Synthetic Metals 220 (2016) 469–476

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Effects of conjugated polymer incorporation on the morphology and energy harvesting of solution-processed, phthalocyanine-based thin films

Gary Z. Cheung[a], Binxing Yu[b], Mengdi Liu[c], Zheng Gong[c], Jesse Kohl[a,1], Christopher E. Petoukhoff[a], Piotr Piotrowiak[c,d], Deirdre M. O'Carroll[a,b,d,*]

[a] Department of Materials Science and Engineering, Rutgers University, 607 Taylor Rd., Piscataway, NJ 08854, USA
[b] Department of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Rd., Piscataway, NJ 08854, USA
[c] Department of Chemistry, Rutgers University, 73 Warren St., Newark, NJ 07102, USA
[d] Institute for Advanced Materials Devices and Nanotechnology, Rutgers University, 607 Taylor Road, Piscataway, NJ 08854, USA

ARTICLE INFO

Article history:
Received 2 May 2016
Received in revised form 12 July 2016
Accepted 16 July 2016
Available online 27 July 2016

Keywords:
Organic semiconductors
Ternary blend
Morphology
Absorption
Photoluminescence

ABSTRACT

Here, we investigate the morphology, spectral absorption bandwidth and energy transfer in solution-processed, phthalocyanine-based thin films blended with conjugated polymer materials with complementary absorption bands. Unary, binary, and ternary solutions of the solution- processable phthalocyanine derivative 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (Oct-Pc) and the conjugated polymers poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and poly(3-hexylthiophene) (P3HT) were used to prepare sub-55-nm-thick unary-phase and blended thin films. Spectroscopic analysis shows that absorption band full-width-at-half-maximum (FWHM) values increase from between 60 nm and 160 nm for the individual materials to greater than 450 nm for the composite ternary-blend thin film due to the complementary bandgap energies and spectral absorption bands of the constituent materials. Additionally, photoluminescence and transient absorption measurements show very efficient transfer of excited-state energy in the wider band-gap materials (donors) to the narrower band-gap material (acceptor). Resonant energy or charge transfer occurs with efficiencies between 90% and 100% for the various blends. Atomic-force microscopy and grazing-incidence, wide-angle X-ray scattering data indicate that P3HT and Oct-Pc exhibit the poorest blending. This correlates with the lowest donor photoluminescence quenching efficiency due to the extended separation of the P3HT chains from Oct-Pc molecules. However, addition of a relatively small fraction of PFO disrupts Oct-Pc crystallinity and enables improved mixing and energy transfer between P3HT and Oct-Pc.

1. Introduction

The limited spectral overlap of conjugated organic molecular and polymer absorption bands with the solar spectrum (absorption spectrum full width at half maximum (FWHM) values are in the range 50 nm to 200 nm at visible wavelengths [1–8]) has led to synthesis of new absorber materials [9–13] and to development of tandem [13,14] and ternary-blend device architectures for broadband solar energy harvesting [1–4]. In a ternary blend, an electron donor or acceptor material is added to a binary blend of two organic semiconductors [2]. Cascading lowest-unoccupied molecular orbital (LUMO) level energies in ternary-blend active materials leads to a transfer of energy typically from the higher bandgap material to the lower bandgap material *via* energy or charge transfer. In that way, the spectral absorption band of blended organic thin films is effectively broadened compared to single-phase (i.e., unary-phase) and binary-blend organic thin films and can yield improved light harvesting across the solar spectrum. The presence (or absence) of a particular energy or charge transfer mechanism typically depends on relative highest-occupied molecular orbital (HOMO) and LUMO energies, the donor-acceptor separation distance, the relative ratios of the materials and spectral overlap between donor emission and acceptor absorption bands. Changes in crystallinity and

---

[*] Corresponding author at: Department of Materials Science and Engineering, Rutgers University, 607 Taylor Rd., Piscataway, NJ 08854, USA.
E-mail address: ocarroll@rutgers.edu (D.M. O'Carroll).

[1] Present address: Science and Technology Division, Corning Incorporated, Corning, NY 14831, USA.

http://dx.doi.org/10.1016/j.synthmet.2016.07.022
0379-6779/© 2016 Elsevier B.V. All rights reserved.

morphology of ternary-blend organic thin films compared to binary-blend thin films have also been reported and can impact the absorption bandwidth and energy transfer favorably or unfavorably depending on the relative ratio, crystallinity and molecular organization of the constituent materials [15,16].

Since bulk-heterojunction (BHJ) thin films consisting of a binary blend of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C61-butric acid methyl ester (PCBM) are the most widely-studied, solution-processable organic thin-film active layers for photovoltaic applications, the majority of studies of organic ternary-blend thin films to date have incorporated a third material into this binary-blend system [2]. Poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT) are two conjugated polymers that have shown potential as the third active material in P3HT:PCBM thin film [5–7]. For example, the P3HT:PCPDTBT:PCBM system, with weight ratio of 0.8:0.2:1, was reported to outperform the P3HT:PCBM 1:1 system in BHJ organic photovoltaic (OPV) devices after a thermal annealing step (power-conversion efficiency (PCE) of 2.8% and 2.5%, respectively) [7]. The proposed mechanism for the performance improvement was a two-step charge transfer process: following excitation, electrons transferred from PCPDTBT to PCBM and, subsequently, the remaining hole carriers on PCPDTBT transferred to P3HT prior to collection at the respective electrode.

Conjugated small molecule absorbers have great potential as sensitizers in OPVs as many have absorption bands that occur in the UV and near-infrared range [8–19]. When incorporated into a ternary system, this allows for a broader absorption band compared to what can typically be achieved with conjugated polymer-based absorber blends. Work by Sharma et al. and Choi et al. demonstrated that P3HT:PCBM devices incorporating solution processable molecules such as diketopyrrolopyrrole with a cyanovinylene-4-nitrophenyl unit (DPP-CN) or 9,18-(di-2-hexyldecyl)-2,11-dimethoxy-9,18-dihydrobenzo[5,6]-s-indaceno[1,2-b]indeno[2,1-h]carbazol-6,15-dione (HMBI) show improved PCE [8,9]. The P3HT:DPP-CN:PCBM ternary blend extended the absorption edge from 630 nm to 750 nm when compared to the binary blend [8]. Due to the cascading relative offsets of the HOMO and LUMO energy levels, charge transfer was the primary mechanism of electronic interaction proposed between the three materials in the P3HT:DPP-CN:PCBM system, similar to that of the aforementioned polymer blend cases. The HMBI:P3HT:PCBM system extended the blue edge of the absorption band of the binary blend from a wavelength of ~400 nm to below a wavelength of 350 nm [9]. The HMBI:P3HT:PCBM system exhibited a long-range, Förster resonance energy transfer (FRET) process from HMBI to P3HT and then a charge transfer process from P3HT to PCBM.

Other small molecule-based ternary-blend systems have employed one or more phthalocyanine derivatives [15–19] to broaden the OPV active layer spectral absorption band and improve overall PCE compared to a binary-blend active layer. Phthalocyanines are particularly attractive as materials for solar energy harvesting because their bandgap energy can be tuned close to the ideal value of 1.4 eV dictated by the Shockley–Queisser limit [20–22]. The main drawback is the limited solubility of most phthalocyanine-derivatives in organic solvents which inhibits their uniform deposition via coating or printing methods. Blending of conjugated polymers with phtalocyanine derivatives, such as copper phthalocyanine (CuPc), has been suggested to improve the stability and performance of CuPc-based OPV devices [23]. However, investigations of the film forming properties, morphology and energy transfer efficiency in sensitized or blended solution-processable phthalocyanine-based thin films have not been reported. Here, the film forming properties, the absorption spectral bandwidth, and the extent and efficiency of energy transfer in thin films of a solution-processable phthalocyanine derivative (2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (Oct-Pc)) sensitized with the conjugated polymers (poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and/or poly(3-hexylthiophene) (P3HT)) are investigated. The complementary absorption bands of the materials generate a broadened absorption spectrum, spanning more than 450 nm, in the ternary-blend thin film. Efficient sensitization of Oct-Pc by both conjugated polymers is demonstrated despite significant differences in the extent of spectral overlap between the conjugated polymers and the Oct-Pc. This study also investigates morphological properties of the organic semiconductor ternary-blend thin films compared to binary blends and the unary-phase films and the effect of blend morphology on the efficiency of energy transfer.

2. Methods

2.1. Materials

The three organic semiconductors were chosen based on the following criteria. (i) Since the film casting technique was solution based, organic semiconductors that were highly soluble in the same organic solvent were selected. This allowed homogeneous blending of the different molecules in solution prior to casting and ensured a high degree of physical interaction between the materials in the cast film, thereby allowing energy/charge transfer to occur [1]. (ii) Each semiconductor was chosen so that its absorption spectrum was spectrally separated to reduce overlap, allowing for a broader absorption band. (iii) Lastly, the emission spectra of the two higher-bandgap-energy semiconductors overlapped with the absorption spectra of the two lower-bandgap-energy semiconductors [24].

Based on the above criteria, the three organic semiconductors chosen for the ternary blend in this study were: poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO; number average molecular weight, Mn = 48,352 Da; polydispersity index (PDI) = 3.74); regioregular P3HT (Mn = 24,091 Da; PDI = 2.2; regioregularity ≥ 96%), and 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (Oct-Pc; molecular weight = 1540.24 Da) [25]. All materials were purchased from Sigma–Aldrich and were used without further purification.

2.2. Film fabrication and characterization

Thin-film samples were fabricated by spin coating solutions of the organic semiconductors, in chloroform, onto glass substrates. The concentrations of the solutions were 2 g L^{-1} for PFO, 5 g L^{-1} for P3HT, and 10 g L^{-1} for Oct-Pc. These concentrations were chosen so that the peak absorbance of each material in the thin films was similar in magnitude and were limited by the solubility of Oct-Pc in chloroform (upper limit of ~12 g L^{-1}). To dissolve the materials in chloroform, solutions were heated to 40 °C and sonicated in a water bath for 30 min. 20 μL of the solution was dynamically dispensed onto a glass substrate spinning at 6000 rpm and the substrate was allowed to spin for 1 min.

Film thickness and surface topography were evaluated using atomic force microscopy (AFM; Veeco Digital Instruments Nanoscope III, tapping mode, antimony-doped silicon AFM probe tips with a nominal tip radius of 8 nm). Prior to film thickness measurements, a region of the organic thin film was physically removed to expose the substrate. Subsequently, AFM scans of a film/substrate region of the sample were acquired and the step size from the top of the film to the substrate surface was extracted from the scans, yielding the film thickness [15].

Grazing-incident wide angle X-ray scattering (GIWAXS) patterns were acquired using the X9 undulator-based beamline in the