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The electronic and structural properties of nonclassical bicyclic thiophene: Monomer, oligomer and polymer

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Abstract

The nonclassical thiophenes have received a great deal of attention because of their unusual electronic structure in several decades. Based on DFT approach, the structural and electronic properties of thieno[3,4-*c*][1,2,5]thiadiazole, as well as of its co-oligomers and copolymers with benzene and thiophene, are investigated theoretically. The changes of nucleus-independent chemical shifts (NICSs) as a method examining conjugational degree are reported. The results show that the conjugational degree is increased with the increase of polymeric number. The density of state (DOS) and crystal orbital overlap population (COOP) are also investigated. The band structure analysis shows that the benzene and thiophene substitutes have quite low energy gap (0.23 and 0.32 eV, respectively). Therefore, those substitutes are implied as intrinsic conductors.

Keywords: Thieno[3,4-*c*][1,2,5]thiadiazole; Electronic structure; NICS

1. Introduction

The conducting polymer is currently the focus of much attention. An important goal is to provide such polymers having small band gaps, which exhibit intrinsic conduction or at least semiconductive properties even in ground state. Although the energy gap will be reduced by various methods, such as new conformational structures, new chemical modifications and new hybrid forms, *etc*., the key step of designing conductive polymer is finding out low energy gap parent molecules. Additionally, the electronic properties of monomers and oligomers are connected tightly with the energy gaps of polymers. Exploring the relationship of them is another fundamental step to molecular design.

A π-conjugated heterocyclic polymer is a promising candidate for low energy gap. Nonclassical thiophenes having special π-electron structure are of particular interest. In 1939, Schomaker and Pauling [1] suggested that an expansion of the sulfur octet could be a special factor in stabilization of the thiophene molecule. Since 1967, the first nonclassical thiophene, thieno[3,4-*c*]thiophene, has been reported [2,3]. Because of their unusual electronic structure, nonclassical thiophenes have attracted many people's attention on experiment [4–10] and theory [11–15]. Thieno[3,4-*c*][1,2,5]thiadiazole (TT), a typical bicyclic nonclassical thiophene, was firstly synthesized by Bower and his co-workers [16]. In 1993, the copolymer, TT and thiophene, was synthesized by Tanaka et al. [17], and it was considered with a low energy gap. In 1996, Yamabe et al. [18] have compared electronic structure of polymer TT with its copolymer thiophene by self-consistent-field crystal orbital (SCF-CO) method.

Here, a type of transtactic block polymerization by TT and its copolymer with benzene and thiophene is studied. We intend to understand the intrinsic electronic characteristics and also to comprehend the relationship of electronic structures between monomers, oligomers and polymers. For this purpose, we start with the electronic features of monomers and oligomers, and then extend them in relevant polymers.

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2. Computational details

In order to gain insight into molecular design, we explain the qualitative features using two different density functional theories (DFT) [19]. The Becke's three-parameter nonlocal exchange function with the Lee–Yang–Parr nonlocal correlation function (B3LYP) [20,21] is used to optimize all the structures of monomers and oligomers. There are no imaginary frequencies for all the optimized structures at the present theoretical level. It implies that all the optimized structures are the global minima on the potential energy surface and stable structures. The block polymers are calculated by periodic boundary conditions (PBC) method [22], and the local spin density approximation (LSDA) DFT method [23] is employed. LSDA method was considered to get good results for PBC computation [24]. Moderate basis set, 6-31G*, is used throughout. All of those calculations are performed by Gaussian 03 package [25].

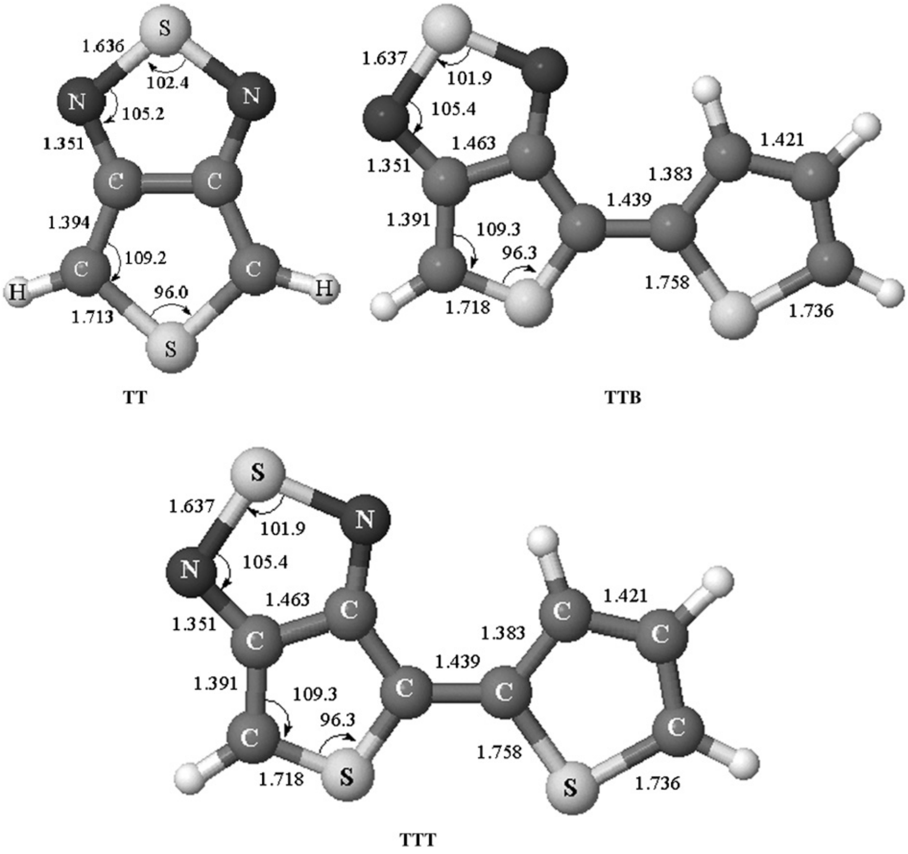
Electronic density topological analyses and nucleus-independent chemical shift (NICS) [26] calculation are carried out at the B3LYP/6-31G* level based on the optimized geometries. The concept of NICS as a measure of the aromaticity of a system was introduced by Schleyer et al. in 1996. The NICS method allows the evaluation of aromaticity, antiaromaticity, and nonaromaticity of single-ring systems and individual rings in polycyclic systems (local aromaticities). This method was used extensively to assess the aromaticity and antiaromaticity of many organic and inorganic compounds, intermediates, and transition states. In this article, NICS is defined as the negative of the magnetic shielding at a ring critical point (RCP) and at 0.5 Å above the RCP, and RCP obtained from the AIM analyses [27]. The topological analyses are gained from atom in molecule (AIM) calculation.

To attain more information about band structure, one isolated structure is extracted from block polymer structure. The single point calculation including full population analysis is performed at the same level (LSDA/6-31G*), based on the optimized structures. Density of state (DOS) and relevant crystal orbital overlap population (COOP) [28] are generated with GaussSum 1.0 [29,30].

3. Results and discussion

3.1. Monomer and oligomer

The optimized structures and geometrical parameters of TT are illustrated in Fig. 1. Inspection of Fig. 1 reveals that the parent molecule (TT) has a rigid planar and high symmetrical geometry. The bond length of central bond for TT, TTB and TTT are illustrated in Fig. 2. In this article, the central bond is denoted as C–C bond, which connects two neighboring central rings. The sketch is shown in Scheme 1. (*e.g.*, in TTB trimer, the central bond is the bond that connects the b2 and c2



TT TTB

TTT

Fig. 1. Optimized structures of monomeric molecules, along with bond lengths (in Å) and angles (in °).

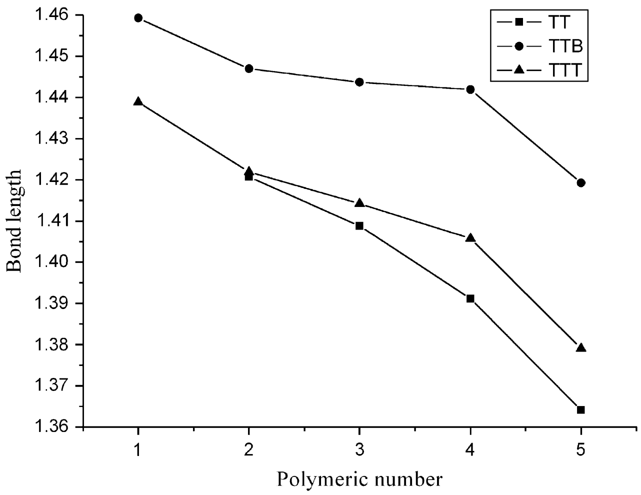
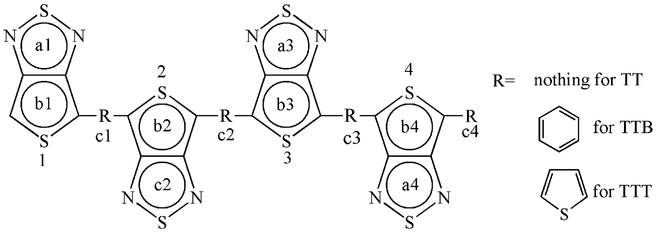


Fig. 2. Bond length of central bond in TT, TTB and TTT (the last point ($n = 5$) denoted as bond length of polymer).



Scheme 1. The sketch of the studied compounds. (In bi-ring, thiadiazole is denoted as ring a and thiophene is denoted as ring b. Ring c is benzene in TTB and thiophene in TTT.)

rings; in tetramer, the central bond is the bond that connects the c2 and b3 rings). In Fig. 2, it can be seen easily that the central bonds become shorter with the increase of the polymeric degree. It indicates that the conjugation degree is increasing.

The complete topological analyses are performed for all the compounds to obtain detailed bonding character. The bond critical points (BCPs), denoted as (3, −1), which represent saddle points in the electron densities between two atoms are examined for all the bonds. In the topological definition, a chemical bond is represented by the bond path. The gradient path links two neighboring nuclei along with maximal ρ_r in any neighboring lines. The charge densities $\rho_{(r)}$, the Laplacian ($\nabla^2_\rho(r)$), the eigenvalues of Hessian matrix (λ_i) at the BCPs, and the Wiberg bond indexes (WBIs) [31] are listed in Table 1. It was shown that $\rho_{(r)}$ and $\nabla^2_\rho(r)$ taken together can be employed to monitor the relative increase or decrease of charge accumulation [32].

The changes of bond length lead to the changes of electronic structure. As listed in Table 1, the electronic density $\rho_{(r)}$ (more positive) and the Laplacian $\nabla^2_\rho(r)$ (more negative) of central bonds increase with the polymeric number. It indicates that the local populations of charge in those bonds are increased. In addition, the other two parameters, ε_{BCP} and WBIs, should be noticed. Both ε_{BCP} and WBIs provide a measure of π-bond character. Based on Bader's AIM theory, ε_{BCP} is bigger and the conjugation is stronger. When the value of WBIs is about 1.0–2.0, the bond displays π character. In Table 1, it is found that with the increase of the polymeric number, the ε_{BCP} and WBIs are increased. It suggests that the π features of the central bonds are strengthened. We consider that the aromatic structures are changed into quinoid structures in polymer. Examining all of those parameters, it can be found that the π feature and conjugational degree of central bond increase with polymeric number. Furthermore, comparing monomers and oligomers with polymers, the bond in latter is shorter. It indicated that the conjugations in polymers are stronger than those in oligomers and monomers.

NICS was used extensively to identify the aromaticity of molecules, because NICS can give a clear indication of ring currents. Furthermore, the changes of NICS at different

Table 1
BCP properties and Wiberg bond index of the central bond[a] in studied compounds

	Polymeric number	$\rho_{(r)}$	$-\lambda_1/-\lambda_2/\lambda_3$	$\nabla^2_\rho(r)$	ε_{BCP}	WBI[b]
TT	Dimer	0.291	0.59/0.49/0.34	−0.741	0.197	1.21
	Trimer	0.298	0.61/0.50/0.34	−0.767	0.220	1.27
	Tetramer	0.310	0.64/0.51/0.33	−0.820	0.255	1.35
	Polymer[c]	0.33	0.68/0.54/0.33	−0.899	0.259	1.28
TTB	Monomer	0.275	0.55/0.48/0.35	−0.681	0.125	1.12
	Dimer	0.281	0.56/0.49/0.35	−0.705	0.144	1.15
	Trimer	0.282	0.57/0.49/0.35	−0.712	0.149	1.17
	Tetramer	0.283	0.57/0.49/0.35	−0.716	0.152	1.17
	Polymer	0.296	0.60/0.50/0.35	−0.757	0.203	1.56
TTT	Monomer	0.283	0.57/0.49/0.35	−0.711	0.161	1.15
	Dimer	0.292	0.59/0.50/0.34	−0.746	0.193	1.22
	Trimer	0.296	0.60/0.50/0.34	−0.762	0.206	1.25
	Tetramer	0.301	0.62/0.50/0.34	−0.782	0.224	1.29
	Polymer	0.317	0.66/0.52/0.33	−0.847	0.275	1.44

[a] See in text.
[b] Attained from NBO analysis.
[c] One isolated structure extracted from the corresponding polymer.

Table 2
Negative NICS for studied compounds at points 0.5 Å above (in parenthesis) and at RCPs

	Ring	Monomer	Dimer	Trimer	Tetramer
TT	a1	13.1(15.1)	13.7(14.1)	13.3(13.6)	12.2(13.1)
	b1	14.7(13.5)	9.9(10.3)	9.0(9.5)	11.3(10.6)
	a2			13.1(13.5)	13.5(13.5)
	b2			6.3(6.8)	4.3(5.1)
TTB	a1	14.1(14.4)	14.0(14.3)	13.7(14.1)	13.7(14.1)
	b1	11.0(11.4)	10.6(11.4)	10.2(10.8)	10.2(10.8)
	c1	7.8(9.5)	5.8(7.4)	5.7(7.3)	5.6(7.3)
	a2		13.5(13.7)	13.3(13.6)	13.4(13.6)
	b2		8.6(9.1)	8.2(8.7)	8.2(8.7)
	c2		7.6(9.3)	5.5(7.1)	5.3(6.9)
	a3			13.5(13.7)	13.3(13.6)
	b3			8.4(9.0)	8.1(8.6)
	c3			7.6(9.3)	5.4(7.0)
	a4				13.4(13.6)
	b4				8.5(9.0)
	c4				7.6(9.3)
TTT	a1	13.9(14.2)	13.7(14.1)	13.5(13.9)	13.3(13.7)
	b1	11.2(11.5)	10.5(10.8)	10.0(10.5)	9.7(10.2)
	c1	11.0(10.2)	8.6(8.0)	7.9(7.5)	8.3(7.7)
	a2		13.0(13.3)	12.8(13.1)	12.7(13.0)
	b2		8.6(8.9)	7.6(7.9)	7.1(7.4)
	c2		12.8(12.3)	8.1(7.6)	7.8(7.2)
	a3			12.7(13.0)	12.7(12.9)
	b3			8.2(8.5)	6.9(7.1)
	c3			10.6(9.9)	8.0(7.5)
	a4				12.5(12.9)
	b4				7.5(8.0)
	c4				10.3(9.8)

position rings in polymer can indicate the conjugational degree. Here, we select NICS as model system to understand the relationship between conjugation degrees and ring current density. The NICSs in different position rings are collected in Table 2. In order to avoid influenced by σ bonds, the NICS(0.5) are also calculated at the same theoretical level. In this paper, the NICS is denoted as the value at point 0.5 Å above ring plane (listed in parenthesis). The position of ring are illustrated in Scheme 1.

Correspondingly, we calculated the NICS of single benzene and thiophene at same theoretical level. NICS and NICS(0.5) of benzene are −9.7 and −11.4, and thiophene are −13.8 and −13.1, respectively. The values in Table 2 indicate that all of the studied compounds have strong local aromaticity. And NICSs in oligomers are smaller than those in single benzene and thiophene. It indicates that the electronic currents above benzene and thiophene rings in oligomer are reducing.

Examining Table 2, for same oligomers, we can find easily that NICSs in terminal ring and in side ring of polymeric axes show only little change. In terminal ring, the changes are less than 15%. For example, in TTB, the values of a1 in monomer to tetramer are approximate and they are 14.4, 14.3, 14.1 and 14.1, respectively. It indicates that the ring current in terminal ring just influences the central section slightly. In other words, the changes of NICSs in side ring (position a) for same oligomer are less than 10%. For example NICSs of a1, a2, a3 and a4 in TTB tetramer are 14.1, 13.6, 13.6 and 13.6, respectively. This is because ring a is far from polymeric axes and the polymeric number just influences slightly the ring current.

Examining middle sections in oligomers, it can be seen easily that the NICSs are different significantly. For TT, b2 is much smaller than b1 (about 28% in trimer and about 52% in tetramer). For TTB, both b ring and c ring that are located on

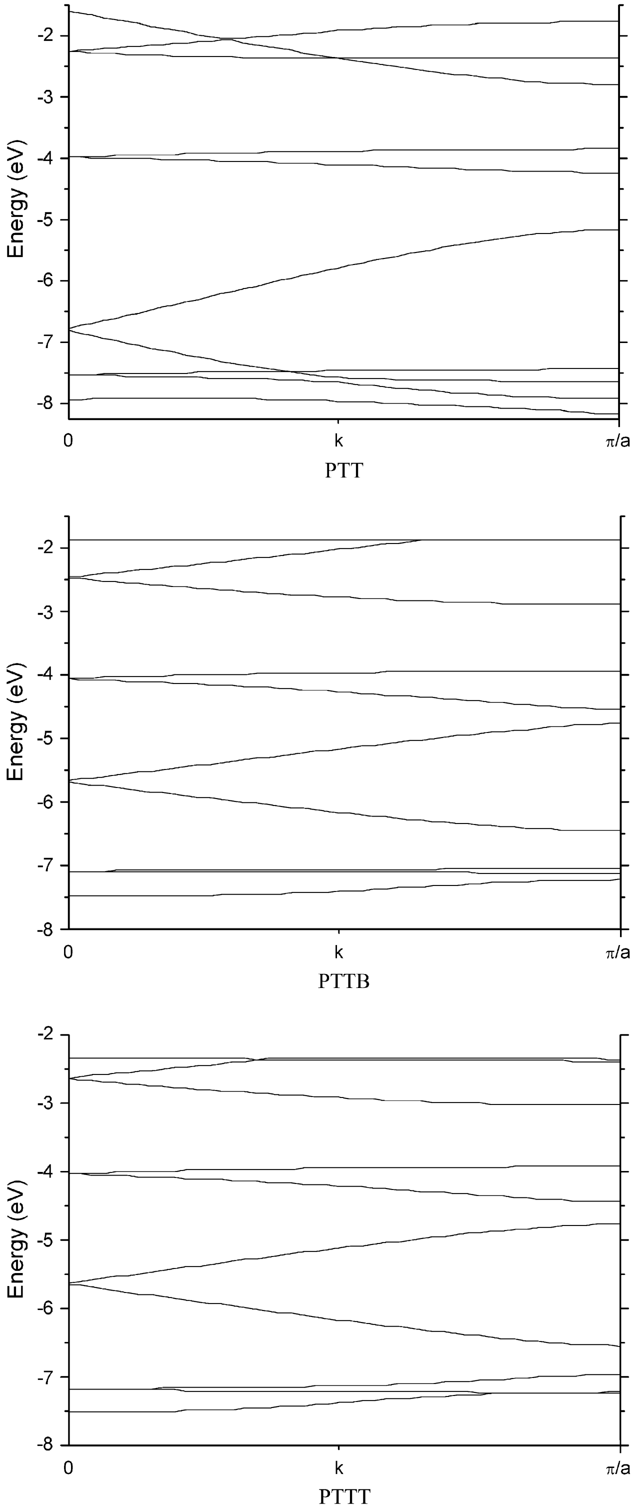


Fig. 3. Band structures of PTT, PTTB and PTTT.

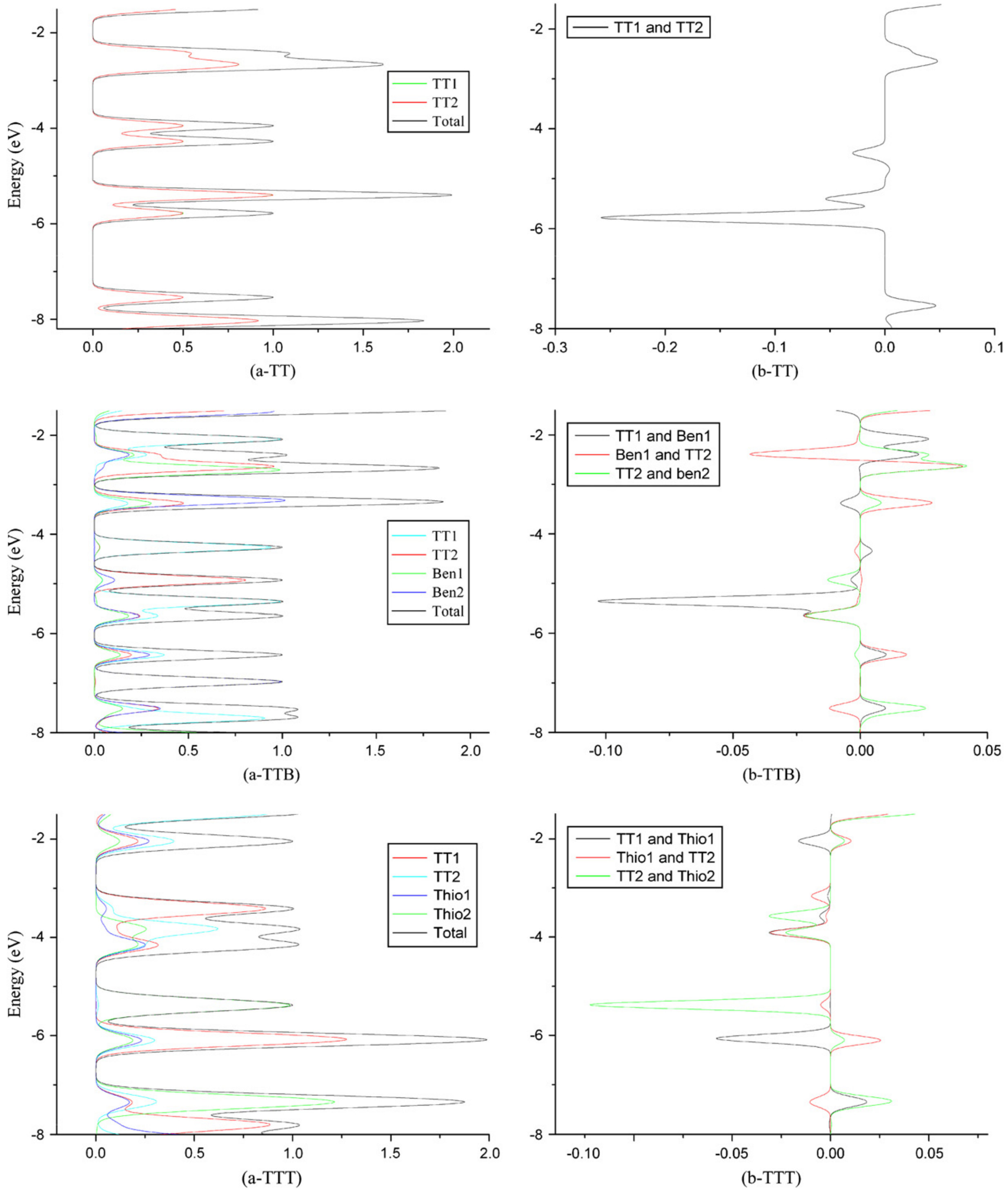


Fig. 4. (a) DOSs and PDOSs of one isolated structure extracted from polymers. (b) COOP diagram corresponding to the polymers.

polymeric axes are also different obviously. Especially, in tetramer, rings b2 and b3 are close to center, their NICSs (8.7 and 8.6) are smaller than those in terminal ring (10.8 for b1 and 9.0 for b4). Ring c has similar situation that the values in c2 and c3 are smaller than those in c1 and c4. This means that the ring currents in central rings are smaller than those in the outer one. TTT have similar behavior, and NICS at central ring are smaller than those at outer one. For example, in TTT tetramer, NICS is 10.2 for b1, 7.4 for b2, 7.1 for b3 and 8.0 for b4; and the corresponding values for c1−c4 are 7.7, 7.2, 7.5 and 9.8, respectively. The fact that NICSs at central ring are smaller than those at outer ring shows that the conjugation in central section is stronger than that in outer section, and the structure in central is closer to quinoid structure. Moreover, it shows that the electronic in central section delocalize to whole molecule, and doesn't loclalize on central section. We consider that the changes of NICSs can examine the conjugational degree.

3.2. Periodic system

To obtain the electronic properties of polymer, a periodic boundary conditions (PBC) calculation is performed. The computed band structures around the Fermi level are illustrated in Fig. 3. Correspondingly, the partial density of state (PDOS) spectra and crystal orbital overlap population (COOP) diagrams are gathered in Fig. 4. The COOP diagrams only illustrate the orbital overlap of C–C bond between two rings. Table 3 collects the HOMO and LUMO energies, the energy gaps of oligomers, the highest occupied band (HOB) energies, the lowest unoccupied band (LUB) energies and the band gaps of polymers. The contribution (percentage) of group to HOB and LUB orbital is listed in Table 4.

3.2.1. PTT

Inspection of Table 3 shows that the energy gap of TT oligomer has a degressive trend (from 3.24 eV for monomer to 0.8 eV for tetramer), whereas its polymer PTT has the widest band gap (0.92 eV) compared with other polymers. Abnormally, the HOB energy of polymer is smaller than HOMO energy of tetramer, and the energy gap of PTT is bigger than tetramer. The reason of this results is that the different computational method is used in molecular system and period system. Investigating Fig. 3, we can find that the band gap between the top of the HOB and the bottom of the LUB is wide, while the valence bandwidths are narrow. It indicates less orbital overlap between HOB and LUB. Analyzing Fig. 4 (a-TT), the same result is obtained. The total occupied DOSs are concentrated at between 5 and 6 eV and at the bottom of those curves, and there is a wide bandwidth between HOB and LUB. Due to the same structure of TT1 group and TT2 group, the curves of their PDOSs are overlapped completely each other. In addition, the contributions of TT1 group and TT2 group to HOB and LUB are completely same (50%, respectively). The COOP curve, Fig. 4 (b-TT), shows that C–C bond between TT1 and TT2 is strongly antibonding near the HOB and weakly bonding near LUB.

3.2.2. PTTB

Similar to TT, the energy gaps of TTB oligomer decrease regularly. Moreover, the energy gap of the polymer is the smallest value (0.23 eV) among all of the polymers. In Fig. 4 (a-TTB) and Table 4, it is found that the gap between HOB (−4.77 eV) and LUB (−4.65 eV) is quite narrow. The occupied DOSs near HOB are wide and multi-segment. It indicates that PTTB is a potential conductor. Inspecting Table 4, we can find that the HOB of TTB almost completely comes from TT2 (96%), and Ben1 has only 4% contribution, the other groups (TT1 and Ben2) have no contribution completely, whereas the four groups contribute to LUB averagely. The COOP curves (Fig. 4 (b-TTB) indicate that C–C bonds TT1–Ben1 and TT2–Ben2 are antibonding, whereas the bond between Ben1 and TT2 is weakly bonding near HOB. Near LUB, the bonds TT1–Ben1 and Ben1–TT2 exhibit weak bonding and antibonding, respectively. Otherwise, the bond TT2–Ben2 is nonbonding.

Table 3
Energies (eV) of HOMO and LUMO and energy gaps for oligomer and polymer

		Monomer	Dimer	Trimer	Tetramer	Polymer[a]
TT	H	−5.99	−5.20	−4.81	−4.56	−5.16
	L	−2.75	−3.27	−3.56	−3.76	−4.24
	E_g	3.24	1.93	1.25	0.80	0.92
TTB	H	−5.47	−4.97	−4.77	−4.67	−4.77
	L	−2.84	−3.14	−3.29	−3.38	−4.55
	E_g	2.63	1.83	1.48	1.29	0.23
TTT	H	−5.32	−4.76	−4.51	−4.35	−4.76
	L	−2.87	−3.26	−3.47	−3.61	−4.43
	E_g	2.45	1.50	1.04	0.74	0.32

[a] For polymer; H means HOB, L means LUB.

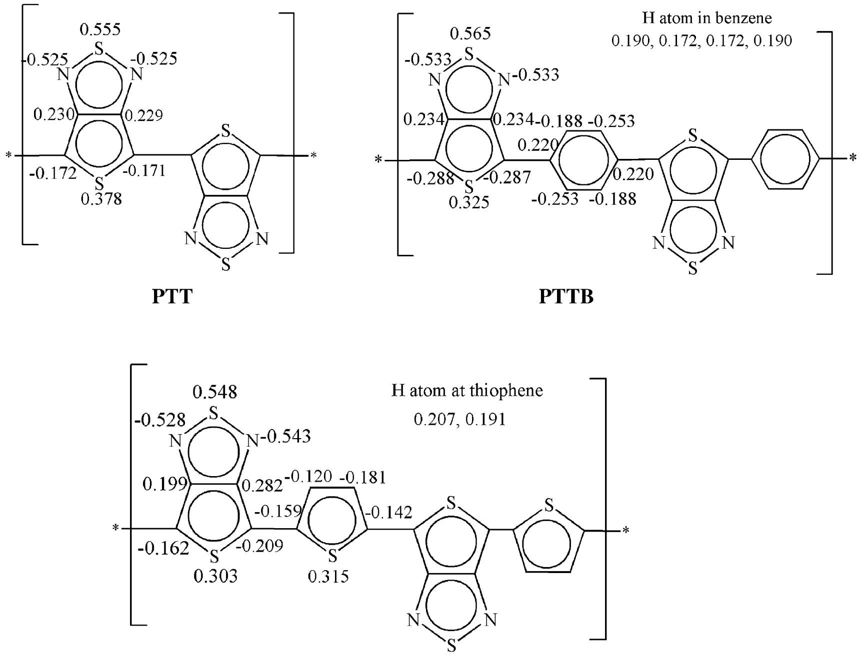
3.2.3. PTTT

For the oligomers of TTT, the energy gap (in Table 3) has the similar decrease behavior. Energy gap between HOB and LUB is 0.32 eV. Similar to TTB, in TTT the occupied DOSs near HOB are wide and multi-segment. Considering Fig. 4 (a-PTTT) and Table 4, it can be easily found that the HOB is contributed completely by group Thio2 (99%), while the LUB is contributed averagely by four groups. Examining COOP b-PTTT plot, it can be found that the bond TT2–Thio2 is strongly bonding close to HOB. Correspondingly, the bond Thio1–TT2 is weakly bonding, and the bond TT1–Thio1 is nonbonding near HOB. On other hand, the three bonds are antibonding near LUB.

Analyzing the energy gap, it can be found that the E_g of PTTB is smaller than that of PTTT. To understand the result, we should take two aspects into consideration. One is aromatic. Examining Table 2, the aromaticity of thiophene is stronger than benzene. The electron is more difficult to be delocalized to the whole molecule. On other hand, the charge distribution also influences the energy gap (donor and acceptor actions). In Fig. 5, the Mulliken charge distribution of studied polymers is illustrated. Inspecting Fig. 5, we can find that the sum transferring charge (0.282) between TT and benzene in PTTB is more than that (0.109) between TT and thiophene in PTTT. Comparatively, the benzene's ability of donating electron is stronger than the thiophene's. Therefore, the donor–acceptor action leads E_g of PTTB less.

Table 4
Contribution (%) of a group to HOB and LUB

		TT1	TT2	Ben1	Ben2	Thio1	Thio2
TT	HOB	50	50				
	LUB	50	50				
TTB	HOB	0	96	4	0		
	LUB	33	24	18	24		
TTT	HOB	0	0			1	99
	LUB	31	25			23	21



PTT **PTTB**

PTTT

Fig. 5. Charge distribution on polymer (for PTTB, sum charge in TT is −0.282 and in benzene is 0.282; for PTTT, sum charge in TT is −0.109, and in thiophene is 0.109).

4. Conclusions

In this paper, the electronic and structural properties of bicyclic nonclassical thiophene, thieno[3,4-*c*][1,2,5]thiadiazole, and its benzene and thiophene substitutes, as well as their transtactic oligomers and polymers are calculated by theoretical method. The change of NICS as a method examining conjugational degree is reported. The change of NICSs shows that the conjugation in central section is stronger than that in outer section, and the structure in central is closer to quinoid structure. The band structure and density of state studies show that the benzene and thiophene substituted compound TTB has a narrow energy band (0.23 eV and 0.32 eV, respectively), and they can be considered as intrinsic conductor.

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