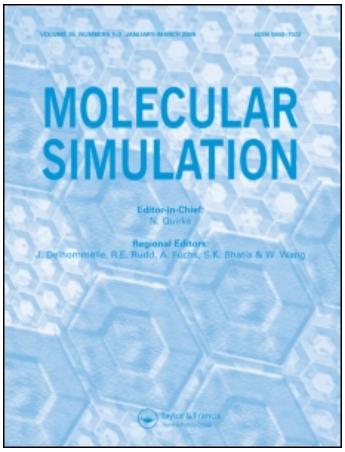

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The electronic properties of poly(*p*-phenylenevinylene) derivatives and their monomers and oligomers

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The electronic properties of poly(*p*-phenylenevinylene) derivatives and their monomers and oligomers

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The electronic structures of monomers, oligomers and polymers of poly(*p*-phenylenevinylene) (PPV) derivatives are calculated and analysed based on density functional theory (DFT) methods. The influences of different substituent groups on the band gaps are discussed. Strong relationships are found between band-gap and bond length alternation (BLA) of polymers, and between band-gap and Wiberg bond index (WBI). Analysis of nuclear independent chemical shift (NICS) reveals that oligomers with similar energy gaps have close values of NICS.

Keywords: PPV; band gap; NICS

1. Introduction

Conducting polymers have attracted strong interest since the discovery of metallic conductivity in polyacetylene in the 1970s [1]. A large number of polymers with low band gaps have been synthesised and found to have good conductivity. It is very important to design small band-gap polymers while searching for good conducting polymers. Generally, conducting polymers can be classified into four types: high-molecular electrolyte, metal organic complex compound, charge transfer complex, and conjugated polymer. With their special structures, π-conjugated polymers are widely studied as functionality materials such as light-harvesting materials and photo- and electro-luminescent materials. The band gaps of π-conjugated polymers are usually reduced by the introduction of substituents, donor–acceptor systems, ladder-type polymers, etc.

Poly(*p*-phenylenevinylene) (PPV) is well known for its applications in light emitting diodes (LED) [2]. Synthesis and systematic investigation of PPV and its derivatives have been developed in the past decades since they exhibit relatively high luminescence efficiencies in electroluminescent diodes [3–11]. Although the electronic and structural properties are well known for PPV, those for the PPV derivatives are still not well characterised. At present, it is difficult to directly calculate some electronic properties of polymers. However, it is convenient to compute the electronic properties of related oligomers. In fact, the electronic properties of reasonably long oligomers (e.g. 10-mer) could match well with the corresponding properties of the polymers. Consequently, it is necessary to understand the relationships between polymers and the corresponding monomers and oligomers.

In this study, PPV is chosen as the backbone and several common substituents such as —F, —CN and —OH are adopted to replace the —H atoms on the aromatic ring of PPV; various polymers are considered, and finally a few polymers with close band gaps or similar structures are adopted. For convenience, the polymers are named based on their side groups (see Scheme 1 or Figure 1): for example, if the two —H atoms in PPV are replaced by the —OH groups, the new polymer is labelled as PO.

2. Computational methods

All quantum chemical calculations were carried out using the density functional theory (DFT) [13] with the 6-31G* basis sets implemented in Gaussian 03 program [12]. The Becke three-parameter hybrid functional with the Lee–Yang–Parr non-local correlation functional (B3LYP) [14,15] was chosen to optimise the structures of monomers and oligomers. Vibrational frequencies calculations were performed to ensure that optimised geometries corresponded to minimums on the potential energy surface (PES). Natural bond orbital (NBO) analysis and nuclear independent chemical shift (NICS) [16] calculations were carried out based on the optimised geometries. NICS values were computed through the gauge-independant atomic orbital (GIAO) [17] method implemented in Gaussian 03. Points at or above ring centres, which are determined by the unweighted mean of the heavy atom

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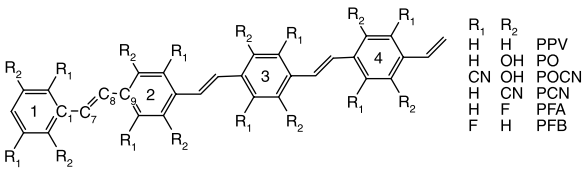

Scheme 1. The structures of the tetramer of the studied polymers; the unit numbers from 1 to 4, are also used in related monomer and oligomers.

coordinates, are often selected to compute NICS jobs. In this paper, however, the chosen points are (above) aromatic ring critical points (RCP) rather than geometrical centres, as suggested by Cossío et al. [18]. RCP is the point where the density of electron is the lowest in the plane [19], and it can be obtained from the atoms in molecules (AIM) analyses. Though NICS (1) (at points 1 Å above the molecular plane) is recommended as being a better measure of the π-electron delocalisation as compared to NICS (0) (at the molecular plane, i.e. at the ring centre) [20, 21], NICS values at four points (RCPs, 0.5, 1.0 and 1.5 Å above RCPs) are all computed in this paper.

The periodic boundary conditions (PBC) method and the pure DFT method of PBEPBE [22] were employed in optimising the geometries of the polymers. Since NBO analysis is not available for polymers, 11 cells of the polymers were chosen in related jobs. The NBO data for the central cell are equal to those of adjacent cells within the limits of computational error and are adopted.

3. Results and discussion

3.1 Band structures

3.1.1 Band gap

The optimised structures along with related bond lengths of polymers are presented in Figure 1. As all of the polymers are highly symmetric, with a symmetric centre, some data are omitted. Band structures of the polymers are shown in Figure 2. Band gaps and energy levels of the HOCOs (the highest occupied crystal orbital) and the LUCOs (the lowest unoccupied crystal orbital) of the polymers are collected in Table 1. Bandwidths of the HO (the highest occupied) and LU (the lowest unoccupied) bands of the polymers also can be found in Table 1. Additionally, we compute the band gaps of POF (replace the two —CN groups in POCN with —F atoms) and PFCN (replace the two —OH groups in POCN with —F atoms), and the related data are also collected in Table 1.

Replacing the H atoms with other atoms or groups on the backbone of PPV does not cause a lot of band gap changes except in the case of POCN. The band gap of POCN is 0.88 eV, while that of PPV is 1.30 eV. But the band gaps of PO, PCN, PFB and PFCN are quite close, within the range of 1.16–1.21; and that of POF, 1.27 eV, is quite close to the one of PPV. It is very strange that the band gap of PFA even increases slightly by 0.03 eV compared with PPV. Maybe, the reason is that the hydrogen bond existing in PFA is much stronger than other polymers.

Let us see the energy levels of the HOCOs and LUCOs first. The changes of the energy levels of the HOCOs and LUCOs of the PPV derivates compared with PPV are listed as follows (the order of the derivates is always PO, POCN, PCN, PFA, PFB, PFCN and POF; the values of HOCO and LUCO are separated by a slash; the calculating formula is: $(E - E_{ppv})/E_{ppv}$): −13.6/−16.9%, 22.1/45.3%, 36.5/56.1%, 8.5/10.8%, 9.2/16.9%, 43.3/67.6% and −1.9/−2.0%. As the energy levels of the HOCOs and LUCOs of the polymers are all below zero, the negative values listed above imply that the energy levels of related polymers are higher than those of PPV. It is obvious that the existence of —OH groups causes the energy level of the HOCOs and LUCOs to increase, while —CN and —F make the two energy levels decrease, especially in the

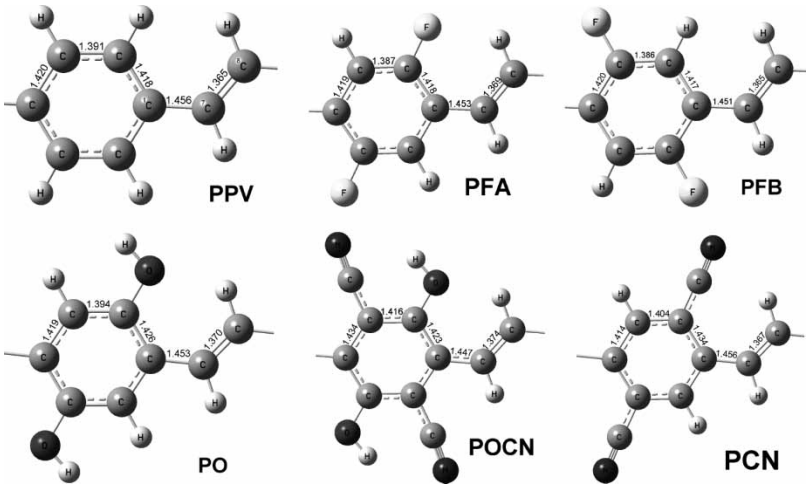

Figure 1. Optimised structures of the polymers along with bond length (units in Å).

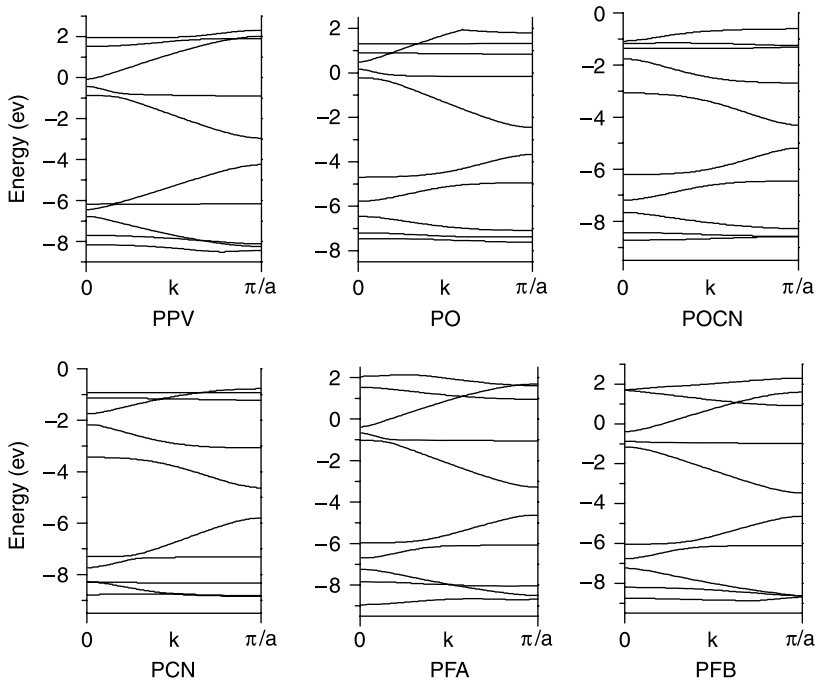

Figure 2. Band structures of the six one-dimensional polymers.

Table 1. Energy gaps and energy levels of the HOMOs and the LUMOs of the monomers and oligomers, band gaps and energy levels of the HOCOs and the LUCOs of the polymers, bandwidths of the HO and LU bands of the polymers (units in eV).

Name		Monomer	Dimer	Trimer	Tetramer	Polymer	Polymer[a]
PPV	H	−6.03	−5.36	−5.11	−4.99	−4.25	1.94
	L	−0.83	−1.60	−1.89	−2.03	−2.96	2.10
	E	5.20	3.76	3.22	2.96	1.30	
PO	H	−5.37	−4.91	−4.67	−4.54	−3.67	1.04
	L	−0.70	−1.34	−1.58	−1.70	−2.46	2.23
	E	4.67	3.57	3.09	2.84	1.21	
POCN	H	−6.47	−6.14	−5.98	−5.90	−5.19	1.00
	L	−2.59	−3.09	−3.35	−3.49	−4.30	1.23
	E	3.89	3.05	2.63	2.41	0.88	
PCN	H	−7.13	−6.69	−6.53	−6.46	−5.80	1.49
	L	−2.64	−3.27	−3.57	−3.73	−4.62	1.20
	E	4.49	3.42	2.96	2.73	1.18[b]	
PFA	H	−6.28	−5.74	−5.52	−5.41	−4.61	1.33
	L	−1.17	−1.97	−2.27	−2.42	−3.28	2.26
	E	5.11	3.77	3.25	2.99	1.33	
PFB	H	−6.28	−5.75	−5.54	−5.39	−4.64	1.41
	L	−1.28	−2.11	−2.43	−2.68	−3.46	2.29
	E	5.00	3.64	3.11	2.72	1.18[b]	
PFCN	H	−7.34	−6.96	−6.83	−6.78	−6.09	1.17
	L	−2.91	−3.56	−3.88	−4.06	−4.94	1.28
	E	4.43	3.41	2.95	2.72	1.16	
POF	H	−5.75	−5.41	−5.19	−5.08	−4.17	0.76
	L	−1.04	−1.77	−2.04	−2.18	−2.90	2.59
	E	4.72	3.64	3.15	2.90	1.27	

[a] H and L refer to bandwidths of the HO and LU bands, respectively. [b] The band gap of PCN is slightly greater than that of PFB.

case of PCN. The substituents have much more effect on the energy level of the LUCOs than that of the HOCOs, no matter whether they cause the energy levels to increase or not. It is not surprising that POCN has the smallest band gap, due to the combining effect of —CN and —OH groups; the energy level of the LUCO altered 45.3%, twice as much as that of the HOCO (22.1%).

The bandwidths of the HO and the LU bands are related to band gaps indirectly. Reducing the bandwidths can narrow the band gap, on one side; and as a result of the relatively smaller space for the electrons to move, the capacity to conduct can weaken, on the other side.

The bandwidths of the HOB (HO band) and LUB (LU band) of PPV are quite close; the difference is only 0.16 eV. The changes of the bandwidths of the HOB and LUB of the polymers, compared with PPV, are shown as follows (the order of the derivates and the calculating formula are the same as above; before slashes are HOBs): −46.4/6.2%, −48.5/−41.4%, −23.2/−42.9%, −31.4/7.6%, −27.3/9.0%, −39.6/−39.0% and −60.8/23.3%. Apparently, the groups of —OH and —F both cause the bandwidth of HOB to decrease sharply and make the bandwidth of LUB increase, while —CN groups cause the two to decrease and have a greater effect on the bandwidth of LUB.

3.1.2 Energy gap

The values of energy gaps of monomers, oligomers and band gaps of polymers are collected in Table 1. Apparently, PPV and PFA have similar band gaps and energy gaps, (monomers differ 0.09 eV, others within 0.03 eV). But the bandwidth of HOB band of PFA is much smaller than that of LUB band, influenced by the —F substituents. PFA and PFB are stereoisomers, and the differences between their energy gaps and band gaps are within the range of 0.11–0.17. The gaps of PO and PCN are close too. The differences of the oligomers range from 0.13 to 0.11 eV, and that of the polymers is only 0.03 eV. POCN is special for its gaps differ much from others (all are above 0.30 eV), and its gaps are the smallest too.

3.1.3 Bond length alternation

The band gaps of linear π-conjugated systems mainly depend on the degree of bond length alternation (BLA) along the polymer backbone [23]. Though the band gap and BLA are not linearly correlated, polymers with small BLAs usually have small band gaps too. If just C_1–C_7–C_8 (defined in the structure of PPV in Figure 1) is considered, the BLAs of the six polymers are: 0.091, 0.083, 0.073, 0.089, 0.085 and 0.086. Obviously, the BLA of POCN is the smallest, which is also very different from the others; it is in agreement with the computational result that the band gap of POCN is the smallest (see Table 1), as mentioned before. The BLAs of the others are close to each other (from 0.083 to 0.091), which indicate that their band gaps are close too; the computational results are from 1.18 to 1.30. The band gap's order cannot be inferred only from the value of the BLAs. On the one hand, the bonds of the aromatic ring are not considered; On the other hand, the rule between the band gap and the BLAs does not always work. As shown in Figure 1, the band lengths of PFA and PFB, a couple of stereoisomers, are nearly the same, and so are the BLAs. But there is a difference of 0.15 between the band gaps.

3.1.4 Wiberg bond index

The Wiberg bond index (WBI) [24] can be used as a measure of π-bond character. The bond displays π character, when the WBI is within the range of 1.0–2.0. The bonds, C_1–C_7 and C_7–C_8 (see Scheme 1 or the structure of PPV in Figure 1), are considered again. The WBI of the two of the polymers can be found in Table 2. It is obviously that the WBI of C_1–C_7 of POCN, 1.169, is largest, while the WBI of C_7–C_8 of POCN, 1.651, is smallest. So the bonds of C_1–C_7 and C_7–C_8 differ least in POCN, which implies that the electrons can move more easily. The values of WBI of other polymers are quite close, the values of C_1–C_7 range from 1.141 to 1.153, and those of C_7–C_8 are in the range of 1.691–1.707. This result indicates that POCN has the smallest band gap and that other polymers have close band gaps again.

The WBI of the three bonds between the adjacent aromatic rings in oligomers are also collected in Table 2 (there were only two bonds in monomer). It was mentioned before that all the energy gaps of POCN are smallest and that those of PPV and PFA are quite close. Apparently, all the values of C_1–C_7 and C_8–C_9 of POCN are the smallest, and those of C_7–C_8 are the largest, compared to the related values of other polymers. And all the WBI of PPV and PFA are close; all the differences are less than 0.15. All the above show that the WBIs of two polymers are close when they have similar band gaps.

3.2 NICS

The concept of nucleus-independent chemical shifts (NICSs) was introduced by Schleyer et al. in 1996, as a magnetic index of aromaticity. NICS is defined as the negative value of the absolute shielding computed at a certain point, usually at or above ring centre. Aside from its lack of direct experimental validations, the NICS method has been used extensively to assess the aromaticity and antiaromaticity of many organic and inorganic compounds, intermediates and transition states.

As a magnetic index, NICS can give a clear indication of ring current, thus it can also give an indication about the capacity to conduct, indirectly.

Table 2. Wiberg bond index of selected bonds (the bonds between two aromatic rings) of monomers, oligomers and polymers.

Name	Unit	Monomer	Dimer	Trimer	Tetramer	Polymer
PPV	1	1.089[a]/1.900[b]	1.114[a]/1.746[b]/1.119[c]	1.115/1.741/1.123	1.115/1.740/1.124	1.141[a]/1.707[b]
	2		1.097/1.889	1.126/1.731/1.124	1.128/1.725/1.128	
	3			1.097/1.889	1.127/1.729/1.124	
	4				1.097/1.889	
PO	1	1.100/1.886	1.125/1.721/1.130	1.127/1.716/1.134	1.127/1.715/1.134	1.153/1.682
	2		1.107/1.876	1.137/1.707/1.134	1.138/1.701/1.139	
	3			1.108/1.875	1.138/1.706/1.135	
	4				1.108/1.875	
POCN	1	1.105/1.873	1.136/1.697/1.140	1.138/1.691/1.145	1.138/1.690/1.146	1.169/1.651
	2		1.112/1.862	1.148/1.682/1.145	1.151/1.675/1.151	
	3			1.113/1.861	1.150/1.680/1.146	
	4				1.113/1.861	
PCN	1	1.097/1.887	1.122/1.729/1.126	1.123/1.724/1.130	1.123/1.724/1.130	1.148/1.691
	2		1.105/1.876	1.133/1.715/1.130	1.134/1.710/1.134	
	3			1.105/1.875	1.134/1.713/1.130	
	4				1.106/1.874	
PFA	1	1.093/1.893	1.117/1.732/1.123	1.119/1.728/1.126	1.119/1.727/1.127	1.144/1.696
	2		1.101/1.882	1.129/1.718/1.127	1.130/1.713/1.131	
	3			1.101/1.881	1.130/1.717/1.127	
	4				1.101/1.881	
PFB	1	1.086/1.900	1.112/1.741/1.118	1.114/1.736/1.122	1.124/1.722/1.134	1.142/1.699
	2		1.094/1.888	1.125/1.725/1.123	1.139/1.703/1.140	
	3			1.094/1.888	1.138/1.709/1.134	
	4				1.102/1.881	

[a] C_1–C_7, [b] C_7–C_8 and [c] C_8–C_9; the three bonds are denoted in Scheme 1.

Table 3. Negative NICS of the monomers and oligomers at RCPs and 0.5, 1.0 and 1.5 Å above RCPs (units in eV).

Name	Unit	Monomer	Dimer	Trimer	Tetramer
PPV	1	8.8/10.6/10.6/7.4	8.5/10.2/10.2/7.2	8.4/10.2/10.2/7.2	8.4/10.2/10.2/7.2
	2		7.7/9.5/9.6/6.8	7.3/9.1/9.3/6.5	7.2/9.1/9.3/6.5
	3			7.6/9.4/9.6/6.7	7.2/9.1/9.3/6.5
	4				7.6/9.4/9.6/6.7
PO	1	11.9/12.4/10.5/6.7	10.8/11.4/10.0/6.5	10.8/11.4/9.9/6.5	10.8/11.4/9.9/6.5
	2		10.6/11.1/9.6/6.2	10.2/10.7/9.3/6.0	10.2/10.7/9.3/6.0
	3			10.5/11.1/9.6/6.2	10.2/10.7/9.3/6.0
	4				10.6/11.1/9.6/6.2
POCN	1	10.8/11.2/9.7/6.3	10.4/10.8/9.3/6.1	10.4/10.8/9.3/6.1	10.4/10.8/9.3/6.1
	2		10.2/10.6/9.0/5.9	9.7/10.1/8.7/5.6	9.7/10.1/8.6/5.6
	3			10.1/10.5/9.0/5.8	9.7/10.0/8.6/5.6
	4				10.1/10.5/9.0/5.8
PCN	1	9.6/11.0/10.4/7.2	9.1/10.6/10.2/7.0	9.2/10.6/10.2/7.0	9.1/10.6/10.2/7.0
	2		8.6/10.0/9.6/6.6	8.2/9.6/9.3/6.4	8.2/9.6/9.3/6.4
	3			8.6/9.9/9.5/6.6	8.1/9.5/9.2/6.4
	4				8.6/9.9/9.6/6.6
PFA	1	11.9/12.4/10.7/7.0	11.6/12.1/10.4/6.8	11.6/12.1/10.4/6.8	11.5/12.0/10.4/6.8
	2		11.3/11.7/10.0/6.5	10.9/11.4/9.7/6.3	10.9/11.3/9.7/6.3
	3			11.2/11.6/10.0/6.4	10.9/11.3/9.7/6.3
	4				11.2/11.6/10.0/6.5
PFB	1	11.3/12.0/10.5/6.9	11.0/11.6/10.2/6.7	10.9/11.6/10.1/6.7	10.9/11.5/10.1/6.6
	2		10.2/10.8/9.5/6.3	9.7/10.4/9.2/6.0	9.6/10.3/9.1/5.9
	3			10.1/10.7/9.5/6.2	9.6/10.2/9.0/5.9
	4				10.0/10.6/9.4/6.2

The NICS values of monomers and oligomers can be found in Table 3. Let us focus on the values of oligomers of the same polymers first. The NICS values of a constitutional unit at the similar part of oligomers are nearly the same; this indicates that the ring currents influence its unit a lot and influence adjacent units quite little. To take PPV as the example, NICS values at or above the RCP of the second aromatic ring of trimer are 7.3/9.1/9.3/6.5, and those of tetramer are 7.2/9.1/9.3/6.5; the second unit of dimer is at the terminal, and the values are 7.7/9.5/9.6/6.8, while those of the related unit of tetramer, which is the fourth unit, are 7.6/9.4/9.6/6.7. The NICS values of the two central units of tetramers are very close too; the difference is within 0.1, e.g. the values of the second and third aromatic ring of POCN are: 9.7/10.1/8.6/5.6 and 9.7/10.0/8.6/5.6; it indicates the similar electronic structure of the two units. In the same oligomer, NICS values at points far from central are larger than those at central, for example, the values of NICS(1) of tetramer of PO are 9.9, 9.3, 9.3, 9.6; it implies that π-electron delocalise to the whole molecule rather than localising at the central section.

It should be noticed that the maximum negative values of NICS are found at about 0.5 or 1.0 Å above RCPs. The value of NICS does not depend purely on the π system. As it is affected by the σ framework of the CC and CH bonds, it is suggested that the NICS values should be calculated at a distance from the plane of the ring to assess the aromaticity and antiaromaticity; thus, the value at 1.0 Å above the plane has become standard [25].

Now, we only examine the values of NICS (1) when comparing oligomers of different polymers. As it is mentioned before, the band gap of POCN is smallest; and all the values of NICS of POCN are smallest compared to others, no matter whether in monomers or in oligomers. The band gap of PFA is slightly larger than that of PPV and is the largest, and the values of NICS at each point of its monomer and oligomers are also the largest too. We also notice the weakness of this method. Let us focus on the central ring of trimer. The value is 9.3 for PPV, PO, PCN, 9.2 for PFB, 9.7 for PFA and 8.7 for POCN. Though the band gap of PPV is 0.12 more than that of PCN, the NICS of the two is nearly the same. Considering that the values of NICS of PFA are always much greater than those of the others and that its band gap is even larger than PPV, if we just examine the values of the others, the method works much better. It may be improved by using a better basis-set and calculating NICS at a suitable point.

4. Summary

A series of monomers, oligomers, polymers of PPV derivatives are involved in this paper. Their structures and electronic properties are calculated based on DFT methods. The analysis of the influences of different types of substituent groups shows that POCN has the smallest band gap with the combining effect of the groups of —OH and —CN. The changes of NICS values reveal that if two polymers of PPV derivates have close band gaps, the values of NICS of their related monomer or oligomers would also be close too.

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