The Use of Combinatorial Materials Development for Polymer Solar Cells

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We use a combinatorial approach to develop molecular plastic solar cells based on soluble fullerene derivatives blended with conjugated polymers. A combinatorial way of sample preparation is well suited to deal with the multitude of possible combinations of the components of such blends. We use high mobility poly(thiophene) and poly(phenylenevinylene) derivatives to be combined with acceptors. Gradients of methanofullerene/polymer concentration were formed by diffusion of the low molecular weight component in the spin-cast polymer matrix. Likewise the gradients of zinc phthalocyanine/C60 were prepared by co-evaporation of the two materials from two sources to make a linear array of photodiode devices. Photo- and electrophysical properties, such as absorption, luminescence, short circuit photocurrent and open circuit photovoltage, were measured using a specially designed installation with a resolution of 70±100 µ. Clear evidence was obtained that the photoconversion efficiency increased with the amount of methanofullerene up to very high levels, in the case of methanofullerene/polymer blends, verifying the important role of the acceptor in the photoconversion. By choosing the optimal ratio between C60 and ZnPc in the evaporated layer it is possible to obtain high photocurrent in the 600–700 nm range, due to the added contribution from photoinduced electron transfer between the two molecules. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

To develop molecular plastic solar cells we need both advanced organic synthesis and supramolecular engineering on the materials level in order to develop efficient device structures based on the photoinduced charge transfer between donor and acceptor moieties. We need a number of different donors/acceptors in order to collect sufficient energy from the solar spectrum. In order to cope with the multiplicity of polymer/acceptor molecules combinations, we have developed a combinatorial technique to generate many different stoichiometries along a concentration gradient. This allows us to study the behaviour of soluble fullerene derivatives when mixed with different conjugated polymers in a systematic fashion.

There is a great need to handle the many possible combinations, and this offers one route to make many compositions along a distance of 20–30 mm, and to investigate them with the help of local probes. With absorption spectroscopy we can evaluate the concentration of the different species (if they have sufficiently distinct spectra); with luminescence spectroscopy we can estimate the degree of photoluminescence quenching due to photoinduced charge transfer; with diode measurements we can evaluate the efficiency of photo-
current generation. The same techniques can be used to evaluate most gradient structures.

In order to increase the energy conversion efficiency we wish to enhance the optical absorption and photocurrent generation in the 600–700 nm range; where the optical absorption of polymers under study is not high enough. Here we use a low molecular weight donor, zinc phthalocyanine, which can be co-evaporated with C$_{60}$ to form the blends. ZnPc has a strong absorption in the mid-visible range, and photoinduced charge transfer between ZnPc and C$_{60}$ is known. It is also known that the ratio between C$_{60}$ and ZnPc, as well as the substrate temperature, can significantly change the photovoltaic properties of the devices. We therefore extended the combinatorial technique to study all the possible ratios between C$_{60}$ and ZnPc in device structures. Forming the gradient of ZnPc in C$_{60}$ is easily done by co-evaporation of both molecules onto a surface from two separate sources at a distance; a gradient will be formed along the space extending in between the two evaporation sources. These structures are then used for evaluation of solar cell performance.

**EXPERIMENTAL**

The chemical reagents used in our research were:

Fullerene C$_{60}$, Fluka Co.

PCBM (6,6) phenyl-C$_{61}$-butyric acid methylester (methanofullerene), Groningen University

ZnPc Zinc Phthalocyanine, Fluka Co.

MDMO-PPV poly[2-methoxy-5-(3',7-dimethyloctyloxy)-1,4-phenylene vinylene], Eindhoven University

PTOPT poly (3-(4-octylphenyl)2,2-bithiophene, Chalmers Technical High School

To generate the diffusion profiles of low molecular weight components in polymers, we put a small drop of the solution of methanofullerene (PCBM, [6,6]-phenyl-C$_{61}$-butyric acid methyl ester), dissolved in a mixture of toluene and chloroform, at the centre of a spin-cast polymer layer. Toluene swells the polymer without dissolving it, while chloroform dissolves the polymer. By varying the ratio between these two solvents, one can control the ratio between methanofullerene diffusion through the swollen matrix and the mutual dissolution of polymer and PCBM. In this way we can obtain concentrations ranging from 0 to 100% of PCBM within a polymer matrix, over lengths 20–30 mm.

To add ZnPc/C$_{60}$ blends in devices, we co-evaporated ZnPc and C$_{60}$ to form mixed layers on the top of polymer layers. The two substances were thermally evaporated in the evaporation chamber from two different boats, separated spatially. The evaporation was carried out simultaneously, with the fluxes being approximately equal. Since the angular distribution of flux from the evaporation boats is Knudsen-like: flux $\sim \cos \theta$, where $\theta$ is the angle between maximal flux direction (perpendicular to the boat plane) and any other flux direction, placing the substrates at the different positions in the evaporation chamber one can vary the ratio of ZnPc:C$_{60}$ varying the angles, under which the substrate sees the evaporation sources, as well as the distances to them.

Thus, the layers having different ratios between C$_{60}$ and ZnPc on top of the polymer films were obtained during one evaporation cycle, allowing the determination of the components’ influence on the photocurrent generated in the structure.

To study the optical and photovoltaic properties of all these structures, the scanning measurement set-up was developed (Fig. 1), allowing the quantitative detection of absorbance, photoluminescence, short circuit photocurrent and open circuit photovoltage with a spatial resolution as high as $\sim$ 100 $\mu$m. Measurements were performed by
means of focusing light from a Xe-lamp (300 mW) or monochromatic light as luminescence excitation beam (WL $\sim$ 430 nm) onto the surface of the sample, which was then moved stepwise using a mechanical drive. The focused spot size is around 100 $\mu$m and each step moves the sample by 30 $\mu$m, thus allowing measurements with the resolution of $\sim$ 100 $\mu$m.

The scanning absorbance measurements are realised by means of projecting a collimated beam from the Xenon lamp through the sample onto a CCD array. In order to measure the photocurrent under short circuit condition and the open circuit photovoltage along the gradient, the films were cast onto ITO substrates and thin aluminium stripes were evaporated after formation of the gradient. The substrate was then attached to the scanning installation holder (Fig. 1) and copper wires were glued as the contacts. A focused light beam from Xe lamp with spot diameter ca. 100 $\mu$m moving along the film was the source of photogenerated charge carriers. Some noise on photocurrent signal appeared during the movement of the light spot along the film.

The photocurrent action spectra (IPCE) were measured by a set-up consisting of Keithley 485 picoammeter and the Oriel MS257 Monochromator Unit. The light source used was a tungsten–halogen lamp (Oriel). The monochromatic light intensity was measured by pyroelectric detector (Oriel). The I–V curves were taken using Keithley 2400 source meter. An Oriel Xenon lamp was used for the simulation of AM0 (78 mW/cm²) radiation conditions.

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**RESULTS**

The scanning absorbance and luminescence spectra of PCBM blended with poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) can be seen from Fig. 2. The ratio between peaks on the absorbance spectra along the gradient direction (Fig. 2(a)), compared with the peak intensities of the absorbance spectra of three reference structures with known ratios between PCBM and polymer, allowed us to interpolate the ratio between MDMO-PPV and PCBM along the whole diffusion profile.

![Absorbance spectra](image1)

![Luminescence spectra](image2)

**Fig. 2.** (a) Scanning absorbance spectra of PCBM-MDMO-PPV (distance between scans 500 $\mu$m). (b) Scanning luminescence spectra of PCBM-MDMO-PPV (distance between scans 500 $\mu$m)
All the scanning measurements results on the PCBM/MDMO-PPV blends are combined in Fig. 3, which shows the luminescence intensity (calculated as square under the luminescence spectrum curve), short circuit photocurrent and approximate volume concentration of PCBM, as estimated from the absorbance spectra. It can be seen that luminescence is quenched completely within the PCBM concentration range of around 3% vol. This demonstrates again that attaining photoin-

Fig. 3. The dependencies of luminescence (crosses), Isc and concentration on the distance (squares) along the diffusion gradient

Fig. 4. The absorbance spectra of the ZnPc/C_{60}/PTOPT structures with the different ratios of ZnPc to C_{60}

duced charge transfer to $C_{60}$ or methanofullerenes in the heterojunction plastic solar cells made of the conjugated polymers with the band gap $C_{60}$ in the range 2.0–2.5 eV is not a problem. The dominant problem is the charge collection efficiency.

Surprisingly the short circuit current of the device increases with the amount of metallofullerene in the blend up to concentrations as high as ca. 90% vol. This observation contradicts the common view that photoinduced electron transfer from polymer to fullerene is the main source of photocurrent. Our results match well with the observed short circuit photocurrent dependency on fullerene concentration obtained by studies of individual photodiodes. As shown in photodiode simulations, much of the photocurrent is actually generated in the acceptor. There is a significant peak at 320–360 nm, which we associate with a $C_{60}$ transition $h_u$-$t_{1g}$ that provides up to 60% of the photocurrent once illuminated by AM0 1 Sun. (It should be noted, however, that the UV content in the AM 1.5 Spectrum is much smaller than in AM0.)

One of the differences between these blends and the bi-layer structures is provided by the nanosize character of the fullerene phase in blends. If, in the bulk fullerene layer, the electron exited to the $t_{1g}$ level can easily drop down to the long-living $t_{1u}$ in the nanodomains of methanofullerenes, this process could be suppressed due to the discrete character of phonon spectrum. This fact probably gives rise to the enhanced quantum efficiency in the near-UV spectral region for solar cells based on blends with phase separation on the nanometer scale.

In an effort to enhance the match of the solar cell absorption with the solar spectrum (Fig. 4), we have investigated the influence of the additional layer containing zinc phthalocyanine, which was known to exhibit weak electron transfer if co-evaporated with $C_{60}$.

The results of the sensitization on the photocurrent action spectra for ZnPc and $C_{60}$ co-evaporated on top of (PTOPT, poly(3-(4-octylphenyl)2,2-bithiophene) for different ZnPc/ $C_{60}$ ratios can be seen from Fig. 5. The device with the components ratio of 1:1 ZnPc:$C_{60}$ showed a significant peak of photocurrent at 590 nm, which we associated with the absorbance band of ZnPc. Photocurrent spectra were taken by illuminating the structures with the monochromatic light and measuring the number

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**Fig. 5.** Current versus wavelength for PTOPT structures with $C_{60}$/ZnPc with different ratios, evaporated on top (see insert for components ratio)
Fig. 6. IPCE spectra of ZnPc/C₆₀ evaporated on top of the PTOPT (see insert for components ratio)

Fig. 7. I–V curves of the structure Al/C₆₀–ZnPc/MDMO-PPV-PCBM/ITO in the dark and under AM0 1 Sun (78 mW/cm²) illumination

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of electrons, collected in the external circuit. Normalizing this value to the light intensity in the given spectral range, we obtained the number of electrons collected in the external circuit per incident photon in dependence on photon energy (the so-called internal photon to electron conversion efficiency, IPCE). The corresponding IPCE spectra of the sensitized structures can be seen from Fig. 6. It is visible that for the range of ratios that corresponds to ca. 1:1 mole (the ratio was estimated based on the results of Giampietro Ruani (Private Communication)) between components, we have a significant improvement in the 600–650 nm range. We know from the communications of the other groups, that the so-called weak photoinduced electron transfer from ZnPc to C60 depends to a great extent on the morphology of the co-evaporated layers, and in our case the 50/50 molar ratio corresponds to the mixed layer structure, which combines maximal charge separation and transport properties.

Though the improvement of IPCE values is rather moderate (ca. 12%) due to the large number of photons within this range in the actual solar spectrum, the photocurrent increase is of the order of 80–100%, and the photocurrent spectra taken under tungsten–halogen lamp illumination give a more adequate picture of the real contribution of ZnPc to the total photocurrent of the solar cell.

The devices which combine the ZnPc/C60 evaporated layers on the top of PCBM/MDMO–PPV blends with optimal concentration of constituents, found by the combinatorial technique exhibited $U_{oc}=0.6$ V, $I_{sc}=1.01$ mA/cm$^2$ (Fig. 7) corresponding to the energy conversion efficiency ca. 0.5% under AM0 (78 mW/cm$^2$) illumination conditions which was 15% more in comparison with the structures without the ZnPc–fullerene layer.

We also carried out the modelling of photon to electron conversion regarding the optical component of electromagnetic field distribution throughout the ZnPc-sensitized photodiode structure. The modelling is based on the results of spectroscopic ellipsometry measurements of the optical constants of the structures and allows simulation of the light absorption, including the interference effects appearing due to the reflection on the interfaces between the layers with different refraction indices.

The results of the modelling showed that the optimal thickness of the ZnPc/C60 layer, maximizing contribution of the sensitizing layer to the photon to electron conversion efficiency is in the range 80–100 nm. Unfortunately our measurements showed that the co-evaporated layers are highly resistive, and the serial resistance of an 80 nm thick layer decreases the total current through the device, thus neutralizing the additional input coming from the ZnPc absorption. We see two possible ways to solve this problem:

1. to add the chemically modified ZnPc with the solubilizing side groups directly to the polymer/acceptor blend;
2. try to optimize the ZnPc/C60 evaporation conditions in order to obtain the layers with lower serial resistance.

CONCLUSIONS

The combinatorial methods along with the scanning spectroscopic and photovoltaic parameter measurements are a convenient tool to investigate bulk-heterojunction photovoltaic solar cells, since they avoid the time-consuming routine of making a blend and then measuring method to study the many possible combinations of the constituents. These combinatorial studies show that the photovoltaic properties of fullerene-based solar cells vary significantly, depending on the morphology of the fullerene phase: whether it is the evaporated film (as in the case of bi-layer structures) or nanodomains (as in the case of the polymer–methanofullerene blends).

When introducing a molecular species for enhanced photoconversion in the green–red range, higher photocurrents are obtained. Putting together the blends and evaporated ZnPc/C60 layers one can combine high conversion efficiencies in the UVA range, coming from methanofullerene absorption with the visible input of a photoinduced charge transfer from polymer to evaporated fullerene layers along with a significant part coming...
from the near-IR range of the visible spectrum due to the sensitization by ZnPc.

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