Gradient Copolymers of Thiophene and Pyrrole for Photovoltaics

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Abstract

The electronic properties of copolymers can be tuned by controlling their monomer ratio, and therefore can potentially be used to improve charge separation in organic photovoltaic devices. Here we show evidence based on density functional theory calculations that it is possible to control the electronic structure of π -conjugated copolymers of thiophene and pyrrole to obtain a gradient in the band gap and both conduction and valence crystal orbital band levels by controlling their composition. Our calculations predict and optimal thiophene monomer fraction range between zero and 40% is needed in order to obtain the largest electronic structure gradients.

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1. Introduction

Organic polymer-based photovoltaic (OPV) devices have recently gained much interest due to their light weight, flexibility, and low-cost of manufacture.[1] These materials usually consist of π -conjugated polymers with band gaps typically near 2 eV. The power conversion efficiency of these devices has been steadily increasing and it has recently reached close to 9%.[1] In light of this, much work has been devoted to the design of suitable polymers for more efficient OPVs.[2, 3]

Recently it has been suggested that both organic and inorganic solar cells with compositional effects across the device exhibit improved performance.[4, 5] Manipulating this gradient allows one to engineer the band gap and electronic orbital levels to control the resulting conducting properties of the material. Such compositional gradients can be achieved in conjugated polymers via various polymerization methods,[6, 7, 8] resulting in gradient copolymers that have a continuously varying composition along the polymer chain. Their study is currently a very active research area,[9, 10, 11, 12, 13] with proposed applications ranging from vibration-damping materials to coatings.[14, 15] However, the effect of compositional gradients on the electronic properties of these π -conjugated polymers has not yet been investigated in the literature. In this work we set out to determine the compositional effects on the electronic structure of copolymers of thiophene (T) and pyrrole (P) (Figure 1) using density functional theory methods.

Thiophene has a relatively high hole mobility and its derivatives are already commonly used in OPVs[1], while pyrrole provides a commensurate structure to control the composition. Polythiophene (PT) and polypyrrole (PP) have experimental band gaps of 2 and 2.81 eV[16, 17] and redox po-

tentials of 1.97 and 1.31 V(SCE), respectively,[18, 19] as well as ionization potentials that differ by over 0.5 eV [20]. Due to these differences, we anticipate that by synthesizing PT and PP into a gradient copolymer or by laying copolymers of differing constant monomer ratio in a graded fashion, a gradient in their electronic structure can be achieved. The difference in redox potentials provides additional motivation for pursuing polymerization via an electrochemical route.

2. Calculations

Figure 1: Schematic structures of the thiophene and pyrrole copolymer employed in this work. The periodic unit cell consists of a total of eight units ($T + P = 8$).

All calculations have been carried out using the split-valence Gaussian-type double-zeta Pople basis set with added polarization functions (6-31G**) and periodic boundary conditions (PBC) as implemented in the *Gaussian 09* suite of programs.[21] All structures have been fully relaxed until the maximum and root mean square atomic forces are less than 0.02 and 0.015 eV/Å, respectively, and the maximum and root mean square atomic displacement between consecutive iterations are less than 10^{-3} and $6 \cdot 10^{-4}$ Å, respectively. We have used eight monomer units ($T + P = 8$ in Figure 1) in each unit cell corresponding to a translational vector of approximately 30 Å and a uniform reciprocal space integration grid of 12 k-points.

First we compare the band gaps from Kohn-Sham band energy differ-

ences for the homopolymers of pyrrole and thiophene obtained within the local spin-density approximation (LSDA)[22, 23, 24], Perdew-Burke-Ernzerhof exchange-correlation functional (PBE)[25], hybrid PBE (PBEh)[26], and the screened exchange hybrid density functional HSE[27, 28, 29] with their corresponding homopolymer experimental values (Table 1). We find that, consistently with previous results for crystals and carbon nanostructures,[29, 30, 31, 32, 20, 33] both hybrid functionals perform better than the non-hybrid ones, with HSE slightly closer to the experimental value than PBEh. Previous results show that in the polymeric limit, band gaps obtained as band energy differences using the HSE screened hybrid functional approach excitation energies obtained from TD-DFT calculations employing the corresponding unscreened hybrid functional PBEh.[31] In view of these results as well as others presented in the literature[34] we determine band gaps as band energy differences from PBC calculations using the HSE screened hybrid functional.

Table 1: Homopolymer band gaps (eV) obtained using different density functionals.

Method	Polythiophene	Polypyrrole
LSDA	1.06	1.79
PBE	1.02	1.75
PBEh	2.38	3.22
HSE	1.70	2.52
Experimental	2 ^a	2.81 ^b

^a Taken from Ref. 16

^b Taken from Ref. 17

3. Results and Discussion

We turn now to the effect of monomer composition on the electronic structure of the copolymers. We model the different copolymers with a periodic unit cell of eight monomers of thiophene and pyrrole as shown schemat-

ically in Figure 1. The ratio of thiophene monomers to the total repeat length is defined here as $X = \frac{T}{T+P}$, where T and P are the number of units of thiophene and pyrrole, respectively. X was varied from zero to one by replacing a pyrrole monomer with a thiophene monomer in the unit cell using a left-to-right replacement scheme (Figure 1). It should be pointed out that other compositional arrangements with the same ratio are also possible within this scheme. For example, a ratio of $X = 0.5$ can be achieved by simply alternating one thiophene and one pyrrole monomer. This particular composition gives a band gap of 1.95 eV in contrast to 1.76 eV for the four thiophene and four pyrrole monomers unit cell. However, alternating single monomer units are more unlikely to be realized experimentally than multiple units and therefore not considered in this work.

At each step in X , the starting structure was fully relaxed with a periodic unit cell of eight monomers. In all calculations a planar structure was enforced and therefore the results presented in what follows correspond to planar structures. For each relaxed structure, the highest occupied crystal orbital (HOCO), lowest unoccupied crystal orbital (LUCO) and band gaps were calculated.

Our copolymer calculations show a gradient relationship between the ratio of monomers and the electronic energy levels. These results are presented in Figure 2 considering the periodic structures schematized in Figure 1. Our calculations support the idea that by controlling the monomer ratio during the synthetic procedure, an electronic structure gradient can be obtained. This gradient in the energy levels provides the basis to produce a charge separation effect in which electrons and holes separate as they move “downhill” within the HOCO and “uphill” within the LUCO (Figure 2) and it constitutes the main result of this work.

Figure 2: HOCO and LUCO levels of thiophene/pyrrole copolymers obtained using PBC at the HSE/6-31G** level of theory. Although the change in band gap is largest as one approaches the pyrrole homopolymer, the over all energy level slope is maintained as X is varied from 0 to 1.

As shown in Figure 2, the gradient in the HOCO and LUCO levels as well as in the band gap as a function of the monomer ratio X shows that this gradient is maximized for monomer ratios X between zero and approximately 0.4. In order to understand the nature of the energy levels presented in Figure 2 we analyze the total and partial density of states (DOS) for several compositions. In Figure 3 we present the total DOS together with the partial contributions originated in the different atomic

species. Figure 4 presents the total DOS with the partial contributions from the different units, i.e. thiophene and pyrrole. In both figures we observe that the valence states tend to be delocalized, with a slight localization as X approaches 0.5. The conduction states include strongly localized levels in the copolymer case. These levels present a progressive shift that is largest going from $X = 0.4$ to $X = 0$. The copolymer valence levels near the energy gap consist of proportional contributions from both thiophene and pyrrole units. However, the conduction levels near the gap region originate mostly from thiophene units (Figure 4).

Figure 3: Total and partial density of states for copolymers corresponding to $X = 0$, $X = 0.25$, $X = 0.5$, $X = 0.75$, and $X = 1$. The partial DOS corresponds to contributions by each element type. The Fermi level is set at zero.

Figure 4: Total and partial density of states of copolymers showing the contributions from each monomer type. The copolymer valence levels consist of nearly proportional contributions from both thiophene and pyrrole, whereas the copolymer conduction levels originates mostly in the thiophene units.

4. Conclusions

By employing DFT methods we find a compositional effect of monomer units in copolymers of pyrrole and thiophene that results in a gradient in their HOCO and LUCO levels. This gradient is greatest for compositions X ranging between zero and 0.4.

The copolymer valence states tend to be delocalized, while the conduction states show strongly localized levels dominated by contributions from T units. Valence states show a more proportional contribution from both T and P depending on the value of X .

Our results suggest that a cell prepared with an arrangement consist-

ing of individual copolymers presenting a compositional gradient along the polymer periodic dimension should enhance the charge separation mechanism of the material. From the multiple methods of experimental synthesis available for gradient copolymers,[6, 7, 8] only those that allow for a careful control of the monomer ratio can potentially be used for charge separation purposes.

While the gradient obtained in this work can mitigate the electron-hole recombination it also increases the band gap of the material beyond 2 eV, which is outside the optimal range for OPV applications. However, following the ideas presented in this work, it is feasible to find a commensurate polymer with a smaller band gap to generate a gradient in the opposite direction thus reducing the band gap distribution of the material while still presenting the desired electronic structure gradient.

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