Enhanced photocurrent response in photocells made with platinum–poly-yne/C_{60} blends by photoinduced electron transfer

A. Köhler [a], H.F. Wittmann [a], R.H. Friend [a], M.S. Khan [b], J. Lewis [c]

[a] *Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK*
[b] *Department of Chemistry, College of Science, Sultan Qaboos University, PO Box 36, Al-Khad 123, Oman*
[c] *University Chemical Laboratory, Lensfield Road, Cambridge CB3 9BB, UK*

Abstract

We report photocurrent and photoluminescence measurements on blends of the organometallic polymer Pt–poly-yne and C_{60}. Due to efficient intersystem crossing, triplet excitons with a binding energy of at least 0.8 eV are created after photoexcitation of Pt–poly-yne. We find that electrons are transferred from Pt–poly-yne onto C_{60} by efficient ionization of the triplet exciton. This process gives rise to a photocurrent quantum yield of up to 1–2% in photocells fabricated in a layer structure of indium–tin oxide (ITO)/Pt–poly-yne and 7 wt.% C_{60}/aluminium. Evidence for the ionization of the strongly bound triplet excitons is provided by studies of luminescence in the blends. There is only partial quenching of the singlet emission band, but complete quenching of the triplet emission band, and the lifetime of the triplet emission at room temperature is reduced from 2 to 0.1 μs upon addition of 7 wt.% C_{60}.

Keywords: Fullerene; Photocurrent; Photocells; Blends; Platinum

1. Introduction

The mechanism of exciton dissociation and the relationship between the exciton binding energy and the generation of free carriers are of current interest. In hydrocarbon polymers such as poly(p-phenylenevinylene) (PPV) there are divergent views about the strength of electron–hole correlation, ranging from negligible interaction [1–3] to strong binding [4–7]. It was recently suggested that the formation of bound electron–hole pairs (excitons) upon photoexcitation of a polydiacetylene effectively inhibits photoinduced electron transfer onto C_{60}, and that thus the presence of photoinduced electron transfer from PPV and poly(3-alkylthiophene) (P3AT) implies the creation of free carriers upon photoexcitation [2]. However, in this work, we show that there clearly is efficient separation of strongly bound triplet excitons on the organometallic polymer Pt–poly-yne by electron transfer onto C_{60}.

Pt–poly-yne (Fig. 1) is a metal complex in a square planar configuration. There is π-electron delocalization along the chain, particularly for the unoccupied states, as mixing occurs between the π^*-orbitals of the conjugated ligands, i.e. the acetylenic groups spaced by a p-phenylene group, and the metal 6p-orbitals [8,9]. The metal ions act as a barrier to this delocalization, so that optical excitations are expected to have the character of molecular excited states. Indeed, the triplet exciton is confined to one monomer unit [10]. Most of the photoexcited states in this organometallic polymer are triplet excitons, as the presence of the heavy metal atom platinum causes a strong intersystem crossing (with an efficiency of 99% at low temperatures [11]) from the singlet manifold at 3.2 eV to the triplet manifold at 2.4 eV. This polymer is therefore special in the sense that the triplet channel is directly accessible to observation in both absorption and luminescence [11], and thus provides a model system to study the role of strongly bound triplet excitons in conjugated polymers. In this respect we note that the binding energy of the triplet exciton is at least as large as the exchange energy to the singlet exciton, i.e. 0.8 eV. This high binding energy will make charge separation difficult, although we found a weak photoresponse in this material attributed to ionization of the triplet exciton [12].

In the present work, we find a long lifetime (2 μs) for these triplet states at room temperature which allows time for diffusion of the excitons to interfaces where charge separation is possible. We used addition of C_{60} to assist in the dissociation of excitons on Pt–poly-yne, since C_{60} is known to be a good electron acceptor. For example, it is dopable with alkali metals, it shows n-type semiconducting behaviour [13], and its high electron affinity has already successfully been used for charge transfer from conjugated polymers [14–16].

2. Experimental methods

Photocells were fabricated in a layer structure of indium–tin oxide (ITO)/Pt–poly-yne and C_{60}/aluminium. Pt–poly-yne and C_{60} were dissolved in dry deoxygenated toluene. The solutions were then mixed to give blends with 7 wt.% C_{60} (purity 99.9%) or 10 wt.% C_{60} (purity 98%). Thin films were spin-coated from this solution. The processing steps were carried out under argon atmosphere, apart from the fabrication of pure Pt–poly-yne devices. The devices have an active area of 0.4 cm². The films had an optical density of about 1.5. They were illuminated by a tungsten lamp dispersed by a Bentham M300 single-grating monochromator. The photocurrent was measured and a bias was applied with a Keithley 237 source-measure unit. To correct for the spectral response of the illumination system the device was replaced by a calibrated UV-enhanced silicon photodiode.

Excitation for the photoluminescence measurements was provided by the 364 or 457 nm line of an argon ion laser. The peak heights of the spectra depend critically on the geometry of the experimental setup and thus vary a little with the experimental conditions. For the time-resolved photoluminescence measurements the tripled output of a Q-switched Nd:YAG laser (355 nm, about 10 ns pulses) was used as an excitation source. The integrated photoluminescence signal for energies below 2.41 eV was detected with a Hamamatsu model R1387 photomultiplier tube and monitored with a fast oscilloscope.

3. Results

The short-circuit photocurrent action spectra for the Pt–poly-yne and the blend with C_{60} are shown in Fig. 1, along with optical absorption spectra. Note that the photocurrent onset is at the threshold for singlet absorption in the Pt–poly-yne in both cases. Upon addition of C_{60} to Pt–poly-yne the quantum yield, i.e. the number of collected charge carriers per incident photons, rises by two orders of magnitude from

Fig. 2. Current spectra of (a) a device with only Pt–poly-yne and of (b) a device with a Pt–poly-yne/C_{60} blend (7 wt.% C_{60}, purity 99.9%) at various applied biases as indicated in the figure. The dashed vertical lines indicate the position of the photocurrent peak at 3.15 eV for forward bias and at 3.25 eV for reverse bias. The spectra are not corrected.

0.01 to 1.6%. Apart from the enhanced response no change in the photocurrent spectrum is seen, in particular no current due to excitation of C_{60} (Fig. 1). Also, no change occurs in the absorption spectra upon addition of C_{60}: neither a superposition of the C_{60} absorption spectrum with the Pt–poly-yne spectrum, nor an appearance of new subgap absorption features (Fig. 1). The latter indicates that no ground state charge transfer occurs.

The position of the photocurrent peak in devices made with only Pt–poly-yne is dependent on the direction of the internal field in the device (Fig. 2(a)). For forward bias (Al negative), the peak response is at 3.25 eV (matching the absorption), whereas, for negative bias, the peak response is shifted to 3.15 eV. This is attributed to the low mobility of electrons in Pt–poly-yne [12]. Fig. 2(b) shows that this shift of photocurrent peak with bias still occurs upon addition of C_{60} (7%, purity 99.9%).

To clarify the origin of the enhanced photocurrent response, the photoluminescence spectra of the different films were compared after excitation into the singlet state. The phosphorescence signal from the triplet at 2.4 eV is quenched considerably more than the fluorescence from the singlet at 3.2 eV (Fig. 3(a)). The same feature is observed in thick solutions (optical thickness equal to or greater than 3, concentration 22 mg/ml). Fig. 3(b) shows the phosphorescence signal of a pure Pt–poly-yne film and the Pt–poly-yne/C_{60} film after excitation into the triplet state. Even although the illumination intensity for the blend film was increased by a
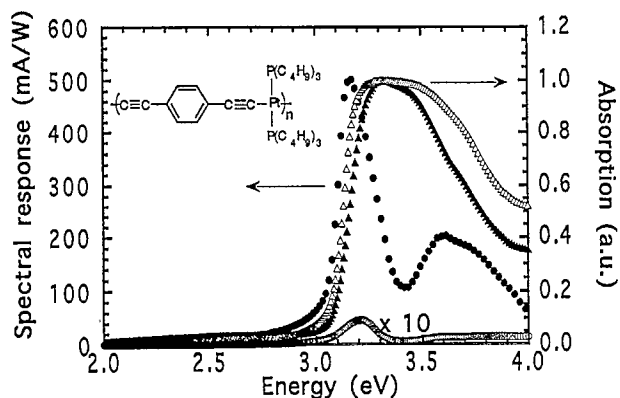

Fig. 1. Photocurrent spectra under short-circuit conditions (circles, left axis) and normalized absorption spectra (triangles, right axis) of Pt–poly-yne (open symbols) and a Pt–poly-yne/C_{60} blend (filled symbols). The blend contains 10 wt.% C_{60} of 98% purity. The photocurrent response for Pt–poly-yne is magnified by a factor of 10. The inset shows the structural formula of Pt–poly-yne.
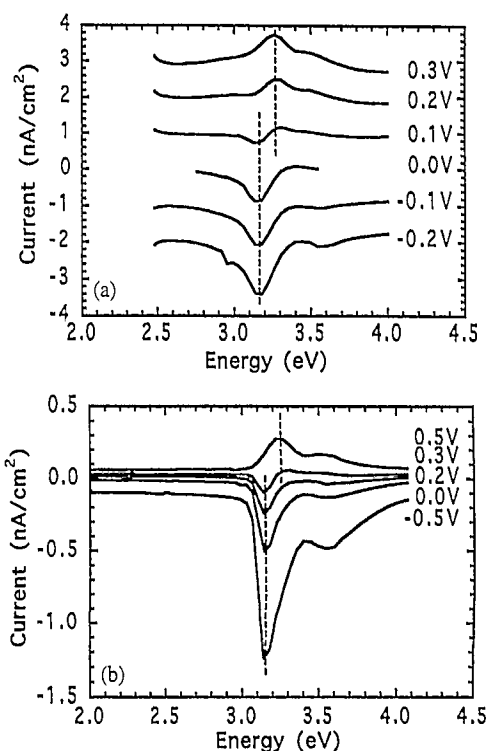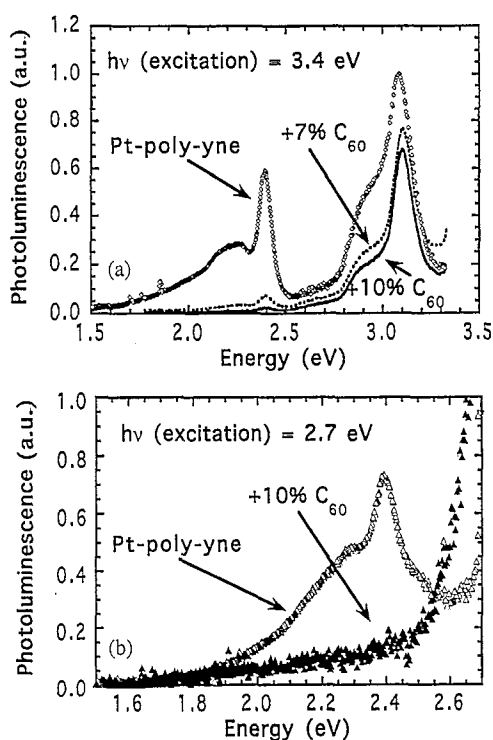
Fig. 3. Photoluminescence spectra of films of (a) Pt–poly-yne (diamonds), Pt–poly-yne with 7 wt.% C_{60} (purity 99.9%) (dotted line) and Pt–poly-yne with 10 wt.% C_{60} (purity 98%) (solid line) after excitation at 3.4 eV into the singlet state, and (b) of Pt–poly-yne (open triangles) and Pt–poly-yne with 10 wt.% C_{60} (filled triangles) after excitation at 2.7 eV into the triplet state.

factor of ten over that used for the data in Fig. 3(a), no phosphorescence signal can be detected.

In a similar way, the lifetime of the phosphorescence signal is reduced by a factor of 20 upon addition of C_{60}. The decay of the luminescence signal in thick solutions (optical thickness equal to or greater than 3, concentration 22 mg/ml) of the Pt–poly-yne and the blend can be fitted mono-exponentially to give a lifetimes of 2.1 and 0.1 µs, respectively (Fig. 4).

4. Discussion

Upon photoexcitation in Pt–poly-yne, the resulting excited states are mostly strongly bound triplet excitons [11,17]. These are confined to one monomer unit [10], have a lifetime of 2 µs at room temperature and a binding energy of at least 0.8 eV. To give a rise to a current, these electron–hole pairs need to be separated. The resulting charge carriers need to be transported through the film and to be collected at the electrode.
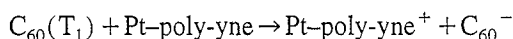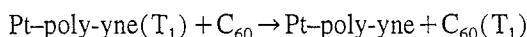
Adding C_{60} to Pt–poly-yne causes an enhanced quantum yield of carriers (Fig. 1). However, the position of the photocurrent peak still depends on the direction of the internal field in the device (Fig. 2), which is an effect caused by electron trapping [12]. This indicates also that the current is still dominated by hole transport. The concentration of about 7% C_{60}, i.e. a ratio of 14:1 for Pt–poly-yne to C_{60}, is too low

to allow a percolation path through the C_{60}. Thus electron transport must still occur via the Pt–poly-yne chains. On the other hand, the photoresponse is found to be strongly enhanced. As addition of C_{60} does not improve absorption or charge transport and collection, this points to an increased charge separation, i.e. the dissociation of the triplet exciton by transfer of the electron onto the C_{60}.

Two mechanisms of charge separation are possible. Firstly, the electron of the triplet exciton on Pt–poly-yne can be transferred directly onto the C_{60} molecule, yielding positively and negatively charged ions:

$$Pt\text{–}poly\text{–}yne(T_1) + C_{60} \rightarrow Pt\text{–}poly\text{–}yne^+ + C_{60}^-$$
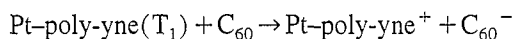
Secondly, the triplet exciton on Pt–poly-yne can transfer its energy to C_{60}, thus exciting a triplet exciton on C_{60}. C_{60} in the triplet state is very electronegative and will easily capture an electron from the triplet excited state of another Pt–poly-yne chain:

$$Pt\text{–}poly\text{–}yne(T_1) + C_{60} \rightarrow Pt\text{–}poly\text{–}yne + C_{60}(T_1)$$

$$C_{60}(T_1) + Pt\text{–}poly\text{–}yne \rightarrow Pt\text{–}poly\text{–}yne^+ + C_{60}^-$$

In either of the two processes the result is the dissociation of the triplet exciton by electron capture of C_{60}.

The photoluminescence measurements have shown that the triplet emission is more strongly quenched than the singlet emission upon addition of C_{60}, and that complete quenching of the triplet exciton occurs after direct excitation into the triplet state (see Fig. 3). Thus, the transfer occurs mainly from the triplet exciton and not from the singlet exciton, since the ratio of phosphorescence to fluorescence would not otherwise be affected. The concentration of C_{60} is low, so that there are not enough C_{60} molecules in the vicinity of a singlet exciton on the Pt–poly-yne chain for dissociation of the singlet exciton, while the long-living triplet excitons can diffuse to the C_{60} molecules, where they are quenched. This is confirmed by the reduction of the triplet lifetime upon addition of C_{60} (Fig. 4).
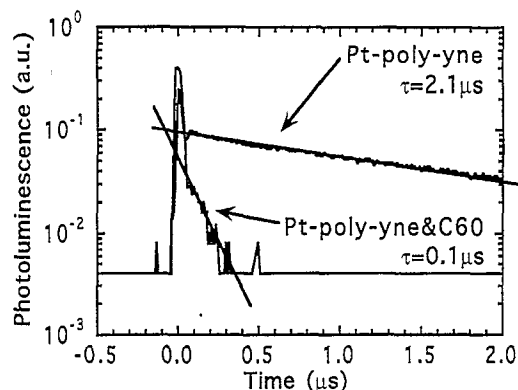

Fig. 4. Time-resolved phosphorescence signals of a Pt–poly-yne solution and a solution of Pt–poly-yne with 7 wt.% C_{60} (purity 99.9%). The decay times are indicated in the figure.

5. Conclusions

We have shown that transfer of electrons from Pt–poly-yne onto C_{60} occurs by ionization of the triplet exciton in Pt–poly-yne. This process occurs efficiently despite the high binding energy of the triplet exciton of at least 0.8 eV, as the long lifetime of the triplet exciton allows for diffusion to the C_{60} sites. This process gives rise to quantum yields of up to 1–2% in photocell structures with ITO and aluminium electrodes.

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