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**Effect of Solvent Additives on the Solution Aggregation of
Phenyl-C₆₁-Butyl Acid Methyl Ester (PCBM)**

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Abstract

High-boiling point solvent additives, employed during the solution processing of active-layer formulations, impact the efficiency of bulk hetero-junction (BHJ) organic solar cells by influencing the morphological / topological features of the multicomponent thin film. Here, we aim at a better understanding of how these additives change the aggregation landscape in the casting solution prior to film deposition via a multi-scale computational study of the aggregation phenomena of phenyl-C₆₁-butyric-acid methyl ester (PCBM) in various solutions. The energetic landscape of PCBM-solvent / solvent-additive intermolecular interactions is evaluated at the electronic-structure level through symmetry-adapted perturbation theory to determine the nature and strength of non-covalent forces important to aggregation. Molecular dynamics simulations highlight how the choice of solvent and solvent additives control the formation of molecular aggregates. Our results indicate that high-boiling point solvent additives change the effective interactions among the PCBM and casting-solvent molecules and alter equilibrium PCBM aggregate size in solution.

1. Introduction.

The potential for roll-to-roll printing and for deposition onto flexible substrates opens the way for organic photovoltaics (OPV) to impact a range of applications including wearable / fabric embedded devices, window coverings, and large-scale building applications. To date, the bulk heterojunction (BHJ) film architecture, developed primarily from spun-cast multicomponent inks, has shown the most promise to offer the required film morphology for efficient, printed OPV. The printing of OPV active layers requires precise control both of the ink formulations and film morphologies derived from multicomponent blends; however, there remain significant challenges to control the BHJ morphology, known to consist of highly variable material phases, through molecular design and processing protocols.¹⁻⁷

Printed organic solar cells are mainly processed with halogenated solvents, owing to the ability of these solvents to solubilize both the electron-rich donor (usually π -conjugated small molecules or polymers) and acceptor (typically substituted fullerenes) components; we note that efforts to replace such toxic, hazardous solvents with “green” solvents now show promise.^{8, 9} The dilute inclusion of high-boiling point additives, including 1,8-diiodooctane, 1-chloronaphthalene, and dichlorobenzene (also used as solvent), to the casting solvent has been demonstrated to aid in the formation of morphological^{10, 11} and topological¹²⁻¹⁴ film features, leading to improved OPV efficiency.¹⁵ However, the effects of these additives are blend dependent, with many instances of additives resulting in detrimental morphologies. Given the highly empirical route pursued in the use of these additives, it is not surprising that there is still limited understanding of how the choice of solvent and additives affects aggregation and the formation of the active-layer morphology.^{9, 11-14, 16-20}

More generally, issues pertaining to fullerene solubility have been of interest for some time, as aggregation in solution and in the solid state can impact materials properties of fullerene-containing films.^{9, 20-26} Though the solution aggregation of C₆₀ has been studied for more than two decades,^{20, 27} there remain many questions concerning the solubility of these highly symmetric, conjugated systems.^{20, 28, 29} Halogenated aromatic solvents are superior to non-halogenated solvents for solvating C₆₀, with some exceptions.^{21, 27} Various hypotheses, ranging from electron transfer between solvent molecules and fullerenes or anion- π -interactions, have been put forward to explain the large solubility of fullerenes in halogenated solvents,^{30, 31} though correlations between the parameter space explored and solubility are scarce.²⁹

Here, to start developing a molecular view of how processing protocols influence the film morphology of fullerene-containing OPV active layers, we report on a multiscale theoretical effort to investigate the solution aggregation of phenyl-C₆₀-butyric acid methyl ester (PCBM),³² a widely used, soluble fullerene.^{9, 23, 33-41} The solvents under consideration are chlorobenzene (CB) and o-dichlorobenzene (DCB), while the additives include 1-chloronaphthalene (1CN) and 1-8-diiodooctane (DIO). We begin by deriving an understanding of the nature and strength of the non-covalent forces at play in fullerene solubility through *ab initio* symmetry-adapted perturbation theory (SAPT) calculations for model complexes. All-atom molecular dynamics (MD) simulations are then used to evaluate the free energies of PCBM dimer interactions under various solvent conditions, as well as the dynamic formation of fullerene aggregates as a function of concentration and solvent. The combination of these studies provides a molecular-scale view of the processes that induce variations in fullerene aggregation in solution, which can influence the morphology and performance of OPV active layers.

2. Computational Methodology

Non-covalent interactions between solvent and solvent-additive molecules with PCBM are analyzed in terms of contributions from exchange-repulsion, London dispersion, electrostatic, and induction effects via symmetry-adapted perturbation theory (SAPT)⁴² with density fitting (which allows for efficient wave-function-based computations).⁴³ SAPT calculations were carried out on complexes made of one PCBM molecule and one solvent or additive molecule. The SAPT0 approximation, which does not include the effect of *intra*-molecular electron correlation, was used given the large system sizes.^{42, 43} The SAPT0 calculations were carried out in conjunction with a truncated aug-cc-pVDZ basis set that neglects diffuse functions on hydrogen atoms and diffuse *d* functions on other atoms, the so-called jun-cc-pVDZ basis set; this basis set was previously shown to give accurate binding energies in non-covalent systems and performed well for the S22 test set of non-covalent interactions when compared to high-quality benchmark data.⁴³⁻⁴⁵ The jun-cc-pVDZ basis set is not defined for iodine; therefore, SAPT0/jun-cc-pVDZ calculations were carried out on a chlorine analog of 1,8-diiodooctane – 1,8-dichlorooctane (DCIO) – to provide an estimate of the interaction potential expected for DIO. The SAPT0 computations were performed with a local version of PSI4.⁴⁶

The relaxed molecular geometries serving as input for the SAPT0 calculations were obtained via density functional theory (DFT), with individual molecules optimized at the B3LYP/6-31G(d,p) level of theory and complexes (*e.g.*, fullerene and solvent or fullerene and additive) optimized at the semi-empirical PM6⁴⁷ level of theory in Gaussian 09;⁴⁸ the semiempirical calculations were carried out to quickly and robustly span the complex interaction space. Subsequently, the distance between the molecules in the complexes was varied to construct an SAPT0 interaction energy profile as a function of distance between the fullerene and the solvent or additive

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3 molecule. We note that, due to the system size, SAPT0 calculations were not carried out on
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5 fullerene dimers, though fullerene-fullerene interactions are known to be highly attractive^{26, 27, 49}
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7 – a feature that we show, as well, through potential of mean force simulations.
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11 All molecular dynamics (MD) simulations were performed using the GROMACS 4.5.5 software
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13 suite.^{50, 51} The OPLS-AA (optimized potentials for liquid simulations – all atom)^{52, 53} force field
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15 was employed for all bond, angle, dihedral, and non-bonded parameters; previous simulations of
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17 PCBM with OPLS-AA have validated the use of this force field for such molecules.^{23, 37, 39, 54}
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19 The particle mesh Ewald (PME) summation with an accuracy of 10^{-5} was applied for long-range
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21 electrostatic interactions. A time step of 2 fs was used for most simulations. The switching cut-
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23 off was employed for short-range interactions with switching enforced from 1.2 nm to smoothly
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25 truncate the forces and energies to zero at 1.4 nm.
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32 Potential of mean force (PMF) calculations, using constrained simulations in GROMACS^{51, 55}
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34 within an NPT ensemble (constant number of molecules, pressure, and temperature) at 300 K
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36 and 1 atm, were carried out to determine the free energies of interaction between fullerene
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38 molecules as isolated dimers and under varying conditions. The constrained *in vacuo* simulations
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40 consisted solely of two PCBM molecules, while solution simulations included 4800 solvent
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42 molecules corresponding to a concentration of 4.2×10^{-4} M (or 4.0×10^{-4} M when 160 solvent
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44 additive molecules were considered); these concentrations correspond to less than 0.5 weight
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46 percent (wt. %) PCBM, less than most experiments. The simulations were equilibrated for at
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48 least 10 ns before starting the constrained simulation protocol. Distances between the centers-of-
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50 mass of the C₆₀ cages for the two PCBM molecules were constrained in intervals of 0.05 nm, and the force
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52 on each PCBM molecule was recorded at 0.1 ps intervals during the 5 ns simulation. The force
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data from the final 2 ns was averaged and the force profile from these simulations were integrated using the trapezoidal rule to obtain the PMF profile. The PMF between two PCBM molecules is (arbitrarily) set to zero at a center-to-center distance of 3.0 nm to set the baseline for the interaction. We note that the loss in entropy (which has a constant value at each distance, defined as $2k_B T \ln \frac{R}{r}$, where R is the distance at which the PMF is set to zero and r is the constrained distance between the two PCBM molecules corresponding to that particular simulation) upon decreasing the constrained distance is not included in the PMF profiles, as it does not affect the nature of the results.

To gain insight into how variations in solvent affect the aggregation of PCBM, simulations were performed for PCBM in pure solvents and solvent-additive mixtures. The simulation cells consisted of 10 PCBM molecules and 800 solvent molecules or 20 PCBM and 1200 solvent molecules, giving PCBM concentrations of 1.23×10^{-2} M (9.2 weight % in CB) and 1.63×10^{-2} M (12 weight % in CB and 9.3 weight % in DCB), respectively; we note that these concentrations represent large PCBM weight fractions, with experimental PCBM weight fractions typically in the range of 1 to 3 weight % (concentrations such as these would require extremely large simulation boxes with millions of atoms to simulate the aggregation effects of 40 to 80 PCBM molecules). These simulations were performed for 100-200 ns. Larger simulations, also with 1.63×10^{-2} M PCBM concentrations, were performed with 80 or 320 PCBM molecules in 4800 or 19600 (only CB) solvent molecules, respectively, to understand the effect of the number of PCBM molecules on aggregation.

To consider the influence of solvent additives on PCBM aggregation, simulation boxes contained: (i) 10 PCBM molecules, 20 additive molecules, and 800 CB molecules; (ii) 20 PCBM molecules, 40

additive molecules, and 1200 CB molecules; or (iii) 80 PCBM, 160 additive molecules, and 4800 CB molecules. The PCBM concentrations in the simulations with 1200 (or 4800) solvent molecules correspond to ca. 11.4 weight % in CB:1CN and 10.8 weight % in CB:DIO, greatly than most experiments. For the largest simulation, which included 320 PCBM molecules, the solvent-additive effect was studied using only DIO (640 solvent additive molecules and 19200 CB molecules). The computational cost of such simulations, with ca. 270,000 atoms, has prevented to date their application to DCB or with the 1CN additive.

3. Results & Discussion

3.1. Intermolecular Interactions

The potential energy surfaces (PES) computed at the SAPT0/jun-cc-pVDZ level of theory (referred to hereafter simply as SAPT0) for fullerene-solvent (either chlorobenzene [CB] or *o*-dichlorobenzene [DCB]) and fullerene-additive interactions are given in Figure 1. To set the baseline, we first focus on interactions between unsubstituted C₆₀ and CB or DCB. Comparing the depth of the potential wells, the C₆₀-DCB interaction is 0.5 kcal/mol more stable than C₆₀ with CB. This is a result of the extra chlorine atom in DCB, which increases each of the three stabilizing (electrostatic, dispersion, induction) terms when compared to the CB-fullerene complex, with the largest impact expectedly on the electrostatic and dispersion terms.

Turning to the C₆₀-additive interactions, the strengths of the interactions follow the order 1-chloronaphthalene (1CN) > unsubstituted naphthalene (NAP) > 1,8-dichlorooctane (DCIO). Though DCIO lacks π -character, when compared to DCB (with two chlorine atoms), the results point to similar dispersion strengths, while the centrosymmetric nature of DCIO (and the resulting zero dipole moment) leads to limited electrostatic and induction interactions (see the

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3 electronic supporting information (ESI) for further details). We recall that DCIO is being used as
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5 a model for DIO (1,8-diiodooctane, see Methodology section) in the SAPT0 calculations. Iodine
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7 is known to strengthen intermolecular interactions when compared to chlorine (a function of
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9 greater dispersion arising from the more polarizable nature of iodine) – a feature observed in
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11 many biomolecular complexes⁵⁶ – at the expense, however, of longer center-to-center distances
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13 due to the large van der Waals radius of the iodine atom;^{56, 57} the large polarizability of iodine
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15 can also lead to stronger halogen bond interactions, due to the large σ -hole on iodine interacting
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17 with the fullerene π -electrons.⁵⁸
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Figure 1: Total SAPT0 interaction energy between (middle) C_{60} -solvent and C_{60} -additive complexes and (bottom) PCBM-solvent and PCBM-additive complexes (the total interaction energy is the sum of the electrostatic, dispersion, induction, and exchange energies computed from SAPT0 methodology). Illustrations of the PCBM-solvent and PCBM-additive complexes (white, grey, red, and green spheres represent hydrogen, carbon, oxygen, and chlorine atoms, respectively) are shown in the top panel.

For both the solvent- and solvent-additive- C_{60} interactions, the large energetic destabilization at small distances (< 0.6 nm) is due to the exchange-repulsion energy that grows exponentially with orbital overlap. These exchange-repulsion interactions increase for the C_{60} -solvent interactions in identical ways for both CB and DCB, while the increase is steeper for ICN and NAP due to greater number electrons (including the aromatic π electrons) that increase the exchange term. Importantly, these destabilizing interactions, which limit C_{60} solubility, can be offset by favorable additional non-covalent interactions.

This is demonstrated by the PCBM-solvent interactions, where the repulsive wall of the potential energy surface rises at a smaller interaction distance (≈ 0.64 nm) when compared to the C_{60} -solvent interactions (≈ 0.68 nm); we have reported on similar effects – closer packing due to enhanced favorable intermolecular interactions – resulting in tighter solid-state packing of functionalized rubrenes.⁵⁹ These differences are indicative of effects due to the fullerene adduct, and correlate with the higher solubility of PCBM in these solvents, especially for PCBM in CB.^{26, 27, 40} Interactions between the solvent chlorine atoms and the phenyl moiety on the PCBM adduct also lead to the wide, flat attractive potential from 0.6 to 0.7 nm for CB (the effect is similar, though to a lesser extent, for DCB), as opposed to the more pronounced Lennard-Jones style valley observed for C_{60} -solvent interactions. Notably, the repulsive part of the PCBM-CB potential onsets at a longer center-to-center distance compared to PCBM-DCB (*ca.* 0.02 nm longer). The attraction at relatively shorter distances for the PCBM-DCB complex indicates that DCB can form a tighter and less dynamic solvent shell around PCBM,²⁸ an important characteristic for fullerene solubility;

Turning to the PCBM-additive interactions, while DCIO reveals a tendency for much weaker binding with PCBM when compared to CB and DCB, 1CN (in particular) and NAP interact rather strongly and at similar center-of-mass distances, results in line with those of C₆₀. Across the solvents and additives considered, the intermolecular interactions with PCBM tend to be stronger with PCBM when compared to C₆₀, a factor directly attributable to the adduct.

It is important to note that the SAPT0-derived noncovalent intermolecular interactions computed here can be related, in part, to the widely used Hildebrand and Hansen solubility parameters. Connecting SAPT0 interaction energies to the solubility parameters can be done in principle by evaluating the orientations of solute-solute, solute-solvent, and solvent-solvent pairs, and including the average number of neighbors from MD simulations or NMR (nuclear magnetic resonance)⁶⁰ spectroscopy. Such an approach has recently been used by Jackson and co-workers, who showed that a combination of MD simulations and SAPT calculations can lead to reasonable evaluations of the solubility parameters of non-electrolyte solvents.⁶¹ Along similar lines, new force fields based on SAPT interaction energies are under development, providing the potential for larger-scale simulations that directly take into account such quantum mechanically determined results to evaluate solubility.⁶²⁻⁶⁴ We have shown with MD simulations using the OPLS-AA force field the ability to evaluate Hildebrand and Hansen parameters for PCBM, DCB, and CB with good qualitative agreement with experiment,^{23, 40} and improved force fields should lead to more accurate results. Within this context, the comparisons made here are qualitative, and provide an upper bound of the non-covalent intermolecular interactions that are critical to determining the solubility parameters. In general, while the above discussed results are interesting and will point to critical differences in the discussion that follows, a comprehensive understanding of how the additives change the energetic landscape and miscibility in polymer-

fullerene mixtures represents a more complex issue that will need to be studied at a much larger level requiring a coarse-grained approach.⁶⁵

3.2 Potential of Mean Force (PMF)

To build a profile of PCBM aggregation under varying solvent conditions, we carried out potential of mean force (PMF) simulations that can relay information about effective intermolecular interactions by averaging over the orientational degrees of freedom. The PMF simulations were undertaken (i) *in vacuo*, (ii) in CB or DCB solutions, and (iii) in CB:1CN and CB:DIO solution conditions, in order to build a complete picture of how the fullerene environment impacts the tendency for fullerenes to interact. Figure 2 shows the potential of mean force between two PCBM molecules as a function of the center-of-mass distance computed using only the fullerene cages of PCBM (using the full PCBM center-of-mass does not yield unequivocal information as it is influenced by the instantaneous orientation of the butyric-acid-methyl-ester adduct). Note that positive PMF energies correspond to effective repulsive interactions (*e.g.*, a large energy barrier that undermines the ability to aggregate), while negative energies relate to favorable interactions.

Figure 2: Potential of mean force (PMF) between two PCBM molecules approaching each other computed from constrained simulations and integrating the force acting on the PCBM molecules at each separation. The center-of-mass distance between fullerene cages was considered as the constraint distance.

For the *in vacuo* simulations, both visual and quantitative analyses indicate that the PCBM molecules effectively sample all the possible orientations at each distance interval. The PMF curve for two PCBM molecules shows a constant, zero PMF beyond 2.0 nm (distances between centers-of-mass), which is consistent with the fact that PCBM molecules effectively do not interact at such large distances. At distances less than 2.0 nm, the PMF continuously decreases, pointing to an increased attractive potential with decreasing distance. Considering the forces

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3 acting on only the C₆₀ cages of PCBM (see ESI), the PMF yields a 7.5 kcal/mol attractive
4 interaction at a 1.0 nm distance between centers-of-mass (in agreement with existing reports),⁶⁶
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6 taking into account the entire PCBM molecule yields an 11 kcal/mol attractive interaction. This
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8 underlines that the adduct groups increase the favorable attractions *in vacuo*; indeed, it is adduct-
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10 induced interactions that lead to the PMF being attractive at 2.0 nm for PCBM versus 1.5 nm for
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12 bare C₆₀ dimers.^{66, 67}
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19 The PCBM PMFs show similar trends for all solution conditions considered. The PMF increases
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21 gradually as the fullerenes are brought into closer contact from 3.0 nm to 2.0 nm, followed by a
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23 weak oscillatory behavior, see Figure 2. This is in marked contrast with *in vacuo* PCBM, and
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25 indicates the presence of solvent-induced repulsive interactions. Three positive peaks with
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27 increasing magnitude are observed at 2.0 nm, 1.5 to 1.6 nm, and 1.2 nm, respectively; note that
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29 the larger the peak magnitude, the lower the probability becomes for two PCBM molecules to
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31 acquire enough energy/velocity to cross the barrier. The valleys at 1.7 nm and 1.4 nm in the PMF
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33 correspond to distances where an integer number of solvent layers (evaluated from C₆₀-solvent
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35 radial distribution functions) can fit between the two PCBM molecules, similar to what is
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37 observed for rigid nanotubes or fullerenes in water.^{67, 68} The energy required to remove a layer of
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39 the solvent shell and/or additive molecules yields the solvent-induced repulsive interaction and
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41 results in the positive peaks in the PMF profile. As the PCBM molecular distance decreases to
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43 less than 1.4 nm, it becomes very unfavorable to remove the remaining solvent molecules
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45 because of the strong PCBM-solvent interactions. Hence, the PMFs show high, positive peaks at
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47 very close distances, whose magnitudes are dependent on the type of solvent and the presence of
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49 solvent additive. Below 1.1 nm, when the solvent molecules can no longer fit between two
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51 PCBM, keeping the PCBM molecules apart (beyond their *in vacuo* preferred separation) is
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energetically unfavorable because of: (i) the attractive potential between PCBM molecules; and (ii) the force exerted on the PCBM molecules from the surrounding solvent. Hence, there is a drive for the fullerenes to aggregate, as indicated by the negative slope, once they are able to eschew the solvent molecules between them. These results are consistent with known trends for fullerenes at close distances,^{9, 67} and point to the large propensity of PCBM to aggregate once the center-of-mass distance between the approaching PCBM molecules is less than 1.10 nm.

The strong intermolecular interactions between solvent, additive, and PCBM result in strong, solvent-induced repulsive PMF among PCBM molecules in solution, though there are modest differences among the systems studied. The largest solvent-induced barrier to PCBM aggregation occurs in pure DCB, while the smallest barrier is in pure CB; based on Boltzmann statistics, the 5 kcal/mol repulsive interaction in DCB decreases the PCBM aggregation probability by approximately a factor of 10^3 when compared to a repulsion on the order of room temperature (0.6 kcal/mol). Interestingly, equilibrium MD simulations for two PCBM, in all solvent conditions studied, show PCBM contacts of 1.5 nm or less to be rare events.

While a flat potential-energy surface minimum is seen for the PCBM-CB interaction in the SAPT0 calculations (Figure 1), we do not observe a similar profile at the maximum barrier between PCBM molecules in CB solvent in the absence of additive molecules; this is mainly due to relatively large thermal vibrations that yield more dynamic solvent molecules close to the adduct moiety. However, the stronger interactions observed between PCBM and CB (due to the adduct) can provide a driving force for the adduct moieties to orient towards the surface of PCBM aggregates, and subsequently within thin films; we note that such tendencies for adduct orientation can influence the interaction with polymer domains and the surfaces of electrodes,

and play a role in the electronic processes critical to OPV internal quantum efficiency, as observed elsewhere.^{69, 70}

In CB:DIO, the barrier height for the PCBM-PCBM interactions slightly increases in the range from 2.0 nm to 1.3 nm when compared to the pure solvent. However, at distances closer than 1.3 nm, the PMF profiles for CB and CB:DIO overlap. This indicates that DIO molecules are excluded from the inter-PCBM volume and the effective repulsion at close distances arises only from CB. In contrast, CB:1CN induces long-range repulsion starting at 2.7 nm between the two PCBM molecules and yields a larger repulsive barrier at 1.2 nm (when compared to pure CB), showing that the larger aromatic molecule provides for more repulsion at close separation when compared to the linear-chain additive.

The PMF profiles of Figure 2 indicate that the PCBM aggregation process consists of a series of jumps to approach PCBM center-of-mass distances of 1.2 nm (*i.e.*, to reach the top of the final barrier), and then a downhill process to aggregate. The distance at which the largest repulsion occurs between the two PCBM molecules, 1.2 nm, corresponds to the PCBM-solvent distance of 0.6 nm where the strongest PCBM-solvent interactions are observed in the SAPT0 calculations, which suggests that a consistent picture is reached between the SAPT0 calculations and MD simulations. However, one has to be careful interpreting the PMF's shown above, as the PMF is a two-body term and the free energy profile between PCBM molecules could be significantly impacted in the presence of either aggregates or other molecules. Nonetheless, the solvent-PCBM or additive-PCBM interactions, as revealed by the SAPT0 calculations and PMF profiles, determine the equilibrium size at which the solvent / additive molecules form a strongly interacting shell around PCBM aggregates and hinder further aggregation. It is also worth remembering that aggregation is a

kinetic phenomenon and hence the kinetic arrest upon spin-casting or during other processing might allow for smaller fullerene domains.

3.3 Aggregation in Solution: Cluster Size

The aggregation of PCBM in solution is dependent on a multitude of factors, among which the PCBM concentration is important. Here, we examine the aggregation of PCBM in the solution conditions described in Section 2 address how the choice of solvent, additive, and PCBM concentration influences aggregation.

Starting with 10 PCBM molecules in a simulation box that contains 800 solvent molecules (1.23×10^{-2} M), the aggregation behavior of PCBM is seen to vary considerably when additives are included. Focusing on the radial distribution function (RDF) of the fullerene cages, the RDF peaks are larger when DIO and 1CN (at 1.2×10^{-2} M concentration) are added to CB. This result underlines that additives, in spite of providing larger repulsive interactions between two PCBMs, can aid in the aggregation of PCBM (Figure 3a). The coordination number (*i.e.*, the number of nearest neighbors) for PCBM defined by the C_{60} cages within 1.5 nm, is larger in the presence of DIO and 1CN than CB alone (Figure 3b).

Energy oscillations in the PCBM-PCBM interactions occur on the order of 20-30 ns, in Figure 3c, the lower energy peaks, near $-500 \text{ kcal mol}^{-1}$, correspond to an aggregated PCBM state, while the high energy state at $-400 \text{ kcal mol}^{-1}$ corresponds to the dispersed state (with maximum cluster sizes of two). This indicates that the time scale of PCBM aggregation in these simulations is on the order of a few tens of nanoseconds (Figure 3c). PCBM in CB yields a maximum cluster size of eight. Here, cluster sizes are calculated by identifying the network of PCBM molecules that

are connected to each other. If the distance between the centers-of-mass of two PCBM molecules is less than 1.1 nm, the molecules are considered as connected; the distance cut-off of 1.1 nm is based on the first peak in the RDF (Figure 3a). The fluctuations in intermolecular distances suggest that the cluster sizes vary, as the PCBM molecules oscillate between dispersed and aggregated states. The probability of non-aggregated PCBM molecules in these simulations is high (> 0.4) due to continuous PCBM aggregation and dissolution events. Comparing the cluster sizes when solvent additives are included (Figure 3d) shows that PCBM aggregates of six, seven, or eight molecules have higher probability in the presence of DIO, whereas in CB:1CN the distribution is similar to that observed in just CB.

These results, in contrast to the observations from the simulations with only two PCBM molecules, indicate enhanced PCBM aggregation behavior when the additive molecules are included, especially DIO. It is useful to note that the PCBM clusters are not kinetically stable as they break and re-form during the simulation trajectory; hence, clusters smaller than six PCBM are also observed. Clusters of this size (6) are the free energy minima in the aggregation landscape (when 10 PCBM molecules are present) and might point to smaller clusters in as-cast BHJ thin films,⁷¹ although, as mentioned before, the aggregation landscape in the presence of donor molecules might be different from what is observed here. Visualization of the simulation trajectories provides direct evidence of the multiple aggregation and dissolution events of PCBM within the 100-200 ns of simulation time, indicating dynamic equilibrium as expected during aggregation processes.

Figure 3: (a) C_{60} - C_{60} center-of-mass radial distribution function, $g(r)$ (magnified peak positions in the inset); (b) C_{60} - C_{60} center-of-mass nearest neighbor coordination numbers, $C(r)$; (c) PCBM-PCBM interaction energy; and (d) cluster size distribution for 10 PCBM molecules from 3 different simulations containing: (i) no additive, (ii) 40 molecules of 1-chloronaphthalene, and (iii) 40 molecules of DIO, in 800 molecules of CB solvent.

The fullerene mean-square displacements (MSD) as a function of solvent conditions point to differences in the dynamic aggregation character. Fullerene diffusion in the initial 1 to 2 ns is identical for systems with and without additives (Figure S4 in the Supplementary Information, SI). This is in contrast to the fullerene MSD when there are only 2 PCBM molecules in various

solvent conditions (Figure S3 in the Supplementary Information), in which the MSD follows the order CB:DIO > CB:1CN > CB > DCB. However, within the 10 PCBM molecule simulations the diffusivity of PCBM in CB:DIO decreases when compared to the diffusion of PCBM molecules in only CB. Although the absolute magnitude of displacement of PCBM molecules is highest in CB:1CN, the slope of the evolution is similar to that observed for only CB and hence the diffusivity is not significantly different. This result indicates that additives influence the diffusion of PCBM and aggregation kinetics in rather different ways. The slower diffusion occurs because of larger clusters formed in DIO (see Figure 3d) when compared to PCBM clusters in just CB solvent.

The simulations discussed above involve only 10 PCBM molecules in solution, and hence aggregation beyond the first shell cannot be quantified. Nonetheless, the results can serve as a useful guide through the complex aggregation processes, as the solubility of fullerenes in these solvents is not well understood.²⁰ When the simulations include 20 PCBM molecules (1200 solvent molecules; 40 additive molecules), the C_{60} - C_{60} radial distribution functions (see Figure 4a) are larger in CB compared to DCB, as are the cluster sizes. When additive molecules are present, the magnitude of the first RDF peak is higher in CB:1CN than in CB:DIO, though the cluster size analysis (Figure 5a) suggests that the biggest aggregates are found in CB:DIO rather than in CB:1CN. The presence of multiple smaller aggregates, apart from the existence of one large cluster, can increase the magnitude of the radial distribution function; to avoid this bias, the cluster-size distributions are important. Hence, the combination of the RDFs and cluster sizes are needed to shed light on the aggregation phenomena.

Figure 4: C_{60} - C_{60} center-of-mass radial distribution functions, $g(r)$ for: (a) 20; (b) 80; and (c) 320 PCBM molecules in the simulation box with ratios of 1:60 (PCBM:solvent) and 1:2:60 (PCBM:additive:solvent), without and with solvent additive molecules.

Simulations with 80 PCBM molecules at identical concentrations point to an increase in the RDF magnitude (comparing Figure 4b and Figure 4a), with PCBM in DCB being an exception. The larger RDF peaks at higher PCBM numbers reveals finite-size effects in the simulations, and shows that increasing the number of PCBM molecules, expectedly, increases aggregation due to larger numbers of PCBM interactions. For PCBM in DCB, surprisingly, the magnitude of the RDF does not increase, suggesting no effective increase in PCBM aggregation when compared to the 20-PCBM molecule simulations.

Larger aggregate sizes are observed in simulations with 80 PCBM molecules, up to 52 PCBM molecules in one cluster, with the biggest aggregates found in pure CB. Even though the largest clusters are observed in CB, the distribution of cluster sizes indicates that all sizes smaller than 52 molecules per cluster are observed during the simulation. In contrast, in DCB: (i) small clusters of less than eight molecules or (ii) clusters with 30-50 PCBM molecules, are generally observed. These differences suggest that there exist variations in cluster size for each solvent, based on the solvent-PCBM and PCBM-PCBM interaction strengths. Along with what is observed in the 20-PCBM molecule simulations, the 80-PCBM results are consistent with smaller PCBM cluster sizes in DCB compared to CB;⁷² interestingly, DCB is known to decrease domain sizes when used as additive with chloroform as the solvent.⁷³ The analysis of the cluster sizes indicates that the simulations reached equilibrium and that the PCBM molecules are able to diffuse and form large PCBM clusters; thus, cluster sizes of *ca.* 10-30 molecules in DCB can be considered energetically not favorable (given their generally low numbers).

The maximum cluster size is near 36 molecules in CB:DIO; however, for CB:1CN, cluster sizes with 30-50 molecules are prominent. Even in 80-PCBM simulations, aggregates with 10 to 20

PCBM molecules are more frequently observed in the presence of DIO compared to larger aggregates, providing an additional contrast to PCBM in pure DCB where aggregates of this size are not observed. The absence of larger clusters with DIO, even though the PCBM molecules can diffuse freely and move closer to other PCBM molecules or existing PCBM clusters during the course of the simulation trajectory, suggests that *DIO both aids in the aggregation of small aggregates and effectively shields PCBM molecules from forming large aggregates*. In fact, smaller PC₇₁BM aggregates are observed in the presence of DIO when compared to just chlorobenzene.⁷⁴

For large aggregates, the entropy lost upon aggregation is much smaller than the enthalpy gained due to aggregation; therefore, there are no observable dissolution or dispersion events in the 80-PCBM simulations, in contrast to what is seen in 10- or 20-PCBM simulations. The formation of such clusters, although partly dynamic, provides support to reports that point to the formation of fullerene aggregates in good solvents.²¹ Notably, the cluster sizes reported here are similar to the aggregate sizes (6 nm and 5 nm for PCBM in CB and DCB solvents, respectively) recently observed in BHJ devices from the analysis of grazing-incidence wide-angle x-ray spectroscopy (GIWAXS) data in CB and DCB solvents.⁷⁵

Finally, the 320-PCBM simulations (Figure 4c) show a decrease in RDF magnitude when compared to the 80-PCBM simulations. This indicates, along with the cluster-size analysis in Figure 5, that the ratio of aggregates compared to isolated molecules does not increase in 320-PCBM simulations. As observed in the 80-PCBM simulations, larger clusters have smaller probabilities in CB:DIO than in pure CB, with the largest clusters containing *ca.* 80 molecules in CB:DIO compared to *ca.* 100 PCBM molecules in CB (but with probabilities lower than 10⁻³).

Nevertheless, the aggregate sizes are on average only modestly larger than in 80-PCBM simulations.

Figure 5: Probability (P) distribution as a function of cluster size in simulations with: (a) 20; (b) 80; and (c) 320 PCBM molecules in the simulation box with ratios of 1:60 (PCBM:solvent) and 1:2:60 (PCBM:additive:solvent), without and with additive molecules.

3.4 Aggregation in Solution: Molecular Orientation and Diffusion

The relative orientation among PCBM nearest neighbors is an important factor that determines many materials properties, including the effective intermolecular electronic couplings critical to charge-carrier transport.^{23, 37, 76} Hence, it is of interest to quantify potential differences in PCBM orientation in solution-phase aggregates as these could manifest in the solid state. To evaluate the 2D orientational probability distribution for PCBM molecules within PCBM center-of-mass distances of 0.975 nm and 1.075 nm, a vector going from the center-of-mass coordinates of the fullerene cage to the methano-bridged carbon is used; the orientational distribution for PCBM in CB is shown as a function of system size in Figure 6. With increasing number of PCBM, the probability distributions at all distances and angles are identical, except for a minor increase in the orientation density from 40° to 120° at a distance of 1.025 nm. On the other hand, the 2D probability plot for PCBM in DCB (Figure 6f) has a dumbbell shape indicating a narrow range of favorable orientations (while the more linear shape in CB is indicative of a broader range of orientations). Importantly, these shapes change in the presence of DIO, with a maximum orientation probability (circular) around 90°; the orientation change is minimal in the presence of the 1-CN additive.

These differences in orientation probability as a function of solvent environment can propagate to different crystalline structures. Although the exact crystalline structures obtained from experiments cannot be quantified from these MD simulations, the nature of the solid-state packing structure can induce modifications of the electronic environment in terms of the ionization (and polarization) energies, electronic couplings, site energies, and other intrinsic and extrinsic electronic parameters. These differences, in turn, can result in variations in exciton dissociation properties (as the size of PCBM domains and the orientation of the adduct chains

impact the charge separation ability)⁷⁷ and in charge-carrier transport properties of active layers developed under different processing conditions. We note that such seemingly subtle changes in processing have been shown to lead to variations in electron mobilities determined in thin-film PCBM transistors.^{23, 41, 78}

Figure 6: Two-dimensional (2D) orientational distribution function for: (a) 20 PCBM molecules in 1200 CB solvent molecules; (b) 80 PCBM molecules in 4800 CB solvent molecules; (c) 320 PCBM molecules in 19200 CB solvent molecules; (d) 80 PCBM molecules in 4800 CB molecules and 160 1CN molecules; (e) 80 PCBM molecules in 4800 CB molecules and 160 1,8-DIO molecules; and (f) 80 PCBM molecules in 4800 DCB molecules.

Apart from establishing differences in aggregate size and molecular orientation of PCBM in various solvent formulations, another important quantification of the solvent effects is to

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3 understand the shape of the aggregates within different solvent conditions. We present in the SI
4 plots of the number of molecules observed as a function of the distance from the center-of-mass
5 of the largest aggregate, as well as representative simulation snapshots from the 80-PCBM
6 simulations. The results indicate that PCBM aggregates are more three-dimensional (3D) in DCB
7 and more two-dimensional (2D) in CB, and that the presence of additives in CB does not really
8 affect the shape of the aggregate (Figure S2 and Figure S3). Interestingly, PCBM is known to
9 crystallize in monoclinic and triclinic co-crystal structures⁷⁹ when grown from DCB and CB,
10 respectively. The monoclinic 1:1 PCBM:DCB co-crystal is more anisotropically packed and has
11 more 2D features in comparison to the 3D packed triclinic co-crystal (2:1, PCBM:CB); we do
12 note, however, that solvent-free PCBM crystallites grown from DCB are more similar with the
13 triclinic co-crystal structure grown from CB.⁸⁰ In general, a 3D, isotropic packing is preferable to
14 a 2D packing to insure efficient electron transport through bulk media.²³

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33 When considering thin-film deposition, the evaporation rate and annealing time are crucial
34 factors, as these directly influence the equilibrium morphology of the active layer.⁸¹ The
35 molecular property that is most directly related to the time scale of morphology formation is
36 diffusion. Although it is expected that PCBM diffusion in the donor-acceptor mixtures used to
37 create BHJ layers is more complex as compared to PCBM diffusion in solution alone, it is useful
38 to differentiate the diffusion behavior of PCBM in the various solvent conditions considered
39 here, see Figure 7.

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51 The slopes of the straight lines in the plots of mean square displacements (MSD) vs. time in
52 Figure 7 are related to the diffusion constant through Einstein's equation.⁵⁵ The MSDs of the
53 PCBM molecules in CB, regardless of the presence of additives, show no significant difference.
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3 In fact, the MSD curves are similar when going from simulations containing 20 PCBM to 320
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5 PCBM (with respect to the slope in the first 8 to 10 ns). The MSD of PCBM molecules in DCB
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7 is one-quarter that of PCBM molecules in any of the CB-based simulations. This is due to the
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9 increased density and molecular weight of DCB. The slower diffusion of PCBM in DCB
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11 indicates the possibility of longer annealing times within the BHJ active layer in the presence of
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13 DCB compared to CB. This is line with recent experiments in which the time required to observe
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15 the peak crystallinity in BHJ active later is three times longer in the presence of DCB than CB.⁸²
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17 We note that the solvents considered here have different drying times.⁸³ While this work
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19 considers the miscibility and aggregation of PCBM under varying solvent conditions, the work
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21 cannot account for the kinetic variations of film formation due to these variations. Nevertheless,
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23 connecting molecular-scale parameters, interaction strengths, and diffusion to active layer
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25 morphology is a very challenging proposition on the basis of all-atom molecular dynamics
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27 simulations; as such, studies are ongoing at the coarse-grained level to begin to make these
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Figure 7: Mean square displacements (MSD) of PCBM molecules in simulations with: (a) 20; (b) 80; and (c) 320 PCBM molecules in the simulation box with ratios of 1:60 (PCBM:solvent) and 1:2:60 (PCBM:additive:solvent), without and with additive molecules.

4. Synopsis

We have carried out a combined electronic-structure and molecular dynamics study to investigate PCBM aggregation under a variety of solvent conditions, including the presence of high-boiling point solvent additives. Our results show that seemingly modest variations in solvent and additive chemical structure can impart notable differences on the propensity for fullerenes to aggregate.

The MD simulations point, in general, to the formation of larger aggregates in chlorobenzene *vs.* dichlorobenzene, which agrees well with experimental results concerning the domain sizes of PCBM in BHJ active layers processed with CB or DCB. This is the direct result of the packing proximity between the solvent and PCBM molecules, as highlighted by the differences in the potential energy surfaces and intermolecular interactions (shown at the SAPT0/jun-cc-pVDZ level of theory and in the top-panel of Figure 8). Additive molecules, here 1-chloronaphthalene and 1,8-diiodooctane, effectively decrease the sizes of PCBM aggregates when used in conjunction with CB (representatively showed in the bottom panel of Figure 8). Similarly, the differences in interaction of solvent and additive molecules with the fullerene, and in particular the adduct moiety, can determine the intermolecular orientations among fullerene molecules.

Figure 8: Pictorial representation of key points from this investigation. (top) *o*-Dichlorobenzene has stronger interactions with fullerene cage and can pack at closer distance than chlorobenzene. (bottom) In chlorobenzene, the addition of DIO decreases aggregate sizes and changes the orientation landscape between the individual PCBM molecules.

Overall, our results pave the way toward a better understanding of the roles that various processing solvents and additives play in the formation of solution-processed thin films, which can lead to the design of better solvent systems for the solution processing of organic materials of interest for a host of electronic and optoelectronic applications. While the analysis presented here provides an important step forward, considerable work still needs to be done in order to

reach control of how changes in chemical and molecular structure impact aggregation in these formulations.

Supplementary Information

Electrostatic, dispersive, exchange, and induction interaction energies of PCBM-solvent and PCBM-additive molecules evaluated from SAPT0, potential of mean force (PMF) between PCBM molecules *in vacuo* considering the whole PCBM molecules and only C₆₀ cages, mean square displacement of two PCM molecules under various solvent conditions, averaged mean square displacement of 10 PCBM molecules in 800 solvent molecules and 20 solvent additive molecules when present, number of molecules as a function of distance from the cluster center-of-mass to give an estimate on the fractal dimension of the cluster, and representative simulation snapshots of the PCBM molecular aggregates in various solvent conditions are reported in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.xxxxxxx

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