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Poly(para-phenylene) with the end structure of CH_2-$(C_6H_4)_n$-H provides nearly zero band gaps in long chains with $n>6$

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It was demonstrated from the molecular orbital theory that CH_2-$(C_6H_4)_n$- in which at least one H atom on the end of poly(para-phenylene) (PPP) is replaced by CH_2 group of the chain, provides nearly zero band gaps in the long chains with $n>6$. This behavior was explained by the band overlap leading to metallic characteristics from the perspective of the intermolecular interaction between ethylene units in the oligomer.

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With the recent advances in the development of conducting polymers, conjugated polymers have received special attention for their use in the design of novel functional materials in mesoscopic systems. Poly(para-phenylene) (PPP) has been known to display metallic conductivity after being doped with oxidizing or reducing agents, and its electronic structure has been of continuing interest from both experimental and theoretical standpoints (for example Refs. 1–4). However, it seems quite interesting if the system itself possesses a conductive property without the use of dopants. Here we report a theoretical study on a structure that can provide energy levels in the middle of a band gap by merely controlling the end structure of the polymers instead of using dopants. It is expected that the end effects of long chains could play an important role in the electronic properties of an entire system, leading to a novel approach to the production of pure conducting polymers having no impurities.

Oligomer of PPP has two possible end structures if we express a finite length as a closed system from an infinite PPP polymer. One is H-$(C_6H_4)_n$-H, given by model 1 in Fig. 1, and the other is $CH_2{=}(C_6H_4)_n$-H, given by model 2 in Fig. 1. The final products shown in Fig. 1 can be considered as combinations of polyene chains of 12 carbon atoms and 3 ethylene molecules.

The magnitude of the HOMO-LUMO gap can be predicted by the orbital symmetry of the polyene, depending on the where the two carbon atoms of ethylene are added, as depicted in Fig. 1. Model 1 shows that ethylenes are added to the loci of the polyene with numbers of 1–4, 5–8, 9–12, and so on. Model 2 shows that they are added to the loci with numbers of 2–5, 6–9, and so on. This work demonstrated that it is important for the system to have a CH_2 group at least at one end of the chain, as in model 2, in order to obtain a lower energy gap. First, we show why the HOMO-LUMO gaps are different between models 1 and 2 by dividing the oligomer into polyene and ethylenes. Through the use of this treatment, we can get an insight into the behavior in the vicinity of the Fermi level for both models on the basis of the HOMO-LUMO gap for polyene.

If the degree of mixing in the molecular orbitals (MO's) of the ethylenes and polyene after their interactions is small, the electronic structure of PPP can be elucidated by using the orbital symmetry of the polyene and ethylenes. For the polyene of 12 carbon atoms, the mixing coefficients from the polyene to PPP for model 1 are given by 0.85–0.90 in d_{ij} in the following equation in spite of the calculation levels as Hückel, other semiempirical, or *ab initio* methods:

$$\varphi_i^{(\mathrm{PPP})}=\sum_j d_{ij}\varphi_j^{(\mathrm{polyene})}+\sum_k \sum_l f_{ik(l)}\varphi_{k(l)}^{(\mathrm{ethylene})}. \quad (1)$$

In the above equation, the j in the first term represents the MO's of polyene, the k in the second term represents the MO's of an ethylene, and l indicates each included ethylene molecule. From the large degree of mixing from polyene to PPP in d_{ij}, it seems reasonable that the behavior in the orbital energy for PPP can be evaluated in terms of the interaction between polyene and ethylenes, because the orbital symmetry of polyene is retained even after the interaction.

In Fig. 2, the energy levels and MO coefficients of the HOMO and LUMO are represented for polyene (on the left), for PPP (in the middle), and for ethylene (on the right). We examined the HOMO and LUMO energy levels of PPP by the orbital interaction between the polyene and the ethylenes. We noted the two interacting carbons of polyene indicated by the square in the figure. It can be seen for model 1-Pe that the HOMO of polyene interacts with π^* orbital of ethylene with in-phase symmetry, while the LUMO of polyene interacts with π orbital with out-of-phase symmetry. In contrast, for model 2-Pe, the HOMO of polyene interacts with π orbital of ethylene with out-of-phase symmetry, while the LUMO of polyene interacts with π^* orbital with in-phase symmetry. As shown in the orbital levels of "product," these schemes mean that the energy gap between the HOMO and LUMO increases after interaction in model 1, while it decreases in model 2 from the point of view of the local interaction between a part of polyene and an ethylene.

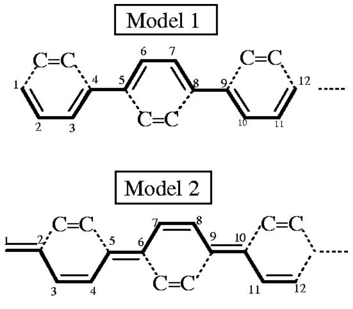

FIG. 1. Two models for PPP.

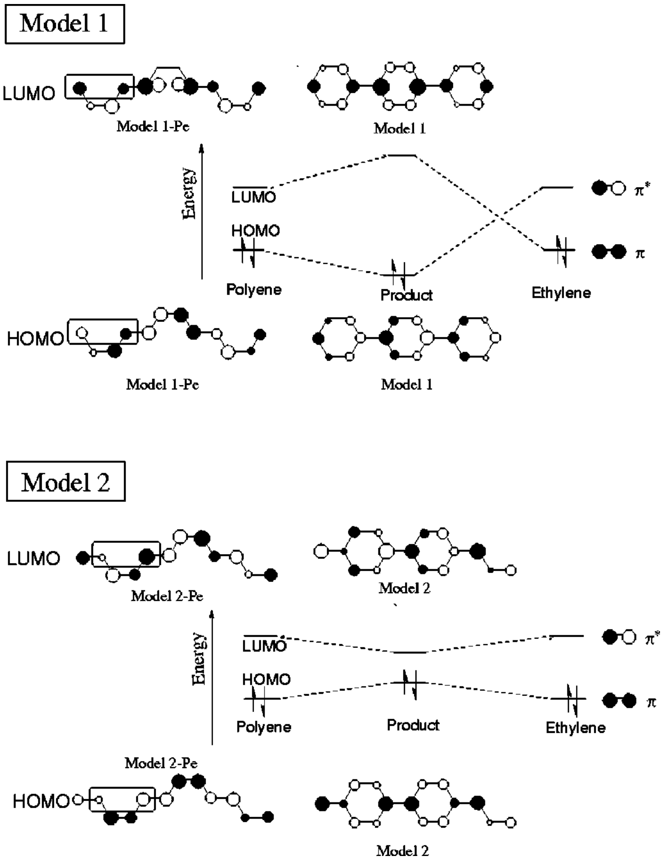

FIG. 2. Orbital interactions between polyene and ethylenes in HOMO and LUMO energies for models 1 and 2.

With $n=1$, 4, and 10 for models 1 and 2, the HOMO and LUMO energies as well as the energy gaps obtained by the GAUSSIAN 98 program package[5] with HF/6-311g** basis set are listed in Table I. As indicated in Fig. 1, the right end of model 2 was terminated by C_3H_4, meaning that 4*n* carbons are included in the parent polyene because it was confirmed that the structure of the right end (-H, CH_2-, or C_3H_4 group) does not depend on its electronic properties, as seen later (compared with the ΔE_g in Fig. 3). The most important point is that the system must be terminated by a CH_2 group at least one end of the chain to get a small HOMO-LUMO gap. Thus, it is sufficient that only the left end is terminated by CH_2. By constraining all atoms to a plane, the geometries are optimized for all parameters. Although the dihedral angles between the benzene rings are twisted with each other for the single chain of model 1 with a neutral charge,[6] the planarization of phenyl rings was observed in crystal.[7,8] The purpose of this study is to examine the end effect for the PPP without including any other factors that might break the π conjugation. Therefore, the phenyl groups of model 1 are assumed to be located in a plane in order to compare the electronic structure of model 2 in the framework of the π conjugated polymers.

TABLE I. Energy levels (a. u.) of HOMO and LUMO for $n=1$, 4, and 10 of models 1 and 2 at HF/6-311g**.

n		1	4	10
Model 1	$[H\text{-}(C_6H_4)_n\text{-}H]$			
LUMO		0.1365	0.0630	0.0440
HOMO		−0.3360	−0.2694	−0.2531
ΔE_g [a]		12.86	9.05	8.08
Model 2	$[CH_2\text{-}(C_6H_4)_n\text{-}C_3H_4]$			
LUMO		0.0611	−0.0053	−0.0969
HOMO		−0.2638	−0.2007	−0.1101
ΔE_g [a]		8.84	5.32	0.36

[a] Energy gap (eV) between HOMO and LUMO.

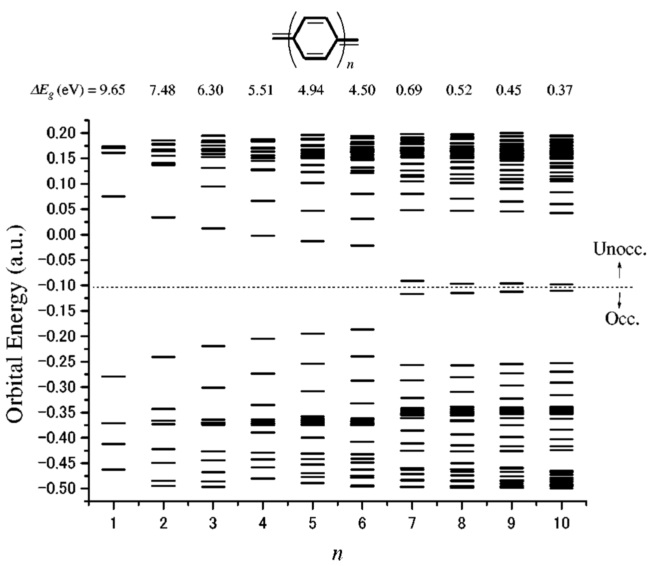

FIG. 3. Energy levels near the Fermi level for $n=1-10$ of model 2 by HF/6-311G**. Energy gaps are also indicated in the upper half.

As shown in Table I, the results for model 2, in which the energy gaps are smaller than those for model 1 for each *n*, are consistent with the prediction from the orbital symmetry shown in Fig. 2. Although the gaps for model 1 also decrease gradually with respect to *n*, the magnitude of the decrease is significant for model 2, especially at $n=10$. The explanation for both models is that the energy band generated from the HOMO or LUMO in the long chain is broadened with an increasing number of units so that the energy gaps between HOMO and LUMO should inherently decrease. Therefore, for model 1, the gap enlarged by interaction between the polyene and ethylenes, as shown in Fig. 2, decreases with the chain length with the result that the bandwidths of the HOMO and LUMO are enlarged. In contrast, for model 2, the gap already narrowed by the orbital interaction is further narrowed by the spread of the bandwidths generated from the HOMO and LUMO. Therefore, the energy gap for model 2 shows a steep decrease with respect to *n*, approaching zero.

To examine the *n* dependency of the band gaps for model 2, the energy levels for $n=1-10$ were plotted, as shown in Fig. 3. Here, the right end of model 2, C_3H_4, is replaced by CH_2, as indicated in the upper half of the figure. We can do so because the end part of another side of the chain barely affects the electronic structure. The reason for this is that the orbital phases between the polyene and ethylenes are only determined by the left-end structure, as shown in Fig. 2. This

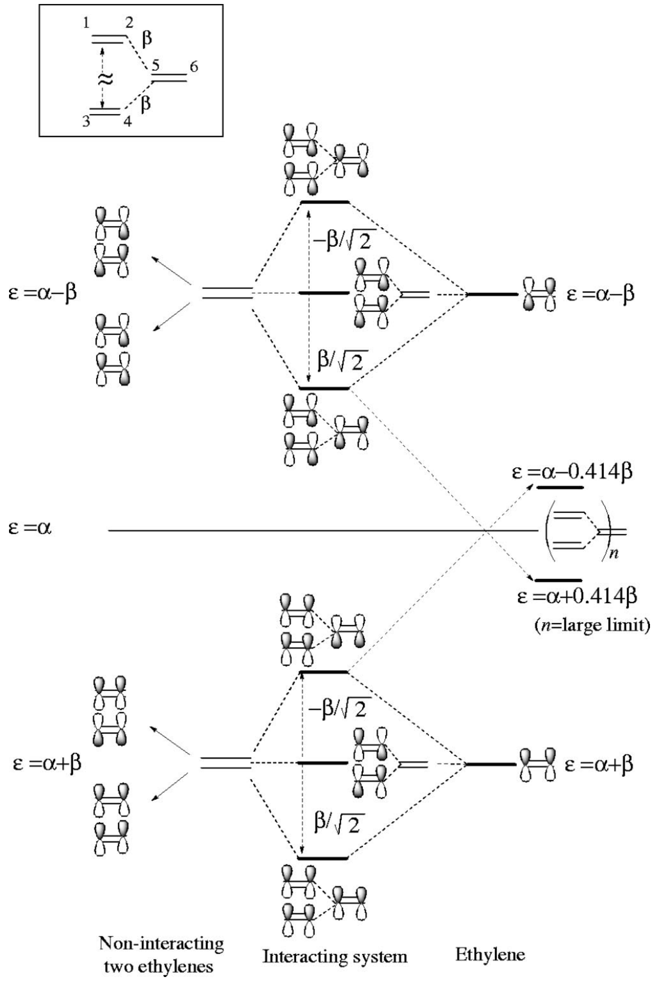

FIG. 4. Interaction scheme for model 2.

was also confirmed numerically from the comparison of the ΔE_g of model 2 in Table I with that in Fig. 3.

The sudden degeneracy with $n>6$ is worth noting in Fig. 3. This phenomena can be anticipated from the orbital interaction in Fig. 2. The parent polyene itself provides a zero band gap at the long chain limit. Thus, further interaction with ethylene leads to a finite gap for model 1 and a negative gap for model 2 leading to zero gap by the HOMO-LUMO mixing. However, to get a clearer insight on *n* dependency, we can analyze the behavior of the HOMO and LUMO energies by constructing the oligomer of model 2 with ethylene units. The model for describing the energy behavior is assumed for the interaction between the two noninteracting ethylenes and an ethylene, as shown in Fig. 4. The one unit in the periodic polymer is considered as three ethylenes indicated at the upper left. By this diagram of orbital interaction, we can analytically discuss the *n* dependency of HOMO and LUMO levels.

The resonance integrals on the basis of the HOMO and LUMO of ethylene are defined by the Hückel method as

$$H^{\rm HOMO}=\int\frac{1}{2}(\chi_1+\chi_2+\chi_3+\chi_4)\hat{H}\frac{1}{\sqrt{2}}(\chi_5+\chi_6)d\tau=\frac{\beta}{\sqrt{2}} \tag{2}$$

and

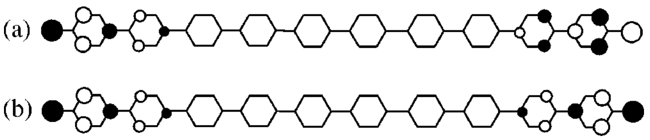

FIG. 5. (a) LUMO and (b) HOMO for $n=10$ of model 2.

$$H^{\rm LUMO}=\int\frac{1}{2}(\chi_1-\chi_2+\chi_3-\chi_4)\hat{H}\frac{1}{\sqrt{2}}(\chi_6-\chi_5)d\tau=\frac{\beta}{\sqrt{2}} \tag{3}$$

respectively. Therefore, the orbital energies are split into the same magnitude after the interaction, as shown in the middle of Fig. 4. For the infinitely large limit of *n*, the HOMO and LUMO of ethylene produce bands with bandwidths written as

$$(\alpha+\beta)+2(\beta/\sqrt{2})\leqslant\varepsilon_i^{\rm HOMO}\leqslant(\alpha+\beta)-2(\beta/\sqrt{2}) \tag{4}$$

and

$$(\alpha-\beta)+2(\beta/\sqrt{2})\leqslant\varepsilon_i^{\rm LUMO}\leqslant(\alpha-\beta)-2(\beta/\sqrt{2}), \tag{5}$$

respectively. As a result, the highest level from the HOMO band provides $\alpha-0.414\beta$ and the lowest level from the LUMO band provides $\alpha+0.414\beta$. This means that the HOMO is changed to an unoccupied level and the LUMO is changed to an occupied level at a more certain *n*, as indicated in Fig. 4, unless the interaction between the HOMO band and LUMO band is considered. Figure 3 represents this specific feature in the vicinity of the Fermi level by HF calculations. The quasidegeneracy at around -0.10 a.u. for $n>6$ means that mixing occurs between the highest MO of the HOMO band and the lowest MO of the LUMO band, producing two nonbonding MO's (NBMO's).

The orbital coefficients for $n=10$ of model 2 are shown in Fig. 5. The symmetric and antisymmetric orbitals are energetically equivalent, because the NBMO's are localized on the end of the polymer. This property near the Fermi level corresponds to the *dis*-joint type in organic molecules with radicals. There might be a possibility that a Peierls system is created by stacking the PPP of model 2, because a half-filled band can be constructed independently from both sides of the stacking system. However, a small interaction between both sides of the chain through the NBMO's can cause a weak interaction such as an interchain interaction in the stacking system of radical molecules. Therefore, we can expect that an appropriate *n* (around 6) that causes a weak interaction in a chain can suppress the structural instability induced by stacking molecules with singly occupied MO's, leading to high conductivity. These types of molecular designs are intimately related to our previous approach in which we demonstrated that an interchain interaction plays an important role in producing high-level conductivity in crystal.[9–11]

In conclusion, it was found that the HOMO-LUMO gaps and the band shapes of PPP reveal completely different features for the two models. The model with an end CH_2 group in the PPP (model 2) plays an important role in producing a narrow band gap in the polymer. In contrast, the model without a CH_2 group in the PPP (model 1) will maintain a finite gap value even in an infinitely long chain. This difference in electronic property, which comes from the end structure of the polymer, cannot be obtained by the conventional tight-binding method for periodic systems, because the tight-binding method does not provide any differences for oligomers with different end structures. The analysis presented here will lead to novel designs of functional materials such as highly conductive crystals and ferromagnetic materials.

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