Aqueous PCDTBT:PC 71 BM Photovoltaic Inks Made by Nanoprecipitation

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Communication

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Abstract

The fabrication of organic solar cells from aqueous dispersions of photoactive nanoparticles has recently attracted the interest of the photovoltaic community, since these dispersions offer an eco-friendly solution for the fabrication of solar cells, avoiding the use of toxic solvents. In this work, aqueous dispersions of pure poly[n-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) nanoparticles, as well as of composite $PC_{71}BM$:PCDTBT nanoparticles, are prepared using the nanoprecipitation post-polymerization method. These dispersions are subsequently used to form the active layer of organic photovoltaic cells. Thin films of $PC_{71}BM$ and PCDTBT are obtained by spray deposition of the nanoparticles' dispersions, and are characterized using a combination of spectroscopic and microscopic techniques. Photovoltaics that incorporate these active layers are fabricated thereafter. The impact of the annealing temperature and of the composition of the active layer on the efficiency of the solar is studied.

FIGURE FOR ToC_ABSTRACT (*see page 16 and last page*)

1. Introduction

Undoubtedly, the interest in organic photovoltaics (OPV) has remarkably increased and became an important topic in materials science during the last decades,[1] thanks to the advantages that organic π-conjugated polymers offer for the fabrication of the photovoltaic active layer, their low cost, flexibility, and lightweight been only some of them, [2] as well as their rapid energy payback time [3].Yet, most of the π-conjugated polymers are processed using toxic organic solvents, mainly chlorinated ones [4] which are not allowed by the international regulations. Therefore, the problem that the photovoltaic industry faces nowadays is related to the replacement of toxic solvents with ecofriendly ones that can still enable processing the semiconducting polymers that form the photovoltaic active layers.

In order to solve this issue one could either directly synthesize polymer particles in an environment-friendly phase, such as water via heterogeneous polymerization, [5] or first synthesize the conjugated polymer via heterogeneous polymerization and, in a second step, disperse this polymer in a bad, yet eco-friendly, medium forming thus nanoparticles. This second approach, i.e. the nanoprecipitation, is the synthetic route that will be explored in this work.

The strength of this process is its universality since whatever material can be processed to form particles, as long as the parent material is soluble into a water-miscible solvent. Typically, THF is used in order to nanoprecipitate π-conjugated polymers in water. [6] THF is particularly advantageous thanks to its low boiling point that allows its evaporation without the need of excess heating which could degrade the material. Moreover, nanoprecipitation is a single-step method to prepare nanoparticles that can be easily adopted by industry. Another advantage is the absence of any stabilizers. In other nanoparticle (NP) preparation methods (e.g. in miniemulsion) the NPs must be encapsulated in a shell of amphiphile molecules that stabilize the nanoparticles in the dispersions and prevent their coalescence or precipitation. Yet, these

molecules are normally insulating and therefore inhibit good charge transport upon film formation, as several authors have highlighted during the last years. [7]

The first organic photovoltaic devices integrating nanoprecipitated particles were reported in 2011 by Darwis *et al.* [8] who prepared poly (3-hexylthiophene-2,5-diyl) (P3HT) nanoparticles in ethanol and subsequently used them to form the active layer. However, due to the very low concentration of their dispersion, four successive spin-coatings were needed to form a thick enough layer, reaching a very low power conversion efficiency of only 0.018%.

P3HT particles have been also combined to the electron acceptor indene-C_{60} bisadduct (ICBA) to form composites nanoparticles in ethanol. Once more, the deposition of several layers was necessary to overcome the problem of low concentration of the dispersions. A thermal annealing step was applied to improve the homogeneity of the active layer and achieve a smoother surface, and the efficiency thus obtained was 3.5% for an inverted solar cell architecture. [9]

Recently, Redmon *and coll* reported the preparation of donor poly[n-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and acceptor [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) NPs in water with potential photovoltaic application. [10] Their approach was focused on detailed assessment of the photo-physical properties of PCDTBT nanoparticles in the absence and presence of $PC_{71}BM$.

Herein we report the preparation of PCDTBT and $PC_{71}BM$ NPs by nanoprecipitation in water for photovoltaic application. The aim of this work was to study the effect of the preparation conditions on the size of the NPs and on the concentration of the aqueous dispersions to achieve eco-friendly aqueous $PC_{71}BM$:PCDTBT photovoltaic inks. The optoelectronic properties of the composite particles as well as of blends of the pure donor/acceptor particles have been studied. Furthermore, we focused on the integration of aqueous dispersions of both the composite particles and of the donor/acceptor blends to form the photovoltaic active layers in photovoltaic devices, by spray-coating deposition. The impact

of the annealing temperature and of the composition of the active layer on the efficiency of the solar cells has been studied. The structure of the active layers is also discussed.

2. Results and discussion

The objective of this study is to prepare stable dispersions of composite $PC_{71}BM$:PCDTBT NPs in water by nanoprecipitation and then use these dispersions as inks for the fabrication of organic photovoltaics. Dispersions of pure PCDTBT and $PC_{71}BM$ particles that are blended in appropriate amounts in aqueous dispersions have been also prepared and tested, to serve as reference samples. These dispersions will be hereafter called blend dispersion. The nanoprecipitation method can be described as follows: the active components PCDTBT and $PC_{71}BM$ are hydrophobic materials and therefore they were first dissolved in THF (a good solvent for both) that is a water-miscible solvent. This solution was rapidly injected into water under stirring. The temperature of the water was fixed at 50°C to ensure miscibility with the initial solution in THF. The THF was subsequently evaporated by placing the solution under argon flow and thus particles dispersed in water have been obtained. Note that this method does not necessitate the use of a stabilizer and that the particles remain dispersed in the medium for 2-3 days without any precipitation. To create the composite NPs both components were solubilized in THF simultaneously, while for the blend dispersions pure PCDTBD and pure $PC_{71}BM$ NPs were synthesized separately and then mixed in the appropriate weight fractions. Details on the procedure we followed are provided in Supporting Information.

As can be seen in **Table 1**, the size of the nanoparticles can be adjusted by tuning the experimental parameters. This study was performed on composite NPs with a fixed composition $PC_{71}BM$:PCDTBT 80:20 wt%. This composition was chosen because it is known to be the most performing one for the fabrication of $PC_{71}BM$:PCDTBT bulk heterojunction photovoltaics.[11,12] Stirring rates between 250 rpm and 1000 rpm have been tested for a fixed initial and final concentration (**Table 1**, samples 1 to 4). The particles size was measured by

dynamic light scattering (DLS) and it was found to exhibit a minimum value of 44 nm for a stirring rate of 750 rpm. In fact, a higher rate of stirring leads to an enhanced mass transfer which can induce rapid nucleation, producing smaller nanoparticles. [13] At a low rate of 250 rpm (**Table 1**, sample 1), stirring is not intense enough to allow the good dispersion of the initial solution in water leading, thus, to bigger particles. On the contrary, at 1000 rpm (**Table 1**, sample 4), stirring is too intense and a vortex is created, that destabilizes the dispersion resulting again in bigger particles.

Table 1.

The concentration of the initial solution of the active components in THF was the second parameter that was varied in order to tune the size of the NPs. The stirring rate was fixed at 500 rpm and the concentration range that was explored was 0.1 – 1 mg/mL (**Table 1**, samples 5 to 9). Increasing the initial concentration resulted in particles with an increasing size from 40 nm to 81 nm. This increase in the particles size is expected and is attributed to the higher density of material (polymer chains plus $PC_{71}BM$ molecules) in the solutions which increases the probability for the formation of larger particles or even aggregates, as has been seen before. [14]

Finally, the particles' size can be tuned by varying the final concentration of the active components in water, keeping a fix initial concentration in THF (**Table 1**, samples 10 to 15 and **Figure 1**). Once more, an increase in the final concentration from 0.025 mg/mL to 0.4 mg/mL gave rise to particles with an increasing size, in agreement with what has been already reported in literature. [15] In fact, below 0.1 mg/mL, the final concentration has a rather low impact on the size of the nanoparticles, since the size increased only from 44 nm to 50 nm, the variation, thus, being smaller than 10 nm. However, above 0.1 mg/mL the size increases rapidly

from 50 nm for a concentration of 0.1 mg/mL to 133 nm for 0.3 mg/mL, until the formation of micrometric aggregates at 0.4 mg/mL.

In order to choose the most appropriate experimental conditions for the preparation of aqueous dispersions that will be used for the formation of the photovoltaic active layer, one should look at the constraints imposed by the target application. First of all, it is generally accepted that the donor or acceptor domain sizes in the active layer should be comparable to the exciton diffusion length (i.e. of the order of 10 nm) in order to limit the excitons loss by recombination. Based on that, the particles size that are targeted herein are the smallest achieved, i.e. between 40-50 nm. Moreover, special care should be taken on the choice of the final concentration of the active components in water, since this will affect the thickness and the homogeneity of the active layer. The target concentration should be high enough to produce a homogeneous film with a thickness in the order of 100 nm, to allow for maximum absorption of the incident light. It is thus necessary to find a balance between a high enough final concentration of the active matter in the aqueous dispersions and small enough particles. Therefore, the experimental conditions that were finally used for the photoactive inks were a stirring rate of 750 rpm, a concentration of the initial solution in THF of 0.5 mg/mL and a final concentration of the active components in water of 0.1 mg/mL, which lead to particles with a diameter of 50 ± 5 nm, as determined by DLS and confirmed by TEM images (**Figure 1b**). It was verified that applying the same conditions for the preparation of pure $PC_{71}BM$ and pure PCDTBT NPs resulted in particles of the same sizes, around 50 nm.

Figure 1.

In view of the eventual use of the composite $PC_{71}BM$:PCDTBT particles for the fabrication of organic photovoltaics, their optical properties have been studied by UV-visible absorption and fluorescence spectroscopies. The absorption and emission spectra of pure $PC_{71}BM$, pure

PCDTBT and blended $PC_{71}BM$ and PCDTBT NPs have been acquired as well, to serve for comparison. The results are presented in **Figure 2**. An excitation wavelength of 395 nm was used for the fluorescence experiments that corresponds to the maximum absorption of PCDTBT.

Figure 2a presents the absorption spectra recorded for pure $PC_{71}BM$ NPs, pure PCDTBT NPs, composite $PC_{71}BM$:PCDTBT 80:20 wt% NPs and the blend of 80 wt% $PC_{71}BM$ + 20 wt% PCDTBT NPs. In case of both composite and blended particles the absorption spectra comprise the absorption features of both PCDTBT and $PC_{71}BM$, those of PCDTBT being less pronounced due to the small fraction of PCDTBT (only 20 wt% in both dispersions). Yet, the two spectra are not the same since the two dispersions absorb differently between 400 nm and 480 nm. In fact, a significant shift of the $PC_{71}BM$ absorption peak from 460 nm for the blend of NPs to 480 nm for the composite NPs is observed. Moreover, our calculations showed that the spectrum of the blend NPs can be deconvoluted in the parent spectra of $PC_{71}BM$ and PCDTBT, respecting the relative weight fractions, which is not the case for the composite particles. These observations suggest that the two materials are in intimate contact within the composite particles. Fluorescence spectroscopy provides further proof on this. The emission spectra of the aqueous dispersions of composite particles for various donor/acceptor fractions are presented in **Figure 2b**, while those of the blended particles are presented in **Figure 2c**. Pure PCDTBT particles emit between 600 and 800 nm. However, when $PC_{71}BM$ is added to form composite NPs the fluorescence of the polymer is strongly quenched for all compositions tested herein, as a result of the coexistence of both $PC_{71}BM$ and PCDTBT in a single composite particle. This is not the case for the dispersions of the blended particles (**Figure 2c**) where the fluorescence of PCDTBT decreases linearly with the decrease of the PCDTBT weight fraction in the blends. No quenching is observed in this case. Note that the quenching of the emission of PCDTBT in case of the composite particles shows that an electron transfer takes place between the donor polymer and the acceptor small molecule. This is a prerequisite for efficient

photovoltaics and demonstrates that the dispersions of composite NPs in water prepared by nanoprecipitation can be used as photoactive inks for the formation of the photovoltaic active layer.

Figure 2.

Motivated by this encouraging result, the aqueous dispersions of the composite $PC_{71}BM$:PCDTBT NPs were used to form the active layer of photovoltaic devices by spray-coating. Spray-coating was chosen due to the low viscosity and low concentration of the inks. Unlike spin coating, this technique prevents severe material losses and allows to deposit higher volume of solution (typically a few mL) in order to compensate for the low solution concentration. [15] The target thickness was 100 nm, and corresponds to that reported in literature to provide the best compromise between good absorbance and low recombination for $PC_{71}BM$:PCDTBT BHJ solar cells.[16]

A study of the surface morphology and roughness has been performed by conventional and conductive AFM. **Figures 3a** and **3b** present respectively the topography and the current images recorded for the layer formed by spraying the composite $PC_{71}BM$:PCDTBT 80:20 wt% particles. The substrate was kept at an elevated temperature (100°C) during deposition to allow for the evaporation of water. This temperature is below the glass transition temperature and the melting temperature of PCDTBT (T_g~130°C[17] and T_m~200°C[18]) and its of $PC_{71}BM$ (T_g~130°C[19] T_m~319°C[20]), therefore a layer of closely packed particles with a high roughness of 30 nm is formed after spray-coating (**Figure 3a**). However, conducting AFM showed that the film appears homogeneous from a charge conduction point of view (**Figure 3b**), in the limits of the uncertainty introduced in the measurement due to the varying contact area between the AFM tip and the surface of the film. [21] This observation implies that the donor and the acceptor not only coexist within the composite particles but also they are very

well mixed, forming a single donor:acceptor phase. Note that in our previous study of the formation of PCDTBT, $PC_{71}BM$ and composite $PC_{71}BM$:PCDTBT particles by the miniemulsion technique, the composite particles appeared on the AFM images as 2-color particles due to the core-shell nature of those particles, as confirmed by small angle neutron scattering. [7] Such core-shell particles have not been observed in case of nanoprecipitation, providing additional evidence that the two materials are very well mixed within each particles, forming a homogeneous entity.

Additional structural characterizations of the nanoprecipitated particles have been performed by means of grazing incidence wide angle x-ray scattering (GIWAXS). The wedge-corrected 2-D scattering images that were recorded for the films of pure $PC_{71}BM$, pure PCDTBT and composite $PC_{71}BM$:PCDTBT 80:20 wt% particles are presented in **Figure S1**. The absence of diffraction peaks in case of the pure $PC_{71}BM$ and PCDTBT particles suggests that both materials are in the amorphous phase. The very large and low-intensity peaks that are apparent in both cases at around 1.8 $Å^{-1}$ are indicative of a rather disordered π-π stacking, in consistence with previous reports. [22] Similarly, the film made out of composite particles does not show any diffraction features, besides the large π-π peak. Therefore, we can confirm the absence of any order in these films, either at the length-scale of a few Å that are probed by X-Rays, or at the nanoscopic/microscopic length-scales probed by AFM. It is noteworthy that the ordering of the donor or acceptor components in the active layers of organic photovoltaics has been recognized as a parameter that favors charge transport in the films, decreasing exciton recombination and, thus, increasing ordering results in increasing device performance. Yet this is not the case for the $PC_{71}BM$:PCDTBT system that is reported to exhibit no crystallization characteristics and morphology is not identified as a critical parameter that affects device efficiency. [23-24]

In case of the particle-formed films studied herein, the fact that the active layers consist of packed particles and not of a homogeneous film is expected to be detrimental for the devices

due to their limited contact which results in non-continuous films. An annealing step that targets the sintering of the particles in order to fill in the interstitial gaps and create a continuous film is necessary. [25-28] Films of composite $PC_{71}BM$:PCDTBT 80:20 wt% particles were annealed during 4 min at various temperatures, starting from the T_g of PCDTBT (130°C) until 180°C with a step of 10°C. The topographic and phase AFM images that were recorded for films annealed at different temperatures are presented in **Figure S2**, in Supporting Information. An 130ºC and an 140°C NPs films present the same aspect as the non-annealed one and well-shaped, spherical particles are apparent. A significant roughness of 30 nm has been measured in all cases. After annealing at 150°C a morphological modification can be noticed; the particles appear blurred at the topography image and roughness decreases to 24 nm, which suggest that they start to sinter and merge. At 160ºC the sintering of the particles is even more pronounced and they continue to merge towards the formation of a continuous film (**Figure 3c**). In the same time discrete conductive domains appear at the current image (**Figure 3d**), which suggests that phase separation between the donor and the acceptor starts taking place. This will be important for the solar cells to be made thereafter, since it suggests the presence of more conductive pathways. A rather homogenous film is obtained when annealing is performed at 170ºC. In these two last cases the roughness decreases further to its minimum value of 20 nm. The sintering of NPs at 160ºC coincides well with the glass transition reported in literature for $PC_{71}BM$. [19] When annealed at 180°C the film appears to be less homogeneous, large domains appear and roughness increases to 30 nm.

Figure 3.

The composite NPs films that were annealed at different temperatures were subsequently integrated in photovoltaic devices. Given the good air stability of all components, the inverted device architecture was chosen, with ZnO being the electron transport layer while Ag deposited

on MoO_3 served as the anode. [29] The sequence of the layers that comprise the photovoltaics is as follows glass/ITO/ZnO/($PC_{71}BM$:PCDTBT NPs)/MoO_3/Ag). Details on device fabrication and characterization are provided in Supporting Information. **Figure 4** presents the current density *vs* voltage (*J vs V*) results obtained for some representative devices annealed at 160°C. In **Table S1** (Supporting Information) the short circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (*FF*) and power conversion efficiency (*PCE*) values, obtained after averaging at least 8 different devices per case, are presented. Different compositions of the composite NPs have been tested for various annealing temperatures. The results for the photovoltaic performance of the 80:20 wt%, 70:30 wt%, 60:40 wt% and 50:50 wt% $PC_{71}BM$:PCDTBT composite NPs are presented in **Table S1** (Supporting Information).

The photovoltaic performance is very poor (PCE < 0.01%) for the non-annealed film (**Figure 4**, black dots) as well as those annealed at 130ºC – 150ºC at any different composition ratios (**Table S1**). This is explained by the poor contact between the NPs, as verified by AFM. However, when annealing is performed at 160ºC, PCE increases, thanks to the sintering of the particles and the continuity induced in the active layer (**Table S1** and **Figure 4**, colored symbols). This increased PCE appears to be primarily driven by the increase in the V_{oc} (**Table S1**). Above 160ºC the PCE appears to decrease slowly. This is attributed to the donor/acceptor phase separation that was discussed above for these elevated temperatures based on the conductive and topography AFM images. In fact, phase separation can lead to a decrease of the donor/acceptor interfaces, which, in turns, results in less efficient exciton dissociation, in consistence with what has been already reported for solution cast films of $PC_{71}BM$:PCDTBT.[24]

In all case, the best performance is obtained for an annealing step at 160ºC. The optimum composition appears to be 70:30 wt%, unlike what is the case for the BHJ $PC_{71}BM$:PCDTBT photovoltaics.[30]

Figure 4.

Finally, devices that integrate the spray-coated films made out of the blend NPs dispersions were fabricated and characterized. Once more, annealing temperatures between 130ºC and 180ºC have been performed, and various weight ratios of the donor – acceptor particles have been tested. The results are presented in **Table S2** in Supporting Information. As expected based on fluorescence data and the absence of energy transfer between the donor and the acceptor, the PCEs are very low, of the order of 0.01% or even lower. Therefore, nanoprecipation of composite NPs is demonstrated to be more adapted for the preparation of photovoltaic inks.

It should be highlighted that no device engineering that could improve performance has been performed on the devices presented in this work. The fabrication conditions were chosen based on those reported in literature for the most performing BHJ $PC_{71}BM$:PCDTBT solar cells.[31] This work focuses on the material used to form the active layer and aims at the demonstration of the effectiveness of nanoprecipitation as an alternative synthetic method for the preparation of aqueous, eco-friendly dispersions destined for industrial photovoltaic applications.

3. Conclusion

To sum-up, we chose the nanoprecipitation method to successfully produce PCDTBT particles as well as composite $PC_{71}BM$:PCDTBT particles in water without stabilizer with tunable size depending on the synthetic conditions. We also studied the NPs' properties. Spray-coating was chosen due to the low viscosity of the inks, in order to deposit a higher volume of solution (mL) and compensate its low concentration. In case of NP-based devices, annealing is a key step to improve the contact between the particles, improving the mixing between the two compounds and getting more homogeneous films. [25-28] The optimum thermal annealing treatment was found to be at 160°C during 4 minutes for the composite NPs supported by AFM.

After integration into solar cells, the thermal annealing led to a strong increase in the efficiency. The best device composed of 70:30 wt% composite NP led to a power conversion efficiency of 0.33%. In further work, different deposition technique will be use to obtain a smoother active layer as ultrasonic spray [32] which could achieve lower roughness than classical spray-coating [33] and so higher PCE values could be expected.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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FIGURE FOR ToC_ABSTRACT