Photocurrent Action Spectra of Perfluoropentacene Thin Films

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Introduction

While the fluorinated analog of pentacene (PEN), perfluoropentacene ($C_{22}F_{14}$, PFP), retains the molecular and electronic structure of the unsubstituted molecule, the electron withdrawing fluorine atoms shift of the HOMO and LUMO-derived states to larger binding energy leading to n-type (electron transporting) semiconductor behavior. [1] TD-DFT calculations predict that the energy and relative strength of the first two singlet exciton transitions also changes. Both the $S_0{\to}S_1$ (B_{1u}) and $S_0{\to}S_3$ (B_{2u}) singlet excitons are shifted to lower energy in PFP compared to the same transitions in PEN, and the magnitude of the transition dipole moment switches in PFP to favor the $S_0{\to}S_3$ transition. These differences are clearly observed in the optical absorption spectra of the thin films [2], and as the $S_0{\to}S_3$ transition of PFP falls within the measurement range of our apparatus, this material offers us a good opportunity to examine the relative photocurrent yield of the $S_0{\to}S_1$ and $S_0{\to}S_3$ singlet excitons in a molecular semiconductor. (The $S_0{\to}S_2$ transition has no appreciable intensity in either molecule.)

In this study, we measure the photocurrent as a function of excitation wavelength for thin film perfluoropentacene devices with either gold or aluminum electrodes. The photon energy range covers both the first and singlet exciton transitions, as well as the most probably position of the charge transfer states and the transport energy gap. A comparison of the photocurrent yield spectra with the *in situ* optical absorption coefficients shows drastic differences between the optical transition probability and the photogeneration yields, reflecting differences in both the charge separation of the excited states and their orientation.

Experimental

PFP (Kanto Denka Kogyo Co. Ltd.) was used as received. Single crystal sapphire [0001] substrates (Shinkosha) were first annealed at 1000 °C in air to expose atomically flat terraces, over which 100 nm aluminum or gold electrodes spaced 0.1 mm apart were vacuum deposited through a metal mask. A thin titanium adhesion layer was used with the gold electrodes. Once placed inside the measurement chamber, the substrates were degassed at 150 °C under ultrahigh vacuum before use. Films were prepared by thermal deposition and the substrate temperature was kept at 50 °C. The deposition rate was 1 ± 0.5 nm min^{-1}. Photocurrent action spectra were evaluated for wavelengths from 400 nm – 1100 nm using a Bunkokeiki SM-25 monochromatic light source and a Keithley 6487 picoammeter-sourcemeter. The incident photon flux was 10^{19} photons m^{-2} and the applied

electric field was 10^5 V m^{-1}. Dark current subtraction was performed for each data point. *In situ* absorption spectra were taken from transmitted light sampled with an optical fiber terminating under the device. Optical absorption coefficients were checked *ex situ* on a reference 40 nm PFP film, prepared identically to the measurement sample but without the metal electrodes.
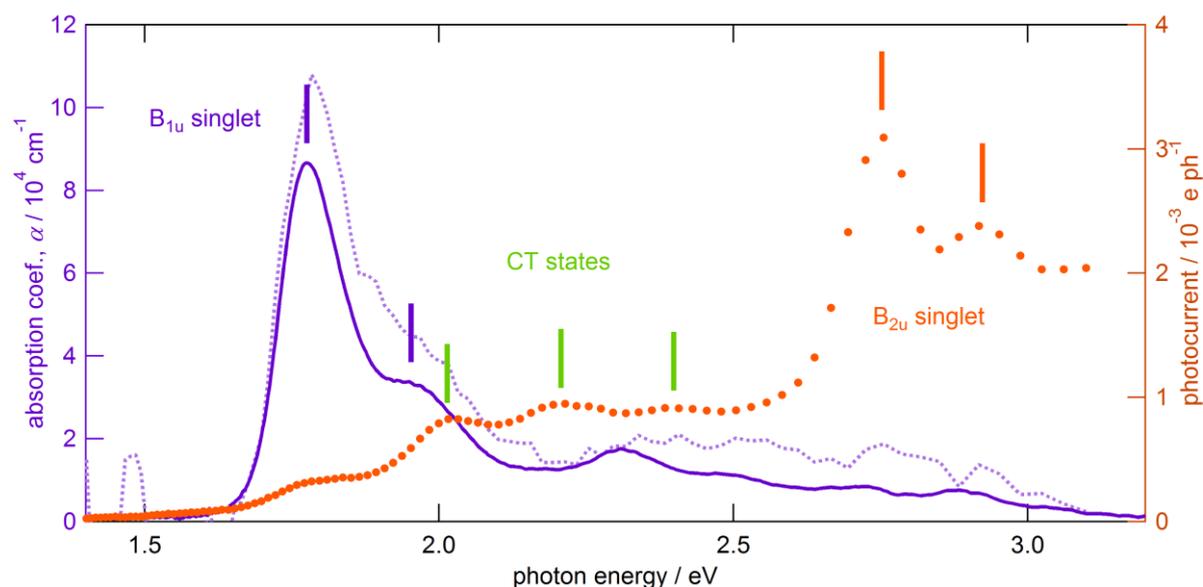
Figure 1. Photocurrent yield (circles) for a 5 nm thick PFP film, with the reference (solid line) and *in situ* (dotted line) absorption spectrum.

Results and Discussion

The dark current in the PFP devices was highly variable, but conductivity was cheifly limited to the first few molecular layers next to the substrate surface. The observed photocurrents are comparatively small. A typical result for a thin PFP film corresponding to this conductive interface region is shown in Figure 1. The *in situ* absorption spectrum is noisy but comparable to the reference: the $S_0{\rightarrow}S_1$ transition starting at 1.8 eV is clearly seen, but the $S_0{\rightarrow}S_3$ transition starting at 2.8 eV is attenuated as a result of the well-ordered, perpendicular orientation of the PFP molecules in the film. The photocurrent spectrum, in contrast, shows a strong signal at 2.8 eV but very little at 1.8 eV. In addition there are a series of regular peaks at 2.0, 2.2, and 2.4 eV which do not correspond to the S_1 manifold that we assign to charge transfer states.

References

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[2] A. Hinderhofer, U. Heinemeyer, A. Gerlach, S. Kowarik, R.M.J. Jacobs, Y. Sakamoto, T. Suzuki, F. Schreiber, J. Chem. Phys., 127 (2007) 194705-194706.