

Theoretical Investigation of New Organic Electroluminescent Materials Based on 4-Azaindole Groups and Oligopyrrole

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Abstract

The electronic properties of four new organic compounds (I-IV) were studied theoretically for application as hole-transporting materials in electroluminescent (EL) devices. We investigated theoretically, the effect of increasing number of pyrrole rings between 4-azaindole end moieties. The time dependent density functional theory (TD-DFT/B3LYP/6-31G(d)) calculated energy gap (E-gap) of the studied compounds decreases in the order of I>II>III>IV; the significant reduction of E-gap of compound IV with 2.7 eV compared to 4.27 eV of compound II is due to the bridging effect of C=C(CO₂H)₂ which remove the steric effect, caused by high dihedral angle between two central pyrrole rings in the non-bridged II. Compound IV possess low-lying lowest occupied molecular orbital (LUMO) energy levels and low lying highest occupied molecular orbital (HOMO) energy levels, may be promising candidate for hole transporting and bright blue to red emitting layer in organic light emitting device (OLED) fabrication.

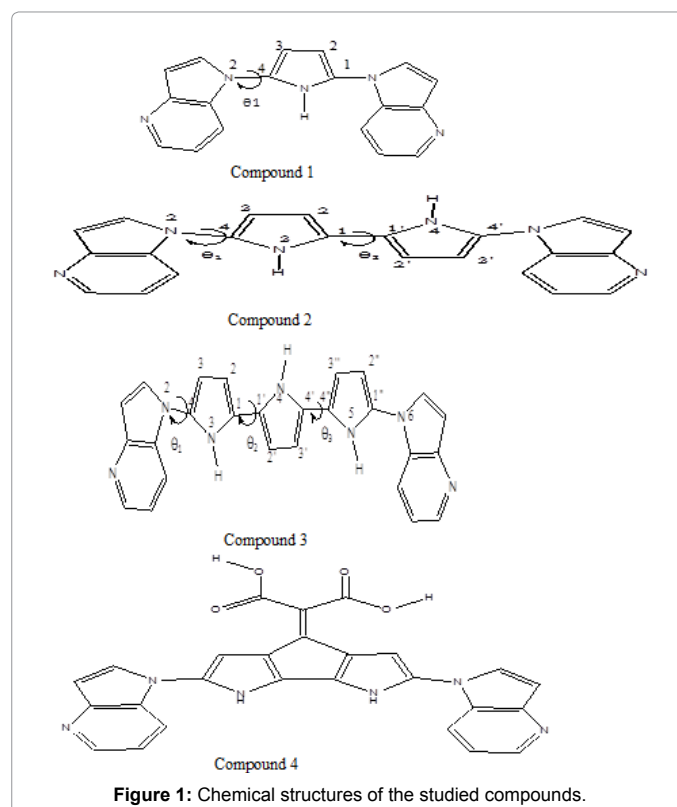
Keywords: Hole-transporting material; Electroluminescent device; Organic light emitting device; Photoluminescence; Chemical structures

Introduction

The study of organic electroluminescence (EL) materials is now a rapidly developing field of material science due to promising practical applications [1]. In spite of the impressive achievement of the last decade, the problem of searching for new effective organic luminescent materials of different emission colours is still topical. Recently, many electronic and optical-electronic devices consisting of organic materials have been demonstrated; organic light emitting devices (OLEDs) require lower energy input, have a wider viewing angle with improved colour contrast, and can be made much thinner. The use of π -conjugated organic compounds as electroluminescent materials in organic light-emitting devices (OLEDs) was originally introduced by Van Slyke over two decades ago [2,3]. Since then, the development of new π -conjugated compounds especially small molecules with superior physical, optical, thermal, and electrochemical properties has become one of the most reviving research areas [4]. Although many fluorescent blue emitters have been reported, such as anthracene derivatives, phenylene derivatives, pyrene derivatives, fluorene derivatives, carbazole derivatives, triarylamine derivatives, and phosphorescent iridium complexes, there is still a clear need for further improvements in terms of efficiency and colour purity compared to red and green emitters [5].

A new type of luminescent compounds based on Oligomers and azaindolyl groups were prepared by Hong et al. [5]. The presence of 4-azaindole moieties at the end group of oligopyrrole greatly enhanced the photoluminescence by increasing the intrinsic stiffness of the polymer backbone; weaken intermolecular interaction [6-8]. The emission spectrum of a conjugated polymer depends basically on its π - π^* band gap, which can be tailored using different structures. In this paper, we present a theoretical study of four new organic electroluminescent material (I-IV) based on (4-azaindolyl) oligopyrrole. We investigated theoretically, the effect of increasing pyrrole ring on 4-azaindole moieties on the structural and optical-electronic properties of the compounds. Then, bridging effect was studied by bridging two central pyrrole rings with electron withdrawing 2-carboxylpropenoic acid group [C=C(CO₂H)₂].

The chemical structures of the materials studied are shown in Figure 1.



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Computational Method

Quantum chemical calculation of the ground state molecular structures of (I-IV) were performed using the Spartan'14 program package on HP 2000 inter (R) core (TM) i3-3110 (M) CPU @ 2.40 GHz processor machine (computer) having 6.00 GB installed memory (RAM) and 750 GB hard disc. The molecules were drawn with SPARTAN' 14 graphical user interface (GUI) and the energy minimization conducted using MMFFaq (Merck Molecular Force Field). MMFFaq, Molecular Mechanics Conformational Distribution gave rise to different conformers for each of the studied compounds with their corresponding energies. The most stable conformer (i.e. conformer with the lowest energy) obtained for each compounds were submitted into SPARTAN' 14 for energy optimization. The influence of increasing number of pyrrole rings on the opto-electronic properties of all the studied compounds were fully optimized at Density Functional Theory (Becke's Three Parameter Hybrid Functional using the Lee, Yang and Parr Correlation Functional-B3LYP) [8]. The basis sets: 6-31G (d) and EDF2 were used for all atoms. We have also examined HOMO and LUMO energies levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. The electronic transition properties, which include the maximum excitation wavelength ($\lambda_{\text{max}}^{\text{abs}}$), excitation energy, relative intensities (oscillating strength), molecular orbitals character and coefficient of the compounds, were studied using Time Dependent Density Functional Theory (TD-DFT) [9].

Results

Optical-electronic properties

The electronic properties of all the studied compounds were obtained by DFT calculations at B3LYP/6-31G (d) and EDF2/6-31G (d) levels. Table 1, Figures 2 and 3 show the analysis of HOMO-LUMO energy gap of the studied compounds.

Highest occupied molecular orbital (HOMO) represents the ability to donate an electron and negative values of HOMO energy is taken as the ionization potential. Using Polarized basis set of B3LYP/6-31G (d), it was found that ionization potential gradually decreased with increasing of the π -conjugation system. The HOMO energy levels of these materials were in the range of -5.75 to -4.83 eV, matching well with most work function of indium tin oxide (ITO) electrode and favouring the injection and transport of holes. Their LUMO energy levels were in the range of -0.91 to -0.81 eV. The HOMO-LUMO energy gaps were calculated to be decreased from 4.84 eV to 4.02 eV with an increase in

	E-LUMO (eV)	E-HOMO (eV)	E-gap (eV)
Compound I (n=1)			
B3LYP/6-31G(d)	-0.91	-5.75	4.84
EDF2/6-31G(d)	-1	-5.57	4.57
Compound II (n=2)			
B3LYP/6-31G(d)	-0.85	-5.12	4.27
EDF2/6-31G(d)	-0.94	-4.98	4.04
Compound III (n=3)			
B3LYP/6-31G(d)	-0.81	-4.83	4.02
EDF2/6-31G(d)	-0.9	-4.70	3.8
Compound IV (n=2)			
Bridged with C=C(CO ₂ H) ₂			
B3LYP/6-31G(d)	-2.46	-5.16	2.7
EDF2/6-31G(d)	-2.56	-5.02	2.46

n: Number of pyrrole rings in the compound; eV: Electron volts; E-gap: LUMO-HOMO; E: Energy

Table 1: Calculated HOMO (eV), LUMO (eV) and Energy gap (eV).

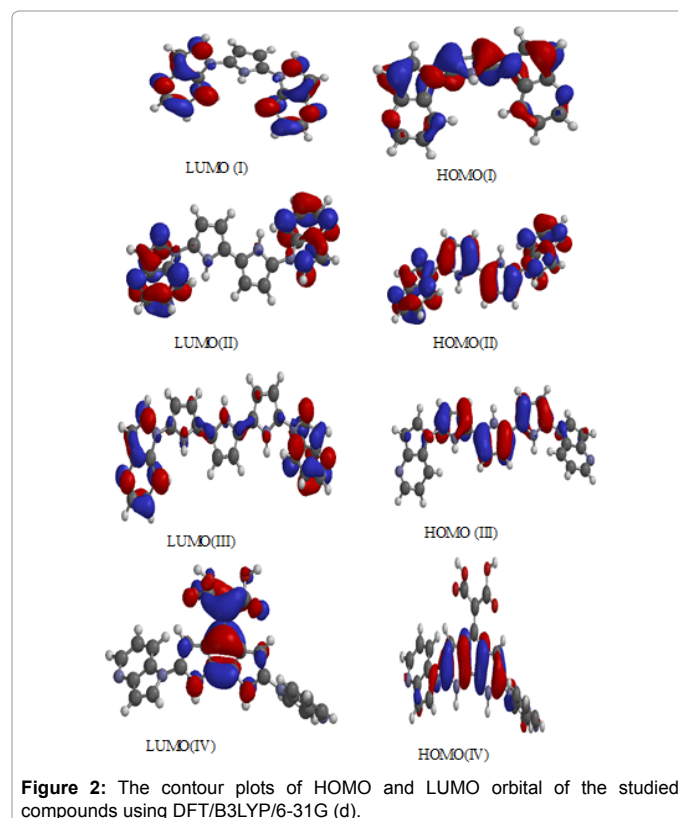


Figure 2: The contour plots of HOMO and LUMO orbital of the studied compounds using DFT/B3LYP/6-31G (d).

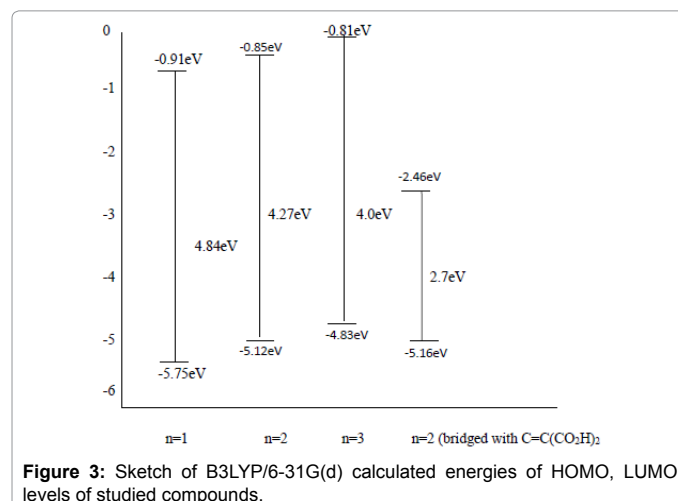


Figure 3: Sketch of B3LYP/6-31G(d) calculated energies of HOMO, LUMO levels of studied compounds.

the π -conjugation length of the oligopyrrole units of the compounds (1-3) and these values are in perfect accordance with those estimated from the electronic transition data [10-12].

The distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of studied compounds was also investigated at the DFT/B3LYP/ 6-31G (d) level for the geometry optimizations. The iso-density surface plot of HOMO and LUMO were exhibited above in Figure 2, it is seen from the figure that the electron density of HOMO is mainly localized on the pyrrolyl moieties while the electron density of LUMO is mainly on the 4-azaindole backbone except compound VI, where is localized on pyrrolyl groups with contribution from 2-carboxylpropionic acid substituent group. The electron transition from the ground state to the excited state will be

Electronic transition	λ_{abs} (nm)	Eex. (eV)	O.S.	MO/character	Coefficient
Structure I (n=1)					
S ₀ -S ₁	290.2	4.2721	0.0585	HOMO-1 LUMO	0.9732
S ₀ -S ₂	287.9	4.3068	0.006	HOMO-1 LUMO	0.97
S ₀ -S ₃	260.7	4.756	0.0117	HOMO-1 LUMO	-0.672
S ₀ -S ₄	260.6	4.7581	0.0005	HOMO-1 LUMO	-0.6897
II (n=2)					
S ₀ -S ₁	330.7	3.7499	0.0867	HOMO-2 LUMO	0.9838
S ₀ -S ₂	329.5	3.7627	0	HOMO-2 LUMO	0.9898
S ₀ -S ₃	290.3	4.2702	1.1505	HOMO-1 LUMO	0.9506
S ₀ -S ₄	261.3	4.7516	0.006	HOMO-1 LUMO	0.6028
III (n=3)					
S ₀ -S ₁	346.3	3.5803	0.1485	HOMO-2 LUMO	0.9593
S ₀ -S ₂	345	3.5934	0.0006	HOMO-2 LUMO	0.9878
S ₀ -S ₃	318.7	3.8901	1.5623	HOMO-2 LUMO	0.9496
S ₀ -S ₄	278.6	4.4502	0.0074	HOMO-1 LUMO	0.8453
IV (n=2) Bridged					
S ₀ -S ₁	639.5	1.9388	0.0145	HOMO LUMO	0.9899
S ₀ -S ₂	390.7	3.1733	0.0014	HOMOLUMO	0.9927
S ₀ -S ₃	382.7	3.24	0.0003	HOMO LUMO	0.9942
S ₀ -S ₄	362	3.4251	0.0003	HOMO-2 LUMO	0.9913

Eex: Excitation energy; O.S.: Oscillator strength; λ_{abs} : Maximum absorption wavelength; MO: Molecular orbital

Table 2: Electronic transition data for the studied compounds obtained by TD-DFT/B3LYP/6-31G (d) calculation.

electron flowing from the pyrrolyl moieties to the azaindoly moieties. The electron density distribution of HOMO and LUMO suggests that the investigated compounds might possess beneficial electron injection and transport properties with the incorporation of electron withdrawing 2-carboxylpropenoic acid group [13].

The calculated band gap (E-gap) of the studied compounds decreases in the order as follows:

I>II>III>IV. The significant reduction of E-gap of compound IV with 2.7 eV compared to 4.27 eV of compound II is due to the bridging effect of C=C(CO₂H)₂. This bridging effect causes a destabilization of both HOMO and LUMO levels; thus, producing the lowest value of the energy gap. The low HOMO energy level of compound IV with -5.16 eV suggests that the compound has high oxidation stability and potential application for charge transport material [14]. For organic polymeric chromophores, this energy gap ranges from 1.4 to 3.3 eV corresponding to light wavelength between 890-370 nm covering the visible region [15] (Table 2).

Absorption and emission properties

The absorption spectra of the studied compounds exhibited three absorption bands at 261-291 nm, 300-362 nm and 383-640 nm due to π - π^* electronic transitions. The low-energy broad band at 383-640 nm is assigned to an intra-molecular charge transfer band from the pyrrole ring to the two 4-azaindole backbone. The lowest-energy electronic transition HOMO \rightarrow LUMO consists mostly of the intra-molecular charge transfer and an average absorption band of 471 nm. Other two absorption bands occur around 339 nm and 276 nm mainly consisting of HOMO-2 \rightarrow LUMO vertical transitions and HOMO-1 \rightarrow LUMO vertical transitions respectively. The excitation energy, oscillator strength, coefficient and main configuration for most relevant absorption bands were listed in Table 2. The presence of the N-H group in the heterocyclic ring influences the excited electronic states. The first four vertical excitation energies are summarized. Only two electronic transitions from ground state (S₀) to third excited electronic state (S₃) have computed oscillator strength been higher than 0.5 while the other electronic transitions, with smaller oscillator strength have a negligible relevance in experimental works [16-19].

Conclusion

Conjugated oligomers and polymers have been studied in great details as electroluminescent materials for usage in organic light emitting devices (OLED). Azaindoly oligomers-based materials have been investigated extensively because of the many attractive properties they possess. Compound IV is the least sterically hindered and may be promising candidate for hole transporting and bright blue to red emitting layer in organic light emitting device (OLED) fabrication.

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