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Substituent Effect on Hole Mobility of Conjugated Polymers in Photovoltaic Cells

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In this work, we have theoretically investigated the substituent effect on hole mobility of the conjugated alternating polymers typically applied in photovoltaic cells. We found that both linear and nonlinear behaviour of binding energy of polarons with respect to their extension size in two series of polymers. The resistances in the process of polaron's jumping between polymer chains are thus different. The experimental relative hole mobility of two kinds of polymers are well explained. Analysis of substituent effect provides insight into obtaining better hole-transport conjugated polymers in future.

Key Words: Substituent effect, Hole mobility, Binding energy, Photovoltaic cells.

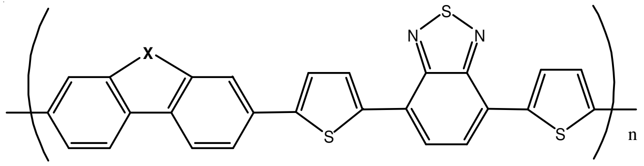
INTRODUCTION

Application of organic semiconductors such as conjugated polymers in photovoltaic cells[1] has extensively broaden the perspective of making use of the solar energy during the past few years[2-6]. A key feature of the conjugated polymer lies in the flexibility of modifying it with soluble side chains, which makes the fabrication of solar cells much easier than that of the inorganic silicon-based materials[7,8]. With new type of conjugated polymers, the ability of wider optical absorption, better charge separation and transport and higher power conversion efficiency in solar cells have been greatly enhanced[9,10]. However, understanding the critical process of power conversion in solar cells remains a great challenge and thus has fundamental significance in developing new photoelectric conversion materials.

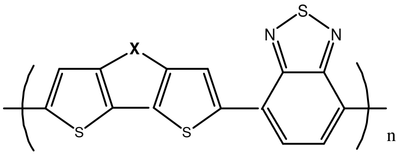
Probing the interplay between mobile charge and the corresponding deformation in the backbone of conjugated polymers is one of the most attracting aspects in the charge transport process. After the separation of the spatially localized electron-hole pairs, or excitons, into free electrons and holes at the bulk hetero-junction (BHJ)[11-14] interface between an electron-donor (D) and an electron-acceptor (A) conjugated material, both the intra-chain and inter-chain charge transport are then controlled by the intrinsic properties of conjugated polymers. For example, the side chains with strong D-A electronic groups are unfavourable to the passing of charge through the polymer chain. Moreover, the rigidity of conjugated polymers can play important role in affecting the charge mobility. In general, conjugated polymers with better rigidity are considered to have larger charge mobility[15].

In the past decade, the hole transport polymers, such as poly[2-methoxy-5-(3,7-dimethyl-octyloxy)-1,4-*p*-phenylene-vinylene] (MDMO-PPV)[16-18], poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV)[19,20] and region-regular poly(3-hexylthiophene) (P_3HT)[19,21] have been extensively investigated. The utilization of these polymeric materials in photovoltaic cells has got the power conversion efficiency between 3.0 and 5.0 % when they are mixed with [6,6]-phenyl C61 butyric acid methyl ester (PCBM). However, the performances of these polymers are somehow limited by their relatively large band gaps[22,23]. A new benzothiadiazole (BT)-containing polycarbazole derivative, [N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4,7'-di-2-thienyl-2',1'3'-benzothiadiazole)] PCDTBT[24], has been presented to show high solubility and a good power conversion efficiency (3.6 %) as well. The structures of two series of BT-containing alternating polymers, P1 series (the polymers P1, P2 and P3 with different functional groups: 2,7-fluorene, 2,7-carbazole and 2,7-dibenxosilole) and P4 series (P4, P5 and P6, with 4H-cyclopenta[2,1-b;3,4-]dithiophene, 4H-dithieno[3,2-b;2',3'-

d]pyrrole, 4H-3,4-dithia-7-sila-cyclopenta[a]pentalene) are shown in Fig. 1. The latter series has a simple D-A resonant structure[25]. In P1 series, the field effect transistor (FET) hole mobility[26] of P2 and P3 reaches ~1 × 10^{-3} $cm^2V^{-1}s^{-1}$. In P4 series, P4 shows a hole mobility[25] as high as 2 × 10^{-2} $cm^2V^{-1}s^{-1}$. And the dithienosilole-BT alternating polymer, P6, also has a relatively high field effect transistor hole mobility[25] of 3 × 10^{-3} $cm^2V^{-1}s^{-1}$.



P1: X=C P2: X=N P3: X=Si n=3



P4: X=C P5: X=N P6: X=Si n=5

Fig. 1. Structures of the studied systems. For P1 series (P1, P2 and P3) repeated units n is set to be 3, while for P4 series (P4, P5 and P6) n is set to be 5, the aim of which is to keep the same number of the carbon atoms along the chain for both series

In this work, we theoretically investigated the charge-induced deformation on the polymer backbone and the self-trap of charge by this kind of deformation. The substituent effect (C, N, Si as bridging atoms) on charge mobility was investigated *via* the polaron's binding energy with respect to the extension size of deformation. Based on this investigation, we successfully explained the difference of charge mobility between P1 and P4 series of hole conducting materials.

COMPUTATIONAL METHODOLOGY

Geometries and electronic properties of all these oligomers were obtained by means of hybrid density functional B_3LYP with the basis set of 6-31G* in Gaussion 03 package[27]. Geometrical optimization for the neutral oligomer was carried out first. Then we added positive charges on the optimized neutral oligomer chain and performed optimization further. In this process, from one ring to six rings at two sides of oligomers were gradually fixed to simulate the size of polarons[28]. In the condensed phase it is difficult for the chain to stretch and thus the intra-chain relaxation is supposed to be the main way in forming the polarons. The reason why we investigated the cases with different restrictions is due to the fact that the polaron will not always maintain the same shape in polymers. Different pieces of the polymer can have different surrounding environment, which may make the relaxation of atoms very different to the case of a free polymer chain. Moreover, in the inter-chain hopping process, the polaron will inevitably decrease its shape until its final jumping to another polymer chain.

Polaron's binding energy was obtained from the energy difference between the total energy of charged polymers without relaxation and that of charged polymers after relaxation.

Due to the fact that the injected charge can give rise to deformation that spans several units of polymer, we therefore used the oligomer of P1 series with n = 3 and P4 series with n = 5 (the number of total carbon atoms along the conjugated chain of both P1 and P4 is the same as 60 carbon atoms) as the protype in researching the properties of polarons. In this work, we replaced the alkyl side chains with H atoms to reduce the computational cost. Moreover, it should be mentioned that for doubly charged oligomers the singlet state and triplet state are nearly degenerated.

RESULTS AND DISCUSSION

Energy gap of polymers: The calculation of energy gaps of polymers is often performed with two methods, namely, the periodic boundary condition calculation approach[29,30] and the oligomer extrapolation approach[28,31,32]. The second method was employed in this work. Strictly, the oligomer extrapolation of energy gap of polymer should be based on the time-dependent calculation of excitation energy. However, the extrapolation based on the HOMO-LUMO gap is also practical due to the fact that the HOMO-LUMO gap is the first order approximation of the excitation energy of oligomer. This approximation is based on the consideration that the excitation configuration from HOMO to LUMO dominantly contributes to the whole excitation configuration of the first excited state. Fig. 2 shows the HOMO-LUMO gaps of the series of oligomers from P1 to P6 as the function of 1/n, the inverse of number of repeating units (from 1 to 5). We can find that the good linear relationship between HOMO-LUMO gaps and 1/n exists in all of these structures and we can extrapolate the final energy gap of these polymers. In Table-1, we can see that the extrapolated energy gaps are in good agreement with the experiments (the errors between the calculations and experiments are less than 0.2 eV).

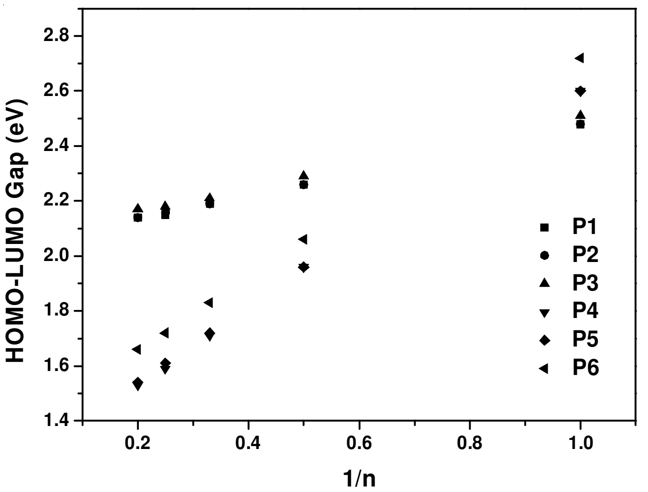


Fig. 2. HOMO-LUMO gaps of P1, P2, P3, P4, P5 and P6 as a function of 1/n, where n is the number of repeating units along the polymer chain

However, on the other hand, one can also find that the extrapolated HOMOs and LUMOs have much larger deviation from experiments. This is due to the limitation of the current approximate exchange-correlation potential in the asymptotical region[33,34]. Therefore the relative good computational HOMO-LUMO gaps are to some extent due to the cancellation of error in HOMO and LUMO energy levels.

TABLE-1
HOMO, LUMO AND HOMO-LUMO GAPS OF OLIGOMERS P1-P6 (UNIT OF eV)

Oligomer	HOMO	Exptl[a]	LUMO	Exptl[a]	Δ_{H-L}	Exptl[a]
P1						
n=1	-5.09		-2.61		2.48	
n=2	-4.93		-2.67		2.26	
n=3	-4.89		-2.71		2.18	
n=4	-4.88		-2.72		2.16	
n=5	-4.87		-2.73		2.14	
Eg(n=∞)	-4.80		-2.75		2.05	
P2						
n=1	-5.07		-2.59		2.48	
n=2	-4.91		-2.65		2.26	
n=3	-4.87		-2.68		2.19	
n=4	-4.86		-2.70		2.16	
n=5	-4.84		-2.70		2.14	
Eg(n=∞)	-4.77	-5.50	-2.72	-3.60	2.05	1.88
P3						
n=1	-5.16		-2.64		2.52	
n=2	-5.01		-2.73		2.28	
n=3	-4.98		-2.77		2.21	
n=4	-4.96		-2.78		2.18	
n=5	-4.96		-2.79		2.17	
Eg(n=∞)	-4.90	-5.70	-2.83	-3.81	2.07	1.85
P4						
n=1	-5.05		-2.45		2.60	
n=2	-4.68		-2.72		1.96	
n=3	-4.55		-2.84		1.71	
n=4	-4.49		-2.90		1.59	
n=5	-4.46		-2.94		1.52	
Eg(n=∞)	-4.30	-5.30	-3.04	-3.57	1.26	1.40
P5						
n=1	-5.00		-2.40		2.60	
n=2	-4.63		-2.67		1.96	
n=3	-4.51		-2.78		1.73	
n=4	-4.45		-2.84		1.61	
n=5	-4.42		-2.87		1.55	
Eg(n=∞)	-4.27		-2.98		1.29	
P6						
n=1	-5.26		-2.54		2.72	
n=2	-4.89		-2.83		2.06	
n=3	-4.78		-2.95		1.83	
n=4	-4.73		-3.01		1.72	
n=5	-4.70		-3.04		1.66	
Eg(n=∞)	-4.55	-5.05	-3.16	-3.27	1.39	1.45

[a]Reference[26]

Geometrical shapes of polarons: The shapes of polarons reflect the deviation of nuclei from their equilibrium positions due to the charge added on the polymer chain. From the view point of non-local interaction between charge and the nuclei, one only takes account of the coupling between them and neglects the deformation of the polymer backbone[35]. While in the present work, we explicitly researched the local-interaction between charge and the polymer backbone, involving the self-trap of charge by the deformation of the chain.

The geometry of polarons reflects, in part, the rigidity of different parts in the conjugated carbon chain of polymer. A perfectly rigid chain will never change its geometry and therefore will never have the polaron effect.

According to our calculations, we found that P1, P2 and P3 have the similar geometries of polarons and so do for P4, P5 and P6. Thus in Fig. 3 we only displayed the geometries of polarons of P1 and P4 with one positive charge and two positive charges. The carbon chain was divided into three parts with the central part containing one unit in P1 and about two units in P4. From top to bottom in Fig. 3a to 3d the carbon chains were allowed to relax with less and less regions restricted at two ends. The averaged deformation in the central region (between two vertical lines) of singly charged oligomer is not significantly different from other parts; in contrast, the deformation in the central region of doubly charged oligomer is much smaller than that in the two sides. It reflects that the delocalization of the one positive charge and the localization of two positive charges in two sides. In the doubly charged case, the two positive charges are separated with each other due to the electrostatic repulsion in between.

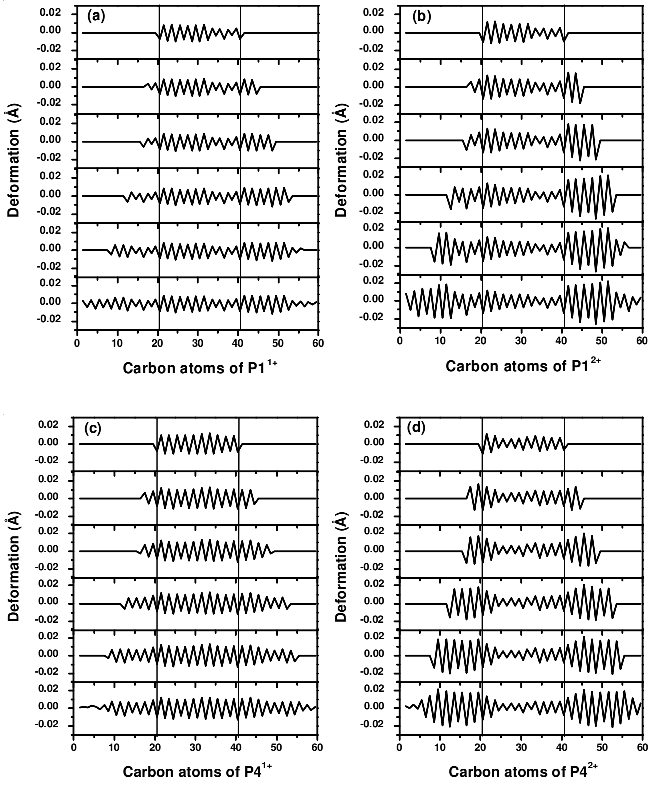


Fig. 3. Deformation of carbon backbone for P1 with (a) one charge, (b) two charges and for P4 with (c) one charge, (d) two charges

There is an apparent invariance in the structure of the central part from bottom to top in Fig. 3. This invariance seems to be quite contradicted to the intuition that when the allowed relaxation region becomes smaller its deformation should be much larger. A reasonable explanation of this phenomenon is that the added charge is still distributed on the whole chain, instead of a small region.

A simple statistical analysis of the averaged deformation is shown in Fig. 4. In both singly and doubly charged cases, for P1 series the averaged deformation curves (Fig. 4a) nearly overlap with each other, while for P4 series (in Fig. 4b) they apparently separate with each other. This behaviour has the counterpart in the binding energy, which will be discussed below.

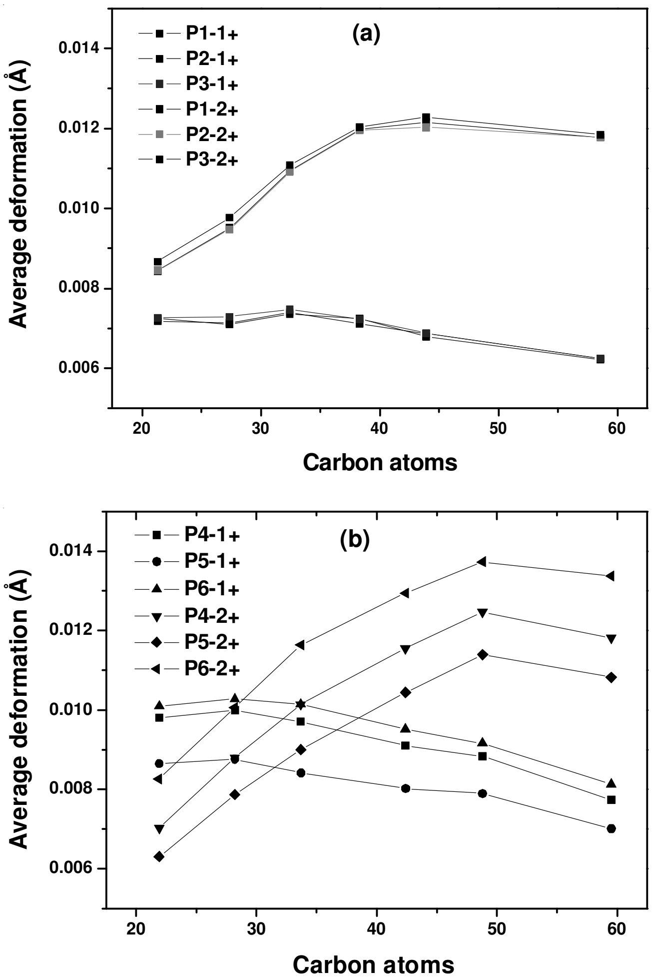


Fig. 4. Average deformation of carbon backbone for (a) P1 series and (b) P4 series, after the injection of one or two positive charges into the oligomer chains

Substituent effect on charge transport: In this work, we mainly considered the transport of hole jumping between chains. Specially, we focused our discussion on the binding energy of polaron and bipolaron. The aim of the analysis of binding energies is to investigate the process in which a polaron or bipolaron gradually escapes from one polymer chain. When a polaron or bipolaron tries to jump away, the deformation on the polymer backbone will gradually decrease and the binding energy will become smaller as well. From the change of binding energy one can also obtain the information of the resistance in the process of their escaping.

Fig. 5 showed that the binding energy of polaron and bipolaron formed in both P1 and P4 series with one and two positive charges. The binding energy of P1 series, as shown in Fig. 5a, has a nonlinear behaviour. The length of allowed relaxation region of about 35 carbon atoms is the inflection point of the curves. In the left of this point the curve is concave and in the right convex. Although the singly charged P1 series have the same behaviour, the order of magnitude of which is much smaller than the doubly charged oligomers. Binding energy of P4 series (Fig. 5b), has an approximately linear behaviour. The slope of changing curves for the singly charged oligomers is smaller than that for the doubly charged oligomers. In the following discussion, we will focus on the change of binding energy for doubly charged P1 and P4 series. The binding energy curve of P1 series indicates that the bipolaron needs to overcome an increased resistance around the inflection point when it tries to jump out of the chain. While for the linear changing behaviour of binding energy in P4 series, the bipolaron only needs to overcome a constant resistance in its escaping process. One can thus realize that the transport of positive charges between chains of P1 series is much more difficult than that of P4 series. And thus the fact that the hole mobility of P4 series is much larger than that of P1 series can be well explained.

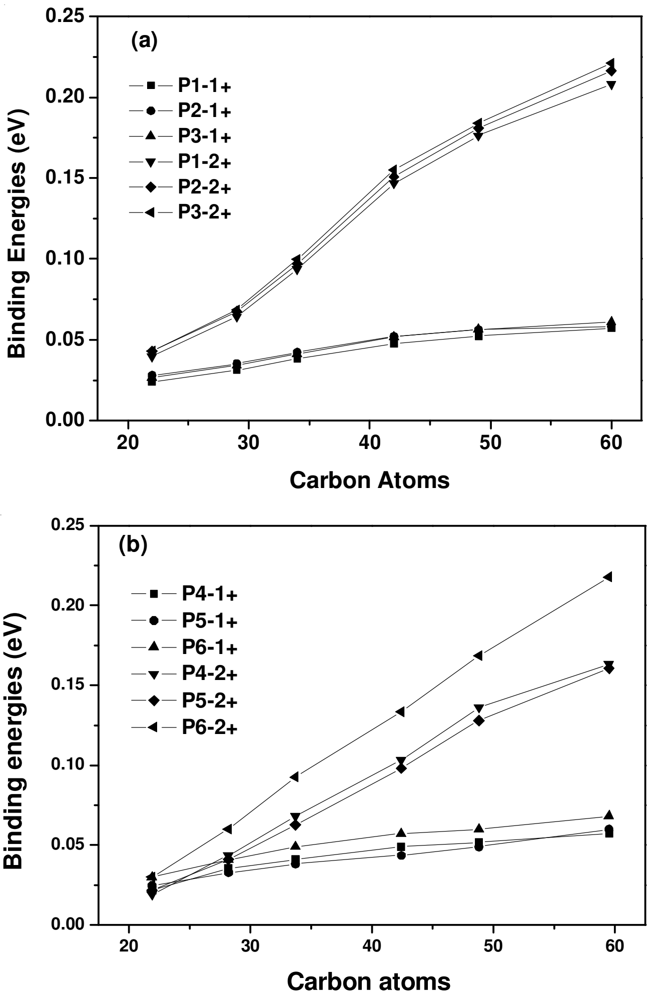


Fig. 5. Binding energy of polarons for (a) P1 series and (b) P4 series with respect to the size of deformation on carbon backbone. When positive charges are injected P1 series show the nonlinear behaviour while P4 series show the good linear behaviour

With a close look at Fig. 5a and 5b, one can find that the change of binding energy in P1 series has nearly the same behaviour that was mentioned before, implying that the substituents of C, N and Si in these polymers have little influence on the transport of bipolaron between polymer chains. While in P4 series the binding energy curves separate with each other. For example, the slope of binding energy of P6 is apparently larger than that of P4 and P5, giving the clue that one can straightforwardly adjust the transport of hole by the chemical modification on these kinds of polymers. This observation gives an idea about the convincible theoretical evidence for explaining why the hole mobility of P6 can be one order of magnitude lower than that of P4 and P5. However, for both P1 and P4 series, there is no significant difference in binding energy between C and N substitution cases, indicating that the substituents with similar radius will not be a good choice in changing the hole transport between chains of these two series.

We can also realize that the binding energy of bipolaron has the same order of magnitude with the energy of a typical vibrational mode of the oligomer. Thus the interaction between the injected positive charge and the local deformation of polymer can be understood as the electro-acoustic (virtual) interaction. The energy released in the self-trap process of bipolaron can excite the vibrational modes. And if the charge absorbs the energy from a vibrational mode it can overcome the binding energy. Therefore, one can probe the interaction between injected charge and vibrational modes from the deformation of backbone of polymer, although it seems that the local deformation and the delocalized vibrational mode are independent with each other.

Conclusion

In this work, we have theoretically investigated the relationship between the size of polarons of two series of conjugated donor material in photovoltaic cells and the corresponding binding energy. We found that the binding energies of polaron change in a nonlinear behaviour in P1 series in contrast to the approximately linear behaviour in P4 series. Substituents of C, N and Si demonstrated different chemical modification effect on the binding energy of injected positive charges. Analysis of the polaron's binding energies can well explain the relative relationship in the hole mobility between P1 and P4 series.

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