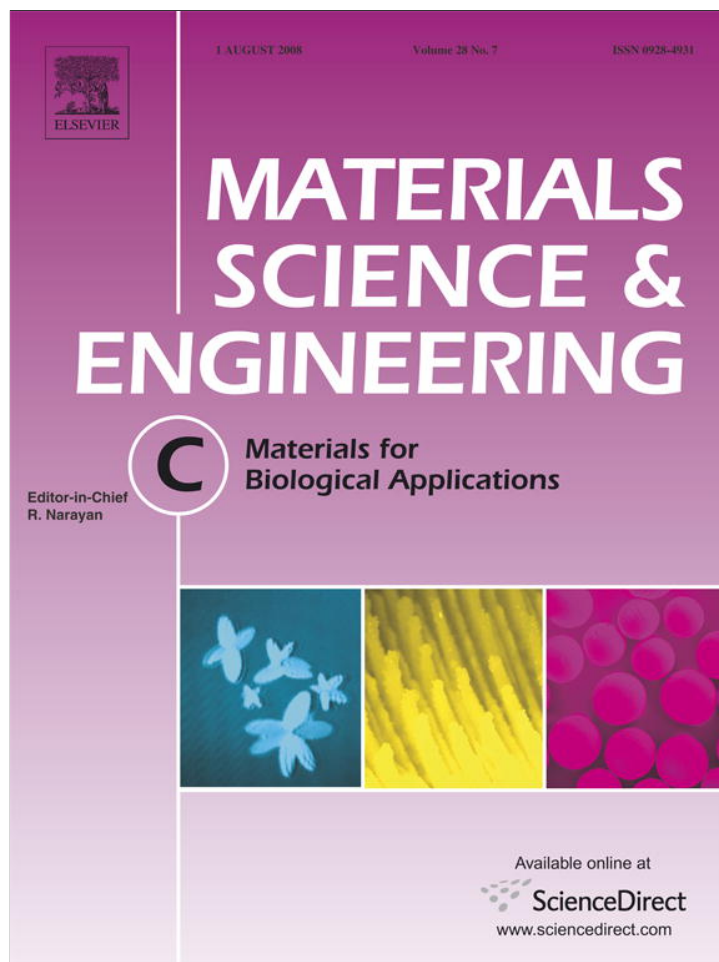


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## On the fluorescence of pyrrole derivative oligomer

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### Abstract

In this work we have investigated the ground state and others electronic properties of the biosensor 3-methyl pyrrole-4-carboxylic acid (MPC) oligomers and related compounds. We considered the systems described by a DFT/B3LYP/6-31G\* type Hamiltonian and explored the effects due to the presence of conformational defects. Furthermore the excited states have been determined by a *post* Hartree–Fock CI methodology.

The results revealed the existence of different electronic patterns for the MPC if compared to the ones existing for the oligopyrrole derivative systems. The response of one of investigated polymers (MPC) was found to be critically dependent on the radicals linked to the studied oligomer chain structure so that the electronic structure analyses should be easily improved by choosing a proper set of preparation parameters to design conducting polymers with desirable properties.

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**Keywords:** Polypyrrole; Theoretical Emission Spectra; Fluorescence; Biosensor

### 1. Introduction

Conducting polymers materials have been extensively studied during the last two decades due to their electronic, electrochemical and optical special properties. The polymers with huge fluorescence intensity have a number of potential advantages over their inorganic counterparts, such as ease of processing, cost of manufacture and greater variety. For this kind of materials, characteristics like conformational structures [1,2], electrical and ferromagnetic behaviors [3], temperature behavior, band structure [4–8] and charge carrier defects [9,10] are well established. In this class of materials the polypyrrole and poly (*para*-phenylenevinylene) derivatives present luminescent properties [11–13]. The polypyrrole has been studied as a protein sensor [14], gas sensor [15–17], junction pyrrole-C-60 [18], and

as composites of (poly)aniline/(poly)pyrrole by electrochemical methods [19]. In an earlier paper we presented the electronic structure calculations for this material systems [20]. In fact, our results showed that these polymers have interesting physical properties but also that the fluorescence process can be modified by chemical methods to yield various light colors by shifting the emission band to the red or blue side of the spectrum.

This opened interesting perspectives in terms of developing sensors based on conducting polymers. The synthesis of 3-methyl pyrrole 4-carboxylic acid (MPC) was obtained through the combined use of condensation, hydrolysis and decarboxylation techniques utilized by Cooper et al. [21]. In this work the use of MPC was reported as a working biosensor for a horse protein (the cytochrome c), but no voltametric response was observed for unsubstituted polypyrrole.

The aim of this paper is to present a theoretical investigation of the geometric, emission (fluorescence) spectroscopic and electronic density of states properties by using a new methodology based on a semiempirical calculation and a Negative Factor Counting

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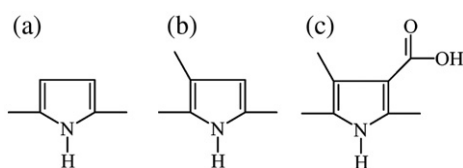


Fig. 1. Schematic representation of the monomer structure of (a) Pyrrole, (b) 3-Methyl Pyrrole and (c) 3-Methyl 4-Pyrrole acidic carboxylic.

methodology, respectively for MPC and two related (poly)pyrroles parents.

## 2. Methodology

We have considered the three structures depicted in Fig. 1. The geometry of the analyzed molecules was fully optimized using semiempirical methods from monomer (m) to pentamer (p). Semiempirical approaches such as the ones contained in MOPAC package [22,23], employed as well density functional theory (B3LYP (Becke's three-parameter hybrid method [24] with Lee, Yang and Parr correlation [18])). The standard 6-31G\* basis sets were used for all B3LYP calculations. The geometries have been carried out using B3LYP [24,25], PM3 [22] and AM1 [23] level. For MOPAC package we utilized a RMS gradient equal to  $0.05 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$ . The criteria for terminating all optimizations, electronic and geometric, were increased by a factor of 100.

The absorption spectra were obtained using the ZINDO package [26–30] with geometries fully optimized and the absorption spectra were calculated at the INDO/S-CI (Intermediate Neglect of Differential Overlap/Spectroscopy-Configuration Interaction) level, with parameters chosen to give the best description of the UV–visible optical transitions [31–34]. This level of approximation was utilized within a restricted closed-shell Hartree–Fock approach to determine the ground state. A total number of 250 configurations were considered for all molecules, including single states. Also, the emission spectra were calculated at an Intermediate Neglect of Differential Overlap/Spectroscopy-Configuration Interaction level [35] modified to simulate the fluorescence lines obtained by a modification of the original ZINDO package created by M.C. Zerner et al. which take into account the excited state geometry (singlet or triplet). We considered all the possible transitions from the first 10-UMOs (Unoccupied Molecular Orbitals) to the last 10-OMOs (Occupied Molecular Orbitals) and introduced a modification of the Mattaga–Nishimoto definition of the  $\gamma$  parameters in order to give a reasonable description of the process [36].

Local electronic density of states (DOS) were also calculated. The geometrical data used in this calculation were coupled by B3LYP geometries. The results obtained indicate that the mixtures between sigma e pi electrons are important. Therefore, we treated the system including all orbitals ( $\sigma$  and  $\pi$ ) per site and represent the electronic Hamiltonian for the  $s$ ,  $p_x$ ,  $p_y$  and  $p_z$  for atoms through first neighbor interactions with tight binding model:

$$H = \sum_i \alpha_i |i\rangle \langle i| + \beta_{i,i+1} |i\rangle \langle i+1| + h.c. \quad (1)$$

The  $\alpha$  index in the Hamiltonian corresponds to the negative of the ionization potential following the Clementi parametrization and  $\beta$  is the interaction between neighbors given by:

$$\beta_{i,i+1} = -(k/2)[I_i + I_{i+1}]S_{i,i+1} \quad (2)$$

where  $k$  is the Hückel constant equal to 2.00,  $I_i = \alpha_i$ , and  $S_{i,i+1}$  correspond to the overlap between the neighbors given by Slater type orbitals (here the geometry came from DFT calculations). The overlaps utilized was obtained by Mulliken, Slater and collaborators formulas [37,38].

## 3. Results and discussion

The neutral and polaron states of those molecules were previously investigated [16] including the absorption spectra showing the stability of these materials in the ground state and the differentiated behavior with relation to the dipole moment values and the cost for polaron formation.

For the sake of completeness we included in this paper the absorption lines of these neutral molecules, so these results allows one to see comparative effects with the new outcomes. For the discussion of the implications we suggest the reading of the paper cited above [16].

Table 1

Dipole moment and energies for calculated geometries of P, MP and MPC in the ground state and the first singlet excited states

Molecular geometry	Dipole moment (Debye)	$\Delta F$ (Kcal/mol)
P(m)	1.9	39.8
P(m) <sup>EX</sup>	1.7	140.4
P(d)	0.0	81.7
P(d) <sup>EX</sup>	2.7	176.7
P(tr)	1.8	121.4
P(tr) <sup>EX</sup>	2.9	206.4
P(tetr)	0.2	162.4
P(tetr) <sup>EX</sup>	1.4	246.4
P(p)	1.8	209.9
P(p) <sup>EX</sup>	1.5	264.5
MP(m)	1.8	31.8
MP(m) <sup>EX</sup>	3.2	134.9
MP(d)	0.0	64.5
MP(d) <sup>EX</sup>	0.0	159.7
MP(tr)	1.7	98.1
MP(tr) <sup>EX</sup>	2.7	182.0
MP(tetr)	0.2	141.0
MP(tetr) <sup>EX</sup>	1.0	213.7
MP(p)	1.7	164.5
MP(p) <sup>EX</sup>	1.6	246.1
MPC(m)	4.4	-60.8
MPC(m) <sup>EX</sup>	6.4	38.9
MPC(d)	0.8	-117.8
MPC(d) <sup>EX</sup>	0.7	-29.7
MPC(tr)	3.3	-179.2
MPC(tr) <sup>EX</sup>	4.0	-99.3
MPC(tetr)	0.3	-240.9
MPC(tetr) <sup>EX</sup>	1.8	-161.9
MPC(p)	3.4	-297.7
MPC(p) <sup>EX</sup>	2.9	-219.1

(m, d, tr and tetr denotes monomer, dimer, trimer and tetramer respectively; <sup>EX</sup> represents excited states).

Table 1 shows the dipole moments and the energies of the monomer (m), dimer (d), trimer (tr), tetramer (tetr) and pentamer (p) of P, MP and MPC, calculated using models with electronic correlation techniques. The most probable geometrical configurations of the P and MP resulted essentially planar for the ground and first singlet excited states. The oligomers dipole moments for antiparallel arrangements are almost equal to zero, if the oligomers have an even number of monomer units, or equal to an integer of the monomer dipole moment, if the oligomers have an odd number of monomer units, as would be expected from a simple summation of non-interacting monomer moments. The dipole moments and heats of formation for the excited states are collected in Table 2 and the calculation indicates that the P species have a slight deviation from planarity for the excited state (about 5° between the rings) and this result is corroborated by the analysis of dipoles showing that for the dimer and the trimer the deviation increases, but it decreases for the tetramer and the pentamer. For MP and MPC molecules the behaviour shows different pattern for odd and even rings provoked by changes on the conjugation lengths and a more detailed analysis of the electronic structure is necessary.

One important fact is that, for each compound, the heat of formation per ring drop off, as the the oligomer size increase, indicating high probabilities for the formation of the various configurations considered. The analysis of the energetic gain was carried out thought the difference between the ground and

Table 2

Principal electronic UV–vis fluorescence transitions as determined from INDO/S-CI methodology for P molecule

Molecule	W.L. (nm)	O.S.	Transition (fluorescence)
P(m)	279	0.78	0.97 L→H>
	183	0.23	0.76 L→H-1>
P(d)	351	0.79	0.99 L→H>
	190	0.68	-0.56 L+1→H>
			-0.77 L+3→H>
P(tr)	432	1.02	-0.99 L→H>
	198	0.59	0.77 L→H-4>
			0.40 L+5→H>
			-0.37 L+3→H>
P(tetr)	164	0.73	-0.65 L+4→H-1>
	475	1.37	0.51 L+1→H-2>
	294	0.18	-0.97 L→H>
	200	0.87	-0.88 L+2→H>
			-0.68 L→H-4>
P(p)			0.36 L→H-4>
			0.35 L+4→H>
	174	0.71	-0.34 L+2→H-4>
			-0.35 L+1→H-3>
			0.24 L+4→H-2>
			0.64 L+4→H-1>
	507	1.65	0.96 L→H>
	271	0.29	0.90 L+3→H>
204	1.03	-0.30 L+2→H-1>	
			-0.55 L→H-5>
			-0.46 L+1→H-4>
			0.47 L+4→H>
		0.96 L→H>	

(H and L represent HOMO and LUMO respectively). The abbreviations W.L. and O.S. denote wavelength and oscillator strength, respectively.

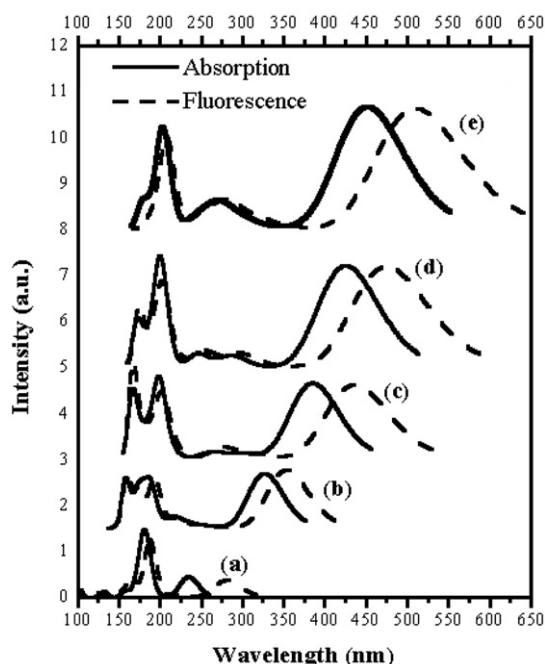


Fig. 2. Simulated absorption and fluorescence spectra of Pyrrole chain, modeled using INDO/S-CI methodology, as a function of the number of oligomer ((a) monomer, (b) dimer, (c) trimer, (d) tetramer and (e) pentamer). These functions were obtained from normalized gaussians weighted by the oscillator strength values.

excited states. One should observe that the MPC has, on the energetic gain, one order higher if compared to the P and MP values. The carboxylic acid has an important contribution on

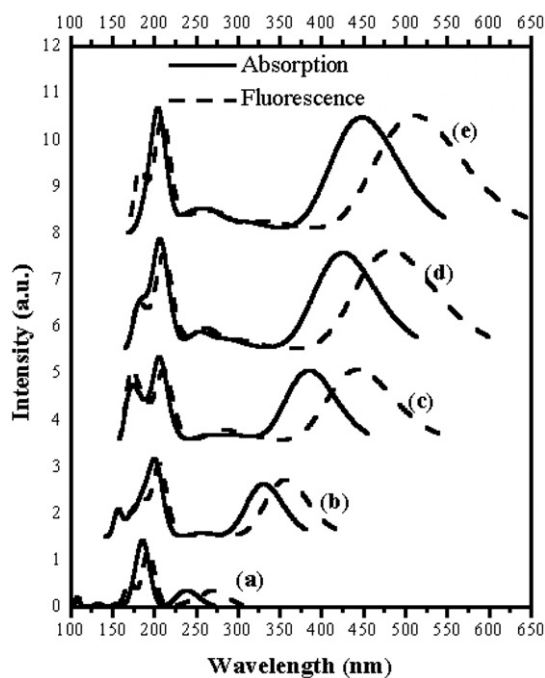


Fig. 3. Simulated absorption and fluorescence spectra of 3-Methyl Pyrrole chain, modeled using INDO/S-CI methodology, as a function of the number of oligomer ((a) monomer, (b) dimer, (c) trimer, (d) tetramer and (e) pentamer). These functions were obtained from normalized gaussians weighted by the oscillator strength values.

these values. The MPC structural analysis shows that the ratio  $\Delta F/\text{ring}$  stabilizes as the number of rings increases.

In the Figs. 2–4 it is shown the theoretical emissions and absorptions spectra for P, MP and MPC performed by ZINDO modified program. These spectra were obtained by describing each of the principal transitions using a suitably weighted Gaussian function normalized to the calculated oscillator strengths.

The emissions spectra show a red shift provoked by relaxation of the first singlet excited state and they are quite similar (monomer with monomer, dimer with dimer and so on.), with the largest band centered in the 380 nm to 520 nm region for P (monomer to pentamer). The MP has the largest band centered in 275 nm to 510 nm. For MPC the largest band is not the first (in eV) band presented provoked by a twisted angle between the rings. The nature of this difference can be understandable from the data of Table 4.

For the P molecule the most important emission line transitions are composed essentially by a single  $|L \rightarrow H\rangle$  transition corresponding to peaks at 279, 351, 475 and 507 nm of the m, d, tr, tetr and p spectra respectively (Fig. 1).

The fluorescence spectra have also other transitions correspondent to the states between  $|L+5\rangle$  and  $|H-5\rangle$ . For the MP molecule (Table 3) the important emission line transitions are composed by a mixing of several transitions and the contributions to the fluorescence spectra corresponding to states between  $|L+4\rangle$  and  $|H-4\rangle$ . In other words, less states contribute to the emission optical transitions.

Table 4 shows the main transitions for MPC molecule. The  $\pi^* - \pi$  transition corresponds to the band centered in 304, 438,

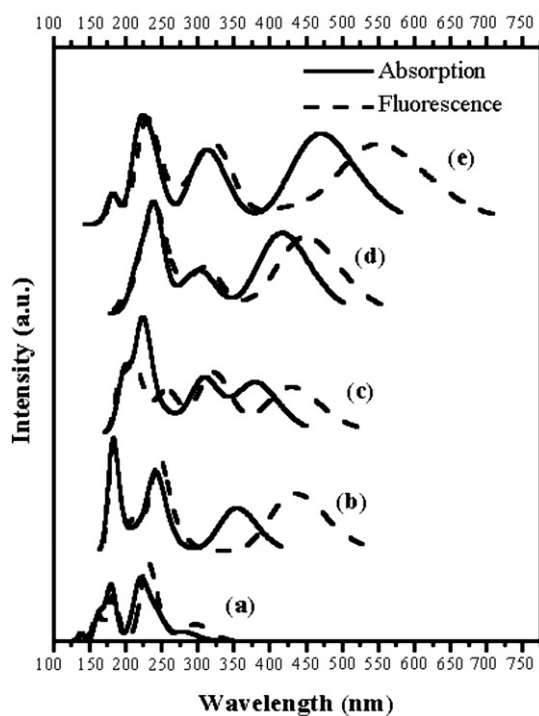


Fig. 4. Simulated absorption and fluorescence spectra of 3-Methyl Pyrrole 4-Carboxylic acid chain, modeled using INDO/S-CI and methodology, as a function of the number of oligomer ((a) monomer, (b) dimer, (c) trimer, (d) tetramer and (e) pentamer). These functions were obtained from normalized gaussians weighted by the oscillator strength values.

Table 3

Principal electronic UV–vis fluorescence transitions as determined from INDO/S-CI methodology for MP molecule

Molecule	W.L. (nm)	O.S.	Transition (fluorescence)
MP(m)	271	0.21	$-0.90 L \rightarrow H\rangle$
	187	0.75	$-0.80 L \rightarrow H-1\rangle$ $0.54 L+1 \rightarrow H\rangle$
MP(d)	355	0.76	$-0.98 L \rightarrow H\rangle$
	204	0.96	$-0.77 L \rightarrow H-2\rangle$ $0.60 L+2 \rightarrow H\rangle$
	189	0.47	$-0.50 L+2 \rightarrow H-1\rangle$ $-0.78 L+1 \rightarrow H-1\rangle$
	442	0.99	$-0.98 L \rightarrow H\rangle$
MP(tr)	288	0.13	$0.87 L \rightarrow H-1\rangle$
	206	0.43	$-0.69 L \rightarrow H-3\rangle$ $-0.38 L+3 \rightarrow H\rangle$ $-0.37 L+5 \rightarrow H\rangle$
	206	0.45	$0.71 L \rightarrow H-4\rangle$ $0.39 L+1 \rightarrow H-1\rangle$
MP(tetr)	172	0.37	$0.33 L+5 \rightarrow H\rangle$ $-0.45 L+2 \rightarrow H-5\rangle$ $-0.40 L+2 \rightarrow H-3\rangle$ $0.31 L+3 \rightarrow H-3\rangle$ $-0.37 L+3 \rightarrow H-2\rangle$
	172	0.36	$0.47 L+2 \rightarrow H-2\rangle$ $0.38 L+4 \rightarrow H-1\rangle$ $0.37 L+5 \rightarrow H-1\rangle$
	482	1.34	$0.97 L \rightarrow H\rangle$
	261	0.19	$0.51 L+4 \rightarrow H\rangle$ $-0.39 L \rightarrow H-2\rangle$
MP(p)	206	1.06	$-0.67 L \rightarrow H-4\rangle$ $0.50 L+4 \rightarrow H\rangle$
	185	0.51	$-0.58 L+5 \rightarrow H-1\rangle$ $0.40 L+4 \rightarrow H-2\rangle$
	509	1.57	$-0.95 L \rightarrow H\rangle$
MP(p)	265	0.11	$0.57 L \rightarrow H-2\rangle$ $0.53 L+3 \rightarrow H\rangle$
	265	0.12	$0.45 L \rightarrow H-2\rangle$ $-0.64 L+3 \rightarrow H\rangle$
	206	1.38	$-0.44 L \rightarrow H-5\rangle$ $-0.41 L \rightarrow H-4\rangle$
	181	0.71	$0.52 L+3 \rightarrow H-4\rangle$ $0.37 L+1 \rightarrow H-2\rangle$ $0.41 L+6 \rightarrow H-1\rangle$

(H and L represent HOMO and LUMO respectively). The abbreviations W.L. and O.S. denote wavelength and oscillator strength, respectively.

432, 453 and 560 nm for m, d, tr, tetr and p oligomers respectively. On other hand, when the molecular geometries are fully optimized the energy of the first transition changes behavior for 2 and 3 units: the energy of this transition decreases, then it increases and decreases again. However, transition distribution have shown that in all cases for MPC the  $|H\rangle$  orbital contains significant contributions to the spectra.

Also it is well-known that organic molecules (including biological molecules and conjugated molecules) have a strong triplet–triplet transition [39–43]. For three, four and five rings of MPC the singlet–singlet transition basically involves four orbitals ( $|H\rangle$ ,  $|H-1\rangle$ ,  $|L\rangle$  and  $|L+1\rangle$ ) but preliminary calculations for phosphorescence spectra show an increase of the transition levels which can be used to orient the molecule and enable the electron transfer.

The electronic density of states (DOS) are shown in Figs. 5 and 6 for polymers utilizing the Hückel methodology described

Table 4  
Principal electronic UV–vis fluorescence transitions as determined from INDO/S-CI methodology for MPC molecule

Molecule	W.L. (nm)	O.S.	Transition (fluorescence)
MPC(m)	304	0.17	0.95 L→H>
	229	0.82	-0.65 L→H-1> 0.69 L+1→H>
	178	0.46	0.61 L+1→H-1> -0.71 L+2→H>
MPC(d)	438	0.61	0.99 L→H>
	245	0.37	-0.46 L→H-3> -0.51 L+2→H> 0.59 L+4→H>
	245	0.53	0.59 L+2→H> 0.54 L+4→H>
	181	0.98	-0.48 L+1→H-3> 0.50 L+3→H-1>
MPC(tr)	432	0.48	0.93 L→H>
	432	0.55	-0.92 L+1→H>
	321	0.30	-0.74 L→H-4>
	257	0.31	-0.48 L+1→H-2> 0.42 L+2→H-2> 0.34 L+5→H>
	202	0.20	0.44 L→H-2> 0.52 L+1→H-2> 0.89 L→H>
MPC(tetr)	453	0.79	0.89 L→H>
	308	0.36	0.43 L+1→H-4> 0.42 L+1→H-2>
	308	0.44	0.45 L+1→H-3> 0.38 L+4→H-1>
	239	0.39	0.49 L+1→H-3> -0.48 L+4→H-1>
MPC(p)	560	0.80	0.72 L→H>
	310	0.45	0.53 L+1→H-1> -0.46 L+2→H>
	230	0.43	0.49 L+2→H-1> -0.39 L+3→H-1>

(H and L represent HOMO and LUMO respectively). The abbreviations W.L. and O.S. denote wavelength and oscillator strength, respectively.

above for neutral systems. Fig. 5 presents for PP, MP and MPC the quasi-1-Dimension DOS because the van Hove singularity presence and several peierls gaps.

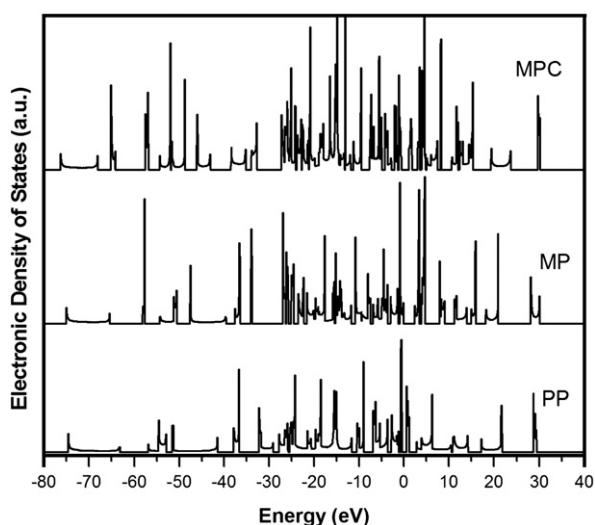


Fig. 5. Full electronic density of states for PP, MP and MPC polymers.

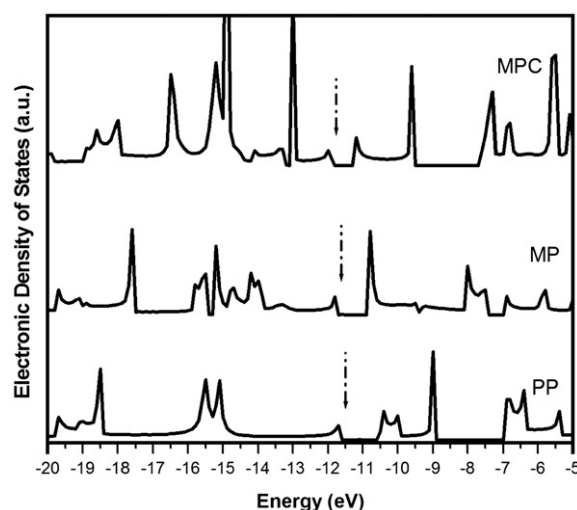


Fig. 6. Zoom around the Fermi level of electronic density of states for PP, MP and MPC polymers. The arrows indicate the position of the HOMO level.

In Fig. 6 exhibit a zoom in the peierls gap region with HOMO equal to  $-11.53$ ,  $-11.61$  and  $-11.79$  eV for PP, MP and MPC polymers, respectively.

Moreover the stokes shift in the Raman spectra increases with the chain length, in agreement with the experiment [39–43]. In general terms, one can say that the P and MP fluorescence spectrum involves a slightly larger number of LUMO levels than in the MPC case.

#### 4. Conclusions and summary

In this work we have calculated the heat of formation and the dipole moments for the neutral ground state and the first singlet excited state of pyrrole, 3-methyl pyrrole and 3-methyl pyrrole 4-carboxylic acid and the results indicate very distinguished behavior.

The analysis of spectroscopy performed by using INDO/S-CI (absorption and fluorescence spectra) with DFT/6-31G\* (geometries) points that the main transitions are due to a mixing of different possible configurations.

Further, suggest that the spectroscopy for the P and MP molecules involves a slightly larger number of unoccupied levels than in the one for MPC molecule.

One can conclude that the anomalous behavior of the protein connection of MPC goes beyond simple singlet–singlet transitions, but also relates changes in the nature of states involved, possibly an interaction of triplet–triplet coupling between the different molecules. This speculation is part of a more complete investigation of organic biosensor systems to be reported elsewhere.

The  $\pi^*-\pi$  [ $\pi-\pi^*$ ] theoretical energy gap values are 2.45 [2.74], 2.43 [2.78] and 2.25 [2.63] eV for P, MP and MPC materials, respectively.

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