Electronic and photovoltaic properties of new materials based on imidazo[1,2-a]pyrazine. Computational investigations

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A quantum chemical investigation has been performed to explore optical and electronic properties of a series of different compounds based π-conjugated molecular materials with fused rings, on imidazo[1,2-a]pyrazines. Different electron-donor side groups as side-chain substituents were introduced in molecular backbone to investigate their effects on the electronic structure. The HOMO and LUMO energy levels as well energy gap E_g of the studied compounds have been calculated and reported. The obtained data suggest that studied molecules are good candidates for organic solar cells.

С использованием квантово-химических методов рассчитаны оптические и электронные свойства соединений на основе ароматических молекул с π-сопряженными связями, а именно имидазо[1,2 a]пиразина. Различные электроно-донорные группы вводились в молекулярную систему для изучения влияния на электронную структуру молекул. Рассчитаны HOMO и LUMO энергетические уровни, а также ширина запрещенной зоны E_g изученных соединений. Результаты исследований позволяют рассматривать эти соединения в качестве перспективных для использования в органических солнечных элементах.

Електронні і фотогальванічні властивості нових матеріалів на основі имидазо[1.2-a]піразину. Комп'ютерне моделювання. *А.Захлоу, С.Чтита, М.Хамалі, Л.Беджит, Т.Лакхліфі, М.Боучріні.*

З використанням квантово-хімічних методів розраховано оптичні і електронні властивості низки сполук на основі ароматичних молекул з π-спряженими звіязками, зокрема імідазо[1,2a]піразіну. Різні бокові електронодонорні групи введено у молекулярну систему для вивчення впливу на електронну структуру молекул. Розраховано HOMO і LUMO енергетичні рівні, а також ширину забороненої зони E_g досліджених сполук . Результати дослідженя дозволяють розглядати ці сполуки як перспективні при використанні в органічних сонячних елементах.

1. Introduction

The interest in π-conjugated polymers increased considerably after discovery that their electrical conductivity increases substantially upon electrochemical doping. This discovery led to the 2000 Nobel Prize in Chemistry awarded to Alan Heeger, Alan Mac Diarmid, and Hideki Shirakawa [1]. By the mid-1980s, several research teams in
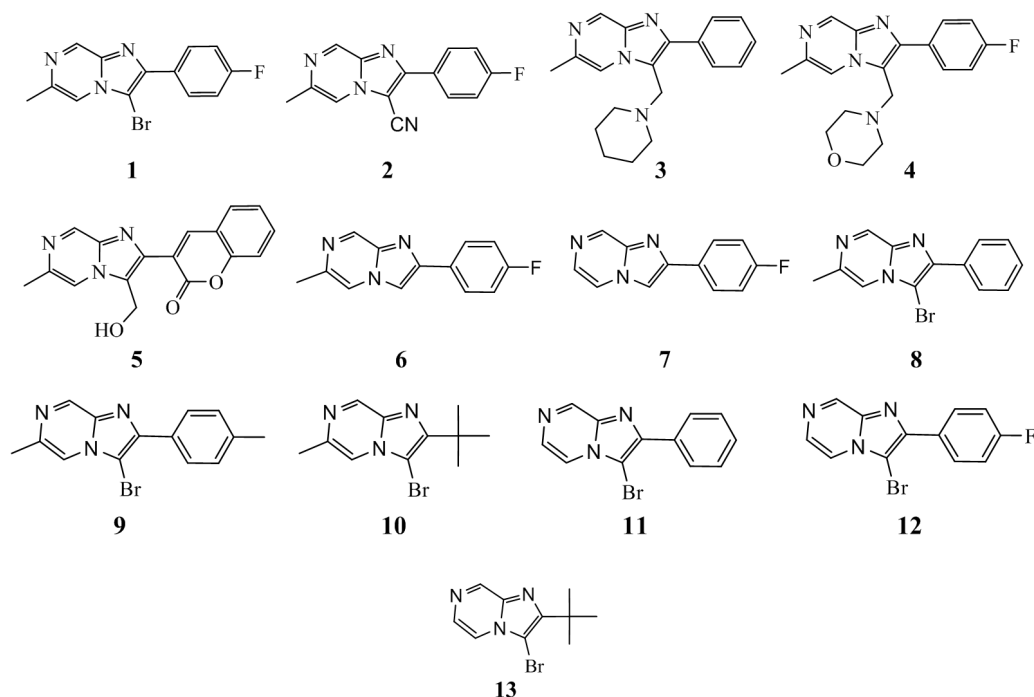
Fig. 1. Structure of the studied imidazo[1,2-a]pyrazines derivatives.

both academia and industry were investigating π-conjugated small molecules and polymers to gain benefit of their unique optical and semiconducting properties [2]. The development of organic semiconductors has focused on organic π-conjugated molecules for application in electronic and photonic devices by virtue of their ability to afford high operating speeds, large device densities, low cost, and large area flexible circuits. These materials which may have interesting optical and electronic properties for applications in microelectronics such as organic field-effect transistor (OFET), light-emitting diodes, sensors, photo-detectors and solar cells [2].

In photovoltaic, one of the most critical issues, besides achieving adequate efficiencies and life times, is to reduce the costs associated with achieving economies of scale. Organic solar cells, which can be processed from solution, have great potential to reach the goal of photovoltaic technology that is economically viable for large-scale power generation, where the organic materials are the key elements for converting light into electricity. Organic photovoltaic materials have many advantages compared to inorganic semiconductors. They are a subject of an increasing interest in recent years due to their advantages of low cost, light weight, processability of the organic materials and potential to make flexible

photovoltaic devices in comparison with the traditional silicon-based solar cells. The mismatch between absorption spectra, low band gap and the solar irradiance spectrum is one of the main reasons for low efficiency and high performance of the organic solar cells devices [3, 4].

In this paper, thirteen compounds based on imidazo[1,2-a]pyrazines (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13 (shown Fig. 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.

2. Theoretical methodology

DFT method of three-parameter compound of Becke (B3LYP) [5] was used in the study of the neutral and polaronic compounds. The 6-31G (d) basis set was used for all calculations [6]. To obtain the charged structures, we start from the optimized structures of the neutral form. The calculations were carried out using Gaussian 03 program [7]. Geometry structures of the 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
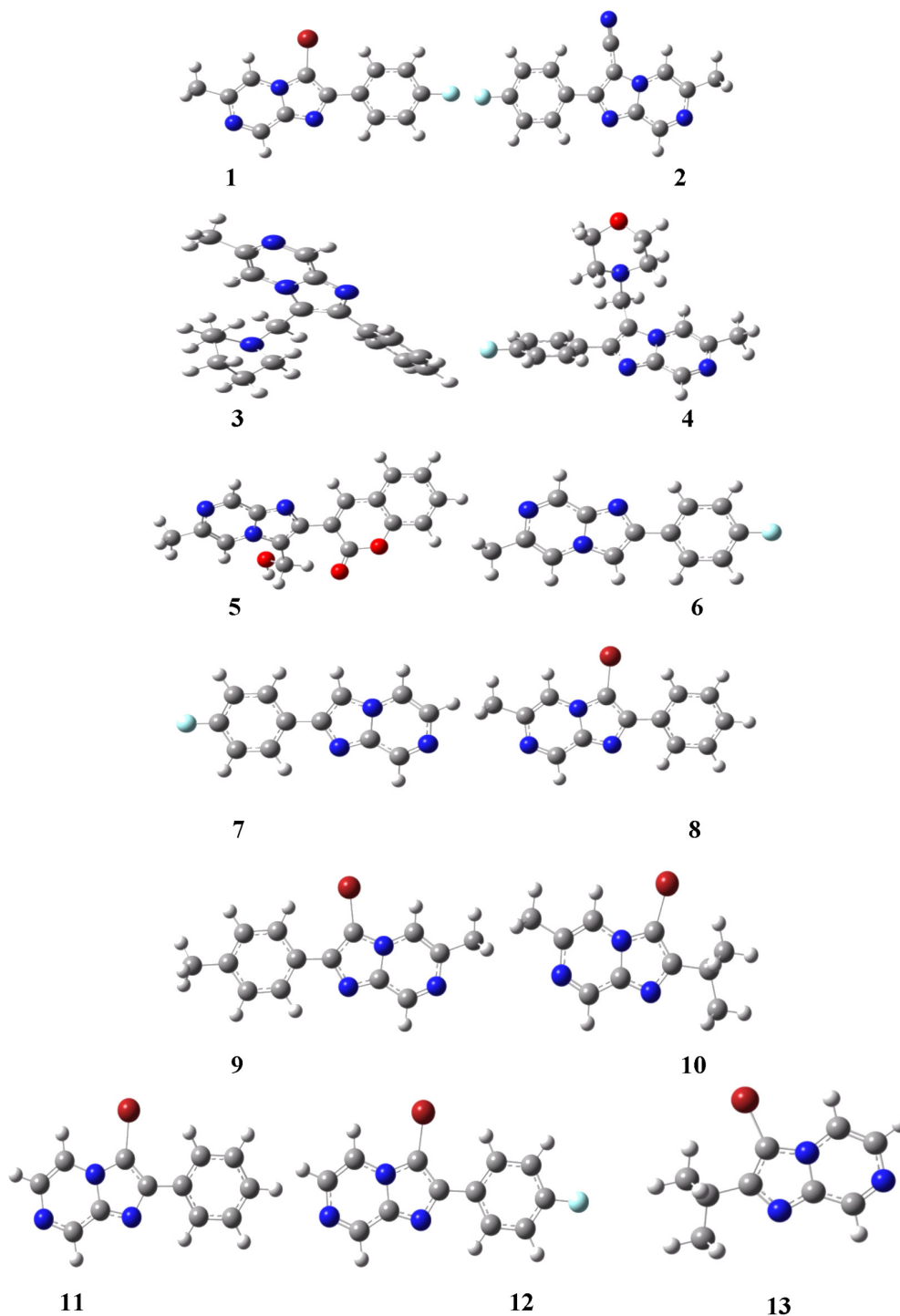
Fig. 2. Optimized structure of the studied compounds (1 to 13) obtained by B3LYP/6-31G (d) level.

energies. The ground state energies and os-cillator strengths were investigated using TD/DFT, calculations on the fully optimized geometries. In fact, these calculation methods have been successfully applied to other conjugated molecules [8].

3. Results and discussion

The result of the optimized structures obtained by B3LYP/6-31G (d) (Fig. 2) shows that they have similar conformations (quasi planar conformation). We found that the modification of several groups attached to

imidazo[1,2-a]pyrazine does not change the geometric parameters.

Table 1 lists the calculated frontier orbital energies and energy Egap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the E_{gap} energy of the studied molecules.

Electronic structures are fundamental for interpretation and understanding of the absorption spectra. It is deduced that the substitution of imidazo[1,2-a]pyrazine in the molecule 1 by different other substituent groups, push up/down the HOMO/LUMO energies in agreement with their electron acceptor/donor character. As shown in Table 2, the HOMO and LUMO energies of 1 to 13 change significantly. This implies that different side substituent structures play key role in electronic properties and the effect of slight structural variations, especially the effect of the motifs branched to the imidazo[1,2-a]pyrazine on the HOMO and LUMO energies is clearly seen. In addition, the energies of E_{gap} of the studied molecules differ slightly from 3.915 eV to 4.806 eV depending on the different structures.

It is known that the architecture of photoactive layer is one of the principle factors of the efficiencies of solar cells. The most efficient technique to generate free charge carriers is bulk heterojunction where the π-conjugated compounds donors are blended with fullerene derivatives as acceptor [9]. In our study, PCEM and derivatives (C_{60}, C_{70}, C_{76}, $C_{78}-C_{2V}$, $C_{78}-D_3$, $C_{84}-D_2$) were included for comparison purposes.

As shown in Table 1, both HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosensitizer. It should be noted that the LUMO levels of the studied compounds Mi ($i = 1-13$) are higher than that of PCEM derivatives which varies from -4.0 to -3.47 eV (C_{60} (-3.47 eV), C_{70} (-3.54), C_{76} (-3.79), $C_{78}-C_{2V}$ (-3.94), $C_{78}-D_3$ (-4.0), $C_{84}-D_2$ (-3.98)) [10].

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 (PCEM derivatives in our case), taking into account the energy lost during photo-charge generation [11]. The

Table 1. Theoretical electronic properties of the studied compounds calculated from the optimized structures by B3LYP/6-31G. Isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level
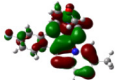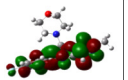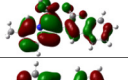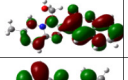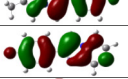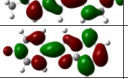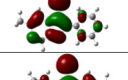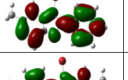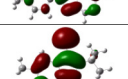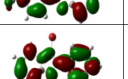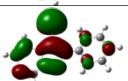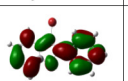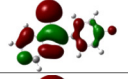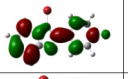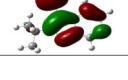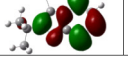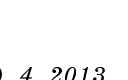
4			-5.528	-1.392	1.758	1.688	1.438	1.288	1.228	1.248
5			-5.989	-1.999	2.291	2.149	1.899	1.749	1.689	1.709
6			-6.044	-1.426	2.274	2.204	1.954	1.804	1.744	1.764
7			-6.131	-1.542	2.361	2.291	2.041	1.891	1.831	1.851
8			-6.075	-1.497	2.305	2.235	1.985	1.835	1.775	1.795
9			-5.931	-1.458	2.161	2.091	1.841	1.691	1.631	1.651
10			-6.065	-1.259	2.295	2.225	1.975	1.825	1.765	1.785
11			-6.172	-1.651	2.402	2.332	2.082	1.932	1.872	1.892
12			-6.151	-1.684	2.381	2.311	2.061	1.911	1.851	1.871
13			-6.154	-1.437	2.384	2.314	2.064	1.914	1.854	1.874

Table 2. Absorption spectra data obtained by TD-DFT methods for the Molecules (1 to 13) of the studied compounds at B3LYP/6-31G (d) optimized geometries

Mi	λ_{Abs}, (nm)	f, a.u.	λ_{Emiss}, (nm)	Stockes Shift, nm
1	308.92	0.2093	339.95	31.03
2	321.44	0.0324	–	–
3	376.36	0.0061	–	–
4	351.83	0.0157	–	–
5	354.27	0.1128	391.95	37.68
6	298.92	0.2545	–	–
7	300.85	0.2577	331.48	30.63
8	306.19	0.1783	348.58	42.39
9	311.09	0.2448	334.48	23.39
10	289.82	0.0733	332.33	42.51
11	309.77	0.1851	436.01	126.24
12	311.53	0.2122	342.43	30.90
13	297.67	0.0824	332.99	35.32

theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression:

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

The obtained values of V_{oc} of the studied molecules calculated according to the equation (1) range from 1.407 eV to 2.603 eV (see Table 1). These values are sufficient for a possible efficient electron injection to PCEM derivatives. Therefore, all the studied molecules can be used as sensitizers. We noted that the best values of V_{oc} are indicated for the studied compounds (1–13) blended with C_{60} or C_{70} and higher value are given for molecule 2 blended with C_{60} (2.603 eV).

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 [12]. In general, as shown in Table 1, the HOMOs of these molecules in the neutral form possess π-bonding character and π-antibonding character between the consecutive subunits while the LUMOs possess π-antibonding character and π-bonding character between the subunits whereas it is the opposite in the case of doped forms.

We have calculated UV-visible spectra of the studied compounds 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 $\lambda_{max}(abs)$ and oscillator strengths f. Excitation to the S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbital. The absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO $\rightarrow$ LUMO transition is predominant in $S_0 \rightarrow S_1$ 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 Molecule 10 (289.82 nm) to Molecule 3 (376 nm). This effect is obviously due to the aromaticity, conjugation and substitution effects in the several studied compounds. Those interesting points are seen both in the studying the electronic and absorption properties.

In order to study the emission photoluminescence properties of the studied compounds M_i, TD/B3LYP method was applied to the geometry of the lowest singlet excited state optimized at the CIS level with 3-21G basis set [13]. As illustrated in Table 2, this could be regarded as 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 the Stokes Shift (SS) are obtained for Molecule 11 (126.24 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 [14].

4. Conclusions

This study is a theoretical analysis of the geometries and electronic properties of various compounds based on pyrazine which displays the effect of substituted groups on the structural and optoelectronic 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 are 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 4.806 eV to 3.99 eV depending on the different structures.

The energy E_{gap} of molecule 3 is much smaller than that of the other compounds.

The Molecule 11 witch have a relatively high value of λ_{max} (absorption), λ_{max} (emission) and the 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 PCEM and derivatives and the subsequent regeneration are feasible in the organic sensitized solar cell. The best values of V_{oc} are obtained for the studied compounds (1−13) blended with C_{60} or C_{70} and the higher value are given for molecule 2 blended with C_{60} (2.603 eV).

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 the organic solar cells.

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