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STUDY OF THE EFFECT OF SUBSTITUTION ON PHTALOCYANINE BASED COMPOUNDS FOR PHOTOVOLTAIC APPLICATION

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ABSTRACT

The research inorganic solar cell has been developed especially in the last decade and has attracted scientific and economic interest triggered by a rapid increase in power conversion efficiencies. In this work, computational study on the geometries and electronic properties of structures composed of phthalocyanine and zinc phthalocyanine which are substituted by different group PcR and PcZn-R. We presented a theoretical study by using DFT method at B3LYP level with 6-31G (d) basis set. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells, so, the HOMO, LUMO, Gap energy and the photovoltaic properties of the studied compounds have been calculated. These properties suggest these materials as a good candidate for organic solar cells.

Keywords: Zinc phthalocyanine, DFT method, Electronically, Properties, Solar cells.

1. INTRODUCTION

The research in the organic π-conjugated molecules has become one of the most interesting topics in the fields of chemistry physics and materials science. Owing to their important specific properties, these new compounds become the most promising materials for the optoelectronic device technology [1], such as LEDS [2], Transistors (TFTs) [3] and solar cells [4].

Solar cells are an attractive renewable energy source, they can provide energy to help meet world's fast growing demands. Well as several types of novel organic [5] and inorganic [6] materials: among those ones, organic solar cells are currently the focus of innovative research for useful properties including flexibility, low cost, low weight and semi-transparent [7]. On the

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other hand, they are manufactured from solution-processing techniques and have unique prospects for achieving low-cost solar energy harvesting, owing to their material and manufacturing advantages. The potential applications of polymer solar cells are broad, ranging from flexible solar modules and semitransparent solar cells in windows, to building applications and even photon recycling in liquid-crystal displays [8]. The most efficient cell design, leading to the highest power conversion efficiencies, is the bulk-heterojunction (BHJ) solar cell [9]. The active layer of BHJ solar cells consists of an interpenetrating network of two types of organic materials, an electron donor and an electron acceptor, and is formed through the control of the phase separation between the donor and acceptor parts in the bulk.

We focus on phthalocyanine (Pc) and metallophthalocyanine (MPc) as original materials for this kind of cells. In fact, these molecules exhibit very high extinction coefficients around 600 nm are considered very good near infrared sensitizers. Additionally, by making use of infrared light, the solar heating of the buildings is reduced, Thereby reducing the demand and power consumption of the air conditioning units [10-13]. Moreover, the structures of Pc and MPc can be easily modified without significantly changing their stability and processability. The photophysical and photochemical properties of these complexes can be altered by introducing different substituents into the peripheral positions of the macrocyclic ring, varying the central metal ions, alternating the axial ligands, or changing the substituted of the macrocycle to strengthen the capacity and solubility of the material [14-18].

In our paper, we will make DFT study of phthalocyanine and Zinc phthalocyanine which are substituted by different group PcR and PcZnR that have been used as semiconductors for a BHJ cell application. A novel the structure of symmetrical substituted Pc, PcR, PcZn and PcZnR (R = OCH$_3$, - COOH, CHC(COOHCN) are shown in (fig.1).

The quantum chemical investigation has been performed to the optical and electronic properties of these compounds. The theoretical knowledge of the HOMO and LUMO energy levels of the components is a basis in studying organic solar cells, so, the HOMO, LUMO and Gap energy of the studied compounds have been calculated and reported.

Pc

PcR

PcZn

PcZnR

R : OMe ; COOH ; CHC(COOHCN)
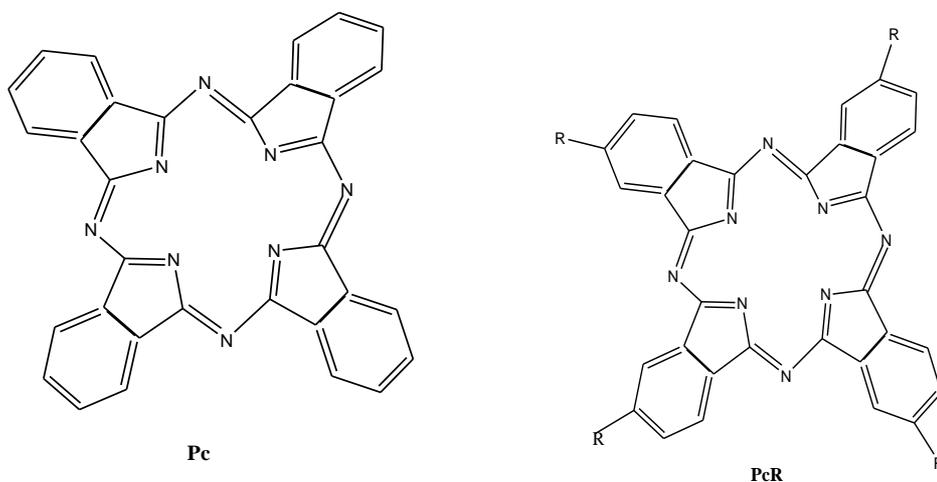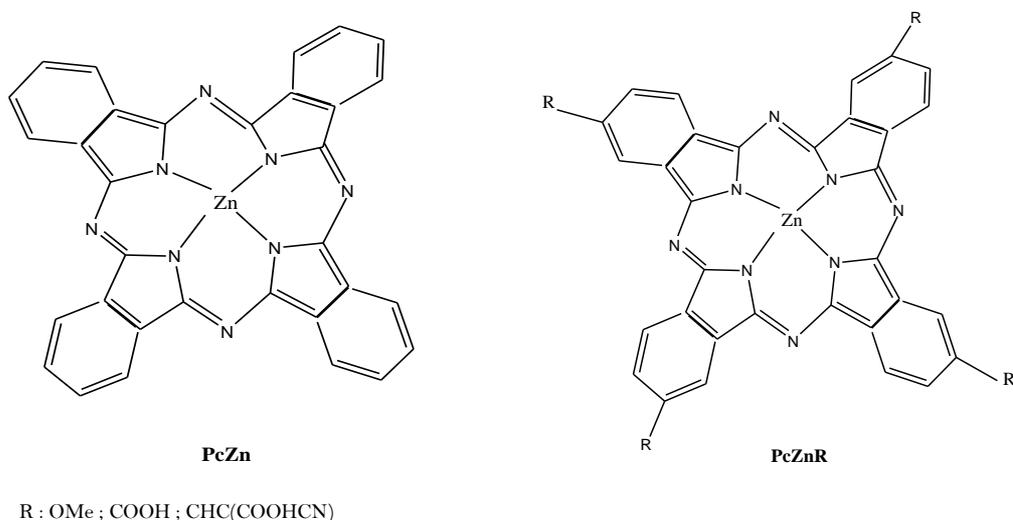
Fig-1. Chemical structures of Pc; PcR; PcZn; PcZnR

2. THEORETICAL METHODOLOGY

The quantum calculations were performed using Gaussian 03 program [19]. The geometries of the resulting conformers were optimized at the DFT level of three-parameter compound functional of Becke (B3LYP) [20]. The 6-31G* basis set was used for all atoms. The geometry structures of neutral and doped molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy Egap 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. In fact, these calculation methods have been successfully applied to other conjugated molecules [21]

3. RESULTATS AND DISCUSSION

The results of the optimized structures obtained by B3LYP/6-31G (d) (Fig.2) show that all the studied phthalocyanine have planar geometries. We found that the modification of several groups attached to does not change the geometric parameters.

Pc

PcOMe

PcCOOH

PcCHC(COOHCN)

PcZn

PcZnOMe

the studied compou
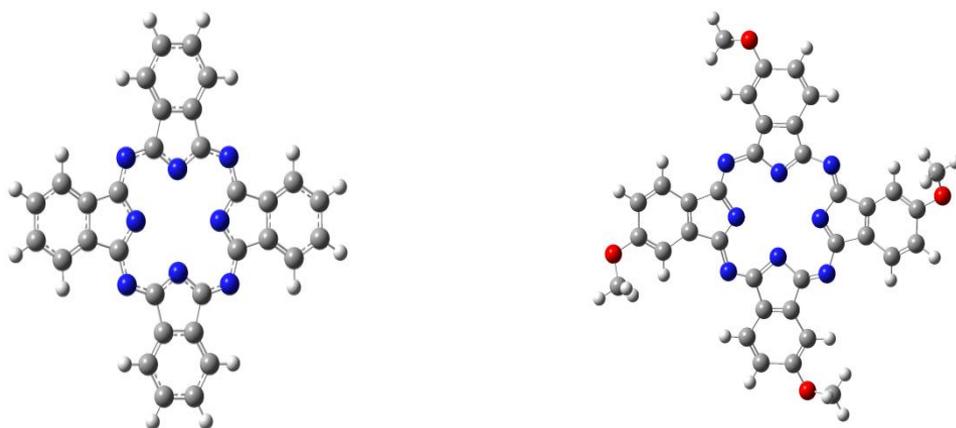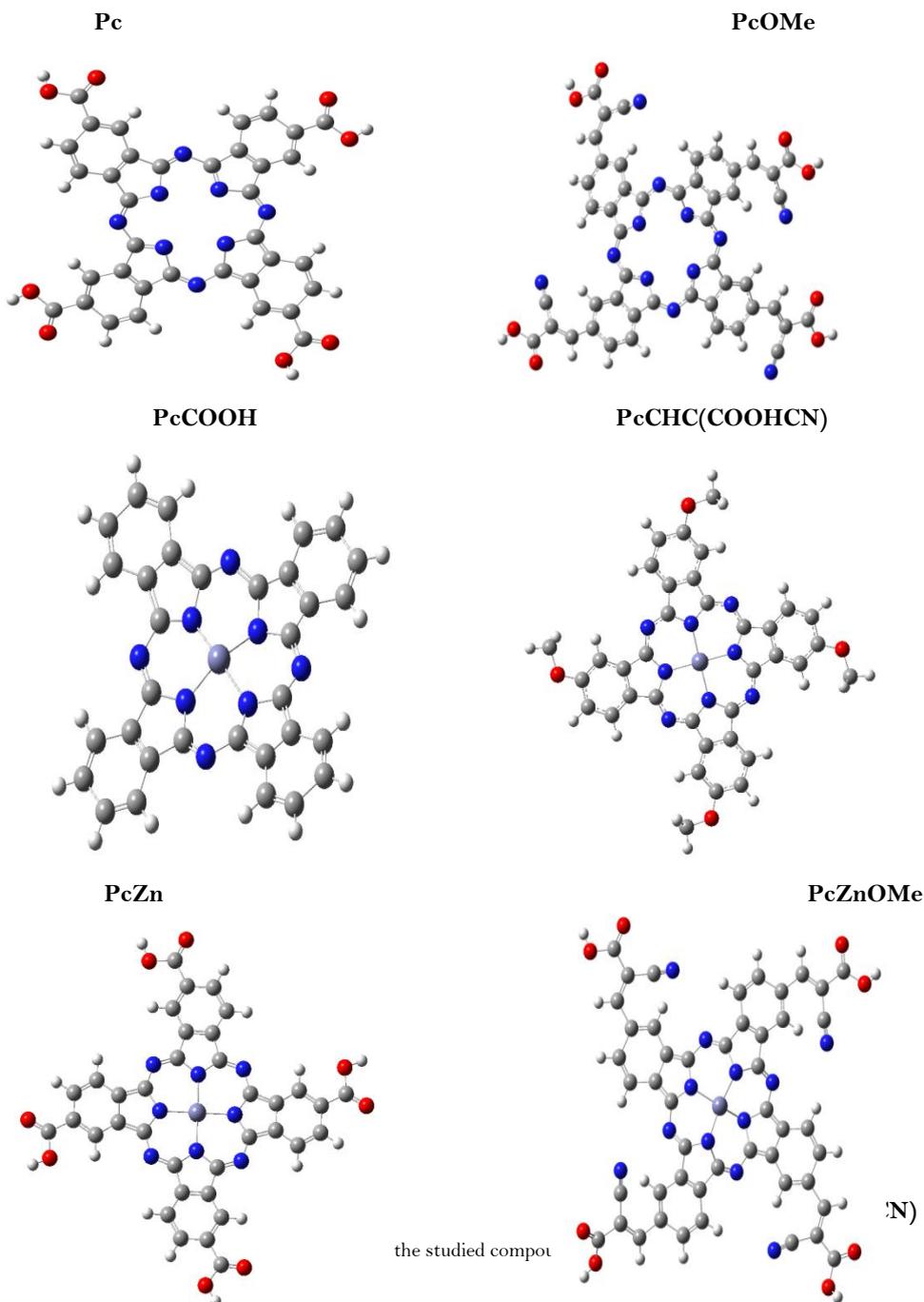
Table 1 and table 2 lists the calculated frontier orbital energies and energy Egap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the studied molecules, also the open circuit photovoltage Voc (eV) and The difference alpha between both the energy levels LUMO of the donor and acceptor PCBM structure (C60, C70, C76, C78-C2V, C78-D3, C84-D3, C84-D2, C84-D2d).

Table-1. Energy Values Of Elumo (eV), EHOMO (eV), Egap AND The Open Circuit Voltage Voc (eV) of The Non-Compexed Phtalocyanine Obtained by B3LYP/6-31G (d).

Molecules	E_{HOMO} (ev)	E_{LUMO} (ev)	Egap (ev)	PCBM C60 (A) Voc (ev)	PCBM C60 (A) alpha (ev)	PCBM C_{60} Voc (ev)	PCBM C_{60} alpha (ev)	PCBM C_{70} Voc (ev)	PCBM C_{70} alpha (ev)	PCBM C_{76} Voc (ev)	PCBM C_{76} alpha (ev)
Pc	-5.757	-4.08	1.67	1.757	-0.38	1.987	-0.61	1.917	-0.54	1.667	-0.29
PcOMe	-5,337	-2,936	2,401	1.337	0.764	1.567	0.534	1.497	0.604	1.247	0.854
PcCOOH	-6.197	-3.690	2,507	2.197	0.01	2.598	-0.22	2.357	-0.15	2.106	0.1
PcCHC(COOHCN)	-6.368	-4.184	2.18	2.368	-0.484	2.598	-0.714	2.528	-0.644	2.278	-0.394
PCBM C60 (A)	-6.1	-3.700									
PCBM C60	-	-3.470									
PCBM C70	-	-3.540									
PCBM C76	-	-3.790									

Molecules	E_{HOMO} (ev)	E_{LUMO} (ev)	Egap (ev)	PCBM C78-C_{2V} Voc (ev)	PCBM C78-C_{2V} alpha (ev)	PCBM C_{84-D3} Voc (ev)	PCBM C_{84-D3} alpha (ev)	PCBM C_{84-D2} Voc (ev)	PCBM C_{84-D2} alpha (ev)	PCBM C_{84} Voc (ev)	PCBM C_{84} alpha (ev)
Pc	-5.757	-4.08	1.67	1.517	-0.14	1.457	-0.8	1.477	-0.1	1.517	-0.13
PcOMe	-5,337	-2,936	2,401	1.097	1.004	1.037	1.064	1.057	1.044	1.087	1.014
PcCOOH	-6.197	-3.690	2,507	1.957	0.25	1.897	0.31	1.917	0.29	1.947	0.26
PcCHC(COOHCN)	-6.368	-4.184	2.18	2.128	-0.244	2.068	-0.184	2.088	-0.208	2.118	-0.234
PCBM C_{78}-C2V		-3.94									
PCBM C_{84}-D3		-4.00									
PCBM C_{84}-D2		-3.98									
PCBM C_{84}-D2d		-3.95									

Table-2. Energy Values of Elumo (eV), Ehomo (eV), Egap and the Open Circuit Voltage Voc (eV) of the Zinc Phthalocyanine Obtained by B3LYP/6-31G (d).

Molecules	E_{HOMO} (ev)	E_{LUMO} (ev)	Egap (ev)	PCBM C60 (A) Voc (ev)	PCBM C60 (A) alpha (ev)	PCBM C_{60} Voc (ev)	PCBM C_{60} alpha (ev)	PCBM C_{70} Voc (ev)	PCBM C_{70} alpha (ev)	PCBM C_{76} Voc (ev)	PCBM C_{76} alpha (ev)
PcZn	-5.190	-2.879	2, 311	1.190	0.803	1.420	0.591	1.35	0.661	1.100	0.911
PcZnOMe	-5.257	-3.004	2,253	1.257	0.696	1.487	0.466	1.417	0.536	1.167	0.786
PcZnCOOH	-5.691	-3.465	2,226	1.691	0.215	1.921	0.005	1.851	0.075	1.601	0.325
PcZnCHC(COOHCN)	-5.682	-3.705	1.970	1.682	-0.005	1.912	-0.235	1.842	-0.165	1.592	0.085
PCBM C60 (A)	-6.1	-3.700									
PCBM C60	-	-3.470									
PCBM C70	-	-3.540									
PCBM C76	-	-3.790									

Molecules	E_{HOMO} (ev)	E_{LUMO} (ev)	Egap (ev)	PCBM C78-C_{2V} Voc (ev)	PCBM C78-C_{2V} alpha (ev)	PCBM C_{84-D3} Voc (ev)	PCBM C_{84-D3} alpha (ev)	PCBM C_{84-D2} Voc (ev)	PCBM C_{84-D2} alpha (ev)	PCBM C_{84} Voc (ev)	PCBM C_{84} alpha (ev)
PcZn	-5.190	-2.879	2.311	0.950	1.061	0.89	1.121	0.91	1.101	0.940	1.071
PcZnOMe	-5.257	-3.004	2.253	1.017	0.936	0.957	0.996	0.977	0.976	1.007	0.946
PcZnCOOH	-5.691	-3.485	2.206	1.451	0.455	1.391	0.515	1.411	0.495	1.441	0.465
PcZnCHC(COOHCN)	-5.682	-3.705	1,97	1.442	0.235	1.382	0.295	1.402	0.275	1.432	0.245
PCBM C_{78-C2V}		-3.94									
PCBM C_{84-D3}		-4.00									
PCBM C_{84-D2}		-3.98									
PCBM C_{84-D2d}		-3.95									

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 and Table 2.

The LUMO energies of Mi (i = 1-8) change significantly by the introduction of metal. This implies the nature of substituted and the metal plays key roles on electronic properties and the effect of structural variations, especially the effect of metal Zn. The variation of the HOMO and LUMO energies is clearly visible. The calculed band gap of phthalocyanine and phthalocyanine substituted are classified in the following order:

$E_g(PcCOOH) > E_g(PcOMe) > E_g(PcCHC(COOHCN)) > E_g(Pc)$

On the other hand, the band gap of Zinc phtalocyanine and Zinc phthalocyanine substituted are classified in the following order:

$E_g(PcZn) > E_g (PcZnOMe) > E_g (PcZnCOOH) > E_g (PcZnCHC(COOHCN))$

From the above analysis, we noted that the LUMO energy levels of the studied molecules are much higher than that of the ITO conduction band edge (-4.7 eV). Thus, the studied molecules Pc, PcOMe, PcCOOH, PcCHC(COOHCN), PcZn, PcZnOMe, PcZnCOOH and PcZnCHC(COOHCN) have a strong ability to inject electrons into ITO electrodes. The experiment phenomenon is quite consistent with previous literature [22]. It is known that the architecture of photoactive layer is one of the principle factors of 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 [23]. In our study, properties of PCBM and derivatives (C_{60}, C_{60A}, C_{70}, C_{76}, C_{78-C2V}, C_{78-D3}, C_{84-D2}, C_{84-D2d}) were included for comparison purposes (fig.3).
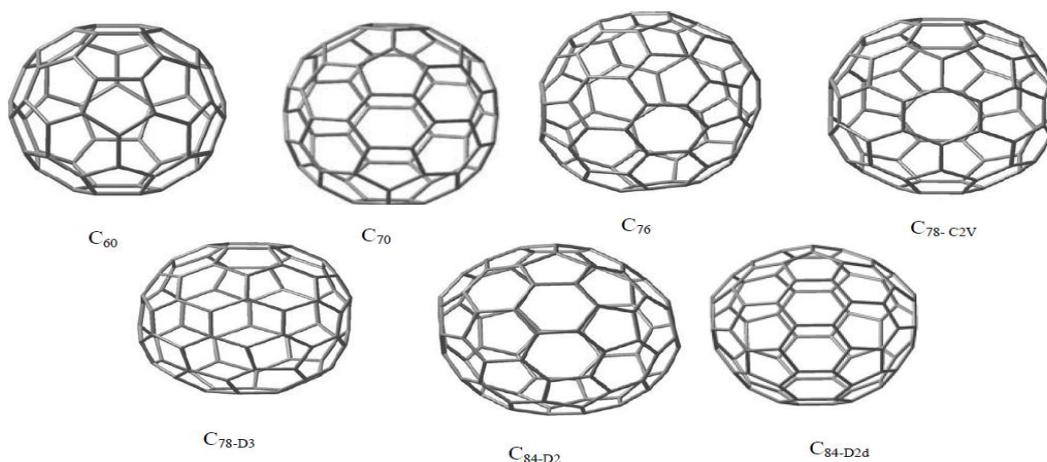
Fig-3. Structure of the investigated fullerenes

As shown in table 1and table 2 both HOMO and LUMO levels of the majority of the studied molecules agree well with the requirement for an efficient photosentizer. It should be noted that the parameter alpha the studied compounds(PcOMe,PcCOOH,PcZn,PcZnOMe and PcZnCOOH) is positif their LUMO levels are higher than that of PCBM derivatives which varies in literature from -4.0 to -3.47 eV (C60 (-3.47 eV) ;C70 (-3.54 eV); C76 (-3.79 eV); C78- C2V (-3.94 eV) ; C78-D3 (-4.0 eV) ; C84-D2 (-3.98 eV) and C84-D2d (-3.95 eV) [9].

Accordingly, the large donor acceptor area can favor charge separation and, hence, increases the conversion efficiency of the cell [24]. To evaluate the possibility of electron transfer from the studied molecules to the conduction band of the proposed acceptors, 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 derivatives in our case). Taking into account the energy lost during the photo-charge generation [25]. The theoretical values of open-circuit voltage Voc have been calculated from the following expression:

Voc = │ EHOMO (Donnor) │ - │ ELUMO (accepteur) │ - 0,3

The obtained values of Voc of the studied molecules calculated according to the equation (1) range from (1.251 eV to 1.516 eV) for PCBM C60(A);(1.481 eV to 1.746 eV) for PCBM C60; (1.411eV to 1.676 eV) for PCBM C70; (1.161 eV to 1.426 eV) for PCBM C76; (1.011 eV to 1.276 eV) for PCBM C78-C2V; (0.951 eV to 1.216 eV) for PCBM C78-D3 ; (0.971 eV to 1.236 eV) for PCBM C84-D2 and (1.001 eV to 1.266 eV) for PCBM C84-D2d (see Table 1 and Table 2).
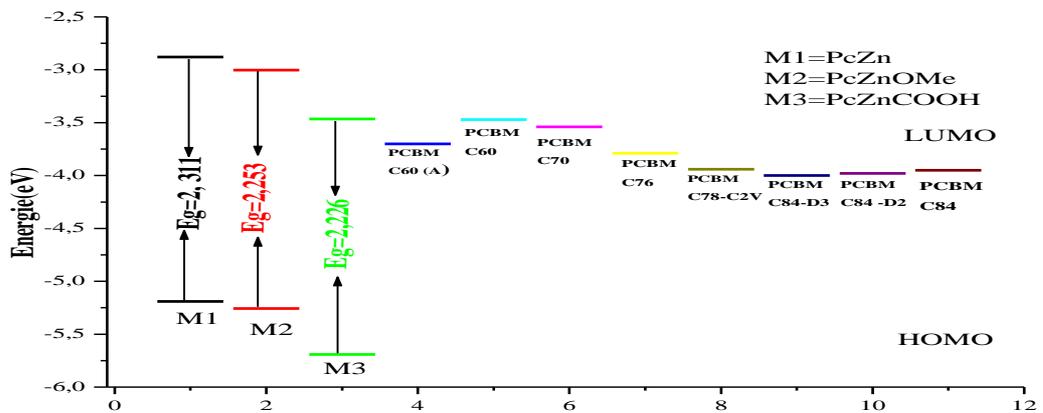
Fig-4. Sketch of DFT/B3LYP/6-31G (d) calculated energy of the HOMO, LUMO levels of studied molecules.
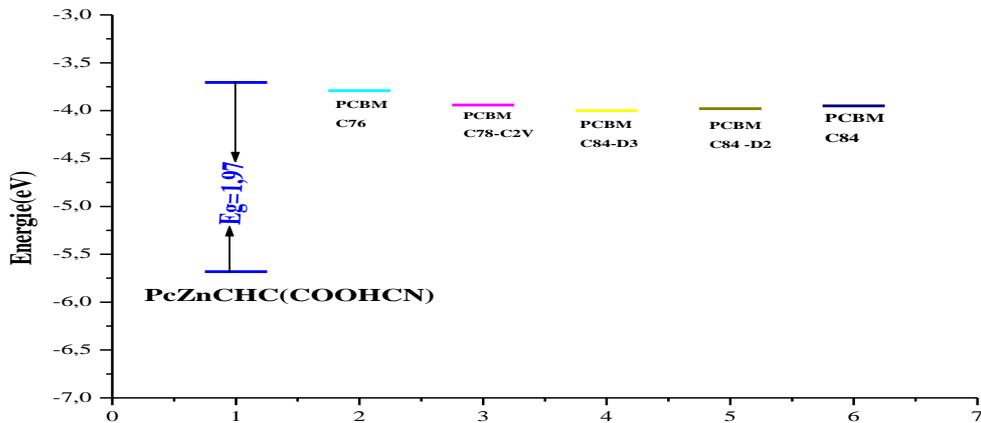
Fig-5. Sketch of DFT/B3LYP/6-31G (d) calculated energy of the HOMO, LUMO levels of PcZnCHC(COOHCN) molecules

These values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as organic solar cell because the electron injection process from the excited molecule to the conduction band of PCBM derivatives and the subsequent regeneration is possible LUMO (D)> LUMO (A)) in the organic-sensitized solar cell. Except for PCBM $C_{60(A)}$, PCBM C_{60} and PCBM C_{70} cannot be used as an acceptor for PcZnCHC(COOHCN) or non-complexed

molecules Pc and PCCHC(COOHCN) since values of LUMO are of these molecules much lower LUMO (D)< LUMO (A)) Therefore the introduction of metal reduces the value of LUMO then studied molecules can be used as organic solar cell, because the electron injection process from the excited molecule to the conduction band PCBM derivatives and subsequent regeneration is possible LUMO (D)> LUMO (A)) in the organic-sensitized solar cell. Except for C_{60}, $PCBM_{60}(A)$, and PCBM C_{70} cannot be used as an acceptor for PcZnCHC(COOHCN) (fig.5).

On the other hand, 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 [26]. In general, as shown in (fig.6) (LUMO, HOMO), the HOMO of these molecules in the neutral form possess a π-bonding character and a π-antibonding character between the consecutive subunits while the LUMO possess a π-antibonding character and a π-bonding character between the subunits whereas it is the opposite in the case of doped forms.

Distribution of HOMO orbitals for uncomplexed phthalocyanine molecule is well developed at the center. However after complexation by Zn metal, it is clear that the LUMO orbital have a weak distribution on the central zinc atom. Thus the effect of the substitution is cleary seem in the LUMO orbital energy distributed in the aromatic rings (benzene and pyrroles) of PcZn.

	HOMO	**LUMO**
Pc		
PcOMe		
PcCOOH		
PcCHC(COOHCN)		

	HOMO	**LUMO**

PcZn

PcZnOMe

PcZnCOOH

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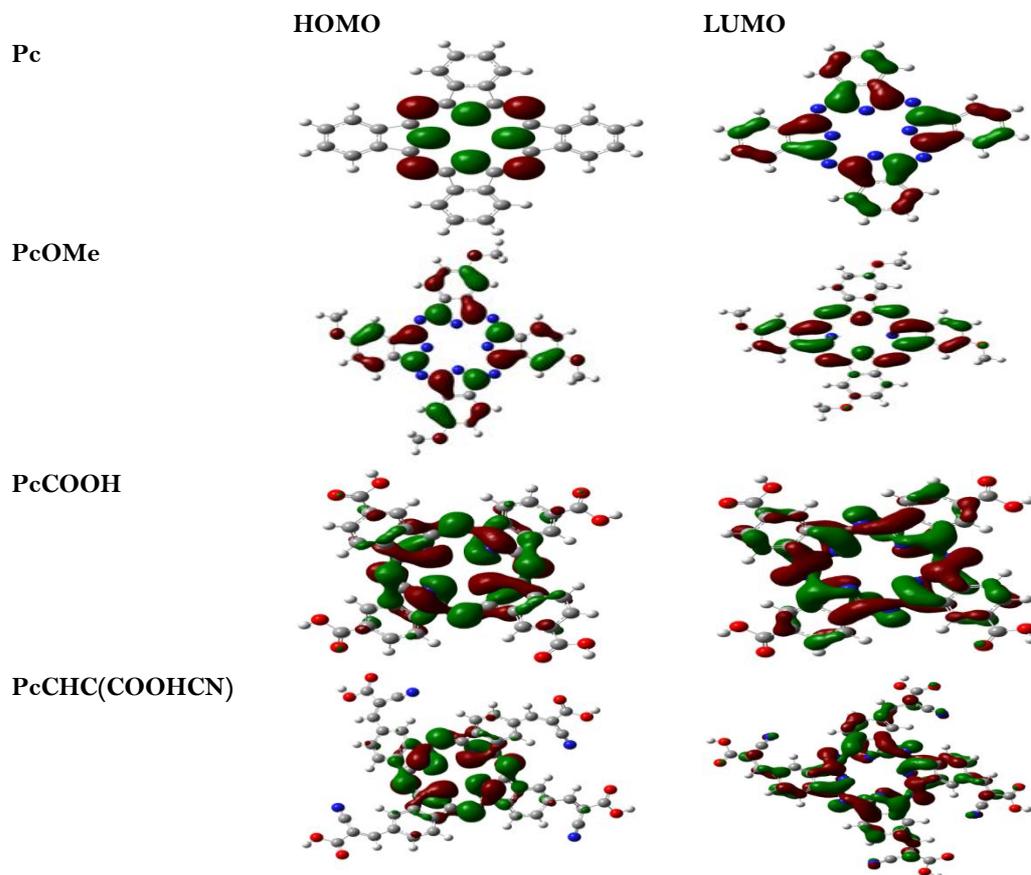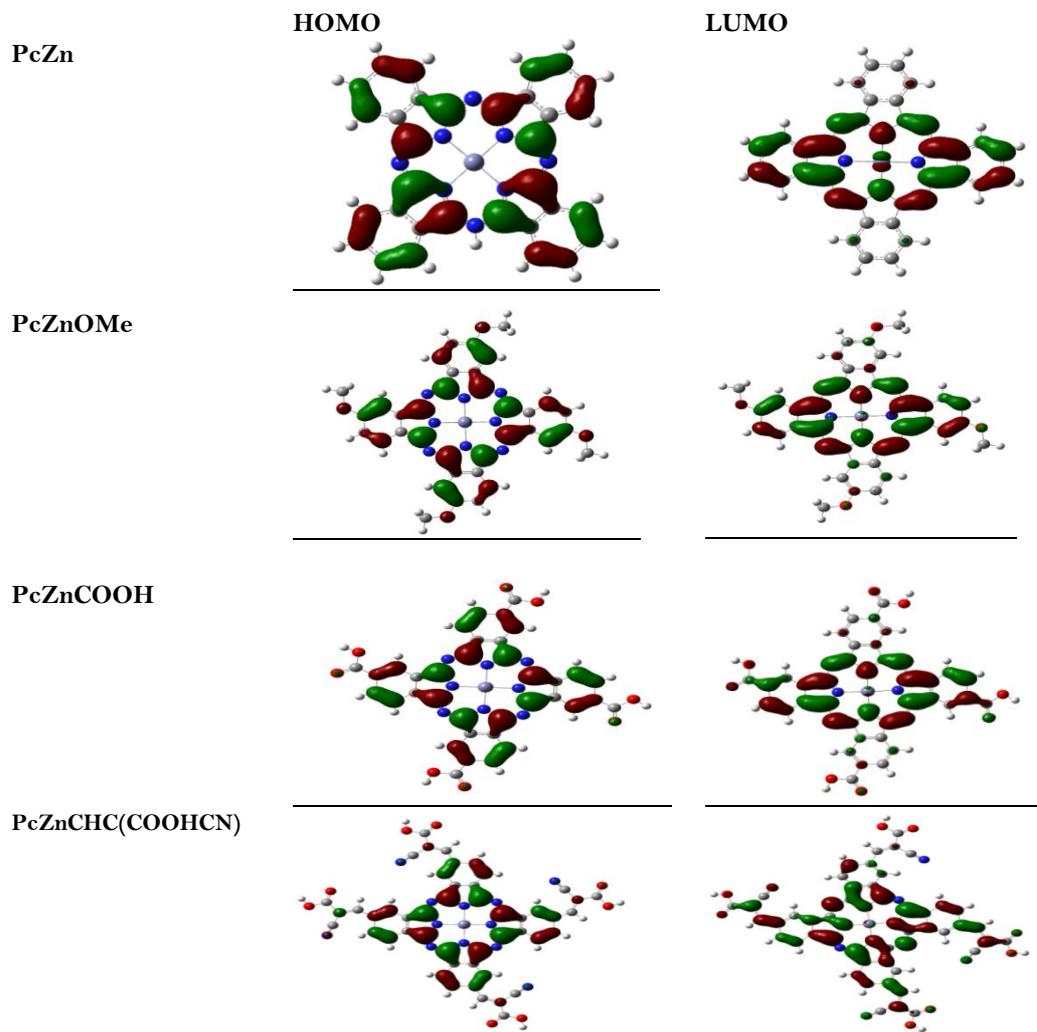
Fig.6. Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level.

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 using TD-DFT starting with optimized geometry obtained at B3LYP/6-31(d) level. The corresponding simulated UV–Vis absorption spectra of Mi, presented as oscillator strength against wavelength, are shown in Figure 6. As illustrated in table II, we can find the values of calculated absorption λ abs(nm) and oscillator strength (O.S) of the studied compounds Mi.

The calculated wavelength λabs of the studied compounds decreases in the following order PcZnCHC(COOHCN) >PcZnOMe >PcZnCOOH>PcZn   which is the same order of the reduction of the acceptor strength. This bathochromic effect of PcZn and PcZnR is obviously due to increased **λ** delocalization. In addition, we note that the broader absorption peak means that

there is a distribution of energy level corresponding to π-π* transition. 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 showing that the LUMO energy is de decreasing on the contrary to increase of the HOMO energy. Data in table 3 shows that there is a bathochromic shift when passing from Molecule PcZn (594.44nm) to Molecule PcZnCOOHCN (646.01). 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 Molecules Mi (1 to 4) Compounds at B3LYP/6-31G (d) Optimized Geometries.

	transition	λ_{abs}(nm)	E_{S0-S1}	O S	MO /character
PcZn	$S_0 \longrightarrow S_1$	594.44	2.0857	0.2292	HOMO -LUMO
	$S_0 \longrightarrow S_2$	584.51	2.1211	0.216	HOMO -LUMO+1
	$S_0 \longrightarrow S_3$	530.20	2,338	0.0020	HOMO-1-LUMO
PcZnOMe	$S_0 \longrightarrow S_1$	614.74	2.0103	0.2010	HOMO-LUMO
	$S_0 \longrightarrow S_2$	603.80	2.053	0.2417	HOMO-LUMO
PcZnCOOH	$S_0 \longrightarrow S_1$	600.05	2.0662	0.4809	HOMO -LUMO
	$S_0 \longrightarrow S_2$	599.58	2.0679	0.4759	HOMO – LUMO+1
	$S_0 \longrightarrow S_3$	436.25	2.8420	0.0000	HOMO-1 -LUMO
PcZnCHC(COOHCN)	$S_0 \longrightarrow S_1$	646.01	1.9192	0.5939	HOMO -LUMO
	$S_0 \longrightarrow S_2$	613.05	2.0224	0.6359	HOMO – LUMO+1
	$S_0 \longrightarrow S_3$	494.71	2.5062	0.0435	HOMO – LUMO+2
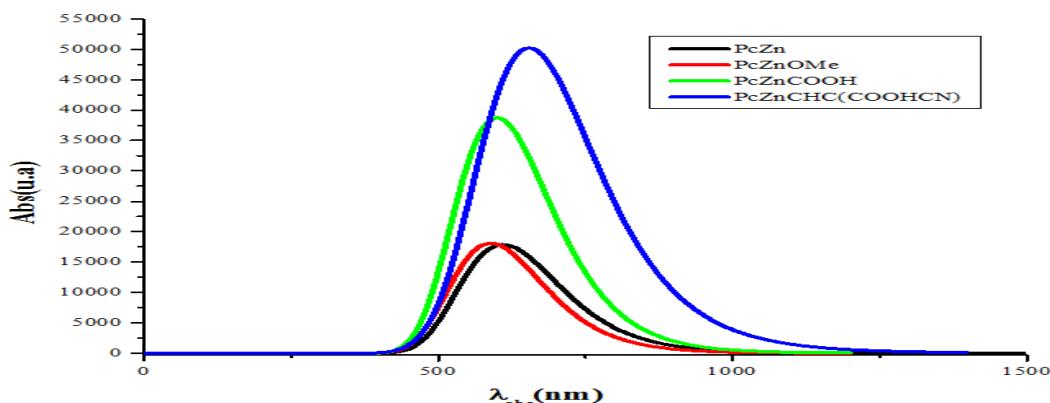
Fig-7. Simulated UV–visible optical absorption spectra of title compounds with calculated data at the TD-DFT/B3LYP/6- 31G(d).

The Scharber model allows to evaluate the efficiency of power conversion for the materials used in photovoltaic applications. The percentage is estimated from the difference between the LUMO energy of the donor and acceptor according to the gap of the donor (fig.8). The percentage values of conversion are presented in the table (4), according to these values; we can choose the best acceptor with an efficiency of the maximum conversion. In Our materials, the

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most effective acceptors are: $PCBMC_{60}$, $PCBMC_{70}$, $PCBMC_{76}$ and $PCBMC_{78-C2V}$. For PcZn, PcZnOMe, PcZnCOOH and PcZnCHC (CNCOOH) the conversion efficiency of 5%, 6%, 7% and 8% respectively.

Tbale-4. Summary Estmates of Ultimate Power Conversion Efficiency of Organic Donor Acceptor Solar Cells

	PcZn	PcZnOMe	PcZnCOOH	PcZnCHC(COOHCN)
PCBMC60(A)	4%	5%		
PCBMC60	5%	[5-6]%		
$PCBMC_{70}$	[4-5]%	6%		
$PCBMC_{76}$	4%	[4-5]%	7%	
$PCBMC_{78-C2v}$	[3-4]%	4%	[6-7]%	8%
$PCBMC_{84-D3}$	3%	[3-4]%	6%	
$PCBMC_{84-D2}$	3%	[3-4]%	6%	
$PCBM_{C84-D2d}$	[3-4]%	4%	6%	
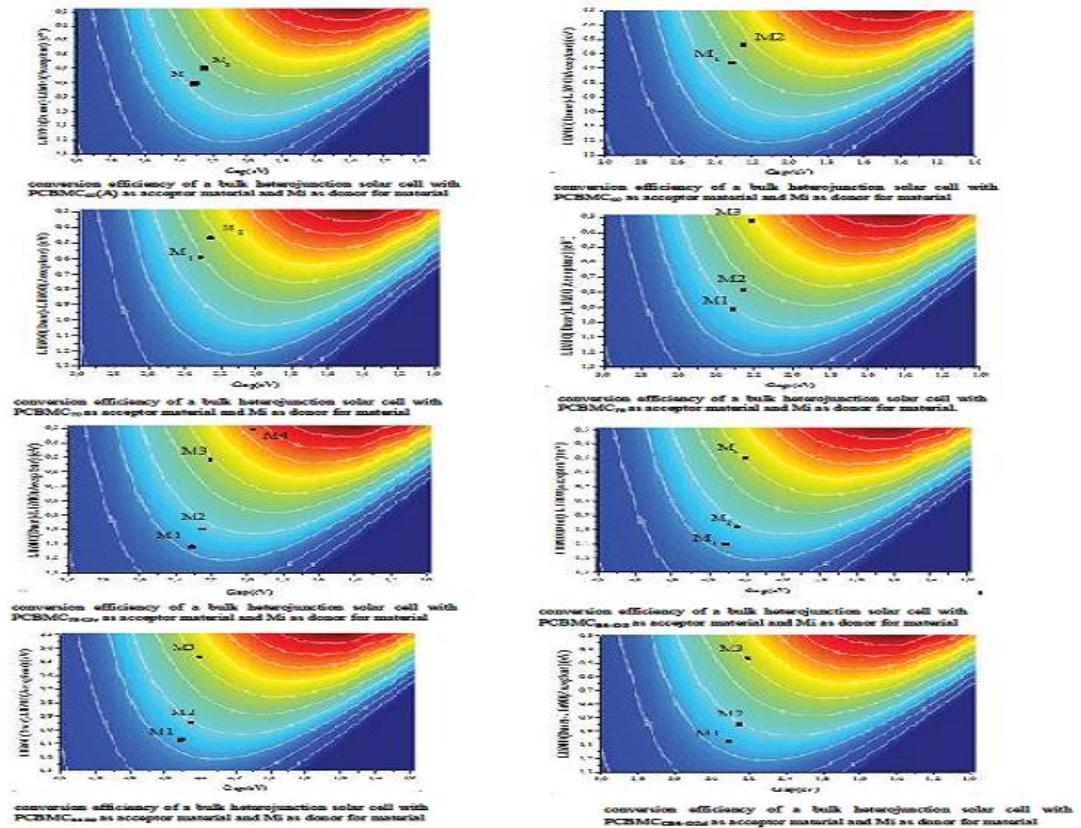
Fig-8. Conversion efficiency of a bulkheterojunction solar cell with PCBM and derivatives as acceptor material and Mi as donor for material.

5. CONCLUSION

This study is a theoretical analysis of the geometries and optoelectronic properties of three various compounds based on the phtalcyanine 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 show 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 energy HOMO and LUMO and energy Egap showed that the energy Egap of the studied molecules differ slightly from 1,970eV to 2.311eV depending on the different structures.

-The energy gap of molecule PcZnCHC(COOHCN) is much smaller than that of the other compounds.

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

- In our materials, the most effective acceptors are: PCBMC60, PCBMC70, and PCBMC76 PCBMC78-C2V. For PcZn, PcZnOMe, PcZnCOOH and PcZnCHC (CNCOOH), the conversion efficiency is about 5%, 7%, 7% and 8% respectively.

- the above results, PcZnCH(COOHCN) composite seems to be a good candidate for photovoltaic application due to its Voc value and its absorption range which is broader than the range of absorption of other copolymers. Based on Scharber model the maximum power-conversion efficiency of the photovoltaic solar cell, with PcZnCHC(COOHCN): $PCBMC_{78-C2v}$ composite as active layer, was around 8%.

-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. 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 cell.

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