

UV photocurrent spectroscopy in poly(*p*-phenylene vinylene) and derivatives

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Abstract

We present photocurrent measurements of poly(*p*-phenylene vinylene) (PPV) and derivatives for photon energies up to 5.0 eV. We observe photocurrent peaks related to the first, second and third absorption peaks, which we associate with the dissociation of a succession of increasingly energetic excitons. We have performed INDO/SCI calculations for the five-ring PPV oligomer, which show different distributions of the electronic charge of the exciton wavefunction over the chain at different excitation energies. We discuss the significance of these states for the photoconduction in PPV and question the applicability of a band-based model.

Keywords: Photoconductivity, Poly(phenylene vinylene) and derivatives, Semi-empirical models and model calculations

1. Introduction

The nature of photoexcited states in conjugated polymers such as poly(*p*-phenylene vinylene) (PPV) is subject of intensive debate [1]. A common concept is that of a bound electron-hole pair, i.e. an exciton, situated energetically below a continuum band. The discussion revolves about the strength of the exciton binding energy, ranging from very small binding energies [2] over intermediate values (0.4 eV) [3] to very strong confinement (up to 0.95 eV) [4]

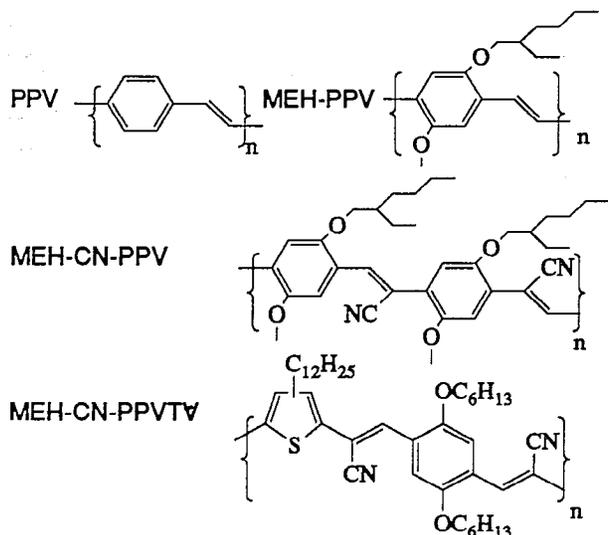


Fig. 1. Structural formulae of the investigated materials

In this paper we present experimental and theoretical results, from which we infer that the notion of a band-based photogeneration model might not be applicable to PPV and its derivatives. We consider the photocurrent in photocells made

with these materials to be caused by the dissociation of different types of excitons associated with the respective absorption peaks.

2. Photocurrent spectra

Photocells were prepared with each one of the materials shown in figure 1 sandwiched between aluminium and semitransparent gold on a quartz substrate. The PPV precursor was converted at 220°C for 10 hs after spin-coating. The short-circuit photocurrent was recorded in air with a Keithly 237 source-measure unit. The photocells were illuminated through the gold electrode with a 150 W Xenon lamp dispersed by a Jobin monochromator fitted with a 1200 g/mm holographic grating blazed at 330 nm. The spectra were corrected for the incident photon number density by measuring the latter with a calibrated silicon photodiode

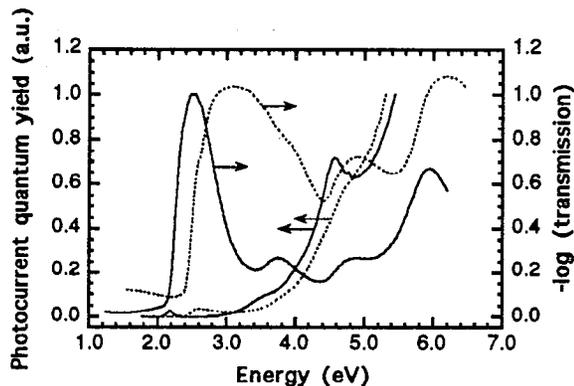


Fig. 2. Absorption and photocurrent spectra of PPV (dotted line) and MEH-PPV (solid line)

Figures 2 and 3 show the absorption spectra and normalised photocurrent quantum yields of PPV, MEH-PPV, MEH-CN-PPV

and MEH-CN-PPVTV. The quantum yields at the first photocurrent peak range between $10^{-2}\%$ and $10^{-4}\%$. All spectra show a strong rise of the photocurrent quantum yield towards photon energies of 5 eV. Superimposed on this rise are features centred at 2.6 eV, 3.8 eV, 4.7 eV for PPV (very weak shoulders), at 2.2 eV, 3.5 eV, 4.5 eV for MEH-PPV, at 1.7 eV, 4.5 eV for MEH-CN-PPV, and at 2.7 eV, 3.2 eV, 3.8 eV, 4.5 eV for MEH-CN-PPVTV. The high energy shoulders are mostly stronger than the first absorption peak, in particular for the cyano-substituted derivatives.

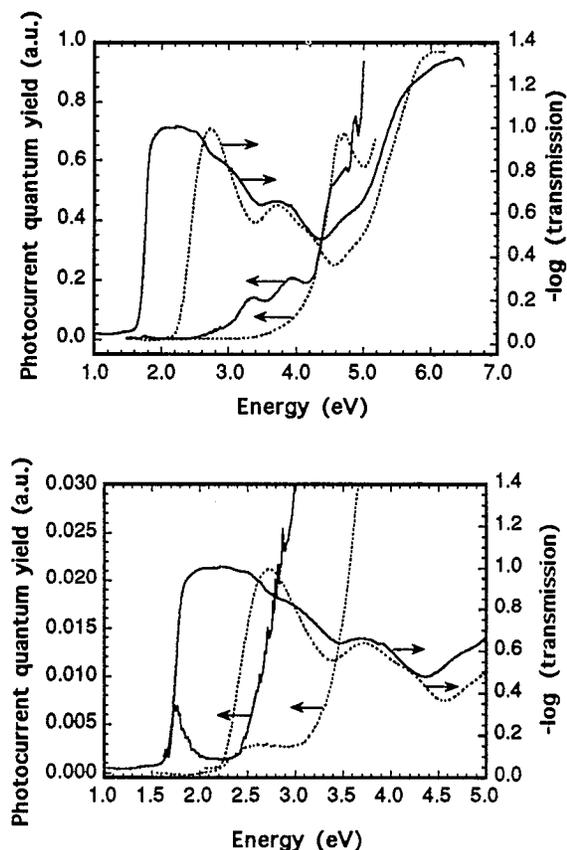


Fig. 3. Absorption and photocurrent spectra of MEH-CN-PPV (dotted line) and MEH-CN-PPVTV (solid line). Bottom figure: smaller scale, same units for photocurrent.

3. INDO/SCI calculations

We performed INDO/SCI calculations for the exciton wavefunction Ψ for the different excited states in a five ring PPV oligomer. All occupied and unoccupied π levels were taken into account in the Configuration Interaction scheme used in these calculations, which is requested for a proper description of the higher-lying exciton wavefunctions. (A similar absorption spectrum can actually be obtained on the basis of a smaller CI active space [5], but such simplified calculation fails in reproducing the correct shape of the wavefunctions for higher-lying excitons). The hole was placed in the middle of the model oligomer, i.e. at site 16. For the excited states contributing to the first absorption peak, the electron density is centred around the hole, while for some of the higher excited states, in particular those contributing to the third absorption peak, the electron

density is large at a distance from the hole and small in the vicinity of the hole (figure 4).

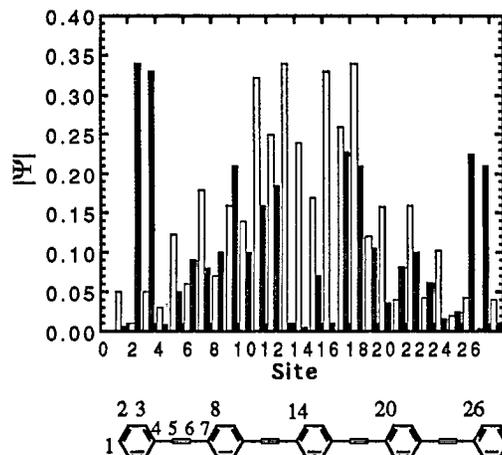


Fig. 4. The five-ring PPV oligomer and the absolute value of the exciton wavefunction as a function of site for excitation into the first absorption peak (white) and into the third absorption peak (black).

4. Discussion

We consider the current rise at high photon energies and the photocurrent shoulders are two different phenomena. On the basis of the work presented above and further unpublished work [6], we attribute the photocurrent shoulders to the dissociation of different types of excitons at the aluminium interface. The different "types" are associated with the different absorption features [7] and we consider their binding energy, that is the activation energy required to obtain two independent carriers, to vary depending on the shape of the wavefunctions and depending on the nature of the excited states involved. For example the wavefunctions of the most prominent excited states located in the third absorption peak are more extended and the analysis of the configuration interaction expansion associated to these states indicates that they involve only transitions from localised to delocalised molecular orbitals and vice versa [6]. The mixing of delocalised and localised orbitals allows for the separation of charge within the exciton (figure 4) and thus facilitates exciton dissociation. The photocurrent yield is therefore larger at 4.5 eV than at the first photocurrent peak (figures 2 and 3).

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