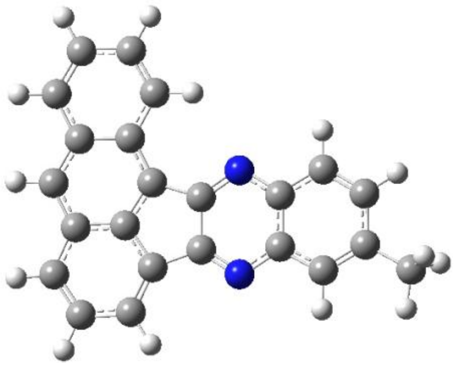
M_3



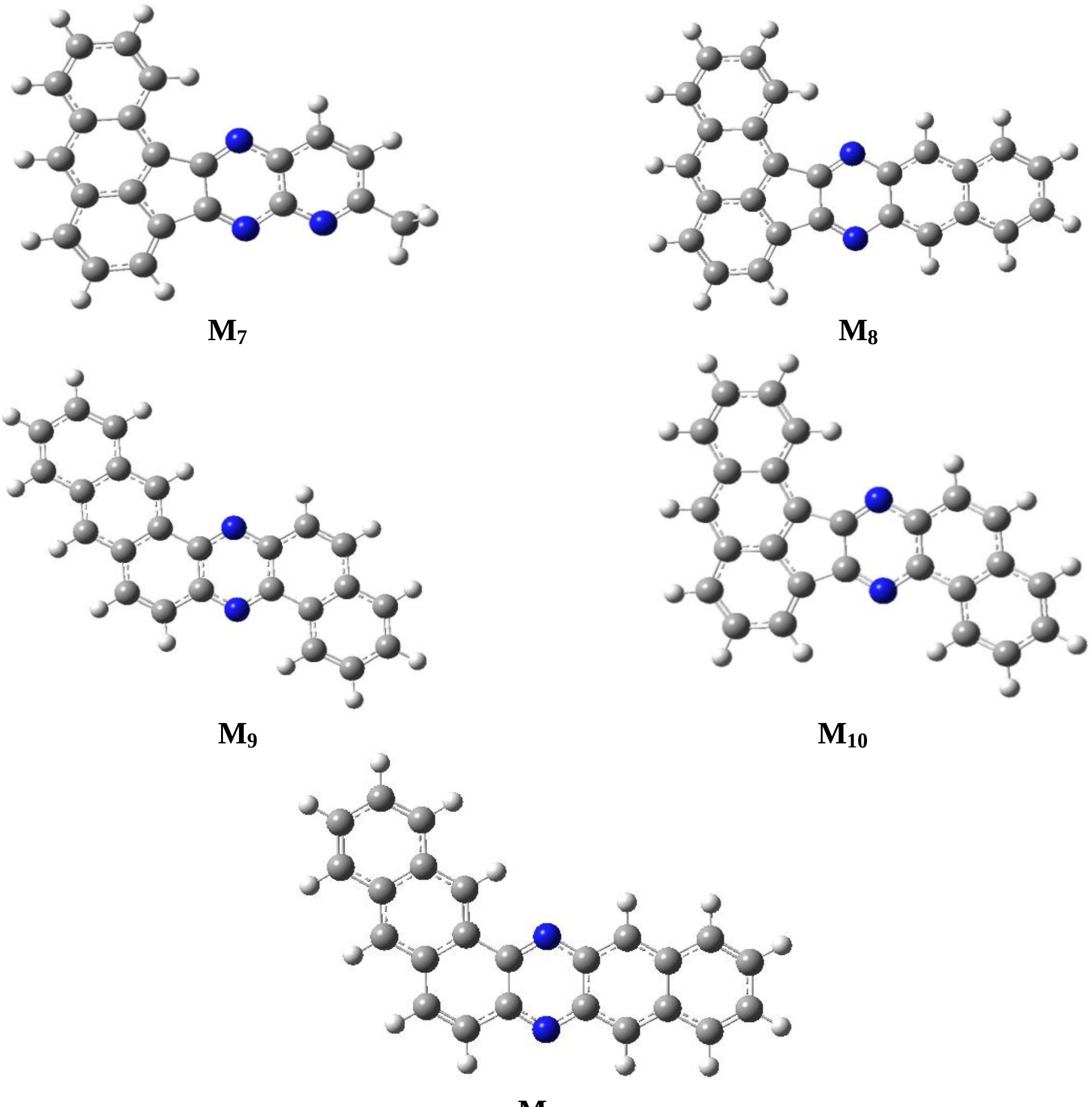
M_4



M_5



M_6



M_7 **M_8**

M_9 **M_{10}**

M_{11}

Figure 2: Optimized structure of the studied compounds Mi (i=1 to 11) obtained by B3LYP/6-31G (d) level

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 E_{gap} energy of the studied molecules.

Table 1: The theoretical electronic properties (HOMO, LUMO and E_{gap}) (in eV) of the studied compounds calculated from the optimized structures by B3LYP/6-31G (d).

MOLEC.	**M_1**	**M_2**	**M_3**	**M_4**	**M_5**	**M_6**	**M_7**	**M_8**	**M_9**	**M_{10}**	**M_{11}**
E_{LUMO} (eV)	**-2.504**	**-2.869**	**-2.731**	**-2.446**	**-2.387**	**-2.342**	**-2.444**	**-2.37**	**-2.103**	**-2.416**	**-2.501**
E_{HOMO} (eV)	**-6.859**	**-7.224**	**-7.053**	**-6.755**	**-6.612**	**-6.465**	**-6.342**	**-5.88**	**-5.483**	**-5.784**	**-5.494**
E_{gap} (eV)	**4.355**	**4.355**	**4.322**	**4.309**	**4.225**	**4.124**	**3.897**	**3.51**	**3.381**	**3.368**	**2.993**

Based on the above presented results, the energy band structures are diagrammed in Figure 3. It is deduced that the substitution, of pyridine ring in the molecule M_1 by different other heterocyclic systems, push up/down the HOMO/LUMO energies in agreement with their electron acceptor/donor character. As shown in table 1, one remark that in the studied molecules (M_2 to M_{10}) the stabilization HOMO levels in comparison with those of compound M_{11}. The HOMO and LUMO energies of M_1 to M_{11} change significantly, the LUMOs for M_1, M_2, M_3, M_4, M_5, M_6, M_7, M_8, M_9, M_{10} and M_{11} are located at -2.504 ; -2.869 ; -2.731 ; -2.446 ; -2.387 ; -2.342 ; -2.444 ; -

2.370 ; -2.103 ; -2.416 ; and -2.501 eV, respectively. The HOMOs for M_1, M_2, M_3, M_4, M_5, M_6, M_7, M_8, M_9, M_{10} and M_{11} are located at -6.859 ; -7.224 ; -7.53 ; -6.755 ; -6.612 ; -6.465 ; -6.342 ; -5.880 ; -5.483 ; -5.784 ; and -5.494 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, the energies of E_{gap} of the studied molecules differ slightly from 2.99 eV to 4.35 eV depending on the different structures. They are classified in the following order $M_1 > M_2 > M_3 > M_4 > M_5 > M_6 > M_7 > M_8 > M_9 > M_{10} > M_{11}$.

On the other hand and from the above analysis, we know that LUMO energy levels of the eleven studied molecules are much higher than that of ITO conduction band edge (−4.7 eV). Thus, molecules in excited states of M_1, M_2, M_3, M_4, M_5, M_6, M_7, M_8, M_9, M_{10} and M_{11} 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 2, both HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosentizer. It should be noted that the LUMO levels of the studied compounds Mi (i=1-11) are higher than that of PCBM [12] (which varies in literature from -3.8 to -4.3 eV). To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of PCBM, the HOMO and LUMO levels are compared.. 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 (Voc) 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 (PCBM in our case), taking into account the energy lost during the photo-charge generation [13]. The theoretical values of open-circuit voltage Voc have been calculated from the following expression:

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

The obtained values of Voc of the studied molecules calculated according to the equation (1) range from 0.83 eV to 1.59 eV (see Table 2), 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 PCBM and the subsequent regeneration is possible in an organic sensitized solar cell.

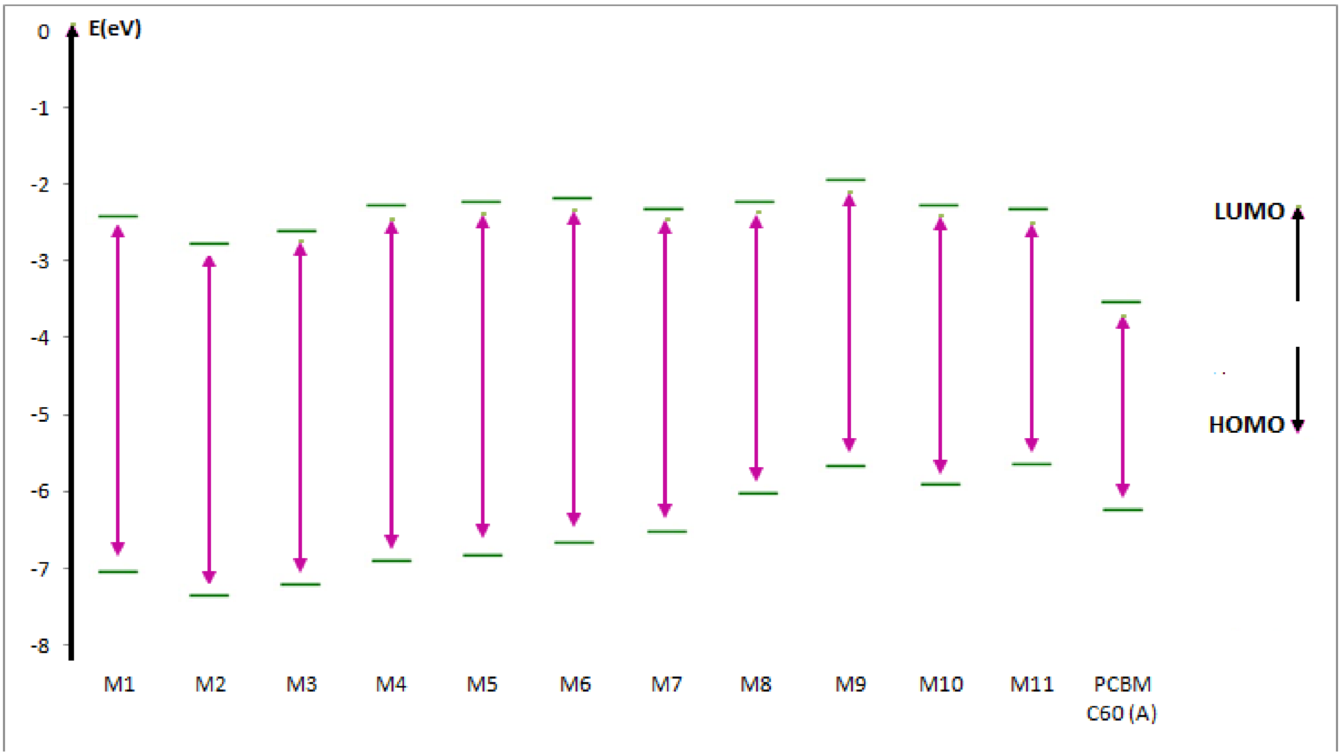
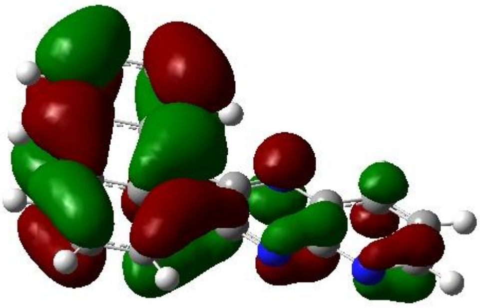


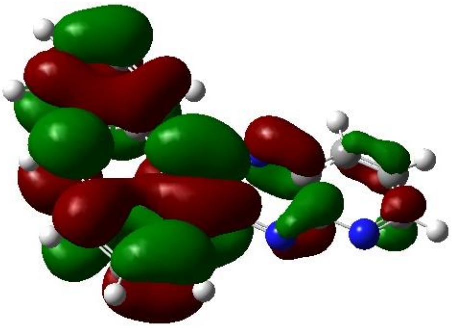
Figure 3: HOMO and LUMO energy levels of the studied compounds, by DFT/B3LYP/6-31G (d) basis set and PCBM.

Table 2: Energy values of E_{LUMO} (eV), E_{HOMO} (eV) and the open circuit voltage V_{oc} (eV).

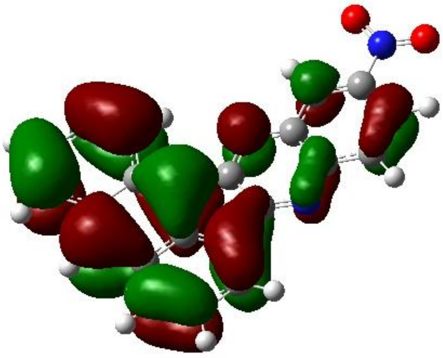
MOLECULE	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**Voc**	**α**
M_1	-6.859	-2.504	2.859	1.196
M_2	-7.224	-2.869	3.224	0.831
M_3	-7.053	-2.731	3.053	0.969
M_4	-6.755	-2.446	2.755	1.254
M_5	-6.612	-2.387	2.612	1.313
M_6	-6.465	-2.342	2.465	1.358
M_7	-6.342	-2.444	2.342	1.256
M_8	-5.88	-2.37	1.88	1.33
M_9	-5.483	-2.103	1.483	1.597
M_{10}	-5.784	-2.416	1.784	1.284
M_{11}	-5.494	-2.501	1.494	1.199
PCBM C_{60} (A)	-6.1	-3.7	---	---

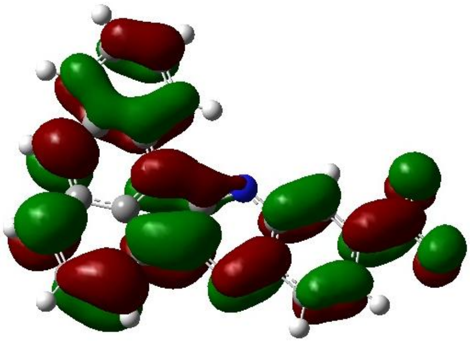
The frontier molecular orbital (MO) contribution is very important in determining the charge-separated states of the studied molecules because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitations properties [14]. In general, as shown in figure 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.



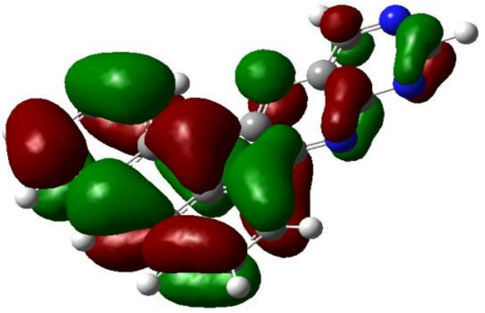


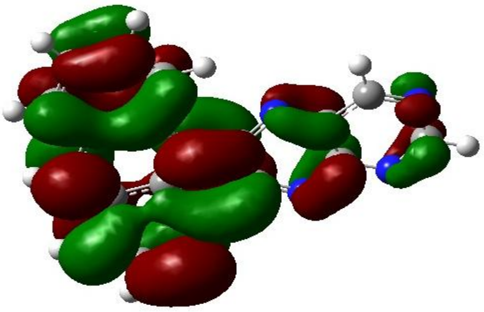
HOMO **M_1** **LUMO**



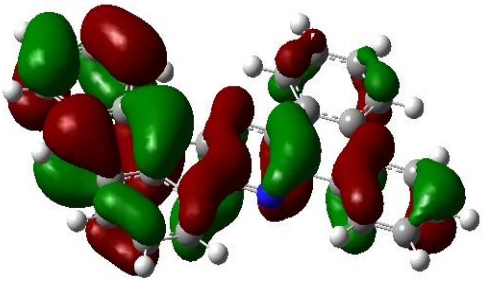


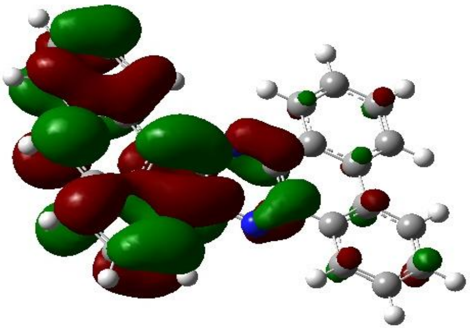
HOMO **M_2** **LUMO**



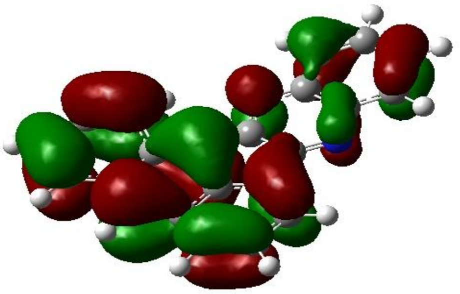


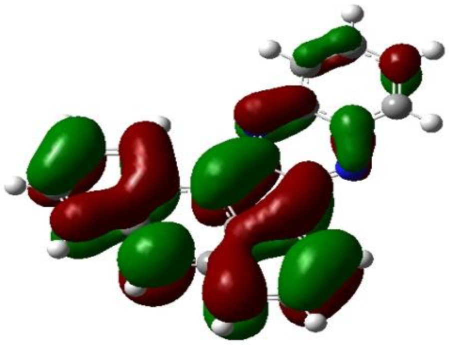
HOMO **M_3** **LUMO**



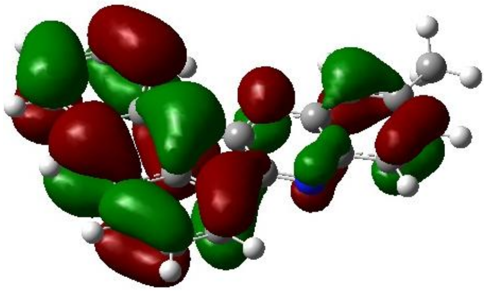


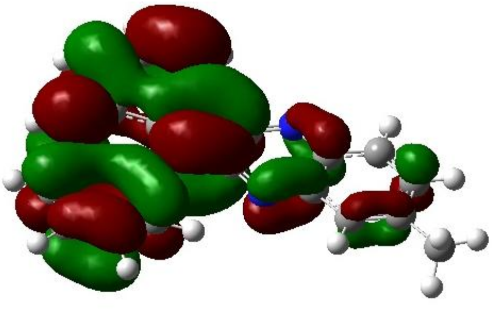
HOMO **M_4** **LUMO**



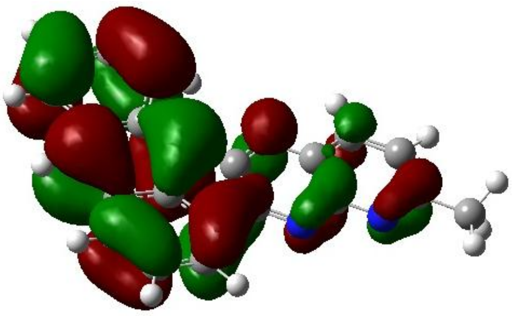


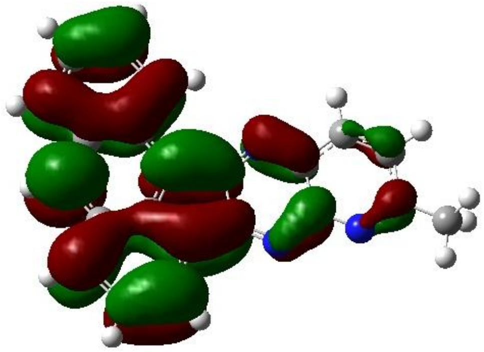
HOMO **M_5** **LUMO**





HOMO **M_6** **LUMO**





HOMO **M_7** **LUMO**

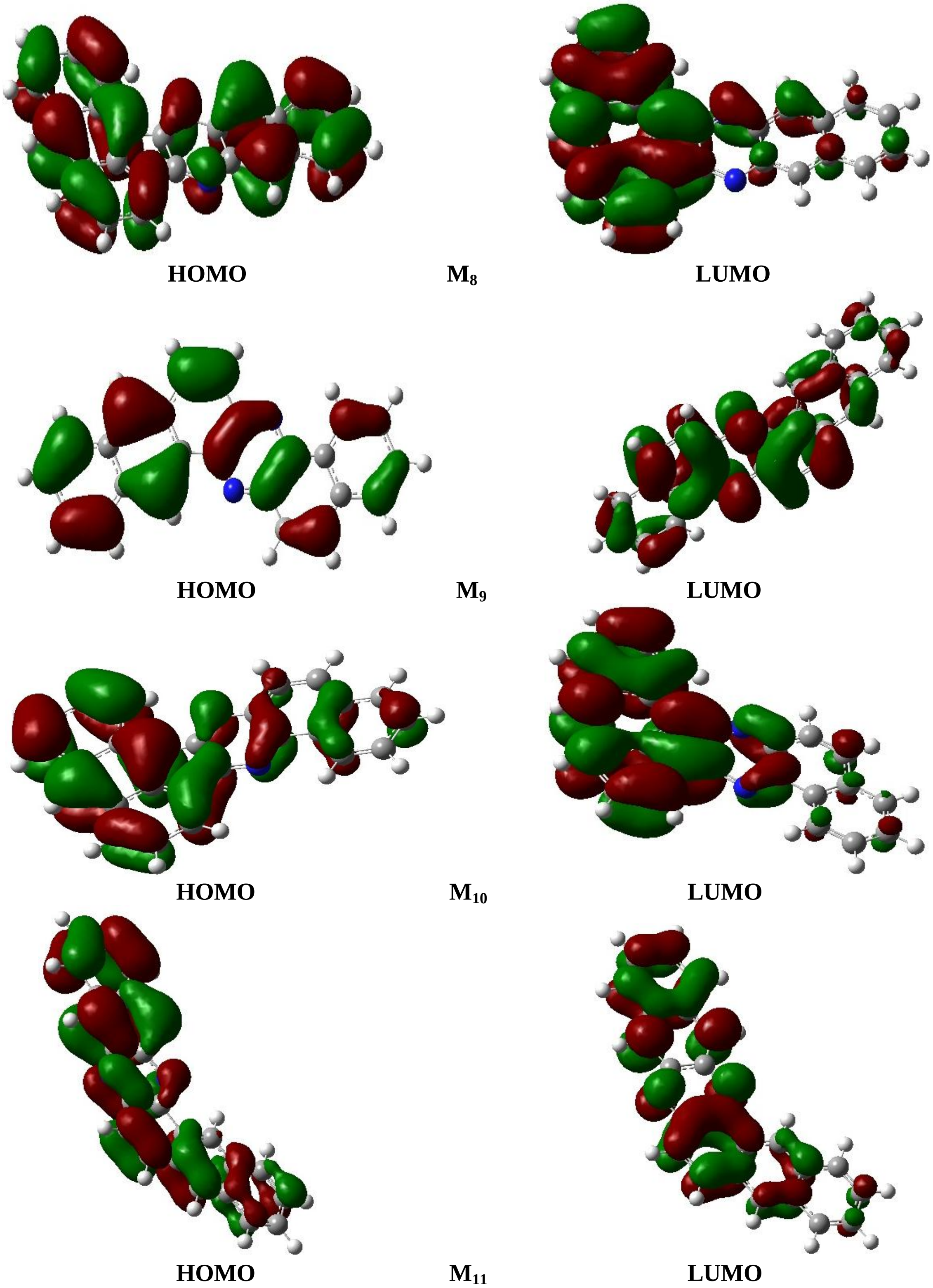


Figure 4: Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level

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 M i (i=1 to 11) using TD-DFT starting with optimized geometry obtained at B3LYP/6-31(d) level. As illustrated in table 5, we can find the values of calculated wavelength λmax and oscillator strengths O.S.

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 5 shows that there is a bathochromic shift when passing from M_1 (424.84 nm) to M_{11} (437.13 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 3: Absorption spectra data obtained by TD-DFT methods for the Mi (i=1 to 11) compounds at B3LYP/6-31G (d) optimized geometries.

MOLEC.	**M_1**	**M_2**	**M_3**	**M_4**	**M_5**	**M_6**	**M_7**	**M_8**	**M_9**	**M_{10}**	**M_{11}**
λ_{max}	424.84	436.12	425.27	445.19	423.66	426.28	427.33	429.86	427.14	434.49	437.13
$E_{activation}$	79.468	77.412	79.389	75.836	79.689	79.198	79.005	78.539	79.038	77.704	77.232
O.S.	0.456	0.624	0.431	0.334	0.43	0.441	0.459	0.522	0.762	0.353	0.322

In order to study the emission photoluminescence properties of the studied compounds Mi, the TD/B3LYP method was applied to the geometry of the lowest singlet excited state optimized at the CIS level with 3- 21G⁄ basis set [15]. The normalized photoluminescence (PL) spectrum of the studied compounds shows a maximum at 488.12 nm for M_1; 500.43 nm for M_2; 443.71 nm for M_3; 548 nm for M_4; 488.01 nm for M_5; 495.23 nm for M_6; 439.91 nm for M_7; 486.19 nm for M_8; 473.66 nm for M_9; 525.65 nm for M_{10} and 455.3 nm for M_{11}. As illustrated in table 4, this could be regarded as an electron transition process that is the reverse of the absorption corresponding mainly to the LUMO-HOMO electron transition configuration. Moreover, the observed red-shifted emission of the PL spectra is in reasonable agreement with the obtained results of absorption. We can also note that relatively high values of Stokes Shift (SS) are obtained for M_4 (102.810 nm). In fact, the Stokes Shift, which is defined as the difference between the absorption and emission maximums (EVA–EVE), is usually related to the band widths of both absorption and emission bands [16].

Table 4: Emission spectra data obtained by TD-DFT methods for the Mi (i=1 to 11) compounds at B3LYP/6-31G (d) optimized geometries

MOLEC.	**M_1**	**M_2**	**M_3**	**M_4**	**M_5**	**M_6**	**M_7**	**M_8**	**M_9**	**M_{10}**	**M_{11}**
λ_{emiss}	488.12	500.43	443.71	548	488.01	495.23	439.91	486.19	473.66	525.65	455.33
λ_{abso}	424.84	436.12	425.27	445.19	423.66	426.28	427.33	429.86	427.14	434.49	437.13
f_{STOKS}	63.28	64.31	18.44	102.81	64.35	68.95	12.58	56.33	46.52	91.16	18.2

Conclusion

This study is a theoretical analysis of the geometries and electronic properties of three various compounds based on the pyrazine 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 4.36 eV to 2.99 eV depending on the different structures. Also we can remark that the energy E_{gap} decreases when going from M_1 to M_{11}. This is probably due to the effect of the conjugated system and aromaticity in the studied compounds.
- The energy E_{gap} of M_{11} is much smaller than that of the other compounds.
- The Molecule M_4 witch have a relatively high value of λ_{max} (absorption), λ_{max} (emission) and Stokes Shift (SS) is expected to have the most outstanding photophysical properties.

- All the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCBM and the subsequent regeneration are feasible in the organic sensitized solar cell.
- 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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