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# Electronic structure investigation of biosensor polymer

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## Abstract

We report a theoretical study of the ground, excited and ionic states of 3-methyl pyrrole-4-carboxylic acid (MPC) oligomers and related compounds which present conformational defects. Our results reveal the existence of differentiated electronic behavior for MPC with relation to oligopyrrole derivatives. These electronic features might explain why MPC works properly as a biosensor for cytochrome C while no voltametric response is observed for unsubstituted poly(pyrrole).

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## 1. Introduction

The search for polymers that could effectively interact with biological systems have attracted much interest due to its potential technological applications in the areas of biological sensors, molecular electronics, surgical plasters containing active ingredients, membranes, etc. [1–8]. Recently, for instance, it has been reported in the literature direct electronic communication between functionalised, conducting polypyrrole and a redox protein in solution [9–14]. They have adopted a novel approach in order to study biological electron transport between proteins and polymeric materials using electrochemically functionalised conducting polymers to produce thin film (<10

nm). The methods employed have potential advantages over more standard techniques used in bioelectrochemistry such as that involving self-assembled monolayer (SAMs): (a) firstly, and perhaps most importantly, they have shown that polymer films can be used to modify a wider range of electrode materials than SAMs, including e.g. C, Au, Pd and Pt.

This provides a methodology where a variety of biologically significant chemical functionalities (necessary for molecular recognition) can be synthesized at the surface through prescriptive monomer synthesis; (b) the functionalised interface can be presented to the biological solution as a stable film (“fragility” of many SAMs); (c) since the polymer’s gross structure is controlled both by the applied electrochemical potential and the counter-ion used during growth, there is the possibility of changing the physical character of the film altering the polymerization conditions.

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Experimental evidences of these direct interactions between biological structures and functionalized polymers are evidenced by the modifications presented in the polymer electrochemical voltammogram [15]. Polypyrrole films have been used for the covalent binding of glucose oxidase to electrode surfaces [16]. Eddowes et al. were the first ones to study the electrochemical potential [17–19] of the cytochrome c. It has been also reported [20,21] reversible electron transfer between Au electrodes and peptide proteins. This opens interesting perspectives in terms of developing based conducting polymers biosensors. The synthesis of 3-methyl pyrrole-4-carboxylic acid (MPC) was obtaining through the combined use of condensation, hydrolysis and decarboxylation techniques [22,23].

Cooper et al. [14] reported the use of MPC as a working biosensor for cytochrome c, but no voltametric response was observed for ethyl ester MPC or unsubstituted poly(pyrrole). This has been attributed to the absence of the of the carboxylic acid groups required to orient the protein and enable electron transfer.

In this work we have theoretically investigated the geometric and spectroscopic properties of a MPC oligomers and some of its related poly(pyrrole) parent structures (Fig. 1).

## 2. Methodology

We have investigated the electronic structure of the compounds shown in Fig. 1, from monomers (m) up to pentamers (p). The geometry of their neutral ground and negative polaron (anion) states were fully optimized using the well-known semi-empirical method Austin method 1 (AM1)/(MO-

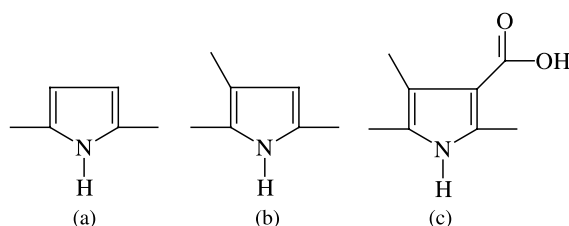


Fig. 1. Schematic representation of the monomer structure of (a) pyrrole (P); (b) MP and (c) MPC.

PAC package) [24–27]. The convergence criterion was modified from standard to maximum *step-size* to 0.005 in order to ensure good quality geometries. The simulated absorption spectra were obtained using the ZINDO-S/CI (Zerner's intermediate neglect of differential overlap—spectroscopy/configuration interaction) package [28–34] with geometries from AM1 calculations. The ZINDO calculations were carried out with parameters chosen to give the best description of the UV–Visible optical transitions [35–38] and using on average 200 configurations including singlet and doublet states.

## 3. Results and discussion

The most probable geometrical conformations for the P and 3-methyl pyrrole (MP) were found to be essentially planar structures for neutral and polaron states. The dipole moment (DM) values of the antiparallel oligomers conformations are almost equal to multiple units of the monomer value, as would be expected from a simple summation of interacting monomer moments.

Table 1  
AM1 results for the structures shown in Fig. 1, from monomer (m) up to pentamers (p)

	Meritaten	G	P	HF-G	HF-P	EP
P (m)		1.9	1.1	39.8	63.3	-1.07
P (d)		0.0	2.9	81.7	81.9	-0.01
P (tr)		1.8	2.9	121.4	108.5	0.58
P (tetr)		0.2	0.1	162.4	144.9	0.79
P (p)		1.8	1.8	209.9	203.4	0.29
MP (m)		1.8	0.6	31.8	54.1	-1.01
MP (d)		0.0	0.0	64.5	64.2	0.01
MP (tr)		1.7	2.7	98.1	85.4	0.57
MP (tet)		0.2	0.2	141.0	131.0	0.45
MP (p)		1.7	3.1	164.5	145.5	0.86
MPC (m)		4.4	4.3	-60.8	-64.4	0.16
MPC (d)		0.8	0.3	-117.8	-148.9	1.41
MPC (tr)		3.3	4.1	-179.2	-214.5	1.60
MPC (tet)		0.3	11.3	-240.9	-275.3	1.56
MPC (p)		3.4	8.3	-297.7	-337.2	1.79

DM (in Debyes) and heats of formation (HF) (in kcal/mol) values for neutral (G) and polaron (P) states are indicated. It is also indicated the values for polaron formation (EP) (in electron-Volts).

In Table 1 we present a summary of AM1 results for the structures shown in Fig. 1.

The values of the heats of formation per ring increase as the number of rings increases indicating that there is an effective electronic stabilisation as expected from the pi electron character of these structures.

The values for the DM and for the polaron formation show a quite differentiated behavior for P, MP and MPC structures. The DM values for MPC structures are higher than those for P and MP, as expected due to the presence of the carboxylic acid group. With relation to the polaron formation values there are remarkable differences for P and MP structures when contrasted to MPC ones. For P and MP structures these values are negative for the monomer, with an increase followed by a decrease (from tetramer to pentamer). For the MPC structures these values are always positives with a constant increase as a function of the number of structural units. From these values we can expect a quite differentiated electrochemical behavior, as experimentally observed.

In the Figs. 2–4 we compare the ZINDO simulated absorption spectra for P, MP and MPC from monomers up to tetramers. These spectra are generated gaussian enveloping the transition energy values weighted by oscillator strength (OS) values.

Although all spectra are similar (monomer with monomer, dimer with dimer and so on), with the largest band centered in the (a) 225–250, (b) 325–350, (c) 375–400, (d) 425–450 and (e) 450 nm region, there are a few differences in the nature of the transitions as we can observe from Table 2.

For P and MP structures the most important transitions are composed essentially by a mixing of  $|H \rightarrow L\rangle$  and  $|H - 1 \rightarrow L + 1\rangle$  configurations with an OS values between 0.7 and 1.4. For MPC structures the most important absorption lines corresponds to different possible transitions,  $|H \rightarrow L\rangle$ ,  $|H - 2 \rightarrow L\rangle$ ,  $|H \rightarrow L + 2\rangle$ ,  $|H \rightarrow L + 1\rangle$ .

For all the structures we observe significant and continuous red shift as the number of units increases, as expected from polymeric systems with effective electronic couplings. Also we observe little differences from trimers to tetramers, suggesting

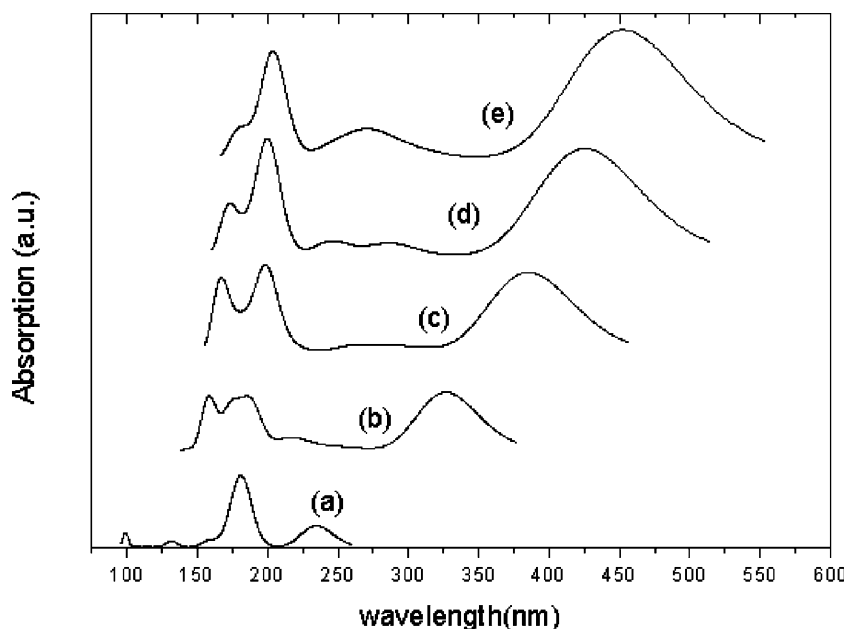


Fig. 2. Simulated absorption spectra of pyrrole chains from ZINDO calculations, as a function of the number of units: (a) monomer; (b) dimer; (c) trimer; (d) tetramer, and (e) pentamer.

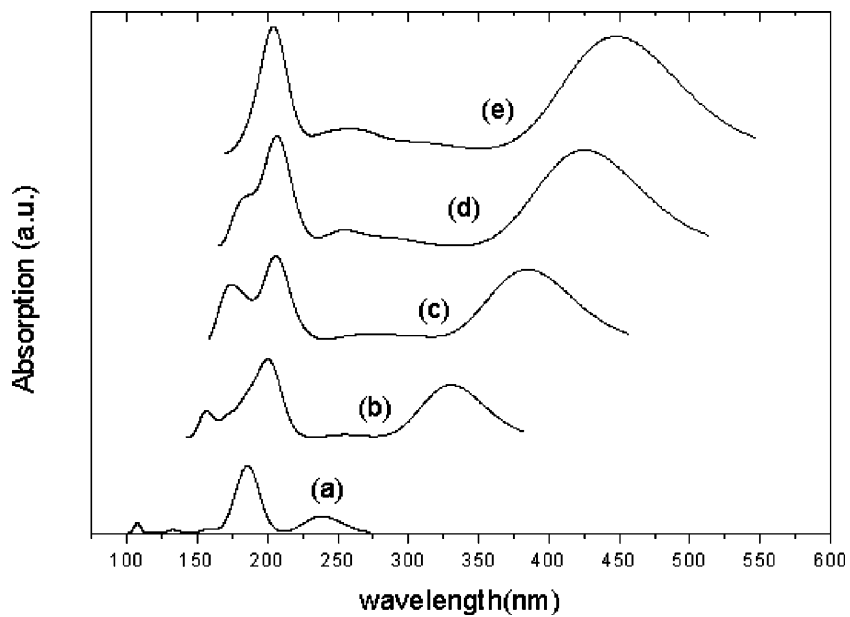


Fig. 3. Simulated absorption spectra of MP chains from ZINDO calculations, as a function of the number of units: (a) monomer; (b) dimer; (c) trimer; (d) tetramer, and (e) pentamer.

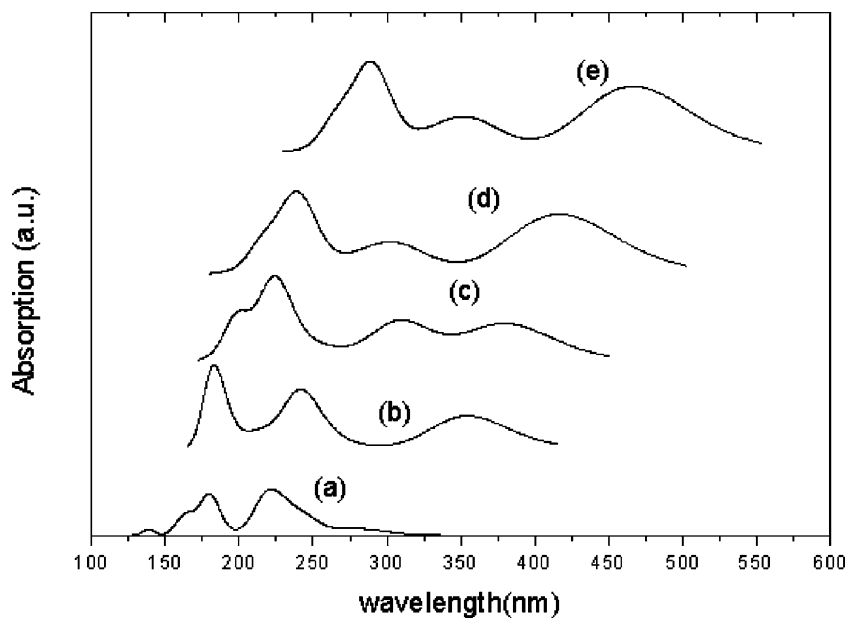


Fig. 4. Simulated absorption spectra of MPC chains from ZINDO calculations, as a function of the number of units: (a) monomer; (b) dimer; (c) trimer; (d) tetramer, and (e) pentamer.

Table 2  
Main electronic transitions from ZINDO calculations

	OS	CI Contributions
P (m)	0.7818	-0.70 H → L + 1⟩ -0.67 H - 1 → L⟩
P (d)	0.7603 0.9282	0.99 H → L⟩ -0.77 H - 2 → L⟩ 0.60 H → L + 2⟩
P (tr)	1.0642 0.8908	-0.98 H → L⟩ -0.17 H - 1 → L + 1⟩ -0.62 H - 4 → L⟩ -0.52 H → L + 3⟩
P (tet)	1.4091 1.0348	0.96 H → L⟩ -0.24 H - 1 → L + 1⟩ -0.62 H - 6 → L⟩ 0.48 H → L + 4⟩
MP (m)	0.8145	-0.63 H → L + 1⟩ 0.57 H - 1 → L⟩
MP (d)	0.9375 0.7227	-0.72 H - 2 → L⟩ 0.63 H → L + 2⟩ -0.98 H → L⟩ -0.11 H → L + 2⟩
MP (tr)	1.0176 0.9323	-0.98 H → L⟩ -0.17 H - 1 → L + 1⟩ 0.63 H - 3 → L⟩ -0.54 H → L + 3⟩
MP (tetr)	1.4247 1.3347	-0.52 H → L + 4⟩ 0.66 H - 4 → L⟩ 0.96 H → L⟩ -0.25 H - 1 → L + 1⟩
MPC (m)	0.6927 0.4247	0.87 H → L + 1⟩ 0.35 H - 1 → L⟩ -0.79 H → L + 2⟩ 0.4319 H - 1 → L + 1⟩
MPC (d)	0.9862 0.8436	0.43 H - 2 → L + 2⟩ 0.43 H - 3 → L + 1⟩ -0.71 H → L + 2⟩ -0.51 H - 2 → L⟩
MPC (tr)	0.5194 0.4669	-0.62 H - 3L + 1⟩ 0.44 H - 1 → L + 2⟩ -0.94 H → L⟩ 0.22 H - 1 → L⟩
MPC (tet)	0.8861 0.7013	-0.70 H → L + 1⟩ 0.47 H → L + 2⟩ -0.96 H → L⟩ -0.17 H - 2 → L⟩

H and L refer to highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively.

that tetramers are representative in terms of electronic behavior of the polymeric systems.

#### 4. Summary and conclusions

We reported theoretical analysis for geometric and spectroscopic features of the structures indicated in Fig. 1, from monomer up to pentamers.

Our results indicate that while the simulated absorption spectra for pyrrole (P); MP and; MPC present many common features there are very differentiated behavior with relation to DM values and cost for polaron formation.

These results, specially with relation to the values for polaron formation are suggestive that the experimentally observed differentiated electrochemical behavior (with relation to cytochrome c) presented by P, MP and MPC structures might be consequence of these electronic features and not simply related to the absence of the carboxylic acid groups required to orient the protein and enable electron transfer as suggested in the literature [14].

This speculation deserves further investigation. If true the incorporation of chemical groups decreasing the cost of polaron formation could lead to new and more effective polymeric biosensors.

This work is part of a more complete investigation on organic biosensor systems to be reported elsewhere [39].

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