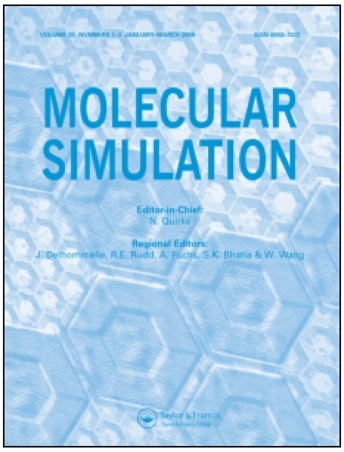

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Theoretical investigation on the geometries and electronic properties of thiophene ring-containing compounds: monomer, oligomer and polymer

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Theoretical investigation on the geometries and electronic properties of thiophene ring-containing compounds: monomer, oligomer and polymer

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In this study, theoretical analysis on the geometries and electronic properties of various conjugated oligomers based on thiophene (Th) or bicyclic non-classical Th units is reported. The dihedral angle, bond length, bond-length alternation, bond critical point (BCP) properties, nucleus-independent chemical shift (NICS) and Wiberg bond index (WBIs) are analysed and correlated with conduction properties. The changes of bond length, BCP properties, NICS and WBIs all show that the conjugational degree is increased systematically with main chain extension. As a result, the highest occupied molecular orbital–lowest unoccupied molecular orbital energy separation (E_g) is decreased upon chain elongation. The E_g of oligomers based on bicyclic non-classical Th unit is much lower than that of Th-based oligomers due to the narrower E_g of bicyclic non-classical Ths compared to Th, which indicates that the narrow E_g of the bicyclic non-classical Ths can be carried over to their polymers by using them as building blocks for the polymers. The band structures and density of states analysis show that the four polymers all have small band gap (<0.9 eV), wide highest occupied bandwidth and relatively small effective mass of hole, which indicate that those proposed polymers may be potential conductors.

Keywords: DFT; bicyclic non-classical thiophene; electronic properties; effective mass

1. Introduction

Currently, a major effort is being made to design novel conjugated polymers that have a small band gap [1–5] in the field of electrically conducting polymers. Polymers with small energy separation between the top of the valence band and the bottom of the conduction band are expected to show not only good intrinsic conductivity but also good non-linear properties [6]. Recent theoretical and experimental investigations have shown that the narrow-band-gap polymers can be obtained by starting from a monomer which already has a small energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [7–9]. So, finding parent molecules with narrow HOMO–LUMO energy separation (E_g) is the key step in designing and synthesising conductive polymers.

For the successful molecular design of a novel parent molecule with narrow energy separation, as well as its corresponding conducting polymer, one needs to explore the relationship between the geometries, electronic structures of the compound and its conduction properties. Furthermore, the connection between the conduction properties of the monomer and that of its corresponding polymer also should be well understood. Once such information has been achieved, the desired electronic properties could be obtained by specific synthesis after successful molecular design [2].

Non-classical thiophenes (Th) have been regarded as promising candidates for the design of a low band gap polymer due to their unusual electronic structures [10–12] since thieno[3,4-*c*]Th (TTh) was synthesised in 1967 [13,14]. Two years later, a typical bicyclic non-classical Th, thieno[3,4-*c*][1,2,5]thiadiazole (TT), was synthesised by Bower and Schlessinger [15]. TT is known to have a small HOMO–LUMO energy separation [10]. The theoretical calculations (at B3LYP/6-31G(d) level) show that the HOMO–LUMO separations of TTh and TT are 2.98 and 3.25 eV, respectively. If the narrow HOMO–LUMO separations of the bicyclic non-classical Ths can be carried over to their polymers by using them as building blocks for the polymers, we should expect intrinsically conductive polymers.

Using this strategy, four novel co-polymers are designed by replacing the phenylene ring of poly(*p*-phenylenevinylene) with TTh, TT, thieno[3,4-*c*]furan (TF, O-substitute of TTh) and Th units in turn, as shown in Scheme 1. These novel polymers are poly(2-vinylTTh), poly(3-vinylTT), poly(3-vinylTF) and poly(2-vinylTh), which are denoted as $(\mathrm{VTTh})_n$, $(\mathrm{VTT})_n$, $(\mathrm{VTF})_n$ and $(\mathrm{VTh})_n$, respectively. In this work, theoretical investigation

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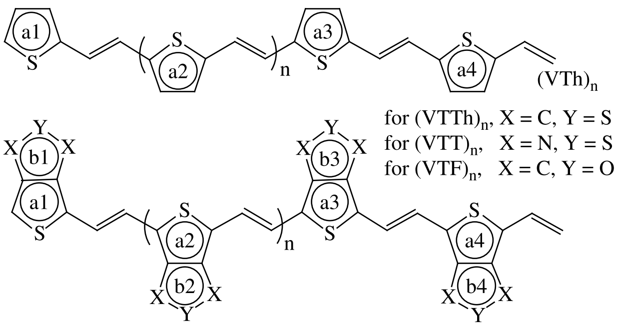


Scheme 1. Chemical structure of the studied polymers.

of the geometric and electronic structures of the four novel polymers, as well as of their monomers and oligomers, is reported. For the purpose of providing an in-depth understanding of the relationship between the chemical and electronic structures of a polymer and its conduction properties, we start with the geometric and electronic features of monomers and oligomers, and then extend them to relevant polymers.

2. Method of calculation

The geometric and electronic structures of the monomers and oligomers are optimised by means of the hybrid density functional theory (DFT) method [16] at B3LYP level of theory (Becke-style 3-parameter DFT) [17,18] with 6-31G(d) basis set. There are no imaginary frequencies for all the optimised structures, which implies that all the optimised structures are the global minima on the potential energy surface and stable structures. Based on the optimised structures, natural bond orbital (NBO) [19–22] analysis, topological analysis of the electron density [23] and nucleus-independent chemical shift (NICS) are calculated with B3LYP/6-31G(d) method.

The local spin density approximation (LSDA) [24] is one of the first DFT methods employed to calculate atomic and molecular properties. It was suggested that the LSDA method be considered to get good results for the calculation of periodic boundary conditions (PBC) [25]. So, the geometry optimisation of polymers is performed by means of DFT method treated in PBC at the LSDA level of theory with 6-31G(d) basis set. The one-dimensional band structure of the conjugated copolymer originates from the interaction of the π-orbitals of the repeating units throughout the polymer chain. The band gap (E_g) of the conjugated copolymer is calculated as the minimum difference between the highest occupied band (HOB) and the lowest unoccupied band (LUB) energy levels at a constant k in this study. The bandwidth is calculated from the spread of energy levels available to carriers within each band. The effective mass of the charge carriers (m_H and m_L) at the edge of the upper valence band or lower conduction band is defined as $m^* = \eta^2[\partial^2 E(k)/\partial k^2]^{-1}$. Additionally, density of states (DOS) is generated with GAUSSSUM 1.0 [26,27]. All the calculations are performed on Gaussian 03 program package [28].

3. Results and discussion

3.1 Optimised geometries and electronic properties

3.1.1 Monomers

The optimised structures and geometrical parameters of $(VTTh)_1$, $(VTT)_1$, $(VTF)_1$ and $(VTh)_1$ are illustrated in Figure 1. The dihedral angle (Φ_1) is the deviation from coplanarity between heterocyclic ring and C=C linkage, as shown in Figure 1. It can be seen that the dihedral angle Φ_1 is equal to zero in all of the studied monomers, which suggests a coplanar conformation of those monomers. If we compare the bond length of the C1—C6 bond of those monomers (in the range of 1.441–1.458 Å) to that of the C—C bond of ethane (1.54 Å), we can find that the C1—C6 bond of these monomers is shorter by around 0.10 Å. On the contrary, the bond length of the C6=C7 bond in those monomers (in the range of 1.341–1.347 Å) is longer than that of the C=C double bond in ethylene (1.20 Å). The bond shortening shows a certain amount of double bond character to the C1—C7 single bond and the bond lengthening shows a decrease in double bond character of C6=C7 bond. The above results also suggest that the π electrons on C6 and C7 atoms are delocalised over the entire framework rather than localised between the two specific nuclei. Besides, the theoretical calculation shows that S5—C4 bond length in $(VTT)_1$ (1.713 Å), $(VTF)_1$ (1.706 Å) and $(VTTh)_1$ (1.704 Å) is shorter than that in $(VTh)_1$ (1.731 Å). And the same situation can be obtained by analysing the S5—C1 bond length. This result suggests that the delocalised degree of π orbital in $(VTT)_1$, $(VTF)_1$ and $(VTTh)_1$ is stronger than that in $(VTh)_1$. The bond length of S5—C4 and S5—C1 decreases in the following order: $(VTh)_1 > (VTT)_1 > (VTF)_1 \approx (VTh)_1$, which indicates that the conjugational degree increases in the order: $(VTTh)_1 \approx (VTF)_1 > (VTT)_1 > (VTh)_1$.

According to the NBO method, the natural atomic charge of an atom is its nuclear charge minus the total electron population on that atom. The natural atomic charge distribution and the sum of natural charge (S_{NC}) for two segments (heterocyclic unit and ethylene unit), as well as the intramolecular charge transfer (D_{CT}), are all shown in Figure 1. The S_{NC} is calculated as the summation of natural atomic charge distribution of the heterocyclic unit or the ethylene unit. For instance, the S_{NC} of TF ring in $(VTF)_1$ is $-0.2666 - 0.1508 - 0.1642 - 0.4759 + 0.5765 + 0.0969 - 0.4115 + 0.0989 + 0.2263 + 0.2267 + 0.2636 = 0.0200$. The absolute value of S_{NC} means the amount of intramolecular charge transfer (D_{CT}) between the heterocyclic unit and the ethylene unit [5,29].

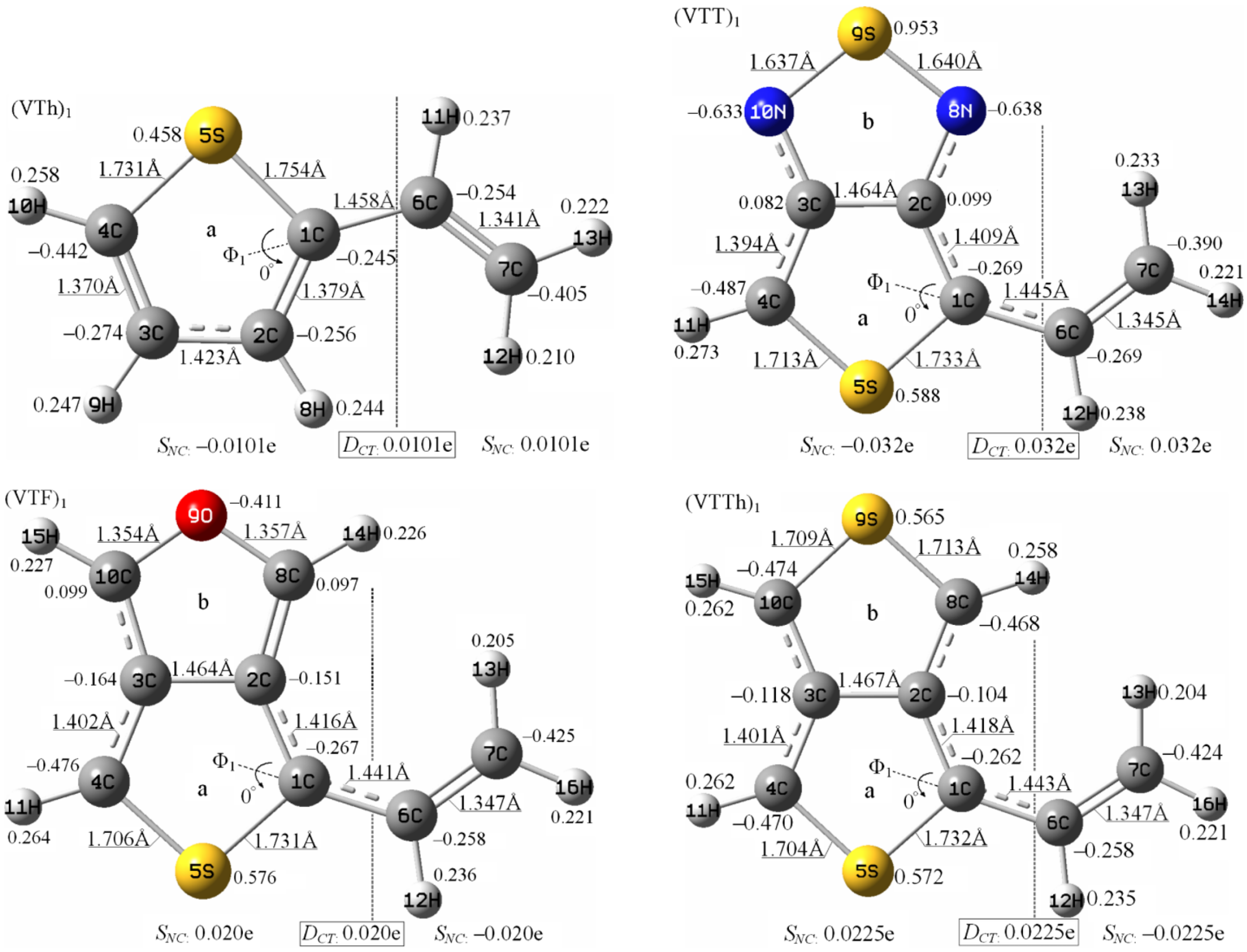
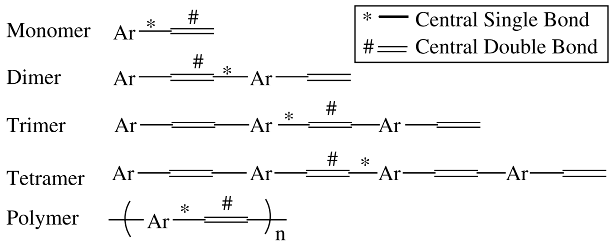


Figure 1. Optimised geometries and natural charge distribution of monomers.

The order of the magnitudes of intramolecular charge transfer D_{CT} obtained from the NBO analysis at B3LYP/6-31G(d) level is $(VTT)_1$ (0.0320 e) $>$ $(VTTh)_1$ (0.0225 e) $>$ $(VTF)_1$ (0.0200 e) $>$ $(VTh)_1$ (0.0101 e). Note that the E_g obtained at the same level decreases in the order: $(VTh)_1$ (6.13 eV) $>$ $(VTT)_1$ (3.24 eV) $>$ $(VTF)_1$ (3.05 eV) $>$ $(VTTh)_1$ (2.98 eV), which is in the reverse trend as that of the magnitudes of intramolecular charge transfer except in the case of $(VTT)_1$. The bigger the magnitude of intramolecular charge transfer is, the narrower the HOMO–LUMO energy gap becomes. The reason is that the intramolecular charge transfer enhances the π-electron delocalisation and thus leads to a decrease in the HOMO–LUMO energy gap [5,11,30]. By inspecting Figure 1, we can find that N10 atom in $(VTT)_1$ has a natural charge of -0.6330 and N10 atom has a natural charge of -0.6380. The large negative charge on N10 and N8 atoms indicates that the unusually large D_{CT} of $(VTT)_1$ is probably a result of the two adjacent imine nitrogen atoms with high electronegativity in the thiadiazole ring, which could significantly localise electrons in thiadiazole ring and thus cause the reduction of the π-electron delocalisation over the entire molecular framework. As a result, the HOMO–LUMO energy gap of $(VTT)_1$ is bigger than that of $(VTF)_1$ and $(VTTh)_1$ in spite of the large D_{CT} value of $(VTT)_1$.

3.1.2 Oligomer

The theory of atoms in molecules (AIM) [23] provides us with a definition of bond critical points (BCP) [31]. Those are saddle points in the electron density (ρ_r) and appear between any two nuclei which are said to be chemically bonded. According to the theory of AIM, any bond can be represented in terms of its BCP properties. These properties have been extensively studied [16,23,31] and have been seen to compactly and accurately characterise the properties of their associated bonds. Hence, we currently examine the electron density (ρ_r), the three curvatures of the density (λ_1, λ_2 and λ_3) and the ellipticity (ε_b) at each BCP of the central single bond (CSB) and the central double bond (CDB). Note that the ε_b is defined as $\lambda_1/\lambda_2 - 1$. In this paper, the C=C linkage which connects



Scheme 2. Sketch map of central bond of the compounds.

two neighbouring heterocyclic units in the central section of a molecule is defined as CDB, and the C—C bonds between the CDB and the heterocyclic unit is defined as CSB, as shown in Scheme 2. Bond length alternation (Δr_c) is defined as the bond length difference between the CSB and the CDB. The intramolecular charge transfer (D_{CT}), HOMO–LUMO gap (E_g), BCP properties, Wiberg bond indexes (WBIs) [32], bond length (r_c) and bond length alternation (Δr) are all listed in Table 1. For the purpose of comparison, those properties of monomers are shown in the same table too.

As shown in Table 1, the bond length of CSB (in the range of 1.384–1.458 Å) in those oligomers is shorter than that of the pure carbon–carbon single bond (1.54 Å). It suggests that there is a certain amount of double-bond character to the CSB. On the other hand, the bond length of CDB (in the range of 1.341–1.405 Å) is longer than that of the pure carbon–carbon double bond (1.33 Å). Along with the main chain extension, the CSB becomes shorter and the CDB becomes longer. For example, from monomer up to tetramer for (VTF), the bond length of CSB decreases from 1.441 to 1.384 Å and that of CDB increases from 1.347 to 1.405 Å. The bond length changes of CSB and CDB show an increased double bond character of the CSB and a decreased double bond character of the CDB. It also indicates that the conjugational degree is increased upon main chain elongation for all the studied compounds. If we examine the values of Δr shown in Table 1, we can find that the bond-length difference between CSB and CDB decreases in the order: monomer > dimer > trimer >tetramer. And that the calculated energy gap decreases in the same order: monomer > dimmer > trimer >tetramer, as shown in Figure 2. It indicates that the minimisation of bond length alternation along the backbone of the studied compounds is an important guideline in band gap reduction. This result also suggests that the polymerisation degree plays an important role in the reduction of HOMO–LUMO energy separation. Besides, the calculation results show that the dihedral angles (Φ) between heterocyclic ring and C=C linkage in (VTh)$_n$, (VTF)$_n$ and (VTT)$_n$ ($n = 2$–4) are all

Table 1. The optimized geometries and electronic properties of the studied oligomers.

	r_c (Å)			ρ_r (a.u.)		ε_b		WBIs[b]			
Compound[a]	CSB[c]	CDB	Δr	CSB	CDB	CSB	CDB	CSB	CDB	D_{CT} (e)	E_g (eV)
(VTh)											
Mo	1.458	1.341	0.117	0.277	0.339	0.108	0.360	1.118	1.874	0.010	4.75
Di	1.445	1.356	0.089	0.282	0.331	0.136	0.328	1.163	1.684	0.012	3.26
Tri	1.441	1.359	0.082	0.284	0.329	0.142	0.320	1.176	1.661	0.012	2.68
Te	1.440	1.360	0.080	0.285	0.329	0.145	0.317	1.181	1.650	0.012	2.38
(VTT)											
Mo	1.445	1.345	0.100	0.281	0.337	0.131	0.346	1.150	1.831	0.032	2.72
Di	1.419	1.373	0.046	0.294	0.321	0.177	0.279	1.255	1.548	0.045	1.63
Tri	1.408	1.383	0.025	0.301	0.315	0.201	0.251	1.312	1.476	0.051	1.06
Te	1.395	1.396	−0.001	0.308	0.308	0.227	0.218	1.384	1.393	0.058	0.67
(VTF)											
Mo	1.441	1.347	0.094	0.276	0.335	0.024	0.353	1.168	1.811	0.020	2.70
Di	1.415	1.377	0.038	0.297	0.318	0.205	0.283	1.285	1.506	0.024	1.57
Tri	1.400	1.389	0.011	0.305	0.311	0.237	0.250	1.362	1.421	0.026	0.94
Te	1.384	1.405	−0.021	0.313	0.302	0.273	0.212	1.453	1.324	0.028	0.53
(VTTh)											
Mo	1.443	1.347	0.096	0.283	0.335	0.143	0.354	1.165	1.815	0.023	2.66
Di	1.419	1.375	0.044	0.294	0.319	0.196	0.288	1.270	1.525	0.025	1.60
Tri	1.406	1.386	0.020	0.302	0.313	0.224	0.259	1.337	1.450	0.028	1.01
Te	1.393	1.399	−0.006	0.309	0.306	0.254	0.226	1.414	1.363	0.029	0.61

[a] Mo, Di, Tr and Te mean the monomer, dimmer, trimer and tetramer respectively.
[b] Attained from NBO analysis.
[c] See in text.

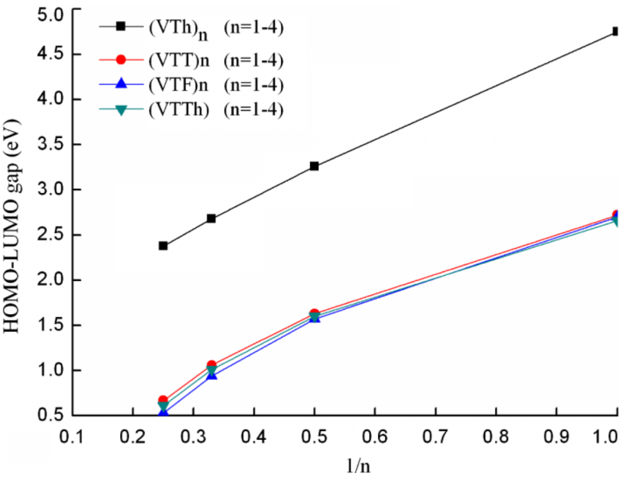


Figure 2. The HOMO–LUMO gap decreases with increased chain length n in oligomers.

zero. However, the dihedral angles in $(VTTh)_n$ ($n = 2$–4), in the range of 2.5–6.8°, are not zero. For example, the dihedral angles Φ_1 and Φ_2 in $(VTTh)_2$ are 5.6° and 6.3°, respectively, as shown in Figure 3. It is the repulsion force between the adjacent hydrogen atoms on the C=C linkage and the heterocyclic unit that results in a non-coplanar conformation of $(VTTh)_2$. Consequently, the twisted conformation of $(VTTh)_n$ ($n = 2$–4) directly leads to the reduction of π-electron delocalisation over the entire molecular framework. It explains why the E_g of $(VTTh)_2$ (1.60 eV) is bigger than that of $(VTF)_2$ (1.57 eV). For the same reason, the E_g of $(VTTh)_3$ (1.01 eV) is bigger than that of $(VTF)_3$ (0.94 eV) and the E_g of (VTTh; 0.61 eV) is bigger than that of $(VTF)_4$ (0.53 eV).

According to the theory of AIM, the electron density ρ_r can be employed to monitor the relative increase or decrease of charge accumulation [5,9]. As listed in Table 1, the ρ_r of CSB is increased upon chain extension. The changes of ρ_r indicate that the local populations of charge in those bonds are increased. The ellipticity (ε_b) of BCP provides a measure for the π character of a bond and structural stability. In addition, the WBIs also provide a measure of π-bond character. When the value of WBIs is in the range of 1.0–2.0, the bond displays π character. Examining Table 1, we can find that the order of WBIs of CSB is monomer < dimmer < trimer < tetramer. This result is due to the participation of more electrons in the CSB formation as the polymeric number increases. However, the trend of the bond length of CSB is monomer > dimmer > trimer > tetramer. It is evident that the bond length is inversely related to bond order. In addition, the ε_b of CSB is also increased upon main chain elongation. The increasing value of ε_b and WBIs indicates that the π features of the CSBs are strengthened. On the contrary, the ρ_r, ε_b and WBIs of CDB are decreased upon chain extension. For example, the WBIs values of CDB in $(VTh)_1$, $(VTh)_2$, $(VTh)_3$ and $(VTh)_4$ are 1.874, 1.684, 1.661 and 1.650, respectively. The decreased values show that the π character of the CDB is weakened. In other words, both CSB and CDB show a more delocalised character upon chain extension. As mentioned above, the changes of bond length, BCP properties and WBIs show that the conjugational degree is increased systematically with chain extension. As a result, the HOMO–LUMO energy separation decreases in the order: monomer > dimer > trimer > tetramer.

The theoretical results also show that the order of the intramolecular charge transfer D_{CT} obtained from the natural atomic charge distribution with 6-31G(d) level for the four types of oligomers is monomer < dimer < trimer < tetramer. We note that the energy gap E_g decreases in the order: monomer > dimer > trimer > tetramer, which is the reverse trend to that of the

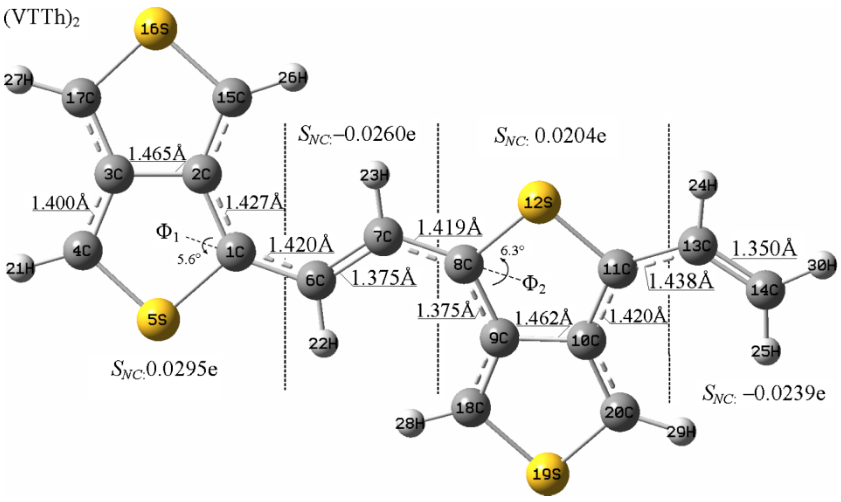


Figure 3. Optimised geometries of $(VTTh)_2$.

intramolecular charge transfer parameter (D_{CT}). That is to say, the more the intramolecular charge transfer is, the narrower the HOMO–LUMO energy gap becomes for the homologous oligomers. The reason is that the intramolecular charge transfer significantly enhances the π-electron delocalisation and thus decreases HOMO–LUMO energy gap. The HOMO–LUMO energy separation of Th [building block for (VTh)], TT [building block for (VTT)], TF [building block for (VTF)] and TTh [building block for (VTTh)] is 6.31, 3.25, 3.05 and 2.98 eV, respectively. It is worthy of note that the E_g of $(VTh)_1$, $(VTT)_1$, $(VTF)_1$ and $(VTTh)_1$ is 4.75, 2.72, 2.70 and 2.66 eV, respectively. Obviously, the HOMO–LUMO energy separation of the building blocks (Th, TT, TF and TTh) is significantly correlated with the E_g of their corresponding monomers. The same results can be obtained by analysing the E_g of dimer, trimer and tetramer. It indicates that the narrow HOMO–LUMO separations of the hetero-aromatic rings can be carried over to their oligomers by using them as building blocks for the oligomers. So, we can find that the E_g of oligomers based on bicyclic non-classical Th unit is much lower than that of Th-based oligomers due to the narrower HOMO–LUMO separation of bicyclic non-classical Ths compared to Th.

3.1.3 NICS analysis

NICS can provide exact information on the electron delocalisation and molecular aromaticity [33]. It has become the most widely used aromaticity probe due to its simplicity and efficiency since its introduction in 1996 [34]. Furthermore, the changes of NICS values along the polymeric backbone can be used to indicate the conjugational degree of the polymer [5]. Some researchers have suggested that NICS(1) (i.e. at points 1 Å above the ring centre) was a better measure of the π-electron delocalisation compared to NICS(0) (i.e. at the ring centre) [33]. So, the NICS values are calculated at positions 1 Å above the ring critical points (RCP) in this study. It is worthy of note that the RCP is obtained from the AIM analysis [23]. For the purpose of discussing the use of NICS as a measure of conjugational degree for oligomers, we have calculated the values of NICS(1) of all the rings in studied oligomers at B3LYP/6-31G(d) level. The NICS(1) values of different rings are listed in Table 2. The positions of ring a_n ($n = 1–4$) and ring b_n ($n = 1–4$) are illustrated in Scheme 1.

As shown in Table 2, all the NICS(1) values are negative, which indicate that all of the studied compounds have local aromaticity. In this paper, we mainly analyse the NICS values from four aspects. Firstly, the NICS(1) values of rings a and b are all more or less decreased upon chain extension. This result shows some decrease of aromaticity with the size of the system. For example, the NICS(1) values of ring a_1 in $(VTT)_1$, $(VTT)_2$, $(VTT)_3$ and $(VTT)_4$ are 10.4, 9.3, 8.9 and 8.5, respectively. The NICS(1) values of ring a_1 decrease by 1.9 from monomer up to tetramer, which indicates that the electronic current above the ring is reduced. The same situation can be obtained by analysing the NICS values in other rings.

Table 2. Negative NICS (ppm) values calculated at points 1 Å above the RCP.

	Ring							
Compound	a_1	a_2	a_3	a_4	b_1	b_2	b_3	b_4
(VTh)								
Monomer	9.7							
Dimer	9.4	8.7						
Trimer	9.3	8.4	8.7					
Tetramer	9.3	8.3	8.3	8.7				
(VTT)								
Monomer	10.4				12.5			
Dimer	9.3	8.3			12.0	12.0		
Trimer	8.9	6.8	7.7		11.8	11.6	11.8	
Tetramer	8.5	5.8	5.7	7.1	11.6	11.3	11.3	11.5
(VTF)								
Monomer	9.8				11.9			
Dimer	8.6	7.5			11.3	11.1		
Trimer	8.0	5.9	6.8		10.9	10.6	10.8	
Tetramer	7.5	4.8	4.7	6.2	10.5	10.1	10.1	10.4
(VTTh)								
Monomer	10.3				11.5			
Dimer	9.3	8.1			11.5	11.4		
Trimer	8.7	6.5	7.4		11.2	11.2	11.4	
Tetramer	7.9	5.4	5.3	6.8	10.5	10.1	10.1	10.5

Secondly, the NICS(1) values in the side ring of the polymeric axes show little change upon chain extension compared to the rings (ring a) which are located on the polymeric axes. In Table 2, the NICS(1) of b_1 in $(VTF)_1$, $(VTF)_2$, $(VTF)_3$ and $(VTF)_4$ are 11.9, 11.3, 10.9 and 10.5, respectively. The NICS(1) values of ring b_1 decrease by 1.4 from monomer up to tetramer. The changes of ring b_1 (1.4) are much less than those of ring a_1 (2.3) from monomer up to tetramer. This is because ring b is far from the polymeric axes and the polymeric number just influences the ring current slightly. Thirdly, it can be seen that NICS values in the terminal ring of polymeric axes show only little change for the same compound by examining Table 2. For example, the NICS(1) of a_1 and a_4 in $(VTTh)_4$ tetramer are 7.9 and 6.8, b_1 and b_4 are 10.5 and 10.5, respectively. This indicates that the ring current in terminal ring only has a limited effect on the central section. Finally, the NICS(1) values in central ring are much smaller than those in terminal rings, especially those in the rings (a) that are located on the polymeric axes. For example, the NICS(1) of a_1, a_2, a_3 and a_4 in $(VTT)_4$ tetramer are 8.5, 5.8, 5.7 and 7.1, respectively. It is evident that the NICS(1) of ring a_2 and a_3 are all much smaller than that of ring a_1 and a_4. On the one hand, this result shows that the π electrons in central section are delocalised over the whole molecule, and are not localised on central section. On the other hand, it also shows that the conjugational degree in the central section is stronger than that in outer one.

3.2 Periodic system

The conduction properties of a polymer are related to its electronic properties. These properties mainly include bandwidth (W_{VB} and W_{CB}), electron effective mass (m_L), effective mass of hole (m_H) and band gap (E_g). Conjugated polymers with relatively smaller band-gap, bigger bandwidth, smaller effective mass are expected to be better conductors of electricity, both intrinsically and extrinsically. The theoretical electronic properties of $(VTh)_n$, $(VTT)_n$, $(VTF)_n$ and $(VTTh)_n$ are listed in Table 3. In addition, we show the one-dimensional band structure and the DOS along the polymer chain of $(VTh)_n$, $(VTT)_n$, $(VTF)_n$ and $(VTTh)_n$ in Figure 4. As shown in Table 3, $(VTh)_n$, $(VTF)_n$ and $(VTTh)_n$ all have relatively small effective mass of hole or electron and narrow band gap (in the range of 0.71–0.82 eV), which indicate that those polymers could have the potential applications as conductors or semiconductors. By examining Table 3, it can also be found that m_L of $(VTT)_n$ is large (5.437 m_e), but the band gap (0.63 eV) is narrow and the effective mass of hole (−1.295 m_e) is relatively small. So, $(VTT)_n$ could also have the potential applications as conductors or semiconductors. The E_g of $(VTF)_n$ (0.82 eV) and $(VTTh)_n$ (0.76 eV) is bigger than that of $(VTh)_n$ (0.71 eV) and $(VTT)_n$. This result can be explained by their geometries. The calculation shows that the dihedral angles (Φ) between two adjacent bicyclic non-classical Th units (or two adjacent Th units) in $(VTh)_n$ and $(VTT)_n$ are zero. However, the dihedral angles in $(VTF)_n$ and $(VTTh)_n$ are 13.6° and 29.1°. It is the repulsion force between the adjacent hydrogen atoms on the C=C linkage and the bicyclic non-classical Th unit that results in the non-coplanar conformation of $(VTF)_n$ and $(VTTh)_n$. The non-coplanar conformation directly leads to the decrease in conjugational degree and the increase in band gaps of $(VTF)_n$ and $(VTTh)_n$. Among those polymers, the $(VTT)_n$ has a smallest band gap of 0.63 eV.

Analysing the band structure illustrated in Figure 4, we can find that the widths of highest unoccupied band (HOB) of the four copolymers are wide. The HOB of $(VTh)_n$, $(VTT)_n$, $(VTF)_n$ and $(VTTh)_n$ are 1.28, 1.12, 0.95 and 0.98 eV in width, respectively. The large bandwidths indicate a smaller effective mass of hole and then the higher carrier mobility. However, the widths of LUB of those polymers based on bicyclic non-classical Ths (including $(VTT)_n$, $(VTF)_n$ and $(VTTh)_n$) are narrower compared to the HOB bandwidths. The narrow lowest unoccupied bandwidths of $(VTT)_n$, $(VTF)_n$ and $(VTTh)_n$ indicate that the relatively poor π-electron delocalisation and potential for relatively strong carrier localisation. The same result can be obtained by analysing the DOS diagram. The narrow band gaps and the wide bandwidths of HOB of the proposed polymers based on bicyclic non-classical Th unit or Th unit indicate that they could have the potential applications as organic semiconductors or conductors.

Table 3. The electronic properties of the studied polymers.

Polymer	HOMO (eV)	LUMO (eV)	W_H (eV)	W_L (eV)	m_L (m_e)	m_H (m_e)	Φ (°)	E_g (eV)
$(VTh)_n$	−4.48	−3.77	1.28	1.14	1.359	−1.295	0	0.71
$(VTT)_n$	−4.86	−4.23	1.12	0.33	5.437	−1.295	0	0.63
$(VTF)_n$	−4.44	−3.62	0.95	0.71	1.295	−1.360	13.6	0.82
$(VTTh)_n$	−4.41	−3.65	0.98	0.57	1.813	−1.360	29.1	0.76

W_H, bandwidth of HOB; W_L, bandwidth of LUB; m_L, effective mass of electron; m_H, effective mass of hole; Φ, Dihedral angle.

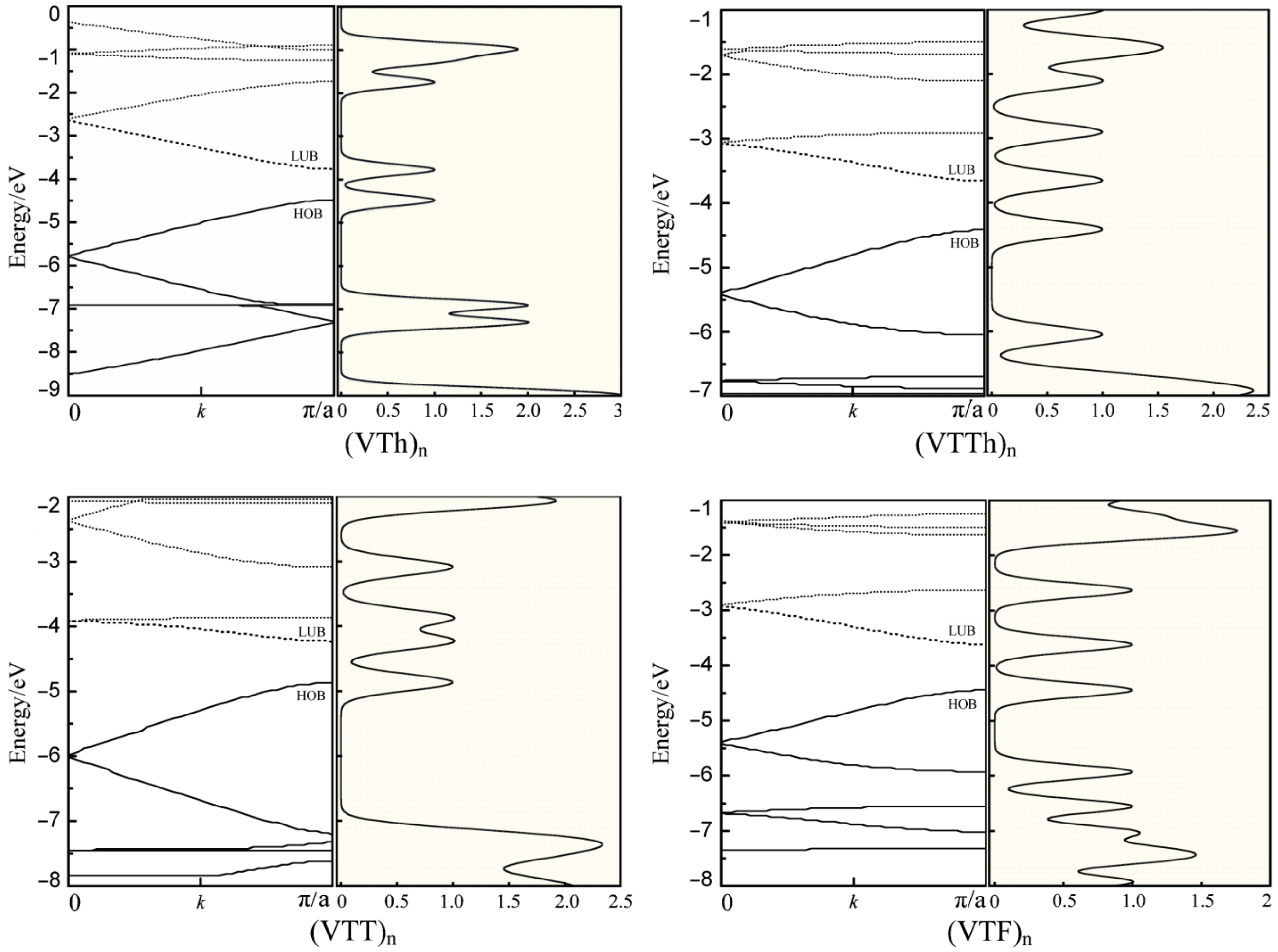


Figure 4. The band structures and DOS of the one-dimensional polymers.

4. Conclusion

The geometries, electronic structures and properties of oligomers based on Th or bicyclic non-classical Th unit were calculated and analysed systematically by DFT method. We find that those oligomers except $(VTTh)_n$ ($n = 2$–4) all have coplanar conformation. The bond length, bond length alteration, BCP properties, NICS and WBIs are employed to study the conjugational degree. The results suggest that those values are correlated tightly with the conjugational degree. The electron density (ρ_r) at BCP, ellipticity (ε_b) and WBIs of CSB are increased and those of CDB are decreased upon chain extension. The bond length alternations (Δr_c) of those studied oligomers are all reduced with the increase of polymeric number. The changes of those values show that the conjugational degree is increased systematically with main chain extension. The changes of NICS also show that the conjugation in central section is stronger than that in the outer section. The investigation on E_g of hetero-aromatic rings (Th, TT, TF and TTh) and their corresponding oligomers indicates that the narrow HOMO–LUMO separation of the bicyclic non-classical Ths can be carried over to their polymers by using them as building blocks for the polymers. In addition, the band gaps and DOS of those one-dimensional infinite systems [$(VTh)_n$, $(VTT)_n$, $(VTF)_n$ and $(VTTh)_n$] were also investigated by means of DFT method treated in PBC. The theoretical studies show that the four copolymers all have a narrow energy band gap (<0.9 eV), a wide HOB bandwidth and a relatively small effective mass of hole. Due to the twisted conformation of $(VTF)_n$ and $(VTTh)_n$, their band gaps are slightly bigger than that of $(VTh)_n$ and $(VTT)_n$. The narrow energy band gap and the large HOB bandwidth of the proposed copolymers indicate that they may be potential candidates for conductive polymers.

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