

Charge and Field Modulation Spectroscopy on Pentacene Thin-Film Devices

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1. Introduction

Organic field-effect transistors (OFETs) have attracted considerable recent attentions for future applications in flexible, large-area and low-cost electronic products. An important issue of OFETs is to reveal the microscopic states of gate-bias-induced charges at organic semiconductor interfaces that provide a clear basis for improving the device characteristics. The fundamental description of the charge states is based on small polarons that readily interact with defects in the form of charge trapping, although no spectroscopic clue to understand polaron states has been reported yet for small-molecule-based OTFTs.

Here we present charge modulation spectroscopy of pentacene thin-films to sensitively detect the absorption of gate-induced polarons. In contrast to the conventional electro-absorption (EA) spectroscopy [1-4], we successfully detect applied-field and charge-induced effects, independently, on the absorbance of pentacene by using field-effect device structures. Indeed, we observe distinguished field-modulation (FM) and charge-modulation (CM) spectra. In FM, a homogeneous Stark shift, expressed by the close resemblance with the 1st derivative of the absorbance, is observed. On the other hand, the CM signal is dominated by bleaching, except for the spectral region around 2 eV, where absorption is increased with the induced hole layer. We interpret this feature as an indication for vibrational energy reconstruction due to the presence of trap states. We found that the obtained field- and charge-modulation (FM/CM) spectra give clear insights into the nature of electronic and polaronic excitations in pentacene.

2. Experimental

The device structure is shown in the inset of Figure 1: On top of a fused-silica or CaF₂ substrate with a semitransparent Au/Ti gate electrode, parylene C (200 – 250 nm) was deposited as the gate insulator. Finally 50 nm pentacene and semitransparent Au (source/drain) electrodes were thermally evaporated to complete the field-effect device structure. It should be noted that the polycrystalline pentacene films have been produced under identical conditions for the field-induced ESR spectroscopy [5,6].

Field modulation is obtained by applying positive gate bias, while charge is modulated by applying negative gate bias. Using a microscope setup, monochromatized light was focused onto one of the source/drain electrodes (for FM and CM) or into the channel region (for CM only). By applying pulsed gate biases at frequencies of 0.1 – 1 kHz, transmis-

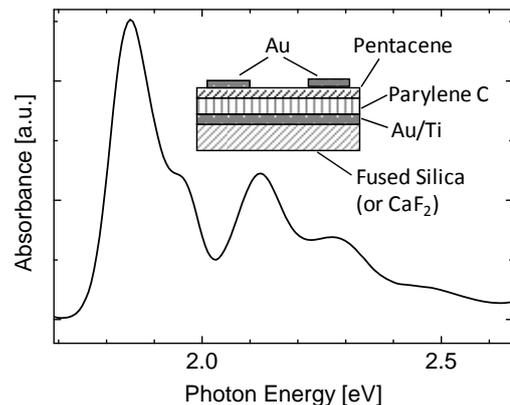


Fig. 1 Absorption spectrum of pentacene. Inset: FET layout.

sion spectra with a good S/N ratio were achieved by using lock-in technique. It is estimated that the maximum applied modulation voltages of @V afford a field strength of 5.7×10^{-5} V/cm within pentacene channel layers in case of field modulation (FM) and a hole density of 2×10^{12} cm⁻² at the pentacene interface in case of charge-modulation (CM).

3. Results and Discussion

Due to the centro-symmetric nature of pentacene, the FM signal is proportional to the square of the applied voltage (V^2). In contrast, the CM signal is proportional to V . Figure 2 shows FM and CM spectra, respectively. The spectra present much different spectral features; the FM signal closely follows the 1st derivative of the absorbance, while the CM signal is dominated by bleaching of the absorbance.

Field-Modulation

In FM (Fig. 2, upper panel), we observe a homogenous nonlinear Stark shift for all the UV/VIS spectral range up to 2.5 eV, as expressed by the quadratic electric field dependence and the close resemblance with the 1st derivative of the absorbance (Fig. 1). Latter is indicative for Frenkel-type excitations. Furthermore, a 1-photon optically forbidden transition to an A_g state is observed at 2.8 – 3.0 eV. In contrast to earlier EA studies [1], there are no indications for CT (charge transfer) exciton formation or other further complications, since the signal can be nicely described by the 1st derivative. The observation of a homogenous Stark shift strongly indicates that all spectral features of pentacene in the UV/VIS region (see Fig. 1) have the same physical origin, i.e. are due to the vibrational progression

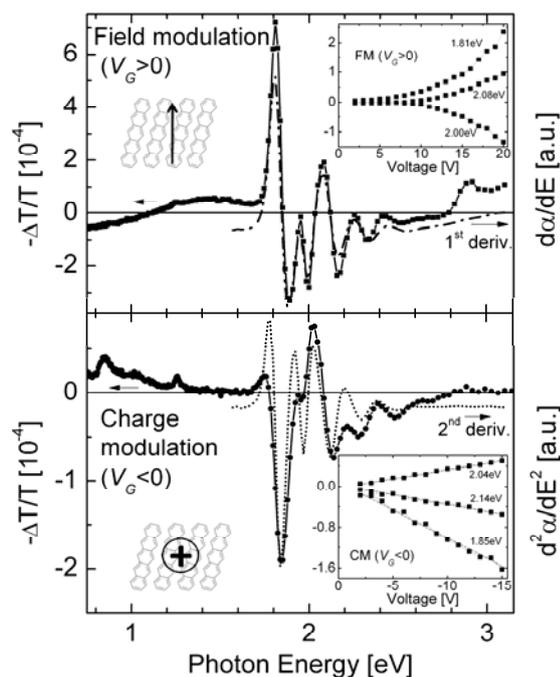


Fig. 2 Upper panel: FM spectrum, together with the 1st derivative of the absorbance. Lower panel: CM spectrum, together with the 2nd derivative of the absorbance. Insets: Voltage-dependence of the FM and CM signal at selected photon energies.

[7] of the same electronic transition. From the second Davydov component, only the shoulder at 1.97 eV is visible.

Charge Modulation

For CM (Fig. 2, lower panel), bleaching due to hole injection is dominant in UV/VIS, as one can easily see from the comparison with the absorbance (Fig. 1), and the signal amplitude is proportional to V , i.e. the injected charge density. At energies around 2 eV, the CM signal indicates *enhanced* absorption. Further, it follows the sign change of the 2nd derivative in this region, which can be assigned to broadening of the spectrum around 2 eV. In order to discuss the origin of this anomaly, it is better we have to consider that our pentacene films have been prepared under nominally identical conditions as in case of electron-spin resonance (ESR) studies revealing multiple trap-and-release (MTR) transport [5] and *extended trap states* [6]. If we adopt the model presented in Ref. 4, we can understand our results as shown in Fig. 3: By the hole injection, cations are formed and visible in the near-IR CM spectrum (Fig. 2 and 3) [7]. These cations, comparable to filled *localized* trap states, interact with the surrounding neutral molecules, effectively forming spatially *extended* trap states. We suggest that this interaction is the cause of an energy reconstruction for some of the vibrational modes, and thus responsible for the CM feature observed around 2 eV.

4. Conclusions

By using FET devices, which allow the truly *separate* measurement of FM and CM spectra, we could show that

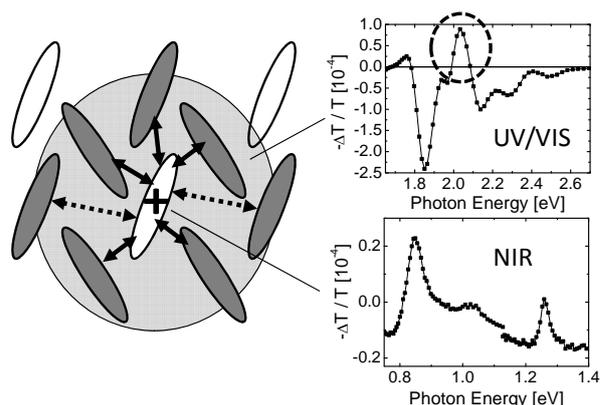


Fig. 3 Schematic representation of a hole-doped pentacene film: The central cation (visible in NIR) interacts with the surrounding molecules, causing a vibrational energy reconstruction.

the absorption spectrum of pentacene in UV/VIS can most likely be explained by simple vibrational progression (and Davydov splitting), because a homogenous Stark shift is observed in FM. The CM data are compatible to hole accumulation, which results in populating spatially extended trap states, in agreement with MTR which is frequently observed in pentacene thin films.

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