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EXCITON BINDING ENERGY OF ELECTRONIC POLYMERS: A FIRST PRINCIPLES STUDY*

LINGYUN ZHU, YUANPING YI, LIPING CHEN and
ZHIGANG SHUAI†

Key Laboratory of Organic Solids
Beijing National Laboratory for Molecular Sciences (BNLMS)
Institute of Chemistry, Chinese Academy of Sciences
100190 Beijing, P. R. China
†*zgshuai@iccas.ac.cn*

Exciton binding energy (E_b) is a key factor for the polymer electronics as well as for the fundamental polymer physics, which has been controversial since long time. Light-emitting polymer requires a large E_b so that the charge recombination dominates. But, the photovoltaic polymers need small E_b to allow efficient charge separation. First-principles Density Functional Theory (DFT) is employed to calculate E_b for polydiacetylene (PDA), *trans*-polyacetylene (PA), polythiophene (PT), poly(2,5-thienylenevinylene) (PTV), and poly(*p*-phenylene vinylene) (PPV). We find that the hybrid B3LYP, B972, PBE1PBE, and B1B95 functionals with 20–25% amount of exact HF exchange can give reasonable results and predict E_b is around 0.1–0.6 eV for these π-conjugated polymers.

Keywords: Exciton binding energy; time-dependent density functional theory; semiconducting conjugated polymers.

1. Introduction

Π-conjugated oligomers and polymers are currently under intensive investigation since they offer a wide range of potential applications in novel electronic or opto-electronic devices, such as organic light-emitting diodes (OLEDs), organic solar cells, and sensors.[1–5] Poly(p-phenylenevinylene) (PPV) and its derivatives have been widely used in electronic devices.[6] Poly(2,5-thienylenevinylene) (PTV) and well-defined oligothienylenevinylenes are known to exhibit lower oxidation potentials and smaller band gaps in comparison to oligothiophenes and

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†Corresponding author.

oligo(p-phenylene-vinylene) with comparable chain lengths.[7] Designing better organic electronic materials requires a comprehensive understanding of the electronic structure of conjugated polymers and the factors affecting it.

The magnitude of the (lowest singlet) exciton binding energy (E_b), defined as the difference between the charge separation gap and the optical gap of $1B_u$ state, has been intensively studied in the past, and is still controversial and hence, is of great interest.[8] Strictly, this definition is only applied to long-chain oligomers. We note that for small-chain oligomers charge gap is smaller than $1B_u$ excitation energy. The charge gap is defined as the energy creating an electron plus the energy creating a hole, namely, when the electron does not interact with the hole, or their separation is infinite. In the long-chain limit, it can be regarded as the gap between the lowest unoccupied (LUMO) and highest occupied (HOMO) molecular orbitals. But, for finite chain length, the two charges (electron and hole) can never be separated from each other. It is thus not well defined for finite system. The optical gap of $1B_u$ state is the vertical excitation energy from the ground state to the first dipole-allowed excited state.

In photovoltaic devices we would like to have a small binding energy, which facilitates the fast separation of charges, while in electroluminescent devices such as LED, a larger E_b is desirable so that the charge recombination dominates. In general, there exist different opinions, whether the lowest optical transition is due to the absorption of free charge carriers (direct interband transitions), weakly bound electron–hole (e–h) pairs (Wannier or charge transfer excitons), or tightly bound (Frenkel) excitons. In this context, E_b varies from a few $k_B T$ to the order of $1\,\mathrm{eV}$ for PPV.[9] The direct measurements of E_b are not straightforward except for the single crystal of polydiacetylene (PDA).[4] It has been argued that electronic correlation effects and electron–photon coupling and their interplay are often not considered appropriately. Furthermore, differences in samples and experimental techniques raised questions on the comparability for the results.[10,11]

Theoretical investigations of E_b of conjugated polymers have been very important both for the semiempirical model study[12] and the DFT/LDA Bethe–Salpeter equation (BSE) or GW approaches.[13] The semiempirical model can be treated nearly exactly for the electron correlation, but the results rely much on the parameters, though the qualitative understanding had been achieved.[12] BSE or GW approach is indeed first-principles; however, from the theoretical ground, whether the Hohenberg–Kohn–Sham framework could accommodate these many-body corrections at the Green's function level is not clear. Further, the final results are not consistent among themselves.[13]

We note that there are two recent progresses in quantum chemistry: (i) Time-Dependent Density Functional Theory (TDDFT) and its successful application to the lowest-lying excited states[14] and (ii) the hybrid GGA Becke three-parameter Lee–Yang–Parr (B3LYP) functional for the quantitative prediction of chemical structure and electronic structures.[15] The combination of the two has been found to be very successful in studying the excitation processes in conjugated systems.[16] Tretiak *et al.* have showed that hybrid density functionals are able to reproduce

the excitonic effects and give the reasonable results for E_b.[17] In this work, we apply TDDFT with different functionals to study E_b for conjugated polymers of polydiacetylene (PDA), trans-polyacetylene (PA), polythiophene (PT), poly(2,5-thienylenevinylene) (PTV), and poly(*p*-phenylenevinylene) (PPV). The purpose of this contribution is to provide the state-of-the-art first-principles calculations for this controversial quantity of electronic polymers.

2. Computational Details

The chemical structures of investigated oligomers comprising PDA, PA, PT, PTV, and PPV are depicted in Fig. 1. The ground-state geometries of the molecules are optimized at the DFT level with different functionals and the 6-31G* basis set, as implemented in the GAUSSIAN 03 package.[18] In all cases, we assume coplanar

(a)

$N = 2n\text{-}1$ BLA=r1-(r2+r3)/2

(b)

$N = n$ BLA=r1-r2

(c)

$N = 2n$ BLA=(r1+r1')/2-(r2+r2')/2

(d)

$N = 3n - 1$ BLA=(r1+r1'+r1'')/3-(r2+r2'+r2'')/3

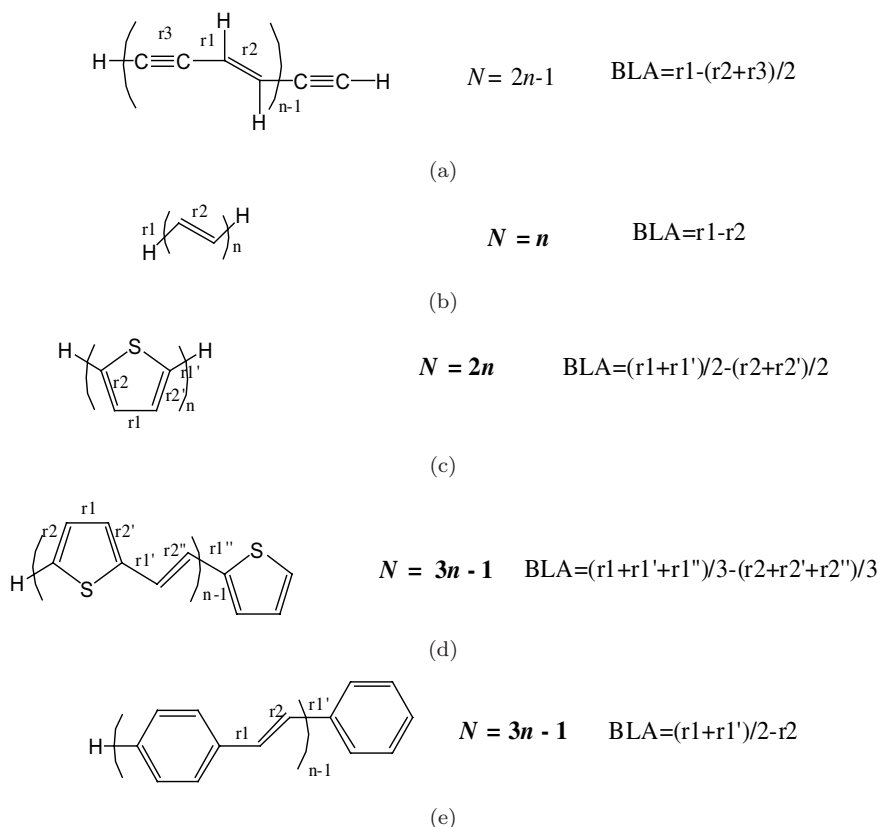(e)

$N = 3n - 1$ BLA=(r1+r1')/2-r2

Fig. 1. Chemical structures of conjugated polymers: (a) polydiacetylene (PDA); (b) *trans*-polyacetylene (PA); (c) polythiophene (PT); (d) poly(2,5-thienylenevinylene) (PTV); (e) poly(*p*-phenylenevinylene) (PPV). N is the number of double bonds along the shortest path connecting the terminal carbon atoms of the molecular backbone. Bond length alternation (BLA) is the difference between the average over the various long and short carbon–carbon bonds along the conjugated polymer chain in the unit cell.

conformations that are imposed by π-delocalization and crystal packing in the films. We performed TDDFT to calculate E_b for PDA, PA, PT, PTV, and PPV, as extrapolated from oligomers with increasing chain lengths. Commonly used functionals, including pure local spin density approximation (LSDA), generalized gradient approximation (GGA, such as BLYP, BP86, BPBE, PBEPBE,BPW91), meta-GGA (such as PBEKCIS), hybrid density functionals (H-GGA, such as O3LYP, B3LYP, B972, PBE1PBE, BHandH, which contain 11.61%, 20%, 21%, 25%, and 50% HF exchange, respectively) and hybrid-meta GGA (B1B95 which contain 25% HF exchange) with the 6-31G* basis set have been used to look at the influence on the results.

3. Results and Discussion

3.1. *DFT functionals' influence on the exciton binding energy of PDA*

As stated above, PDA is the experimentally best-characterized polymeric system for E_b. In the theory part, to predict the exciton binding energies of conjugated polymers accurately, we firstly investigate the influence of exchange-correlation functionals on E_b of PDA. We performed TDDFT calculations on the PDA oligomers with LSDA, GGA (BLYP, BP86, BPBE, PBEPBE, BPW91), meta-GGA (TPSS, PBEKCIS, TPSSKCIS), H-GGA (O3LYP, B3LYP, B972, PBE1PBE, BHandH), and hybrid-meta GGA (B1B95) functionals on the basis of DFT-optimized ground-state geometries with the corresponding functionals.

To obtain E_b of PDA polymer, we firstly fit the evolution of the HOMO–LUMO gap and the $1B_u$ transition energy with the chain length using the empirical expression proposed by Kuhn.[19] And then E_b of the PDA polymer is obtained as the difference between the extrapolated value of HOMO–LUMO gap and the extrapolated value of $1B_u$ excitation energy at the limit of infinite length. The corresponding results calculated at the level of different functionals are shown in Table 1.

Bond length alternation (BLA), is defined as the difference between the average over the various long and short carbon–carbon bonds along the conjugated polymer chain in the unit cell, which plays an important role in interpreting the electronic structures of conjugated molecules.[20,21] The calculation of BLA values for PDA, PA, PT, PTV, and PPV oligomers are shown in Fig. 1. The HOMO–LUMO gap is approximately in linear relationship with the BLA at HF or various DFT levels.[20,21]

From Table 1, we find that the HF method has the largest BLA, while pure DFT theory (LDA, GGA, and M-GGA) has the smallest BLA in the range of 0.07–0.08 Å. Hybrid DFT calculated BLA is within 0.09–0.13 Å, which gives the closest values with the experiment results (0.13–0.17 Å).[22] With the increase of the amount of HF exchange, the BLA value also increases.

The evolution of HOMO–LUMO gap is the same as that of BLA. HF method predicts the HOMO–LUMO gap to be 8.01 eV, which is unreasonably larger than the experimental value (~ 2.4 eV).[23] This large error is partly ascribed to the

Table 1. Extrapolated HOMO–LUMO gap, and optical gap ($1B_u$ state) energies for PDA polymer using Kuhn fit expression with different functionals in unit of eV, and extrapolated BLA values using linear fits. Calculated E_b, of PDA polymer is the difference of extrapolated value of HOMO–LUMO gap and optical gap.

Polymer	Theory		χ[a]	BLA (Å)	HOMO–LUMO gap	Optical gap	E_b
$(PDA)_\infty$	HF		100	0.168	8.01	3.50	4.51
	LDA	LSDA	0	0.069	0.50	0.56	−0.06
	GGA	BLYP	0	0.080	0.60	0.62	−0.02
		BP86	0	0.077	0.57	0.61	−0.04
		BPBE	0	0.077	0.58	0.62	−0.04
		PBEPBE	0	0.076	0.57	0.61	−0.04
		BPW91	0	0.077	0.58	0.62	−0.04
	M-GGA	PBEKCIS	0	0.078	0.59	0.63	−0.04
	H-GGA	O3LYP	11.61	0.090	1.16	1.07	0.09
		B3LYP	20	0.105	1.72	1.44	0.28
		B972	21	0.105	1.79	1.48	0.31
		PBE1PBE	25	0.107	2.00	1.59	0.41
		BHandH	50	0.125	3.71	2.34	1.37
	HM-GGA	B1B95	25	0.110	2.18	1.68	0.50
	Expt.			0.13–0.17 [b]	2.4[c]	2.0[d]	0.5[e]

[a]χ, percentage of HF exchange in the functional; [b]Ref. 22; [c]Ref. 23; [d]Refs. 24, 25; [e]Ref. 4.

neglect of electron correlation. However, LDA and pure DFT theory (GGA and M-GGA), including exchange and correlation terms, estimate the HOMO–LUMO gap to be 0.5–0.6 eV, which is also unreasonably smaller compared with the experiment (~ 2.4 eV). The hybrid DFT functionals, B3LYP, B972, PBE1PBE, and B1B95, including 20%–25% HF exchange provide the most reasonable result (1.7–2.2 eV), although it is slightly smaller than the experiment.

For optical gap of $1B_u$ state of PDA polymer, HF overestimates it while LDA and pure DFT underestimate it compared with the experiment (~ 2.0 eV).[24,25] The hybrid B3LYP, B972, PBE1PBE, and B1B95 functionals calculated optical gaps are a bit smaller (1.4–1.7 eV) than the experiment, while BHandH calculated value (2.3 eV) is overestimated than the experiment.

For E_b of PDA polymer, the HF value is too large due to the large overestimation of the HOMO–LUMO gap since no electron correlation correction is included in the calculation; however, LDA and pure DFT yield negative E_b which is ascribed to the calculated degree of BLA and HOMO–LUMO gap too small. Only by mixing HF exchange with local and gradient-corrected (nonlocal) exchange-correlation functionals of DFT, hybrid DFT methods give much better results (positive E_b). O3LYP functional, including 11.6% amount of HF exchange, estimates the value of E_b of PDA to be 0.09 eV, which is too small than the experimental value (0.5 eV).[4] With the increase in the amount of HF exchange, the calculated E_b becomes larger. BHandH functional (including 50% amount of HF exchange) calculated E_b of PDA (1.37 eV) is substantially overestimated compared with the experiment. The B3LYP, B972, PBE1PBE, and B1B95 functionals with 20%–25% amount of

exact HF exchange predict E_b of PDA polymer within 0.3–0.5 eV, which provide
the most reasonable results with the experimental value. So, in the following inves-
tigation, we will use B3LYP, B972, PBE1PBE, and B1B95 four-hybrid functionals
to study E_b of the PA, PT, PTV, and PPV conjugated polymers.

3.2. *Exciton binding energies of PA, PT, PTV, and PPV polymers*

We use B3LYP, B972, PBE1PBE, and B1B95 four-hybrid functionals to study E_b
of PA, PT, PTV, and PPV four-conjugated polymers. In this paper, we only list
the results of BLA values, HOMO–LUMO gaps, and optical gaps at the level of
commonly used B3LYP functional.

Tables 2–5 list the BLA values, HOMO–LUMO gaps, and optical gaps of PA,
PT, PTV, and PPV oligomers calculated by TDDFT/B3LYP/6-31G* method.
(i) With the increase in chain length, the calculated BLA values decrease in $1/N$ lin-
ear approximation (see Fig. 2). With the heteroatom, PT and PTV have the smaller
BLA compared with PA and PPV. Therefore, PT and PTV have more delocalized
π-electrons. (ii) We note that PTV oligomers have smaller HOMO–LUMO gaps in
comparison with PT and PPV oligomers with comparable chain lengths. This is in
good agreement with the experimental results that PTV and its oligomers exhibit
lower oxidation potentials and smaller band gaps in comparison to oligothiophenes
and oligo(p-phenylene–vinylene) with comparable chain lengths.[7] (iii) We also find
that for small oligomers ($(PA)_2$, $(PA)_3$, $(PTV)_2$, $(PT)_2$ and $(PPV)_2$), the calculated

Table 2. BLA value, HOMO–LUMO gap, and optical gap ($1B_u$ state) energies for PA
oligomer and polymer (TDDFT/B3LYP/6-31G*) in unit of eV.

Compound	BLA(Å)	HOMO–LUMO gap	Optical gap	
			Cal.	Expt.
$(PA)_2$	0.1168	5.62	6.04	6.25[a], 5.92[b]
$(PA)_3$	0.1038	4.49	4.87	4.93[c], 4.95[d], 5.13[d]
$(PA)_4$	0.0955	3.79	4.14	4.41[e]
$(PA)_5$	0.0897	3.32	3.63	3.98[f]
$(PA)_6$	0.0853	2.98	3.25	3.65[f]
$(PA)_7$	0.0818	2.72	2.96	
$\vdots$				
$(PA)_{21}$	0.0646	1.59	1.54	
$(PA)_{22}$	0.0642	1.56	1.50	
$(PA)_{23}$	0.0638	1.54	1.47	
$(PA)_{24}$	0.0634	1.52	1.44	
$(PA)_{25}$	0.0631	1.50	1.41	
$(PA)_\infty$ (Kuhn fit)		1.34	1.19	
$(PA)_\infty$ (Linear fit)	0.0553	1.02	0.85	
Expt.	0.07–0.09[g]			1.5–1.8[g]

[a]Ref. 26; [b]Refs. 27–31; [c]Ref. 32; [d]Ref. 33; [e]Ref. 34; [f]Ref. 35; [g]Ref. 36.

Table 3. BLA value, HOMO–LUMO gap, and optical gap ($1B_u$ state) energies for PT oligomer and polymer (TDDFT/B3LYP/6-31G*) in unit of eV.

Compound	BLA(Å)	HOMO–LUMO gap	Optical gap	
			Cal.	Expt.
$(PT)_2$	0.0597	4.22	4.03	4.05[a]
$(PT)_3$	0.0557	3.45	3.27	3.49[a]
$(PT)_4$	0.0521	3.03	2.84	3.16[a]
$(PT)_5$	0.0510	2.78	2.57	2.99[a]
$(PT)_6$	0.0498	2.61	2.38	2.85[a]
$(PT)_7$	0.0490	2.50	2.25	
$(PT)_8$	0.0477	2.41	2.14	
$(PT)_9$	0.0472	2.35	2.07	
$(PT)_{10}$	0.0474	2.31	2.01	
$(PT)_\infty$ (Kuhn fit)		2.13	1.82	
$(PT)_\infty$ (Linear fit)	0.0436	1.80	1.47	
Expt.				2.0[b]

[a]Ref. 37; [b]Ref. 38.

Table 4. BLA value, HOMO–LUMO gap, and optical gap ($1B_u$ state) energies for PTV oligomer and polymer (TDDFT/B3LYP/6-31G*) in unit of eV.

| Compound	BLA(Å)	HOMO–LUMO gap	Optical gap	
			Cal.	Expt.
$(PTV)_2$	0.0631	3.63	3.57	3.45[a]
$(PTV)_3$	0.0583	2.84	2.76	2.85[a]
$(PTV)_4$	0.0556	2.45	2.34	2.56[a]
$(PTV)_5$	0.0541	2.24	2.09	
$(PTV)_6$	0.0523	2.11	1.92	2.29[a]
$(PTV)_7$	0.0522	2.02	1.81	
$(PTV)_8$	0.0516	1.95	1.72	2.18[a]
$(PTV)_9$	0.0513	1.91	1.66	
$(PTV)_{10}$	0.0510	1.87	1.61	
$(PTV)_\infty$ (Kuhn fit)		1.76	1.48	
$(PTV)_\infty$ (Linear fit)	0.0481	1.49	1.17	
Expt.				1.80[b]

[a]Ref. 39; [b]Ref. 40.

excitation energies are in good agreement with the experimental values with the difference being less than 0.2 eV. However, for large oligomers, the transition energies tend to be underestimated by the TDDFT method, and the deviations with respect to the experimental data become larger with the chain length increasing. This can be partially ascribed to the overestimation of long-range electron correlation effects in the TDDFT method.[43] On the other hand, it should be noted that our theoretical calculations were performed on the fully coplanar geometries, whereas most spectroscopic measurements were carried out in solutions. The solvent effects can induce a twist between the oligomer rings and then make the excitation energy increased. For example, both theory and experiment have shown that the

Table 5. BLA value, HOMO–LUMO gap, and optical gap ($1B_u$ state) energies for PPV oligomer and polymer (TDDFT/B3LYP/6-31G*) in unit of eV.

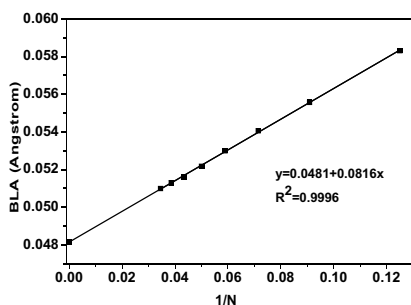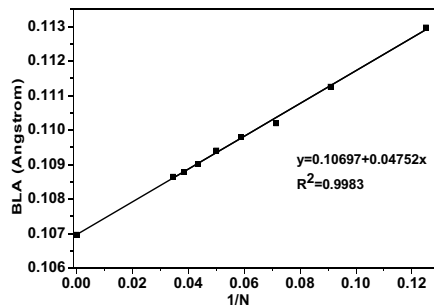| Compound	BLA(Å)	HOMO–LUMO gap	Optical gap	
			Cal.	Expt.
$(PPV)_2$	0.1175	4.15	4.01	4.01[a]
$(PPV)_3$	0.1130	3.39	3.21	3.44[a]
$(PPV)_4$	0.1113	3.05	2.82	3.20[a]
$(PPV)_5$	0.1102	2.86	2.60	3.08[a]
$(PPV)_6$	0.1098	2.75	2.46	3.01[a]
$(PPV)_7$	0.1094	2.67	2.37	2.97[a]
$(PPV)_8$	0.1090	2.62	2.31	4.01[a]
$(PPV)_9$	0.1088	2.59	2.27	4.01[a]
$(PPV)_{10}$	0.1087	2.56	2.23	
$(PPV)_\infty$ (Kuhn fit)		2.47	2.12	
$(PPV)_\infty$ (Linear fit)	0.1067	2.22	1.84	
Expt.				2.45[b]

[a]Ref. 41; [b]Ref. 42.
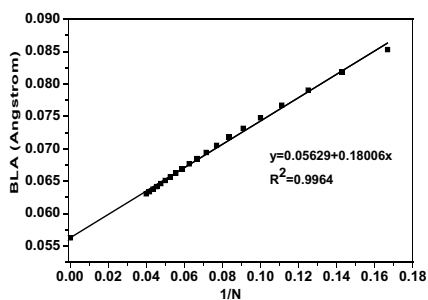
(a) PA
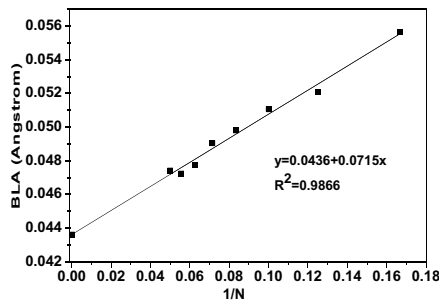
(b) PT

(c) PTV

(d) PPV

Fig. 2. BLA values calculated at the B3LYP/6-31G* level as a function of 1/N for PA (a), PT (b), PTV (c) and PPV (d) units respectively. The solid lines are linear fits by considering N ≥ 6 for PA and N ≥ 3 for PT, PTV, and PPV.
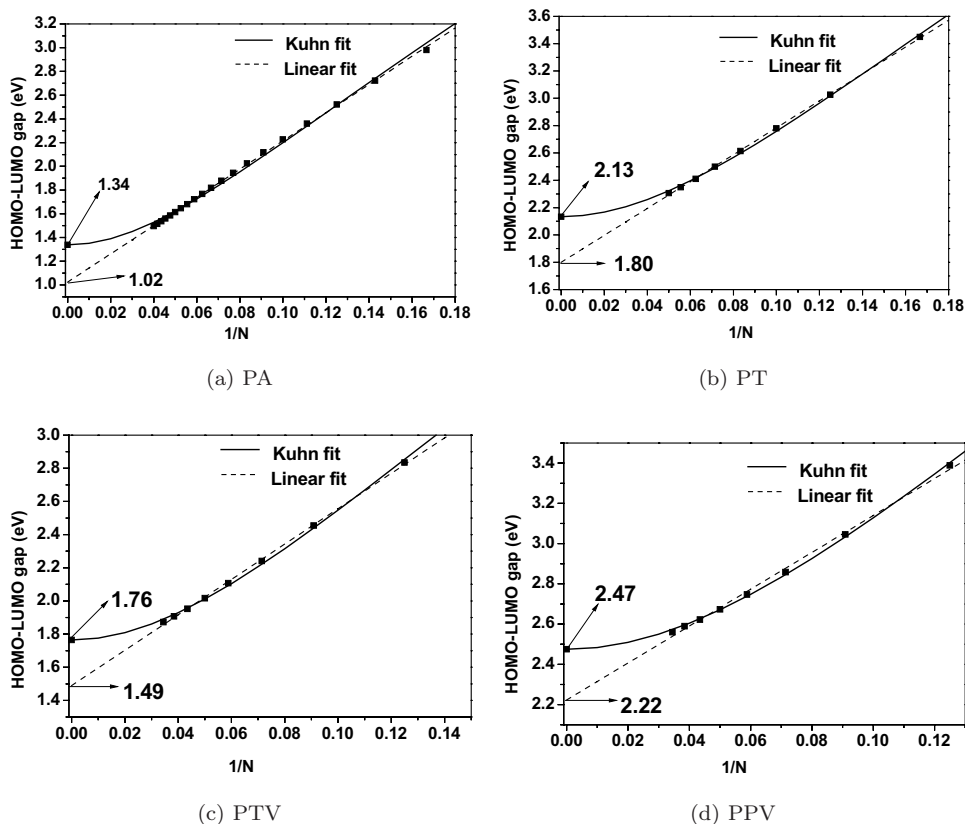
Fig. 3. LUMO–HOMO gap calculated at the TDDFT/B3LYP/6-31G* level as a function of $1/N$ for PA (a), PT (b), PTV (c) and PPV (d) units, respectively. The solid lines are Kuhn fits. The dashed lines are linear fits. Kuhn fits are drawn by considering $N \geq 6$ for PA and $N \geq 3$ for PT, PTV, and PPV.

PT oligomers are not planar but subject to a strong rotational disorder.[44] However, in solid state, the ring torsions can often be suppressed. Thus, our strategy to fix the planar structure is more relevant for the materials in electronic devices.

We plot the HOMO–LUMO gap and the $1B_u$ transition energy as a function of $1/N$ in Figs. 3 and 4, where N is the number of double bonds along the shortest path connecting the terminal carbon atoms of the molecular backbone (Fig. 1). We fit the evolution of the HOMO–LUMO gap and the $1B_u$ transition energy with $1/N$ using the Kuhn fit; the extrapolated $1B_u$ excitation energies for PA, PT, PTV, and PPV polymer are obtained as 1.19 eV, 1.82 eV, 1.48 eV and 2.12 eV, respectively; the experimental values are 1.5–1.80 eV,[36] 2.0 eV,[38] 1.80 eV,[40] and 2.45 eV[42] for PA, PT, PTV, and PPV polymers, respectively. Our results are underestimated by *ca.* 0.3 eV compared with the experimental values. For the sake of comparison, we also show the linear fits in Figs. 3 and 4 as dashed lines. We find that the extrapolated
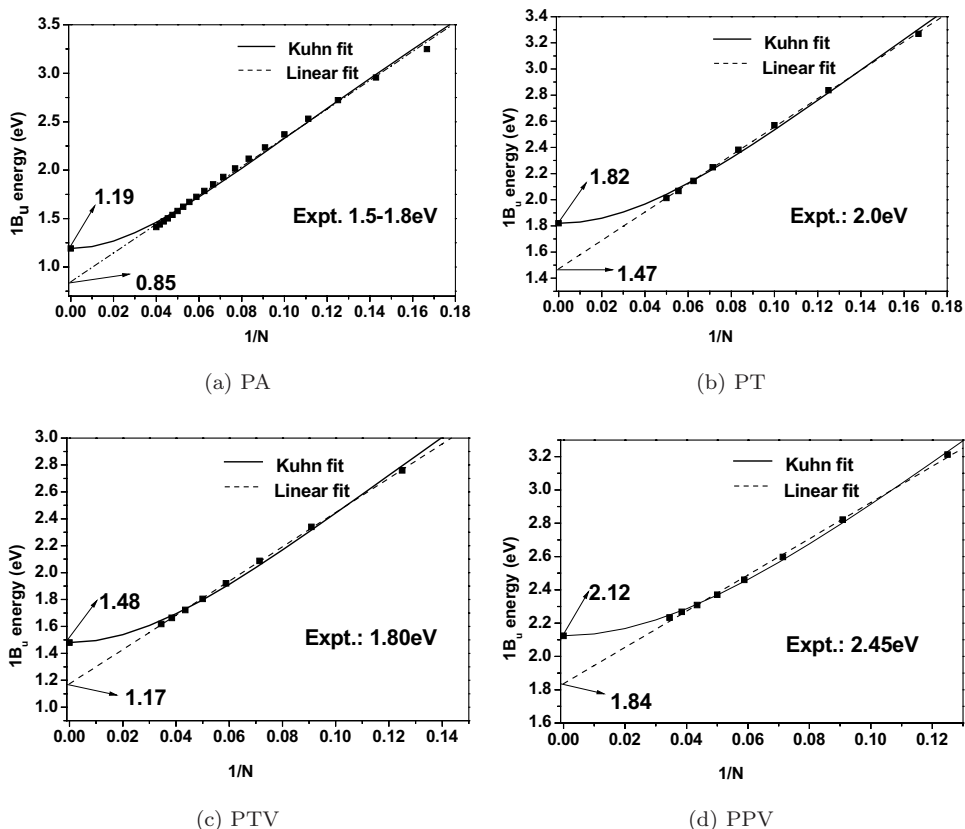
Fig. 4. $1B_u$ excitation energy calculated at the TDDFT/B3LYP/6-31G* level as a function of $1/N$ for PA (a), PT (b), PTV(c) and PPV(d) units, respectively. The solid lines are Kuhn fits. The dashed lines are linear fits. Kuhn fits are drawn by considering $N \geq 6$ for PA and $N \geq 3$ for PT, PTV, and PPV.

HOMO–LUMO gap and $1B_u$ excitation energies of the polymers from the linear fits are obviously smaller than those from the Kuhn fits. The extrapolated $1B_u$ excitation energies of the polymers from the linear fits are far away from the measured value for these four polymers, which are underestimated by *ca*. 0.6 eV. Thus, the convergence of $1B_u$ excitation energies cannot be represented by a linear function; it has to be described with a Kuhn function as mentioned above.[45] However, in terms of E_b of polymers, their differences between linear fits and Kuhn fits are minor, due to the cancellation.

In Table 6, we list the calculated results for E_b of four conjugated polymers using B3LYP, B972, PBE1PBE, and B1B95 DFT functionals. The E_b obtained from four functionals are in the range of 0.1–0.6 eV. From Fig. 5 we find that with the increase of BLA, E_b firstly decrease and then increase. The E_b of these four polymers with different functionals are all in the order of PA < PTV < PT < PPV.

Table 6. Calculated and experimental exciton binding
energies (in eV) for PA, PT, PTV, and PPV conju-
gated polymers at the level of different functionals.

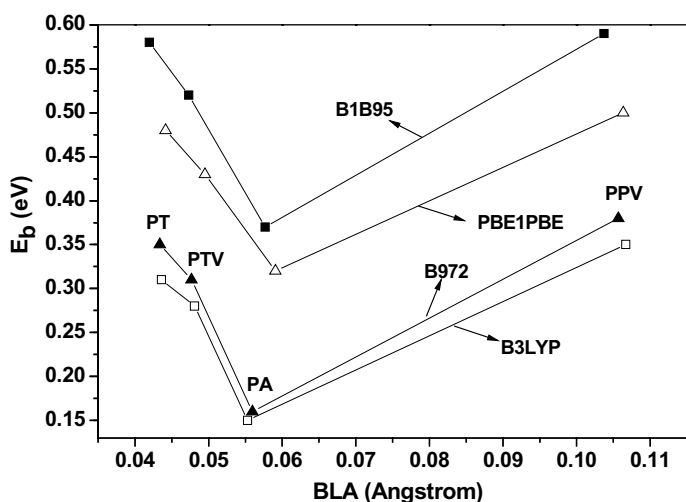| Theory	PA	PT	PTV	PPV
B3LYP	0.15	0.31	0.28	0.35
B972	0.16	0.35	0.31	0.38
PBE1PBE	0.32	0.48	0.43	0.50
B1B95	0.37	0.58	0.52	0.59
Expt.	0.1[a]			0.2–0.45[b]

[a]Ref. 46; [b]Ref. 47.

Fig. 5. Evolution of E_b of PA, PT, PTV, and PPV conjugated polymers at the level of B3LYP, B972, PBE1PBE, and B1B95 functionals with the BLA values.

B3LYP and B972 functionals which include about 20% HF exchange show better performance for the evaluation of E_b for conjugated polymers. The calculated E_b for PA polymer is about 0.2 eV. Our results support the experimental findings that E_b in PA are *ca.* 0.1 eV.[46] PBE1PBE- and B1B95-functionals-calculated E_b for PA are 0.32 eV and 0.37 eV, respectively, which are a bit overestimated than the experimental results. B3LYP and B972 functionals estimated E_b of PPV is *ca.* 0.4 eV, which is consistent with the experimental results in the weak-to-intermediate range (0.2–0.45 eV).[47] PBE1PBE and B1B95 functionals calculated results are also overestimated than the experimental values. For PT and PTV polymers, B3LYP and B972 functionals estimated E_b are *ca.* 0.35 eV and 0.30 eV, respectively, which are smaller than that of PPV. PTV has smaller E_b value due to the smaller HOMO–LUMO gap than PT and PPV vide supra. Although the smaller E_b of PTV can be expected to improve the efficiency of photovoltaic devices, it cannot be widely

used as the materials for organic solar cells in comparison with PT.[48–50] However, the pthotovoltaic properties of PTV can be improved by the modulation of its molecular structures.[51]

We note that there are small differences for exciton binding energies of polymers between our calculations and the experiments, because our calculations are for the isolated polymer chains, whereas the experimental E_b are measured in the solid state, solid-state; effects (like dielectric screening effects) have been neglected in the calculations.[13]

4. Conclusions

To summarize, we have investigated E_b of PDA, PA, PT, PTV, and PPV using TDDFT method. Commonly used functionals, including LSDA, GGA (BLYP, BP86, BPBE, PBEPBE, BPW91), meta-GGA (PBEKCIS), hybrid GGA (O3LYP, B3LYP, B972, PBE1PBE, and BHandH, which contain 11.61%, 20%, 21%, 25%, and 50% HF exchange, respectively) and hybrid M-GGA (B1B95 which contain 25% HF exchange) have been used to compare with.

The B3LYP, B972, PBE1PBE, and B1B95 functionals with 20%–25% amount of exact HF exchange predict E_b of PDA polymer within 0.3–0.5 eV, which provide the most reasonable results with the experiment value of 0.5 eV.

For PA, PT, PTV, and PPV conjugated polymers, the E_b obtained from B3LYP, B972, PBE1PBE, and B1B95 functionals are in the range of 0.1–0.6 eV and in the order of PA < PTV < PT < PPV. B3LYP and B972 functionals which include about 20% HF exchange can give the most reasonable results when compared with the experimental values.

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