Research Article

DFT and EPR Study of Spin Excitations in Oxidized Thiophene-Based Conjugated Oligomers

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Abstract: Comparison of data obtained using the density functional theory (DFT) and electron paramagnetic resonance (EPR) method made it possible to establish the composition and state of spin charge carries in the poly(3, 4-ethylenedioxythiophene) (PEDOT) and poly(3-alkylthiophene) (P3AT) oligomers. The coexistence of several polarons on the P3AT chain, the properties of which are governed by the structure of the substituents, is identified. All terms of the spin Hamiltonians of different oligomers were obtained, and their high-resolution EPR spectra were calculated. The structure of the P3AT substituents is shown to influence the polaron spin state and hyperfine interaction with its own microenvironment. The prospects of the approaches used in the work to develop electronic and spintronic elements with spin-controlled parameters are shown.

Keywords: alkylthiophene oligomer, density functional theory, electron paramagnetic resonance, ethylenedioxythiophene oligomer, poly(3-alkylthiophene) oligomers

1. Introduction

Organic polymeric materials with an extended π-conjugated structure are widely synthesized and studied due to their potential for use in molecular electronics, photonics and spintronics [1-3]. Such materials are commonly used as an active matrix of different donor-acceptor devices, e.g, nanosensors, diodes, field effect transistors, band filters, solar cells, in which energy transfer is carried out by highly mobile topological distortions, solitons, polarons or bipolarons [4, 5]. The unusual properties of these carriers and their microenvironment predetermine the uniqueness and peculiarity of the entire molecular element. For example, light irradiation of a donor-acceptor photovoltaic cell leads to the generation of energetic excitons in its matrix. The dissociation of such excitations on the polymer chain with an aromatic conformation is accompanied by the transfer, for example, of an electron to the corresponding acceptor and the formation of a positively charged polaron with a quinoid conformation and an unpaired electron. The charges so separated start to transfer the converted light energy to a potential consumer. The efficiency of energy conversion by such elements is largely determined by the methods of synthesis, as well as the structural and electronic properties of their ingredients. It depends significantly on the number, spin state, dynamics and stability of polaron charge carriers. Magnetic properties of a system with unpaired electrons are described by the spin Hamiltonian characterizing by the Landé g-factor of a spin and its hyperfine coupling (HFC) with neighboring nuclei possessing nonzero nuclear spin

[6]. These main parameters provide essential details about the chemical environment and spin density of the electronic wave function. They partly depend on the spin population, its state and play a key role in the electronic and magnetic properties of the entire system. Spin HFI initiates intermolecular charge/spin transfer and therefore changes an effective g-factor of the spin system. However, the complex problem of increasing the efficiency and functionality of organic donor-accepter devices has not yet been solved thoroughly.

The search for the most effective ingredients of such devices can be carried out by quantum chemical modeling their expectable electron and band properties using density functional theory (DFT), see, e.g., [7-11]. Processes occurring in organic compounds are usually carried out with the participation of spin charge carriers. Therefore, one of the most effective methods for studying such systems are electron paramagnetic resonance (EPR) spectroscopy [12-14]. Combined DFT and EPR approach appeared to be the more informative and complementary method used for the study of various organic spin systems, see, e.g., [15-20].

In this paper, the results of the study of spin properties of polarons stabilized in the poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3-alkylthiophene) (P3AT) oligomers using the DFT in combination with EPR method is reported. This allowed us to obtain and analyze the correlations of spin state and composition of polarons depending on the properties of the polymer matrix.

2. Methodical section

Oxidized poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3-alkylthiophenes) (P3AT) oligomers with different alkyl substituents R, H (P3HyT), CH_3 (P3MeT), C_2H_5 (P3EtT), and C_3H_7 (P3PrT) were used as model systems. The synthesis, characteristics and areas of application of these compounds are well described in the literature [21, 22]. In this work, the drawing was carried out using the Accelrus/Symux Draw v.4.0 program, followed by their preliminary structural optimization using the software Avogadro v.1.2.0. These systems with polarons excited on their chains are presented in Figure 1.
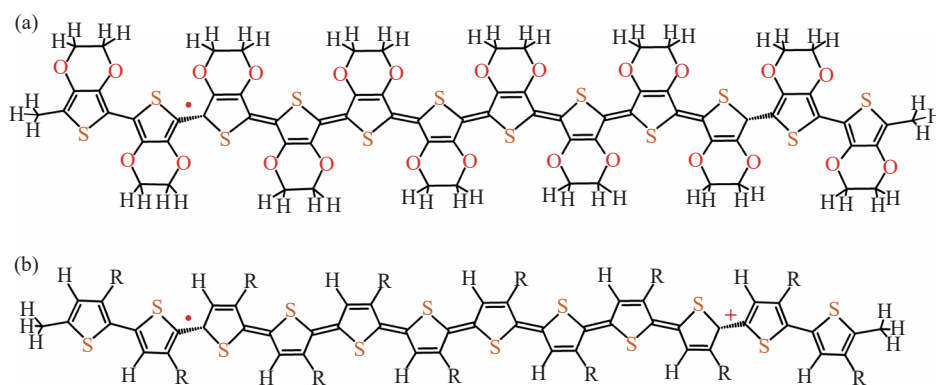

Figure 1. Schematic representation of polarons $P^{+\bullet}$ with a spin $S = 1/2$ and positive elemental charge e formed on the PEDOT (a) and P3AT with R = H, CH_3, C_2H_5, C_3H_7 (b) oligo12mer chains

The energy levels of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, E_{HOMO} and E_{LUMO}, respectively, as well as the band gap, $E_g = E_{LUMO} - E_{HOMO}$ of the samples were calculated after their DFT structural optimization using the quantum chemical program packet Orca v.5.0.4 [23] with the B3LYP functional. For the comparison, the atomic spin density was determined in both the Mulliken [24] and Löwdin [25] formalisms. The data obtained from such orbital population analysis reflect the tendency of the electron and spin density shift in macromolecules, however, they could not reflect the actual populations obtained using experimental methods. Nevertheless, these data can be used in interpreting, for example, the redistribution of charge density and spin population in organic compounds of different structures. The anisotropic and averaged spin-spin HFC constants A and

Landé g-factors of the samples under study were determined using the EPRnmr module with the EPRII basis sets for ^{1}H to ^{16}O and TZVPP ones for ^{32}S nuclei.

These parameters were then used for numerical calculation and visualization of respective high-resolution D-band (with $v_e = \omega_e/2\pi = 140$ GHz and $B_0 = 4{,}996$ mT) EPR spectra using the software EasySpin v.5.2 software [26]. This spectral waveband was chosen for the most accurate interpretation of EPR spectra of paramagnetic centers excited in organic systems. Visualization of energy and structure configurations was performed using the Avogadro v.1.2.0 program [27].

3. Results and discussions

The energy levels of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, E_{HOMO} and E_{LUMO}, respectively, as well as the band gap, $E_g = E_{LUMO} - E_{HOMO}$ of the samples were calculated after their structural optimization according to the density functional theory (DFT) using the quantum chemical program packet Orca v5.0.4 [23] with the B3LYP functional. The band gap sub-energies of the samples under study at parallel and opposite spin orientations relative to the direction of the external magnetic field are presented in Table 1.

Figure 2 demonstrates the distance distribution of spin density ρ_i on all atoms constituting thiophene-based PEDOT (^{16}O, ^{1}H, ^{32}S, ^{12}C) as well as P3Hy and P3MeT (^{1}H, ^{32}S, ^{12}C) oligomers, calculated in the Mulliken formalism. The Figure evidences that this parameter of all atoms except for ^{32}S changes in a zigzag form along the main x-axis of these systems. Such conformational feature arises from the different spatial situations of identical atoms in the oligomer networks. Nevertheless, the effective/averaged over atoms dependences indicate the presence of spin charge carriers on the chains of oligomers under study. Besides, one might expect a symmetric, centered distribution of spin density along the polaron. However, the Figure evidences that the above-mentioned dependences of P3HyT become asymmetrical as its hydrogen atoms in position 3 are replaced by CH$_3$ substituents, that is at P3HyT → P3MeT transition. More evidence and clarity of this effect can be interpreted from the analysis of simpler spin dependencies obtained for the sulfur atoms included in the thiophene rings of the oligomers.

Table 1. The band gap of the samples which polaron spin is oriented along and opposite of an external magnetic field, $E_g^{\uparrow\uparrow}$ and $E_g^{\uparrow\downarrow}$, respectively, parameters of polarons determined from Eq.(1) and their concentration ratio S_1/S_2 calculated for PEDOT and P3AT oligo12mers by using the Orca package

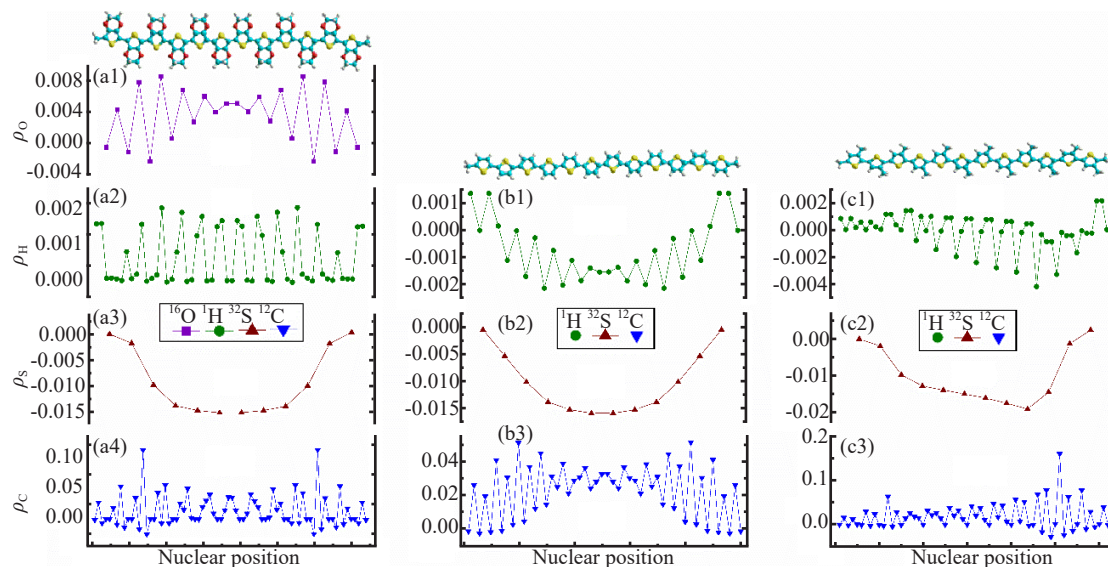| Parameter	PEDOT	P3HyT	P3MeT	P3EtT	P3PrT
$E_g^{\uparrow\uparrow}$, eV	1.588	2.021	1.645	1.641	1.640
$E_g^{\uparrow\downarrow}$, eV	0.642	0.406	0.704	0.585	0.588
ρ_0	0.012	0.024	0.024	0.023	0.023
ρ_1	-0.290	-0.566	-0.925	-0.850	-0.842
n_{c1}	4.412	4.065	5.109	5.016	5.030
w_1	5.787	8.658	10.703	9.937	9.968
ρ_2	-0.296	-0.571	-0.158	-0.173	-0.169
n_{c2}	8.654	8.924	9.248	9.177	9.163
w_2	5.806	8.689	3.297	3.313	3.280
S_1/S_2	0.978	0.987	18.944	15.286	15.139

Figure 2. Spin population on each nuclear constituting the PEDOT(a_i), P3HyT(b_i), and P3MeT(c_i) oligo12mers (shown schematically in the top) calculated according the Mulliken approach using the Orca program with EPRnmr module, B3LYP functional, 6-311 G basis set for ^{1}H to ^{16}O, and TZVPP one for ^{32}S nuclear. The total ρ value of spin population on all atoms of oligomers is equal to one

Figure 3 shows the dependences of the spatial change in spin density on the sulfur nuclear cross the topological quasiparticles stabilized in the chains of PEDOT and P3AT oligo12mers. As can be seen from the Figure, the PEDOT and P3HyT oligomers demonstrate the simplest spin density dependences. They become more complex as the sulfur atoms in the third position of the latter are replaced by an alkyl substituent. In this case, the length of such substituents weakly affects the amplitude and shapes of the corresponding dependences. It was assumed that they consist of at least two contributions of spin charge carriers formed on the chain of P3AT oligomers. It was found that these dependences can be most accurately described by the following equation:

$$\rho(n) = \rho_0 + \frac{2\rho_1}{\pi}\frac{w_1}{4(n-n_{c1})^2 + w_1^2} + \frac{2\rho_2}{\pi}\frac{w_2}{4(n-n_{c2})^2 + w_2^2} \tag{1}$$
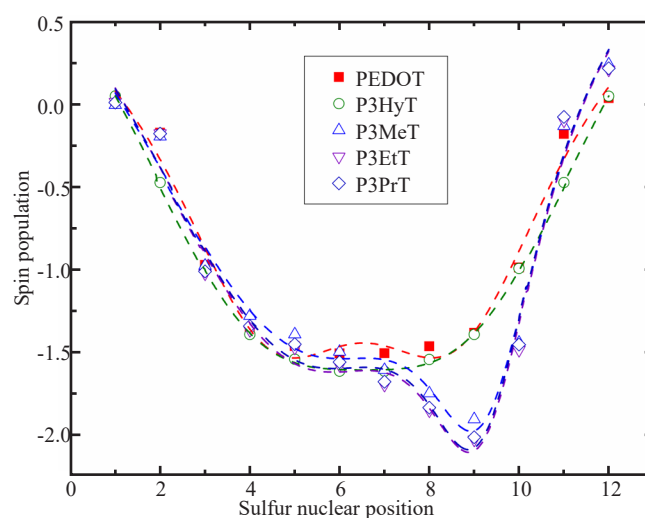

Figure 3. Spin population on serum nuclear constituting the PEDOT and various P3AT oligo12mers calculated according the Mulliken approach using the Orca software with EPRnmr module, B3LYP functional, 6-311 G basis set for ^{1}H to ^{16}O, and TZVPP one for ^{32}S nuclear

Where n is the atomic position number ρ_i are the constants, w_i is the half-height width, and n_{ci} is the extremal atomic position along the main molecular x-axis. The dependences calculated from Eq.(1) using respective parameters also summarized in Table 1 are shown by dashed lines. This fact confirms the coexistence in such systems of spin charge carriers with a different spin, conformational and magnetic parameters. Such carriers, quite obviously, must also be characterized by different dynamic parameters. To explain this phenomenon, the following remark can be made. As can be seen from Figure 1, both the C_2 and C_3 atoms of the PEDOT and P3HyT thiophene circles are bound to identical substituents. This identity is violated in the case of P3AT oligomers with other substituents. Besides, all C-C bonds are different in length as are the C-H ones due to their different types. This should be due to the formation of their chains of several polarons, which, however, do not merge into bipolarons. This can be explained by the fact that when two polarons merge into a bipolaron, one would expect their unpaired electrons to merge. As a result, the corresponding P3AT should transition to a diamagnetic, spinless state. However, such a transition does not occur. The concentration ratios S_1/S_2 of polarons excited in the compounds under study are summarized in Table 1 as well. These data indicate nearly equal concentrations of both polarons stabilized in oligomers with identical substituents of the C_2 and C_3 atoms, this ratio changes by more than an order of magnitude when replacing hydrogen of C_3 with other molecular groups.

The main parameters of the spin Hamiltonian characterizing the spin state and the interaction of polarons in the studied cation-radical oligo12mers, calculated using the Orca program packet with the EPRnmr module, are given in Table 2. When calculating the tensor magnetic resonance parameters, the following orientations of the axes were chosen: the x-axis is directed along the main polymer axis, the y-axis lies in the plane of the thiophene rings, and the z-axis is located perpendicular to these two axes. D-band EPR spectra simulated for the systems under study using the EasySpin software are presented in Figure 4. Several conclusions can be made from the analysis of the presented data. First, the values of the g-factor of polarons stabilized in PEDOT exceed those of spin charge carriers excited in P3AT. Second, the spectral splitting g_x-g_z determined for P3AT first increases when the hydrogen atoms are replaced by methyl substituents, and then decreases again with the Me $\rightarrow$ Et $\rightarrow$ Pr elongation. The latter circumstance may arise due to the improvement of the oligomer's morphology upon the transition from P3MeT to P3EtT and then to P3PrT. The magnetic resonance parameters calculated in the present work appeared to lie near those, determined experimentally for spin systems with PATAC [28] and P3AT [29-32] active matrices. Finally, from the analysis of the data presented in Table 2, one can note a tendency towards strengthening the hyperfine spin-spin interaction in P3AT with elongated substituents, which may be a result of the higher number of hydrogen atoms. It should be noted that these conclusions were made from the analysis of the effective Hamiltonian described separate or series of spin charge carriers excited in an organic system.

Table 2. The main and averaged values of effective g-tensor and spin-spin hyperfine coupling constants A_i calculated for PEDOT and P3AT oligo12mers using the Orca software package with respective basis sets

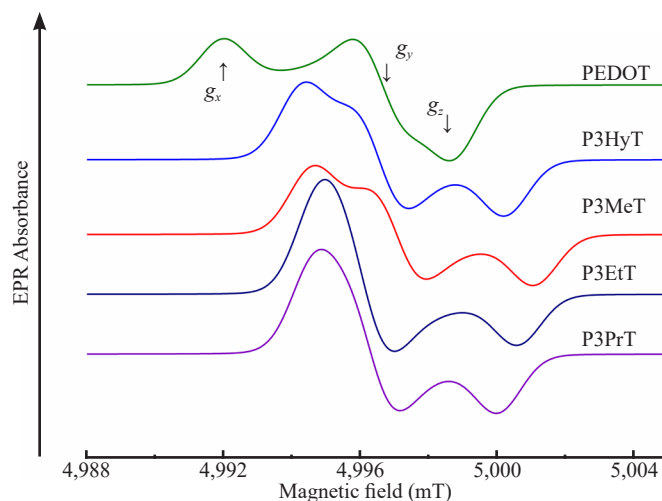| Parameter	PEDOT	P3HyT	P3MeT	P3EtT	P3PrT
g_x	2.00376	2.00283	2.00271	2.00264	2.00269
g_y	2.00189	2.00191	2.00173	2.00207	2.00201
g_z	2.00103	2.00043	2.00009	2.00028	2.00051
g_{iso}	2.00222	2.00172	2.00150	2.00166	2.00174
A_x, MHz	48.01	-1.52	35.87	58.23	54.70
A_y, MHz	26.11	-1.18	-13.54	6.77	11.47
A_z, MHz	36.99	0.27	-13.65	15.01	10.49
A_{iso}, MHz	37.03	-0.81	2.89	27.00	25.55

Figure 4. D-band EPR spectra of the PEDOT, P3HyT, and P3MeT calculated by using EasySpin software

4. Conclusions

The energy and spin parameters of topological distortions of the chains of oxidized oligo12mers PEDOT and P3AT were studied using DFT and EPR methods. The results obtained allowed us to detect the stabilization of independent polarons on the chains of these compounds. The parameters of such charge carriers were found to be similar for identical substituents in positions 3 and 4 of thiophene monomers. However, they changed significantly when the hydrogen substituent of P3HyT was replaced by an alkyl one. The spin densities on all atoms of the studied oligomers were calculated. A narrowing of a part of the spin density was identified due to the specificity of formation, relaxation, and interaction of polarons with their own microenvironment. All anisotropic parameters of the spin Hamiltonians of the studied oligomers with different side substituents were obtained, and high-resolution EPR spectra of these compounds were calculated.

The methods and approaches proposed in the work can also be used to study the structural, electronic and spin properties of a wide range of organic donor-acceptor compounds with spin charge carriers. The influence of orbital hybridization of macromolecular substituents on polaron spin states seems to have broader implications for the design of conjugated polymers and their composites with tailored electrical and magnetic properties. So, the data obtained can be used to develop further new high-performance nanoelectronic devices with spin-dependent electronic parameters. In particular, the fact of the coexistence of several independent polarons in organic systems may prove to be key to the creation of new solar cells, multicore processors, active bandpass filters, other devices with spin-controller parameters.

Acknowledgments

Conflict of interest

The authors declare no competing financial interest.

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