

Limonene as a Green Solvent for Depositing Thin Layers of Molecular Electronic Materials with Controlled Interdiffusion

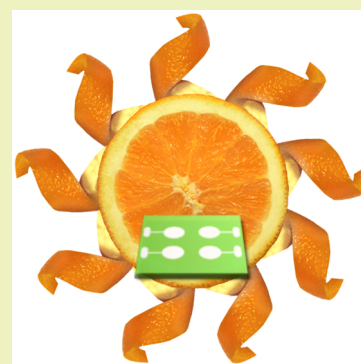
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ABSTRACT: In the fabrication of thin-film electronic devices such as solar cells, molecular components are often deposited from solution by spin-coating. Toxic chlorinated solvents are widely used in this process, and environmentally benign alternatives are desirable. Ideally, these alternatives should be inexpensive, derived from renewable sources, and able to dissolve typical molecular electronic materials. Moreover, they should allow the creation of thin films in which the interdiffusion of different components can be controlled to optimize the performance of the resulting device. In an initial survey, we have examined the deposition of layers of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), which are benchmark molecular semiconductors that have been widely used together in solar cells as electron donor and acceptor, respectively. We have found that solutions in limonene (which is a green solvent produced by citrus fruits and other plants) are particularly effective for depositing PCBM on P3HT to create bilayer architectures. Wetting of the P3HT underlayer is improved when limonene is used in place of standard chlorinated solvents, and interdiffusion of PCBM and P3HT is reduced, as established by TOF-SIMS measurements. Our results underscore the potential of unconventional green solvents such as limonene for use in fabricating molecular thin-film electronic devices.

KEYWORDS: Limonene, Thin-film devices, P3HT, PCBM, Interdiffusion, Green solvents



INTRODUCTION

Thin-film electronic devices such as light-emitting diodes, solar cells, and transistors have traditionally been made from inorganic components. Increasingly, however, these classical materials are being replaced by carbon-based molecular substitutes.^{1–3} Motivation for developing these new materials is provided by their increasingly impressive performance and by unique properties that include high flexibility, low density, and ease of deposition by simple low-energy methods such as spin-coating. Moreover, molecule-based devices do not typically contain highly toxic elements, can be designed to facilitate recycling,^{4–6} and can in principle be made by green methods from renewable starting materials.^{7–9}

In general, fabricating effective thin-film devices requires that active components with diverse compositions be brought together in ways that achieve a delicately adjusted balance between intermixing and segregation on the nanometric scale. The right balance is particularly hard to achieve in molecule-based devices because the intrinsic mobility of the components can facilitate extensive intermixing or large-scale separation of phases, particularly when solvents are present. A degree of interdiffusion is needed when the goal is to create architectures such as bulk heterojunctions (BHJs), in which interpenetrated phases are separated on the nanoscale but nevertheless remain in intimate contact.^{10,11} In the field of molecular photovoltaic devices, BHJs define an effective way to structure electron donors and acceptors so that excitons produced by the

absorption of light can lead efficiently to the separation of charges and their subsequent migration. More highly nanostructured heterojunctions with optimized dimensions promise to yield devices with even better power-conversion efficiencies and fully reproducible performance;^{12–14} in all such devices, however, interdiffusion of the components will lead to equilibrium and the loss of key nanostructural features. As a result, it is important to learn how to control interdiffusion involving adjacent domains of different composition so that the integrity of nanostructures is not compromised at their interfaces.

In the present study, we have surveyed solvents that can dissolve typical molecular semiconductors and allow adjacent thin films of these substances to be deposited by spin-coating in ways that minimize interdiffusion of the components. For our tests, we selected two benchmark compounds that have been widely used together as active components in thin-film photovoltaic devices: poly(3-hexylthiophene) (P3HT), which serves as an electron donor, and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), a fullerene derivative that acts as an electron acceptor (Figure 1).^{15,16} These two materials intermix well enough to allow them to form useful BHJs, but conditions such as exposure to solvents or long annealing at elevated

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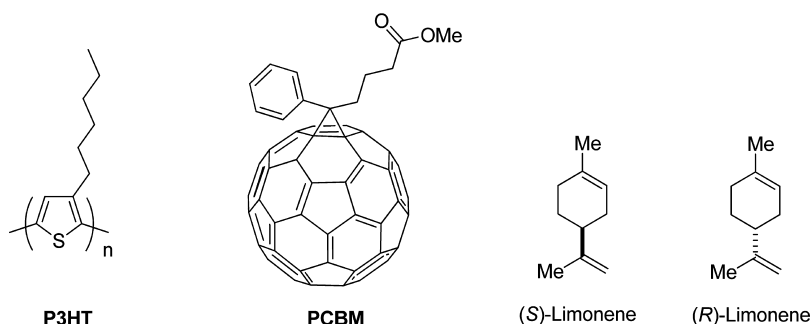


Figure 1. Structures of compounds of interest in depositing thin layers of molecular electronic materials.

temperatures can lead to extensive separation of phases and degraded performance.

To assess the feasibility of conserving nanostructured architectures with minimal interdiffusion, we examined layer-by-layer depositions of thin films of P3HT and PCBM by spin-coating. In such depositions, the use of solvents that only slightly dissolve the underlayer can be expected to minimize interdiffusion.¹⁷ Such solvents are described as orthogonal. For example, creating a thin film of PCBM on an underlayer of P3HT with minimal interdiffusion is expected to be facilitated by solvents that dissolve PCBM well and P3HT poorly. Widely used orthogonal solvents for depositing these materials by spin-coating include dichloromethane and other halogenated compounds;^{17–32} however, interdiffusion is still extensive.^{17–24}

Moreover, layers of P3HT are poorly wetted by solutions in dichloromethane, thereby leading to nonuniform deposition of adlayers and irreproducible fabrication of devices. The most effective solvents will presumably be those that can wet underlayers yet cannot dissolve them effectively.

A recent publication by Machui et al. provided Hansen solubility parameters for dozens of solvents, as well as estimates of their ability to dissolve P3HT and PCBM.³³ Included among the solvents is the natural product limonene (Figure 1), and the published data encouraged us to test it as a green substitute for dichloromethane and other halogenated solvents in fabricating thin-film devices. Its boiling point (176 °C) is low enough to ensure virtually complete elimination of traces after the deposition of adlayers. Although limonene is increasingly used as a renewably produced solvent,³⁴ it has only recently been employed in the production of thin-film devices,³⁵ and its use in creating nanostructured layers with controlled interdiffusion has not been reported.

Limonene is a chiral molecule, and both (*S*)-limonene (also known as *L*-limonene) and its (*R*)-enantiomer (*D*-limonene) are produced abundantly by various citrus fruits and other plants. Racemic limonene can be obtained easily by heating the pure enantiomers. (*S*)-Limonene has the smell of turpentine, and its (*R*)-enantiomer has a lemony odor. Limonene has very low toxicity to humans, and both enantiomers are currently registered in the U.S. Code of Federal Regulations as substances that are generally recognized as safe (GRAS) for use as flavoring agents and adjuvants in food for human consumption.^{36,37} Moreover, limonene is inexpensive enough to be widely employed as a major component of industrial cleaning agents and degreasers. Because P3HT and PCBM are both achiral molecules, the performance of (*S*)-limonene, (*R*)-limonene, and racemic limonene as green solvents for the deposition of thin layers will be identical. Arbitrarily, we

selected the (*S*)-enantiomer for our studies, but the (*R*)-enantiomer or the racemic compound will be equally effective.

In our work, we used measurements of contact angles and analyses of composition by time-of-flight secondary-ion mass spectrometry (TOF-SIMS) to show that limonene is more effective than dichloromethane for wetting underlayers of P3HT and for minimizing interdiffusion of P3HT and PCBM when adjacent layers are deposited by spin-coating.

EXPERIMENTAL SECTION

Deposition of Adlayers of PCBM on P3HT. We designed glass substrates with standardized patterns of indium tin oxide for use in fabricating thin-film photovoltaic devices, and the substrates were manufactured for us by commercial suppliers. The substrates were cleaned ultrasonically, first in deionized water, and then successively in acetone, 95% aqueous ethanol, and isopropanol (15 min each). The cleaned substrates were exposed to UV/ozone for 15 min. A 50 nm layer of PEDOT:PSS (Clevios PH 1000) was subsequently deposited on the substrates by spin-coating. The coated substrates were annealed at 110 °C for 30 min and transferred to a glovebox under N₂. P3HT (One Material) was deposited by spin-coating at 1000 rpm, using solutions in chlorobenzene with concentrations varying from 5 to 20 mg/mL to give layers with thicknesses in the range of 20–150 nm. An adlayer of PCBM (Solaris Chem) was then deposited by spin-coating, using solutions in (*S*)-limonene (10 mg/mL at 1000 rpm) or dichloromethane (10 mg/mL at 4000 rpm) to give layers with thicknesses of 25 nm. Thicknesses of layers were measured by profilometry (Dektak 150) in each step of the fabrication. (*S*)-Limonene (96%) was supplied by Acros Organics.

Contact Angles on Films of P3HT. Films were produced by spin-coating as described above, and 2 μ L drops of solvent were dispensed on the surface by syringe. Contact angles were then measured by goniometry.

Measurements of Composition by Time-of-Flight Secondary-Ion Mass Spectrometry (TOF-SIMS). A TOF-SIMS Model IV instrument (ION-TOF GmbH) was used to acquire depth profiles in dual-beam mode, in which two separate ion beams are used in alternating sequence to erode the sample and to analyze an area in the center of the crater. A beam of Cs⁺ at 400 eV was used to etch a crater of 200 μ m \times 200 μ m in the sample, while a beam of Bi⁺ at 15 keV was used for analysis in a region of 50 μ m \times 50 μ m. Charge compensation was provided by a low-energy electron flood gun throughout the profiles. Negative secondary ions were collected and analyzed according to their mass to obtain elemental and chemical information about the samples.

RESULTS AND DISCUSSION

Machui et al. estimated the solubilities of P3HT and PCBM in limonene to be 0.2 and 7.4 mg mL^{−1}, respectively.³³ Our measurements confirmed that these values are approximately correct. The nearly 15-fold higher solubility of PCBM established the potential suitability of limonene as an orthogonal solvent and suggested that it would be superior to

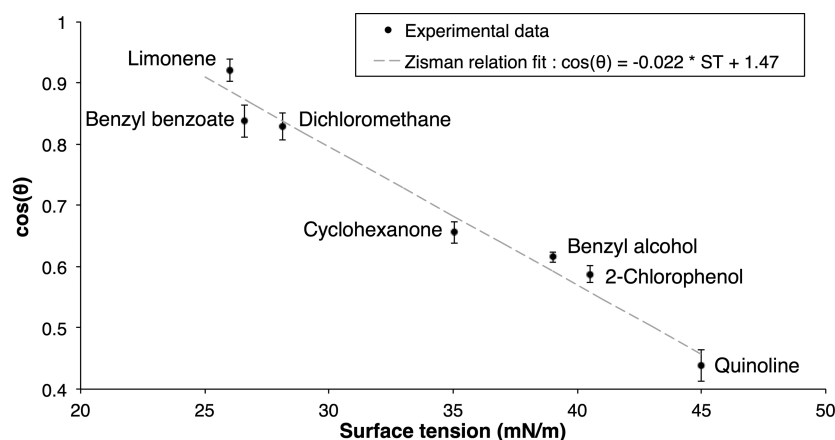


Figure 2. Wetting of films of P3HT by various solvents selected for their ability to dissolve PCBM preferentially, as assessed by a graph showing the cosine of contact angles ($\cos(\theta)$) as a function of surface tension (ST). Error bars represent standard deviation. The broken line confirms that the Zisman relationship is respected (linear dependence of $\cos(\theta)$ on ST).

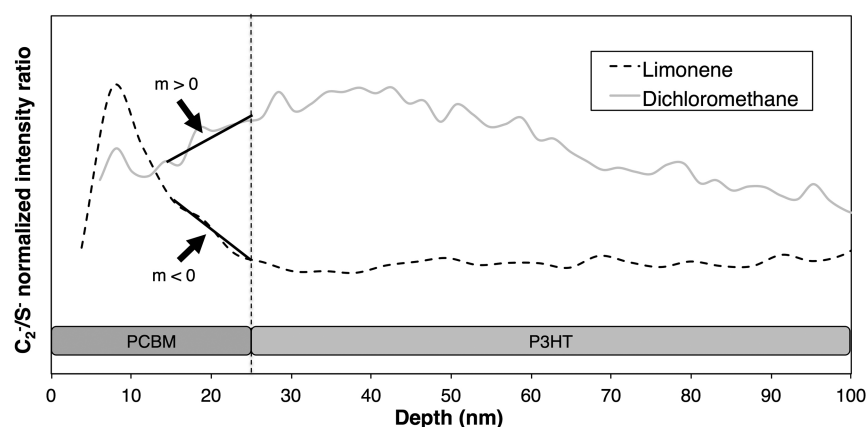


Figure 3. Ratio of the intensities of the ions C_2^- and S^- measured by TOF-SIMS as a function of depth for bilayers made by using either (S)-limonene or dichloromethane to deposit PCBM on P3HT. The slope m as a function of depth in the range 10–25 nm is highlighted by a solid line.

conventional halogenated solvents such as chlorobenzene and chloroform, which were estimated by Machui et al. to dissolve PCBM better than P3HT by factors of only 4 and 2, respectively.

We then examined the ability of (S)-limonene to wet films of P3HT, as assessed by using goniometry to measure contact angles. For comparison, we also tested dichloromethane and a set of five other solvents selected because their Hansen parameters suggested particularly high preferences for dissolving PCBM relative to that for dissolving P3HT (50- to 1000-fold), as assessed by Machui et al.³³ Our data, summarized in Figure 2, reveal that limonene has an exceptional ability to wet layers of P3HT, compared with that of other solvents that have high degrees of orthogonality. It is noteworthy that the Zisman relationship is respected by films of P3HT, and the cosine of the contact angle varies linearly with the surface tension of the solvent employed. As a result, this relationship can be used to search for solvents that are even more effective than limonene in wetting P3HT.

We then assessed the extent of nanoscale interdiffusion occurring in bilayer architectures created by spin-coating solutions of PCBM in (S)-limonene and dichloromethane on top of existing layers of P3HT. Depth profiling by dual-beam TOF-SIMS was used to study the composition of the bilayers as a function of depth. Two characteristic ions were selected to distinguish P3HT from PCBM. S^- was chosen as a marker

because it can only be derived from P3HT, and C_2^- was used to follow the distribution of PCBM because it is more abundant than in P3HT. C_{60}^- ions were not detected during depth profiling, presumably because etching by Cs^+ destroys molecular structure, even at the relatively low energy of 400 eV. As a result, C_{60}^- ions could not be used to assay PCBM. Figure 3 shows the intensity ratio C_2^-/S^- as a function of depth for bilayers made by using spin-coating in either (S)-limonene or dichloromethane to deposit PCBM. Intensities cannot be compared directly because the two species assayed have different ionization probabilities, so normalized curves were used for comparison. The thicknesses of the two layers, as measured by profilometry, are also shown at the bottom of the graph. In all samples, the layer of PCBM was nominally 25 nm thick, without considering the effects of interdiffusion.

Figure 3 reveals that the slope of the plots in the range of 10–30 nm is negative for bilayers made with limonene. This indicates an initially high ratio of PCBM to P3HT, which decreases as the nominal position of the interface is approached, and the composition becomes primarily P3HT. In sharp contrast, the slope of the plot in the same region is positive for bilayers made with dichloromethane. This suggests very substantial interdiffusion of P3HT and PCBM near the nominal position of the interface. Our results thereby show that intermixing of P3HT and PCBM is reduced when limonene is

used as an orthogonal solvent for creating well-defined bilayer architectures.

CONCLUSIONS

Our work has established that bilayer architectures of P3HT and PCBM can be created with controlled interdiffusion of the components, using spin-coating in (S)-limonene as a green alternative to dichloromethane and other chlorinated solvents. Our selection of limonene was made on the basis of Hansen parameters suggesting a high preference for dissolving PCBM relative to P3HT. Moreover, limonene proved better than dichloromethane for wetting P3HT, thereby reducing the probability of forming nonuniform adlayers by spin-coating. TOF-SIMS demonstrated that intermixing of P3HT and PCBM in bilayer architectures can be reduced significantly by using limonene to replace dichloromethane as the solvent for spin-coating. Our work underscores the potential of using limonene, as well as other inexpensive solvents of low toxicity derived from renewable sources, in the fabrication of thin-film molecular electronic devices.

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The authors declare no competing financial interest.

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