

Supporting information for:

Distinguishing the influence of structural and energetic disorder on electron transport in Fullerene multi-adducts

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Coarse grain fullerene force field

Here we extend the Girifalco^{S1,S2} coarse grain buckminsterfullerene (C₆₀) forcefield. The general principle in the creation of this simple forcefield is in the smearing out of the effective Lennards-Jones interactions of 60 graphitic-like carbons over the surface of a sphere the experimental size of a C60 fullerene. We believe this to be directly transferable to the interaction of the fullerene cages in functionalised adducts.

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Our intent is to simulate the various PCBM adducts with a simple two-bead model for the fullerene cage and the side-chain, modelled entirely with Lennard-Jones interactions for computational efficiency. This model for the side-chain of a single spherical super-atom is likely to be better for more symmetric sidechains than PCBM such as indene-functionalised fullerenes.

We take the interaction parameters for the fullerene cage to be identical to those derived by Girifalco for C_{60} ; the atomistic model we use to inform about effective sidechain parameters that reproduce the exclusion of fullerene nearest neighbours seen in the radial distribution function.

We created an atomistic model for mono-PCBM based on the OPLS⁷ empirical force-field, with the reference geometry from a gas-phase quantum chemistry calculation (b3lyp/6-31g*), and the fullerene cage simulated as arbitrarily stiff. This we used to do molecular dynamics on a small ensemble (2564 molecules, 20 *ps* of simulation time) to generate radial distribution functions which we used to fit the free parameters in our coarse-grain molecular dynamics model.

In our coarse-grain model, we choose the interaction energy of the sidechain bead to be the same as the Girifalco parameter for the fullerene site, scaled by the mass of the sidechain (190 Da versus 720.6 for C_{60}).

We then compared coarse-grain radial distribution functions to the atomistic model, varying the effective bond length of the fullerene-sidechain connection, and the effective van-de-Waals radius of the sidechain.

$$V_{LJ} = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right)$$

The complete set of parameters which describes the coarse grain forcefield is $\epsilon_{C60} = 26.823$ kJ/mol, $\sigma_{C60} = 0.895$ nm (Girifalco); $\epsilon_{PBM} = 10.0$ kJ/mol, $\sigma_{PBM} = 0.704$ nm; the C60-PBM bond being $r = 0.64$ nm (fitted in this work).

Having fitted a coarse grain model for mono PCBM, we then extended this to the various fullerene isomer adducts by added extra mono-PCBM sidechain sites at the positions of the

adducts.

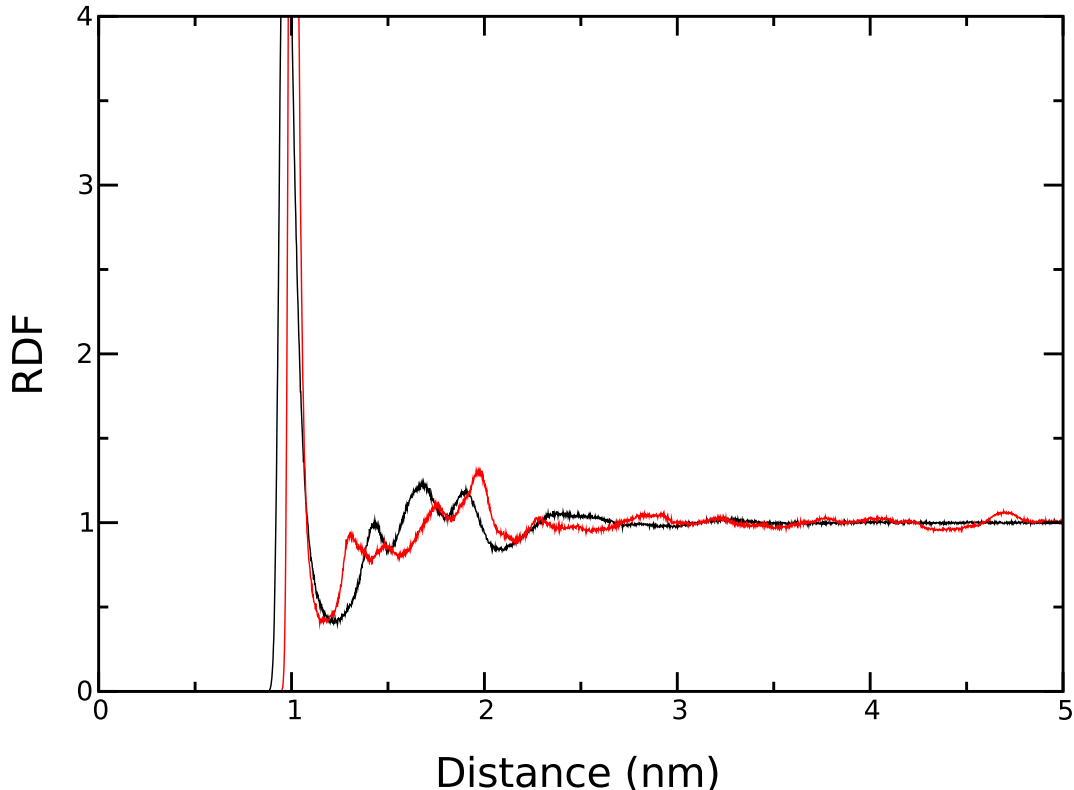


Figure S1: Radial distribution functions C_{60} centres for molecular dynamics simulations of both the coarse grain force field (black), and atomistic OPLS derived force field (red). Distributions for the atomistic representation were taken from the centre of mass of the 61 carbons making up the cage. The coarse grain representation is between the carbon pseudo atoms. The atomistic molecular dynamics was 2564 molecules over 20 *ps* of simulation time. The coarse grain simulation was 100'000 molecules over 200 *ps* of simulation time. We interpret the discrepancy between the nearest neighbour separation for the atomistic and coarse grain representations to be due to the approximate nature of our atomistic forcefield, which was not fitted to experimental fullerene separations but rather uses the default OPLS atom types with a stiff representation for the fullerene cage. Conversely, the coarse grain forcefield uses the carefully fitted Girifalco parameters.

The parameters for the irreducible set of bis and tris isomers were generated by computationally expedient direct enumeration of all possible configurations. Reduction of the set was made with a simple canonical representation (TODO: angles in table for the Supp

Info?).

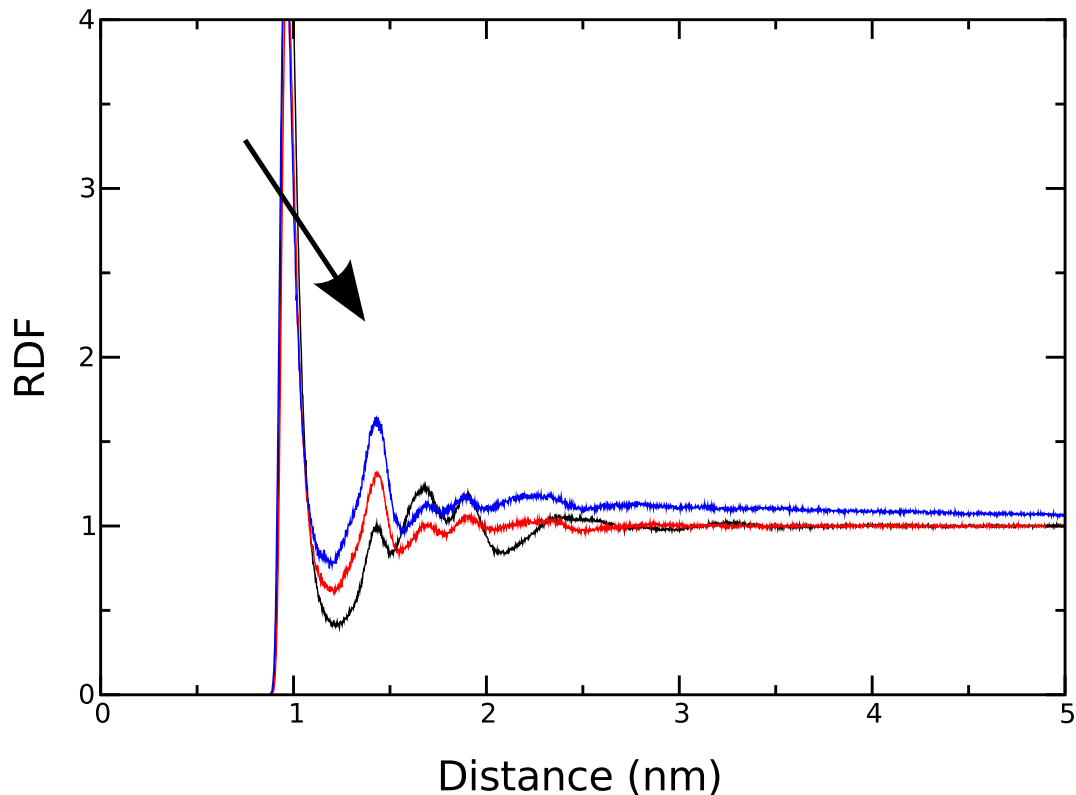


Figure S2: Radial distribution functions of $C_{60} - C_{60}$ for mono (black), bis (red) and tris (blue). The effect of steric hindrance in the increasing number of sidechains can be seen in the decrease of nearest neighbours, and an increase in next nearest neighbours. The isomer pure mono phase has notably more structure than the mixed isomers of bis and tris.

Fullerene sidechain enumeration

C_{60} has 90 bonds between the 60 atoms. 30 of these are 6,6 coordinating (1.37 Å long - along two hexagonal facets) and have more double-bond like character. The remaining 60 bonds are 5,6 coordinating (1.448 Å long). PCBM is formed by 4+2 cycloaddition. These sidechains are believed (ref - that synth paper) to wholly coordinate with the 6,6 bonds.

The 8 unique bis isomers, and 45 tris isomers, have been identified and their point group derived in previous work (ref, Hirsch?). However we did not find a computationally readable list of structures which would be directly useful in constructing our coarse grained model.

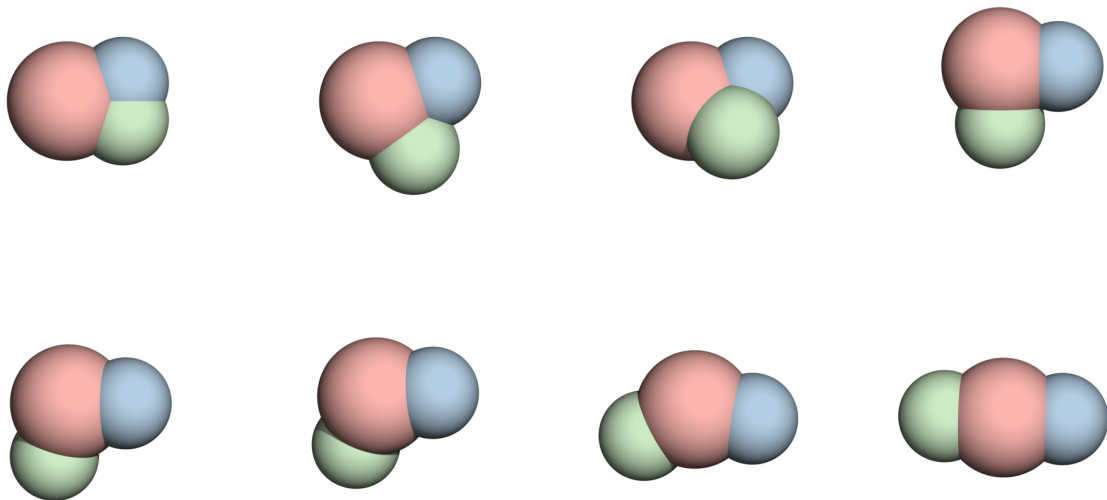


Figure S3: The 8 unique bis isomers, at the coarse grain level. From left to right the isomers are: C1, C2, C3, E, T4, T3, T2, T1.

The bis isomers can be enumerated (identified) by hand and are defined in our coarse grain model simply as the internal angle between the two sidechains. Of the 9 unique isomers, two are equitorial, which for our coarse grain model results in equivalent 90-degree angles.

Identifying unique tris isomers is much more difficult, so we developed a computational method to directly enumerate the isomers and calculate the coarse-grain specification of angles between the three sidechains.

First we read in the coordinates of a C60 molecule with (0,0,0) defined as the centre of the fullerene. We then identify the 6,6 bonds by spacing ($<1.4\text{\AA}$) between atoms. The midpoint of these bonds, and thus the attachment point of the sidechains, was found by averaging the cartesian positions of the two bonded atoms.

We can then enumerate over all possible permutations of these bonds (30 options, 3

Table S1: Inter-sidechain angles for bis isomers, degeneracy from number of ways possible of constructing this unique isomer. All isomers have the same 4-fold degeneracy due to the C4 symmetry of bond location, except for the T1 isomers

Isomer	$\theta_{A,B}$	degeneracy
E	90	4
C2	60	4
C3	72	4
C1	36	4
T3	144	4
T4	108	4
T2	120	4
T1	180	1

selections leading to 24360 permutations, which can be immediately simplified by inspection to 812 permutations by taking 2 selections of 29 options if we choose the first location for the first sidechain). Three inter-sidechain angles are then generated (arcos of the dot production) from these sets of 3 coordinates (a,b;a,c;b,c).

As the order in which we specify the inter-sidechain angles does not matter, we are free to rearrange. By reordering these angles in ascending order, we can identify degenerate configurations by direct comparison.

The newly calculated set of three angles is compared against a list of uniquely defined isomers, and either appended to this list if found to be unique, or discarded and the degeneracy counter of that (already identified) isomer incremented.

With a simple bit of trigonometry and enumeration we directly discover the 45 unique tris isomers and their symmetry derived degeneracy, and can directly generate the angle specification suitable for an empirical force field specification, and a relaxed set of coarse grain coordinates for visualisation and the generation of a dense initial structure for molecular dynamics.

Molecular dynamic assemblies for transport simulations

100'000 kDa simulations...

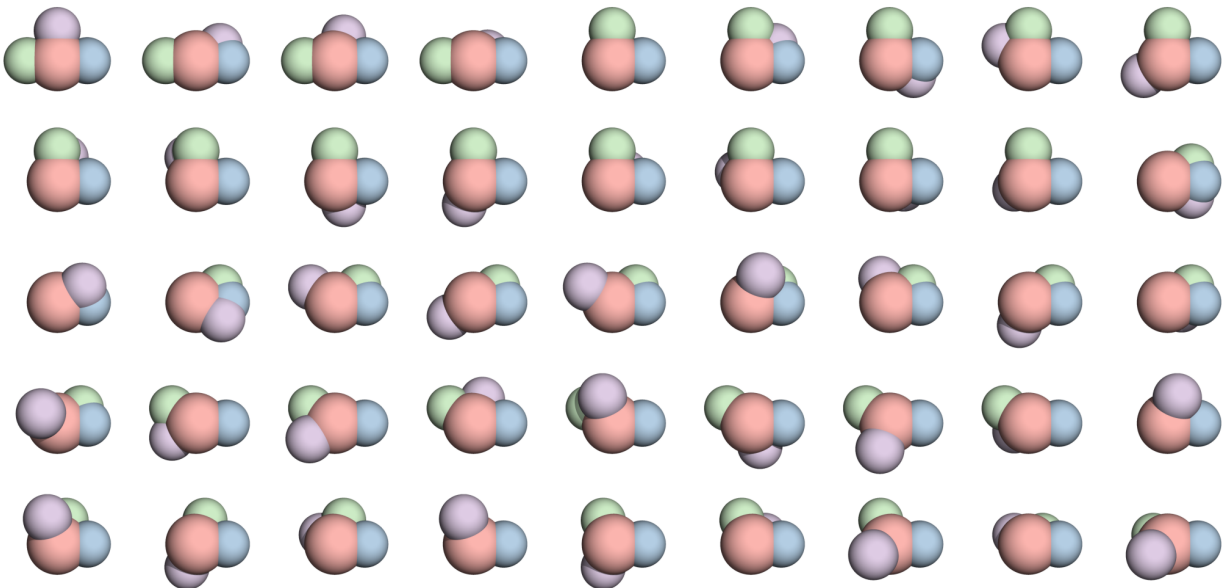


Figure S4: The 45 unique tris isomers, at the coarse grain level, as generated automatically by the method described here.

Transport simulations

We approximate the electron transfer integral between fullerenes with an isotropic approximation where $J \propto \exp(-\alpha d)$ where d is inter-fullerene cage distance and α is 0.5^{-1} .

Our choice of an isotropic transfer integral is due to the simplicity of extracting this single dimension d from the coarse-grain molecular-dynamics simulation, without needing to consider the attitude of individual molecules. Our previous work^{S3} shows that the variation in transfer integrals between unfunctionalised fullerenes varies by [TODO: check this] a factor of two, a relatively small effect compared to variations due to packing.

The cyclo-addition of fullerenes to form the functionalised adducts we study in this work profoundly alters the electronic structure of the fullerene (each addition consumes a (pi orbital) conjugated [TODO: not right wording] electron in forming the sidechain bond). Even different isomers have explicitly different molecular orbital energy levels.^{S4}

Here we use an isotropic transfer integral to approximate the full treatment which would require electronic structure calculations of a wide range of different fullerene adduct isomers.

Table S2: Inter-sidechain angles for all 45 enumerated tris isomers, with a statement of the degeneracy (number of ways possible of constructing this unique isomer).

$\theta_{A,B}$	$\theta_{A,C}$	$\theta_{B,C}$	degeneracy
36	36	36	1
36	36	60	3
36	36	72	3
36	60	60	3
36	60	72	6
36	60	90	6
36	72	90	6
36	72	108	6
36	90	108	6
36	90	120	6
36	108	120	6
36	108	144	6
36	120	120	3
36	120	144	6
36	144	144	3
36	144	180	6
60	60	108	3
60	60	120	3
60	72	72	3
60	72	90	6
60	72	120	6
60	90	108	6
60	90	144	6
60	108	108	3
60	108	144	6
60	120	144	6
60	120	180	6
60	144	144	3
72	72	108	3
72	72	144	3
72	90	120	6
72	90	144	6
72	108	120	6
72	108	180	6
72	120	144	6
72	144	144	3
90	90	90	2
90	90	180	3
90	108	120	6
90	108	144	6
90	120	144	6
108	108	108	1
108	108	144	3
108	120	120	3
120	120	120	1

We postulate that the variation in real-world mobilities can be explained through the variation of fullerene-fullerene packing caused by the various sidechains, and by the consideration of the varying isomer energy levels^{S4} as a Gaussian distribution imposed on the site-energies in the semi-classical Marcus equation.

Simulations of time of flight transients were carried out using the ToFeT package.[?]

Transport Simulations

In a similar fashion to previous work^{S3} we wish to use an isotropic analytic function for the variation of the transfer integral J between two fullerenes. Previous we showed that for a fullerene adduct, where the adduction breaks the highest I_h point group symmetry of the fullerene, the transfer integral is still fairly isotropic.^{S5}

Here we undertake projective-method calculations of the transfer integral^{S6} between representative fullerene adducts. Our aim is to confirm that the effective transfer integral $J \approx J_0.exp(-\lambda d)$ applies as a function of distance, and to find whether the λ factor varies between fullerene adducts.

Internal reorganisation energy

Some mobs

Acknowledgement

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Table S3: Inner sphere reorganisation energies of Mono, Bis and Tris PC–60BM fullerenes. All units meV.

Isomer	λ_{neut}	λ_{ion}	λ_{tot}
mono	77.91	77.49	155.40
bis-C1	111.52	182.64	294.16
bis-C2	108.54	158.89	267.43
bis-C3	81.38	83.31	164.69
bis-E1	88.82	89.49	178.31
bis-T1	138.30	151.32	289.62
bis-T2	80.30	80.93	161.23
bis-T3	125.77	166.20	291.97
bis-T4	87.66	95.56	183.22
tris-E,E,E	108.42	105.41	213.84
tris-E,E,T1(1)	99.51	100.82	200.33
tris-E,E,T1(2)	94.62	98.86	193.49
tris-E,T3,T2	93.97	92.93	186.90
tris-E,T4,T2	98.54	106.46	205.00
tris-E,T4,T3	100.51	100.06	200.56
tris-T3,T3,T3	137.97	173.63	311.60
tris-T4,T3,T3	200.30	226.34	426.64
tris-T4,T4,T2	149.22	148.26	297.48
tris-T4,T4,T4	136.01	166.56	302.57

Table S4: Inner sphere reorganisation energies of Mono, Bis and Tris Methano fullerenes. All units meV.

Isomer	λ_{neut}	λ_{ion}	λ_{tot}
mono	68.80	68.83	137.63
bis-c1	70.42	70.57	140.99
bis-c2	70.45	73.48	143.93
bis-c3	78.69	72.39	151.08
bis-e1	69.79	74.79	144.58
bis-t1	69.37	69.01	138.38
bis-t2	78.85	79.53	158.38
bis-t3	75.42	72.98	148.40
bis-t4	70.03	68.63	138.66
tris-EEE	105.49	78.63	184.12
tris-EET1-1	76.11	76.12	152.22
tris-EET1-2	72.66	72.96	145.62
tris-ET3T2	73.33	75.39	148.72
tris-ET4T2	75.29	72.51	147.80
tris-ET4T3	76.80	73.70	150.50
tris-T3T3T3	82.08	75.01	157.09
tris-T4T3T3	77.78	78.22	155.99
tris-T4T4T2	74.82	74.58	149.40
tris-T4T4T4	82.84	75.88	158.73
c70-mono	92.31	87.75	180.07
c70-bis-4158	98.25	96.06	194.31
c70-bis-5657	87.27	89.48	176.75
c70-bis-6768	96.07	96.10	192.17

Table S5: Simulated mobility by Time of Flight (using the ToFET code), with varying energetic disorder. Units are mobility — cm^2/Vs , energetic disorder — meV

σ	$0. \times 10^{-3}$	56×10^{-3}	121×10^{-3}
M	4.40×10^{-3}	2.72×10^{-3}	0.837×10^{-3}
B	2.27×10^{-3}	1.30×10^{-3}	0.329×10^{-3}
B-E1	1.88×10^{-3}	1.09×10^{-3}	0.277×10^{-3}
T	1.20×10^{-3}	0.589×10^{-3}	0.126×10^{-3}
T-EEE	0.623×10^{-3}	0.429×10^{-3}	0.0854×10^{-3}

Supporting Information Available

The data set and analysis codes, COARSEGRAINPCBM, are available as a source code and data repository on GitHub.^{S7} This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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