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Development of non-halogenated binary solvent systems for high performance bulk-heterojunction organic solar cells

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ABSTRACT

Halogenated solvents such as dichlorobenzene (DCB) are commonly used in the fabrication of bulk-heterojunction (BHJ) organic solar cells. However, most halogenated solvents are very toxic. This report provides a route to eliminate halogenated solvents based on Hansen Solubility Parameters (HSPs) for manufacturing high efficiency BHJ solar cells. The device performances fabricated from several different binary solvent systems were compared to that from DCB. For the investigation of different gel behavior of solvent mixtures, Hansen solubility parameters and viscosity were mainly considered for the selection of binary solvent mixture candidates. Upon the addition of 20 vol.% benzaldehyde (BA) to p-xylene (p-XL), the device performances were improved in power conversion efficiency (PCE) from 3.1% to 3.8% and external quantum efficiency (EQE) from 63% to 70%. The solar cell devices fabricated using p-XL/BA binary solvent mixtures exhibited PCE comparable to that from DCB.

1. Introduction

There have been tremendous efforts for the development of solution processable high performance bulk-heterojunction (BHJ) organic solar cells for the last couple decades. In order to improve device performances by modifying the morphology of the organic active layers [1], solvent annealing [2–4], thermal annealing [4–6], and solvent additives [7,8] have been utilized for the fabrication of solution-processed bulk-heterojunction solar cells. The most commonly used solvents in the fabrication of solution processable solar cells tend to be halogenated solvents due to their superior performance [9]. However, most of the halogenated solvents used in the fabrication process are toxic which prevents their usage in large scale organic solar cell manufacturing. Also, nearly all halogenated solvents have a global warming potential greater than that of carbon dioxide. Thus, in order to eliminate halogenated solvents in the solution processing of BHJ solar cells, an alternate processing route based on Hansen Solubility Parameters (HSPs) has been introduced in our previous work [10], which can be utilized to predict molecular affinities, solubility, and solubility-related phenomena [11,12].

In order to select good candidates for binary solvent mixtures, Hansen Solubility Parameters (HSPs), describe the total cohesion energy, E, by three contributions: the dispersion interactions, E_d, permanent dipole-permanent dipole molecular inter actions, E_p, and the hydrogen bonding molecular interactions, E_h. This energy is directly related to the solubility parameters (δ), which are the square root of the cohesion energy density (E/V) [13].

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

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Fig. 1 illustrates the HSPs for a number of different solvents. The solvents that can dissolve the P3HT and PCBM mixture (chloroform [$CHCl_3$], ortho-dichlorobenzene [o-DCB], chlorobenzene [CB], biphenyl, mesitylene [MS], carbon tetrachloride [CCl_4], diethylbenzene, ethylbenzene, toluene and xylene [XL]) are grouped together in HSPs space that define the interaction radius (R_0) wherein solvents dissolve the polymer and solvents outside of the volume defined by R_0 will not dissolve the polymer. As DCB tends to yield devices with better performance, a mixture that matches its solubility parameters (δ_d = 19.2, δ_p = 6.3, δ_h = 3.3 $MPa^{1/2}$) would be desired. Based on the HSPs selection rules, the composition of 27–73 vol.% MS–AP with δ_d = 19.2, δ_p = 6.3, δ_h = 2.9 $MPa^{1/2}$ was predicted. However, in our previous report we showed that solutions using MS–AP systems exhibited a gel behavior that led to thin film morphologies which were different than those from DCB solutions and consequently, the best device performance was observed from far from the predicted composition at a 80–20 vol.% MS–AP mixture [10]. These discrepancies might be due to the mismatch of several liquid properties such as viscosity, electron density, and the normal boiling point of the component solvents. Furthermore, such behavior may provide a unique opportunity for the formation of well-defined polymer and PCBM domains due to the formation of the solid network of the polymer. In order to study the effect of several liquid properties on device performance, we developed other binary solvent systems that also exhibit gel behavior but possess solution properties similar to those of halogenated solvents through the tuning of solubility and viscosity of the solutions. MS–AP, pXL–AP, and pXL–BA combinations were selected as binary systems to study considering viscosity, density, and boiling point along with the HSPs of the component solvents.

2. Experimental details

2.1. Materials and device fabrication

PEDOT:PSS (Poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate)) was purchased from Baytron AG (Clevios P VP AI 4083), P3HT (poly(3-hexylthiophene)) was purchased from Rieke Metals (4002E), PCBM (phenyl-C61-butyric acid methyl ester) was purchased from Solenne B.V., and BCP (bathocuproine) was purchased from TCI Co. DCB (99%), MS (99.0%), AP (99%), p-XL (99%), and BA (99%) were all purchased from Sigma–Aldrich and stored in a dry nitrogen glove box.

2.2. Device fabrication

Bulk-heterojunction solar cells based on P3HT/PCBM blend were fabricated in the following simple device stack structure: ITO/PEDOT:PSS/P3HT:PCBM/BCP/Al. Patterned ITO (Indium tin oxide) substrates were scrubbed and cleaned with sequential sonication of deionized water, acetone, and isopropyl alcohol followed by UV-zone treatment for 40 min. The cleaned ITO-coated glass substrates were modified by spin-coating a thin layer (~40 nm) of PEDOT:PSS (Clevios, 4083) and cured at 190 °C for 30 min in air. P3HT and PCBM were dissolved in a 1:1 ratio to 1.0 wt% in mixtures of MS–AP, p-XL–AP and p-XL–BA by heating and stirring for 2 h at 75 °C in a nitrogen atmosphere. These solutions were then cooled slowly to ambient temperature until the systems form gel-type solutions. For comparison devices, the P3HT:PCBM blend (1.5 wt%, 1:1 weight ratio) was dissolved in DCB and stirred for 24 h at 40 °C. The polymer blended films were spin-coated in a nitrogen-filled glove box onto the PEDOT:PSS modified substrate. The spin conditions were modified for each solution to maintain a thickness of 60 nm for all the active layers. The as-cast films were dried overnight in nitrogen atmosphere at ambient temperature. After drying, the samples were thermally annealed at 140 °C for 30 min. Finally, BCP (14 nm) and Al cathode (100 nm) layers were deposited in a vacuum thermal evaporation chamber built by Travato Man. Inc. on top of the active layer and each device had an active area of 0.04 cm^2.

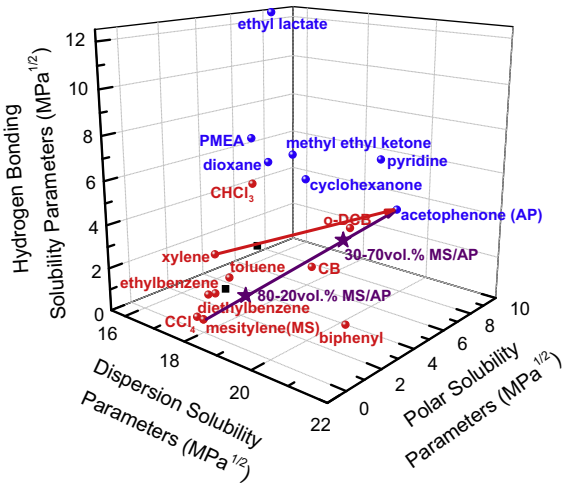

Fig. 1. Hansen Solubility Parameters (HSP) for selected solvents and solvent mixtures. Solvents in red are considered as good solvents for P3HT/PCBM blend and in blue are non-solvents. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.3. Device characterization

The current density–voltage characteristics were measured using a solar simulator (Newport, 150 W) with an AM 1.5G filter in a nitrogen filled glovebox at room temperature. The intensity of illumination was set for 100 mW/cm^2 using a Si reference Hamamatsu cell (Model C24 S1787-04) calibrated by the National Renewable Energy Laboratory (NREL), USA. The spectral mismatch of the solar simulator was estimated to be less than 10%. External quantum efficiency data were measured with monochromatic light by varying the excitation wavelength from 300 to 1100 nm at intervals of 10 nm, under a white bias light of 100 mW cm^{-2} (Optronics Laboratories, Inc.). The surface morphology of the thin films was measured using atomic force microscopy (Park Systems XE-150)