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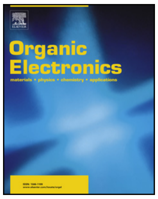

Environmentally friendly preparation of nanoparticles for organic photovoltaics

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ABSTRACT

Aqueous nanoparticle dispersions were prepared from a conjugated polymer poly[thiophene-2,5-diyl-*alt*-5,10-bis((2-hexyldecyl)oxy)dithieno[3,2-*c*:3′,2′-*h*][1,5]naphthyridine-2,7-diyl] (PTNT) and fullerene blend utilizing chloroform as well as a non-chlorinated and environmentally benign solvent, *o*-xylene, as the miniemulsion dispersed phase solvent. The nanoparticles (NPs) in the solid-state film were found to coalesce and offered a smooth surface topography upon thermal annealing. Organic photovoltaics (OPVs) with photoactive layer processed from the nanoparticle dispersions prepared using chloroform as the miniemulsion dispersed phase solvent were found to have a power conversion efficiency (PCE) of 1.04%, which increased to 1.65% for devices utilizing NPs prepared from *o*-xylene. Physical, thermal and optical properties of NPs prepared using both chloroform and *o*-xylene were systematically studied using dynamic mechanical thermal analysis (DMTA) and photoluminescence (PL) spectroscopy and correlated to their photovoltaic properties. The PL results indicate different morphology of NPs in the solid state were achieved by varying miniemulsion dispersed phase solvent.

1. Introduction

Ever increasing global energy consumption has led to a tremendous rise in fossil fuel emissions, resulting in air pollution and global warming [1]. The urgent need for the development of clean and renewable energy sources has attracted immense attention of both scientific and industrial researchers [2,3]. Undoubtedly, solar energy is one of the best candidates to fulfil the current and future energy needs [4,5]. Organic photovoltaics (OPVs) enjoy significant advantages over traditional solar technology due to their lightweight, flexibility, ease of manufacturing, scalability and low cost [6–9]. Continued research into OPV technology has led to significant improvements in the device performance with power conversion efficiency (PCE) of up to 13% being reported [10]. However, OPVs are commonly prepared via spin-coating the active materials on small indium tin oxide (ITO) coated glass substrates from non-environmentally friendly halogenated solvents [11], which is counterproductive to achieving scalable and environmentally friendly fabrication of OPVs.

In recent years a number of publications have focussed on developing alternative OPV fabrication methods, which are scalable at low cost such as roll-to-roll printing [8,12–14]. Although remarkable success has been achieved in printing OPVs on flexible substrates, most of the best performing materials used for printing are still processed from chlorinated solvents such as *ortho*-dichlorobenzene (*o*-DCB) [15]. The large-scale use of chlorinated solvents is harmful to human health and has a detrimental impact on the environment [16,17]. Moreover, the usage of chlorinated solvents increases the cost of large-scale fabrication of OPVs, which results from expensive halogenated solvent recovery systems. The harmfulness and high cost of chlorinated solvents used for processing photoactive materials in OPV fabrication is one of the main hurdles to be overcome before the knowhow of fabricating high performing OPVs can be transferred from a lab-scale to an industrial scale fabrication. Thus, it is of utmost importance to develop green deposition methods by utilizing benign and non-chlorinated

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solvents [18–20].

OPVs with active layers processed from a water or alcohol based nanoparticle dispersion has been reported in recent years [21–24]. These nanoparticles are processed from donor-acceptor blends either through a miniemulsion process with the presence of surfactant [25–28] or a precipitation method [21–23,29]. Furthermore, conjugated polymer nanoparticles were also reported to be synthesized by direct Suzuki-Miyaura dispersion polymerization [30–32]. In the miniemulsion method, the organic solvent utilized to dissolve the active materials should ideally have high vapour pressure as well as be immiscible with water. Most procedures reported in the literature to date use harmful chlorinated solvents, such as chloroform ($CHCl_3$) [21,33], chlorobenzene [34] or *o*-DCB [26]. Compared to conventional bulk heterojunction (BHJ) OPV fabrication, the NP method is still environmentally superior considering (a) the volume of chlorinated solvents utilized is comparably less; (b) the roll-to-roll printing of solar cells is free from chlorinated solvents as they can be removed in a closed loop system prior to printing. Considering that the upscaling of OPVs with NP active layers will lead to an increase in the consumption of solvents used to prepare NPs, it is timely to consider the use of industrially relevant solvents during the preparation of the NPs of the photoactive materials in addition to the subsequent deposition.

In this paper, we report for the first time the preparation of water-dispersed nanoparticles using a relatively benign and industrially relevant solvent, *o*-xylene, as the miniemulsion dispersed phase solvent, and successfully demonstrate the fabrication of solar cells with comparable device parameters to BHJ OPVs [19]. The nanoparticles were prepared from a wide bandgap semicrystalline conjugated polymer namely poly[thiophene-2,5-diyl-*alt*-5,10-bis((2-hexyldecyl)oxy)dithieno[3,2-*c*:3′,2′-*h*][1,5]naphthyridine-2,7-diyl] (PTNT) [35] and $PC_{71}BM$ (phenyl C_{71} butyric acid methyl ester). PTNT polymer was chosen in this study as it was demonstrated to perform well in an active layer thickness of up to 400 nm [35], which makes it a relevant polymer for devices fabricated via printing. To gain a better understanding of the influence of the miniemulsion dispersed phase solvent on the nanoparticle properties, PTNT:$PC_{71}BM$ NPs prepared using chloroform as the miniemulsion dispersed phase solvent were also studied. Size distribution, optical, thermomechanical and photovoltaic properties of PTNT:$PC_{71}BM$ nanoparticles prepared using *o*-xylene (NP-xylene) were systematically studied and compared with those processed from chloroform (NP-chloroform). A maximum PCE of 1.65%, with a short circuit current density (J_{SC}) of 4.75 mA/cm^2 was achieved from nanoparticles prepared using *o*-xylene as the miniemulsion dispersed phase solvent as compared to a 1.04% PCE and 2.84 mA/cm^2 of J_{SC} for the dispersions prepared using chloroform as the miniemulsion dispersed phase solvent.

2. Experimental

2.1. PTNT synthesis

Polymer PTNT (Fig. 1) was synthesized by Stille coupling copolymerization from monomer 2,7-dibromo-5,10-bis((2-hexyldecyl)oxy)dithieno[3,2-*c*:3′,2′-*h*][1,5]naphthyridine(dibromo-NT) and 2,5-bis(trimethylstannyl)thiophene as previously reported [35]. The molecular weight was measured by size exclusion chromatography (SEC) in 1,2,4-trichlorobenzene (1,2,4-TCB) at 150 °C. Detailed synthetic procedure and SEC operational conditions are included in Supplementary Information. $M_n = 55.7$ kg/mol, $M_w = 163.2$ kg/mol were determined relative to polystyrene standards. Through square wave voltammetry, the HOMO and LUMO energy levels of PTNT are estimated to be −5.9 and −3.6 eV, respectively [35]. Bulk heterojunction (BHJ) solar cells processed using PTNT:$PC_{71}BM$ (1:2 wt ratio) processed from *o*-DCB solution have been reported to achieve a PCE of 5% in a conventional configuration [35] and 5.1% in an inverted structure [36].

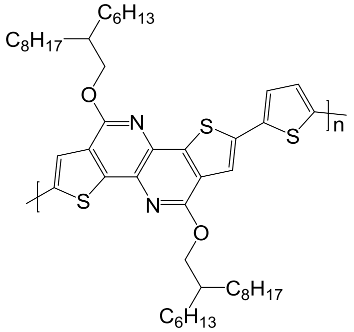

Fig. 1. Chemical structure of PTNT.

2.2. Nanoparticle preparation

$PC_{71}BM$ was purchased from Solenne BV. PTNT:$PC_{71}BM$ nanoparticles were prepared with the weight ratio of 1:2 through the miniemulsion method [33,37]. The weight ratio was chosen based on the best performance of BHJ devices from a PTNT:$PC_{71}BM$ blend without solvent additive [35]. PTNT (10 mg) and $PC_{71}BM$ (20 mg) were dissolved in 540 µL of organic solvent (chloroform or *o*-xylene) at 35 °C with stirring at 500 rpm for 2 h. Meanwhile the aqueous phase was prepared by dissolving sodium dodecyl sulphate (SDS) (33 mg) in 2.8 mL of MilliQ water. After ensuring complete dissolution of PTNT and $PC_{71}BM$, the aqueous phase was combined with the organic phase under stirring at 1200 rpm. A macroemulsion was then formed by stirring the mixture at 1200 rpm at 30 °C for approximately 1 h. To generate the miniemulsion, Vibra-Cell ultrasonic processor VCX 750 with 1/8″ stepped probe was introduced to ultra-sonicate the macroemulsion at 30% amplitude for 3 min. Then the miniemulsion was transferred immediately to a heating block and stirred at 1200 rpm to form a stable water dispersion of NPs after complete removal of the residual organic solvent. For nanoparticles prepared using chloroform, the miniemulsion was heated at 60 °C for 3 h to ensure the complete removal of chloroform whereas in the case of using *o*-xylene, a NPs dispersion was achieved by heating at 75 °C for 6 h. Additional water was added every hour to compensate for the water loss, which otherwise results in aggregation of material and precipitation on the wall of the vials. To minimise unwanted SDS from negatively impacting the device performance [27], centrifugal dialysis was introduced to remove excess free surfactant in the dispersion as well as concentrate the active materials in the water dispersion, giving the final dispersion a solids content of 6 wt% in 0.5 mL water.

2.3. Nanoparticle characterization

Scanning electron microscopy (SEM) was performed using an ultra-high resolution field-emission gun scanning electron microscope (Zeiss Merlin) at an accelerating voltage of 2 kV with magnification ranges of 50,000–150,000 X. All SEM samples were spin-coated (3000 rpm for 1 min) from diluted nanoparticle water dispersion with 1 wt% of solids content on conductive silicon substrate. The size distribution of PTNT:$PC_{71}BM$ (1:2 wt ratio) NPs prepared from different organic solvents were characterized from SEM images with a circular Hough transform algorithm [37,38]. In the varied annealing temperature study, all films were pre-dried at 90 °C for 4 min immediately after spin-coating for consistency with device fabrication.

The ultraviolet–visible (UV-vis) study was performed on a Perkin Elmer UV-vis-NIR Lambda950 spectrophotometer. The photoluminescence (PL) measurements were performed on a Varian Cary Eclipse fluorescence spectrophotometer at the excitation wavelength of 450 nm. The PL measurements of NP water dispersions were performed on diluted NP-xylene and NP-chloroform dispersion with the same concentration. Measurements of the solid state were performed on spin