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PBC-DFT study of the electronic properties of 1,3,4-thiadiazole polymers: Substitution linkage effects

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ABSTRACT

In this paper, the structural and electronic properties of poly-1,3,4-thiadiazole-based systems PTDz have been investigated using first-principles calculations in periodic forms. Of particular interest is the band gap modulation through substitution linkages. Specifically, H has been substituted by ethynyl and vinylene in PTDz, leading to poly1,3,4-thiadiazole ethynylPTDzE and poly1,3,4-thiadiazole vinylenePTDzV, respectively. These substitutions linkages lead to suppression of the band gap or HOMO-LUMO gap. Overall, a wide range of band gaps can be achieved through substitutions.

Keywords: PBC-DFT, 1,3,4-thiadiazole polymers, Substitution linkage effects.

INTRODUCTION

The discovering for renewable energy sources has sparked considerable interest in the modulate of electronic and photonic applications in photovoltaic devices[1-4], lasers[5], light emitting diodes (LED)[6-11], field effect transistors (FET)[12-17] based on organic molecules and π-conjugated polymers[18,19]. Compared to many types of conventional inorganic semiconducting material-based technologies, polymer devices are light weight, flexible, chemical stable, potentially less expensive to fabricate and have an ultrafast optoelectronic response[20-24]. They also exhibit a nearly continuous tunability of the energy levels and bandgaps that can be tailored by molecular synthesis, versatile material design and device fabrication process, and low cost solution-process ability for industrial manufacturing on a large scale[19,25-28].

The design of novel conjugated polymers with narrow band gaps requires an intensive investigations of the relationships between the chemical intuition of synthesis and the electronic properties. It has already been reported that the electronic properties of conjugated polymers can be tuned without much efforts by chemical modification. The application of computational predictive density functional theory (DFT) methods combined with chemical intuition leads to facilitate the tailoring during the search for new conjugated polymers. An important contribution of the computational research, which is inherently more time and cost-efficient, is the reduction in the number of potential targets for experimental synthesis. Two different theoretical approaches by using first-principles computations are available to evaluate the band gaps of polymers. The first approach is to investigate the band gap for a series of discrete oligomers with increasing size, and extrapolation to infinite chain length is followed[29-37]. This is a reliable method, but it is difficult to predict band structures from molecular calculations. This is in part due to the fact that realistic theoretical descriptions of the polymer involve heavy computational costs. The second approach is based on standard solid state methods to model an idealized infinite polymer chain. Band structure calculations, according to periodic boundary conditions, Bloch functions, and translational symmetry, are an important theoretical tool in the exploring new conducting polymers[36-40]. It is generally accepted that band gaps predicted for conducting polymers using the theoretical level of DFT coupled with PBC were in excellent agreement with experimental values.

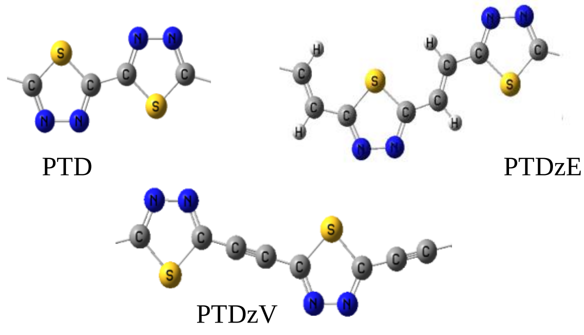
Most of the physical properties of solids are directly or indirectly related to the electronic band structure. The most useful information may extracted from the band structure involves: (1) the value of the bandgap; (2) the direct or indirect nature of the band gap; and (3) the band dispersion or the slope of the bands involved in the band gap.

1,3,4-Thiadiazole (TDz) is a small unit that a growing interest as an electron deficient unit having two electron-withdrawing imine (C=N) groups[41-46]. The molecular and electronic structure of TDz is isoelectronic with five- and six-membered heterocycles, as like as thiophenes, pyrazines and thiazoles. TDz oligomer have received substantial attention due to their aromaticity and isoelectronicity[47,48]. TDz containing liquid crystals have shown good luminescence and wide range mesophases[49]. Some of TDz derivatives form highly ordered structures over a long range[50]. Thiadiazole polymers are not efficient at light harvesting, but they have been incorporated during the fabrication of solar cells as acceptors[51-52]. The derivatives of TDz, has been synthesized, however, poly1,3,4-thiadiazole (PTDz), has not been reported yet. Early calculations were carried out by Flores-Holguin and Glossman-Mitnik for the electronic properties of PTDz using B3LYP/3-21G* method through an extrapolation scheme from oligomers[47]. They predicted that the PTDz is linear, planar and possibly aromatic material, with the extrapolated value of HOMO–LUMO gap for $N \rightarrow \infty$ is 3.626 eV, almost independent of the solvent. They suggested it would be interesting for technical applications to decrease this value by replacing the terminal hydrogens with electron-acceptor and electron-donor groups, as in push–pull polymers. Other alternative have been explored; for example, the electronic properties of the donor–acceptor of fluorene-1,3,4-thiadiazole oligomers have been investigated by Flores-Holguin *et.al* via applying the B3LYP/6-31G(d) chemical model[53]. Using extrapolation analysis, they found that the gap energy decreases to 2.16 eV for polymer. Also, they predicted that the UV–Vis absorption spectra within the visible region of the spectrum. In addition, the electron acceptor character shown by fluorene-1,3,4-thiadiazole, which are suitable for bulk heterojunction solar cells. Although there have been rapid technological developments in the applications of polymers, many aspects of the basic physics of the PTDz are not well established and its properties are not fully understood. It is believed that the present investigation will be very useful for understanding the structural properties and the band gap of the new TDz systems, which provides a basis for constructing TDzpolymerbased electronic devices. Consequently, many calculations of the properties of TDz carried out by using simple models such as that of an isolated, perfect straight chain where the solid state effects are not included.

In the present work, the structural and electronic properties of 1,3,4-thiadiazole-based systems have been investigated using first-principle density functional theory calculations in periodic forms. It is well-known experimentally that the energy band gap of organic molecules can vary, by ≈ 0.3 eV in the presence of ethynyl linkage[11,24]. The focusing on effect of functional groups (ethynyl[54,55] and vinylene[56,57]), as linkage terminal, that significantly enhances π-conjugation by delocalizing electrons along the backbone, leading to TDz polymers with narrow band gaps. The DFT calculations utilize the generalized gradient approximation functional of HCTH[58,59], that developed by Hambrecht−Cohen−Tozer−Handy exchange-correlation functional and the double numeric and polarized (DNP) basis set with fully periodic boundary conditions (PBC) to obtain accurate band gaps in these conjugated polymers[60]. The majority of bond distances, bond angles and atomization energies prediction, reproduce well the experimental HOMO-LUMO gap, and vibrational frequencies analysis regarding the excellent performance of HCTH methodology[61]. Dunning’s correlation-consistent numerical basis sets (DNP), which is a p-polarized double-zeta numerical basis set and its accuracy is comparable to that of Pople’s Gaussian-type 6-31G** basis set[62-67]. DNP have attracted great attentions recently due to the compactness and rapid convergence in DFT calculations[66,67]. In addition, the performance of numerical basis sets, which is used in the DFT program package (DMol3), have been successfully employed in calculations on sulfur-containing molecules[68,69].

2 Theoretical calculations

Periodic calculations were performed using DFT within the generalized gradient approximation of the HCTH407[70] feature within the DMol3 module implemented in Materials Studio software suite (Accelrys Inc.)[71]. Molecular geometries, and band structures have been predicted for three conjugated polymers based on 1,3,4-thiadiazole (TDz) end-capped by linkage groups (pure, ethynyl −C≡C− and vinylene −CH=CH−) in polymeric form, where PTDz (poly 1,3,4-thiadiazole), PTDzE (poly 1,3,4-thiadiazole ethynyl), PTDzV (poly 1,3,4-thiadiazole vinylene), as showed in figure-1. All calculations have been performed using the double numerical plus polarization basis set (DNP), and employing norm-conserving pseudopotentials. This basis set used to increasing the speed of calculations and the basis set superposition error is small. The DNP has a polarization p-function added on hydrogen atoms, as well as a polarization d-function added on non-hydrogen atoms have been used with the electron smearing of 0.001 Hartree. The tolerances of energy, gradient, and displacement convergence were 2×10^{-5} Hartree, 4×10^{-3}Hartree/Å, and5×10^{-3} Å. The fine grid sizes (corresponding to a k-point separation of 0.04 A^{-1}). The global orbital cutoff was performed with fine quality value of 4.0 Aº. The optimizations were carried out without any symmetry constraints. Since the electronic properties of polymers depend on the constituent monomers, we have started with studying the properties of monomers. Unlike many plane-wave DFT packages, DMol3 does not optimize lattice constants[72], therefore the molecules within the unit cell were optimized within the cell parameters specified during the following steps. The first step involves the optimization of structure and geometry of the oligomer of 4-monomers. The second step is the specifying of crystal lattice constant (a) according to the length of a two repeating units. Further, a vacuum layer (b and c lattice constants) of about 15A° is used to avoid interlayer interactions. The third step is the triclinic crystalline form of two repeating units followed by the evaluation of band structure of the crystal. The five-membered rings alternate their directions in homopolymers, so that the unit cell contains two rings. PTDz, PTDzV and PTDzE having periodic unit cell of length 7.6 A, 11.6 A and 11.2 A, respectively. Band structures in the positive region of the first Brillouin zone (between k=0 and k=π/a, Γ→X) were calculated along the k-vector of the one dimensional polymers with 50×1×1 k-points. The lowest 4 unoccupied and highest 4 occupied bands in the positive region of the first Brillouin zone were plotted. The vertical electronic excitation of the absorption spectra, including wavelengths and oscillators strengths were systematically investigated using TDDFT calculations with HCTH/DNP method on the fully DFT-optimized structure of the ground states. The lowest excitation energies were calculated within the range 35 singlet excited states. The polymers here have chain length of about 9-14 nm. The segment of this chain length contains 12 monomers, which mimics the optical properties of polymers with infinite chain quite well.


PTD

PTDzE

PTDzV

Fig. 1 — Unit cell structures of the PTDz,

3 Results and Discussions

3.1 Electronic Properties

As summarized in figure 2, there is no significant difference between HOMO energy level of TDz molecule and that of TDzE and TDzV. All of these molecules exhibit deeper HOMO energy levels (< - 6.4 eV) due to the electron deficiency of the TDz units. TDzE and TDzV have significantly lower LUMO energy levels than that of TDz, suggesting that the π-conjugation between TDz and the ethynyle / vinylene units is better than the pure TDz.

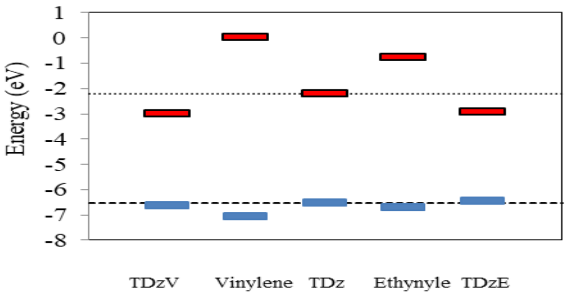


Fig. 2 — HOMO (blue) and LUMO (red) energy levels of TDzV, vinylene, TDz, ethynyle and

Fig. 2 — HOMO (blue) and LUMO (red) energy levels of TDzV, vinylene, TDz, ethynyle and TDzE molecules.

The main goal of this theoretical study is to determine the band structur and optical properties of PTDz, PTDzE and PTDzV. These polymers are predicted to appear in a totally flat structure, probably caused by the intramolecular dipole-dipole interaction. The already mentioned planarizing effect of TDz oligomer turn out to be completely flat[47]. The calculated band structures for the one-dimensional nature of PTDz, PTDzE and PTDzV are compared in figures 3, 4 and 5 using the conventional symmetry direction from Γ to X points in Brillouin zone. The band structure for PTDz has a direct bandgap of 2.022 eV between the valence band maximum and the conduction band minimum at Γ. The largest direct bandgap (3.647 eV) is found at the X point. This value is in good agreement with the theoretical prediction of Flores-Holguin and Glossman-Mitnik, who have determined 3.626 eV, by using the extrapolated approach[47]. By looking on the energy bands of PTDzE and PTDzV (Fig. 4 and 5), one immediately notice a qualitative similarity of the band structures of these polymers with PTDz. The significantly smaller calculated energies of the direct transitions are 1.695 and 1.476 eV at Γ point, respectively. The most relevant difference in the band structure can be seen at the zone edge (X point), where the occupied bands converged at the zone boundary. This suggests that the coupling arrangement between linkage group and TDz in the backbone of polymer can result in an effective reduction in the band gap of the polymer. Moreover, the calculated band gap may decreases due to the conjugated length backbone of these repeating units. It has been experimentally reported that the presence of an ethynyl group (–C≡C–) as a linkage group decreases the maximum wave length of absorption spectrum by a magnitude of about 0.3 eV[73,74].According to this, linkage group implies a clear improvement in the conducting character of this kind of polymers. The three polymers are semiconductors and their energy gaps are small enough to allow electrons to be thermally promoted into the conduction hand. Compounds with a direct bandgap are optically active and are suitable for photonic and optoelectronic devices. Bandgaps for PTDzE and PTDzV provide the evidence of their absorptions in red regions of the visible spectrum are smaller than that of PTDz, which prominent near-IR absorption of the green regions of the visible spectrum. The valance band width (VBW) for PTDz and PTDzV obtained values of 0.479 eV and 0.51 eV, respectively, whereas for PTDzE the VBW is a little larger of 0.64 eV. The bandwidth of valence band is similar for PTDz because there is no significant difference between HOMO energy level as mentioned above. The small valance band curvature of these polymers lead to larger effective mass and lower charge carriers mobility

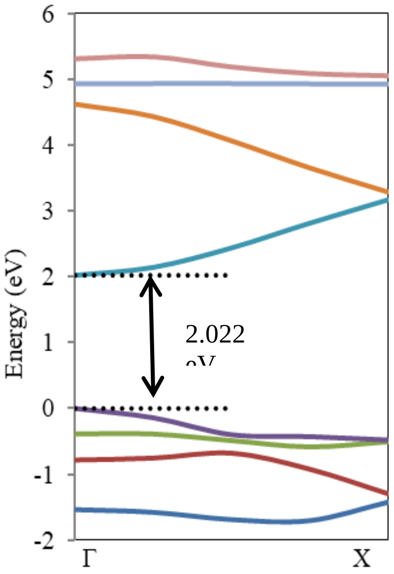


Fig. 3: The band structure of PTD

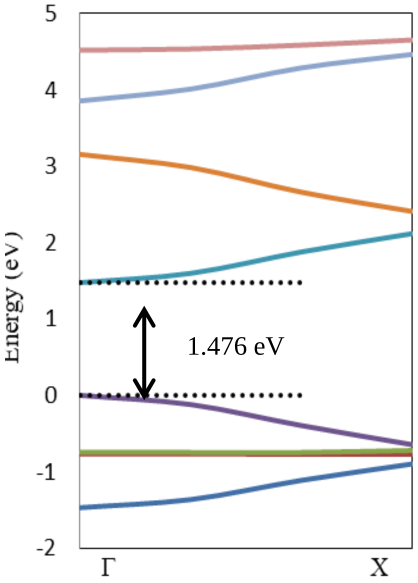


Fig. 4: The band structure of PTDzE.

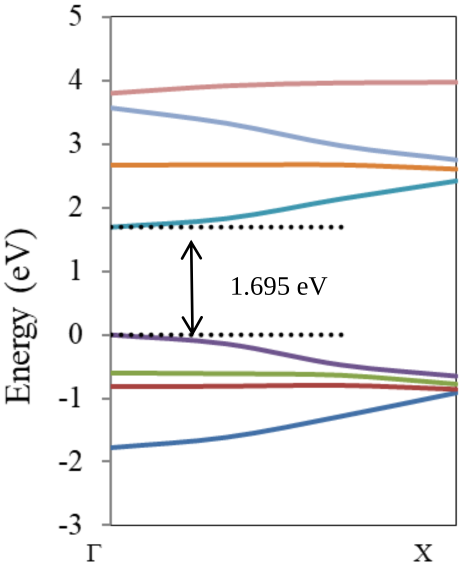


Fig. 5: The band structure of PTDzV.

A narrow bandwidth of conduction band of polymers is observed. For series polymers, the bandwidth of conduction band for PTDz, PTDzE, and PTDzV are 1.146, 0.71, and 0.67 eV, respectively. The fact that less disperse bands indicate weaker interactions between adjacent orbitals belong an isolated chain. Nearly flat bands indicate localization, low group velocity and the kinetic energy of charge carriers are quenched in these bands.

3.2 Optical properties

The corresponding simulated UV–Vis absorption spectra of the studied polymers, presented as oscillator strength against wavelength are shown in Fig. 6. The transition along the chain direction is favorable, this reveals the one-dimensional nature of the polymer crystals. PTDz have three absorption peaks at 438, 485, and 526 nm. The first absorption peak correspond to the $\pi \rightarrow \pi*$, while the another two peaks are attributed to the intramolecular charge transfer (ICT) transition. The absorption simulations of PTDzE and PTDzV are both have four excitation peaks, which for PTDzE at 496, 565, 604 and 658 nm, while for PTDzV at 540, 687, 629 and 749 nm. All these four peaks are lay within the visible region and to carry characteristics of intramolecular charge transfer (ICT). In comparison with the wave length of maximum absorption λ_{max} of PTDz, there is about 127 and 191 nm red-shift for PTDzE and PTDzV, respectively. PTDzV exhibits an electronic bandgap, defined as the onset of the $\pi \rightarrow \pi*$ absorption, of 1.476 eV and a λ_{max} of 626 nm, making it deep blue in color. Usually, the complete localization of the electronic wavefunction means their transition becomes a typical charge transfer (CT) transition, which is desirable for the efficient energy transfer[75].

The absorption wavelengths arising from S0→S1 electronic transition increase progressively with the decreasing of the band gap energies of the studied polymers. Moreover, PTDzE and PTDzV have an intense absorption (high oscillator strength) comparing with the PTDz. This effect is obviously due to the conjugated length in these compounds. In the scheme of band structure, these transitions are vertical, starting from the lower energy separation, which corresponds to k = 0 (the optical gap), and extending up to the highest values of the separation between the two bands. According to the PBC/DFT results, the lowest energy transition is no longer formed by the VB-CB pair. For PTDz, PTDzE and PTDzV excitation to the S1 state corresponds exclusively to the promotion of an electron from the second valance band 2nd VB to the first conduction

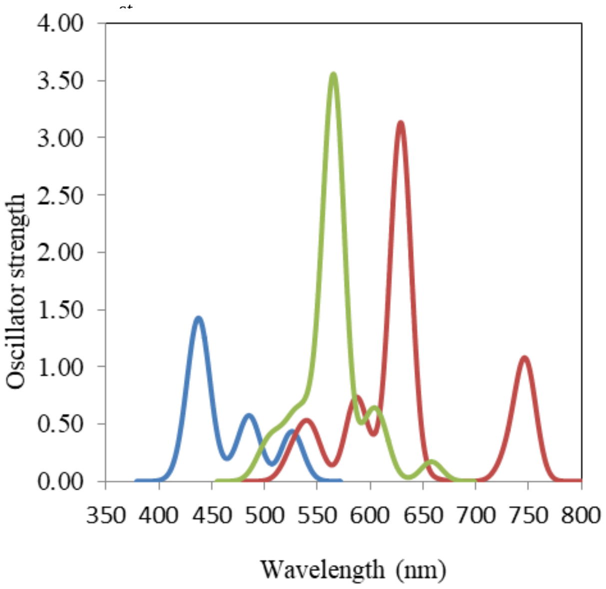


Fig. 6: The UV–Vis absorption spectra of PTDz (blue), PTDzV (green) and PTDzE (red).

boundary conditions (PBC) in conjunction with TDTDF calculations to rationalize the critical role that linkage group plays in these polymers. The PBC-DFT and TDDFT calculations performed the theoretical HCTH level with DNP basis set. The molecular structures of the three polymers differ from each other only in terms of linkage groups, such a difference leads to significant changes in the energy gaps and optoelectronic properties with the former showing much greater absorption in the visible region. The results strongly emphasize that the existing of ethynyland vineylene linkages is a more effective way of lowering the band gap in poly 1,3,4-thiadiazole conjugated systems. In addition, PTDzV shows the most extended absorption wavelength (λ_{onset}= 749nm) due to the improved conjugation length.Finally, the present work draw attention toward the vinylene/ethynyle-linked 1,3,4-thiadiazole polymer as narrow bandgap materials with very interesting electronic properties.

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