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# Theoretical investigations on the electronic and optical characteristics of fused-ring homopolymers: Comparison of oligomer method and PBC–DFT method

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## ABSTRACT

The electronic and optical characteristics of conjugated polymers are the curial parameters for their photovoltaic and photonic applications. Here, the electronic and optical properties of six selected homopolymers were studied using two methods: oligomer method and PBC–DFT method. The calculated results show, PBC/B3LYP/6-31G\* is preferable to weakly conjugated homopolymers, while the oligomer approach using linear fit at B3LYP/6-31G\* level, reproduced well band gaps for stronger conjugated homopolymers. The results also indicate that the calculated absorption spectra using TD-B3LYP/6-31G\* at trimer model are in agreement with the available experiments, however the Meier fit of oligomers highly overestimates the experimental data.

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## 1. Introduction

Recently, organic electronics has gained considerable interests due to its applications in organic light-emitting diodes (OLEDs) [1–3], organic thin film transistors (OTFTs) [4–6], organic photovoltaic cells (OPVs) [7–9], etc. Vast amounts of new materials are experimentally discovered with theoretical explanation providing only post-facto justification of the observed structures and devices [10–12]. In 10 years, however, theories (in particular computational chemistry methods) together with rational design techniques directs the successful synthesis of the organic electronic materials used in organic semiconductor devices [13], especially in solar cell applications [14]. This opens vast opportunities for new material designs [15].

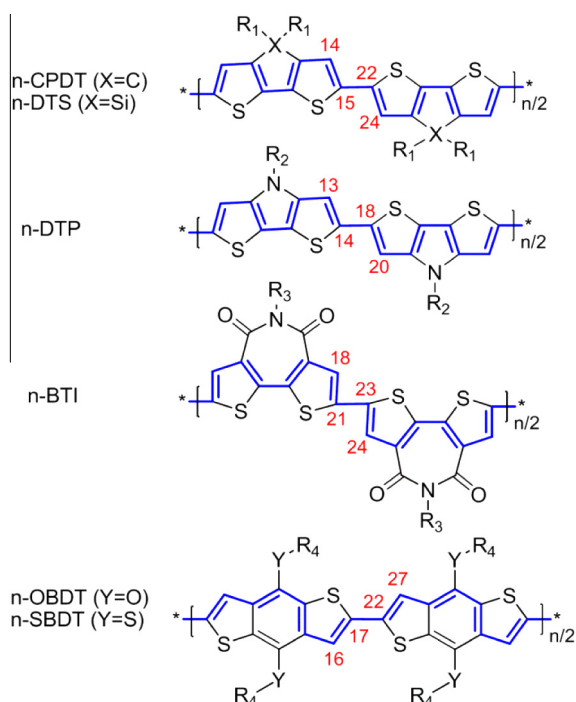
Rational design of the all-plastic optoelectronic devices on the basis of conjugated polymeric materials has many challenges that involve experimental and theoretical chemistry and physics [16]. To design organic electronic materials with better performances requires a comprehensive understanding of the electronic structure and optical properties of conjugated polymers and other related parameters. Quantum-chemistry approaches have been generally used to rationalize experimental data of organic molecules and to predict many important properties of yet unknown materials [17]. A traditional and classical method to calculate a band gap is the so-called oligomer approach, in which the properties of oligomers are first calculated, and then extrapolated to ideal infinite polymers [12,18–21]. Recent studies indicated that the

method involving periodic boundary condition (PBC) can also reliably predict the band gaps of conjugated polymers [22–25]. However, predictions from different theoretical methods and experimental results obtained for a given conjugated backbone generally differ significantly, so that assessing the reliability of a given methodology for the predictions of the polymer properties is an important task [16], in particular, the comparisons between different theoretical methods is urgently needed, and could help to settle down the debates on the methodology for precisely predict band gap and other related properties.

In this Letter, six fused-ring analogs of homopolymers, as shown in Figure 1, poly(cyclopentadithiophenes) (*n*-CPDT) [26,27], poly(dithienosilole) (*n*-DTS) [28], poly(dithienopyrrole) (*n*-DTP) [29,30], poly(*N*-alkyl-2,2'-bithiophene-3,3'-dicarboximide) (*n*-BTI) [31], poly(dialkoxy-benzo[1,2-b:4,5-b']dithiophene) (*n*-OBDT) [32] and poly(dithioalkoxy-benzo[1,2-b:4,5-b']dithiophene) (*n*-SBDT) [32] were investigated on the inherent band gaps and absorption spectra using theoretical quantum-chemical methods. A comparison has also been implemented between the oligomer method (with three fits: linear fit, Kuhn fit, and Meier fit) and PBC–DFT (the periodic boundary condition–density function theory) method. We show that, for band gaps, PBC/B3LYP/6-31G\* calculations is preferable to weakly conjugated homopolymers, while the oligomer approaches with linear fit, at B3LYP/6-31G\* level, reproduces very well the band gaps of strongly conjugated homopolymers. Time-dependent density functional theory (TD-DFT) with trimer model calculations roughly satisfied the experimental absorption spectrum, while the Meier fits of the oligomers (*n* = 1–5, 8) overestimate the experimental data.

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**Figure 1.** Chemical structures of selected homopolymers.  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  shown in molecular structures all denote alkyl-branched chains. The numbers (in red) in these structures indicate the dihedral angles studied in this Letter. The bonds marked with blue color are the backbones for selected molecules. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 2. Methods and computational details

### 2.1. Theoretical background

The polymer properties such as  $\pi$ - $\pi^*$  transition and HOMO–LUMO (the highest occupied molecular orbital–the lowest unoccu-

pled molecular orbital) gap can be estimated usually by plotting those oligomer properties as a function of  $1/n$  or  $1/N$ , where  $n$  is the repeating units contained in oligomers, and  $N$  is the number of double bonds along the shortest path connecting the terminal carbon atoms of the molecular backbone contained in oligomers [16]. For these selected oligomers,  $N$  equals to  $4n$ . It is widely accepted that the oligomer method offers a reasonable estimated band gap by extrapolating the y intercept from the linear fit (shown in Eq. (1)) of the LUMO–HOMO gap against the reciprocal of the number of monomer units ( $1/n$ ) [33–36].

$$E_g = a + b \frac{1}{n} \quad (1)$$

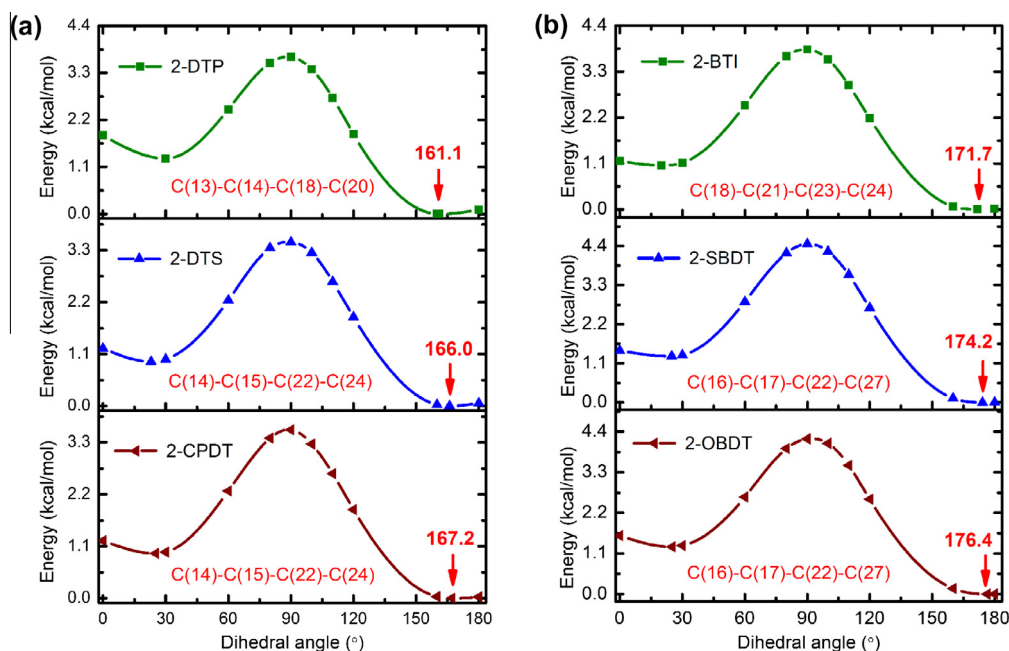
where  $E_g$  is the band gap energy,  $a$  is identified as  $E_g$  of a polymer ( $n = \infty$ ) and  $b$  is directly proportional to the effective conjugation. In reality, both theoretical and experimental data were proved to suffer from saturation effect once  $n \approx 12$ , which leads to a ill-estimation of  $E_g$  when carrying out such linearization [18]. Several non-linear semi-empirical extrapolation methods were proposed over the past years. Meier et al. [37] suggested an exponential fit using three empirical parameters, as shown in Eqs. (2a) and (2b), which correctly describes the chain-length dependence of different oligomeric series with respect to  $1/n$ .

$$E_g = E_{g,\infty} + (E_{g,1} - E_{g,\infty})e^{-a(n-1)} \quad (2a)$$

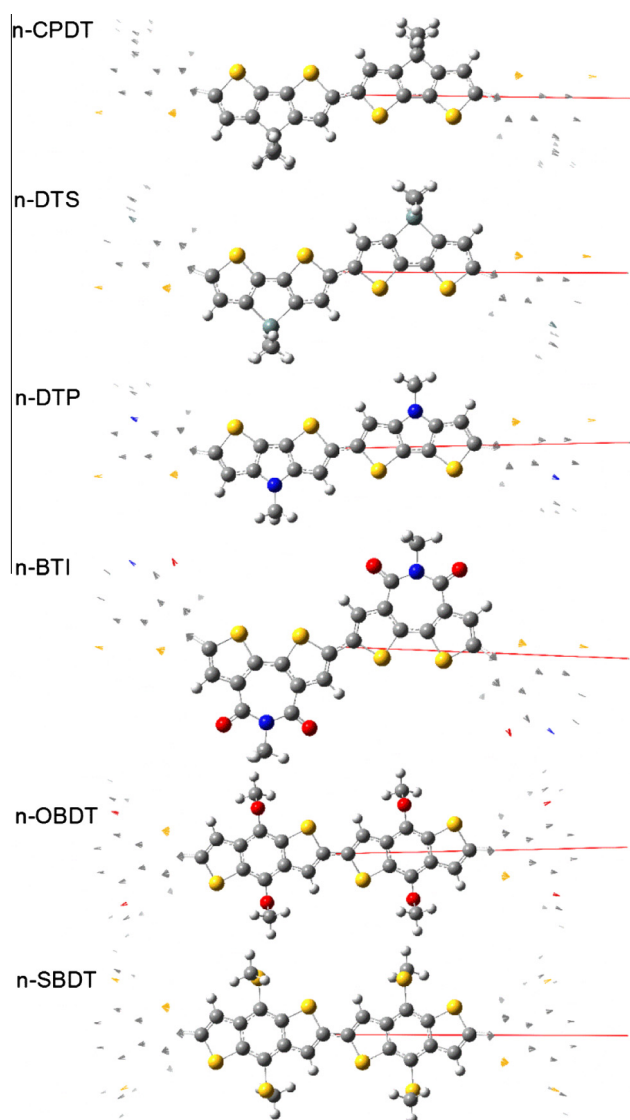
$$\lambda = \lambda_{\infty} - (\lambda_{\infty} - \lambda_1)e^{-b(n-1)} \quad (2b)$$

where  $E_{g,1}$  and  $\lambda_1$  are the excitation energy, and the maximum absorption and fluorescence wavelength, respectively, when  $n = 1$ ;  $E_{g,\infty}$  and  $\lambda_{\infty}$  are the corresponding properties for  $n = \infty$ ,  $a$  and  $b$  are parameters which indicate how fast the limit of convergence is approached. A more physical approach based on classical mechanics calculated the evolution of the excitation energy with increasing chain length by a model based on the idea of Lewis and Calvin [38,39], as shown in Eq. (3),

$$E_g = E_0 \sqrt{1 + 2 \frac{k'}{k_0} \cos \frac{\pi}{N+1}} \quad (3)$$



**Figure 2.** Torsion energy curves of six selected homopolymers, calculated at B3LYP/6-31G\* using the dimer ( $n = 2$ ) model, as a function of dihedral angle (shown in Figure 1). The dihedral angles of the minimum-energy structures are indicated by the red arrows in the torsion energy curves. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Figure 3.** Optimized ground-state structures of the unit cells of n-CPDT, n-DTS, n-DTP, n-BTI, n-OBDT, and n-SBDT, calculated at PBC/B3LYP/6-31G\* level.

**Table 1**  
LUMO–HOMO gaps of all these investigated oligomers ( $n = 2–9$ ) at B3LYP/6-31G\* level.

	<i>n</i> -CPDT	<i>n</i> -DTS	<i>n</i> -DTP	<i>n</i> -BTI	<i>n</i> -OBDT	<i>n</i> -SBDT
$n = 2$	2.927	2.917	3.195	2.961	3.308	3.274
$n = 3$	2.474	2.477	2.686	2.589	2.950	2.903
$n = 4$	2.236	2.274	2.435	2.421	2.786	2.723
$n = 5$	2.082	2.153	2.309	2.327	2.684	2.622
$n = 6$	2.005	2.068	2.248	2.269	2.624	2.559
$n = 7$	1.938	2.020	2.183	2.232	2.592	2.519
$n = 8$	1.894	1.991	2.128	2.207	2.560	2.486
$n = 9$	1.860	1.960	2.101	2.189	2.542	2.466

where the formal double bonds of a polyene are regarded as  $N$  identical oscillators.  $k/k_0$  usually is about  $-0.45$ .  $E_0 = h\sqrt{k_0/4\pi^2\mu_0}$ , where  $h$ ,  $k_0$  and  $\mu_0$  are the Planck constant, the force constant, and the reduced mass of the isolated oscillator, respectively. A linear relationship of the  $E_g$  can be obtained from the Kuhn approximation by representing the squares of the band gap against the cosine of  $\pi/(N + 1)$ .

Recently, method involving PBC is also believed to be able to well predict the band gaps of conjugated polymers, especially for

**Table 2**

The calculated band gaps by oligomers approach with three fits (linear fit, Kuhn fit and Meier fit), and PBC–DFT calculations, along with experimental data.

	<i>n</i> -CPDT	<i>n</i> -DTS	<i>n</i> -DTP	<i>n</i> -BTI	<i>n</i> -OBDT	<i>n</i> -SBDT
Line fit	1.54	1.67	1.77	1.94	2.30	2.22
Kuhn fit	1.80	1.90	2.04	2.14	2.50	2.43
Meier fit	1.84	1.96	2.11	2.19	2.54	2.46
PBC	1.73	1.83	1.89	2.12	2.45	2.41
Exp.	1.7–1.8 <sup>a</sup>	1.91 <sup>b</sup>	1.7–2.0 <sup>c</sup>	2.0 <sup>d</sup>	2.21, 2.37 <sup>e</sup>	2.07, 2.15 <sup>f</sup>

<sup>a</sup> From Ref. [26,27].

<sup>b</sup> From Ref. [28].

<sup>c</sup> From Ref. [29,30].

<sup>d</sup> From Ref. [31].

<sup>e</sup> From Ref. [32].

<sup>f</sup> From Ref. [32].

these homopolymers [35]. The theoretical band gaps of polymers are the differences between the highest occupied crystal orbital (HOCO) and lowest unoccupied crystal orbital (LUCO) values.

## 2.2. Computational methods

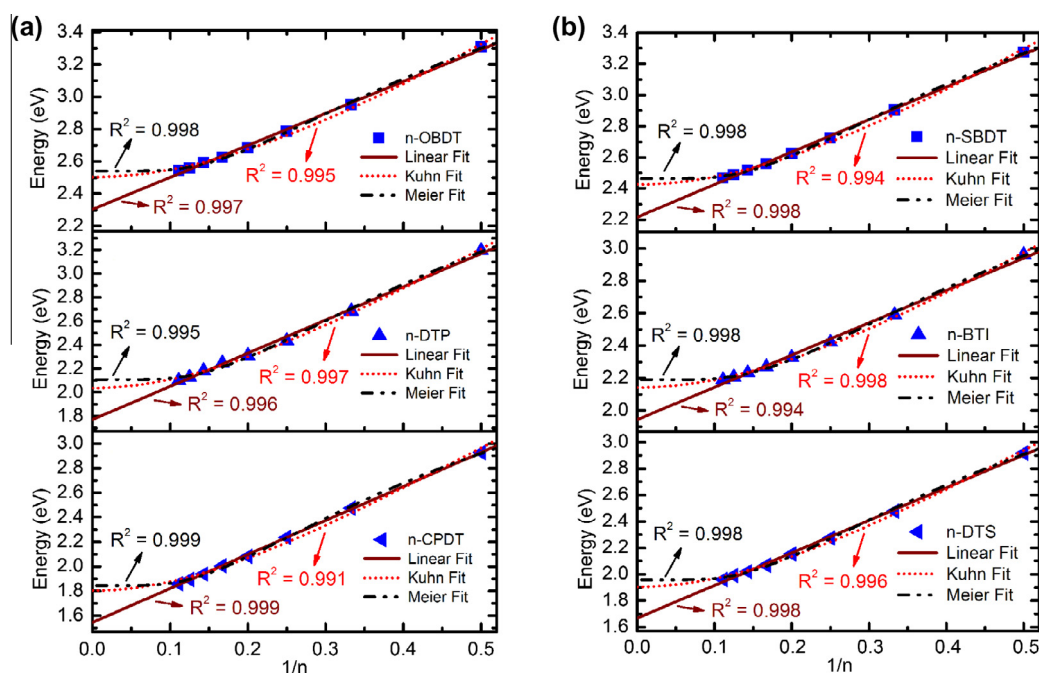
The geometric and electronic structures of these oligomers ( $n = 2–9$ ) were studied by DFT [40], and the optical absorption spectra of these oligomers ( $n = 1–5, 8$ ) were calculated using TD-DFT [41–44]. All calculations were carried out in the GAUSSIAN 03 package [45]. To simplify the calculations, all alkyl-branched chains ( $R_1, R_2, R_3$  and  $R_4$ , shown in Figure 1), were replaced by methyl groups, and the terminals of the repeating units are saturated with hydrogen atoms [46]. The DFT method was treated according to Becke's three parameter gradient-corrected exchange potential and the Lee–Yang–Parr gradient-corrected correlation potential (B3LYP) [47,48]. All polymers (*via* PBC) and oligomers were initially calculated with the polarized split-valence 6-31G\* (or 6-31G(d)) basis set which has been proven to be a reliable basis set for homopolymer systems [22]. All calculations were performed without any symmetry constraints and only in the gas phase.

## 3. Results and discussion

### 3.1. Dihedral angle and bond length of backbone

Figure 2 shows the torsion energy as a function of dihedral angle between the repeating units, for example, in 2-CPDT ('2' denotes the repeating unit number) the dihedral angle is C(13)–C(14)–C(22)–C(24), as shown in Figure 1. There are two low torsion energy states in all of energy curves, one of which is the *cisoid*, the other is *transoid*. In comparison, those structures with *transoid* conformations are the most stable structures with the minimum energy, and the corresponding dihedral angles are 167.2°, 166.0°, 161.1°, 171.7°, 174.2°, and 176.4° for 2-CPDT, 2-DTS, 2-DTP, 2-BTI, 2-SBDT, and 2-OBDT, respectively. All of the minimum energy structures are almost planar systems, which contribute to the performance of these materials. Another parameter of bond length alternation (BLA) is also calculated in this Letter, which is generally defined by the difference between single bands and double bonds, but for complicated structures of the model components, it is difficult to draw obvious definitions [49], and the quantitative behavior is still a matter of debate [50]. In this Letter, we only consider and investigate the BLAs of sampler components of *n*-CPDT, *n*-DTS and *n*-DTP. The BLAs are calculated as the differences between the average bond lengths of single bonds and double bonds. The BLAs of 2-CPDT, 2-DTS and 2-DTP are 0.044, 0.048, and 0.028 Å, respectively. With the increase of the number of units, the BLAs of three components decreased





**Figure 4.** LUMO–HOMO energy gap fitting versus the reciprocal numbers of monomer unit for (a) *n*-OBDT, *n*-DTP, and *n*-CPDT, respectively (from top to bottom); (b) *n*-SBDT, *n*-BTI, and *n*-DTS, respectively (from top to bottom). Note that energy gaps of oligomers are calculated at B3LYP/6-31G\*, and the fitting method includes linear fit, Kuhn fit, and Meier fit.

**Table 3**

The calculated absorption spectra of the oligomers ( $n = 1-5, 8$ ) and experimental value for corresponding polymers.

	<i>n</i> -CPDT	<i>n</i> -DTS	<i>n</i> -DTP	<i>n</i> -BTI	<i>n</i> -OBDT	<i>n</i> -SBDT
$n = 1$	316.1	341.8	284.0	349.6	341.7	332.9
$n = 2$	451.2	464.2	411.3	461.3	404.4	407.4
$n = 3$	545.3	556.6	498.1	540.2	460.2	467.8
$n = 4$	616.7	619.3	560.9	589.1	495.2	507.3
$n = 5$	674.2	665.0	603.5	621.2	519.6	532.9
$n = 8$	768.6	739.7	676.3	667.1	552.6	570.7
Meier fit	836.2	783.5	714.2	685.8	573.5	591.7
Exp.	560–613 <sup>a</sup>	498 <sup>b</sup>	506–600 <sup>c</sup>	524 <sup>d</sup>	483 <sup>e</sup>	505 <sup>f</sup>

<sup>a</sup> From Ref. [26,27].

<sup>b</sup> From Ref. [28].

<sup>c</sup> From Ref. [29,30].

<sup>d</sup> From Ref. [31].

<sup>e</sup> From Ref. [32].

<sup>f</sup> From Ref. [32].

gradually. However the relationship of conjugated effect and BLA are not sensitive for current components for the limited calculated molecules.

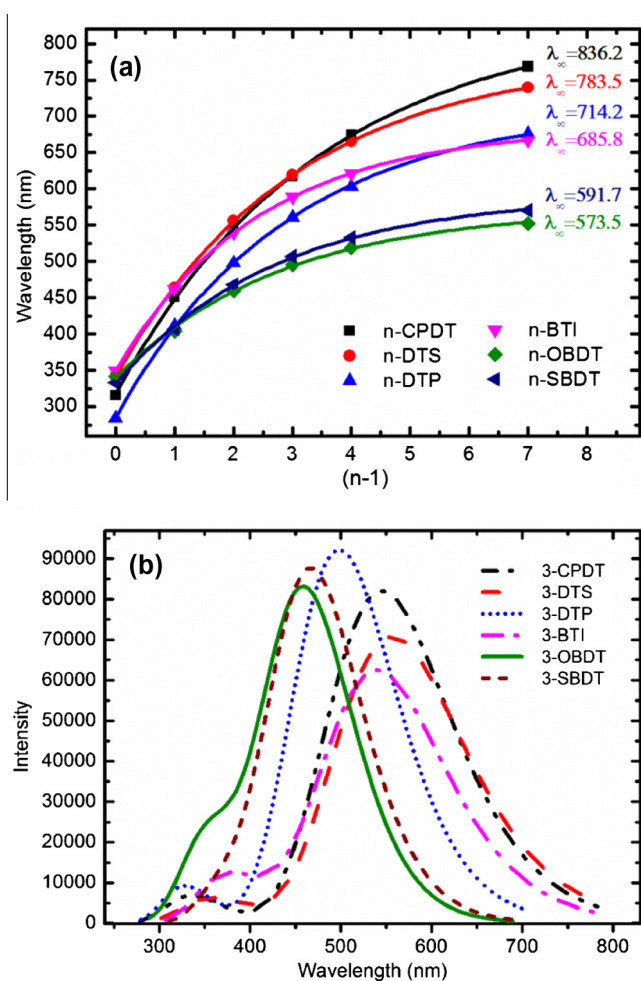
The lengths of bridged bonds (i.e., the carbon–carbon single bond between two consecutive oligomers) for the six dimers (C(15)–C(22) for 2-CPDT and 2-DTS; C(14)–C(18) for 2-DTP; C(21)–C(23) for 2-BTI, and C(17)–C(22) for 2-OBDT and 2-SBDT) are within 1.441–1.446 Å, which are  $\sim 0.1$  Å shorter than that of ethane (1.54 Å). This is due to the partial double-bond character on the bridge bond caused by  $\pi$ -bonding interaction, thereby strengthening and shortening the bridge bond. The results demonstrate that all of the stable structures are aromatic and the  $\pi$ -electrons are delocalized over the entire dimer frameworks. In the basis of the analysis of stable molecular structures, we use the PBC model and built up unit cell with one dimer ( $n = 2$ ) in *transoid* conformation for all calculations. Figure 3 shows the B3LYP/6-31G\* optimized ground-state structures of unit cells of all the investigated polymers (*via* PBC). The optimized ground-state structures (the figures are shown in Supporting information) of all the

investigated oligomers ( $n = 1-9$ ) show good planarity and *transoid* conformations.

### 3.2. The calculated band gaps

The calculated band gaps (defined as LUMO–HOMO) for these conjugated oligomers ( $n = 2-9$ ) of all homopolymers were shown in Table 1. With increase repeating units, the band gaps of all oligomers decrease gradually, while the differences of band gaps between each two consecutive oligomers become smaller. For example, the difference of band gaps between the dimers ( $n = 2$ ) and the trimers ( $n = 3$ ) in all oligomers are at least  $\sim 0.35$  eV, while these values decrease to be as small as  $\sim 0.035$  eV between the octamers ( $n = 8$ ) and the nonamers ( $n = 9$ ). The calculated and experimental band gaps for six polymers were summarized in Table 2. HOMO–LUMO values for the polymers were obtained from the oligomer method ( $n = 2-9$ ) using three typical fits (linear fit, Kuhn fit, and Meier fit). HOCO–LUCO values were calculated with PBC/B3LYP/6-31G\* method. The experiments of six homopolymers, as shown in Table 2, are 1.7–1.8 eV for *n*-CPDT [26,27]; 1.91 eV for *n*-DTS [28]; 1.7–2.0 eV for *n*-DTP [29,30]; 2.0 eV for *n*-BTI [31]; 2.21, 2.37 eV for *n*-OBDT [32]; and 2.07, 2.15 eV for *n*-SBDT [32]. Figure 4a and b show the fitting curves (linear fit, Kuhn fit, and Meier fit), along with the regression coefficient ( $R^2$ ) for six selected oligomers.

PBC/B3LYP/6-31G\* calculated results, as shown in Table 2, are close to the corresponding experiments for all six polymers. In particular, for *n*-CPDT, *n*-DTS, and *n*-DTP, the predicted band gaps of 1.73, 1.83, and 1.89 eV closely match the experiments. For oligomer method, the predictions by linear extrapolation for *n*-BTI, *n*-OBDT, and *n*-SBDT (1.94, 2.30, and 2.22 eV, respectively) are much closer to experimental band gaps than those predictions by the Kuhn fit and Meier fit, also the calculations by PBC calculations (2.12, 2.45, 2.41 eV for *n*-BTI, *n*-OBDT, and *n*-SBDT). The better predictions by linear fit here which is reported to be possible ill-estimation for the saturation effect are probably related to the molecular conjugation properties. For the selected molecules, the



**Figure 5.** (a) Convergence of the absorption spectra of the oligomers ( $n = 1-5, 8$ ) with increasing number  $n$  of repeating units (Meier fit). (b) The calculated absorption spectra on the trimer model.

polymers of  $n$ -BTI,  $n$ -OBDT, and  $n$ -SBDT are proved to be slightly more conjugated than other three ones of  $n$ -CPDT,  $n$ -DTS, and  $n$ -DTP with the molecular planarity shown in Figure 2. For strongly conjugated polymers, the saturation effect may commence at longer chain length [22], and these predictions of components within finite units ( $n = 1-9$ , it is not too long chain length) by linear fit will be correct.

### 3.3. Optical absorption spectra

The vertical singlet-singlet electronic transition energies and optical absorption spectra of the selected oligomers ( $n = 1-5, 8$ ) were calculated by TD-B3LYP/6-31G\* (considering the first 10 excited states). Table 3 summarizes the calculated maximum absorption wavelengths (MAWs) for the oligomers, the MAWs from Meier fit (Eq. (2b)) and the experimental MAWs for all homopolymers. The estimated MAWs by Meier fit also are shown in Figure 5a. The MAWs fitted by Meier fit are 836.2, 783.5, 714.2, 685.8, 573.5, and 591.7 nm for  $n$ -CPDT,  $n$ -DTS,  $n$ -DTP,  $n$ -BTI,  $n$ -OBDT, and  $n$ -SBDT, respectively, which highly overestimate the corresponding experimental values (560–613 [26,27], 498 [28], 506–600 [29,30], 524 [31], 483 [32], and 505 nm [32], respectively), by comparison, the calculations from the oligomers of trimers and tetramers (except for  $n$ -DTS) closely match the experimental MAWs. We hence plotted the calculated MAWs on the trimer

model, as shown in Figure 5b. The calculated MAWs (3-CPDT: 545.3 nm, 3-DTS: 556.6 nm, 3-DTP: 498.1 nm, 3-BTI: 540.2 nm, 3-OBDT: 460.2, and 3-SBDT: 467.8 nm) are approximately consistent with the experiments (560–613 [26,27], 498 [28], 506–600 [29,30], 524 [31], 483 [32], and 505 nm [32]) for  $n$ -CPDT,  $n$ -DTS,  $n$ -DTP,  $n$ -BTI,  $n$ -OBDT, and  $n$ -SBDT, respectively) with very small offset. Figure 5b also clearly shows the peak absorption spectra of all the oligomers/polymers are around 500 nm, which will be good candidates for organic solar cell.

## 4. Conclusion

In this letter, the band gaps and optical spectra of six selected special fused-ring analogs of oligomers ( $n = 2-9$ ) are theoretically investigated using oligomer method (B3LYP/6-31G\* with linear fit, Kuhn fit and Meier fit) and PBC-DFT. The results demonstrate that, for the band gap calculations, the oligomer method using linear fit is suitable for those strongly conjugated structures, while, the PBC-DFT method calculations (at B3LYP/6-31G\* level) will match weakly conjugated homopolymer experimental data. The absorption spectra calculations indicate that the TDDFT calculations on the trimers ( $n = 3$ ) at B3LYP/6-31G\* level are roughly in agreement with the available experiments, while, the Meier fit of the oligomers ( $n = 1-5, 8$ ) highly overestimate the experimental data.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2013.03.068>.

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