MODELLING THE EFFECT OF NON-PLANARITY ON LUMINESCENCE ENERGY OF CONJUGATED POLYMERS

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Abstract

We present theoretical investigations of structural and electronic properties of ground-state and low-lying excited singlet states in isolated chains of conjugated polymers using a self-consistent quantum molecular dynamics method. With this approach, we have determined the energy of both states as function of the twist angle between two planar segments of the same polymer chain, for polymer chains with variable length. The conjugated polymers investigated here are poly(para-phenylene vinylene) (PPV) and polydiacetylene (PDA). Our results show that the energy of the excited-state increases more than that of the ground-state, as the twist angle increases up to 90º degrees. The change in the twist angle of both polymers leads to a blueshift in luminescence transition energy, the effect being stronger in PPV when the planar segments have similar sizes. The predicted blueshift in both polymers is dependent on the chain length, the effect being more pronounced for shorter-chains.

1. Introduction

Conjugated polymers are very promising semi-conducting materials for applications in electronic, optoelectronic and photonic devices [1]. Photoluminescence and electroluminescence studies of conjugated polymers have suggested that luminescence transition energies are sensitive to conformational changes [2,3]. Furthermore, a blueshift in photoluminescence energies with increasing temperature was observed [2] and that effect was attributed to lattice fluctuations due to torsional displacements away from planarity.

Although these recent experimental studies have shown that polymer conformation has an influence on its luminescence, the effect of rotational displacement of the conjugated segments away from planarity on ground-state and excited-state properties of each polymer molecule are not fully understood. Theoretical methods combining molecular dynamics with self-consistent quantum mechanics methods are ideally suited to study such effects in conjugated polymers where atomic positions and electronic structure are coupled problems.

In recent years, many theoretical approaches using *ab initio* band structure calculations have been carried out for describing the ground-state properties of conjugated polymers, but the predicted torsional energy surface reported for poly(para-phenylene vinylene) (PPV) does not agree with experimental findings [4].

In this work we calculated the torsional energy surface of individual PPV and PDA chains in their ground-state and low-lying excited singlet-state and assess the influence of the twist angle between two conjugated segments within the polymer chain for the luminescence transition energy. The results reported here for chains of different length and varying-length conjugated segments were obtained using CNDO (Complete Neglect

of Differential Overlap) combined with molecular dynamics. This method has already proved to be a successful tool for conformational studies in previous works [5,6].

2. Details of the calculations

The ground-state and low-lying singlet excited-state calculations were carried out using the CHEMOS code [7,8]. The self-consistent quantum-chemical molecular dynamics method implemented in this code is based on two main linked components. One part is the electronic structure calculations using the standard quantum chemistry method called CNDO, which generates forces on each atom that are self-consistent to a chosen degree without numerical differentiation. The other part is molecular dynamics, which provides ion dynamics using the self-consistent forces. The CHEMOS code has further facilities to include external force fields.

Before any dynamical simulation of internal rotation of two conjugated segments around a specific bond is performed, the polymer chain is fully relaxed. The rotational processes are then simulated by a non-damped molecular dynamics using full self-consistent forces at each time-step.

In dealing with twisting, the atoms placed at one side of that bond are rotated clockwise whilst the atoms placed on the other side are only allowed to move within its conjugated plane. Thus, in additional to the quantum-mechanical force, each atom in the rotating segment is subjected to an external force tangential to the circular path. This procedure allows one to perform dynamical rotation with simultaneous geometry optimization. Tangential forces are varied at each time-step to keep a nearly constant

angular velocity. In the limit of infinitely slow motion, we expect the potential energy surface to remain very close to the minimum-energy surface.

3. Results

Following the procedure described above, we calculated the torsional potential energy for an isolated chain of PPV and PDA as a function of the torsional angle between two conjugated segments. We have focused our calculations on the rotation around the carbon-carbon bond shown in Fig. 1.

Fig. 2 shows the rotational energy profile for the ground-state and the low-lying excited singlet state. Note that when the rotational angle is zero the polymer chain is planar with all-trans conformation. Our results show qualitatively similar torsional energy profiles for PDA in the ground-state and singlet excited-state, which however differ markedly from a quantitative point of view: the rotational energy is much higher in the singlet excited-state. These results also suggest that a planar conformation with a twist angle of 180º is the most stable one. The results for PPV suggest that the low-lying excited singlet state has also a planar conformation, whereas a non-planar conformation with a twist angle of approximately 30º is predicted to be the most stable one for the ground-state. Although in qualitative agreement with the experimental diffraction data [9], CNDO predicts non-planarity of PPV in its ground-state with larger twisting. In all cases, the orthogonal form corresponds to the highest rotational barrier, which is larger for the excited-state.

The rotational energy profile of both conjugated polymers in its ground-state is mainly determined by the competition of two effects. One is the resonant stabilization (π-

electron conjugation effect) and other is the steric hindrance (repulsion due to overlap of the wave functions). The balance between these two effects results in a planar conformation for PDA and a deviation from planarity for PPV, a non-intuitive result.

The dependence of the maximum rotational barrier on the length of the rotating segment is shown in Fig. 3 for an isolated chain of PPV and PDA with an even and an odd number of monomer units. The predicted trends for both chain lengths are similar for PPV and considerably different for PDA. This latter result in probably due to the difference in energy when the formed exciton is centered on a double bond linking two diacetylene units as compared to the energy of an exciton centered on a triple bond within a diacetylene unit. In Fig. 3, the maximum rotational energy of PPV chains in the excited-state increases as the fraction of their maximum conjugated length rotating increases up to 0.5. Negligible change was predicted for the ground-state.

Fig. 4 shows the effect of chain length on the maximum rotational energy for the low-lying singlet excited-state of PPV and PDA with different fractions of its maximum conjugated length rotating. For both polymers, the rotational barrier increases as the chain length decreases.

4. Discussion

A neutron-scattering study directly confirms the presence of temperature-dependent non-planarity of PPV [10]. As the temperature rises the degree of non-planarity increases. According to our results, when the torsion angles along the polymer chains increase, the energy of the low-lying singlet excited-state increases more than that of the ground-state. As a consequence, a blueshift of the luminescence transition energy occurs, something

which has been observed in temperature-dependent photoluminescence experiments in PPV [11] and can be explained by the present work. We point out that although PDA has lack of ring torsional degrees of freedom, both PPV and PDA show the same trend as a function of rotational displacement of conjugated segments away from planarity, which suggests that a similar temperature-dependent photoluminescence effect may exist for PDA. However, presently we are unaware of any temperature-dependent optical absorption experiments that have recorded thermochromism in PDA.

A blueshift of luminescence transition energy with increasing torsion angle from two conjugated polymers with a planar backbone (PDA), and a non-planar backbone (PPV) in the ground-state supports the argument that the blueshift in photoluminescence energy should reflect the temperature dependence of torsional fluctuations. The blueshift effect should be more pronounced for shorter-chains that have higher torsional energies in the excited-state.

5. Conclusions

We have presented systematic torsional-dependent energy studies of ground-state and low-lying excited singlet states for two conjugated polymer chains with different backbone conformations in ground-state. Both conjugated polymers show a blueshift of their transition energies between the excited-state and the ground-state when increasing the torsion angle between planar conjugated segments, an effect which is independent of their backbone conformation in the ground-state. These results also suggest that the temperature-dependent torsional displacements away from planarity are a plausible explanation for the blueshift of the luminescence energies of conjugated polymers with

increasing temperature. If the singlet excitons that are created in the polymer backbone remain localized on the shorter chains, we would expect a stronger blueshift.

Quantum molecular dynamics calculations, such as those reported here, are a useful tool for providing a physical interpretation of experimental data but also information that is so far impossible to obtain from the experiments.

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Figure Captions

Figure 1 – The optimized molecular structure of an isolated chain of (a) PPV and (b) PDA with 16 repeat monomer units and two perpendicular conjugated planar segments of the same length.

Figure 2 – Rotational energy profile for internal rotation around C – C bonds in (a) PPV and (b) PDA as indicated in Fig. 1, for the ground-state (bottom position) and low-lying singlet excited-state (top position). The rotational angle zero corresponds to planar all-trans conformation.

Figure 3 – The dependence of the maximum rotational barrier on the length of rotating segment for an isolated chain of (a) PPV and (b) PDA with 15 (squares) and 16 (triangles) monomer units. The open and closed indicate the data points that were calculated explicitly for the low-lying singlet excited-state and the ground-state, respectively. The curves are simply a guide to the eye.

Figure 4 – The effect of chain length on the maximum rotational energy of (a) PPV and (b) PDA for the low-lying singlet excited-state and the following fractions of its maximum conjugated length rotating: 0.25 (squares), 0.33 (circles), 0.40 (triangles) and 0.50 (stars). The marks indicate the data points that were calculated explicitly. The curves are simply a guide to the eye.
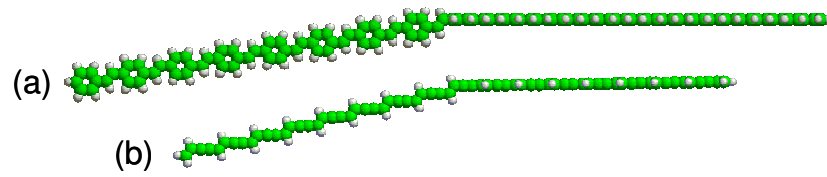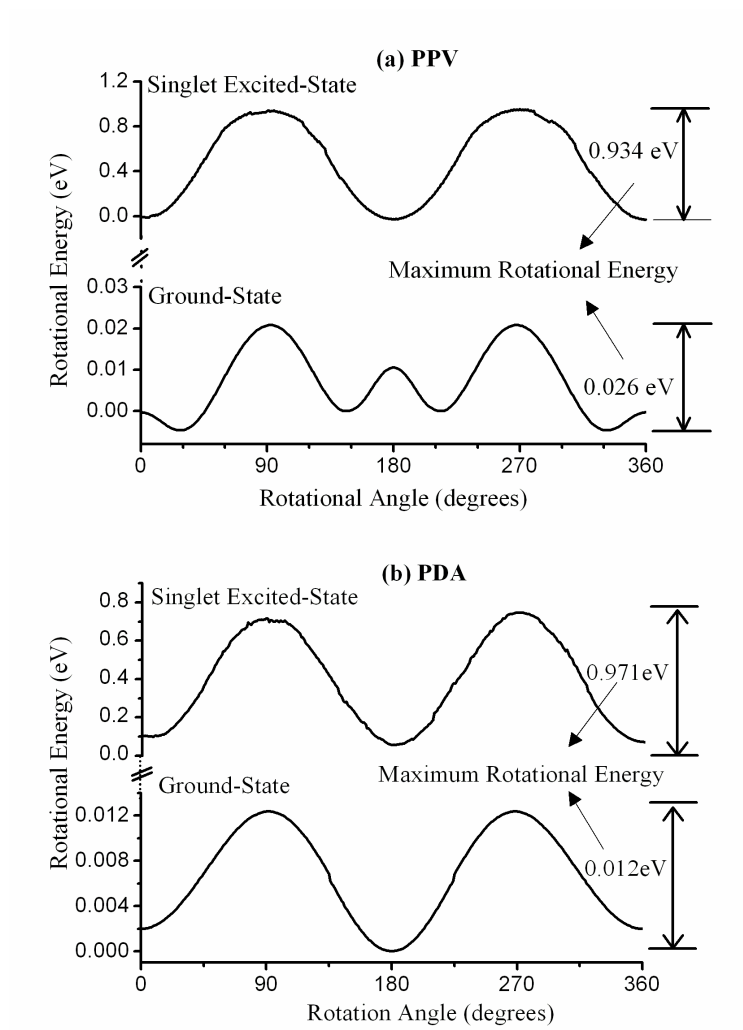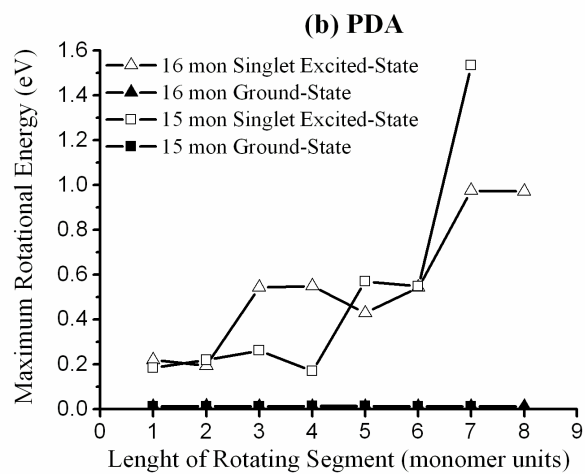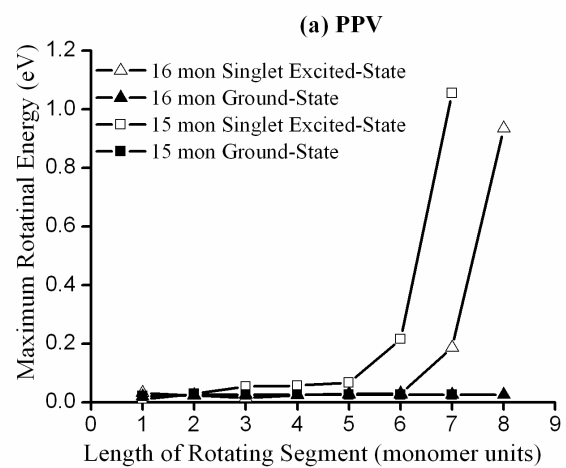
Fig 1.

Fig 2.

Fig. 3

(a) PPV

(b) PDA

Fig. 4

(a) - PPV