

On the inapplicability of electron hopping models for the organic semiconductor Phenyl-C61-butyric Acid Methyl Ester (PCBM)

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Supporting information (corrected)

1 Computational Methods

Geometry optimization of the PCBM molecules in the tc and mc structures were carried out for unit cell dimensions that were fixed to the experimental values.¹ $a = 13.833 \text{ \AA}$, $b = 15.288 \text{ \AA}$, $c = 19.249 \text{ \AA}$, $\alpha = 80.259^\circ$, $\beta = 78.557^\circ$, $\gamma = 80.406^\circ$ for tc and $a = 13.756 \text{ \AA}$, $b = 16.634 \text{ \AA}$, $c = 19.077 \text{ \AA}$, $\alpha = 90.000^\circ$, $\beta = 105.289^\circ$, $\gamma = 90.000^\circ$ for mc. The tc structure contains 4 PCBM molecules per unit cell and 4 chlorobenzene solvent molecules and the mc structure 4 PCBM molecules and 2 ortho-dichloro-benzene solvent molecules. The orbitals were expanded in plane waves with a reciprocal space energy cutoff of 90 Ry and the exchange correlation energy was calculated according to Perdew, Burke and Ernzerhof (PBE).² Dispersion interactions were accounted for in two ways (i) by dispersion corrected atom-centred Goedecker-Hutter pseudo-potentials,³ denoted PBE-DCACP, and by the dispersion correction according to Grimme,⁴ denoted PBE-D. All calculations were carried out for the Γ point. After optimization, the maximum nuclear gradient was 2.6×10^{-3} Hartree/bohr for the tc structure and 5×10^{-4} Hartree/bohr for the mc structure. To obtain sc, hex and bcc model structure we constructed unit cells containing one PCBM molecule and optimized the geometry to 5×10^{-4} Hartree/bohr for a series of lattice constants until an energy minimum was obtained. These optimizations were carried out for the PBE-DCACP functional only. The fcc-C₆₀ structure was obtained similarly using 4 PCBM molecules per unit cell. The cohesive energy per fullerene molecule, E_c , was calculated as $E_c = (E_{\text{pbc}} - nE_g)/n$ where E_{pbc} is the total potential energy per unit cell in periodic boundary conditions (pbc), E_g is the potential energy of a fullerene molecule in the gas phase using the gas phase optimized structure and n is the number of fullerene molecules per unit cell. In case of tc- and mc-PCBM the solvent molecules were deleted before E_{pbc} was calculated.

Electronic coupling matrix elements, H_{ab} , were calculated using the fragment orbital density functional theory (FODFT) approach of Ref. 5 in combination with the electronic structure method detailed above,

$$H_{ab} = \langle \phi_D^{N+1} | h_b^{\text{KS}} | \phi_A^{N+1} \rangle, \quad (1)$$

where N is the number of electrons of neutral PCBM, h_b^{KS} is the one-particle Kohn-Sham Hamiltonian constructed from the $2N + 1$ orbitals of the isolated electron donor molecule PCBM⁻ and the isolated electron acceptor molecule PCBM (A), ϕ_D^{N+1} is the SOMO orbital of the negatively charged donor molecule PCBM⁻, and ϕ_A^{N+1} the SOMO orbital of the negatively charged acceptor molecule PCBM⁻. In order to preserve the Hermitian property, the final coupling matrix element was obtained as the average of H_{ab} and H_{ba} . For a discussion of the approximations underlying Eq. 1 we refer here to our recent work.^{5,6}

The reorganization energy λ was assumed to equal the sum of an inner-sphere contribution, λ_i , and an outer-sphere contribution λ_o , $\lambda = \lambda_i + \lambda_o$. The inner-sphere contribution was obtained according to the standard 4-point scheme,

$$\lambda_i = [E_C(\mathbf{R}_N) + E_N(\mathbf{R}_C)] - [E_C(\mathbf{R}_C) + E_N(\mathbf{R}_N)] \quad (2)$$

where \mathbf{R}_C and \mathbf{R}_N denote the geometry at the minimum of the potential energy surface of the negatively charged PCBM⁻ (C) and neutral PCBM (N), and E_C and E_N are the potential energies of N and C, respectively. The outer-sphere contribution was estimated using the Marcus formula⁷

$$\lambda_o = (\Delta q)^2 (1/\epsilon_{\text{op}} - 1/\epsilon_s) (1/r - 1/R), \quad (3)$$

where ϵ_s and ϵ_{opt} are the static and optical dielectric constants, r the cavity radius for C and R the center-to-center distance between two fullerenes. We use the experimental parameters for fcc-C₆₀, $\epsilon_s = 4.4$,^{8,9} $\epsilon_{\text{op}} = n^2 = 4.0$ (at 1.06 \mu m),^{10,11} $r = 5.02 \text{ \AA}$.

2 Frontier orbitals of C₆₀ and PCBM

The lowest unoccupied orbital (LUMO) of C₆₀ is of t_{1u} symmetry and 3-fold degenerate.¹⁷ **Vertical** insertion of an excess electron leaves the symmetry of the orbitals unchanged, resulting in a 3-fold degenerate **singly**

occupied molecular orbital (SOMO) for unrelaxed C_{60}^- . An electronic state of this manifold is depicted in Figure S1 (A). **After ionic relaxation of the anion the three levels become quasi-degenerate.** For $PCBM^-$, the 3-fold degeneracy is lifted due to the presence of the side chain. The SOMO of $PCBM^-$ still resembles very closely the SOMO of C_{60}^- with the nodal plane oriented parallel with respect to the side chain (see Figure S1 (B)). The SOMO+1 and the SOMO+2 are 40 and 240 meV, respectively, above the SOMO. The nodal plane of these states include the side chain as shown in Figure S1 (C), (D). The energetic order of the orbitals is the same for the six different side chain conformations found in the tc (four) and mc (two) crystal structure, hence the orbital energies were averaged over all six structures. The energy spacing between SOMO and SOMO+1 of $PCBM^-$ is not more than $1 - 2k_B T$ at room temperature, which means that the two orbitals are in fact quasi-degenerate and that both of them contribute to electron transfer. The SOMO+2 is too high in energy to contribute significantly at ambient temperature. Thus, the number of orbitals mediating electron transfer reduces from three for C_{60}^- to two for $PCBM^-$. The coupling matrix elements presented in the main text are for the SOMO of $PCBM^-$, only, which suffices to show that hopping models are not applicable.

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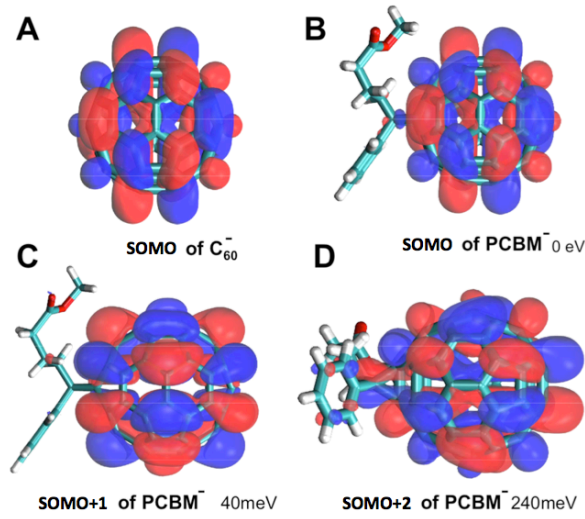


Figure S1: Singly occupied molecular orbital (SOMO) for gas phase C_{60}^- (A) and $PCBM^-$ (B), SOMO+1 of $PCBM^-$ (C) and SOMO+2 of $PCBM^-$ (D). Energy levels indicated for PCBM are averaged over different side chain conformations.

Table S1: Bond lengths of the long and short covalent bond, d_l and d_s , respectively, lattice constant a and cohesive energy E_c of PCBM and C_{60} (calc = calculated, exp = experimental, lit = literature). All calculations were carried out with the PBE-DCACP functional if not stated otherwise.

	d_l (Å)		d_s (Å)		a (Å)		E_c (eV)		
	calc	exp	calc	exp	calc	lit	PBE-DCACP	PBE-D	lit
PCBM									
tc	1.454	1.447 ^a	1.399	1.388 ^a	-	13.757 ^{ab}	-1.41	-1.91	-
mc	1.451	1.447 ^a	1.399	1.388 ^a	-	13.833 ^{ac}	-1.30	-1.76	-
sc	1.453	-	1.399	-	10.25	9.9 ^e	-1.09	-1.07	-1.27 ^e
hex	1.453	-	1.399	-	10.00 ^d	9.7 ^e	-0.97	-0.79	-1.05 ^e
bcc	1.453	-	1.399	-	13.06	11.1 ^e	-0.87	-0.73	-0.95 ^e
gas	1.454	-	1.399	-	-	-	-	-	-
C_{60}									
fcc	1.452	1.455 ^f	1.398	1.391 ^f	14.25	14.15 ^g	1.37	1.48	1.789 ^h
gas	1.453	1.458 ⁱ	1.399	1.401 ⁱ	-	-	-	-	-

^aRef.¹

^b $b = 16.634\text{Å}$, $c = 19.077\text{Å}$, $\beta = 105.29^\circ$.

^c $b = 15.288\text{Å}$, $c = 19.249\text{Å}$, $\alpha = 80.26^\circ$, $\beta = 78.56^\circ$, $\gamma = 80.41^\circ$.

^d $c = 12.00\text{Å}$.

^eRef.,¹⁵ LDA.

^fRef.,²³ at 5 K, sc-structure.

^gRef.,¹⁴ at 255 K.

^hRef.¹⁶

ⁱRef.,²⁴ at 730° C.

Table S2: Electron transfer parameter for hexagonal, sc and bcc PCBM in the respective minimum energy structures.

ET direction	R (Å)	H_{ab} (meV)	λ (meV)	ΔE_{ad}^\ddagger (meV)	k_{ET} (Hz)
sc					
[010]	10.25	32.7	139	9	9.23×10^{12}
[001]	10.25	6.1	139	29	5.05×10^{11}
[100]	10.25	2.3	139	33	6.71×10^{10}
$[\bar{1}0\bar{1}]$	14.50	0.5	148	37	2.65×10^9
$[0\bar{1}1]$	14.50	0.5	148	37	2.65×10^9
[110]	14.50	0.2	148	37	4.19×10^8
[101]	14.50	0.1	148	37	1.04×10^8
[011]	14.50	0.0	148	37	$< 1.04 \times 10^8$
$[\bar{1}10]$	14.50	0.0	148	37	$< 1.04 \times 10^8$
hex					
[100]	10.00	73.9	138	-7	1.97×10^{13}
[010]	10.00	6.4	138	28	5.63×10^{11}
[110]	10.00	4.7	138	30	2.98×10^{11}
[001]	12.00	2.9	143	33	1.02×10^{11}
bcc					
[111]	11.31	1.2	142	34	1.70×10^{10}
[001]	13.06	0.8	146	36	7.01×10^9
$[\bar{1}\bar{1}1]$	11.31	0.6	142	35	4.16×10^9
[010]	13.06	0.4	146	36	1.74×10^9
$[11\bar{1}]$	11.31	0.3	142	35	1.03×10^9
$[\bar{1}\bar{1}1]$	11.31	0.1	142	35	1.13×10^8
[100]	13.06	0.1	146	36	1.08×10^8