

有機半導体の電子構造の研究

Density of Frontier States and Electronic Transitions of Molecular Semiconductors

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Introduction

Molecular semiconductors are notable for the similarity of their solid state electronic structure with that of the single component molecule. In the absence of significant band dispersion, the distribution in energy of the electronic states of the molecular solid can be accurately modelled by the energy of the molecular orbitals calculated with single-molecule density functional theory (DFT). Only the separation between the occupied and virtual states requires empirical adjustment. This shift is needed to account for the polarization energy and final state effects, which are not addressed in the calculations natively.

Methods

Gaussian 09 software package. The molecular structure is optimized and the energy levels calculated using the B3LYP functional and 6-311+g(d) basis set, typically. The time dependent (TD) calculations are done at the same level of theory.

Results and Discussion

Summary: The simulated DOS and simulated optical spectra of pentacene (PEN) and perfluoropentacene (PFP) molecules were compared.

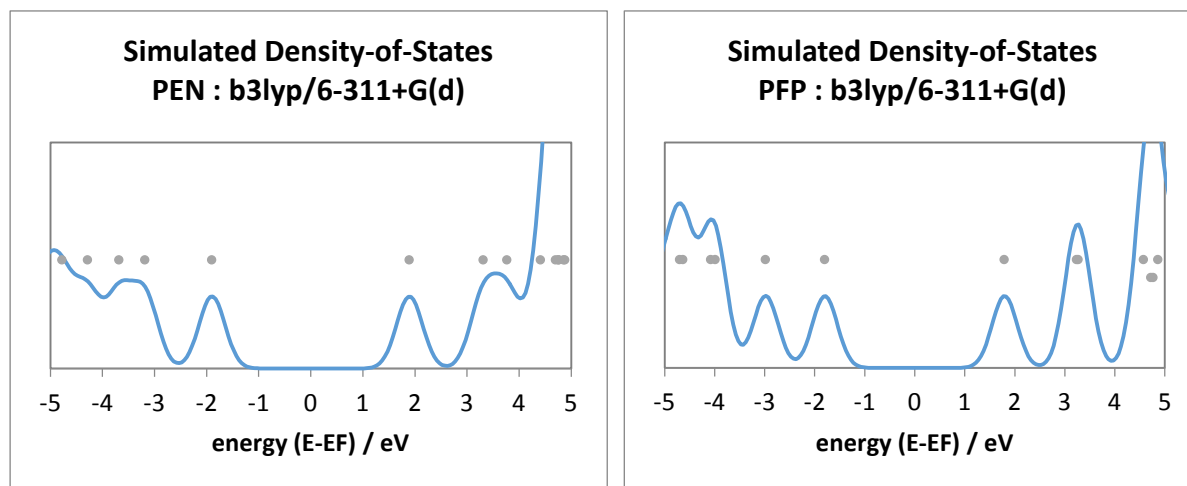


Fig. 1. The simulated density of states for PEN and PFP molecules.

The simulated DOS is shown in Fig. 1. The Fermi energy is positioned midway between the HOMO and LUMO levels. The component peaks are Gaussians of fixed width $\sigma = 0.55$ eV centered on the eigenvalues. The DFT energies of the occupied and virtual states have each been rigidly shifted away from the Fermi energy by 0.8

eV to account for polarization and final state effects. We note that the HOMO–LUMO separation energy is quite similar, 3.8 eV for pentacene and 3.6 eV for perfluoropentacene.

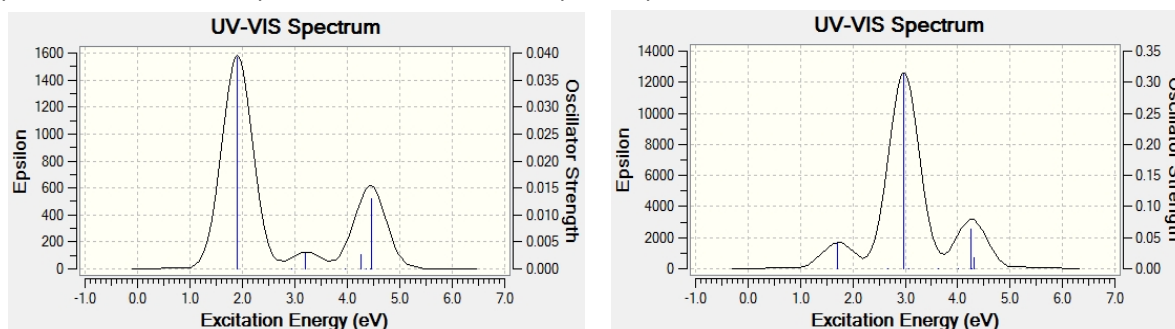


Fig. 2. The simulated optical spectra of PFP (left) and PEN (right).

Fig. 2 shows the simulated UV–VIS spectra. Of special note is the increase in the oscillator strength of the second active singlet transition, B_{2u} , in PFP, and the overall shift of the singlet states to lower energies. The PFP B_{2u} singlet falls within the range of our photoconductivity apparatus, so we expect from these calculations that PFP should be an interesting molecule to study as we can compare the photocurrent yield for the B_{1u} ($\text{HOMO} \rightarrow \text{LUMO}$, $S_0 \rightarrow S_1$) and B_{2u} (primarily $\text{HOMO} \rightarrow \text{LUMO}+1$, $S_0 \rightarrow S_3$) excitations simultaneously.

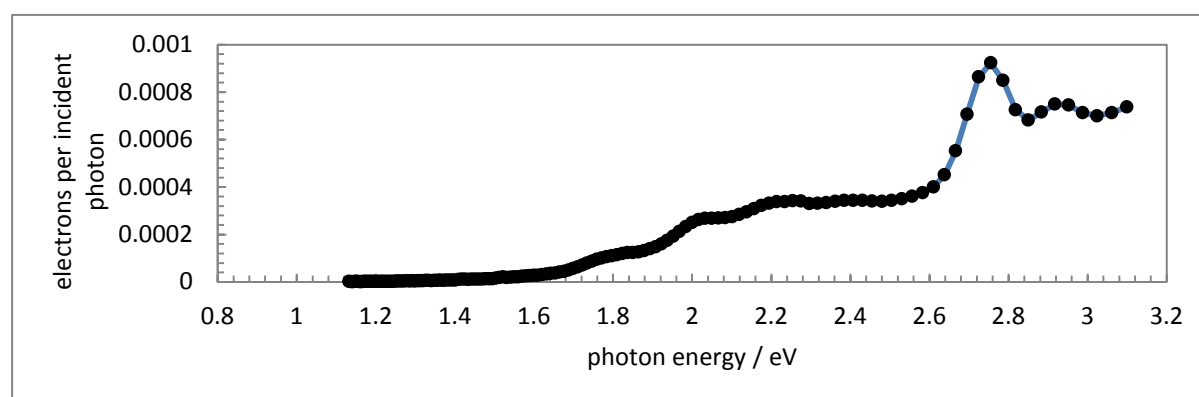


Fig. 3. Photocurrent yield spectrum for 4.5 nm PFP thin film on sapphire substrate.

The peak at about 2.8 eV in Fig. 3 is attributed to the $S_0 \rightarrow S_3$ transition, while the lower energy peaks are the sequence of vibronic structures originating from the $S_0 \rightarrow S_1$ excitation. The relative intensities can, using the Gaussian TD calculations and the known symmetry, be used to evaluate the orientation of the molecules relative to the incident light.

参考論文

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