



Photoluminescence Studies on the Supramolecular Interactions Between a Pyrrolidinofullerene and Zinc- Phthalocyanine Used in Organic Solar Cells

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Abstract: We present a study of supramolecular interactions between a highly soluble pyrrolidinofullerene bearing three chelating pyridyl groups (PyF) and zinc-phthalocyanine (ZnPc). Photoluminescence quenching shows a non-diffusive concentration dependency, which can be explained by the formation of a non-covalently bonded supramolecular dyad. A further indication for such a complexation is

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observed by a significantly increased solubility of ZnPc in CH_2Cl_2 upon addition of PyF. Solar cells fabricated from a thin evaporated layer of ZnPc and a spincoated layer of PyF show short-circuit current densities of approximately 4 mA/cm^2 with open circuit voltages around 400 mV under 100 mW/cm^2 simulated AM1.5 illumination.

Keywords: Fullerene, phthalocyanine, organic solar cell, complex, photoluminescence, quenching

INTRODUCTION

In recent years, a lot of effort has gone into the search of organic donor-acceptor systems for providing an efficient light induced charge transfer (1) in order to produce organic solar cells (2). Fullerenes as electron acceptors play a very important role in most of these concepts. Fullerenes with attached pyridinyl groups have been studied because of the formation of non-covalent, self-assembled complexes with highly absorbing organic compounds such as metalized porphyrins (3). We study the complexation of a highly soluble pyrrolidinofullerene compound bearing three chelating pyridyl groups (PyF) (4) with zinc-phthalocyanine (ZnPc), a donor material well suited for the use in organic solar cells (5). Using a scheme of in situ complexation during fabrication, we fabricate a photovoltaic device exhibiting open circuit voltages of about 400 mV and a short-circuit current density of over 4 mA/cm^2 . This exceeds the performance of a similar cell using a fullerene without specific coordination interaction with zinc-phthalocyanine. These studies underline results published earlier on this topic (6) by giving further proof of the complexation between PyF and ZnPc.

RESULTS AND DISCUSSION

ZnPc has a very low solubility in most organic solvents. In toluene though, enough ZnPc can be solved to probe its photoluminescence (PL). The PL of ZnPc is strongly quenched by fullerenes due to an efficient photo-induced charge transfer process. To study this process, small amounts of PyF are added to the dilute solution of ZnPc in toluene while the ZnPc PL is monitored. As a reference, the same procedure is done with the soluble fullerene derivate 1-(3-methoxycarbonyl) propyl-1-phenyl [6,6] C_{61} (PCBM), which has no pyridyl groups attached and will form no complex with ZnPc. In both cases, a rapid decrease of PL intensity is observed with an increase in fullerene concentration (Figure 2 right).

To quantify the process, the relative PL intensities are plotted against the molar concentration of the fullerene added to the solution in a Stern–Volmer plot (Figure 2 left). A purely diffusion driven quenching mechanism will give a straight line in this plot. The gradient of this is called the Stern-Volmer

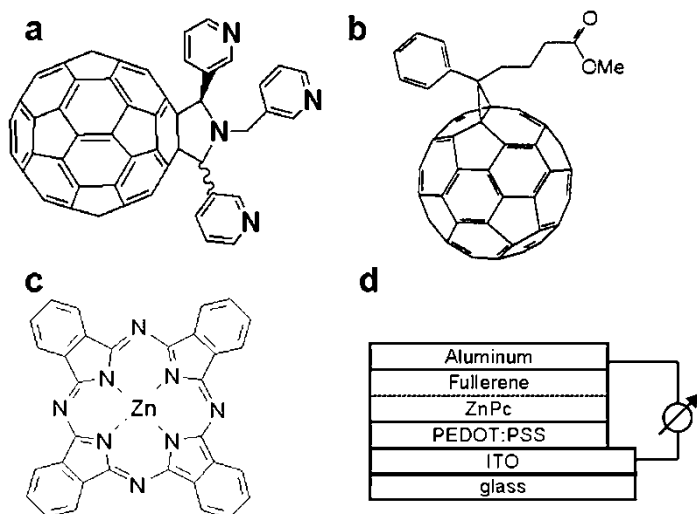


Figure 1. Structure formulae of the materials used in this study: (a) pyrrolidinofullerene bearing three chelating pyridyl groups (PyF); (b) 1-(3-methoxycarbonyl) propyl-1-phenyl [6,6] C₆₁ (PCBM); (c) zinc-phthalocyanine (ZnPc); (d) schematic layout of the solar cells.

constant K_{sv} , which is directly related to the quenching rate via:

$$K_{sv} = k_q/k_f = \tau_f \cdot k_q$$

k_f : Fluorescent rate; k_q : Quenching rate; τ_f : Fluorescence lifetime

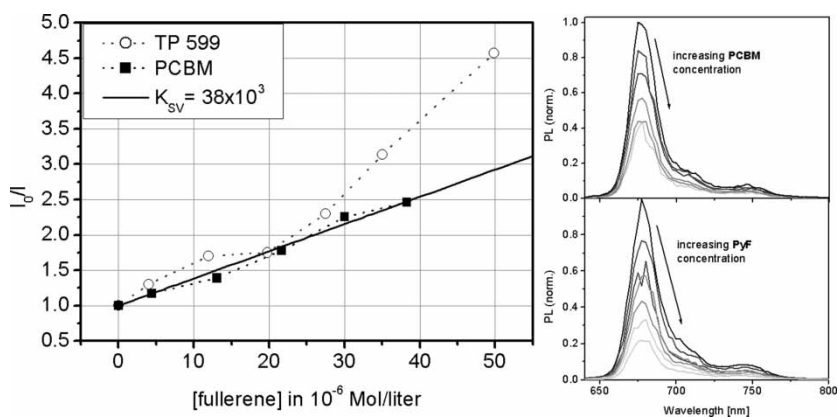


Figure 2. Right: PL spectra of ZnPc in Toluene with increasing amount of fullerenes added. Left: Stern–Volmer plot for the quenching of ZnPc in Toluene by PCBM and PyF.

For the quenching of the ZnPc PL by PCBM, this behaviour is quite clearly observed. A $K_{sv} = 38\,000\text{ dm}^3/\text{mol}$ is derived from the plot. Together with $\tau_f \approx 3\text{ ns}$ (7) and the ZnPc concentration of about 0.1 mg/ml , this leads to a value of $k_q \approx 10^9/\text{s}$.

The quenching of ZnPc with PyF, however, shows a superlinear behaviour in the Stern–Volmer plot, which can be attributed to a non-diffusive encounter of the donor and acceptor molecules. As ZnPc and PyF will be linked together by the non-covalent bonding, this is a further strong indication for the proposed supramolecular interactions.

In contrast to PyF, ZnPc shows an extremely low solubility in halogenated methanes, such as CHCl_3 or CH_2Cl_2 . A thin film ($\sim 40\text{ nm}$) of vacuum evaporated ZnPc retains most of its colour after immersion in CH_2Cl_2 , while it is washed away completely in a highly dilute solution of PyF in CH_2Cl_2 . This is a further indication for the formation of supramolecular complexes, which lead to an enhanced solubility of ZnPc. But even with the effect of increased solubility of the complex, the amount of ZnPc in a mixed solution is too small to assure a high absorption in a solar cell structure where a blend of ZnPc and PyF is spincoated to form a “bulk heterojunction.”

The deposition of the fullerene compound onto an evaporated layer of ZnPc is performed by putting a drop of solution ($\sim 10\text{ mg}$ PyF per ml CH_2Cl_2) onto the rotating substrate at very high spinning speeds (8000 rpm). The fast evaporation of the solvent assures that the film of ZnPc is not disrupted and a “diffuse bilayer junction” between PyF and ZnPc is probably formed.

The photovoltaic performance of solar cells fabricated using this technique is displayed in Figure 3. To study the influence of the complex

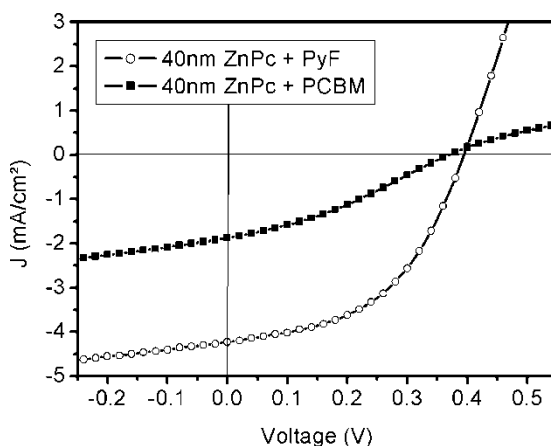


Figure 3. I-V-characteristics of solar cells fabricated with PCBM and PyF on ZnPc under 100 mW simulated AM1.5 illumination.

formation on the device parameters, we compare the performance of solar cells comprising PyF and PCBM as acceptor materials. The open circuit voltages of both devices are around 400 mV, the main difference being in the short-circuit current density and the fill factor. Both are significantly higher in the case of PyF.

Acceptor material	V_{oc} (V)	J_{sc} (mA/cm ²)	FF
PyF	400	4.2	0.48
PCBM	380	1.9	0.33

The structure of the interface between ZnPc and PyF may be strongly influenced by the formation of the supramolecular complexes. We propose two favourable aspects of the complexation: First, the orientation of the two molecules in the complex may enhance the overlap of the π -orbitals, thus increasing the charge-transfer rate. Second, the increased solubility of the complex may ensure a more favourable nanomorphology at the interface, which will enhance the stability of charge separation and ensures a better transport of the charges to the electrodes.

In conclusion, we have studied the supramolecular interactions between a pyrrolidinofullerene compound and zinc-phthalocyanine. These interactions lead to an improvement of organic solar cells when occurring in situ during the film formation. We propose that this concept of coordination between donor-acceptor moieties might also be applied in the production of other organic optoelectronic devices to improve their performance.

EXPERIMENTAL

The structure formulae of the used materials as well as a schematic of the solar cells are shown in Figure 1. The quenching studies were performed with an Edinburgh Instruments LP920 flash photolysis spectrometer using a Coherent Infinity Nd:YAG laser running at 355 nm as excitation source. The photoluminescence of a solution of ~ 0.1 mg/ml ZnPc in toluene was measured before and after adding small amounts of concentrated fullerene solution. The solubility was probed by putting 15×15 mm glass slides covered with ~ 40 nm of ZnPc into CH_2Cl_2 and a solution of 0.5 mg PyF per ml CH_2Cl_2 followed by gentle shaking for about 5 minutes.

The solar cells were prepared by cleaning a slide of ITO-covered glass, followed by spincoating a PEDOT:PSS solution (Baytron PH). The ZnPc layer had a thickness of 40 nm and was evaporated in high vacuum (10^{-6} mbar) from a heated ceramic crucible. The substrate temperature was kept at about 70°C. On this layer, the PyF was spincast as discussed in the results section. As back electrode, about 100 nm of Aluminum were

evaporated. IV-characteristics of the solar cells were measured under 100 mW simulated AM1.5 conditions in an argon glovebox.

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