Photocurrent measurements on aggregates in ladder-type poly(p-phenylene)

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Abstract

We report measurements of the photovoltaic effect on single layer devices made with a ladder-type poly-(paraphenylene) (LPPP). Besides the photocurrent in the blue spectral range associated with π to π^* intra-chain absorption we observe an additional response in the yellow part of the spectrum centred at 2.25 eV. We also observe a weak absorption feature at the same energy, and we consider that both arise from absorption into π electron states formed over several aggregated polymer chains. The photocurrent due to excitation of these states is enhanced by two orders of magnitude compared to blue excitation and vanishes under reverse bias (i.e. ITO negative). We find that the photocurrent response due to the aggregate states is more sensitive to oxygen exposure than the response due to intra-chain absorption.

1. Introduction

Poly(para-phenylene)s are of interest as high-efficient blue-emitting luminescent polymer [1,2], and there has been considerable interest in the development of derivatives with improved luminescent and processing properties. A series of ladder polymers, LPPPs, have been developed by Scherf and Müllen [1,2], and these show a range of interesting properties. The structure of the ladder polymer used here is shown in Fig. 1. The planar configuration of the LPPP increases inter-chain order, reduces the bandgap compared to PPP [3,4] and leads to a well-defined conjugation length [5]. In solution, LPPPs show highly efficient photoluminescence, with blue emission associated with intra-chain excitation [6]. In the solid state an additional emission shifted to the yellow part of the spectrum can be observed, which is accompanied by a strong reduction of luminescence efficiency [6,7]. The yellow photoluminescence feature arises because of inter-chain interactions [7–9], which might be present in the ground state, i.e. aggregated states, or which might be caused by interaction in the excited state, i.e. excimers [10]. In solution, the distance between polymer chains is too large for inter-chain interaction to occur. In the solid state, these effects can be suppressed by the addition of spacer groups to the chain which hinder inter-chain interaction [7].

Aggregated states are found in aromatic molecules such as anthracene [11], and different models are currently discussed to account for the electronic excitation spectra of rigidly bridged aromatic chromophores [12]. Aggregation might also be expected to occur in many conjugated polymers. For example various poly(p-phenylene)s (PPP) prepared in differ-

R'= -1.4-C_6H_4-$C_{10}H_{21}$
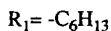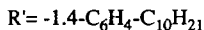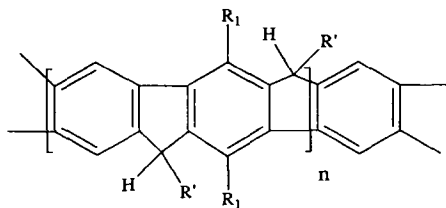
R_1= -C_6H_{13}

Fig. 1. Structural formula of the ladder-type PPP used in this work.

ent ways show a broad unstructured red-shifted emission which might be due to formation of aggregated chains [13,14].

It has been shown that molecular aggregation can allow inter-chain charge-transfer [11]. If excitons extend over several chains the possibility of three-dimensional motion of the electron or hole leads to a better chance avoiding geminate recombination and to increase the exciton splitting rate. Indeed, the increase of yellow emission in LPPP is connected to a decrease of overall luminescence efficiency [7]. We note also that the lifetime of the emission due to inter-chain interaction is found to be longer than the lifetime of the blue emission [15].

The rate of exciton splitting is the key parameter for photogeneration of charge-carriers [16]. Charge transfer onto neighbouring conjugated chain segments leading to bound polaron pairs is suggested to be the dominant mechanism to account for the existence of photoconductivity in PPV [17]. Photovoltaic measurements on LPPP are a useful tool to investigate the photophysics of excited states generated by absorption in the aggregated, yellow, states and in the intra-chain, blue, states.

2. Experimental methods

Photovoltaic devices of ITO/LPPP/aluminium have been fabricated in a sandwich structure as described elsewhere [6]. The polymer was spin-coated from a chloroform solution of 3 wt% onto ITO-coated glass substrates to give films of thickness of about

250 nm. Aluminium contacts were thermally evaporated onto the top of the film, defining the active device area to about 5 mm². The devices were stored under inert gas atmosphere. The photocurrent was measured with the light incident through the ITO. The light source was a 100 W tungsten lamp (Bentham IL 1) dispersed by a single-grating Bentham M300 monochromator with a resolution of 2 nm. A Keithley 237 source-measure unit was used to monitor the current flowing through the sample and to apply a dc bias voltage. The data are corrected for the spectral response of the illumination system and the dark current. The former was done by replacing the sample with a calibrated silicon photodiode. Absorption spectra were taken with a Perkin Elmer 19 spectrometer. All spectra were taken at room temperature and in air.

3. Results

The luminescence properties of LPPPs with different side-chains have been reported previously [6]. The LPPP used here shows a yellow emission that is characteristic of this group.

Fig. 2 shows the photocurrent spectra of LPPP under forward and reverse bias. For comparison the absorption spectrum is also shown. Under forward bias (Fig. 2a) the photocurrent spectrum matches the absorption spectrum very closely in the blue spectral range. In the yellow part of the spectrum an additional photocurrent peak can be observed peaking at 2.25 eV. The energy of this peak is very close to the energy reported for the yellow luminescence associated with possible excimers [8,9]. The photocurrent peak is broad and structureless as is the related luminescence feature [6,9]. This yellow peak is not present in the photocurrent action spectrum under reverse internal field (Fig. 2b). In the blue spectral range the current peak precedes the absorption peak for the internal field in short-circuit condition or reverse bias.

In the absorption spectrum of a drop-cast sample with the same optical density than the film used in the device, we observe a weak absorption feature between 2.0 and 2.5 eV (Fig. 3). In the yellow spectral range at 2.25 eV 0.14% of the incident photons are absorbed (absorption coefficient $\alpha = 25$
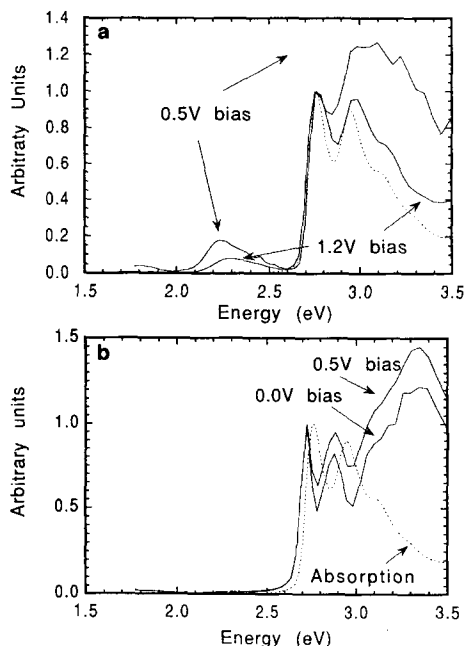
Fig. 2. Spectral response (solid line) in a device in a sandwich structure of ITO/LPPP/aluminum under (a) forward bias and (b) under reverse bias. For comparison the absorption spectrum of this film is also shown (dotted line). The data are corrected for the spectral response of the illuminating system. Note that under forward bias there is a additional photocurrent peak in the yellow part of the spectrum (2.3 eV).

± 20 cm^{-1}). The same absorption coefficient is found in a drop-cast sample which is about 9 μm thick as estimated by comparison of the optical density at 2.65 eV between the two samples. For comparison the luminescence spectrum for excitation at 2.60 eV is also shown. Note that we see only aggregate emission for excitation at this energy. The energy difference between absorption peak and photoluminescence peak from the aggregate is 0.1 eV, while this Stokes' shift for the non-aggregated chains (data not shown here) is 0.2 eV. After correction for absorption and reflection in the photovoltaic device we obtain the following table for values of the quantum yield for photogeneration of charge carriers:

Note that the efficiency of exciton dissociation on the aggregated chains is enhanced with respect to the single polymer chain by a factor of 350 at 0.5 V bias and 150 at 1.2 V bias.

In contrast to the blue photocurrent, the yellow photocurrent disappears for reverse internal field. Fig. 4 shows the current–voltage characteristics for the ITO/LPPP/Al device taken under illumination with blue light, yellow light and in the dark. The I/V curve taken under illumination with blue light is clearly separated from the dark I/V curve and shows a typical diode behaviour. The open-circuit voltage, at which the polymer is expected to have flat bands, is 0.2 V. The I/V curve taken under yellow light follows the dark I/V curve up to 0.2 V and separates at higher bias.

Exposing the device to air is found to decrease the current in both cases, in the dark and under illumination. The photocurrent in the yellow spectral range decays more quickly than the blue photocurrent, both taking several hours. Upon annealing, the original
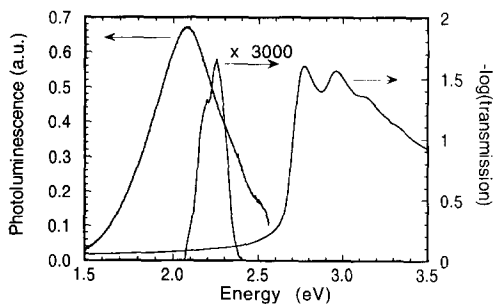

Fig. 3. Absorption spectra of a drop-cast film of the LPPP shown as − log(transmission): the absorption of the aggregated chains shows clearly after subtraction of the baseline. For comparison the photoluminescence spectrum after excitation at 2.60 eV is also shown. No correction for reflection is made.
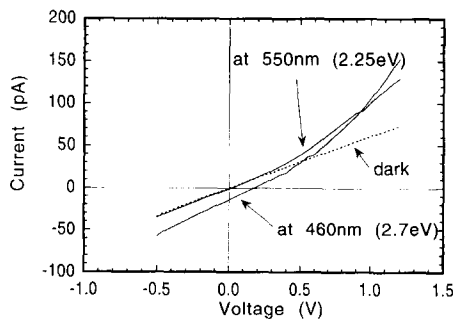

Fig. 4. Current–voltage characteristics of a ITO/LPPP/aluminium device. The data are taken without illumination (dotted line), at the energy of the first blue photocurrent peak (2.7 eV) and at the energy of the yellow photocurrent peak (2.25 eV).

response can be recovered, followed by a quicker decay if further exposed to air. From the decrease of the dark current we conclude that the effect of oxygen on LPPP is not only a quenching of the photoexcited carriers but also a reduction of the overall carrier mobility. Quenching of photoexcited excitons might occur in addition to the trapping of charge carriers. The latter might affect the states of the aggregated chains more due to their longer lifetime [15].

4. Discussion

4.1. Spectral response of photocurrent and absorption

The red-shifted broad unstructured peak in the luminescence spectra was previously considered to be due to the emission of excimers [18], i.e. aggregation of chains stabilised by interaction in the excited state. However, the existence of a photocurrent signal in the yellow part of the spectrum shown in Fig. 2 indicates optical excitation at an energy well below the blue absorption band. The presence of absorption is confirmed by the absorption spectrum (Fig. 3) and the yellow luminescence by subgap excitation [15]. This indicates that the LPPP chains interact and form aggregates with a common ground state. We consider that the excited state at 2.25 eV might be due to the π–π^* transition of these aggregates. The difference in the energies of the peaks in absorption and emission of the aggregate states is small (0.1 eV). This implies relatively little exciton diffusion to lower-energy sites within the aggregate sites.

LPPPs have a high π–π^* gap, i.e. relatively weak delocalisation of π orbitals along the chain, into which the wavefunction of a conjugated segment is squeezed in. Spreading out onto adjacent molecules might therefore be energetically favourable. The formation of aggregates might be assisted by the rigid and planar structure of LPPPs, similar to fused-ring aromatic chromophores such as anthracene, naphthalene and perylene, which form aggregates either in ground or excited state [11,12].

On photoexcitation, the wavefunction of the excitation formed still extends over the aggregated molecules. The spatial separation of electron and hole anticipates a lower exciton binding energy and therefore a higher exciton dissociation probability. This enhancement of the photocurrent quantum yield for the aggregate with respect to the single chain is summarised in Table 1. The spatial separation caused by inter-chain interactions also reduces radiative recombination, consistent with the decrease of overall luminescence efficiency in devices with strong yellow emission [6,7]. In addition, theoretical calculations carried out for crystalline PPP indicate that the three-dimensional character of the crystalline area tends to cause strong inter-chain interaction which reduces excitonic effects in the crystalline bulk [4].

If the bias applied to the device is increased, the difference between the quantum yield of the single chain and the aggregated chains decreases (Table 1). Possibly field-assisted exciton dissociation [16,18] competes with dissociation assisted by charge-transfer.

Under reverse internal field (Fig. 2b) the photocurrent reaches a maximum at a photon energy lower than the absorption peak. This is typical for many polymer photovoltaic devices, and has been explained by a limited range for electrons due to trapping effects [16,19]. The location of the photocurrent peak under reverse bias is determined by the trade-off between absorption depth and electron range. The fact that the photocurrent spectrum under forward bias matches the absorption spectrum indicates that holes can cross the film without being trapped.

Leditzky and Leising [20] suggest that direct ionisation occurs after photoexcitation without excess energy and that the charge separation occurs even at sub-bandgab excitation energy. This suggestion is based on two facts, first the location of the blue photocurrent peak before the absorption peak and

Table 1
Comparison of the quantum yields (electron/absorbed photon) obtained for the aggregated chains (at 2.25 eV) and single chains (at 2.60 eV). Absorption in the film and reflection at the back electrode are taken in account

Energy (eV)	Quantum yield (%)	
	at 0.5 V bias	at 1.2V bias
2.60	0.002	0.1
2.25	0.7	15

second the coincidence of the blue photocurrent peak with the photoluminescence peak. However, the former only occurs beyond the onset of absorption, and the latter might easily be coincidental due to the relative small Stokes shift in LPPPs. We therefore conclude the location of the photocurrent peak does not indicate subgap ionization.

4.2. Bias dependence of photocurrent

From Figs. 2 and 3 is evident that absorption into the aggregate states occurs. The existence of blue and yellow luminescence after excitation in the blue spectral range [6] indicates energy transfer into aggregate states. We consider here possibly contributing processes for generating charge carriers by photoexcitation in the LPPP. Firstly, light of energy 2.8 eV is absorbed on a single polymer chain and an exciton is created. The exciton dissociates on the polymer chain by the mechanism discussed above. This gives a photocurrent in the blue spectral range. Secondly, light with 2.8 eV is absorbed by the polymer chain and creates an exciton. The exciton migrates onto the aggregate and dissociates there. By this process, excitons on the aggregate also contribute to the photocurrent in the blue spectral range. Thirdly, light with 2.3 eV is absorbed by the aggregate, creating an exciton there which subsequently dissociates, giving raise to a photocurrent in the yellow spectral range.

The current–voltage curves taken at different illumination energies (Fig. 4) show the coincidence of flat-band condition and onset of yellow photocurrent. Also, Fig. 2 shows a photocurrent in the yellow spectral range only if the device is under forward bias (ITO positive with respect to aluminium), but not under reverse bias.

Under reverse bias holes are pulled towards the ITO electrode and electrons are pulled to the aluminium electrode. If the aggregates were formed near to the ITO interface, trapping of electrons crossing the polymer film could account for the disappearance of the current. However the coefficient for the aggregate absorption is found independent of film thickness indicating a distribution of aggregates throughout the whole film depth. The bias dependence observed could be caused by photoionisation of the aggregates at the ITO interface. We note that

due to the low absorption coefficient the polymer film is illuminated at both electrodes. The offset between the electrode workfunction and the polymer Fermi level is about 0.5 eV larger for ITO than for aluminium. This causes a larger potential drop at the ITO interface which might explain the asymmetric response. The increased electrical field at the interface might initiate the complete separation of the relatively long-living [15] electron–hole pairs which are already spatially separated on the aggregate. From the very different quantum yields for yellow and blue excitation and the symmetrical response upon blue excitation we infer that this mechanism does not affect the excited states on a single chain.

The thermally stimulated current (TSC) measurements of Leditzky and Leising [5] indicate the presence of traps at 0.1 and 0.4 eV above the HOMO level of the bulk chain. Leditzky and Leising assign the trap levels of 0.4 eV to the presence of distortions of the local electronic structure which might result from structural peculiarities such as partial agglomeration. They note that these features might also act as traps for singlet excitons. It might be possible that the aggregates observed in our measurements are the partial agglomeration they discuss.

4.3. Oxygen dependence of current

A stronger yellow fraction in the luminescence spectrum in LPPP sample was reported to occur upon annealing. This was commonly attributed to the assistance of the heat on the formation of excimers [8]. In the light of our results, it is likely that, by annealing the device, not only aggregation is assisted, but also oxygen is expelled, which improves the transport properties of the polymer. Exciton or carrier migration from the single chain onto the low energy aggregate sites is more likely to occur resulting in a enhanced yellow luminescence with respect to the blue one.

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