Photophysics and photovoltaic device properties of phthalocyanine–fullerene dyad:conjugated polymer mixtures

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Abstract

The phthalocyanine–fullerene dyad Pc-C60 is an intramolecular donor–acceptor system that can be used as photoactive material in photovoltaic devices. The photocurrent shows maxima below 400 and 700 nm, but only a small response in the range around 500 nm. To improve the spectral match to the solar emission spectrum, an energy transfer process from the conjugated polymer poly [2-methoxy-5-(3′,7′-dimethyloctyloxy)-1-4-phenylene vinylene] MDMO-PPV (antenna system) to the dyad compound can be used. The photophysics of the energy transfer process was studied with luminescence measurements and sub-picosecond time-resolved transmission changes. The influence of the polymeric antenna system on the photovoltaic device properties was measured with spectrally resolved photocurrent (IPCE) measurements. Photocurrent in nearly the full visible spectral range was obtained. In addition, Pc-C60 was also added as third component to MDMO-PPV:PCBM mixtures. The photocurrent around 700 nm was increased, however with reduction in the short-circuit current under white light illumination.
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1. Introduction

For the investigation of photoinduced electron transfer processes in organic molecules, both, a strong fundamental interest for the photophysics, and also the tentation to use the systems for applications like solar energy conversion devices, have boosted a great experimental and theoretical effort. Dyad systems composed of electron-acceptor molecules covalently linked to photoactive donors are candidates to perform photoinduced electron transfer [1–7]. Due to their outstanding electronic and optical properties, fullerenes as electron accepting units in combination with phthalocyanines as electron donors appear particularly promising. Recently, charge transfer states with lifetime of 3 ns have been reported for phthalocyanine–fullerene dyad compounds in solution [8], as well as long living photoinduced charge separation (lifetime 0.2 ms) in the solid state [9]. The long lifetime of the charge separated state opens a possibility to collect the charges at suitable electrodes and to use such electron transfer systems in organic photovoltaic applications. Indeed, photovoltaic devices using films of phthalocyanine–fullerene dyad (Pc-C60) were built and characterized [9]. The devices showed photocurrent in the spectral ranges below 400 and around 700 nm. However, the photocurrent in the range between the two absorption maxima was found to be low.

As has been shown in a preliminary study [10], energy transfer from a light absorbing-conjugated polymer to the dyad (antenna system) may enhance the spectral range of the photocurrent, which improves the spectral mapping to the solar spectrum. In the present paper, the use of the conjugated polymer poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1-4-phenylene vinylene] (MDMO-PPV) as antenna system performing energy transfer to the phthalocyanine-fullerene dyad is described. Photophysical studies including luminescence measurements and investigations of time-resolved transmission changes in the sub-ps range are shown. Spectrally resolved photocurrent measurements of devices build with MDMO-PPV:Pc-C60 show current response not only below 400 and around 700 nm, but also around 500 nm, thus covering nearly the full visible spectral range. Moreover, we show that the incorporation of the dyad molecule into polymer/fullerene blends, as used in bulk heterojunction plastic solar cells [11], gives rise to an enlarged spectral response of the devices, however with reduction in the short circuit current under white light illumination.

2. Experimental

The synthesis of the phthalocyanine–fullerene dyad Pc-C60 has been described in a previous paper [12]. The structures of the dyad and of substituted Zn-phthalocyanine (ZnPc) as a reference compound, and the conjugated polymer MDMO-PPV (Covion), which is used as antenna system for energy transfer to the dyad, are shown in Fig. 1.

Thin film samples for optical measurements were prepared by spin coating with 1500 rpm from toluene or chlorobenzene solution onto fused silica substrates. Luminescence measurements were performed with excitation at 476 nm from an
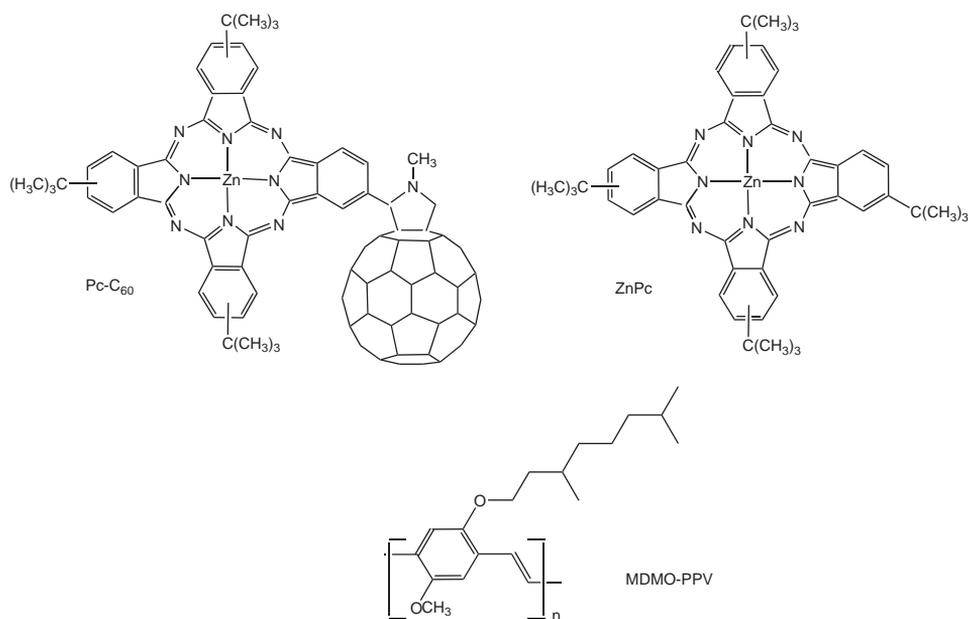
Fig. 1. Structure of the compounds.

argon ion laser. Time-resolved transmission changes have been measured with a sub-100 fs laser system using pump and probe technique. Normalized transient transmission changes $-\Delta T/T$ were measured by spectrally filtering the probe beam and combining differential detection with lock-in amplification. The set-up of the system has been described elsewhere [13]. Photovoltaic devices were built on transparent indium tin oxide (ITO)-coated glass, covered with a thin film of PEDOT:PSS (Baytron P from Bayer AG) to improve the ohmic contact with the organic semiconductor. On top of it, the active layer ($\sim$100–150 nm) was prepared by spin coating from toluene or chlorobenzene solution. The top electrodes were vapour deposited through a shadow mask, using films of LiF and Al [14]. The photovoltaic device characteristics were measured under illumination intensity of 80 mW/cm^2 of white light from a solar simulator (Steuernagel). A lock-in technique was used to measure the incident photon to current efficiency (IPCE). With this technique the number of electrons produced from the cell under short-circuit conditions are related to the number of incident photons [15].

3. Results and discussion

3.1. Photoluminescence studies

Evidence for energy transfer from MDMO-PPV to phthalocyanine is found from luminescence measurements. Fig. 2 compares the luminescence spectra of MDMO-
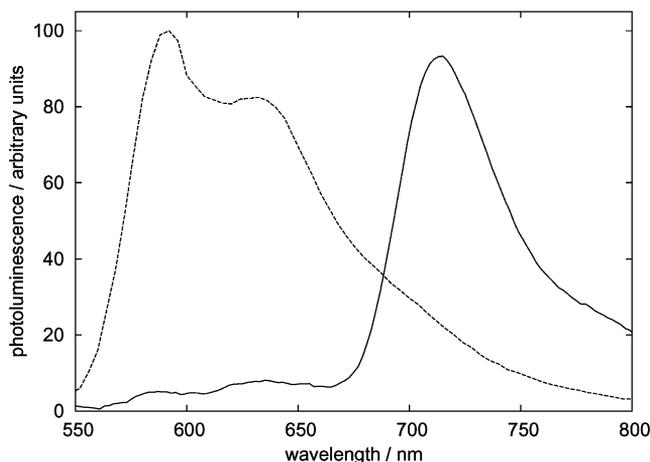
Fig. 2. Luminescence spectra of MDMO-PPV (dashed curve) and of a mixture of MDMO-PPV with 5% ZnPc (solid curve). Films prepared from 5 mg/ml toluene solution. Excitation at 476 nm.

PPV (dashed curve) and of a mixture of MDMO-PPV with 5% ZnPc (solid curve). With excitation at 476 nm, where only MDMO-PPV absorbs, the luminescence of the pure polymer can be seen in the range around 600 nm. In the mixture, the MDMO-PPV luminescence around 600 nm is quenched, and luminescence from ZnPc at 720 nm occurs. Since the absorption of ZnPc at 476 nm is very weak, the results are strong indications for energy transfer from the conjugated polymer to phthalocyanine.

3.2. Time-resolved transmission measurements

To study the kinetics of the energy transfer reaction, time-resolved transmission changes of the MDMO-PPV:ZnPc mixture have been measured. Spectra obtained at different delay times after the excitation pulse are shown in Fig. 3. Two distinct negative absorption regions (bleaching) around 500 and 700 nm can be seen. The broad negative feature around 500 nm is correlated with the bleaching of the absorption of MDMO-PPV and shows the depopulation of the ground state after absorption of the excitation pulse. The bleaching decays within about 10 ps. Simultaneously another negative absorption feature at 700 nm occurs, which is attributed to the bleaching of the ground state absorption of phthalocyanine (Q band), due to the energy transfer from MDMO-PPV to ZnPc.

To determine, if the energy transfer reaction occurs not only in mixtures with phthalocyanine, but also with the dyad compound, similar studies have been performed with MDMO-PPV:Pc-C60 mixtures. Fig. 4 shows time traces of the spectral features at 540 nm (bleaching of the ground state absorption of MDMO-PPV) and at 700 nm (bleaching of the ground state absorption of phthalocyanine) for mixtures MDMO-PPV:ZnPc and MDMO-PPV:Pc-C60. As can be seen, the rates for
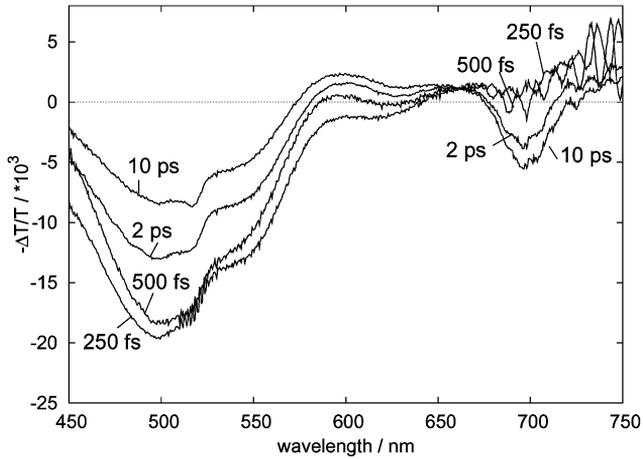
Fig. 3. Time-resolved transmission changes after excitation at 476 nm of a mixture of MDMO-PPV with 5% ZnPc. Film preparation conditions as for Fig. 2.

all spectral changes are quite similar, indicating a similar energy transfer process in both mixtures.

3.3. Photovoltaic measurements

Utilizing the energy transfer process described in the previous section, MDMO-PPV may be used as antenna system for photovoltaic applications of Pc-C60. In addition to the absorption below 400 and 700 nm from Pc-C60, which has been shown to give rise to photocurrent in these spectral regions [9], the absorption of MDMO-PPV around 500 nm is expected to contribute also to the photocurrent. Fig. 5 shows the IPCE spectra of photovoltaic devices made with Pc-C60 (solid curve) and with Pc-C60:MDMO-PPV mixtures (10%, 25% and 50%). Indeed, the absorption range around 500 nm contributes to the photocurrent. In the series measured, the highest IPCE value around 500 nm was found with the Pc-C60:MDMO-PPV (10%) mixture (dashed curve), however with decrease in the photocurrent related with the Pc-C60 absorption features below 400 and around 700 nm. The open circuit voltage with white light illumination at 80 mW/cm^2 was 0.5 V, which is significantly larger compared with the 0.32 V obtained with pure Pc-C60 devices [9]. However, the short circuit current in the mixture is lower (reflected also by the lower current in the maxima of the IPCE curve), indicating charge transport problems within the device.

With increasing MDMO-PPV concentrations (dotted and dash-dotted curves in Fig. 5), the IPCE efficiencies decrease further. However, the relative contribution from the MDMO-PPV absorption at 500 nm relative to the peaks at 360 and 700 nm increases. With the mixtures, the photocurrent response covers nearly the full visible spectral range. For practical applications, improvement of the charge transport
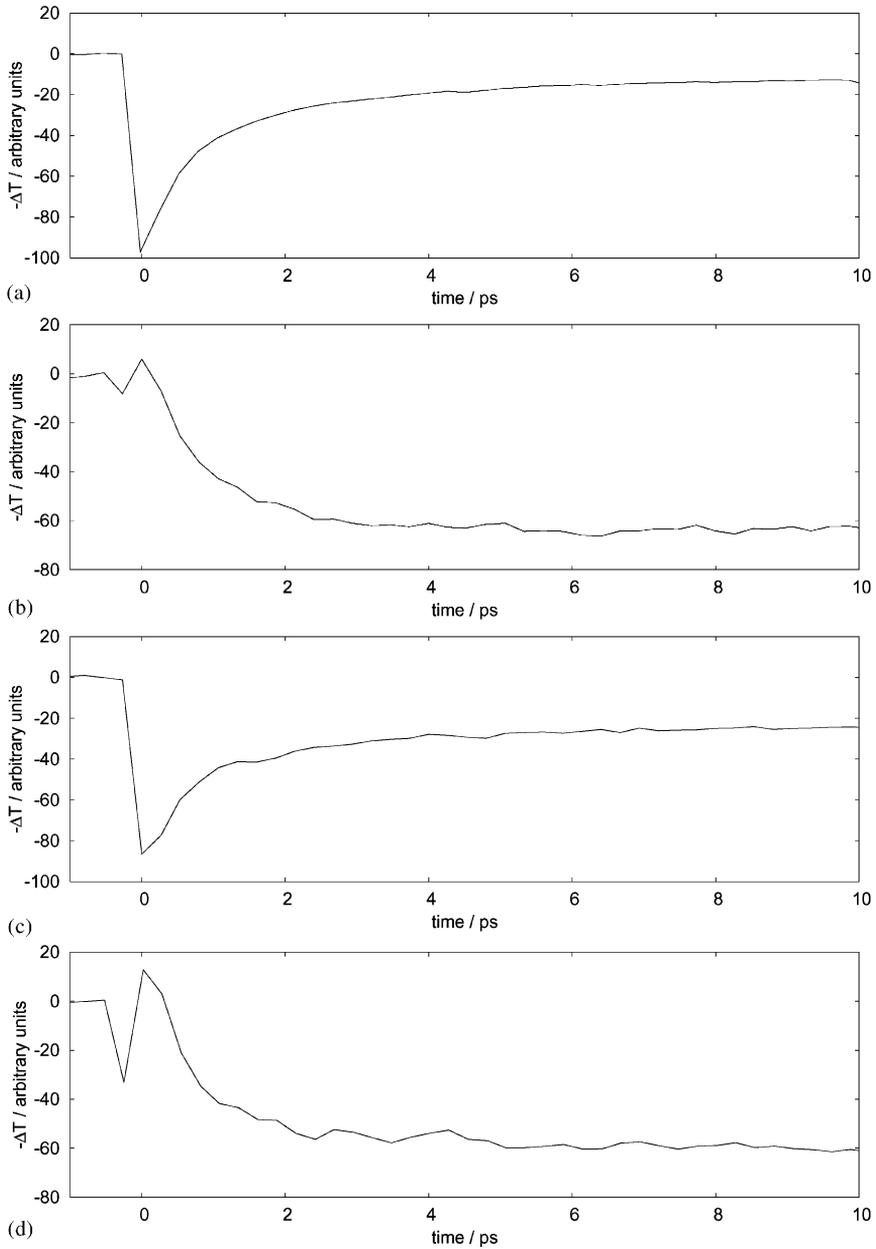
Fig. 4. Time traces of the features at 540 and at 700 nm for mixtures MDMO-PPV:ZnPc and MDMO-PPV:Pc-C60. (a) MDMO-PPV:ZnPc, 540 nm, (b) MDMO-PPV:ZnPc, 700 nm, (c) MDMO-PPV:Pc-C60, 540 nm, and (d) MDMO-PPV:Pc-C60, 700 nm.
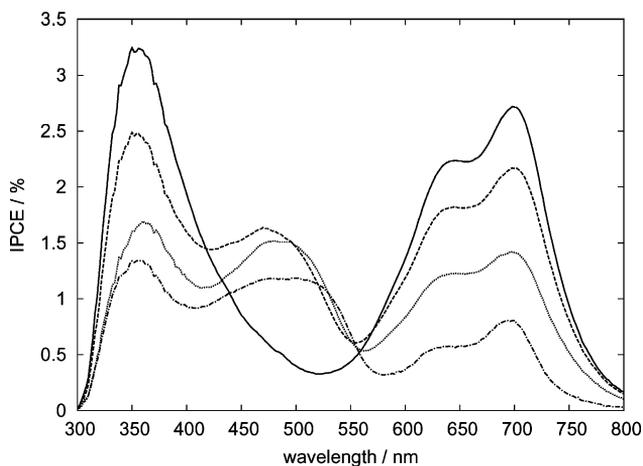
Fig. 5. IPCE (incident photons to current efficiency) curves of photovoltaic devices made with Pc-C60 (solid curve, prepared from 16 mg/ml chlorobenzene solution) and with Pc-C60:MDMO-PPV mixtures (dashed curve 10% MDMO-PPV, prepared from 12 mg Pc-C60 + 1.2 mg MDMO-PPV per ml chlorobenzene solution; dotted curve 25% MDMO-PPV, prepared from 10.8 mg Pc-C60 + 2.7 mg MDMO-PPV per ml chlorobenzene solution; dash–dotted curve 50% MDMO-PPV, prepared from 3 mg Pc-C60 + 3 mg MDMO-PPV per ml chlorobenzene solution).

properties of the devices is necessary for the enhancement of the photovoltaic properties.

As another strategy for extending the spectral range of the photocurrent in organic photovoltaic devices, Pc-C60 was also added as third component to MDMO-PPV:PCBM mixtures (PCBM = methanofullerene [6,6]-phenyl C61-butyric acid methyl ester). Devices with MDMO-PPV:PCBM have been used successfully in organic photovoltaics and showed power efficiencies of 2.5% under AM1.5 conditions [11]. However, the spectral response of devices with MDMO-PPV:PCBM is limited by the absorption of MDMO-PPV to the spectral range below 550 nm. By adding Pc-C60 to the system an enlargement of the spectral range of the photocurrent especially in the range around 700 nm (absorption of Pc-C60) is expected. Fig. 6 compares the photocurrent of MDMO-PPV:PCBM devices with devices made with the ternary mixtures MDMO-PPV:PCBM:Pc-C60. As can be seen, in the range of 700 nm the photocurrent is significantly increased. Obviously, photoinduced charge separation within the dyad molecule PC-C60 contributes in this spectral range also to the photocurrent of the device. However, the large photocurrent in the range around 500 nm obtained with MDMO-PPV:PCBM devices is strongly decreased. Again, charge transport problems in the ternary mixture either due to morphology problems or due to unfavourable energetic properties of the acceptor levels in the two fullerenic compounds PCBM and Pc-C60 may be the reason for the decrease in the overall efficiency. High-resolution investigation techniques like atomic force microscopy (AFM) or transmission
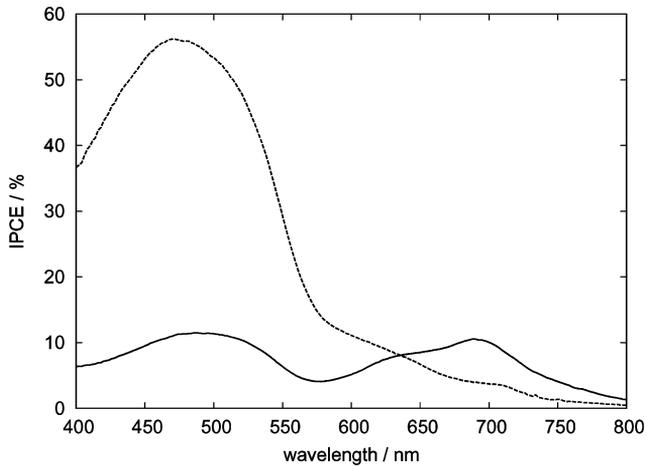
Fig. 6. IPCE curves of MDMO-PPV:PCBM devices (dashed curve) and of devices made with the ternary mixture MDMO-PPV:PCBM:Pc-C60 (25%:52.5%:22.5%). Films prepared from 5 mg/ml chlorobenzene solution.

electron microscopy (TEM) are expected to yield a better insight in the morphological structure [16]. By controlling the morphology and/or influencing the energetic properties (e.g. different chemical substitution) a significant improvement of the device properties seems reasonable.

4. Conclusions

With luminescence and sub-ps time resolved transmission measurements the energy transfer process from MDMO-PPV to the phthalocyanine–fullerene dyad compound Pc-C60 was studied. Based on the results, MDMO-PPV was used as antenna system in photovoltaic devices using Pc-C60 as donor–acceptor system for charge separation. In spectrally resolved IPCE measurements, a photocurrent around 500 nm correlated with energy transfer from MDMO-PPV to Pc-C60 occurs, in addition to the Pc-C60 related photocurrent below 400 and 700 nm, thus covering nearly the full visible spectral range. The extension of the absorption range can be used for a better matching of the photocurrent spectrum to the solar emission spectrum. In addition, Pc-C60 was also added as a third component to MDMO-PPV:PCBM mixtures. Devices made with this ternary mixture showed an increase of the photocurrent in the range of 700 nm, compared with MDMO-PPV:PCBM devices. However, both in MDMO:Pc-C60 and in MDMO-PPV:PCBM:Pc-C60 devices, low short-circuit currents indicate charge transport problems. Improvement of the charge transport properties of the devices is necessary to enhance the photovoltaic performances.

Acknowledgements

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