Solvent-dependent structure formation in drying P3HT : PCBM films studied by molecular dynamics simulations

Citation for published version (APA):

Negi, V., Lyulin, A., & Bobbert, P. A. (2016). Solvent-dependent structure formation in drying P3HT : PCBM films studied by molecular dynamics simulations. *Macromolecular Theory and Simulations*, 25(6), 550-558.
<https://doi.org/10.1002/mats.201600075>

Document license:

Unspecified

DOI:

[10.1002/mats.201600075](https://doi.org/10.1002/mats.201600075)

Document status and date:

Published: 01/11/2016

Document Version:

Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Solvent-dependent structure formation in drying P3HT:PCBM films studied by molecular dynamics simulations

*Vikas Negi, Alexey Lyulin, Peter Bobbert**

September 23, 2016

Molecular Materials and Nanosystems, Department of Applied Physics, Eindhoven University of
Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands

Email: p.a.bobbert@tue.nl

Abstract

We study phase separation in the donor-acceptor blend poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) during evaporation of a solvent using coarse-grained molecular dynamics simulations. To this end, an equilibrated P3HT:PCBM:solvent mixture is placed in an elongated simulation box, after which solvent molecules are removed at regular time intervals from a region above

the film. Three often-used solvents are considered: chloroform (CFM), chlorobenzene (CLB), and orthodichlorobenzene (oDCB). The coarse-grained solvent-solvent interaction parameters are tuned to reproduce the atmospheric boiling temperatures, while the PCBM-solvent interaction parameters are tuned to reproduce the PCBM solubilities. Other parameters are taken from literature. During evaporation, we observe the formation of a crust that is depleted of solvent, in which aggregation of P3HT and PCBM occurs. In agreement with experiment, the top region of the dry film is rich in PCBM for the cases of CLB and oDCB, and rich in P3HT for the case of CFM, while the very top layer of the film is always rich in P3HT. We ascribe this vertical separation to a competition between the tendency of P3HT to move to the surface due to its low surface energy and the different tendencies of PCBM to be dragged along to the surface by the evaporating solvent depending on its solubility. Also in agreement with experiment, the P3HT-PCBM interface area is larger for CLB and oDCB than for CFM. For CLB and oDCB, we find an indication for a spinodal P3HT-PCBM decomposition starting from the top and bottom surface, whereas for CFM the phase separation appears to be initiated in the bulk of the film.

1 Introduction

The traditional silicon-based technology currently used to harness the energy of the sun is still not economically competitive with fossil fuel-based power generation.^[1] Apart from improvements in efficiency of photovoltaic cells, their production cost needs to be reduced as well. Due to cheaper starting materials, photovoltaic devices based on organic semiconductors such as conjugated polymers have potential as a cost-effective alternative. Other advantages are device flexibility, solution processability and suitability for industrial-scale reel-to-reel production. Some of the most promising organic photovoltaic (OPV) cells are based on the bulk heterojunction (BHJ) design in which

two different organic semiconductors, an electron-donor material (usually a semiconducting polymer) and an electron acceptor material (usually a fullerene derivative) are blended together to form the photovoltaic active layer. When coated onto a substrate, using solvent deposition techniques such as spin coating or doctor blading, the two components phase separate to form a heterojunction with a large internal interfacial area, which is crucial for the OPV device performance.

The mechanism of power generation in an OPV cell is the following. Absorption of a photon by the polymer leads to the formation of an exciton, which migrates to the donor/acceptor (DA) interface. Here, electron transfer from the donor to the acceptor takes place forming charge transfer (CT) excitons, which are dissociated into free charges that are transported to the electrodes and generate the photocurrent.^[2] The exciton diffusion length, i.e., the distance an exciton diffuses before it decays, is of the order 10 nm in most semiconducting polymers.^[3] Thus, it is crucial that a photogenerated exciton can reach a DA interface within this distance.

The active layer in an OPV cell is usually 100-200 nm thick, which is much larger than the exciton diffusion length. The problem of the resulting length scale mismatch has fueled most of the research focused on fine-tuning the morphology of BHJ-based devices. Various experiments have shown that many basic electronic properties that determine the ultimate OPV device efficiency, such as charge-carrier mobility and recombination rates, are strongly dependent on the BHJ morphology.^[4, 5] The BHJ morphology in turn depends, among other things, on the processing and drying conditions, the choice of solvents, and the molecular weight of the polymer.^[6] Post-processing treatments, such as thermal^[7, 8, 9] or solvent-vapor annealing,^[10] are known to enhance the device performance by altering the BHJ morphology. It has also been established that the addition of a co-solvent can drastically alter the morphology, leading to better device efficiencies.^[11, 12] Experiments suggest that the solubility of the electron acceptor component plays a crucial role in determining the final film morphology, affecting the final device performance.^[13] The use of different solvents for the same DA combination can lead to different vertical stratification profiles.^[14] It is thus evident that predicting the right processing conditions to obtain the best BHJ morphology is crucial for improving the OPV device efficiency.

There is still not a clear understanding of the dependence of the lateral and vertical phase separation profiles of the DA blends on the solution-processing conditions.^[14] Therefore, morphology optimization is predominantly still a trial-and-error process, making the investigation of new kinds of DA blends very time-consuming. Moreover, most of the presently used solvents are toxic and therefore cannot be used on an industrial scale. Non-toxic alternatives should be investigated, but this is also a time-consuming process. Thus, there is a clear need to understand the role played by solvents in determining how the phase separation occurs in a drying film.

Computer simulations based on molecular dynamics (MD) can help to develop a fully predictive atomistic model for the final film morphology. The solvent evaporation process has been modeled previously using continuum-based approaches.^[15, 16] However, these approaches are usually generic and do not use interaction parameters based on the solubilities of the D and A components, which have been experimentally shown to be of great importance.^[13, 14] Also, atomic-scale film morphologies obtained using MD can be further used to carry out charge-transport simulations and study exciton dynamics at the DA interface.^[17, 18] Hence, MD simulations would be able to establish a direct link between the factors determining the film morphology, like the choice of solvents and the processing conditions, and the resultant OPV device performance.

Using MD simulations, we focus in this work on the role played by the solubilities of the D and A components on structure formation in a drying film of the well-characterized DA blend poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM). One of the earlier MD studies of these blends has focused on the effects of annealing after film formation.^[19] The large-scale MD simulations in that work, spanning a time scale of a few microseconds, demonstrate that it is possible to study effects of annealing on the DA phase separation by MD simulations, despite the fact that experimentally the annealing process typically takes a few hours. This observation is important for the present work, because the entire solvent evaporation process occurring during spin coating, from a DA solution to the final dry film, occurs on time scales of usually a few hundred milliseconds to a few seconds (the latter when using co-solvents).

In the present work, by using a powerful supercomputer and a coarse-grained model, we can

reach a simulation time scale of a microsecond, which is sufficient to observe various interesting aspects of the phase separation process. We investigate the evaporation and phase separation process for three different often-used solvents: chloroform (CFM), chlorobenzene (CLB), and orthodichlorobenzene (oDCB). Importantly, we reproduce the experimental solubilities of PCBM in the investigated solvents^[20] by fine-tuning the PCBM-solvent interaction parameters. Hence, our simulations can highlight the role played by the individual solvents. We note that a previous MD study of the effects of solvent evaporation on the morphology of a P3HT:PCBM blend^[21, 22] focused exclusively on the bulk dynamics and ignored surface effects, which are known to influence the final film morphology. Also, in the coarse-grained (CG) model used in that work both the P3HT unit and the PCBM molecule are represented by only one bead, which might not be sufficient to capture the correct phase separation dynamics in a drying film. By contrast, we simulate evaporation of a solvent from a supported P3HT:PCBM film including surface effects and use coarse-grained molecular dynamics (CGMD) based on a model in which the P3HT unit is represented by three and the PCBM molecule by five beads.^[23] All MD simulations have been carried out using the GPU-enabled GROMACS simulation package, which is currently one of the fastest codes available and demonstrates excellent scaling capabilities.^[24, 25, 26, 27] The trajectory analysis and subsequent visualizations have been done using VMD^[28] and OVITO.^[29, 30, 31]

2 Computational setup

2.1 Model and force field

P3HT is one of the most widely studied conjugated polymers and thus there exist various atomistic and CG models in the literature. For our work, we choose a three-bead model for P3HT and a five-bead model for PCBM (see Supporting Information S1).^[23] It has recently been established that a three-bead model for P3HT gives more accurate predictions of experimental values for fluid phase densities and various thermomechanical properties than a one-bead model.^[32] The authors

of Ref. 23 have performed an extensive test of their CG force-field parameters by matching several simulated and measured properties. They model short-ranged bonded interactions, such as bond stretching, angle bending, and torsional potentials, based on the harmonic approximation. Regarding long-range interactions, they use the Coulomb potential to model electrostatic interactions and the Lennard-Jones (LJ) form to model the van der Waals interaction:

$$V_{\text{LJ}}(r_{ij}) = 4\epsilon \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\left(\frac{\sigma}{r_{ij}} \right)^6 \right) \right). \quad (1)$$

We model our solvent molecules CFM, CLB, and oDCB as single neutral beads interacting via the LJ potential Eq. (1). The parameters σ (nm) and ϵ (kJ/mol) have been tuned to yield the correct experimental densities at room temperature ($T = 298$ K) and the boiling points of the solvents (see Supporting Information S2). Our P3HT polymer chain length is set to 40 monomer units (7 kDa), corresponding to a length of 16 nm. It should be noted that this is rather small as compared to experimental polymer molecular weights routinely used for fabricating OPV cells (30-40 kDa), but such relatively short chain lengths have shown good phase separation behavior in annealing studies done using CGMD simulations.^[19] It is difficult to estimate the right polymer solubility for such short chains. We choose the interaction parameters ϵ_{PS} between the polymer (P) and each of the three solvents (S) such that $\epsilon_{\text{PS}} - (\epsilon_{\text{PP}} + \epsilon_{\text{SS}})/2$ is about 0.2 kJ/mol. This corresponds to the required “good” solvation behavior of the polymer in the three solvents. The experimental persistence length is close to 2.4 ± 0.3 nm^[33] and thus our chains are long enough to model the flexible polymer conformations in a solution and avoid simulating a “rod-like” behavior (see Supporting Information S3).

We note that using a simple mixing scheme to determine the off-diagonal parameters $\epsilon_{\text{P'S}}$ for PCBM-solvent (P'S) interactions does not reproduce the correct solubility behavior of PCBM. The parameters $\epsilon_{\text{P'S}}$ are instead set to values reproducing the experimental solubilities in the different solvents.^[20] At a PCBM concentration close to the solubility limit for the solvent we see the formation of small PCBM clusters that grow in size as the concentration is increased; see **Figure 1** for the case of PCBM dissolved in CFM. We have not included electrostatic interactions in

Figure 1: (a) Snapshot of a simulation after reaching equilibrium of PCBM (red beads) dissolved in chloroform (CFM, not shown here for clarity) at a concentration of 20 mg/ml. Since the concentration is below the solubility limit of PCBM in CFM (28 mg/ml), the PCBM is uniformly dispersed. (b) Snapshot for a PCBM concentration of 40 mg/ml, which is above the solubility limit. Clusters of PCBM molecules are clearly visible. The same behavior is observed for the other solvents. The sizes of the simulation boxes are $40 \times 40 \times 40 \text{ nm}^3$ (a) and $32 \times 32 \times 32 \text{ nm}^3$ (b).

our current simulations. Neglecting these interactions seems to have no effect on the equilibrated properties (such as the density and radial distribution function of a PCBM system; see Supporting Information S4) and greatly reduces the computational load, allowing us to probe much longer time scales. Also, it has been recently established that for polymer chains dissolved in a solvent,^[34] the van der Waals interactions play a much bigger role in determining the chain conformations than electrostatic interactions.

It should be noted that CG force fields lead to accelerated dynamics as compared to atomistic force fields, because of a smoother potential energy surface. For the CG scheme used by us, an acceleration factor of about 10 has been reported.^[23] Thus the CG simulation time needs to be multiplied by this factor in order to obtain the equivalent atomistic simulation time. In the rest of the paper, we mention the CG simulation times unless specified otherwise.

2.2 Simulation technique

We simulate solvent evaporation from a supported P3HT:PCBM:solvent film. The starting configuration for each solvent system consists of 450 P3HT chains and 3318 PCBM molecules dissolved in the solvent such that both the P3HT and PCBM concentrations are 50 mg/ml for the P3HT:PCBM:CFM (3.5:3.5:93 wt %) and P3HT:PCBM:CLB (4:4:92 wt %) systems, and 30 mg/ml for the P3HT:PCBM:oDCB (2.5:2.5:95 wt %) system. We note that the concentrations for the CLB and oDCB solutions are below their solubility limits for PCBM, whereas for CFM the PCBM concentration is above the solubility limit. Due to the low solubility of PCBM in CFM, we would need a very large number of solvent beads (about 1.8 million) to start with a configuration below the respective solubility limit, which would greatly increase the computational workload. We checked that for the oDCB and CLB systems the trend in the phase separation process does not depend on whether the initial PCBM concentration is below or above the solubility limit. We expect this to be the same for the CFM system. Hence, we chose to start evaporation from an equilibrated CFM solution at 50 mg/ml as for the CLB system. The P3HT and PCBM components are always present in a 1:1 weight ratio.

In a first stage, the equilibration stage, the solution is equilibrated at a temperature of 298 K and a pressure of 1 bar. We control the temperature using a velocity-rescaling thermostat^[35] with a time constant of 0.1 ps and implement an isotropic pressure coupling using the Berendsen barostat^[36] with a time constant of 5 ps to control the pressure. A leap-frog integrator with a time step of 3 fs is used to obtain the trajectory of the beads. The neighbor lists are built using the Verlet cut-off scheme. Periodic boundary conditions in all three directions are used. Typical box sizes in this stage are $50 \times 50 \times 50 \text{ nm}^3$.

Once equilibrated, in a second stage, the evaporation stage, the system is placed in a new elongated box with two walls at $z = 0$ and $z = z(\text{box}) = 1160 \text{ nm}$ and the simulation is continued. Before doing so, the periodic boundary conditions in the z -direction are removed, completing molecules that are “broken” by the periodic boundary conditions. The system is then put at a small distance above $z = 0$ to ensure that all molecules are within the new box. The periodic boundary conditions

in the x - and y -directions are kept. The wall at $z = 0$ acts like a substrate supporting the blend, while the wall at $z = z(\text{box})$ determines the free space available for evaporation of the solvent. The LJ parameters σ of the z -dependent interaction between the top wall ($z = z(\text{box})$) and all the individual beads are chosen in such a way that the solvent can move into the free space ($\sigma = 6$ nm), while the P3HT and PCBM stay within the film ($\sigma = 1100$ nm). The parameters σ_{WP} , ϵ_{WP} (wall-P3HT) and $\sigma_{\text{WP}'}$, $\epsilon_{\text{WP}'}$ (wall-PCBM) with the bottom supporting wall ($z = 0$) are set to $\sigma_{\text{WP}} = \sigma_{\text{WP}'} = 4$ nm and $\epsilon_{\text{WP}} = \epsilon_{\text{WP}'} = 1$ kJ/mole for both P3HT and PCBM, so that there is no preference for either of the two components to move towards this wall; see Supporting Information S1 for more details.

The pressure in the elongated box is controlled using a semi-isotropic coupling implemented with the Berendsen barostat with the compressibility set to 0 for the z -direction and 1.0×10^{-5} bar $^{-1}$ for the x - and y -directions. Once the evaporation stage starts, solvent beads begin to leave the film surface and fill up the empty space between the film and the top wall at (see Supporting Information video). In order to allow for continuous evaporation of solvent from the film, the existing vapor needs to be removed from the box. To this end, the simulation is in a first cycle interrupted when the average vapor density above a cutoff distance of 100 nm from the film surface has increased to a value of 2.5 kg/m 3 for each solvent. This happens after time intervals of about 5 ns for CFM, 10 ns for CLB, and 20 ns for oDCB (see Supporting Information S5). In the next removal cycles we use these time intervals between successive interruptions. This procedure is repeated until the solvent concentration in the film is below 2 wt %, resulting in total CG simulation times of about 240 ns for CFM, 440 ns for CLB, and 540 ns for oDCB. The different time intervals and total simulation times reflect the different volatilities of the solvents, with CFM having the highest volatility and oDCB the lowest. This way of vapor removal approximates a continuous evaporation process, while at the same time limiting the number of interruptions. We note that the evaporation speed in our simulations will be faster than under usual laboratory conditions. However, our simulations correctly account for the different volatilities of the three solvents and we therefore expect that the simulated trends in the film formation process can be extrapolated to experimental time scales.

Figure 2: Snapshot of the P3HT:PCBM:CFM system at the bottom of a $45 \times 45 \times 1160 \text{ nm}^3$ simulation box during the evaporation stage with 14 wt % of P3HT as well as PCBM.

Figure 2 gives a snapshot of the P3HT:PCBM:CFM system during the evaporation stage after about 110 ns of CG simulation time (about $1.1 \mu\text{s}$ atomistic time), when the amount of P3HT and PCBM is 14 wt % for each. The CFM beads are evaporating along the elongated z -axis. We note that since CLB and oDCB are less volatile than CFM, it takes a longer time to reach the same stage for those solvents: about 150 ns for CLB and about 400 ns for oDCB.

3 Results and discussion

3.1 P3HT and PCBM density profiles

In **Figure 3** we show for the three solvents the vertical density profiles of P3HT and PCBM during evaporation, along the z -direction of the simulation box. The results for the different solvents are ordered from left to right according to their measured boiling points at atmospheric pressure (CFM: 61°C , CLB: 131°C , oDCB: 180°C).

Figure 3: Evolution of the vertical layer-averaged density profiles of P3HT (top panels) and PCBM (bottom panels) during solvent evaporation for the three different solvents: chloroform (CFM, left), chlorobenzene (CLB, middle), and orthodichlorobenzene (oDCB, right). The different curves are for different weight percentages of P3HT and PCBM in the simulation box. The starting P3HT:PCBM:solvent weight percentages are 3.5:3.5:93 (CFM), 4:4:92 (CLB), and 2.5:2.5:95 (oDCB). The profile for the almost dry film (2 wt % of solvent, 49 wt % of P3HT and PCBM each) are indicated by the black lines.

We observe peaks in the density of both P3HT and PCBM at the top surface, which grow during evaporation. These peaks indicate the formation of a “crust” that is rich in both PCBM as well as P3HT and depleted of solvent. Crust formation under evaporation has been described in the context of concentrated polymer solutions.^[37] It is identified as a non-equilibrium feature and is predicted by kinetic models for evaporation. Crust formation in MD simulations of a polymer and a solvent has been reported before.^[38] It is consistent with predictions from various numerical kinetic modeling schemes.^[39] Any experimental solvent deposition technique will also be a non-equilibrium process, where the final morphology will be a kinetically frozen state. We therefore conclude that crust formation in the deposition of OPV films should occur experimentally under evaporation conditions that are sufficiently far from equilibrium. We note that the peaks at the bottom surface in Figure 3 also point at the formation of a crust at this surface. We attribute these peaks to a quick “evaporation” of the small solvent molecules from the film to a thin layer very close to the bottom of the simulation box that is inaccessible to the larger PCBM molecules and P3HT chains.

Whereas the previous studies of crust formation concerned binary mixtures, we have in our case ternary mixtures. Therefore, crust formation will in our case also be determined by the interplay between surface energies and differences in solubilities of P3HT and PCBM. It is clear from Figure 3 that both the height and the shape of the peaks is different for P3HT and PCBM, showing that the composition of the crust is not homogeneous. The thick red lines in Figure 3 are the density profiles for the almost dry film. We observe that the profiles for CLB and oDCB in the almost dry film are rather similar, but deviate from those for CFM.

In order to obtain a better view on the composition of the film during drying and the phase separation between P3HT and PCBM, we plot in **Figure 4-6** for the different solvents the profiles of the density fractions of P3HT and PCBM in the film at three different stages in the evaporation process. The phase separation can initiate from the top surface, bottom surface, or uniformly across the film. The fluctuations in the density fractions give an indication about the instabilities present in the film during evaporation of the solvent.

Figure 4: Vertical profiles of the layer-averaged density fractions of P3HT and PCBM at three different moments in the evaporation process, for the P3HT:PCBM:CFM system. The corresponding weight percentages of P3HT and PCBM in the simulation box are indicated.

As can be seen in Figure 5 and 6, for the cases of CLB and oDCB the top region is rich in PCBM and poor in P3HT. This can favor OPV device efficiency, as the cathode is usually deposited on the top surface. The final morphology has a thin P3HT layer on the top surface, in agreement with experiments.^[14] Its occurrence is a result of the lower surface energy of P3HT^[40] as compared to PCBM and is thus a thermodynamically driven effect. By contrast, Figure 4 shows that for the case of CFM the top region is rich in P3HT.

The enrichment of the top region by PCBM for the cases of CLB and oDCB and by P3HT for the case of CFM is fully in agreement with experiments.^[14] These experiments also demonstrate the impact on the performance of the final OPV cells. We explain the differences in enrichment by the different solubilities of PCBM in the three different solvents. The solubility of PCBM in CLB and oDCB is considerably higher than in CFM, which is reflected by a stronger attraction between the PCBM and CLB or oDCB molecules as compared to CFM molecules. As a result, while the solvent is moving upwards to replenish the evaporating solvent at the top surface, it drags along the

Figure 5: Same as figure 4, for the P3HT:PCBM:CLB system.

Figure 6: Same as figure 4, for the P3HT:PCBM:oDCB system.

PCBM more strongly for the cases of CLB and oDCB than for the case of CFM. This finally leads to an enrichment of PCBM in the top layers for the cases of CLB and oDCB.

We now turn our attention to the different modes inducing the phase separation process between P3HT and PCBM. For the cases of CLB (Figure 5) and oDCB (Figure 6), at the intermediate stage of evaporation (middle panels) large differences between the density fractions of P3HT and PCBM are observed in the interior of the film. This is compatible with a phase separation mode that proceeds via spinodal decomposition, starting from the top and bottom surface, as observed in experiments on a P3HT:PCBM:CLB system.^[41] On the contrary, for the case of CFM (Figure 4) no large differences between the density fractions are observed in the interior of the film. This is compatible with a phase separation mode initiated in the bulk of the film, which does not lead to significantly different layer-averaged density fractions.

3.2 P3HT-PCBM interfacial area

In order to make a connection to the OPV cell performance, we want to have a measure for the P3HT-PCBM interfacial area as well as the volumes of the P3HT and PCBM components for the almost dry films for the three different solvents. To this end, we use the surface construction technique implemented in the visualization tool OVITO.^[29, 30, 31] This technique makes use of a polyhedral mesh constructed on a set of points based on the Delaunay tessellation, and a probe sphere determining a surface area and a volume of this set of points that depends on the radius of the probe sphere. We apply this technique to quantify the P3HT-PCBM interfacial area and the volume occupied by these two components.

In **Figure 7** we show top snapshots of the almost dry film obtained with the three different solvents. In the top panels, the P3HT beads are indicated in green and the PCBM beads in red. We observe that the top layers in the case of CFM contain more P3HT than in the cases of CLB and oDCB, in accordance with the analysis in the previous subsection. The bottom panels provide a three-dimensional view of the PCBM component as obtained with the surface construction tech-

Figure 7: Top views of the almost dry film morphology obtained with the three different solvents: chloroform (CFM, left panels), chlorobenzene (CLB, middle panels), and orthodichlorobenzene (oDCB, right panels). In the top panels the P3HT (PCBM) beads are indicated by green (red) spheres with their corresponding van der Waals radii. The bottom panels provide a three-dimensional view of the PCBM component, defined using the surface construction technique explained in the main text. The sizes of the areas shown is about $43 \times 43 \text{ nm}^2$ for CFM, $45 \times 45 \text{ nm}^2$ for CLB, and $48 \times 48 \text{ nm}^2$ for oDCB. The P3HT-PCBM interfacial areas obtained with the three solvents are 6.18×10^3 , 7.35×10^3 , and $7.24 \times 10^3 \text{ nm}^2$ with the corresponding probe sphere radii set to 0.8255, 0.8505, and 0.8895 nm, respectively.

nique, using as input the positions of the beads of the different components. The radius of the probe sphere was chosen close to the first peak in the pair correlation function of the C_{60} beads of the PCBM and fine-tuned such that the obtained volume of the PCBM component is for all three cases $3.12 \times 10^3 \text{ nm}^3$. In the case of CFM the P3HT-PCBM interfacial area is smaller than in the cases of CLB and oDCB, which indicates a coarser phase separation. This observation is in accordance with experiments demonstrating that a decreasing solubility of the acceptor component leads to a coarser morphology,^[13] and provides an explanation for the general finding that OPV cells made with CLB and oDCB as solvents perform better than those prepared with CFM.

4 Summary, conclusions, and outlook

We have investigated the P3HT:PCBM film formation process during evaporation of a solvent using coarse-grained molecular dynamics simulations. We considered three solvents with increasing boiling-point temperatures: chloroform, chlorobenzene, and orthodichlorobenzene. During evaporation, we observed the formation of a crust that is depleted of solvent, in which the aggregation of P3HT and PCBM occurs. Morphological properties of our almost dry films that are crucial for the performance of the final organic photovoltaic devices match well with those of films fabricated under laboratory conditions, such as the solvent-dependent vertical P3HT-PCBM segregation profile and the size of the P3HT-PCBM interfacial area.

We conclude that surface effects play a very important role in determining the aggregation of the P3HT and PCBM components. P3HT always tends to move towards a surface, because of its low surface energy, and in doing so competes with PCBM. For PCBM, it is the solubility that determines how much of it accumulates in the surface region. For a solvent with a high PCBM solubility, like chlorobenzene and orthodichlorobenzene, more PCBM is transported to surface region than for a solvent with a low PCBM solubility, like chloroform.

By tracking the layer-averaged P3HT and PCBM density fractions in the vertical direction during evaporation we tried to obtain insight in the modes responsible for the P3HT-PCBM phase separation. For the cases of chlorobenzene and orthodichlorobenzene, we find an indication for a spinodal decomposition starting from the top and bottom surface, whereas for chloroform the phase separation seems to be initiated in the bulk of the film. However, more information is needed to form a complete picture of the phase separation process. For this, a link has to be made with continuum approaches based on Flory-Huggins theory. A possible pathway is to obtain the Flory-Huggins interaction parameters of our P3HT:PCBM:solvent systems from molecular dynamics simulations and to use these in phase-field modeling studies.^[15, 16]

5 Supporting Information

Description of force-field parameters, bulk properties of the solvents, bulk properties of P3HT, bulk properties of PCBM with and without electrostatics, vapor density simulations of the solvents above the film (PDF); simulation video of the solvent evaporation for the case of chloroform (AVI).

5.1 Notes

The authors declare no competing financial interest.

6 Acknowledgement

The authors thank MSc Charley Schaefer, Dr Martijn Wienk, and Prof.dr René Janssen for fruitful discussions. This work is part of the Industrial Partnership Programme (IPP) “Computational sciences for energy research” of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organisation for Scientific Research (NWO). This research programme is co-financed by Shell Global Solutions International B.V. This work was carried out on the Dutch national supercomputer Cartesius with the support of SURF Cooperative.

Keywords: molecular dynamics, organic electronics, solar cells, structure-property relations, thin films

References

- [1] Lewis, N. S. *Science* **2007**, *315*, 798–801.

- [2] Bakulin, A. A.; Rao, A.; Pavelyev, V. G.; van Loosdrecht, P. H. M.; Pshenichnikov, M. S.; Niedzialek, D.; Cornil, J.; Beljonne, D.; Friend, R. H. *Science* **2012**, 335, 1340–1344.
- [3] Shaw, P. E.; Ruseckas, A.; Samuel, I. D. W. *Advanced Materials* **2008**, 20, 3516–3520.
- [4] Scarongella, M.; Paraecattil, A. A.; Buchaca-Domingo, E.; Douglas, J. D.; Beaupre, S.; McCarthy-Ward, T.; Heeney, M.; Moser, J.-E.; Leclerc, M.; Frechet, J. M. J.; Stingelin, N.; Banerji, N. *J. Mater. Chem. A* **2014**, 2, 6218–6230.
- [5] Jamieson, F. C.; Domingo, E. B.; McCarthy-Ward, T.; Heeney, M.; Stingelin, N.; Durrant, J. R. *Chem. Sci.* **2012**, 3, 485–492.
- [6] Liu, F.; Chen, D.; Wang, C.; Luo, K.; Gu, W.; Briseno, A. L.; Hsu, J. W. P.; Russell, T. P. *ACS Applied Materials & Interfaces* **2014**, 6, 19876–19887, PMID: 25350382.
- [7] Li, G.; Shrotriya, V.; Yao, Y.; Yang, Y. *Journal of Applied Physics* **2005**, 98.
- [8] Parnell, A. J.; Dunbar, A. D. F.; Pearson, A. J.; Staniec, P. A.; Dennison, A. J. C.; Hamamatsu, H.; Skoda, M. W. A.; Lidzey, D. G.; Jones, R. A. L. *Advanced Materials* **2010**, 22, 2444–2447.
- [9] Yin, W.; Dadmun, M. *ACS Nano* **2011**, 5, 4756–4768, PMID: 21563761.
- [10] Zhao, Y.; Xie, Z.; Qu, Y.; Geng, Y.; Wang, L. *Applied Physics Letters* **2007**, 90.
- [11] Kouijzer, S.; Michels, J. J.; van den Berg, M.; Gevaerts, V. S.; Turbiez, M.; Wienk, M. M.; Janssen, R. A. J. *Journal of the American Chemical Society* **2013**, 135, 12057–12067, PMID: 23863101.
- [12] Collins, B. A.; Li, Z.; Tumbleston, J. R.; Gann, E.; McNeill, C. R.; Ade, H. *Advanced Energy Materials* **2013**, 3, 65–74.
- [13] Troshin, P. A.; Hoppe, H.; Renz, J.; Egginger, M.; Mayorova, J. Y.; Goryachev, A. E.; Peregu-dov, A. S.; Lyubovskaya, R. N.; Gobsch, G.; Sariciftci, N. S.; Razumov, V. F. *Advanced Functional Materials* **2009**, 19, 779–788.

- [14] Ruderer, M. A.; Guo, S.; Meier, R.; Chiang, H.-Y.; Korstgens, V.; Wiedersich, J.; Perlich, J.; Roth, S. V.; Muller-Buschbaum, P. *Advanced Functional Materials* **2011**, *21*, 3382–3391.
- [15] Wodo, O.; Ganapathysubramanian, B. *Computational Materials Science* **2012**, *55*, 113 – 126.
- [16] Wodo, O.; Ganapathysubramanian, B. *Applied Physics Letters* **2014**, *105*.
- [17] Groves, C. *Energy Environ. Sci.* **2013**, *6*, 3202–3217.
- [18] Nelson, J.; Kwiatkowski, J. J.; Kirkpatrick, J.; Frost, J. M. *Accounts of Chemical Research* **2009**, *42*, 1768–1778, PMID: 19848409.
- [19] Carrillo, J.-M. Y.; Kumar, R.; Goswami, M.; Sumpter, B. G.; Brown, W. M. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17873–17882.
- [20] Machui, F.; Langner, S.; Zhu, X.; Abbott, S.; Brabec, C. J. *Solar Energy Materials and Solar Cells* **2012**, *100*, 138 – 146, Photovoltaics, Solar Energy Materials, and Technologies: Cancun 2010.
- [21] Lee, C.-K.; Pao, C.-W. *The Journal of Physical Chemistry C* **2014**, *118*, 11224–11233.
- [22] Lee, C.-K.; Pao, C.-W.; Chu, C.-W. *Energy Environ. Sci.* **2011**, *4*, 4124–4132.
- [23] To, T. T.; Adams, S. *Phys. Chem. Chem. Phys.* **2014**, *16*, 4653–4663.
- [24] Berendsen, H.; van der Spoel, D.; van Drunen, R. *Computer Physics Communications* **1995**, *91*, 43–56.
- [25] Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. *Journal of Chemical Theory and Computation* **2008**, *4*, 435–447, PMID: 26620784.
- [26] Lindahl, E.; Hess, B.; van der Spoel, D. *Molecular modeling annual* **2001**, *7*, 306–317.
- [27] Van Der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A. E.; Berendsen, H. J. C. *Journal of Computational Chemistry* **2005**, *26*, 1701–1718.

- [28] Humphrey, W.; Dalke, A.; Schulten, K. *Journal of Molecular Graphics* **1996**, *14*, 33 – 38.
- [29] Edelsbrunner, H.; Mücke, E. P. *ACM Trans. Graph.* **1994**, *13*, 43–72.
- [30] Stukowski, A. *Modelling and Simulation in Materials Science and Engineering* **2010**, *18*, 015012.
- [31] Stukowski, A. *JOM* **2014**, *66*, 399–407.
- [32] Root, S. E.; Savagatrup, S.; Pais, C. J.; Arya, G.; Lipomi, D. J. *Macromolecules* **2016**, *49*, 2886–2894.
- [33] Heffner, G. W.; Pearson, D. S. *Macromolecules* **1991**, *24*, 6295–6299.
- [34] Jackson, N. E.; Kohlstedt, K. L.; Savoie, B. M.; de la Cruz, M. O.; Schatz, G. C.; Chen, L. X.; Ratner, M. A. *Journal of the American Chemical Society* **2015**, *137*, 6254–6262, PMID: 25920989.
- [35] Bussi, G.; Donadio, D.; Parrinello, M. *The Journal of Chemical Physics* **2007**, *126*.
- [36] Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. *The Journal of Chemical Physics* **1984**, *81*, 3684–3690.
- [37] P.G. de Gennes, *Eur. Phys. J. E* **2002**, *7*, 31–34.
- [38] Peter, S.; Meyer, H.; Baschnagel, J. *The Journal of Chemical Physics* **2009**, *131*.
- [39] Okuzono, T.; Ozawa, K.; Doi, M. *Phys. Rev. Lett.* **2006**, *97*, 136103.
- [40] Wang, X.; Ederth, T.; Inganas, O. *Langmuir* **2006**, *22*, 9287–9294, PMID: 17042544.
- [41] Vaynzof, Y.; Kabra, D.; Zhao, L.; Chua, L. L.; Steiner, U.; Friend, R. H. *ACS Nano* **2011**, *5*, 329–336, PMID: 21189029.

Figure 8: TOC Graphic

7 For Table of Contents use only

A coarse-grained molecular dynamics based approach is used to model solvent evaporation from a supported P3HT:PCBM film. Based on the different solubilities of PCBM in various solvents, P3HT or PCBM enriched layers are found on the top surface which is in agreement with experiments.