**A Computational Insight on Designing Low Electronic Energy Gap (Benzothiadiazole/ Benzoselenadiazole – Pyrrole) copolymers**

Pınar Seyitdanlioglu Sirina, Pervin Unal Civcirb,\*, Canan Unaleroglua,\*

aHacettepe University, Department of Chemistry, Beytepe Campus, 06800, Ankara, Turkey

bAnkara University, Department of Chemistry, Faculty of Science, 06100 Ankara, Turkey

\*Corresponding author e-mail: [pervin.unal.civcir@science.ankara.edu.tr](mailto:pervin.unal.civcir@science.ankara.edu.tr)

\*Corresponding author e-mail: canan@hacettepe.edu.tr

**Abstract**

Organic conductive polymers have great significance due to their wide range of applications in optoelectronics and material sciences. In this study, pyrrole-benzothiadiazole/benzoselenadiazole based type green polymers were undertaken computational work to investigate the solubility of polymers. Structural, electronic, and optical properties of eight different polymers were predicted using DFT and TD-DFT at B3LYP/6-31G level on semi-empirical PM6-optimized geometries. It has been shown that the calculation results of synthesized green polymers are in great agreement with the experimental results. Alkylated 4**,**7-di(1*H*-pyrrol-2-yl)benzo-[c][1,2,5]thiadiazole (**PB1**) and 4,7-di(1*H*-pyrrol-2-yl)benzo[c][1,2,5]selenadiazole (**PB7**) monomers were studied to investigate the effect of alkyl chains on their electronic and optical properties. Butyl substituted more soluble polymers were shown to have low electronic energy gaps (1.27-1.55 eV). Moreover, the electronic energy gap values ​​of the studied polymeric structures are in the appropriate range of technological applications (1.24-2.18 eV). The approach utilized in this study can be used to design new semi-conducting polymers.

**Keywords**

Electronic energy gap, semi-conducting polymers, green polymers, alkylated polymers

1. **Introduction**

Low band gap conducting polymers have attracted great interest due to their remarkable advantages such as lightweight, ease of workability, low cost, electric, magnetic and optical properties. These features enable them to be applied in technological fields such as electrochromic devices, sensors, solar cells, light-emitting diodes, transistors, and artificial muscles [1-10]. The design of conducting polymers is of great importance in developing new materials for many applications. One of the most efficient approaches to develop conducting polymers with a low band gap is based on the strategy that can be achieved by combination with electron-donating (donor) and withdrawing (acceptor) units within the polymer chain [11-13]. To construct a polymer backbone with the desired optical and electronic properties, quinoxaline, diketopyrrolopyrrole, and benzothiadiazole are mostly used groups due to their good performances as an acceptor, while many groups can be used as donors such as thiophene, pyrrole derivatives [12,14-17]. Among these, pyrrole/benzothiadiazole based donor-acceptor conjugated polymers have lately received great attention due to their superior optical properties as a neutral-state green polymer [15-17]. These green polymers are very significant for red, green, blue (RGB) devices. Recently, L. Toppare et al. realized a pioneering study on the electrochemical polymerization of 7-di(1*H*-pyrrol-2-yl)benzo-[c][1,2,5]thiadiazole and 4,7-di(1*H*-pyrrol-2-yl)benzo[c][1,2,5]selenadiazole and the resulting polymers make simultaneous absorptions with a narrower band gap (1.08, 1.12 eV) in both red and blue regions [17]. Another remarkable experimental study on 7-di(1*H*-pyrrol-2-yl)benzo-[c][1,2,5]thiadiazole oligomers indicating the relation of the gradual bathochromic shift and chain elongation had previously been done by H. A. M. van Mullekom et al [18]. More recently, U. Salzner reported a theoretical study showing the effect of donor-acceptor monomers on the optical and electronic properties of conductive polymers. Among them, poly [7-di (1*H*-pyrrol-2-yl) benzo-[c][1,2,5] thiadiazole] came forward as a promising material for various applications [19]. It is well known that linear alkyl chains positively affect the band gap of conductive polymers and increase their solubility. Moreover, it has been indicated that copolymers with alkyl side chains are more soluble in various solvents [20-23].

In this study, we computationally investigated how the alkyl chains on 4**,**7-di(1*H*-pyrrol-2-yl)benzo-[c][1,2,5]thiadiazole and 4,7-di(1*H*-pyrrol-2-yl)benzo[c][1,2,5]selenadiazole affect the optical, electronic, and structural properties of corresponding polymers to contribute to the development of new soluble materials with a low electronic band gap. We first, chose methyl-substituted 7-di(1*H*-pyrrol-2-yl)benzo-[c][1,2,5]thiadiazole because of the computational cost and searched how the methylation at different positions of pyrrole affect the generation of low electronic band gap polymers (**Figure 1**, **PB1**, **PB2**, **PB3**, **PB4**, **PB5**).



**Figure 1**. Structures of the studied monomers

1. **Computational details**

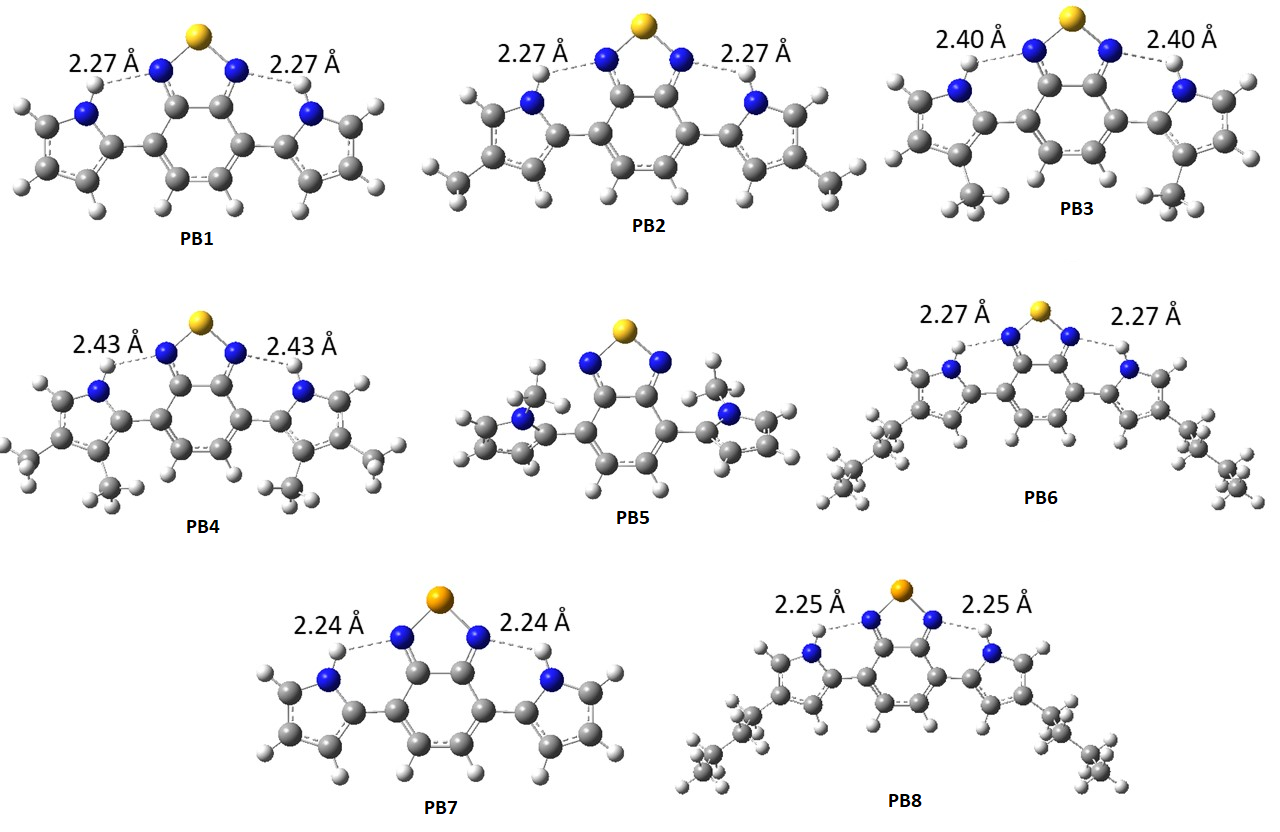
All calculations were performed with Gaussian 09W (Revision D.01) and GaussView 5.0.8 molecular visualization program. Monomers were designed in the order of pyrrole- benzothiadiazole-pyrrole, which represents a donor-acceptor-donor model (D-A-D) (Figure 1). In the first step, scan analysis was done for each oligomer to determine the conformer with the lowest energy values using a semi-empirical quantum mechanical PM6 method (*n*=1 to 3, where *n* is the number of monomer units). Scan analysis results of monomer, dimer, and trimer units of all structures were given in Supplementary material **Figure S17** to **Figure S40**. Next, ground-state geometries of the most stable conformers were optimized in the gas phase with a semi-empirical PM6 method. All stationary points were confirmed equilibrium structures (no imaginary frequencies) through vibrational analysis. The electron correlation effect was investigated by using Density Functional Theory, B3LYP (Becke three-parameter hybrid exchange functional combined with Lee-Yang-Paar correlation functional). It is known that the B3LYP method gives quite a correct energy gap for various polymers[24,25].

After optimization work, the electronic energy gap (Eg=EHOMO-ELUMO) for monomers and oligomers were calculated by using the B3LYP/6-31G. Calculations of the electronic energy gap were continued on the oligomers with the elongation of the alkyl chain and adding monomers one after another until the difference of EgapeV to be able to estimate the Egap value of related polymer.

The computed energy gap values are used to estimate Egap values for corresponding polymers by plotting Egap values of monomers and oligomers against the reciprocal of the monomer units (1/n) of oligomers. Then, linear regression and extrapolation procedures were applied to the approximate energy gap of related polymers. Time-Dependent Density Functional Theory calculations were performed using the B3LYP/6-31G level of theory to investigate the electronic structures for all optimized monomers and oligomers**.**

1. **Results and Discussion**

The most stable structures of **PB1**-**PB8** monomers are gathered in Figure 2. The nitrogens of pyrroles and benzothiadiazole on the corresponding most stable conformers of monomers **PB1**, **PB2**, **PB3**, **PB4**, **PB6**, **PB7,** and **PB8** were in a syn position to each other and this conformation provided the formation of the intramolecular hydrogen bond, making the structure more stable than the other conformations. The optimized structures of **PB1**, **PB2**, **PB3**, **PB4**, **PB5**, **PB6**, **PB7,** and **PB8** oligomers in ball & bond type and tube type are given in Supplementary material **Figure S1** to **Figure S16**. In the optimized dimer units, monomers in the global minima are in an anti position to each other that decrease both the electronic repulsion of electron lone pair of pyrrole nitrogens and the steric interaction of methyl groups. A similar backbone structure has been observed in the trimer units. For this reason, conformation analysis has not been performed in oligomers larger than trimers. The geometric parameters of optimized **PB1**-**PB8** monomer-trimer units are given in **Table S1** and **Table S2**. The C-C bond lengths in the bridges are almost 1.45 Å, which is shorter than the single bond length and longer than the double bond length. This shows that all studied structures are close to the quinoid form that contributes to the delocalization of π-electron to the overall structure providing the lower energy gap. Since X-ray crystallography data of monomers are not available in the literature to our knowledge, we are not able to compare our calculation results with experimental data.

****

**Figure 2.** Optimized structures of monomers at semi-empirical/PM6

In the optimized geometry of **PB1** monomer (**Figure 2**), the syn position of nitrogens of donor component pyrrole and acceptor benzothiadiazole provides a convenient geometry to make intermolecular hydrogen bonding (2.27 Å). In this geometry of **PB1**, the dihedral angle φ1 is 0.0, which shows a planar structure (Table S2). However, the dihedral angle (φ3, φ6) between repeating monomer units (n=2-3) ranged between -150.0˚ and -151.0˚ (**Table S2**), showing slightly away from planarity.

Calculations were continued with the B3LYP/6-31G level of theory to estimate the energy of the highest occupied molecular orbital (EHOMO) and the energy of the lowest unoccupied molecular orbital (ELUMO). The contour diagrams of HOMO and LUMO molecular orbitals of all monomers are shown in **Figure 3** and simulated HOMO and LUMO molecular orbitals of all pentamers are given in **Figure S41** in Supplementary material. The contour diagrams of monomers in **Figure 3** show that there is a strong electron density localization spreading over the entire chain for pyrrole-benzothiadiazole derivatives (**PB1**-**PB6**) at the HOMO level, while a strong electron density localization on the benzoselenadiazole ring for the selenadiazole derivatives (**PB7**-**PB8**). In the case of LUMO orbitals, the electron density of pyrrole-benzothiadiazole derivatives (**PB1**-**PB6**) is mostly on the benzothiadiazole ring, whereas it is spread over the entire monomer unit in the pyrrole-benzoselenadiazole derivatives (**PB7**-**PB8**). The contour plots of pentamers show that all the oligomers, except **PB5**, have a strong electron density localization along the main chain of the HOMO and LUMO orbitals.

|  |  |  |
| --- | --- | --- |
| **Monomer HOMO Orbitals** | | **LUMO Orbitals** |
| **PB1** |  |  |
| **PB2** |  |  |
| **PB3** |  |  |
| **PB4** |  |  |
| **PB5** |  |  |
| **PB6** |  |  |
| **PB7** |  |  |
| **PB8** |  |  |

**Figure 3.** Simulated HOMO and LUMO molecular orbitals of all monomers

A small band gap is an essential feature for conductive polymers. Poly[7-di(1*H*-pyrrol-2-yl)benzo-[c][1,2,5]thiadiazole] has been experimentally studied system and has a band gap within semi-conductive range (1.12 eV). Therefore, monomer **PB1** was chosen first to indicate the consistency of calculation results with the experimental data. As given in the **Table 1,** the experimental bandgap and the calculated electronic energy gap values of poly[7-di(1*H*-pyrrol-2-yl)benzo-[c][1,2,5]thiadiazole are 1.12 eV and 1.68 eV (B3P86-30%), 4.52 eV (wB97XD) respectively [17, 19]. In this work, the estimated electronic energy gap from the calculations at the B3LYP/6-31G level for n=1-5 repeating units is 1.27 eV, which is highly close to the experimental result. After describing the polymer structure with the insilico method, the polymer was investigated to impart solubility by the addition of alkyl groups on poly[7-di(1*H*-pyrrol-2-yl)benzo-[c][1,2,5]thiadiazole. Mono-alkylated **PB2**, **PB3**, and **PB5,** dialkylated **PB4** monomers have been taken into the calculation with DFT-B3LYP/6-31G. Similar intramolecular hydrogen bond formation as in the monomer **PB1** was observed for **PB2**, **PB3,** and **PB4** monomers (2.27 Å, 2.40 Å, 2.43 Å, respectively). Mono alkylated **PB2** monomer retained its planar structure (Table S2). However, methyl groups on **PB3** and **PB4** partiallydistorted planar structure 30.7˚ for **PB3** [ φ1: C(3)-C(4)-C(5)-C(6)] and 31.9˚ for **PB4** [φ1: C(3)-C(4)-C(5)-C(6)] ), and as a result, the intramolecular hydrogen bond became longer than it was on **PB1** and **PB2** monomers. These intramolecular hydrogen bonds made them a more stable conformer. The planarity in the **PB5** monomer was disrupted by replacing the NH hydrogen with a methyl group. Dihedral angles φ1of **PB5** are -51.6o, -51.5o, and -51.5o for monomer, dimer, and trimer, respectively, and φ3 [φ3:C(11)-C(12)-C(13)-C(14)] are 78.2o (dimer) and 78.6o (trimer) and φ6 [φ6:C(23)-C(24)-C(25)-C(26)] is 78.6o. This distortion in the structure negatively affects the mobility of pi electrons and increases the electronic energy gap value to 2.18 eV.

Among the polymers given in **Table 1**, the polymer of **PB2** has a lower electronic band gap (1.36 eV). This result indicated that the most suitable location for the alkylation of monomers is the C(2) of pyrrole. Therefore, after this finding, the n-butyl substituted **PB6** monomer was chosen to carry out the effect of the lengthened alkyl group on the electronic band gap. J. Roncali et al. reported that increasing the length of the alkyl chain (up to C10H21) on poly(3-alkylthiophenes) has a positive effect on the energy gap. In order to investigate whether the electronic energy gap of the polymer will be positively affected by increasing the length of the alkyl chain in the studied monomer units, calculations were made for **PB6** by connecting n-butyl to the 2 position of the pyrrole ring in **PB1**. It is observed that the estimated electronic band gap of **PB6** was 1.27 eV, which is the same as that of **PB1** and even smaller than **PB2** (1.36 eV). This result indicated that polymer of linear alkyl chain substituted 4,7-bis(4-butyl-1*H*-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole (**PB6**) has the required low electronic band gap value for the conductive polymer and the alkyl groups increase the solubility.

After obtaining these results, calculations were made for another previously synthesized semi-conductive green/light blue polymer poly[4,7-di(1*H*-pyrrol-2-yl)benzo[c][1,2,5]selenadiazole] **PB7** using B3LYP/6-31G(d,p) level of theory. The stable conformer of **PB7** is similar to **PB1** and **PB2** monomers, the dihedral angle φ1 (Table S2) is 0.0˚, which shows a planar structure. The estimated electronic band gap was found 1.25 eV (1.08 eV experimental). Considering the results obtained from the **PB6** polymer, n-butyl substituted 4,7-bis(4-butyl-1*H*-pyrrol-2-yl)benzo[c][1,2,5]selenadiazole (**PB8**) was studied. When the calculations were made for the **PB8** polymer using the same functional (B3LYP) and basis set 6-31G, the determination coefficient of the Egap-1/n plot was seen to be distant from 1 (0,6689). Therefore, the calculations were repeated with the same functional, but the basis set was expanded to 6-31G (d,p). When the calculations were accomplished, the determination coefficient of the Egap-1/n graph approached 1 and the Egap value for **PB8** polymer chain was found to be 1.55 eV. Egap-1/n graphs, graph equations, and R-squared values for all structures are given in **Figure 4.** As can be seen from **Table 1**, HOMO energies increase while LUMO energies decrease during polymerization, and in consequence, electronic band energies decrease.

PB6; y = 0.8497x + 1.268  
R² = 0.9859

1/n

Egap

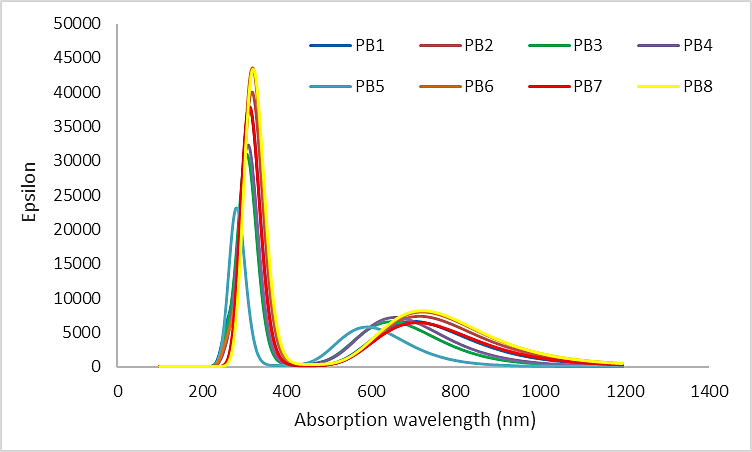
**Figure 4.** Egap-1/n graph of oligomer series and graph equations and R-squared values

**Table 1.** HOMO, LUMO and electronic energy gaps of monomers, oligomers, and polymers\*

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | EHOMO | ELUMO | Electronic energy gap | Egap, Experimental | Electronic energy gap, Calculated [19] | |
|  |  |  |  |  |  | B3P86-30% | wB97XD |
| **PB1** | Monomer | -4.83 | -2.68 | 2.15 |  | 2.83 | 5.68 |
| Dimer | -4.47 | -2.76 | 1.71 |  | 2.24 | 5.06 |
| Trimer | -4.36 | -2.80 | 1.56 |  | 2.04 | 4.86 |
| Tetramer | -4.31 | -2.82 | 1.49 |  | 1.95 | 4.77 |
| Pentamer | -4.28 | -2.83 | 1.45 |  | - | - |
| Polymer |  |  | 1.27 | 1.12 (O) [17] | 1.68 | 4.52 |
| **PB2** | Monomer | -4.73 | -2.62 | 2.11 |  |  | |
| Dimer | -4.41 | -2.68 | 1.73 |  |  | |
| Trimer | -4.36 | -2.71 | 1.66 |  |  | |
| Tetramer | -4.26 | -2.73 | 1.53 |  |  | |
| Pentamer | -4.24 | -2.74 | 1.50 |  |  | |
| Polymer |  |  | 1.36 |  |  | |
| **PB3** | Monomer | -4.88 | -2.54 | 2.35 |  |  | |
| Dimer | -4.51 | -2.60 | 1.91 |  |  | |
| Trimer | -4.40 | -2.63 | 1.77 |  |  | |
| Tetramer | -4.35 | -2.65 | 1.71 |  |  | |
| Pentamer | -4.33 | -2.65 | 1.68 |  |  | |
| Hexamer | -4.32 | -2.66 | 1.66 |  |  | |
| Polymer |  |  | 1.50 |  |  | |
| **PB4** | Monomer | -4.88 | -2.54 | 2.35 |  |  | |
| Dimer | -4.51 | -2.60 | 1.91 |  |  | |
| Trimer | -4.40 | -2.63 | 1.77 |  |  | |
| Tetramer | -4.35 | -2.65 | 1.71 |  |  | |
| Pentamer | -4.33 | -2.65 | 1.68 |  |  | |
| Polymer |  |  | 1.62 |  |  | |
| **PB5** | Monomer | -5.16 | -2.56 | 2.60 |  |  | |
| Dimer | -5.09 | -2.61 | 2.49 |  |  | |
| Trimer | -5.08 | -2.63 | 2.45 |  |  | |
| Tetramer | -4.88 | -2.65 | 2.23 |  |  | |
| Pentamer | -4.88 | -2.65 | 2.23 |  |  | |
| Hexamer | -4.88 | -2.66 | 2.23 |  |  | |
| Polymer |  |  | 2.18 |  |  | |
| **PB6** | Monomer | -4.71 | -2.61 | 2.10 |  |  | |
| Dimer | -4.39 | -2.67 | 1.72 |  |  | |
| Trimer | -4.30 | -2.70 | 1.60 |  |  | |
| Tetramer | -4.19 | -2.73 | 1.46 |  |  | |
| Pentamer | -4.15 | -2.74 | 1.41 |  |  | |
| Hexamer | -4.15 | -2.75 | 1.40 |  |  | |
| Polymer |  |  | 1.27 |  |  | |
| **PB7** | Monomer | -4.73 | -2.60 | 2.13 |  |  | |
| Dimer | -4.37 | -2.68 | 1.69 |  |  | |
| Trimer | -4.25 | -2.71 | 1.54 |  |  | |
| Tetramer | -4.20 | -2.73 | 1.47 |  |  | |
| Pentamer | -4.17 | -2.75 | 1.43 |  |  | |
| Hexamer | -4.15 | -2.75 | 1.40 |  |  | |
| Polymer |  |  | 1.25 | 1.08 [17] |  | |
| **PB8** | Monomer | -4.63 | -2.55 | 2.08 |  |  | |
| Dimer | -4.34 | -2.57 | 1.77 |  |  | |
| Trimer | -4.36 | -2.58 | 1.78 |  |  | |
| Tetramer | -4.25 | -2.60 | 1.65 |  |  | |
| Pentamer | -4.22 | -2.55 | 1.67 |  |  | |
| Hexamer | -4.26 | -2.61 | 1.65 |  |  | |
| Polymer |  |  | 1.55 |  |  | |

\* All values are given in eV

UV-VIS absorption spectra were simulated at TD-DFT method at the B3LYP/6-31G level for **PB1**, **PB2**, **PB3**, **PB4**, **PB5**, **PB6**, **PB7** and TD-DFT/B3LYP/6-31G (d,p) method for **PB8** oligomer from the optimized ground-state structures in the gas phase. UV-VIS absorption spectra simulations of all the optimized monomers are shown in **Figure 5**. As expected from green polymers, two independent absorption bands are observed in the near UV and the orange region in all monomers as seen in **Figure 5**.



**Figure 5.** UV-VIS absorption spectra of all optimized monomers

TD-DFT calculations for oligomers consisting of 1-5 and 1-6 monomer units are given below in **Figure 6** with simulated UV-VIS spectra. It can be seen from Table 2 that a clear red-shift on the wavelengths was observed as the oligomer chains lengthen. UV-VIS spectra of **PB1** and **PB7** polymers in the literature were given as 392 nm/753 nm and 384 nm/738 nm, respectively [17].

**Table 2.** TD-DFT data of all optimized monomers and oligomers

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  |  | f | λmax (nm) | Electronic Transition  HOMO→LUMO |
| **PB1** | Monomer | 0.16 | 700 | 69->70 |
|  | Dimer | 0.61 | 878 | 137->138 |
|  | Trimer | 1.10 | 984 | 205 ->206 |
|  | Tetramer | 1.61 | 1047 | 273 ->274 |
|  | Pentamer | 2.10 | 1088 | 341 ->342 |
| **PB2** | Monomer | 0.18 | 715 | 77 -> 78 |
|  | Dimer | 0.58 | 879 | 153 ->154 |
|  | Trimer | 1.01 | 971 | 229 ->230 |
|  | Tetramer | 1.46 | 1024 | 305 ->306 |
|  | Pentamer | 1.90 | 1056 | 381 -> 382 |
| **PB3** | Monomer | 0.16 | 647 | 77 -> 78 |
|  | Dimer | 0.53 | 804 | 153 ->154 |
|  | Trimer | 0.93 | 880 | 229 ->230 |
|  | Tetramer | 1.34 | 920 | 305 ->306 |
|  | Pentamer | 1.76 | 943 | 381 -> 382 |
|  | Hexamer | 2.18 | 958 | 457 -> 458 |
| **PB4** | Monomer | 0.18 | 658 | 85 -> 86 |
|  | Dimer | 0.48 | 791 | 169 ->170 |
|  | Trimer | 0.78 | 848 | 253 ->254 |
|  | Tetramer | 1.18 | 890 | 337 ->338 |
|  | Pentamer | 1.43 | 900 | 421 -> 424 |
| **PB5** | Monomer | 0.14 | 591 | 77 -> 78 |
|  | Dimer | 0.29 | 618 | 153 ->154 |
|  | Trimer | 0.37 | 629 | 229 ->230 |
|  | Tetramer | 0.60 | 697 | 305 ->306 |
|  | Pentamer | 0.62 | 697 | 381 -> 382 |
|  | Hexamer | 0.64 | 697 | 457 -> 458 |
| **PB6** | Monomer | 0.20 | 722 | 101 ->102 |
|  | Dimer | 0.58 | 892 | 201 ->202 |
|  | Trimer | 0.94 | 973 | 301 ->302 |
|  | Tetramer | 1.42 | 1076 | 401 -> 402 |
|  | Pentamer | 1.81 | 1128 | 501 -> 502 |
|  | Hexamer | 2.11 | 1145 | 601 -> 602 |
| **PB7** | Monomer | 0.16 | 709 | 78 -> 79 |
|  | Dimer | 0.60 | 894 | 155 ->156 |
|  | Trimer | 1.09 | 1000 | 232 ->233 |
|  | Tetramer | 1.70 | 1066 | 309 ->310 |
|  | Pentamer | 1.97 | 1107 | 386 -> 387 |
|  | Hexamer | 2.40 | 1135 | 463 -> 464 |
| **PB8** | Monomer | 0.20 | 721 | 110 ->111 |
|  | Dimer | 0.55 | 867 | 219 ->220 |
|  | Trimer | 0.86 | 918 | 328 -> 329 |
|  | Tetramer | 1.04 | 941 | 437 -> 438 |
|  | Pentamer | 1.19 | 944 | 546 -> 547 |
|  | Hexamer | 1.40 | 947 | 655 -> 656 |

**Figure 6.** UV-VIS absorption spectra of all monomers and oligomers

1. **Conclusions**

Here, theoretical calculations have been performed to predict the structural, electronic, and optical properties of a series of monomers and oligomers **PB1**-**PB8** having benzothiadiazole/benzoselenadiazole and pyrrole units. Structural variations were studied to investigate the alkyl chain elongation effects on the electronic and optical properties of corresponding polymers. Results indicate that when the alkyl groups cause a diverge from 0˚ and 180˚ of dihedral angles between the donor and acceptor groups in the monomer units the electronic energy gap increases. The substitution of the alkyl groups to the β-positions of the pyrrole can be a good option for both keeping the band gap at small values and obtaining high solubility for pyrrole-benzothiadiazole/ benzoselenadiazole-pyrrole (D-A-D) type polymers. Furthermore, quantum chemical calculations showed that the electronic energy gaps of all studied polymer structures are in the appropriate range of technological applications (1.24-2.18 eV). It is important to note that this theoretical approach makes the possible predictive investigation of electronic, structural, and optical properties of new variant polymers bearing benzothiadiazole/ benzoselenadiazole and pyrrole units.

**Acknowledgements**

The calculations reported in this paper were partially performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources). P. S. S. acknowledges TUBITAK-BIDEB for the 2211 scholarship program.

**Appendix S1. Supplementary material**

**References**

[1] W. Lu, A. G. Fadeev, B. Qi, B. R. Mattes, *J. Electrochem. Soc.* 2004,**151,** H33, 10.1149/1.1640635.

[2] U. Lange, N. Roznyatovskaya, V. Mirsky, *Anal. Chim. Acta* 2008, **614,** 1, 10.1016/j.aca.2008.02.068.

[3] B. Dong, D. Y. Zhong, L. F. Chi, H. Fuchs, *Adv. Mater.* 2005,**17,** 2736, 10.1002/adma.200500938.

[4] J. Koh, J. Kim, B. Kim, E. Kim, *Adv. Mater.* 2011, **23**, 1641, 10.1002/adma.201004715.

[5] L. Dou, J. You, J. Yang, C. C. Chen, Y. He, S. Murase, T. Moriarty, K. Emery, G. Li, Y. Yang, *Nat. Photonics* 2012, **6**,180, 10.1038/nphoton.2011.356.

[6] [R. Xia](https://www.sciencedirect.com/science/article/pii/S1566119903000314?casa_token=D4MoM46kg0gAAAAA:p5RPwczRX7Dmsy0k2lqjM-HTJCP2TOO2MXDReE8oQex2M1cxEM_gAptvmB-GUgUzk97zxt1sdw#!), [G. Heliotis](https://www.sciencedirect.com/science/article/pii/S1566119903000314?casa_token=D4MoM46kg0gAAAAA:p5RPwczRX7Dmsy0k2lqjM-HTJCP2TOO2MXDReE8oQex2M1cxEM_gAptvmB-GUgUzk97zxt1sdw#!), [Y. Hou](https://www.sciencedirect.com/science/article/pii/S1566119903000314?casa_token=D4MoM46kg0gAAAAA:p5RPwczRX7Dmsy0k2lqjM-HTJCP2TOO2MXDReE8oQex2M1cxEM_gAptvmB-GUgUzk97zxt1sdw#!), [D. D. C. Bradley](https://www.sciencedirect.com/science/article/pii/S1566119903000314?casa_token=D4MoM46kg0gAAAAA:p5RPwczRX7Dmsy0k2lqjM-HTJCP2TOO2MXDReE8oQex2M1cxEM_gAptvmB-GUgUzk97zxt1sdw#!), *Org. Electr.* 2003, **4**, 165, [10.1016/j.orgel.2003.08.009](https://doi.org/10.1016/j.orgel.2003.08.009).

[7] O. Inganäs, M. Berggren, M. R. Andersson, G. Gustafsson, T. Hjertberg, 0. Wennerström, P. Dyreklev, M. Granström, *Synth. Met.* 1995, **71**, 2121, [10.1016/0379-6779(94)03194-B](https://doi.org/10.1016/0379-6779(94)03194-B).

[8] O. Bubnova, M. Berggren, X. Crispin, *J. Am. Chem. Soc.* 2012, **134**, 16456, 10.1021/ja305188r.

[9] J. Liu, M. Agarwal, K. Varahramyan, *Sens. Actuators B Chem* 2008, **135**, 195, 10.1016/j.snb.2008.08.009.

[10] F. T. Otero, J. M. Sansinena, *Adv. Mater.* 1998, **10**, 491, 10.1002/(SICI)1521-4095(199804)10:6<491::AID-ADMA491>3.0.CO;2-Q.

[11] H. Huang, P. G. Pickup, *Chem. Mater.* 1998, **10**, 2212, 10.1021/cm9801439.

[12] Z. Xua, M. Wang, J. Zhaob, C. Cuib, W. Fana, J. Liu, *Electrochim. Acta* 2014, **125**, 241, 10.1016/j.electacta.2013.12.097.

[13] U. Salzner, *J. Phys. Chem. B* 2002, **106**, 9214, 10.1021/jp020141i.

[14] Y. Gao, X. Zhang, H. Tian, J. Zhang, D. Yan, Y. Geng, F. Wang, *Adv. Mater.* 2015, **27**, 6753, 10.1002/adma.201502896.

[15] F. B. Emre, F. Ekiz, A. Balana, S. Emre, S. Timur, L. Toppare, *Sens. Actuators B Chem.* 2011, **158**, 117, 10.1016/j.snb.2011.05.052.

[16] O. Atwani, C. Baristiran, A. Erden, G. Sonmez, *Synth. Met.* 2008, **158**, 83, 10.1016/j.synthmet.2007.12.013.

[17] D. Baran, G. Oktem, S. Celebi, L. Toppare, *Macromol. Chem. Phys.* 2011, **212**, 799, 10.1002/macp.201000744.

[18] H. A. M. van Mullekom, J. A. J. M. Vekemans, E. W. Meijer, *Chem. Eur. J.* 1998, **4**, 1235, 10.1002/(SICI)1521-3765(19980710)4:7<1235::AID-CHEM1235>3.0.CO;2-4.

[19] U. Salzner, *J. Chem. Theory Comput.* 2014, **10**, 4921−4937, 10.1021/ct500816c.

[20] J. Roncali, R. Garreau, A. Yassar, P. Marque, F. Gamier, M. Lemaire, *J. Phys. Chem.* 1987, **91**, 6706, 10.1021/j100311a030.

[21] S. Pelz, J. Zhang, I. Kanelidis, D. Klink, L. Hyzak, V. Wulf, O. J. Schmitz, J. C. Gasse, R. Frahm, A. Pütz, A. Colsmann, U. Lemmer, E. Holder, Eur. *J. Org. Chem.* 2013, **2013** 4761, 10.1002/ejoc.201300357.

[22] B. Fu, J. Baltazar, A. Ravi Sankar, P. H. Chu, S. Zhang, D.M. Collard, E. Reichmanis, *Adv. Funct. Mater.* 2014, **24**, 3734, 10.1002/adfm.201304231.

[23] C. Lee, T. H. Woo, M. Lee, *Mol. Cryst. Liq. Cryst.* 1998, **316**, 205, 10.1080/10587259808044492.

[24] S. Ghosh, N. A. Kouamé, L. Ramos, S. Remita, A. Dazzi, A. Deniset-Besseau, P. Beaunier, F. Goubard, P. H. Aubert, H. Remita, *Nat. Mater.* 2015, **14**, 505-511, 10.1038/NMAT4220.

[25] P. Ünal Civcir, *Comput. Theor. Chem.* 2018, **1128**, 70, 10.1016/j.comptc.2018.02.013.