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Packing and Disorder in Substituted Fullerenes

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Abstract

Fullerenes are ubiquitous as electron-acceptor and electron-transport materials in organic solar cells. Recent synthetic strategies to improve the solubility and electronic characteristics of these molecules have translated into a tremendous increase in the variety of derivatives employed in these applications. Here, we use molecular dynamics (MD) simulations to examine the impact of going from mono-adducts to bis- and tris-adducts on the structural, cohesive, and packing characteristics of [6,6]-phenyl-C₆₀-butyric acid methyl ester (PCBM) and indene-C₆₀. The packing configurations obtained at the MD level then serve as input for density functional theory calculations that examine the solid-state energetic disorder (distribution of site energies) as a function of chemical substitution. The variations in structural and site-energy disorders reflect the fundamental materials differences among the derivatives and impact the performance of these materials in thin-film electronic devices.

I. Introduction

Materials derived from fullerene derivatives are extensively used as active elements in organic electronic devices, in particular in organic photovoltaics (OPV).¹⁻⁵ The ability to use synthetic methods to tune their solution processability and (opto)electronic properties,⁶ coupled with the propensity of these spherical/ellipsoidal molecules to form three-dimensional aggregate networks with extended percolation pathways in the solid state, have made fullerenes the electron-acceptor material of choice for OPV.⁷ While substituted fullerenes have been the target of a multitude of theoretical investigations (based on quantum-chemical calculations, all-atom molecular dynamics (MD) simulations, and coarse-grained simulations) and experimental studies,^{1, 8-21} there remain fundamental characteristics to be better understood in order to improve the design of new fullerene-based materials.

Earlier work explored the impact of the number of solubilizing adducts appended on the fullerene framework, *i.e.*, mono-, bis-, and tris-substitutions, on the packing structure and electronic characteristics (including site-energy disorder) in thin films of [6,6]-phenyl-C₆₀-butyric acid methyl ester (PCBM). Major aspects of interest included the variation in coordination numbers of PCBM multi-adducts as well as the description of the percolation pathways based on the varying thresholds of magnitudes of electronic coupling among neighboring molecules.⁹ An important conclusion was that the coordination numbers, as well as the percolation lengths, decreased as a function of the number of fullerene adducts. Kinetic Monte Carlo studies pointed to reduced electron mobilities in multi-adduct PCBM when compared to mono-adduct PCBM, due to increased reorganization energy, isomeric disorder,⁸ and structural disorder.¹¹ In these studies, however, the magnitudes of the electronic disorders due to inductive effects from neighboring molecules and intra- and intermolecular vibrations,

were not quantified and simply considered on an empirical basis. The exact nature and extent of disorder are, however, key elements for an in-depth understanding of the charge-transport properties.²² Hence, an accurate evaluation, in particular, of how disorder evolves as a function of the number of adducts would be a significant step towards this understanding. This is the major objective of the present work.

We report here on a comprehensive theoretical investigation focusing on the evolution of energetic disorder (due to variations in site energies) as a function of the number of fullerene adducts. We discuss the influence of the number, nature, and substitution pattern of the adducts on the C₆₀ fullerene cage for the compounds shown in Figure 1.

II. Computational Details

Molecular dynamics (MD) simulations of the mono-, bis-, and tris- adducts of PCBM (chemical formulas -(C₇₂H₁₄O₂), -(C₈₄H₂₈O₄), and -(C₉₆H₄₂O₆), respectively) and indene-C₆₀ (chemical formulas -(C₆₉H₈), -(C₇₈H₁₆), and -(C₈₇H₂₄), respectively), see Figure 1, were carried out using the GROMACS 4.6.2 software suite. Bis-isomers were chosen such that the distance between the adduct moieties on the fullerene cages is small (at position *ee* for bis2, making this bis-adduct less symmetric) in one of the isomers and the largest in another (at position *trans-1* for bis1, making this bis-adduct more symmetric). A recent study indicates that the anisotropy of the polarizabilities are the lowest and highest for bis2- and bis1- isomers, respectively.²³ The adduct positions on the tris-adducts are selected from a combination of adduct positions in the two bis-isomers. The OPLS-AA²⁴ (Optimized Potentials for Liquid Simulations-All Atom) force-field parameters were used to simulate the fullerenes, as we and others have shown that this force field

accurately predicts many of the bulk properties of C_{60} , PCBM, and indene- C_{60} ^{11, 18, 20, 21, 25-27}

Simulations of amorphous PCBM and mono-indene- C_{60} have been described in our previous publications.²⁶⁻²⁸ The phenyl-butyric acid methyl ester adduct ($C_{12}H_{14}O_2$) induces a dipole moment in PCBM, whose magnitude (between 1.5 and 5 D) varies with the orientation of the ester group with respect to the phenyl group; the indene adduct (C_9H_8) brings a dipole moment of *ca.* 3 D. We have recently shown that these variations in adduct polarity affect the cohesive characteristics of pure fullerene and P3HT:fullerene blend thin films.²⁷

Figure 1: (From left to right) Mono-, bis1-, bis2-, and tris- adducts of PCBM (top panel) and indene- C_{60} (bottom panel). The mono-, bis- and tris- adducts of indene- C_{60} are generally referred to as ICMA, ICBA, and ICTA, respectively. Note that there are many isomers possible depending on the positions of the adducts on the [6,6] or [6,5] or [5,5] ring of the fullerene molecule.

For the sake of completeness, we briefly recall our simulation procedure. It consists of randomly placing 512 (in some cases 400) fullerene molecules in a simulation box at a density < 0.3 gm/cc, followed by NPT equilibration (constant number of molecules, pressure, and temperature) at 1000 K and 1 atm. The equilibrated simulation box is further simulated for 2 to 10 ns before, gradually, cooling the system down to 100 K in discrete steps of 50 K every 500 ps. The final 250 ps of these discrete interval simulations are then used to compute the thermodynamic and physical properties. The density vs. temperature plots are used to identify first-order phase transitions, as described elsewhere.^{28, 29} Rigorously speaking, first-order phase transitions involve discontinuity in the order parameter; however, since here we only consider changes in the slope of density as a function of temperature, we refer to these as pseudo first-order phase transitions. To analyze the structural order within the fullerene simulations, we compute the Steinhardt (or bond-order) parameters,^{30, 31} which are based on the orientations and numbers of neighboring molecules. A bonding criterion of 1.1 nm (*i.e.*, only molecules that are less than 1.1 nm away when taking the center of mass-to-center of mass distances between neighbors) is considered for the analysis.

Following previous work,²⁷ we use the charge equilibration method to compute the extent of energetic disorder among the highest-occupied molecular orbital (HOMO) eigenvalues of the fullerene radical-anions, which represent the site energies of the fullerene anions. The overall energetic disorder consists of two contributions, referred as *dynamic* disorder (σ_D) and *static* disorder (σ_S). The dynamic disorder is related to electron-vibration interactions that result in time-dependent variations of the site energies. The static energetic disorder arises from the modulations in site energies due to the permanent loss of site equivalency as the system approaches / corresponds to an amorphous phase. In order to evaluate the total disorder, we

relied on 200 clusters within the ensemble of 512 molecules, each containing a central molecule and the nearest-neighbor molecules within a radius of 1.2 nm (center-of-mass distances from the central molecule). The atomic positions of the neighboring molecules are represented as point charges, with point charges iteratively optimized at the long-range corrected density functional theory (DFT) ω B97XD/6-31G(d,p) level. The range-separation parameter ω was optimized (tuned) using a non-empirical procedure.³² This approach was shown earlier to describe accurately the energy levels of extended π -conjugated molecules.^{32, 33} The tuned ω values are 0.150, 0.115, 0.118, and 0.110 Bohr⁻¹ and 0.147, 0.130, 0.134, and 0.122 Bohr⁻¹ for mono-, bis1, bis2, and tris-adducts of indene-C₆₀ and PCBM, respectively. The reorganization energies upon charging of the isolated multi-adduct fullerenes are also computed using the non-empirically tuned ω B97XD functional; we refer the reader to our recent publication for a full description of this methodology.²⁷

To study the dynamic disorder (σ_D) of the HOMO eigenvalues of the fullerene anions as a function of time, 20 independent clusters were identified (200 frames separated by at least 50 fs). We also simulated single (isolated) fullerene-derivative molecules in boxes whose sizes were obtained from the 512-molecule simulations and used the trajectory coordinates (200 frames separated by at least 50 fs) to compute the relaxation energies for the derivatives considered in this study. The associated relaxation energy values of the anion (denoted as $\lambda_{A,MD}$) are computed as $\lambda_{A,MD} = (\sigma_D)^2 / (2k_B T)$.³⁴ The σ_D values are calculated as the standard deviation of the 200-site energies and are accurate within 0.01 eV. The degree of static disorder was obtained by subtracting the dynamic disorder from the total disorder (see below).

Finally, we note that, here, we have not attempted to fully quantify the electron mobilities; this could be done subsequently via kinetic Monte Carlo simulations based on the atomic coordinates

obtained from the MD trajectories and on the electronic couplings (transfer integrals) between nearest-neighbor molecules, in combination with the static and dynamic disorder parameters. However, we discuss explicitly the major components that directly modulate these electron mobilities among our series of fullerene derivatives, *i.e.*, the numbers of (connected) nearest-neighbor molecules and the extent of disorder.

III. Results & Discussion

1. Packing, Nearest Neighbors, Percolation, and Cohesive Energy

As underlined in the Introduction, understanding the packing of fullerene derivatives in the amorphous bulk is essential for evaluating the charge-carrier transport properties of these technologically relevant materials. Electron transport is determined by the topological routes in the corresponding networks, which depend on the number of nearest-neighbor contacts among adjacent molecules. Therefore, for each substituted fullerene, it is of interest to evaluate the radial distribution functions and coordination numbers, based on the center-of-mass distances between C₆₀ moieties. The main results are collected in Figures 2, 3, and 4. As reported by Nelson and co-workers, the mono-adducts have the largest number of nearest neighbors followed by the bis- and then the tris- adducts.¹¹

At this stage, it is important to note that there are two substitution patterns examined in this study for the bis-substituted fullerenes (bis1 and bis2, see Figure 1), as these are generally found as mixtures with significant isomeric heterogeneity. Also, we recall that, within MD simulations, a useful measure of packing density can be found in the radial distribution functions (RDFs). The RDFs correspond to the ratio between the local packing of molecules and the average packing

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2
3 within bulk and hence point to differences in the local packing environments of the molecules
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5 under study.
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9 In the case of the PCBM species, the fullerene cages of bis1-PCBM lead to a slightly closer
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11 packing (see inset in top-right panel of Figure 2) compared to bis2-PCBM, as identified by the
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13 very similar first peaks of the RDFs. This result can be rationalized by the fact that the presence
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15 of two adducts close to each other in bis2-PCBM shields more effectively the molecules from
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17 each other and increases to some extent the average separation distance between the C₆₀ cages
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19 when compared to bis1-PCBM. The RDF differences are not significant beyond the initial valley
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21 at 1.1-1.2 nm. As expected, tris-PCBM has the smallest RDF first peak due to increased
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23 separation between the fullerene cages.
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Figure 2: Radial distribution functions (RDFs) between the C_{60} centers-of-mass for the mono- and multi-adduct PCBM (top) and indene- C_{60} (bottom) systems.

The coordination numbers (see Figure 3) of the C_{60} cages indicate that the number of nearest neighbor molecules decreases with the number of adducts: The mono-adduct has 8.0 neighbors; the bis-adducts, 5.0 neighbors; and the tris-adduct, 3.7 neighbors. Note that the neighbors within the first shell, especially within a distance of 1.2 nm, are of highest interest with regard to the electronic characteristics; the number of nearest neighbors indeed directly affects the transport pathways available and, as a result, impact the charge-carrier transport properties.

The normalized cluster sizes are shown in Figure 4. When the cluster sizes are analyzed through connection criteria based on center-of-mass distances of less than 1.1 nm, all the monoadduct PCBM molecules are found to be connected to other molecules in the simulation box for the entirety of the simulation time; this results in a normalized cluster size and probability of 1. However, in the cases of bis1-PCBM and bis2-PCBM, a few molecules in the simulation box disconnect from the cluster due to thermal fluctuations (more frequently so for the bis2-adduct than the bis1-adduct of PCBM); this results in a probability of less than one to find the normalized cluster size of 1. Interestingly, in the case of the PCBM tris-adduct, there exist a few molecules (one to five molecules out of the 512 molecules in the simulation box) that remain not connected to other molecules; hence, the normalized cluster size of 1 is not observed in that instance. This observation underlines that, within the corresponding thin films, a number of trap states can be expected due to the presence of isolated/disconnected molecules.^{14, 35}

The indene- C_{60} multi-adducts qualitatively follow packing trends similar to those for the PCBM species. However, here, the packing differences between the bis-adduct isomers are negligible in terms of RDFs and coordination numbers. Also, the presence of a few molecules that remain disconnected from other molecules in the simulation box is observed only in the case of the indene- C_{60} tris-adduct.

Figure 3: Coordination numbers as a function of distance between the C_{60} cages for the mono- and multi-adduct PCBM (top) and indene- C_{60} (bottom) systems.

Figure 4: Normalized cluster size distributions for the mono- and multi-adduct PCBM (top) and indene-C₆₀ (bottom) systems. A normalized cluster size of one indicates all the molecules in the simulation box are connected. Only nearest neighbor molecules that are less than 1.1 nm away from each other (based on center-of-mass distances) are considered for the calculation of the cluster sizes.

We have previously shown that a slightly higher coordination number for the indene-C₆₀ mono-adduct results in a higher tensile modulus when compared to the PCBM analog.²⁷ Similarly, the indene-C₆₀ bis-adducts have a larger number of nearest neighbors (~6.0) when compared to the PCBM bis-adducts (~5.0). This result is indicative of the fact that the indene moieties (at least when used as bis-adducts) do not significantly impede close contacts between adjacent fullerene cages; hence, these molecules pack more tightly when compared to fullerenes containing the phenyl-butyric-acid-methyl-ester adducts. Even though the indene-C₆₀ tris-adduct has a higher coordination number than the PCBM tris-adduct (due to a relatively more compact nature), a larger number of isolated molecules is found in the amorphous indene-C₆₀ tris-adduct simulations when compared to the PCBM tris-adduct. Thus, in the case of the tris-adducts, the indene moieties can sometimes shield more effectively the C₆₀ cages from their neighbors, while it is difficult to completely shield the C₆₀ cages with the longer and flexible butyric-acid-methyl-ester adducts. Nevertheless, the fact that isolated molecules are present in both tris-adduct packings confirms the experimental proposition that such isolated molecules can impede electron transport.^{36, 37}

In order to examine material miscibility, which is a key parameter in the formation of BHJ active layers in OPV, we now turn to an evaluation of the Hildebrand³⁸ and Hansen³⁹ solubility parameters, see Table 1. The Hildebrand parameter is characterized by δ_T (in units of $(\text{cal}/\text{cm}^3)^{1/2}$) and is defined as the square root of the cohesive energy density (the total interaction energy among molecules within a specific volume). The Hildebrand parameter is related to the Hansen parameters (δ_D , δ_P , and δ_H , corresponding to the dispersion, electrostatic, and hydrogen-bonding interaction energies, respectively) through the relationship $\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$.^{39, 40} We observe a consistent decrease in the δ_T value (about $0.5 (\text{cal}/\text{cm}^3)^{1/2}$) with increasing substitution

of the fullerene cage: From $10.7 \text{ (cal/cm}^3)^{1/2}$ [mono] to $10.2 \text{ (cal/cm}^3)^{1/2}$ [bis] and $10.0 \text{ (cal/cm}^3)^{1/2}$ [tris] for the PCBM compounds, and from $10.0 \text{ (cal/cm}^3)^{1/2}$ [mono] to $9.5 \text{ (cal/cm}^3)^{1/2}$ [bis] and $9.0 \text{ (cal/cm}^3)^{1/2}$ for the indene- C_{60} compounds; the bis-adduct isomers result in the same δ_T for each fullerene species. As the number of adducts increases, the contributions from dispersion interactions decrease; however, the contributions from electrostatic interactions, which include polar and hydrogen-bonding interactions, $(\delta_P + \delta_H)$, increase. The bis2 adduct of indene- C_{60} is, however, an exception, the reasons for which are discussed next. For the sake of completeness, we also report the experimentally evaluated parameters for C_{60} that has a δ_T of $9.8 \text{ (cal/cm}^3)^{1/2}$ with dispersion and electrostatic contributions of 9.6 and $1.9 \text{ (cal/cm}^3)^{1/2}$, respectively.⁴¹ From simulations, we obtain a comparable δ_T value of $9.4 \text{ (cal/cm}^3)^{1/2}$ but with all contributions coming from dispersion interactions.

Table 1: Hildebrand and Hansen parameters for the multi-adduct fullerene derivatives. The term referred to as $\delta_P + \delta_H$ is evaluated as $(\delta_P^2 + \delta_H^2)^{1/2}$.

Hildebrand/Hansen parameters (cal/cm ³) ^{1/2}						
	PCBM			Indene- C_{60}		
	δ_T	δ_D	$\delta_P + \delta_H$	δ_T	δ_D	$\delta_P + \delta_H$
mono ²⁷	10.7	9.9	4.0	10.0	9.8	2.0
bis1	10.2	9.2	4.4	9.5	9.2	2.3
bis2	10.2	9.1	4.6	9.5	9.3	1.8
tris	10.0	8.6	5.1	9.0	8.6	2.6

The ($\delta_P + \delta_H$) electrostatic contributions for all fullerene derivatives studied here arise from the interactions among the adducts, as the carbon atoms on the fullerene cages do not carry point charges within the OPLS-AA force field. The variations in these contributions can be illustrative of packing changes within the multi-adducts. In particular, an increase in the $\delta_P + \delta_H$ values suggests closer packing of adduct moieties. The increase in δ_D can be mainly attributed either to increased C_{60} - C_{60} interactions or C_{60} -adduct interactions. For PCBM, increasing the number of adducts contributes to increased electrostatic interactions, with these interactions stronger in bis2 when compared to bis1. The trend is not clear for indene- C_{60} , as the decrease in the electrostatic interactions and increase in dispersion interactions for the bis2 adduct indicate rather close packing of the fullerene cages and adducts when compared to bis1. This observation is also confirmed by the RDFs among the fullerene cages and the adducts, which show a larger first peak for the bis2 adduct than for the bis1 adduct. For the tris-adducts, we observe increased adduct-adduct interactions for both indene- C_{60} and PCBM.

Experimentally, the higher power conversion efficiency (PCE) obtained in the case of indene- C_{60} bisadduct-based BHJ solar cells, especially when poly-3-hexyl-thiophene (P3HT) is used as electron-donor component,^{36, 42} is considered to result from a better miscibility between P3HT and these fullerene derivatives. The corresponding experimental values of δ_P , δ_D , and $\delta_P + \delta_H$ for P3HT are $9.76 \text{ (cal/cm}^3)^{1/2}$, $9.02 \text{ (cal/cm}^3)^{1/2}$, and $3.67 \text{ (cal/cm}^3)^{1/2}$, respectively.⁴³ The comparison of these parameters with those from Table 1 indeed points to the best match, and thus a better miscibility, for P3HT with bisadducts of indene- C_{60} (although caution has to be exercised when comparing the solubility parameter values of pure phases to the BHJ morphology). Apart from solubility parameters, processing conditions, such as choice of solvent, annealing temperature, nature of the donor and acceptor molecules, and mixing weight ratio in

the blend, etc., can potentially change the overall device efficiency.⁴² We also note that for the systems studied here, the change in adduct moiety changes the electron affinity of the fullerene derivatives and hence the open-circuit voltage of such P3HT-ICBA devices compared to P3HT-PCBM devices.^{42,44} With respect to design rules, bis- and tris-adducts that do not hinder significant C₆₀-C₆₀ interactions are optimal systems since they can be expected to provide both denser packing with large numbers of neighbors as in the case of mono-adducts and increased solubility in processing solvents. In this context, recent reports indicate that substitution of indene in bis-adducts or tris-adducts by dihydromethano groups provides enhanced solubility and also increased efficiency, in spite of the short and rigid nature of these groups.⁴⁵⁻⁴⁷

2. Analysis of the Pseudo First-Order Phase Transitions

We now turn to the pseudo first-order transitions, which are based on the evaluation of density vs. temperature plots. The results are collected in Table 2. The temperatures at which these transitions occur are indicative of the annealing temperatures required to enhance the thin-film morphological characteristics coming from molecular rearrangements. However, the exact annealing temperatures depend on whether the materials undergo a glass transition or rearrange at temperatures close to the melting point (in the case of systems that do not undergo a glass transition, these first-order phase transition temperatures indicate the maximum annealing temperatures). For example, PCBM undergoes a glass transition at *ca.* 131 °C, which is much lower and difficult to predict from molecular simulations than the melting point at ~270 °C, and finally decomposes at *ca.* 390 °C.^{48,49}

The melting temperatures are found to decrease with an increasing number of adducts. This trend can be expected since the overall interaction energy (cohesive energy) deduced from the Hildebrand parameters decreases. The decreasing number of C_{60} neighbors, because of the increased number of adducts or due to adduct positions, allows for a larger magnitude of the translational motion of the fullerene cage with increasing temperature, which acts to lower the transition temperature.^{50, 51} We note that the calculated melting temperatures are consistently higher than the experimental values by at least 100 K; the reason is that, within the simulations, super-heating effects are observed when determining the transition points, which tends to increase the simulated transition temperatures.²⁶ While alternate methodologies are available for determining these transition temperatures more accurately,²⁹ for the purpose of comparison among the fullerene derivatives, the results we obtain here provide reliable trends.

Table 2: Pseudo first-order phase transitions calculated from a series of simulations at varying temperatures for the fullerene derivatives considered in this study. The error bars for the density are less than 0.003 g/cc.

Fullerene System	Density@ 300 K (g/cc)	Pseudo First Order Phase Transition (K)
PCBM		
mono	1.507	690-700
bis1	1.418	595-605
bis2	1.417	595-605
tris	1.325	565-575
Indene_ C_{60}		
mono	1.563	640-650
bis1	1.471	610-630
bis2	1.485	540-560
tris	1.397	470-490

The mono and multi-adducts of indene-C₆₀ are consistently calculated to have lower melting temperatures and higher densities than the PCBM derivatives, which is consistent with their lower Hildebrand parameters. Interestingly, the bis1 adduct of indene-C₆₀ has a somewhat higher transition temperature, even though the overall interaction energy deduced from the Hildebrand parameters is stronger in bis1 PCBM. This discrepancy is due to the slightly more ordered packing in bis1 indene-C₆₀ compared to other bis-adducts of indene-C₆₀ and PCBM,^{30, 52} as evaluated from the bond order parameter calculations (we recall that the distribution of the number of nearest molecules we discussed earlier (see Figure 2) showed insignificant differences). We note that, even in calorimetry experiments on indene-C₆₀ bis-adducts, no endothermic peaks indicative of melting are observed while the gravimetric analysis indicates that the indene-C₆₀ bis-adduct decomposes around 270°C. These results confirm that the first-order transition in these adducts are not easily observable and that these materials are inherently glassy, rather than crystalline, as in the case of mono-adducts.⁵³⁻⁵⁵ A recent study indicates that the electron mobility in thin-film devices of ICBA can be up to 0.1 cm²V⁻¹s⁻¹, when ICBA-substrate interactions are tuned and the films are annealed at as high as 200 °C.⁵⁵ Finally, as seen in the Hildebrand parameters, the lowest transition temperature is observed for the tris-adduct of indene-C₆₀ and the difference between the transition temperatures is highest between the tris-adducts of indene-C₆₀ and PCBM.

3. Energetic Disorder

We now focus on understanding the extent of energetic disorder in the thin films of the fullerene derivatives. We first evaluate the reorganization energies, *i.e.*, the change in energy associated

with geometry relaxations upon redox processes. In general, smaller reorganization energies go hand in hand with better charge-carrier transport properties.²²

We recall that in the context of electron-transfer theory the intramolecular reorganization energy consists of the sum of two geometry relaxation energies: the first one related to adding an electron to the neutral molecule, denoted here as λ_A ; and the second one related to removing an electron from the molecular anion, denoted here as λ_N . Our calculations of λ_A for the mono, bis, and tris-adducts of indene- C_{60} yield values (see Table 3) in the range of 0.082-0.094 eV; the neutral relaxation energies (λ_N) are within the same range. The largest reorganization energy (0.189 eV) is found for the symmetric bis-adduct of indene- C_{60} , while the other indene-adducts have slightly smaller reorganization energies (*ca.* 0.17 eV).

Table 3: DFT estimates of the relaxation energies of anion and neutral molecules (λ_A and λ_N) and reorganization energies (λ) computed from the adiabatic potential energy surfaces using the optimally-tuned ω B97XD functional. The $\lambda_{A,MD}(\sigma_D)$ relaxation energies are computed from the standard deviation of the distribution of HOMO eigenvalues for the anionic fullerene derivatives.

Single Molecule Anion (λ_A) and Neutral (λ_N) Relaxation Energies and Overall (λ) Reorganization Energies (eV)								
	Indene- C_{60}				PCBM			
	λ_A	$\lambda_{A,MD}(\sigma_D)$	λ_N	λ	λ_A	$\lambda_{A,MD}(\sigma_D)$	λ_N	λ
mono	0.083	0.09 (0.068)	0.082	0.165	0.089	0.11 (0.077)	0.088	0.177
bis1	0.094	0.09 (0.069)	0.095	0.189	0.096	0.12 (0.078)	0.091	0.187
bis2	0.086	0.09 (0.067)	0.084	0.170	0.218	0.23 (0.108)	0.092	0.310
tris	0.082	0.11 (0.074)	0.086	0.168	0.149	0.16 (0.090)	0.071	0.220

The reorganization energies of the multi-adduct PCBMs are significantly larger than that of the mono-adduct PCBM, except for the bis1-adduct of PCBM. The relaxation energies λ_A and λ_N in the mono adduct and bis1-adduct are only slightly asymmetric; for example, λ_A for bis1 PCBM is 0.096 eV and λ_N is 0.091 eV, resulting in a reorganization energy of 0.187 eV. As the bis2 adduct of PCBM has less symmetry than the bis1 adduct, the HOMO electron density in the bis2 anion is more localized, which leads to a further increase in the difference between $\lambda_A = 0.218$ eV and $\lambda_N = 0.092$ eV, and a total reorganization energy of 0.310 eV. We also observe a larger reorganization energy for the tris-adduct of PCBM compared to the mono-adduct (with a value approximately half the sum of the bis1 and bis2 values). Thus, while the relatively rigid indene adduct does not significantly alter the radical-anion and neutral molecular geometries and consequently the relaxation energies, multiple substitutions with phenyl-butyric-acid methyl ester increase the relaxation energies and would be detrimental for charge transport.^{22, 56} The results are also indicative that the adduct positions affect electron localization and, hence, the reorganization/relaxation energy when using phenyl-butyric-acid methyl ester substituents. We would like to mention that the excess electron in the DFT optimized structures of anionic fullerene multi-adducts is delocalized over the fullerene cage; however, the interaction between the adduct moiety and the fullerene cage can influence the extent of delocalization.

As mentioned earlier, the dynamic disorder depends on electron-vibration interactions. The standard deviation of disorder (σ_D) is related to the reorganization energy through the equation $\sigma_D^2 = 2\lambda_A k_B T$; it can be computed through a combination of time-dependent MD simulations and DFT calculations, as described previously.²⁷ The results obtained from these calculations, see Table 3, are comparable to the relaxation energies obtained from the potential energy

surfaces. We stress again that these results point to larger reorganization energies for the multi-adduct PCBM. Hence, care must be taken when designing larger, *flexible* adducts for fullerenes.

In amorphous films, there occurs a substantial amount of static disorder in addition to dynamic disorder. We have shown recently⁵⁷ that the disorder derived from an ensemble average accounts for both static and dynamic components and can therefore be referred to as the total disorder. When these two components are statistically independent, as is the case here, and each exhibit a Gaussian distribution, the total disorder can be represented as a convolution of static and dynamic components, $\sigma_T^2 = \sigma_D^2 + \sigma_S^2$. This formula was used to derive the results reported in Table 4.

Table 4: Overall disorder computed from the distribution of HOMO eigenvalues of the anionic fullerene derivatives with the point charges of the surrounding first-neighbor molecules included from a single frame of a MD trajectory. The σ_T values are accurate within 0.01 eV, 0.01 eV, and 0.02 eV for mono-adducts, bis-adducts, and tris-adducts, respectively.

Anion Disorder in the Condensed Phase						
σ (eV)						
	Indene-C ₆₀			PCBM		
	σ_T	σ_S	σ_D	σ_T	σ_S	σ_D
mono	0.10	0.07	0.07	0.13	0.10	0.08
bis1	0.11	0.08	0.07	0.14	0.11	0.08
bis2	0.16	0.14	0.07	0.15	0.10	0.11
tris	0.12	0.10	0.07	0.12	0.08	0.09

The total disorder obtained for the mono-adduct PCBM is 30% larger than that of the mono-adduct indene-C₆₀. Taking into consideration the difference in relaxation energy or σ_D (since λ is proportional to σ^2 , differences in λ translate into smaller differences in σ) between the mono-adducts of indene-C₆₀ and PCBM, we obtain static disorders of 0.07 eV and 0.11 eV for the indene and PCBM mono-adducts, respectively. The >50% larger static disorder in PCBM would suggest a smaller electron mobility in PCBM amorphous thin films when compared to films of indene-C₆₀. In contrast, indene-C₆₀ amorphous films were found experimentally to have electron mobilities on the order of 0.04 - 0.07 cm²V⁻¹s⁻¹, which are in the same range as those reported for PCBM, 0.05 - 0.10 cm²V⁻¹s⁻¹.^{58, 59} An explanation for this observation is that the mono-adduct of indene-C₆₀ has been shown to have poor film forming capability when compared to PCBM (when using halogenated solvents);²³ this suggests that the actual disorder in such indene-C₆₀ films could be larger than what is estimated in our work.

In the case of the bis-adducts of indene-C₆₀, the largest standard deviation is computed for the static disorder of the bis2 adduct, 0.14 eV. It is useful to recall that the bis2 adduct has a smaller pseudo first-order transition (melting) temperature when compared to bis1, indicative of potentially easier routes to disrupt local packing; this is consistent with larger variations in the first-neighbor environments. Thus, the differences in the packing environments translate into higher total and static disorders for the bis2 adduct of indene-C₆₀ with respect to the bis1 adduct. In the case of PCBM, there are no significant differences in the disorder parameters between the bis1 and bis2 adducts, which is consistent with the similar pseudo first-order transition temperatures, see Table 2.

Comparing the bis-adducts of indene-C₆₀ and PCBM, the average total disorder of the bis-adducts of indene-C₆₀ is 0.01 eV lower than the average of the bis-adducts of PCBM. Recent

impedance spectroscopy measurements⁶⁰ of disorder in an indene-C₆₀ bis-adduct films within an hybrid-bilayer perovskite solar cell, yield a value of 0.188 eV, which is slightly higher than the maximum value of 0.16 eV we have calculated for the bis2 adduct. The measured higher degree of disorder compared to our results can be attributed, at least partly, to the presence of various interfaces within the devices and of isomeric mixtures of indene-C₆₀ bis-adducts.

The results collected in Table 4 indicate that, among the PCBM compounds, tris-adducts have the lowest total and static disorders. In the case of indene-C₆₀, the σ_T and σ_S values derived for the tris-adduct are larger than those for the mono-adduct but smaller than the averaged values estimated for the bis-adducts. We note, however, that the films of bis-adducts and tris-adducts usually represent mixtures of various isomers. Field-effect transistor measurements point to reduced electron mobilities in multi-adducts of PCBM and indene-C₆₀ when compared to their mono-adduct counterparts.^{37, 58, 59} Kinetic Monte Carlo studies from Nelson and co-workers on a PCBM-adduct series attributed^{8, 11} this trend to increased isomeric disorder with an increase in the number of adducts. Based only on the dependence of the electron affinity on the isomer chemical structure, isomeric disorder can be as large as 70 meV in bis-adducts of indene-C₆₀ and PCBM and larger than 100 meV in tris-adducts.^{8, 11, 36} As mentioned above, our calculations also indicate that there could be significant differences in the static disorder among isomers. Therefore, further investigations are required to provide an analysis of the nature and extent of disorder for isomeric mixtures and how that disorder impacts the magnitude of the electron mobilities computed on the basis of the simulations results.

IV. Conclusions

A computational approach that combines molecular dynamics simulations and density functional theory was used to investigate how the nature and number of solubilizing adducts appended to C₆₀ impact major solid-state parameters associated with charge-carrier transport in thin films. The methodology allows us to describe the topological connectivity within the bulk to pinpoint the differences between the types of disorder (dynamic and static disorders).

At the single-molecule level, our results for the substituted fullerenes indicate that:

- i) The dynamic disorder / reorganization energy are smaller for the indene-based adducts, when compared to the fullerene derivatives based on butyric-acid-methyl-ester adducts.
- ii) The larger butyric-acid-methyl-ester adducts slightly increase the reorganization energy, an effect in part due to the ability of the long chains to influence the electron localization on the fullerene cage. This influence is different for neutral and radical-anion moieties and varies with adduct position, leading to an asymmetry in the related relaxation energies. This result suggests that large adducts can be detrimental to the charge-carrier transport characteristics of fullerenes.

From the solid-state packing studies, the following conclusions can be drawn:

- i) The smaller indene-based adducts provide denser packing and a larger number of nearest neighbor molecules compared to the PCBM-based fullerene derivatives.
- ii) Smaller rigid adducts can provide directionality to the interactions, because of entropic considerations, which can influence the formation of ordered phases (partly

ordered phases in the bis1 adduct of indene-C₆₀) that possess lower structural and energetic disorders.

- iii) There is no clear correlation between the degree of disorder and the number of adducts, since disorder increases when going from mono- to bis-substituted molecules but decreases upon addition of the third adduct.
- iv) The substitution pattern, as seen in particular in the case of bis-indene adducts, can have a strong effect on the static disorder.
- v) Overall the polar, flexible butyric acid ethyl ester adducts lead to larger static and dynamic disorders when compared to the indene adducts.
- vi) In the thin-film simulations, the numbers of isolated molecules are found to be higher in tris-adducts of indene-C₆₀ and tris-PCBM. Such disconnected molecules can behave as energetic traps due to their low electronic connectivity and are detrimental to electron transport.

Overall, the main message from our work is that smaller adducts that lead to limited adduct-adduct interactions can fulfill their role in terms of increased solubility without increasing the extent of disorder and compromising the number of nearest neighbors and pathways for electron transport.

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Table of Contents Graphic:

Isolated
molecules acting
as *traps* in
fullerene
multiadducts