

Theoretical calculation on relationship between molecular structure and band gap of benzo[1,2-b:4,5-b']dithiophene based homopolymer

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Abstract In order to guide the synthesis of new materials with low band gaps, quantum-chemical methods have been increasingly applied to predict the band gaps of conjugated polymers. Softwares such as Material Studio, Gauss View, Gauss 03 and Gauss 09 calculation program were used in this paper. Semi-empirical AM1 method was applied to calculate the optimal geometric structure of selected three benzo[1,2-b:4,5-b']dithiophene homopolymers, namely PBDTV, H2 and H3. Using the generalized density function theory based on B3LYP/6-31G*, B3LYP/6-311G* and M062X/6-311G* level calculation of polymers' band gaps. The results indicate that whether there is enough interspace between adjacent subunits, long alkoxy side chain is advantageous to the band gap decrease, and otherwise it will bring steric hindrance to destroy the coplanarity of polymer chain which is disadvantageous to the band gap decrease. The band gaps of polymers mainly depends on the molecular structure, generally speaking, the more coplanarity of main chain, smaller dihedral angle, smaller difference between the bond length of single and double bonds in the main chain, resulting in narrower band gap.

Keywords Theoretical calculation · Structure–property relationship · Band gap · Coplanarity

1 Introduction

In the past few years, bulk-heterojunction polymer solar cells (PSCs) have attracted considerable attention ascribe to their advantages of low-cost, light weight, and the

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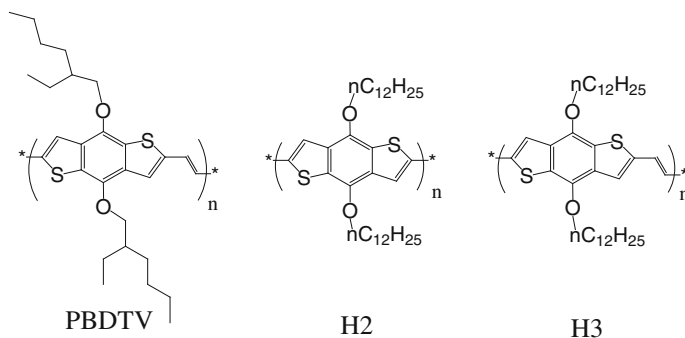


Fig. 1 Molecular structures of three polymers

capability to fabricate flexible large-area optoelectronic devices by solution-process [1–5]. Although PSCs have made several recent advances toward commercialization [6], with a few polymers reaching power conversion efficiencies higher than 6% in the typical bulk heterojunction (BHJ) devices [7–10]. But as impressive and important as these polymers are, they still do not meet the targeted 10% efficiency that is required for broad commercialization. [11] Since one of the limiting parameters for photovoltaic energy conversion is the mismatch of the absorption spectrum of the active layer and the solar emission, the optical band gap of the polymer used is of crucial importance for increasing the efficiency. Therefore, in the past decade, much effort has been devoted to the design and synthesis of new polymer photovoltaic materials, which have low band gaps. Recently, Jianhui Hou [12] developed a series of low band gap polymers based on benzo[1,2-b:4,5-b']dithiophene (BDT), presenting excellent efficiency. BDT attracted some interest as a common unit in conjugated polymers [13], but some of the important properties of this unit have not been explored fully. BDT has two merits. First, BDT has a large planar conjugated structure and easily forms π - π^* stacking, which improves mobility. As reported, polymers based on BDT and thiophene exhibit a hole mobility of $0.25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, one of the highest values for conjugated polymers [14]. Hence, it is reasonable to expect the BDT-based polymers to have good mobility. Second, since band gap of conjugated polymers is generally very susceptible to steric hindrance, if we want to investigate the effects on band gap and molecular energy levels of different units, we must consider the steric hindrance between two adjacent units is very small, as 4,9-bis-alkoxy-BDT has no substituent on 1, 3, 5 and 7 positions. This makes BDT an ideal conjugated unit for new photovoltaic material design.

Many new polymers based on BDT have been synthesized successfully [15–17], with excellent performance on PSCs. In order to investigate the BDT further, softwares such as Material Studio, Gauss View, Gauss 03 and Gauss 09 calculation program were used in this paper. Three BDT homopolymers PBDTV, H2 and H3 were selected as research object which shown in Fig. 1. Semi-empirical AM1 method was applied to calculate the optimal geometric structure of selected three photovoltaic polymers, and generalized density function theory (DFT) based on B3LYP/6-31G*, B3LYP/6-311G* and M062X/6-311G* level were used to calculation of the polymers' band gaps.

2 Experiment section

2.1 Computational methods

B3LYP is a widely used hybrid DFT method. Its exchange-correlation functional can be expressed as [18, 19]

$$E_{xc} = AE_X^{Slater} + (1 - A)E_X^{HF} + B\Delta E_X^{Becke88} + E_C^{VWN} + C\Delta E_C^{LYP} \quad (1)$$

where the three parameters, A, B, C are 0.80, 0.72, and 0.81, respectively. E_x , E_c represent exchange and correlation energy. Slater and Vosko–Wilk–Nusair (VWN) [20] functionals are used to account for local exchange, correlation parts, respectively; while, Becke88 and LYP functionals are used to express the non-local (GGA) exchange and correlation parts, respectively. By selectively mixing exact exchange, and by explicitly including correlation, the B3LYP gaps come very close to the corresponding optical excitation energy. It is generally accepted that, for conjugated oligomers, extrapolating the linear curve of the HOMO–LUMO gap against the reciprocal of the number of monomer units ($1/n$) affords a prediction of the band gap for the corresponding polymer [21–27].

Thus, in this paper the geometries of the oligomers were optimized at an RHF level using a semi-empirical AM1 method [28]. And then the band gaps were calculated using the DFT at B3LYP/6-31G* and B3LYP/6-311G* levels with the Gaussian-03 program [29]. Two types of basis sets were chosen for comparing of the accuracy of the calculations.

However, the HOMO–LUMO bandgaps calculated by B3LYP functional are not agreement with the differences between the ionization potential (IP) and electron affinity (EA) and the first excitation energies well, and it should take into account the optimized effective potential, self-interaction correction, and the asymptotic behavior of the exchange-correction potential for calculating HOMO and LUMO energies [30]. Thus, in order to obtain more accurate HOMO–LUMO bandgaps, hybrid meta-generalized gradient-approximations functional M062X was selected for computing orbital energies at M062X/6-311G* level implemented in the Gaussian-09 program [31]. In comparison to B3LYP functional, M062X are the best functional for applications involving main-group thermochemistry, kinetics, noncovalent interactions, and electronic excitation energies to valence and Rydberg states [32].

2.2 Band gaps calculation

The band gaps in conjugated polymers are governed by their chemical structures. Therefore, the detailed band gap theoretical calculations were carried out on the polymer structures. All band gaps were obtained by DFT (B3LYP/6-31G*) and DFT (B3LYP/6-311G*) with the Gaussian-03 program and DFT (M062X/6-311G*) with the Gaussian-09 program. The theoretical quantity of E_g for direct comparison with the experimental band gap should be the transition (or excitation) energy from the ground state to the first dipole-allowed excited state [33]. At the molecular level, E_g

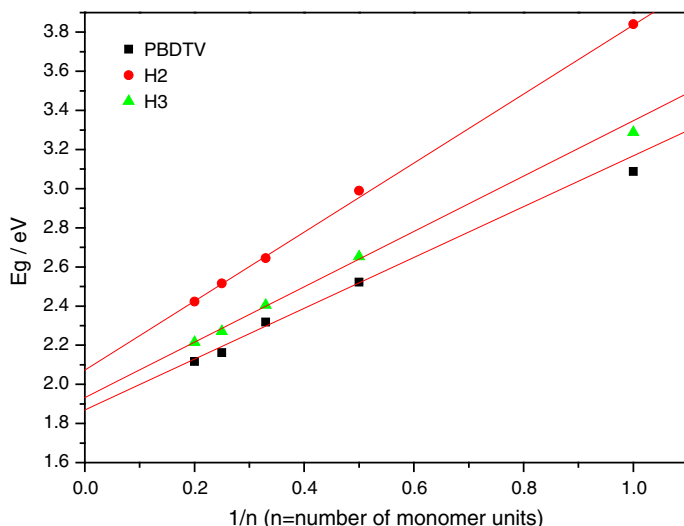


Fig. 2 The band gaps by B3LYP (6-31G*) as a function of reciprocal chain length n in oligomers of PBDTV, H2, and H3

corresponds to the adiabatic transition energy [34]. However, the crudest estimate, but most widely used due to its low cost, is based on the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), when $n = \infty$ [33,35,36]. Band gaps for infinite chains (polymer) of PBDTV, H2, and H3 were determined by plotting band gaps in oligomers against the inverse of the number (n) of monomer units and extrapolating the number of units to infinity. The HOMO–LUMO gaps of the oligomers, and the extrapolated band gaps of polymers are presented in Figs. 2, 3, and 4, respectively.

The calculated band gaps of polymers PBDTV, H2 and H3 with B3LYP (6-31G*), B3LYP (6-311G*) and M062X (6-311G*) basis function are shown in Figs. 2, 3, and 4. Among them, the finally calculated band gaps of PBDTV are 1.87, 2.10, and 2.42 eV, respectively (PBDTV experimental band gap is 2.34 eV [37]). The calculated band gaps of H2 are 2.07, 2.35, and 2.75 eV, respectively (H2 experimental band gap is 2.49 eV [12]). The calculated band gaps of H3 are 1.93, 1.96, and 2.28 eV, respectively (H3 experimental band gap is 2.21 eV [12]). It shows a comparable good theoretical result for the gaps and indicates a combination of semi-empirical geometry optimization followed by a hybrid functional DFT calculation for the energy levels of molecular oligomers provides a reliable and computationally efficient method for predicting bandgaps of conjugated polymers.

2.3 Methods comparison

For comparison, results obtained from B3LYP/6-31G*, B3LYP/6-311G* and M062X/6-311G* method are listed in Table 1. It is apparent from the results in Table 1 that the band gaps of three homopolymers calculated by B3LYP or M062X show the

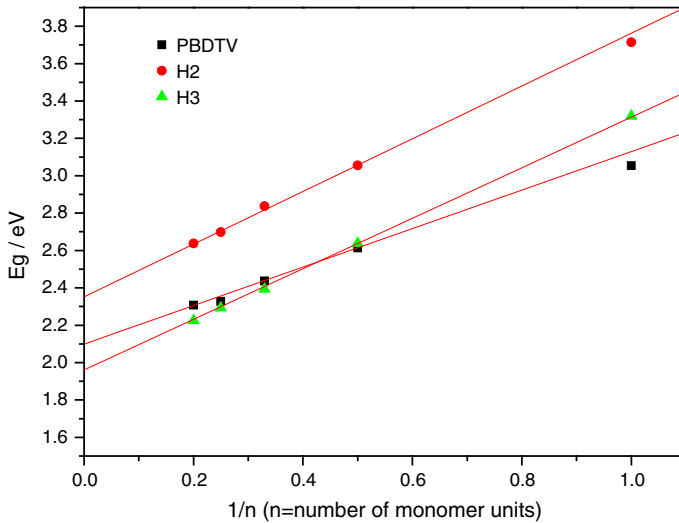


Fig. 3 The band gaps by B3LYP (6-311G*) as a function of reciprocal chain length n in oligomers of PBDTV, H2 and H3

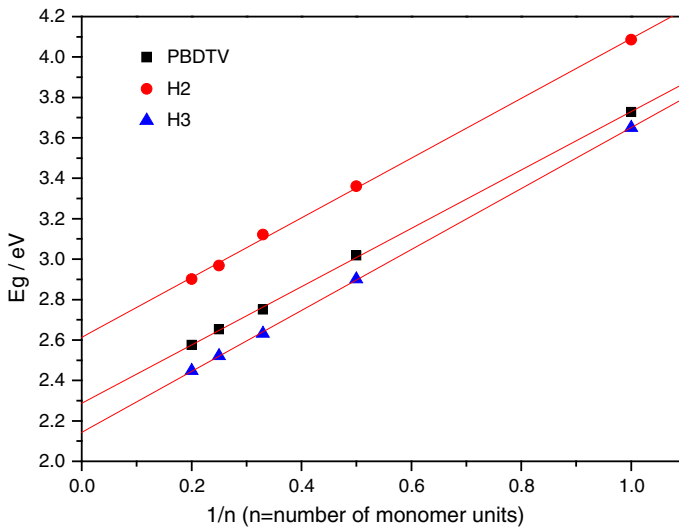


Fig. 4 The band gaps by M062X (6-311G*) as a function of reciprocal chain length n in oligomers of PBDTV, H2 and H3

similar results. And, all the calculation of band gap values of polymers PBDTV, H2 and H3 compared with the experimental values has a good match. This may be due to the HOMO–LUMO gaps of PBDTV, H2, and H3 are generally small (less than 3 eV), systems with many delocalized electrons, the obtained results are much closer to the experimental values than in case of saturated hydrocarbons, mostly because of the smaller numeric values. The difference between the calculated values and experimental

Table 1 The HOMO–LUMO band gaps by B3LYP of PBDTV, H2 and H3

Oligomer	No. of monomer	Band gap (eV)		
		B3LYP/6-31G*	B3LYP/6-311G*	M062X/6-311G*
PBDTV	1	3.086	3.060	3.728
	2	2.523	2.616	3.018
	3	2.320	2.439	2.75
	4	2.170	2.327	2.653
	5	2.119	2.313	2.575
	∞	1.87	2.10	2.42
	Experiment	2.34		
H2	1	3.845	3.718	4.085
	2	2.990	3.060	3.361
	3	2.652	2.842	3.121
	4	2.525	2.703	2.968
	5	2.425	2.639	2.901
	∞	2.07	2.35	2.75
	Experiment	2.49		
H3	1	3.297	3.314	3.651
	2	2.652	2.643	2.901
	3	2.407	2.399	2.632
	4	2.273	2.298	2.521
	5	2.219	2.225	2.448
	∞	1.93	1.96	2.28
	Experiment	2.21		

values is probably due to the fact that the theoretical calculations are in gaseous phase, while the experimental band gaps values are obtained in solutions or in thin films. In comparison of calculated value B3LYP/6-31G* with B3LYP/6-311G* basis function, B3LYP/6-311G* is more close to the experimental value. And in comparison of B3LYP/6-311G* and M062X/6-311G* method, M062X/6-311G* shows a better match with the experimental value.

2.4 Optimized geometry

The main chain structure of trimers PBDTV, H2 and H3 are shown in Fig. 5 and each carbon atom is marked number. The dihedral angle data of trimers PBDTV, H2 and H3 are summarized in Table 2. It can be seen from the Table 2, the maximum dihedral angle values of trimers PBDTV, H2 and H3 are 15.914°, 38.840° and 13.487°, respectively. Analysis of the above dihedral angle data can be found that there is a little coplanarity difference of polymers PBDTV, H2, and H3, and the order of dihedral angle maximum values is H2 > PBDTV > H3, it shows that the calculated results are

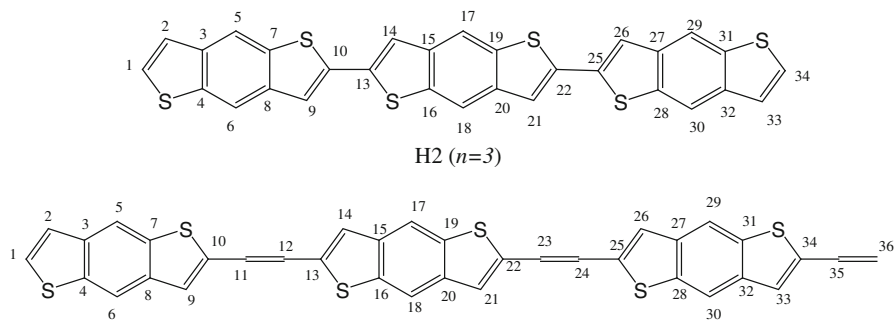


Fig. 5 The conjugated oligomers (PBDTV, H2, H3 $n = 3$) main chain structure. H2 ($n = 3$), PBDTV, H3 ($n = 3$)

Table 2 Dihedral angles of PBDTV, H2 and H3 ($n = 3$) by AM1 optimized geometry

Dihedral angles/(deg)	Molecules		
	PBDTV	H2	H3
(9,10,13,S)	–	38.840	–
(21,22,25,S)	–	–15.227	–
(9,10,11,12)	2.536		–13.487
(11,12,13,14)	3.749		–3.386
(21,22,23,24)	2.525		2.801
(23,24,25,26)	4.128		3.386
(33,34,35,36)	–15.914		1.080

basically in agreement with their experimental band gaps order (2.49, 2.34, 2.21 eV). The geometry optimized molecular structures are shown in Fig. 6. From Fig. 6, we can be more intuitively find that the main chain coplanarity of polymer H3 is best, PBDTV is second, whereas the molecular main chain of H2 showed large torsion. Thus, the simulation results are consistent with their band gap situation, we can conclude that as the dihedral angle decreasing, the coplanarity of polymer is better, and the band gap is smaller.

2.5 Substitution influence

Commonly, alkyl attached to the molecular backbone can lead to a band gap decrease in the BDTs. This behavior is a result of the electron-releasing effect created by the introduction of the alkyl side chains. The decrease in the band gap is due to the electronic substituent effect created by the introduction of the alkyl side chains and is larger than the steric hindrance imparted by the alkyl side chains [38]. Hence, these steric hindrances are usually neglected. Nevertheless, our calculation results show that alkyl substituents induce obvious steric hindrances and increased band gap for

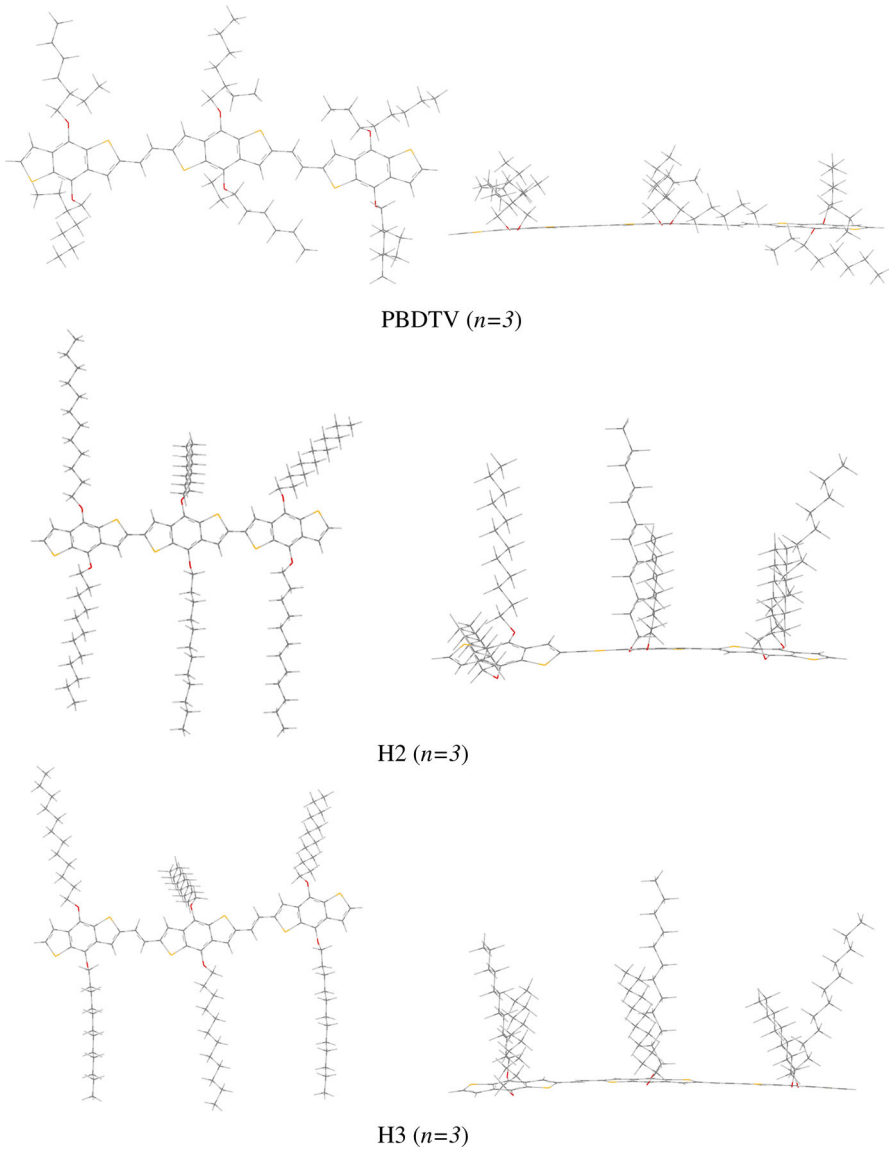


Fig. 6 AM1 Optimized geometries of PBDTV, H2 and H3 ($n = 3$), PBDTV ($n = 3$), H2 ($n = 3$), H3 ($n = 3$)

BDT homopolymers mainly depends on their interspace distance between adjacent subunits.

Compared to PBDTV and H3, both are BDT unit connected by alternating $-C=C-C-$ bond, and polymer PBDTV side chain is isooctyl alkoxy, while H3 side chain is a linear twelve alkoxy, and the interspace distance between the subunits is large enough (13.45 and 12.87 Å, respectively), as shown in Fig. 7, in comparison with their experimental band gap values, PBDTV (2.34 eV) is slightly bigger than

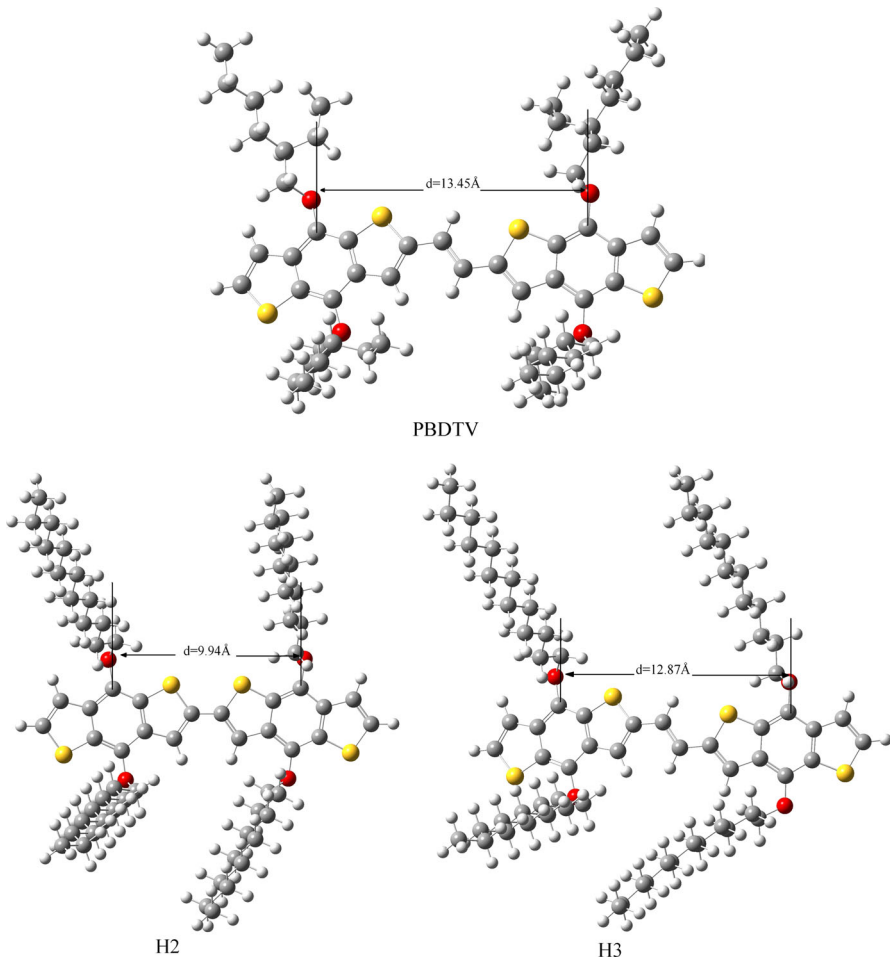


Fig. 7 The adjacent units interspace distance of polymers PBDTV, H2 and H3

that of H3 (2.21 eV), it indicates that the longer linear alkoxy side chains is more advantageous to the band gap decrease [39], and the side chain steric hindrance is also very small. However, compared to PBDTV and H2, we find that even though the polymer H2 introduced twelve alkoxy long side chain, but the band gap is still bigger than PBDTV, this is mainly due to the molecular structure of H2 is directly connected by $-C-C-$ bond between BDT subunits, leading to the interspace distance between the adjacent BDT subunits is small, linear distance between side chains of H2 is around $\sim 9.94 \text{ \AA}$, and PBDTV is about $\sim 13.45 \text{ \AA}$, as shown in Fig. 7. Therefore, although twelve alkoxy long side chain is more advantageous to reduce the energy gap, but it also bring large steric hindrance damaged the coplanarity of molecular chain, reducing the conjugate effect, and offsetting the band gap decrease, unfavorable to the band gap decrease, and finally show the band gap of polymer H2 (2.49 eV) is bigger than that of polymer PBDTV (2.34 eV). Compared H2 with H3, there are all the same

twelve alkoxy long side chain, H2 is connected by $-C-C-$ bond between adjacent BDT subunits while H3 is connected by $-C-C=C-C-$ bond between adjacent BDT subunits, therefore, H3 has a larger interspace distance between its subunits, the linear distance between the adjacent BDT subunits is about $\sim 12.87 \text{ \AA}$, while H2 is about $\sim 9.94 \text{ \AA}$, resulting in smaller steric hindrance in H3 than that of H2. Therefore, the coplanarity of H3 is better than that of H2, this is also agreed with the band gap values (2.49, 2.21 eV).

Thus, we can conclude that in the case of the polymer main chain has enough space between adjacent subunits, and the polymer with longer length of alkoxy side chain is advantageous to the band gap decrease, such as polymer PBDTV and polymer H3, Fig. 6. But in the case of the polymer main chain has not enough interspace between adjacent subunits, although introduction of longer alkoxy side chain can reduce the band gap, but at the same time bring steric hindrance, and offset the lower band gap effect, instead of destroying polymer chain planarity, not well for band gap decreased. In addition, polymer with branched side chain has better solubility than that of with linear alkoxy side chain, such as polymer PBDTV monomer is a pale yellow oily liquid [37], and polymers H2, H3 monomers are white solid [12]. Anyhow, the calculation results show that the better coplanarity of polymer main chain, the longer of conjugation length, and resulting in lower band gap.

Table 3 C–C bond lengths of PBDTV, H2, H3 ($n=3$) by AM1 optimized geometry

Bond ^a	Bond distances (Å)		
	PBDTV	H2	H3
D(1,2)	1.495	1.358	1.357
S(2,3)	1.522	1.458	1.445
D(3,4)	1.509	1.455	1.417
S(4,6)	1.499	1.402	1.388
D(6,8)	1.515	1.411	1.407
S(8,9)	1.530	1.443	1.435
D(9,10)	1.514	1.380	1.370
S(10,11)	1.520		1.430
D(11,12)	1.488	S(10,13)	1.375
S(12,13)	1.510	1.441	1.434
D(13,14)	1.508	1.382	1.368
S(14,15)	1.526	1.440	1.432
D(15,16)	1.506	1.423	1.448
S(16,18)	1.491	1.391	1.381
D(18,20)	1.519	1.421	1.409
S(20,21)	1.525	1.446	1.430
D(21,22)	1.499	1.379	1.368
S(22,23)	1.508		1.438
D(23,24)	1.486	S(22,25)	1.356
S(24,25)	1.508	1.441	1.438

^a S/D denotes C–C single/double bond and the data were taken from the structures optimized at the AM1

The C–C bond lengths of the optimized oligomers ($n=3$) are listed in Table 3. For PBDTV, H2 and H3, C–C single bond distances are longer than that of C=C double bonds indicating that the PBDTV, H2 and H3 polymers have more aromatic character. Thus, aromatic forms are a more stable conformation for PBDTV, H2 and H3 molecules. We note that the C–C single-bond distances of PBDTV, H2 and H3 within the scope of 1.491–1.530, 1.391–1.458 and 1.381–1.445 Å, respectively. And the C=C double-bond distances of PBDTV, H2 and H3 within the scope of 1.486–1.519, 1.358–1.455 and 1.375–1.448 Å, respectively. Thus, the difference distances between the C–C single-bond and C=C double-bond are 0.005–0.011, 0.003–0.033 and 0.003–0.006 Å for PBDTV, H2 and H3 respectively. Therefore, the order of the difference distances between the C–C single-bond and C=C double-bond is H2 > PBDTV > H3, which illustrate that the charge delocalization on the main chain of the polymer H3 is best and band gap is smallest, and H2 is worst and band gap is biggest, this is in good agreement with the results of dihedral angle values.

3 Conclusion

The BDT homopolymers band gaps were successfully calculated using the DFT at B3LYP/6-31G*, B3LYP/6-311G* and M062X/6-311G* levels, and all the calculations were performed with the Gaussian-03 or Gaussian-09 program. The geometries were optimized at an RHF level using a semi-empirical AM1 method. The calculated band gaps are in good agreement with the experimental values. In comparison of calculated value B3LYP/6-31G* with B3LYP/6-311G* basis function, B3LYP/6-311G* is more close to the experimental value. And in comparison of B3LYP/6-311G* and M062X/6-311G* method, M062X/6-311G* shows a better match with the experimental value. The results indicate that the band gaps of BDT homopolymers mainly depends on the molecular structure, generally speaking, the more coplanarity of main chain, smaller dihedral angle, smaller difference between the single and double bond length, resulting in narrower band gap. In addition, whether there is enough interspace between adjacent units in BDT homopolymer, longer alkoxy side chain is advantageous to the band gap decrease.

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References

1. J. Peet, J.Y. Kim, N.E. Coates, W.L. Ma, D. Moses, A.J. Heeger, G.C. Bazan, Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols. *Nat. Mater.* **6**, 497 (2007)
2. C. Soci, I.-W. Hwang, D. Moses, Z. Zhu, D. Waller, R. Gaudiana, C.J. Brabec, A.J. Heeger, Photoconductivity of a low-bandgap conjugated polymer. *Adv. Funct. Mater.* **17**, 632 (2007)
3. L. WeiShi, Y. Yohei, F. Takanori, S. Akinori, S. Shu, T. Seiichi, M. Hiroyasu, S. Sono, T. Masaki, A. Takuzo, Amphiphilic molecular design as a rational strategy for tailoring bicontinuous electron donor

- and acceptor arrays: photoconductive liquid crystalline oligothiophene-C60 dyads. *J. Am. Chem. Soc.* **130**, 8886 (2008)
4. H. YouJun, Z. GuangJin, M. Jie, Z. MaoJie, L. YongFang, Poly(thienylene-benzothiadiazole-thienylene-vinylene): a narrow bandgap polymer with broad absorption from visible to infrared region. *Polymer* **50**, 5055–5058 (2009)
 5. B. Laju, G. Xiaoyang, Y. Bo, X. Zhiyuan, Y. Donghang, G. Yanhou, W. Fosong, Monodisperse co-oligomer approach toward nanostructured films with alternating donor–acceptor lamellae. *J. Am. Chem. Soc.* **131**, 13242 (2009)
 6. G. Dennler, M.C. Scharber, C.J. Brabec, Polymer–fullerene bulk-heterojunction solar cells. *Adv. Mater.* **21**, 1323 (2009)
 7. S.H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J.S. Moon, D. Moses, M. Leclerc, K. Lee, A.J. Heeger, Bulk heterojunction solar cells with internal quantum efficiency approaching 100%. *Nat. Photonics* **3**, 297 (2009)
 8. L. Yongye, F. Danqin, Y. Wu, S.-T. Tsai, L. Gang, R. Claire, Y. Luping, Highly efficient solar cell polymers developed via fine-tuning of structural and electronic properties. *J. Am. Chem. Soc.* **131**, 7792 (2009)
 9. H. Jianhui, C. Hsiang-Yu, Z. Shaoqing, C. Ruby I., Y. Yang, W. Yue, L. Gang, Synthesis of a low band gap polymer and its application in highly efficient polymer solar cells. *J. Am. Chem. Soc.* **131**, 15586 (2009)
 10. C. Hsiang-Yu, H. Jianhui, Z. Shaoqing, L. Yongye, Y. Guanwen, Y. Yang, Y. Luping, W. Yue, L. Gang, Polymer solar cells with enhanced open-circuit voltage and efficiency. *Nat. Photonics* **3**, 649 (2009)
 11. M.C. Scharber, D. Muhlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec, Design rules for donors in bulk-heterojunction solar cells—towards 10% energy-conversion efficiency. *Adv. Mater.* **18**, 789 (2006)
 12. H. Jianhui, P. Mi-Hyae, Z. Shaoqing, Y. Yan, C. Li-Min, L. Juo-Hao, Y. Yang, Bandgap and molecular energy level control of conjugated polymer photovoltaic materials based on benzo[1,2-b:4,5-b']dithiophene. *Macromolecules* **41**(16), 6012–6018 (2008)
 13. K. Hiraiishi, T. Yamamoto, New π -conjugated polymers constituted of dialkoxybenzodithiophene units: synthesis and electronic properties. *Synth. Met.* **130**, 139 (2002)
 14. P. Hualong, L. Yuning, W. Yiliang, L. Ping, O. Beng, Z. Shipping, X. Gu, Low-temperature, solution-processed, high-mobility polymer semiconductors for thin-film transistors. *J. Am. Chem. Soc.* **129**, 4112 (2007)
 15. H. Chao, W. ZhongWei, C. KangLi, S. BaoQuan, Z. Qing, Synthesis and photovoltaic properties of new conjugated polymers based on di(2-furyl)thiazolo[5,4-d]thiazole and benzo[1,2-b:4,5-b']dithiophene. *Polymer* **54**(3), 1098–1105 (2013)
 16. T. Hua, D. XianPing, Y. JunTing, Z. BaoFeng, W. YaFei, L. Yu, Z. WeiGuo, W. HongBin, C. Yong, A novel benzo[1,2-b:4,5-b']dithiophene-based conjugated polymer with a pendant diketopyrrolopyrrole unit for high-performance solar cells. *Macromolecules* **46**(1), 113–118 (2013)
 17. D. RuoMeng, Y. Long, G. Xia, H. Ye, W. Peng, Z. ShaoQing, Z. JianPing, H. LiJun, H. JianHui, Application of two-dimensional conjugated benzo[1,2-b:4,5-b']dithiophene in quinoxaline-based photovoltaic polymers. *Macromolecules* **45**(7), 3032–3038 (2012)
 18. A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652 (1993)
 19. A. Frisch, M.J. Frisch, *Gaussian 98 User's Reference* (Gaussian Inc., Pittsburgh, 1998)
 20. S.H. Vosko, L. Wilk, M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.* **58**, 1200–1211 (1980)
 21. U. Salzner, P.G. Pickup, R.A. Poirier, J.B. Lagowski, Accurate method for obtaining band gap in conducting polymers using a DFT/hybrid approach. *J. Phys. Chem. A* **102**, 2572–2578 (1998)
 22. S. Yang, P. Ollishevski, M. Kertesz, Bandgap calculations for conjugated polymers. *Synth. Met.* **141**, 171–177 (2004)
 23. M. Kertesz, C.H. Choi, S. Yang, Conjugated polymers and aromaticity. *Chem. ReV.* **105**, 3448–3481 (2005)
 24. S.S. Zade, M. Bendikov, From oligomer to polymers: convergence in the HOMO–LUMO gaps of conjugated oligomers. *Org. Lett.* **8**(23), 5243–5246 (2006)
 25. G.R. Hutchison, Y.-J. Zhao, B. Delley, A.J. Freeman, M.A. Ratner, T.J. Marks, Electronic structure of conducting polymers: limitations of oligomer extrapolation approximations and effects of heteroatoms. *Phys. Rev. B* **68**, 035204-1–035204-3 (2003)

26. G. Taubmann, Calculation of the Huchkel parameter β [beta] from the free-electron model. Chem. Educ. **69**, 96–97 (1992)
27. J.S. de Melo, L.M. Silva, L.G. Arnaut, R.S. Becker, Singlet and triplet energies of α -oligothiophenes: a spectroscopic, theoretical, and photoacoustic study: extrapolation to polythiophene. J. Chem. Phys. **111**, 5427–5433 (1999)
28. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model. J. Am. Chem. Soc. **107**, 3902 (1985)
29. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman et al., *GAUSSIAN 03, Revision B.01* (Gaussian Inc., Pittsburgh, 2003)
30. C.-G. Zhan, J.A. Nichols, D.A. Dixon, Ionization potential, electron affinity, electronegativity, hardness, and electron excitation energy: molecular properties from density functional theory orbital energies. J. Phys. Chem. A **107**, 4184–4195 (2003)
31. Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. Theor. Chem. Account. **120**, 215–241 (2008)
32. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P.I. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N.J. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, *Gaussian 09, Revision B.01* (Gaussian Inc, Wallingford, 2009)
33. Z. Zhengxi, W. Yongfeng, L. Yun, Time-dependent density functional theory study on polyazopyrrole and polyazothiophene. Macromolecules **36**, 9585 (2003)
34. J. Gierschner, J. Cornil, H.J. Egelhaaf, Optical bandgaps of π -conjugated organic materials at the polymer limit: experiment and theory. Adv. Mater. **19**, 173 (2007)
35. O. Kwon, M.L. McKee, Theoretical calculations of band gaps in the aromatic structures of polythieno[3,4-b]benzene and polythieno[3,4-b]pyrazine. J. Phys. Chem. A **104**, 7106 (2000)
36. L. Yang Li, J.K. Feng, A.M. Ren, J.Z. Sun, The electronic structure and optical properties of carbazole-based conjugated oligomers and polymers: a theoretical investigation. Polymer **47**, 1397 (2006)
37. H. Youjun, Z. Yi, Z. Guangjin, M. Jie, G. Xia, Z. Bo, Z. Maojie, Z. Jing, L. Yongfang, Z. Fengling, I. Olle, Poly(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene vinylene): synthesis, optical and photovoltaic properties. Appl. Polym. Sci. A Polym. Chem. **48**, 1822–1829 (2010)
38. K. Colladet, S. Fourier, T.J. Cleij, L. Lutsen, J. Gelan, D. Vanderzande, L.H. Nguyen, H. Neugebauer, S. Sariciftci, A. Aguirre, G. Janssen, E. Goovaerts, Macromolecules **40**, 65 (2007)
39. J. Gierschner, J. Cornil, H.J. Egelhaaf, Optical bandgaps of π -conjugated organic materials at the polymer limit: experiment and theory. Adv. Mater. **19**(2), 173–191 (2007)