

Complexation of pyrrolidinofullerenes and zinc-phthalocyanine in a bilayer organic solar cell structure

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Bilayer organic solar cells were prepared using zinc-phthalocyanine (ZnPc) and a novel, highly soluble pyrrolidinofullerene bearing three chelating pyridyl groups (PyF). The formation of supramolecular complexes between the two compounds is indicated by a significantly increased solubility of ZnPc in dichloromethane upon addition of the PyF. Spin-coating a film of PyF on a vacuum-evaporated film of ZnPc results in a solar cell yielding short circuit current (I_{sc}) densities of 3 mA/cm² and open-circuit voltages (V_{oc}) of about 0.4 V under 100 mW/cm² simulated AM1.5 illumination. Solar cells prepared by substituting the PyF with a fullerene derivative forming no complexes with ZnPc show significantly lower photovoltaic conversion efficiencies. © 2005 American Institute of Physics. [DOI: 10.1063/1.2146070]

Significant advances in the field of organic semiconductors enable the development of cheap and flexible solar cells comprising thin photoactive layers of organic materials.¹ These efforts can be distinguished in two approaches to produce thin organic films: thermal evaporation^{2,3} and casting from solution.^{4,5}

In the first approach, metal phthalocyanines are an adequate choice as absorbing layer because of their strong absorption coefficient ($\alpha > 10^5$ cm⁻¹) over a wide range of the solar irradiation spectrum and their sufficient charge transport properties. The phthalocyanines are combined with a material having high electron affinity, such as C₆₀ or perylene derivatives. An efficient photoinduced charge transfer process^{6,7} separates the positive and negative charges, providing a high efficiency for charge generation. The charges have to move to the respective electrodes fast enough to avoid recombination.

In the second approach, a conjugated polymer is utilized as main absorbing material and electron donor and blended with an electron accepting material.^{5,6} The mixture provides a large interface for an efficient charge transfer throughout the whole photoactive volume, forming a "bulk heterojunction." If both phases are above the percolation limit, separate channels for the extraction of the respective charges can be formed. The most widely used electron acceptor in these solar cells is 1-(3-methoxycarbonyl) propyl-1-phenyl [6,6] C₆₁ (PCBM),⁸ which provides excellent charge transfer in combination with a wide range of conjugated polymers.⁴

Recently, a novel family of soluble fullerene derivatives bearing chelating pyridyl groups was synthesized using a route based on the generation of azomethine ylides from picolylamines and aldehydes in a [2+3] cycloaddition reaction with [60] fullerene. Such derivatives are known to form supramolecular dyads with metalloporphyrins.^{9,10} Low-cost production and environmental stability make these compounds interesting for various applications.

In the following we present a study on the complexation between a pyrrolidinofullerene compound bearing three chelating pyridyl groups (PyF) and zinc-phthalocyanine (ZnPc). A route to combine these materials in a bilayer thin-

film organic solar cell is described and the performance of these cells is studied in comparison with reference cells fabricated using PCBM as electron acceptor. The results show a strong enhancement of the photovoltaic activity due to the complexation of the donor and acceptor molecules as compared to noncomplexed structures. The used materials and the solar cell structure are shown in Fig. 1.

The absorbance spectra of the fullerene solutions [0.5 mg fullerene per 1 ml dichloromethane (DCM)] are measured before and after adding 2 mg ZnPc in 3 ml solution followed by gentle stirring and filtering through a 0.45 μ m membrane filter. As a reference, 2 mg ZnPc is added to 3 ml pyridine, stirred and filtered through a 0.45 μ m membrane filter.

The solar cells are prepared on indium-tin-oxide (ITO) covered glass. On this, a layer of PEDOT:PSS (BAYTRON PH) with a thickness of about 70 nm is spincoated. About 25 nm of ZnPc is deposited by thermal evaporation in high vacuum (approximately 10⁻⁶ mbar), followed by placing a

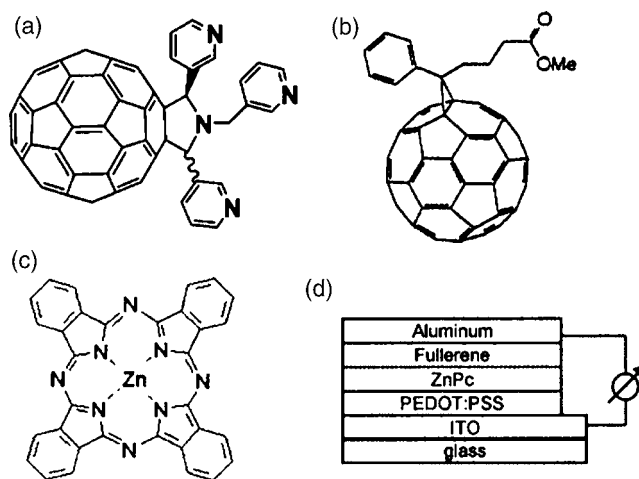


FIG. 1. Structure formulas of the materials used in this study: (a) pyrrolidinofullerene bearing three chelating pyridyl groups (PyF), (b) 1-(3-methoxycarbonyl) propyl-1-phenyl [6,6] C₆₁ (PCBM), (c) zinc-phthalocyanine (ZnPc), (d) schematic layout of the solar cells.

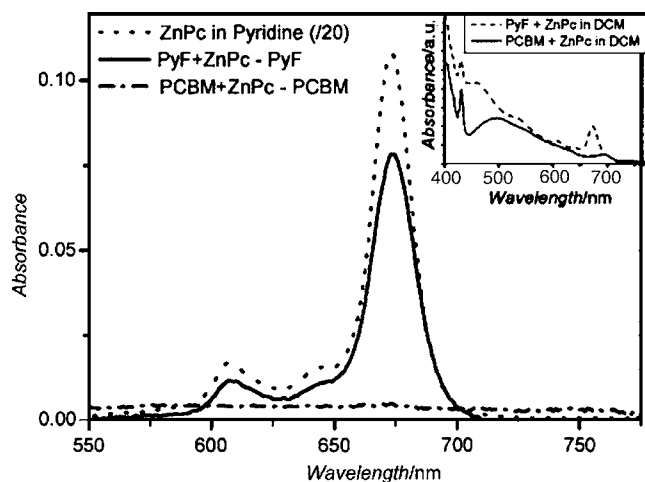


FIG. 2. Difference in the absorption spectra of fullerene solutions before and after the addition of small amounts of ZnPc (solid and dashed-dotted); absorption spectrum of ZnPc in pyridine (dotted, divided by 20). Inset: absorption spectra of the fullerene solutions with added ZnPc.

single drop of the fullerene solution in DCM on the substrate at high spinning speeds (6000–8000 rpm). The samples are transferred to an argon glovebox, where 100 nm of aluminum is evaporated as a back electrode. The active area is approximately $4 \times 2 \text{ mm}^2$.

The PyF solution is prepared and stored in ambient atmosphere while the PCBM solution is kept protected against oxygen and water except for the time of spincoating. The ZnPc-layer is exposed to oxygen after the evaporation to assure the doping necessary to provide good charge transport.¹¹

I-V-characteristics are recorded on a solar simulator (AM1.5, 100 mW/cm^2). The incident photon to collected electron efficiency is measured using chopped monochromatized light from a Xe lamp and a lock-in amplifier.

ZnPc shows very poor or no solubility in most organic solvents, with the exception of pyridine, where a complex with a coordination bond between the zinc and the nitrogen of the pyridine ring is formed. Between ZnPc and DCM there is no complexation and ZnPc is completely insoluble in DCM.

As shown in Fig. 2, this changes significantly upon adding PyF in the solution. The absorption spectrum of a solution of 0.5 mg PyF per 1 ml DCM (solid line in Fig. 2) shows a clear contribution of the ZnPc *Q*-band absorption. A concentration of about $15 \mu\text{g}$ ZnPc per 1 ml solution can be deduced, using a literature value for the molar extinction coefficient ($\epsilon_{674 \text{ nm}} = 2.818 \times 10^5 \text{ cm}^{-1}/\text{M}$) of ZnPc in pyridine.¹² This corresponds to a ratio of one ZnPc per ~ 19 PyF molecules. The difference spectrum shows a high similarity with the absorption spectrum of ZnPc in pyridine (dotted line in Fig. 2), indicating the formation of a complex between the pyridyl groups in PyF and the zinc atom in ZnPc.

The difference spectrum of PCBM in DCM before and after addition of ZnPc (dashed-dotted line in Fig. 2) shows no changes. This means no increase in ZnPc solubility, an indication that there is no coordination between PCBM and ZnPc.

Figure 3 shows the *I-V* characteristics of the solar cell structures. The amount of PCBM and PyF in the solar cells in both cases corresponds roughly to 50 nm thick films,

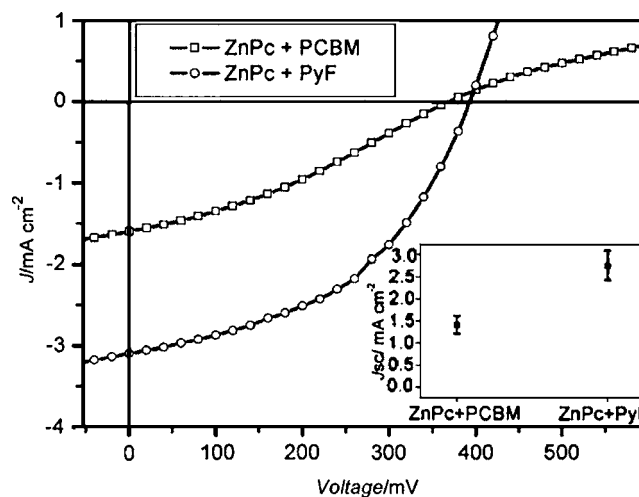


FIG. 3. *I-V* curves of typical solar cells with an active layer of 25 nm ZnPc covered with different fullerenes measured under 100 mW of simulated AM1.5 irradiance. Inset: Photocurrent densities under 100 mW AM1.5 irradiance of 8 cells each for an active layer of 25 nm ZnPc covered with different fullerenes. All devices had an active area of about 0.1 cm^2 .

nearly independent on the concentration (10 mg/ml to 25 mg/ml) of the fullerene solution and the spincoating speed (6000 rpm to 8000 rpm) used, what is probably due to the special spin coating technique as described above and the high volatility of DCM (boiling point $T_b = 40^\circ \text{C}$). The exchange of DCM with chlorobenzene or chloroform results in significantly reduced solar cell output parameters and lower reproducibility.

In the optimal configuration, solar cells fabricated from ZnPc and PyF (round symbols) show short circuit current densities of around 2.7 mA/cm^2 , open circuit voltages of around 400 mV, and fill factors of around 0.4. This corresponds to a power conversion efficiency of approximately 0.5%. In inert argon atmosphere, the performance stays stable over weeks. Contact to ambient atmosphere leads to degradation, presumably due to oxidation of the aluminium.

Solar cells fabricated from ZnPc and PCBM show short circuit current densities of around 1.3 mA/cm^2 , open circuit voltages of around 380 mV, and fill factors of around 0.3. Significant counterdiode behavior is observed.

To explain the superior photocurrent generation in the PyF solar cells, we propose a higher interfacial interaction between the donor and the acceptor due to the specific organometallic coordination interaction between the PyF and the ZnPc. The ordering between ZnPc and PyF¹⁰ may result in a higher overlap of the π -electron wave functions of the donor and acceptor moieties. Additionally, the solubility of the PyF-ZnPc-complex may lead to a more diffuse interface, which can increase the charge transfer probability.¹³ In organic field effect transistors (OFETs), PyF shows significantly lower electron mobilities than PCBM,¹⁴ ruling out a better charge transport in the PyF as reason for the higher photocurrent.

Figure 4 shows the incident photon to collected electron efficiency (IPCE) spectra of the solar cells and the absorption spectra of the active layers. Especially dominant in both spectra is the broad *Q*-band of the solid state ZnPc between 600 and 800 nm. Below 550 nm, the fullerenes give the stronger contribution to the photocurrent. The lower values for the IPCE in the PCBM cell correspond to the lower short

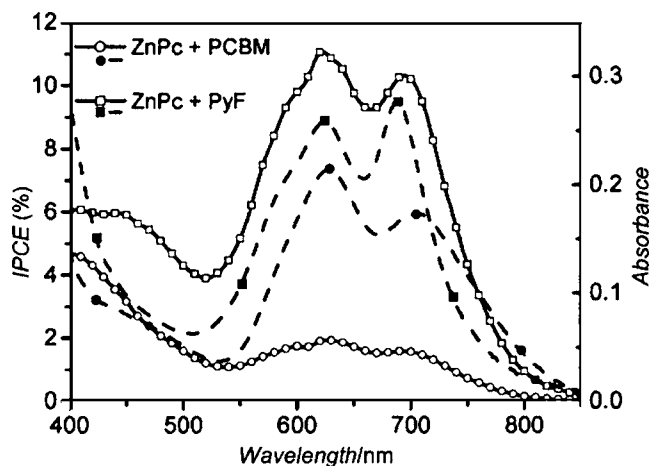


FIG. 4. Incident photon to collected electron efficiency (IPCE) spectra of solar cells with an active layer of 25 nm ZnPc covered with PCBM (solid line, open circles) and PyF (solid line, open squares). Absorption spectra of 25 nm ZnPc covered with PCBM (dashed line, full circles) and PyF (dashed line, full squares).

circuit current densities in the I - V measurements on the solar simulator. Noteworthy is the weighting of the spectral contributions to the IPCE for the different fullerene compounds. With PCBM, the relative ZnPc contribution to the photocurrent generation is considerably smaller than in the cells fabricated with PyF. As the absorption spectra do not indicate a higher contribution of the PCBM absorption, this might be due to a change in the relative efficiencies of the charge transfer between the fullerenes and the ZnPc.

In conclusion, we have prepared solar cells by combining an evaporated layer of ZnPc and a novel highly soluble pyridyl-substituted fullerene derivative and investigated the intermolecular interactions. Relatively high short-circuit current densities of over 2.5 mA/cm^2 were achieved with solar cells of ZnPc and PyF using a special spincoating technique to deposit the fullerene layer.

The complex formation of the pyridyl-substituted fullerenes with ZnPc increases the photovoltaic performance

in this kind of organic solar cells. We propose that an intermolecular complexation between donor and acceptor moieties in organic photovoltaic devices may enhance the charge transfer also in other systems. The performance is yet exceeded by solar cells made from thermally evaporated phthalocyanines and C_{60} ,^{15,16} but with further optimisation of the charge transport properties of the pyrrolidinofullerene material, this gap may be narrowed.

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