Theoretical analysis on the electronic structures and properties of PPV fused with electron-withdrawing unit: Monomer, oligomer and polymer

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A B S T R A C T

The geometries and electronic properties of five novel co-polymers which are obtained by replacing phenylene ring in poly(p-phenylenevinylene) (PPV) with five different fused heterocycles, as well as their corresponding monomers and co-oligomers, have been studied using DFT method. The dihedral angle, bond length, bond-length alternation, electron density at bond critical points (BCPs), nucleus-independent chemical shift (NICS) and Wiberg bond index (WBI) are analyzed and correlated with conduction properties. The bond length between the C=C linkage and the aromatic ring unit in the studied compounds is decreased and the double bond character is increased along with main chain extension. The changes of BCPs, WBIs and NICSs also show that the conjugational degree is increased with main chain extension and the electronic properties of the studied compounds vary systematically with the electron-withdrawing capacity of the fused heterocycles. The changes of NICS also show that the conjugation in central section is stronger than that in outer section. The band structure analysis shows that the energy gaps of the five novel polymers (in the range of 0.17–0.77 eV) are all much lower than that of PPV (1.3 eV). The proposed new coplanar conjugated polymers may be potential conductors.

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1. Introduction

Because of the attractive thermal, mechanical, electronic, optical and optoelectronic properties, the conjugated polymers have been widely studied for many years [1]. One of the most important goals is to develop narrow-band gap polymers in the field of materials science. Indeed, a narrow band gap can be obtained by starting from a monomer which already has a narrow HOMO–LUMO energy separation [2]. Hence, to find out low energy gap parent molecules is the key step of designing conductive polymer. To successfully molecularly engineer new polymers, it is necessary to have a complete understanding of the intrinsic electronic characteristics and of the relationship between the electronic structure of the compound and its conduction properties. Exploring the connection between the geometries, electronic structures and conduction properties of monomers and oligomers is another fundamental step to molecular design.

Poly(p-phenylenevinylene) (PPV) is an organic semiconductor with a optical gap of 2.5 eV [3–5], which has been broadly studied due to the interests in many areas of materials research, such as in

organic light-emitting displays (LEDs) [6], field-effect transistors (FETs) [7], solar cells [8] and switching devices [9] and so forth. Furthermore, when an organic conjugated system combines with donor–acceptor groups or fused with other conjugated ring, its band gap may be further reduced [10,11].

In this study, five new co-polymers are designed by the fusion of pyrazine or thiadiazole ring onto the vacant sites of the phenyl ring in PPV (denoted as $(PV)_n$ in this paper), which are named as $(VQ)_n$ (poly-(5-vinylquinoxaline)), $(VBT)_n$ (poly(4-vinylbenzo[c][1,2,5]thiadiazole)), $(VPQ)_n$ (poly(5-vinyl-[1,4]pyrazino[2,3-g]quinoxaline)), $(VTQ)_n$ (poly-(4-vinyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline)) and $(VBBT)_n$ (poly(4-vinylbenzo[1,2-c:4,5-c']bis[1,2,5]thiadazole)) as shown in Scheme 1. Their corresponding fused heterocyclic units are quinoxaline (Q), 2,1,3-benzothiadiazole (BT) [12], pyrazinoquinoxaline (PQ), thiadiazoloquinoxaline (TQ) and benzobis[1,2,5]thiadiazole [13] (BBT) (Scheme 1). These systems containing Q, BT, PQ, TQ or BBT units seem to possess several advantages in having a narrow band gap. First, these fused heterocyclic units all contain two or more electron-deficient imine nitrogens, they can serve as efficient electron-withdrawing units [14]. Second, TQ, BT and BBT units containing hypervalent sulfur atom have a high electron affinity [10]. Semi-empirical calculations have shown that particularly BBT is an extremely electron-deficient subunit which is attributed to the hypervalent sulfur atom [15]. Third, these systems have no steric repulsion between the adjacent

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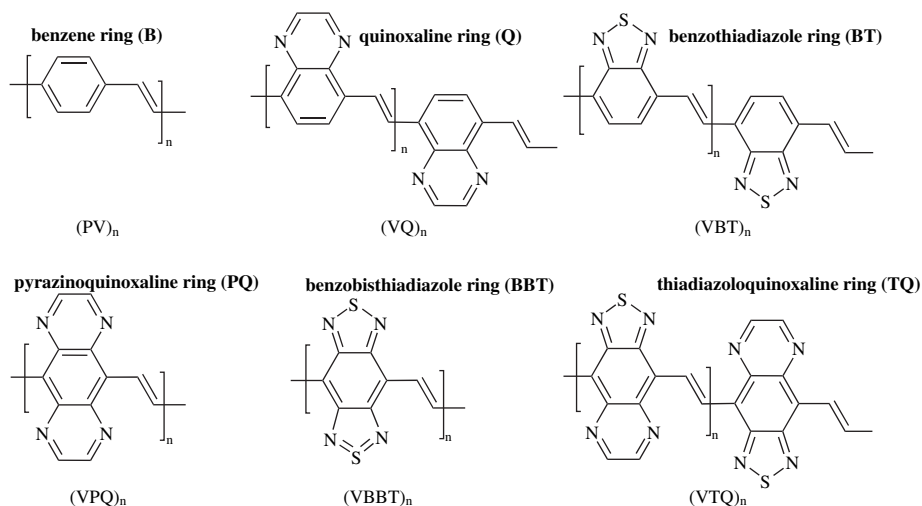
Scheme 1. Molecular structures of studied conjugated polymers.

heterocyclic units, leading to a planar geometry. Finally, the HOMO–LUMO separations of these heterocyclic units are narrow compared with that of benzene (B) due to the less aromaticity [16]. The theoretical HOMO–LUMO separations (at B3LYP/6-31G(d) level) of B, Q, BT, PQ, TQ and BBT are 6.8 eV, 4.77 eV, 4.26 eV, 3.71 eV, 3.20 eV and 2.64 eV, respectively. Obviously, the HOMO–LUMO separations of heterocyclic units are all much lower than that of benzene.

In this paper, theoretical analysis on the geometries and the electronic structures of the five new compounds and PPV, as well as of their oligomers, is reported. The geometry structures, electronic structures and the conduction properties of oligomers and polymers, aiming at providing an in-depth understanding on the correlation of the electronic structures with the conduction properties, are explored theoretically. For this purpose, we start with the electronic features of monomers and oligomers, and then extend them in relevant polymers.

2. Methodology

The geometry and electronic structure of the studied monomers and oligomers are optimized by the hybrid density functional theory (DFT) [17] method at the B3LYP level of theory (Becke-style 3-parameter density functional theory) using the Lee–Yang–Parr correlation function [18,19] with 6-31G(d) [20] basis set performed on Gaussian 03 program package [21]. The polymers are calculated by periodic boundary conditions (PBC) method [22], and the electron correlated PBEPBE method [23] is employed. In this study, one full unit cell was used for the calculation of an isolated, infinite, and one-dimensional polymer in the gaseous phase, starting from the geometry of the central portion (one or two repeat unit, Scheme 1) of the corresponding polymers. There are no imaginary frequencies for all monomers and oligomers at the present theoretical level. It implies that all the optimized structures are the global minima on the potential energy surface and stable structures.

Electronic density topological analyses and nucleus-independent chemical shift (NICS) [24] calculation are carried out at the B3LYP/6-31G(d) level based on the optimized geometries. The topological analyses are obtained from the atom in molecule (AIM) calculation. The NICS is defined as the negative value of the isotropic magnetic shielding computed at or above the geometrical center of the ring. Systems with significantly negative NICS values are aromatic, and systems with strongly positive NICS values are anti-aromatic [25,26]. In this study, two NICS values are calculated at two positions in the studied oligomers: the ring critical point (RCP) and at 0.5 Å above the RCP, which are denoted as NICS(0),

NICS(0.5), respectively. RCP was obtained from the AIM analyses [27]. The natural bond orbital (NBO) [28–31] analysis is also carried out at the B3LYP/6-31G(d) level on the basis of the optimized geometries. Additionally, density of state (DOS) is generated with GAUSSSUM 1.0 [32,33].

3. Results and discussion

3.1. Optimized geometries and electronic properties of monomers, oligomers and periodic systems

The optimized structures and geometrical parameters of monomers involving $(PV)_1$, $(VQ)_1$, $(VBT)_1$, $(VPQ)_1$, $(VTQ)_1$ and $(VBBT)_1$, as well as the sum of natural charge for two segments, are shown in Fig. 1. Inspecting Fig. 1, it can be seen that the sum of natural charges in aromatic ring unit is negative and that in ethylene unit is positive. It indicates that the charges are partly transferred from ethylene units to the aromatic ring units in these monomers. Accordingly, the aromatic ring units (B, Q, BT, PQ, TQ and BBT) all serve as electron-withdrawing units in these compounds. The sum of transferring charge between aromatic ring units and ethylene units in $(PV)_1$, $(VQ)_1$, $(VBT)_1$, $(VPQ)_1$, $(VTQ)_1$ and $(VBBT)_1$ are 0.020, 0.048, 0.054, 0.078, 0.085 and 0.089, respectively. The magnitudes of sum transferring charges in these monomers suggest that the order of electron-withdrawing power of these aromatic ring units is: BBT > TQ > PQ > BT > Q > B. The bond lengths of the C=C linkages in $(PV)_1$, $(VQ)_1$, $(VBT)_1$, $(VPQ)_1$, $(VTQ)_1$ and $(VBBT)_1$ are 1.339 Å, 1.339 Å, 1.340 Å, 1.343 Å, 1.344 Å and 1.345 Å, respectively. Besides, the C–C bond lengths between the C=C linkages and the aromatic rings in $(PV)_1$, $(VQ)_1$, $(VBT)_1$, $(VPQ)_1$, $(VTQ)_1$ and $(VBBT)_1$ are 1.472 Å, 1.471 Å, 1.468 Å, 1.467 Å, 1.464 Å and 1.456 Å, respectively. Obviously, the bond length of C=C linkage is increased and the bong length of C–C bond is decreased from $(PV)_1$ to $(VBBT)_1$. The bond length changes proved that the electron-withdrawing character of the fused heterocycle has an important influence on the structures. The dihedral angles (Φ_1) in these monomers between aromatic ring and linkage are all zero, as shown in Fig. 1. Moreover, the dihedral angles in the studied oligomers and polymers are zero too. So, these compounds all are coplanar polymers.

In order to obtain detailed bonding character, the completely topological analyses are performed for all the studied compounds. The charge densities (ρ_r), the Laplacian $(\nabla_\rho^2(r))$, the eigenvalues of Hessian matrix (λ_i) at the BCPs, and the Wiberg bond indexes (WBIs) [29], as well as the bond length (r_c) of the central single
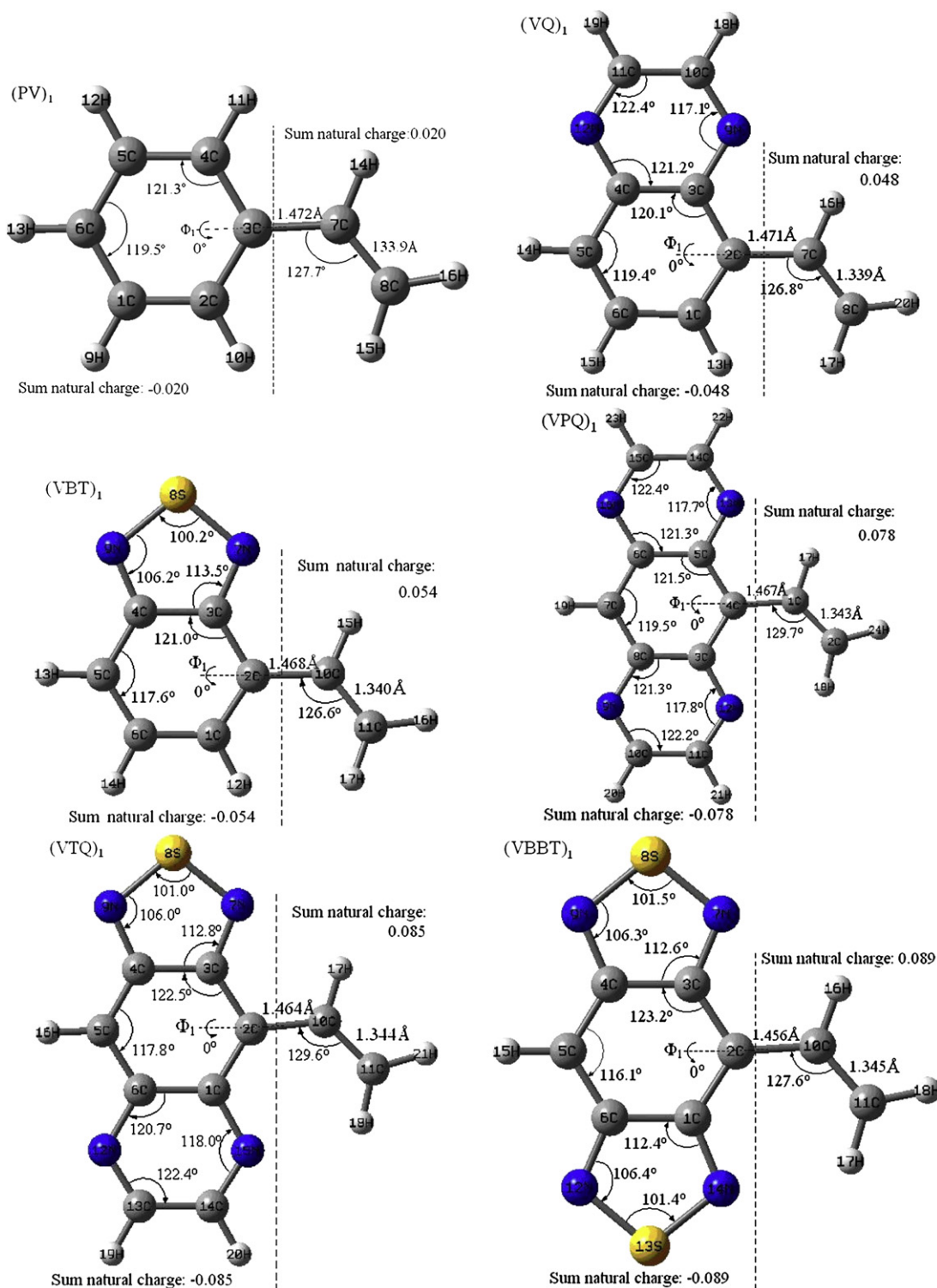
Fig. 1. Optimized geometries and natural charge distribution of monomers.

bond (CSB) and the central double bond (CDB) are listed in Table 1. 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 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. One of the C=C linkages which connect two neighboring aromatic ring units in each studied compound are defined as a CDB, in the same way, one of the C–C bonds between the C=C linkage

and the aromatic ring units is defined as a CSB, as shown in Scheme 2. Inspecting Table 1, generally, we can find that the bond length of the central double bond (in the range of 1.339–1.345 Å) in these compound is larger than that of C=C (1.33 Å) in ethane. On the contrary, the bond length of the central single bond (in the range of 1.395–1.472 Å) is smaller than that of the C–C (1.54 Å) in ethylene. Along with the increase of the polymeric degree, the central single bond becomes shorter and the central double bond becomes longer. The bond length changes show the difference between double

Table 1
BCP properties and Wiberg bond index of CSB[a] and CDB (italic) in studied compounds

	Polymeric number	r_c		$\nabla^2_\rho(r)$		ρ_r		ε_{BCP}		WBIs[b]	
(PV)	Monomer	1.472	*1.339[c]*	−0.681	*−0.985*	0.272	*0.342*	0.085	*0.354*	1.089	*1.900*
	Dimer	1.463	*1.350*	−0.693	*−0.955*	0.276	*0.336*	0.102	*0.323*	1.114	*1.746*
	Trimer	1.461	*1.351*	−0.697	*−0.951*	0.277	*0.335*	0.105	*0.318*	1.126	*1.731*
	Tetramer	1.460	*1.352*	−0.698	*−0.949*	0.277	*0.335*	0.106	*0.316*	1.128	*1.725*
	Polymer[c]	1.456	*1.365*	−0.641	*−0.870*	0.273	*0.321*	0.156	*0.251*	1.092	*1.916*
(VQ)	Monomer	1.471	*1.339*	−0.680	*−0.982*	0.272	*0.341*	0.079	*0.343*	1.089	*1.896*
	Dimer	1.459	*1.352*	−0.698	*−0.948*	0.278	*0.335*	0.099	*0.300*	1.126	*1.726*
	Trimer	1.459	*1.357*	−0.693	*−0.938*	0.277	*0.332*	0.106	*0.294*	1.144	*1.693*
	Tetramer	1.458	*1.358*	−0.695	*−0.936*	0.277	*0.331*	0.107	*0.292*	1.148	*1.685*
	Polymer	1.448	*1.369*	−0.686	*−0.833*	0.278	*0.319*	0.085	*0.289*	1.149	*1.694*
(VBT)	Monomer	1.468	*1.340*	−0.686	*−0.984*	0.273	*0.341*	0.085	*0.345*	1.089	*1.894*
	Dimer	1.455	*1.353*	−0.707	*−0.948*	0.279	*0.334*	0.108	*0.302*	1.133	*1.716*
	Trimer	1.449	*1.358*	−0.718	*−0.936*	0.282	*0.331*	0.116	*0.292*	1.158	*1.671*
	Tetramer	1.448	*1.360*	−0.721	*−0.933*	0.283	*0.331*	0.118	*0.288*	1.163	*1.661*
	Polymer	1.442	*1.372*	−0.701	*−0.824*	0.281	*0.318*	0.093	*0.295*	1.162	*1.675*
(VPQ)	Monomer	1.467	*1.343*	−0.677	*−0.974*	0.272	*0.339*	0.086	*0.326*	1.111	*1.866*
	Dimer	1.455	*1.363*	−0.696	*−0.920*	0.278	*0.328*	0.100	*0.261*	1.163	*1.657*
	Trimer	1.451	*1.366*	−0.705	*−0.911*	0.280	*0.326*	0.107	*0.251*	1.181	*1.630*
	Tetramer	1.448	*1.369*	−0.710	*−0.906*	0.281	*0.325*	0.111	*0.244*	1.191	*1.612*
	Polymer	1.416	*1.405*	−0.732	*−0.764*	0.294	*0.301*	0.162	*0.175*	1.136	*1.863*
(VTQ)	Monomer	1.464	*1.344*	−0.686	*−0.976*	0.274	*0.339*	0.095	*0.325*	1.116	*1.858*
	Dimer	1.447	*1.366*	−0.715	*−0.916*	0.282	*0.327*	0.116	*0.257*	1.183	*1.628*
	Trimer	1.436	*1.371*	−0.742	*−0.904*	0.288	*0.324*	0.128	*0.240*	1.217	*1.580*
	Tetramer	1.431	*1.375*	−0.753	*−0.893*	0.291	*0.321*	0.136	*0.226*	1.240	*1.544*
	Polymer	1.404	*1.413*	−0.750	*−0.775*	0.300	*0.296*	0.206	*0.104*	1.457	*1.300*
(VBBT)	Monomer	1.456	*1.345*	−0.706	*−0.974*	0.278	*0.338*	0.105	*0.322*	1.128	*1.842*
	Dimer	1.430	*1.373*	−0.754	*−0.901*	0.291	*0.323*	0.141	*0.240*	1.230	*1.563*
	Trimer	1.417	*1.383*	−0.784	*−0.876*	0.298	*0.317*	0.164	*0.212*	1.293	*1.487*
	Tetramer	1.400	*1.399*	−0.825	*−0.839*	0.307	*0.308*	0.195	*0.171*	1.386	*1.380*
	Polymer	1.395	*1.416*	−0.791	*−0.735*	0.305	*0.294*	0.203	*0.175*	1.558	*1.242*

[a] See in text.
[b] Attained from NBO analysis.
[c] One repeat unit extracted from corresponding polymer.

bond and single bond is decrease, and the conjugation degree is increased upon chain extension. It can be easily found that the order of the bond length of CSB is $(PV)_n$ (1.456) > $(VQ)_n$ (1.448) > $(VBT)_n$ (1.442) > $(VPQ)_n$ (1.416) > $(VTQ)_n$ (1.404) > $(VBBT)_n$ (1.395) by examining individual compound. However, the order of the bond length of CDB is inverse. This trend is tightly related to the electron-withdrawing capacity of the fused heterocyclic units in the polymers. The same results can be obtained by analyzing the monomers or oligomers. These analyses indicate that the electron-withdrawing power of the fused heterocyclic units in the main chain has an important impact on the structures.

According to Bader's theory of Atoms In Molecules (AIM), the BCPs are points of minimum electron density $\rho(r)$ along the bond. Laplacian of the charge density, $\nabla^2_\rho(r)$, which determines the regions of space wherein electronic charge of molecule is locally concentrate and depleted [34], provides electronic structures. 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 [34,35]. The ellipticity (ε_{BCP}) of the BCP is a measure of the ratio of the rate of intensity decrease in the two directions perpendicular to the bond path. The ellipticity provides a measure for the π character of a bond and structural stability. In addition, WBIs provide a measure of π-bond character too. When the value of WBIs is in the range of 1.0–2.0, the bond displays π character.

As shown in Table 1, both electronic density $\rho(r)$ (more positive) and Laplacian $\nabla^2_\rho(r)$ (more negative) of CSB increase with the polymeric number. It indicates that the local populations of charge in these bonds are increased. The ε_{BCP} and WBIs are also increased upon chain elongation, which suggest that the π features of the central single bonds are strengthened. On the contrary, the $\rho(r)$, $\nabla^2_\rho(r)$ (less negative), ε_{BCP} and WBIs of CDB are decreased upon chain extension. The decreased values show that the π characters of the central double bonds are weakened. In conclusion, both central single bond and central double bond in the studied systems show a more delocalized character upon chain extension. Abnormally, compared the polymer with relevant oligomers, the topological properties of CSB and CDB in some studied polymers are irregular. For example, $\rho(r)$, WBIs, ε_{BCP} and $|\nabla^2_\rho(r)|$ of CSB in $(VBT)_n$ are smaller than those in the corresponding oligomers. The similar situation is happened in CDB. The reason of this result may be that the different computational method is used in molecular system and period system, as mentioned in Section 2.

The concept of NICS as an efficient and simple criterion in probing aromaticity was proposed by Schleyer and co-workers [25,26,36] in 1996. Systems with significantly negative NICS values are aromatic and systems with strongly positive NICS values are anti-aromatic. Non-aromatic cyclic systems should therefore have NICS values about zero. Moreover, the changes of NICS value at different position rings in polymer can be used to indicate the conjugational degree [35]. For the purpose of comprehend of the relationship between conjugation degrees and
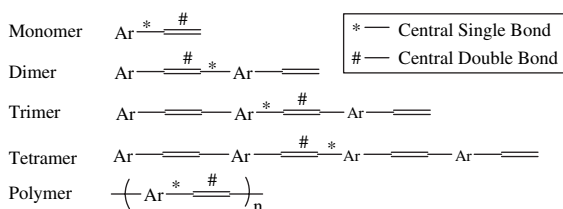
Scheme 2. Sketch map of central bond of the compounds.

Table 2
Negative NICS for studied compounds at points 0.5 Å above and at RCPs

	Ring	Monomer		Dimer		Trimer		Tetramer	
		0	0.5	0	0.5	0	0.5	0	0.5
(PV)	a1	8.8	10.6	8.5	10.3	8.4	10.2	8.4	10.2
	a2			7.7	9.5	7.3	9.1	7.2	9.1
	a3					7.6	9.5	7.2	9.1
	a4							7.6	9.4
(VQ)	a1	9.0	11.0	8.5	10.4	8.4	10.4	8.3	10.3
	a2			7.7	9.5	7.1	9.0	7.0	8.9
	a3					7.6	9.5	6.9	8.9
	a4							7.5	9.4
	b1	6.7	9.9	6.5	9.7	6.5	9.7	6.5	9.7
	b2			6.8	9.9	6.7	9.7	6.6	9.7
	b3					6.8	9.9	6.6	9.7
	b4							6.8	9.9
(VBT)	a1	6.0	7.9	5.5	7.5	5.4	7.4	5.4	7.4
	a2			4.8	6.8	4.2	6.2	4.1	6.1
	a3					4.7	6.7	4.1	6.1
	a4							4.6	6.6
	c1	15.9	16.6	15.6	16.3	15.5	16.2	15.7	16.4
	c2			15.7	16.2	15.5	16.0	15.4	15.9
	c3					15.8	16.3	15.4	15.9
	c4							15.8	16.3
(VPQ)	a1	11.4	13.1	10.2	12.0	10.0	11.8	10.0	11.7
	a2			9.0	10.8	7.7	9.5	7.5	9.2
	a3					8.7	10.4	7.3	9.1
	a4							8.6	10.4
	b1	5.6	8.7	5.4	8.5	5.3	8.4	5.3	8.4
	b2			5.8	8.8	5.6	8.7	5.6	8.6
	b3					5.7	8.8	5.5	8.6
	b4							5.7	8.7
(VTQ)	a1	9.6	11.3	8.2	10.0	7.9	9.7	7.8	9.6
	a2			7.0	8.8	5.4	7.2	4.9	6.7
	a3					6.5	8.3	4.7	6.6
	a4							6.4	8.2
	b1	4.2	7.1	3.9	6.9	3.9	6.8	3.9	6.8
	b2			4.1	7.1	4.1	7.1	4.1	7.1
	b3					4.2	7.2	4.1	7.1
	b4							4.0	7.0
	c1	16.5	17.4	16.1	16.9	16.0	16.8	15.8	16.6
	c2			16.2	16.9	15.5	16.1	15.3	15.9
	c3					15.8	16.5	15.2	15.9
	c4							16.0	16.6
(VBBT)	a1	8.7	10.5	6.6	8.5	5.6	7.6	4.5	6.5
	a2			5.5	7.4	2.6	4.6	0.4	2.5
	a3					4.3	6.3	0.1	2.2
	a4							3.0	4.9
	c1	15.4	16.2	14.7	15.5	14.3	15.1	13.9	14.6
	c2			15.0	15.6	14.0	14.6	13.3	13.8
	c3					14.6	15.2	13.3	13.8
	c4							14.1	14.7

ring current density, the NICS values of all the rings in studied compounds are been calculated at the B3LYP/6-31G(d) level. In order to avoid the influence of s bonds, the NICS(0.5) is also calculated at the same theoretical level. The NICS(0) and NICS(0.5) of different rings are listed in Table 2. The positions of rings are illustrated in Scheme 3.

From Table 2, it can be easily seen that all NICS values of rings are negative, which indicates that all of the studied compounds have strong local aromaticity. We can analyze the NICS from three aspects. First, comparing monomers with oligomers of the same compound, we can find that the NICS values in monomers are bigger than those in oligomers, and along with the chain lengthening the NICS values decrease. For example, in (VBBT) oligomer, the NICS(0.5) values of ring a_1 in monomer, dimmer, trimer and tetramer are 10.5, 8.5, 7.6 and 6.5, respectively. The same results can be obtained by analyzing the NICS values in other ring, such as pyrazine ring (ring b) and thiadiazole ring (ring c). The decrease of

NICS values indicates that the electronic currents above ring in oligomers are reduced. Second, although the NICS values are all more or less decreased upon main chain extension, we also can find that NICS values in terminal ring of polymeric axes show only little change for the same oligomer. From monomer up to tetramer, the changes of NICS values are all less than 8% in ring b_1 and less than 10% in ring c_1. For instance, the NICS (0.5) values of c_1 in $(VTQ)_1$, $(VTQ)_2$, $(VTQ)_3$ and $(VTQ)_4$ are 17.4, 16.9, 16.8 and 16.6, respectively. It indicates that the ring current in terminal ring only have a limited effect on the central section. Finally, the NICS values in side ring of polymeric axes also show little changes for the same oligomer, and the changes of NICS values in side ring (position b and c) are all less than 6%. For example, NICS values of b_1, b_2, b_3, and b_4 in $(VPQ)_4$ tetramer are 8.4, 8.6, 8.6 and 8.7, respectively. The changes are only 0.3 between b_1 and b_4. This is because ring b and ring c are far from polymeric axes and the polymeric number just influences the ring current slightly.

From Table 2, it can also be seen that the NICS values in central ring are smaller than those in terminal ring for trimers and tetramers. For instance, in $(VBBT)_4$ tetramer, the ring c_2 and c_3 are close to center, their NICS values (13.8 and 13.8) are smaller than those in terminal ring (14.6 for c_1 and 14.7 for c_4). This means that the ring currents in central rings are smaller than those in the outer one. It shows that the electron in central section delocalize to whole molecule, and is not localized on central section. In other words, the conjugation in central section is stronger than that in outer section. As shown in Scheme 3, benzene ring (ring a) is located on polymeric axes, the situation of benzene ring is different from ring b and ring c. For (PV) oligomer, from monomer up to tetramer, the NICS(0.5) values in ring a_1 are 10.6, 10.3, 10.2 and 10.2, respectively. The changes are 3.8%. For (VQ), (VBT), (VPQ), (VTQ) and (VBBT), the changes of NICS values in ring a_1 are 6.4%, 6.3%, 10.7%, 15.4% and 38.1%, respectively. The order of the NICS values changes is $(PV) < (VQ) \approx (VBT) < (VPQ) < (VTQ) < (VBBT)$ which is almost the same order as the electron-withdrawing capacity of the fused heterocyclic unit in these compounds. The similar results can be obtained by analyzing the NICS values in ring a_2 and a_3. This means that the electron-withdrawing power of the fused pyrazine and thiadiazole ring on the vacant sites of the phenyl ring has an important impact on NICS values. In other words, the electron-withdrawing units lead to the loss of aromaticity of the central benzene ring unit on the polymeric axes and strengthen the delocalized character of benzene ring unit.

3.2. HOMO–LUMO gaps and the band structure

The HOMO and LUMO energies, the energy gaps of monomers and oligomers, the highest occupied band (HOB) energies, the lowest unoccupied band (LUB) energies and the band gaps of polymers are all listed in Table 3. To obtain more information about the electronic properties of polymer, a periodic boundary conditions (PBC) calculation' is performed. The computed band structures around the Fermi level are shown in Fig. 2. Further more, for the sake of further comprehend of the relationship between electronic structure and band gap, the difference (Δr_c/Å) on the bond length and the difference ($\Delta \rho_r$) on the charge density at BCPs between the central single bond and the central double bond are listed in Table 3 too.

Analyzing Table 3, the calculated HOMO energies of oligomers are increased and the LUMO energies are decreased regularly upon chain extension. As a result, the calculated band gap decreases in the order monomer > dimmer > trimer > tetramer. It indicates that the polymerization degree has an important effect on energy gap. Furthermore, the oligomers containing electron-withdrawing groups (fused heterocyclic units) have lower energy gap by comparison with (PV) oligomers. The order of the energy gap of the
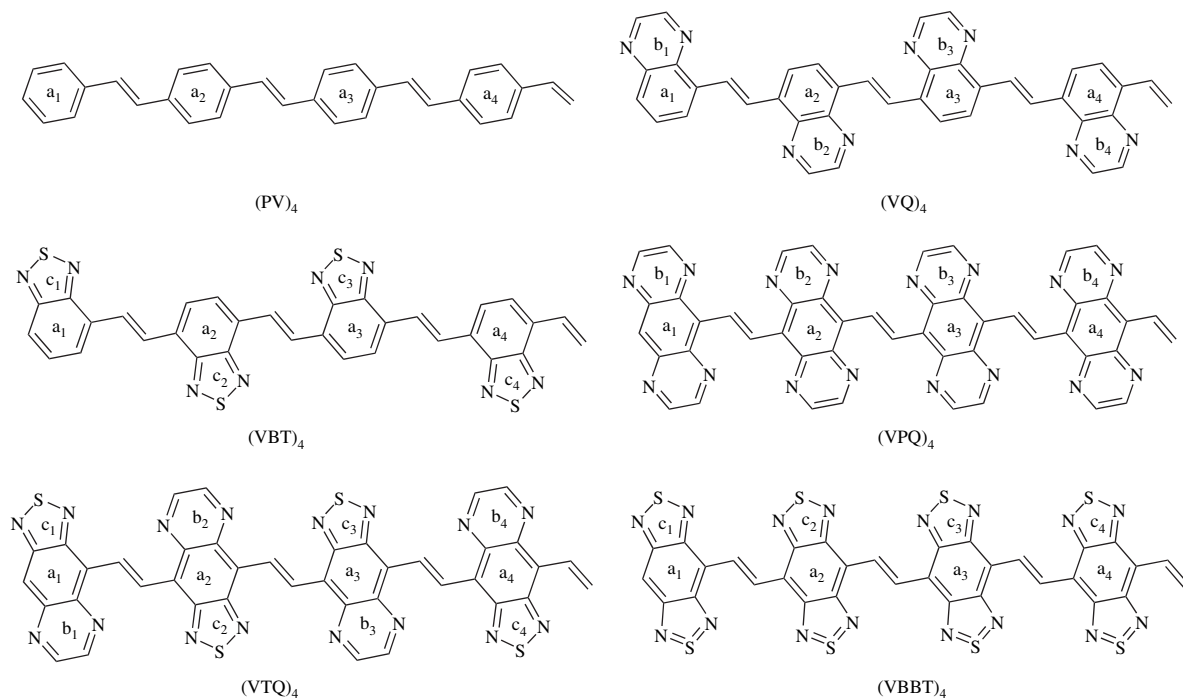
Scheme 3. Chemical structures of the tetramers ((a_1–a_4) benzene; (b_1–b_4) pyrazine; (c_1–c_4) thiadiazole).

studied oligomers with same polymeric number is (PV) > (VQ) > (VBBT). This decreased band gap shows that the electron-with-drawing capacity of fused heterocyclic units is another important effect in these conjugated compounds. Fig. 2 shows the one-dimensional band structure along the polymer chain. The highest occupied bands (HOB) and lowest unoccupied bands (LUB) band-widths of all the polymers are also calculated. The HOB band-widths of $(PV)_n$, $(VQ)_n$ $(VBT)_n$, $(VPQ)_n$, $(VTQ)_n$ and $(VBBT)_n$ are

1.90 eV, 1.03 eV, 1.06 eV, 1.12 eV, 0.93 eV and 1.41 eV, respectively. Comparatively, the HOB and LUB bandwidths of $(VQ)_n$ $(VBT)_n$, $(VPQ)_n$, $(VTQ)_n$ and $(VBBT)_n$ are all smaller than that of $(PV)_n$, which indicate that the π-electron delocalization of these poly-mers is weaker and the carrier localization is stronger than that of $(PV)_n$. However, on the other hand, from the band structure of all the six polymers shown in Fig. 2, it can be found easily that the band gap of $(VQ)_n$ (0.77 eV), $(VBT)_n$ (0.53 eV), $(VPQ)_n$ (0.17 eV), $(VTQ)_n$ (0.45 eV) and $(VBBT)_n$ (0.73 eV) are much lower than that of $(PV)_n$ (1.30 eV). It indicates that they may be potential conductors.

In this paper, the bond-length alternation is defined as the differ-ence on the bond length between the central single bond and central double bond. Examining Table 3, for these compounds with same polymeric number, it can be easily found that the absolute values of Δr_c and $\Delta \rho_r$ are smaller; the energy gaps are lower. For example, in dimers, the absolute values of Δr_c and $\Delta \rho_r$ decrease in the order: $(PV)_2$ (0.113 Å for Δr_c, 0.060 for $\Delta \rho_r$) > $(VQ)_2$ (0.107 Å for Δr_c, 0.057 for $\Delta \rho_r$) > $(VBT)_2$ (0.102 Å for Δr_c, 0.055 for $\Delta \rho_r$) > $(VPQ)_2$ (0.092 Å for Δr_c, 0.050 for $\Delta \rho_r$) > $(VTQ)_2$ (0.081 Å for Δr_c, 0.045 for $\Delta \rho_r$) > $(VBBT)_2$ (0.058 Å for Δr_c, 0.032 for $\Delta \rho_r$), as a result, the energy gap also de-creases in the same order: $(PV)_2$ (3.76 eV) > $(VQ)_2$ (2.99 eV) > $(VBT)_2$ (2.69 eV) > $(VPQ)_2$ (2.14 eV) > $(VTQ)_2$ (1.80 eV) > $(VBBT)_2$ (1.36 eV). Similarly, the same results can be obtained by analyzing monomers, trimers, tetramers or polymers. This trend is completely consistent with the electron-withdrawing power of the fused heterocyclic units in the studied compounds. The energy gaps of oligomers based on (VBBT) are decreased upon the polymeric number regularly, never-theless, the energy gaps of the polymer $(VBBT)_n$ (0.73 eV) are larger than those of tetramer (0.47 eV) instead. The reason of this result may be that the different computational method is used in molecular system and period system. From the analysis above, we can draw a conclusion that the bond-length alternation can be reduced by replacing of the benzene ring in PPV with quinoxaline ring, benzo-thiadiazole ring, pyrazinoquinoxaline ring, thiadiazoloquinoxaline ring or benzobisthiadiazole ring. The electron-withdrawing capacity of fused heterocyclic units plays a very important role on the reduction of the bond-length alternation.
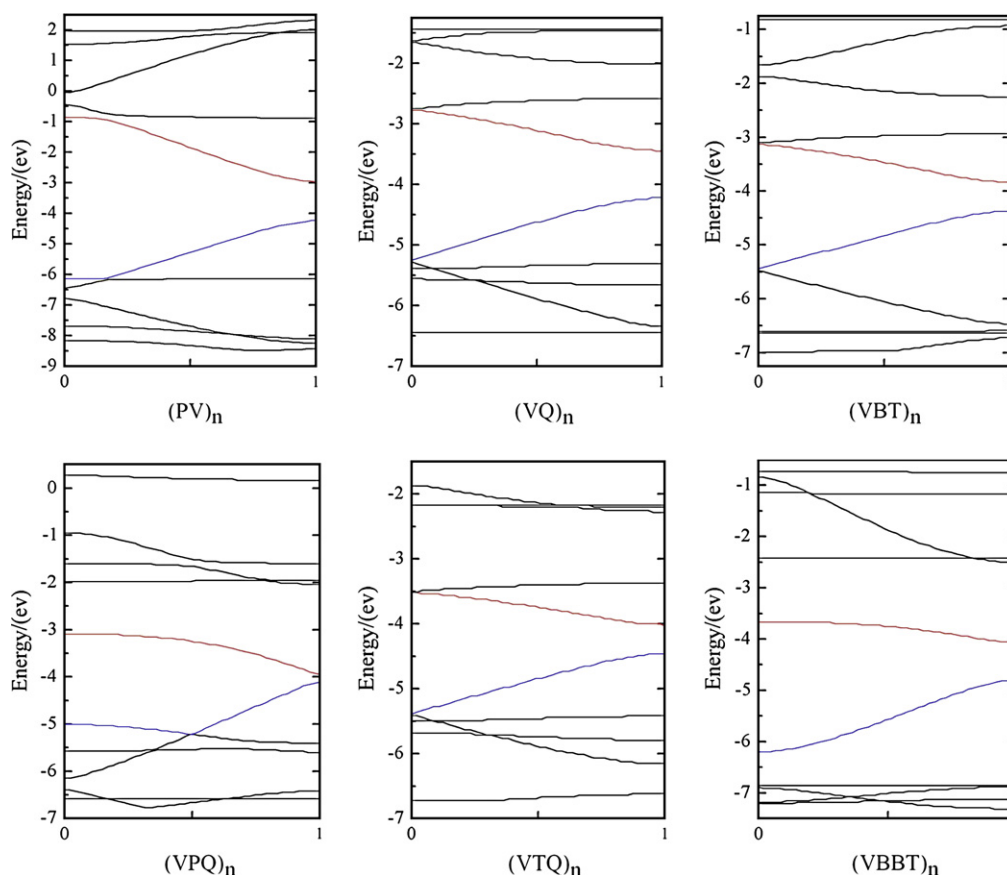
Table 3
Energies (eV) of HOMO and LUMO and energy gaps (eV) as well as the bond-length difference (Δr_c/Å), charge density difference ($\Delta \rho_r$) at BCPs between the central single bond and the central double bond for oligomer and polymer

Compound		(PV)	(VQ)	(VBT)	(VPQ)	(VTQ)	(VBBT)
Monomer	H	−6.03	−6.06	−6.10	−5.95	−5.92	−5.80
	L	−0.83	−2.04	−2.43	−2.87	−3.22	−3.54
	Eg	5.20	4.02	3.67	3.07	2.70	2.26
	Δr_c	0.133	0.131	0.129	0.124	0.120	0.111
	$\Delta \rho_r$	−0.069	−0.069	−0.068	−0.066	−0.065	−0.060
Dimer	H	−5.36	−5.39	−5.51	−5.24	−5.28	−5.20
	L	−1.60	−2.40	−2.82	−3.09	−3.47	−3.84
	Eg	3.76	2.99	2.69	2.14	1.80	1.36
	Δr_c	0.113	0.107	0.102	0.092	0.081	0.058
	$\Delta \rho_r$	−0.060	−0.057	−0.055	−0.050	−0.045	−0.032
Trimer	H	−5.11	−5.10	−5.23	−4.94	−4.97	−4.90
	L	−1.89	−2.55	−2.97	−3.22	−3.62	−4.05
	Eg	3.22	2.55	2.26	1.72	1.35	0.85
	Δr_c	0.109	0.102	0.091	0.084	0.065	0.034
	$\Delta \rho_r$	−0.058	−0.055	−0.049	−0.046	−0.036	−0.019
Tetramer	H	−4.99	−4.97	−5.12	−4.77	−4.80	−4.70
	L	−2.03	−2.65	−3.09	−3.29	−3.73	−4.23
	Eg	2.96	2.32	2.03	1.48	1.07	0.47
	Δr_c	0.108	0.100	0.088	0.080	0.055	0.001
	$\Delta \rho_r$	−0.058	−0.054	−0.048	−0.043	−0.030	−0.001
Polymer[a]	H	−4.25	−4.22	−4.37	−4.10	−4.46	−4.80
	L	−2.95	−3.45	−3.84	−3.93	−4.01	−4.07
	Eg	1.30	0.77	0.53	0.17	0.45	0.73
	Δr_c	0.091	0.079	0.070	0.011	−0.008	−0.022
	$\Delta \rho_r$	−0.047	−0.041	−0.037	−0.007	0.004	0.012

[a] H means HOB, L means LUB.

Fig. 2. Band structure of polymers.

4. Conclusion

Structure and electronic properties of co-oligomers (from monomer up to tetramer) and co-polymers with electron-withdrawing units involving benzothiadiazole, quinoxaline, pyrazinoquinoxaline, thiadiazoloquinoxaline or benzobisthiadiazole were studied by DFT method. The theoretical results suggest that all studied compounds are the coplanar conformation. The electron-withdrawing effect of the fused heterocyclic units can reduce bond-length alternation along the backbone of the studied compounds. Further more, the electron-withdrawing capacity of the fused heterocycle is stronger, the difference between C–C bond and the C=C linkage is smaller in these studied oligomers with the same polymerization degree. The changes of band length, electron density at BCPs, NICS and WBIs are employed to exam the conjugational degree, and the results show these values are closely related to conjugational degree. The changes of NICSs also show that the conjugation in central section is stronger than that in outer section. The band structure analysis shows that $(VQ)_n$, $(VBT)_n$, $(VPQ)_n$, $(VTQ)_n$ and $(VBBT)_n$ have quite low energy gap (0.77 eV, 0.53 eV, 0.17 eV, 0.45 eV and 0.73 eV, respectively). Therefore, the proposed new coplanar conjugated polymers can be considered as intrinsic conductor.

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