

Long-lived photoinduced charge separation for solar cell applications in phthalocyanine–fulleropyrrolidine dyad thin films†

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The photophysical properties of a new dyad molecule composed of a covalently linked Zn-phthalocyanine (antenna/donor) and a C₆₀ derivative (acceptor) have been investigated. We report experimental evidence of long-lived charge separation in the solid state with a lifetime several orders of magnitude higher than in solution. Such a long lifetime, unusual for phthalocyanine–fullerene dyads, is the basis for possible photovoltaic applications. A first demonstration of a working solar cell using phthalocyanine–fullerene dyads as the active material is presented. Though the power conversion efficiency under simulated solar illumination of 80 mW cm⁻² is found to be moderate (0.02%), it is an encouraging result for application of C₆₀ dyad molecules to photovoltaics.

Introduction

Photoinduced electron transfer in organic molecules is an intensively investigated process in natural as well as in artificial systems. Both the strong fundamental interest in the photo-physical process itself and the desire to mimic synthetically the solar energy conversion which occurs in biological systems have caused a great deal of experimental and theoretical effort to be directed towards these ends.¹ Dyads composed of electron acceptor molecules covalently linked to photoactive donors are candidate materials to perform photoinduced electron transfer.^{2–6} Due to their strong electron-accepting properties, fullerenes (*e.g.* C₆₀, C₇₀) are used as building blocks for these artificial photosynthetic systems.² Several dyads,³ triads⁴ and more complex systems² have been synthesised recently using mostly porphyrin derivatives as donors and C₆₀ as the acceptor.^{2,4} These molecules are able to perform long-lived (up to a few hundred ms⁵) intramolecular charge separation in solution. For this reason, they are considered very promising mimics for photosynthetic systems.^{2,7}

In biological photosynthetic systems, the energy conversion process is initiated by efficient absorption of light in antenna molecules. The energy of the excited state is then transferred to the reaction centre, where charge separation occurs. Efficient light absorption and charge separation are the fundamental steps, not only for natural photosynthesis, but also for photovoltaic devices. In fact, the separation of electrons and holes in an organic solar cell follows roughly the same scheme.^{7,8}

The performance of organic photovoltaic devices^{8,9} is based

on two basic processes: the dissociation of excitons and the transport of the resulting separated charges to electrodes. To achieve these processes effectively, asymmetry between a fast forward and a very slow backward electron transfer is necessary. In conjugated polymer/fullerene-based photoactive devices, the forward electron transfer can be faster than 50 fs, as has been shown by recent measurements,¹⁰ while the back electron transfer is retarded to the micro- or millisecond timescales.^{11,12} This propitious asymmetry is due to the low reorganisation energy of the fullerene molecule.¹³

In spite of the success of porphyrin–fullerene dyads in performing charge separation, and the chemical similarities between porphyrins and phthalocyanines, previous studies of phthalocyanine–fullerene dyads have not revealed any charge-separated states.^{14,15} Recently, charge-transfer states with lifetimes of 3 ns have been reported for the first time in phthalocyanine–fullerene dyad compounds in solution.¹⁶ Nevertheless, for effective use of such a molecule in photovoltaic applications, a longer charge-separated state lifetime is necessary in the solid state to avoid recombination and increase the chances of positive and negative charges reaching the electrodes.

In the present study, we have investigated the solid-state photophysical properties of a recently synthesised fulleropyrrolidine–phthalocyanine dyad having a Zn-phthalocyanine derivative as the antenna/donor and a covalently attached C₆₀ derivative as the acceptor,¹⁷ which showed, in a preliminary study, experimental evidence for photoinduced electron transfer.¹⁸ The suitability of such a molecule for photovoltaic applications has been tested by the construction and characterisation of photovoltaic devices which employ it as the active material.

Experimental

Thin film samples for optical measurements were prepared by spin-coating from toluene solution onto fused silica substrates.

†Electronic supplementary information (ESI) available: plots of the refractive index, extinction coefficient and dielectric function of Pc-C60. See <http://www.rsc.org/suppdata/jm/b2/b212621d/>

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Transmittance and reflectance spectra were measured with a Varian Cary 3G UV-Vis spectrophotometer. The dielectric function was calculated from the reflectance and transmittance data with the software package SCOUT (M. Theiss Software, Aachen, Germany).

Photoinduced absorption (PIA) measurements on zinc tetratert-butylphthalocyanine (ZnTBPC) and phthalocyanine–fulleropyrrolidine (Pc-C60) films were performed using a diode laser at 685 nm for excitation, while the *N*-methylfulleropyrrolidine (C60-P) film was excited with the UV multiline (maximum at 363.8 nm) of an Ar⁺ laser. The laser beam was chopped mechanically with a frequency of about 70 Hz, providing the reference for a lock-in amplifier (SR 830, Stanford Research Systems).

Samples were mounted on the cold finger of an optically accessible cryostat under dynamic vacuum, at a constant temperature of 90 K. A 120 W tungsten halogen lamp provided the light for the transmission measurements. The transmission signal (with and without laser light on the sample) was detected with a Si–InGaAsSb photodiode after passing through a monochromator. The spectral dependence of the negative ratio of the photoinduced changes in sample transmission ($-\Delta T$), corrected for the weak photoluminescence, was plotted after normalisation to the transmission (T). The lifetime of the photoinduced features was characterised by measuring the frequency dependence of the signal up to 3000 Hz.¹⁹

Photovoltaic devices were built on transparent indium tin oxide (ITO)-coated glass. The substrate was covered with a thin film of PEDOT:PSS (Baytron P from Bayer AG) by spin-coating to improve the ohmic contact with the organic semiconductor. On top of it, the active layer (~100–150 nm) was prepared by spin-coating from a toluene solution. The top electrodes were vapour-deposited through a shadow mask, using films of LiF and Al. The configuration LiF/Al was chosen to obtain a good ohmic contact between the metal and the active layer.²⁰ The active area was 6 mm². The device fabrication and characterisation was performed under Ar atmosphere.

I/*V* characteristics were measured using a Keithley 2400 SMU unit under illumination with white light of intensity 80 mW cm⁻² from a Steuernagel Solar Simulator. 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.²¹ Light intensity correction was performed using a calibrated Si photodiode.

Results and discussion

Photophysical characterisation

In Fig. 1, the chemical structure of phthalocyanine–fulleropyrrolidine (Pc-C60) is shown. The details of the chemical synthesis of this novel dyad have been reported elsewhere.¹⁷ Similar phthalocyanine–fullerene dyads with larger spacers have been synthesised in the past.^{14,15} However, experimental evidence for charge separation was not found in these compounds. The length and nature of the spacer seem to be very critical, since they control the distance and angular position of the donor and acceptor parts and, consequently, the interaction of wavefunctions. These electronic interactions influence both the rate and quality of the photophysical activities of the molecule, like electron and/or energy transfer.²²

The high optical quality of Pc-C60 and ZnTBPC films permits direct and reproducible measurement of reflectance and transmittance data for the determination of the dielectric function and the absorption coefficients. To overcome the problem of obtaining homogeneous films of the fullerene reference compound (C60-P) a blend with PMMA [poly(methyl methacrylate)] was used. The dielectric function was

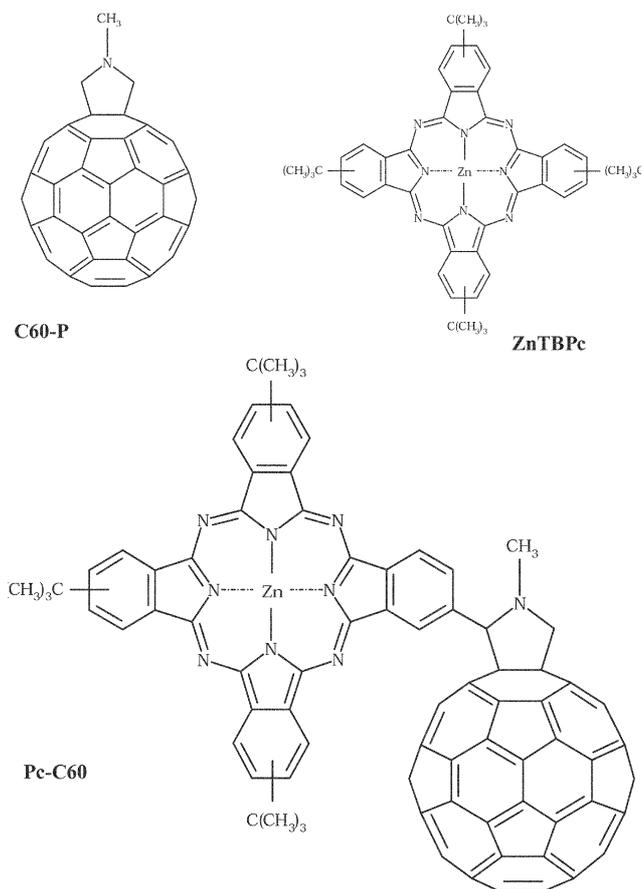


Fig. 1 Chemical structure of the phthalocyanine–fulleropyrrolidine dyad (Pc-C60) and the component molecules ZnTBPC and C60-P.

then calculated using a model for a homogeneously dispersed spherical filler (C60-P) within a matrix (PMMA). In Fig. 2, the absorption spectra for the two parent molecules ZnTBPC and C60-P, as well as the Pc-C60 dyad are compared. The dielectric functions, refractive index and extinction coefficient of Pc-C60 are reported in the ESI.†

Two main absorption features dominate the spectrum of ZnTBPC in thin films, *i.e.* the Soret band at 340 nm, and the two components of the Q-band at 635 and 681 nm. C60-P shows the main absorption peak at 317 nm, and a long and weak tail extending over the whole visible range.

The absorption spectrum of Pc-C60 shows noticeable differences from the sum of the spectra of the two parent molecules. In particular, Pc-C60 shows a Soret band at 337 nm and the two components of the Q band at 640 and 685 nm, with

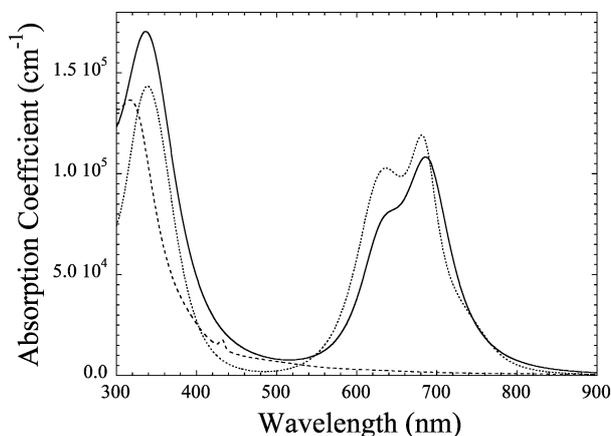


Fig. 2 Absorption coefficients at 300 K of thin films of Pc-C60 (continuous line), ZnTBPC (dotted line) and C60-P (dashed line).

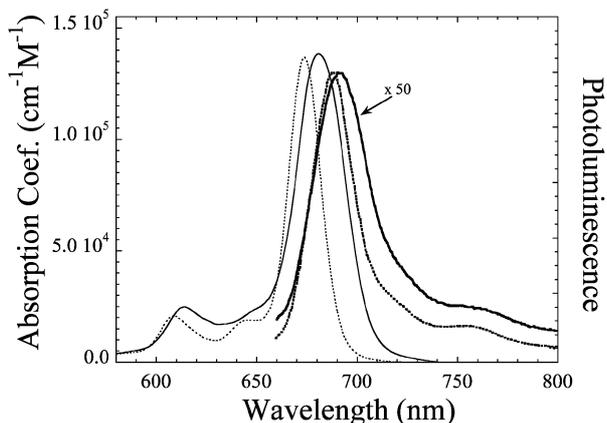


Fig. 3 Absorption (thin lines) and emission (thick lines) spectra of Pc-C60 (continuous lines) and ZnTBPC (dashed lines) in 5×10^{-6} M CHCl_3 solutions. Photoluminescence excitation at 650 nm.

different relative intensities compared to the parent molecule's spectrum. The dissimilarities can be ascribed both to hindered π - π stacking of the phthalocyanines in the Pc-C60 film due to the bulky fulleropyrrolidine and to ground state charge-transfer interactions. Evidence for a weak charge-transfer interaction has even been reported recently for co-evaporated films of Zn-phthalocyanines and C_{60} .²³ However, ground state interaction considerations are ambiguous in the solid state, since the Q band of phthalocyanines is also strongly influenced by intermolecular packing.²⁴

In Fig. 3, the absorption and the photoluminescence spectra of Pc-C60 and ZnTBPC in chloroform solution are shown. The absorption spectrum of Pc-C60 shows a clear shift of the Q-band with respect to that for ZnTBPC. This is a clear sign of a strong electronic interaction between the two parent molecules in the dyad. In particular, the differences in the 700–850 nm spectral region of the emission spectra have been interpreted by Guldi *et al.* as evidence for a charge-transfer interaction in the Pc-C60 dyad.¹⁶ In solutions of the same molar concentration, the dyad molecule shows a photoluminescence intensity which is 50 times lower than that observed for ZnTBPC. The quenching of the photoluminescence in solution is again a strong indication of intramolecular charge separation, as confirmed by picosecond transient absorption measurements, which gave a lifetime for the charge-separated state of 3 ns.¹⁶ However, the existence of charge separation in solution is not sufficient to confirm the suitability of the Pc-C60 dyad for solid-state solar energy conversion devices. In principle, intramolecular charge separation can be followed

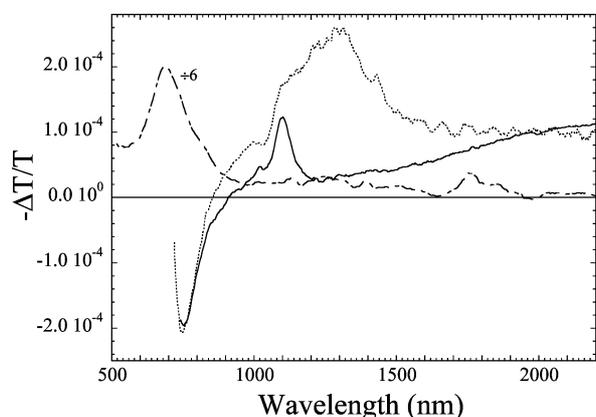


Fig. 4 Photoinduced absorption spectra of Pc-C60 dyad (continuous line), ZnTBPC (dotted line) and C60-P (dashed line) films. Excitation at 685 nm and UV multiline Ar^+ laser; $T = 80$ K.

either by recombination on the same molecule (favoured in solution) or by intermolecular charge separation, which is necessary for solar energy conversion purposes in the solid state, due to the longer lifetime and the necessity to transport the photoinduced charges to the opposite electrodes.

Photoinduced absorption spectra of thin films of Pc-C60 dyad and of the parent molecules are shown in Fig. 4. The spectrum of ZnTBPC shows a negative signal at 750 nm due to the bleaching of the ground state absorption (see Fig. 2) and a large broad absorption feature at ~ 1300 nm that we tentatively assign to a triplet transition. The PIA spectrum of a thin film of C60-P dispersed in the inert matrix (dashed line) is also presented in Fig. 4. The spectrum is dominated by a narrow feature peaking at 690 nm, which is assigned to a triplet transition, as reported in the literature for C_{60} .^{25,26} The PIA spectrum of the Pc-C60 dyad (solid line) has three main features: the bleaching of the ground state absorption at 750 nm, a narrow absorption peak at 1100 nm, and a broad absorption feature around ~ 2200 nm. The narrow band at 1100 nm is characteristic for the anion of the fullerene derivative.²⁷ The nature of the broad feature in the far infrared is uncertain, it is possibly due to a charge-separated state. The strong absorption peak at 1300 nm in the ZnTBPC spectrum disappears completely in the dyad spectrum.

In Fig. 5, the modulation frequency dependence of the absorption features at 1100 (fullerene anion) and 2100 nm (possibly related to the charge-separated state) in the Pc-C60 PIA spectrum is reported. By fitting the data using a model developed for the study of the dynamics of photoexcitation in amorphous materials, which are generally governed by dispersive phenomena,¹⁹ mean lifetimes of about 0.2 ms are obtained for both spectral features.

The lifetime in the solid state of about 0.2 ms is several orders of magnitude longer than has been reported for the molecule in solution,¹⁶ which is a clear indication that the stabilisation of the charge-transfer state in this material is aided by the intermolecular interaction. The long-lived charge separation provides the possibility of using the dyad as the active material in photovoltaic devices.

Photovoltaic devices

As compared to devices built by vacuum vapour deposition techniques using mono- and/or multilayers of small molecules,^{28–31} the Pc-C60 dyad system has the advantage of possible solution deposition and the use of a single layer. In the bulk heterojunction approach, which has been successfully realised for conjugated polymer/fullerene solar cells,^{8,9,32} problems with macroscopic phase separation of the components, giving rise to inefficient charge separation and transport, may occur.^{6,33} In a dyad system, where the donor and acceptor

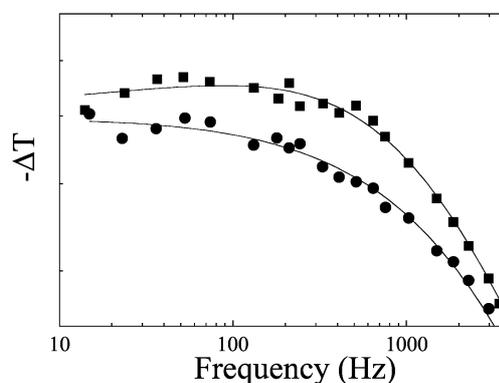


Fig. 5 Modulation frequency dependence of the 1100 (●) and the 2100 nm (■) features of the Pc-C60 spectra. The continuous lines are obtained following a fitting procedure.¹⁹

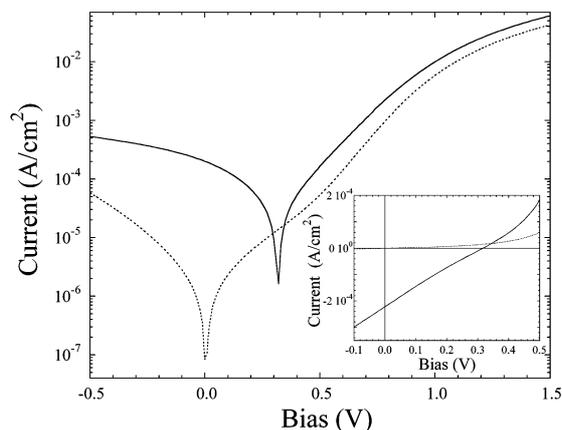


Fig. 6 Semilogarithmic and linear (inset) representations of the current density–voltage characteristics of a Pc-C60 cell. The continuous line represents data obtained under 80 mW cm^{-2} white light illumination, while the dashed line plots data measured in the dark.

part are covalently linked, problems with phase separation are avoided. Moreover, an important issue for improving the efficiency of photovoltaic devices is the selection and development of new molecules having good overlap of their absorption spectrum with the terrestrial solar emission spectrum and high absorption coefficients.²¹ Since the maximum of the solar photon flux is around 700 nm, materials efficiently absorbing light in this region are desirable. These requirements are satisfied by the phthalocyanine–fulleropyrrolidine dyad, where the donor and acceptor are covalently linked and the absorption maximum occurs at 700 nm (Fig. 2).

Solar cells using thin films of Pc-C60 as the active material were fabricated by spin-coating from toluene solution in the configuration described in the Experimental section. The current–voltage characteristics are displayed in Fig. 6. Diode behaviour with a rectification ratio of ~ 10 is observed. Under white light illumination at 80 mW cm^{-2} through the ITO electrode, an open circuit voltage of 0.32 V and a short circuit current of 0.2 mA cm^{-2} have been measured. From the data, a fill factor of 0.26 and a power conversion efficiency of 0.02% were calculated.

Fig. 7 reports the spectrally resolved photocurrent of the Pc-C60 device. The spectrum shows a maximum at about 700 nm, which is the same wavelength where the absorption spectrum of a film of comparable thickness has a maximum. The effective production of photocurrent at 700 nm compared to the value around 400 nm is highly important in the effort to achieve the most effective harvesting of solar light. However, the poor

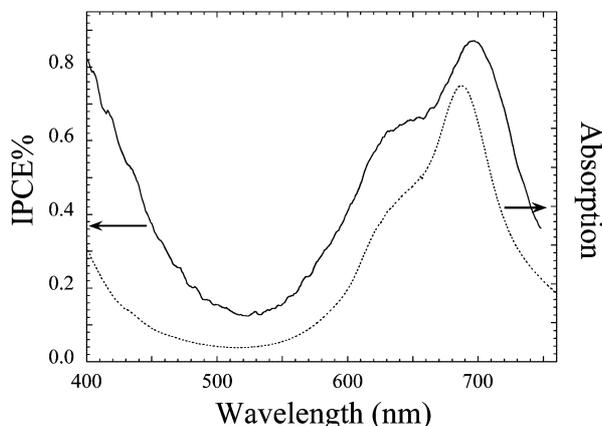


Fig. 7 IPCE measurement of the device using Pc-C60 dyad as the active material. The IPCE spectrum (continuous line) is compared with the absorption spectrum (dotted line).

performance obtained in these test devices with regard to power efficiency needs improvement. Further investigation will be necessary to optimise the device structure and exploit the potential for photovoltaic applications of this new dyad molecule.

Conclusions

We have reported the photophysical characterisation of a novel dyad molecule having a Zn-phthalocyanine derivative as the antenna/donor and a C₆₀ derivative as the acceptor, and fabrication of photoactive devices using this material. We have presented evidence for long-lived photoinduced charge separation in this molecule, which is a prerequisite for its application in photovoltaic devices. Since the absorption maximum of the dyad occurs at 700 nm, this molecule is of great interest for solar cell applications. We have demonstrated working photovoltaic devices which, for the first time, use phthalocyanine–fullerene dyad molecules as the active material. Though the power conversion efficiency under simulated solar illumination of 80 mW cm^{-2} was found to be moderate (0.02%), it is nevertheless an encouraging result for application of C₆₀ dyad molecules to photovoltaics.

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