Supporting Information for:

Mechanistic Insight into the Attachment of Fullerene Derivatives on Crystal Faces of Methyl Ammonium Lead Iodide Based Perovskites

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Table S1: The number of PCBM and CB molecules between the two perovskite surfaces in the simulated systems is provided.

Model system	Number of molecules		
	PCBM	CB	Deposited PCBM
(110) surface	100	5186	35
(100) surface	100	4820	27

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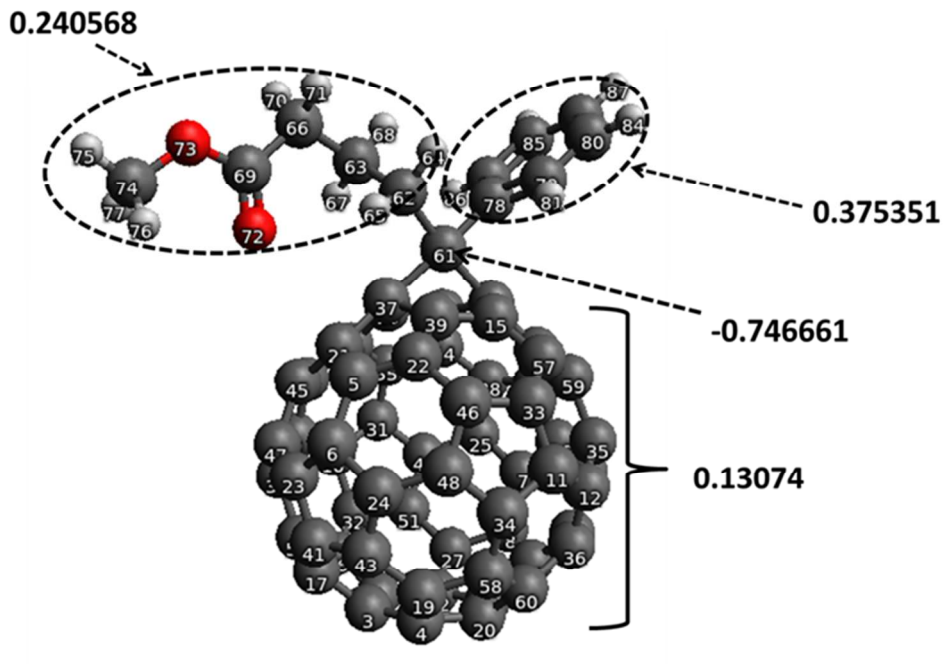

Figure S1: Molecular structure of PCBM with specific serial numbers for atoms is presented. For the convenience, the net partial charges of some key atomic groups are highlighted. Dark grey: C atoms; light grey: H atoms; red: O atoms.

Table S2: Partial charges of a PCBM in chlorobenzene obtained from density functional theory are shown. The indices of atoms in the first column of the table are consistent with the serial numbers presented in Figure S1.

Atom	Coordinates			Charge *(e)*
	X	Y	Z	
1 C	0.148	-0.120	0.159	-0.0309
2 C	0.191	-0.138	0.027	0.0512
3 C	-0.185	0.462	-0.028	-0.0226
4 C	-0.143	0.444	-0.159	0.0032
5 C	-0.250	-0.082	-0.049	0.0983
6 C	-0.317	0.035	-0.087	-0.0664
7 C	0.323	0.290	0.086	-0.0291

8 C	0.256	0.406	0.049	0.0241
9 C	-0.161	0.169	0.315	0.0004
10 C	-0.046	0.244	0.342	-0.0009
11 C	0.052	0.080	-0.342	0.0108
12 C	0.166	0.155	-0.315	-0.0313
13 C	0.008	-0.136	0.193	-0.1014
14 C	0.201	-0.010	0.238	0.0661
15 C	0.094	-0.172	-0.076	0.0264
16 C	0.288	-0.047	-0.030	-0.0141
17 C	-0.283	0.371	0.030	0.0395
18 C	-0.089	0.497	0.076	-0.0041
19 C	-0.196	0.335	-0.239	-0.0385
20 C	-0.002	0.460	-0.193	0.0085
21 C	-0.215	-0.104	0.090	0.0351
22 C	-0.143	-0.134	-0.132	0.0233
23 C	-0.351	0.135	0.014	0.0090
24 C	-0.279	0.104	-0.208	-0.0084
25 C	0.284	0.220	0.208	0.0233
26 C	0.356	0.190	-0.014	-0.0158
27 C	0.148	0.458	0.131	-0.0400
28 C	0.220	0.428	-0.090	0.0056
29 C	-0.151	0.027	0.290	-0.0296
30 C	-0.263	0.223	0.227	0.0215
31 C	0.084	0.179	0.345	-0.0013
32 C	-0.029	0.375	0.282	0.0051
33 C	0.034	-0.051	-0.282	0.0355
34 C	-0.078	0.146	-0.345	0.0149
35 C	0.269	0.101	-0.227	0.0288
36 C	0.156	0.298	-0.290	-0.0131
37 C	-0.085	-0.169	0.093	0.1090
38 C	0.295	0.077	0.183	-0.0484
39 C	-0.040	-0.188	-0.044	0.1129
40 C	0.339	0.058	0.046	0.0448
41 C	-0.334	0.266	-0.046	-0.0352
42 C	0.046	0.512	0.043	0.0336
43 C	-0.289	0.247	-0.183	0.0452
44 C	0.090	0.493	-0.094	-0.0289
45 C	-0.247	-0.008	0.186	-0.0616
46 C	-0.106	-0.067	-0.249	-0.0503
47 C	-0.317	0.114	0.147	0.0146
48 C	-0.176	0.055	-0.288	-0.0020
49 C	0.181	0.270	0.287	0.0024
50 C	0.322	0.211	-0.148	-0.0080
51 C	0.112	0.391	0.248	0.0060
52 C	0.252	0.332	-0.187	-0.0029
53 C	-0.026	-0.036	0.293	0.0911

54 C	-0.247	0.349	0.169	-0.0393
55 C	0.093	0.041	0.321	-0.0676
56 C	-0.127	0.427	0.197	0.0023
57 C	0.132	-0.103	-0.198	-0.0747
58 C	-0.088	0.283	-0.322	-0.0236
59 C	0.252	-0.025	-0.170	-0.0102
60 C	0.032	0.360	-0.293	0.0384
61 C	0.102	-0.509	0.081	-0.7466
62 C	-0.025	-0.579	0.051	0.5973
63 C	-0.134	-0.558	0.159	0.0202
64 H	-0.020	-0.686	0.023	-0.1422
65 H	-0.059	-0.525	-0.040	-0.0378
66 C	-0.271	-0.612	0.119	-0.2628
67 H	-0.140	-0.451	0.180	-0.0540
68 H	-0.102	-0.607	0.251	0.0216
69 C	-0.336	-0.535	0.005	0.7985
70 H	-0.341	-0.608	0.204	0.0779
71 H	-0.267	-0.718	0.090	0.0371
72 O	-0.295	-0.432	-0.044	-0.6167
73 O	-0.450	-0.596	-0.035	-0.4632
74 C	-0.522	-0.529	-0.141	0.3314
75 H	-0.609	-0.591	-0.160	-0.0218
76 H	-0.459	-0.522	-0.230	-0.0170
77 H	-0.552	-0.429	-0.109	-0.0278
78 C	0.223	-0.566	0.024	0.6475
79 C	0.232	-0.665	-0.077	-0.3628
80 C	0.354	-0.708	-0.125	-0.0130
81 H	0.140	-0.707	-0.118	0.1510
82 C	0.345	-0.513	0.075	-0.2839
83 C	0.473	-0.656	-0.070	-0.1299
84 H	0.359	-0.782	-0.204	0.0850
85 C	0.468	-0.560	0.031	-0.0113
86 H	0.337	-0.435	0.150	0.1163
87 H	0.569	-0.691	-0.107	0.0998
88 H	0.560	-0.520	0.072	0.0766

Estimation of ΔG values

In our simulated systems, both surfaces have positively charged atoms, such as Pb in case of (110) surface and H for (100) surface, which directly associate with the carbonyl oxygen atom of PCBM due to strong electrostatic interactions. On the other hand, for the same reason, the corresponding energy barriers for desorption of PCBMs from the perovskite surfaces and diffusion along the surfaces are extremely high. As a result, only the energy barrier for deposition of PCBM from solution to substrate plays a significant role in the overall growth of monolayer of PCBM on the perovskite surface. Applying the above assumptions to classical heterogeneous nucleation theory, the rate of cluster deposition (N_D) is given as,[1-3]

$$N_D = R^{\alpha} e^{\frac{(-\Delta G)}{k_b T_s}} \quad (1S)$$

where, R is the rate of attempts (particle/ns) for deposition of PCBMs on the perovskite surface and α is a constant related to the theoretical cluster size, which is considered as 1 in the present study. Here, k_b is the Boltzmann's constant, T_s is the substrate temperature that is 400K for the simulated systems and ΔG is the thermodynamic barrier for deposition of individuals PCBMs from solution to perovskite surface. We estimated ΔG values for both surfaces, for the sake of qualitative comparison, by using the ratio of N_D and R directly obtained from the MD simulations, and presented in Table S3. Ultimately, the nearly identical estimates of ΔG for both systems signify that the extent of deposition of PCBMs on different perovskite surfaces is not distinct energetically. However, the deposition is dependent on kinetics of each system based on processing conditions. Since the temperature and concentration in the simulated surfaces were identical, our model systems have similar kinetics resulting in very similar success to attempt ratios, shown in Table S3, for deposition.

Table S3: Estimated values of ΔG, in terms of total number of deposited PCBM and total number of attempts for deposition, are presented for both perovskite surfaces.

Model system	N_D/R	ΔG (eV)
(110) plane	7.66×10^{-3}	0.167
(100) plane	7.12×10^{-3}	0.170

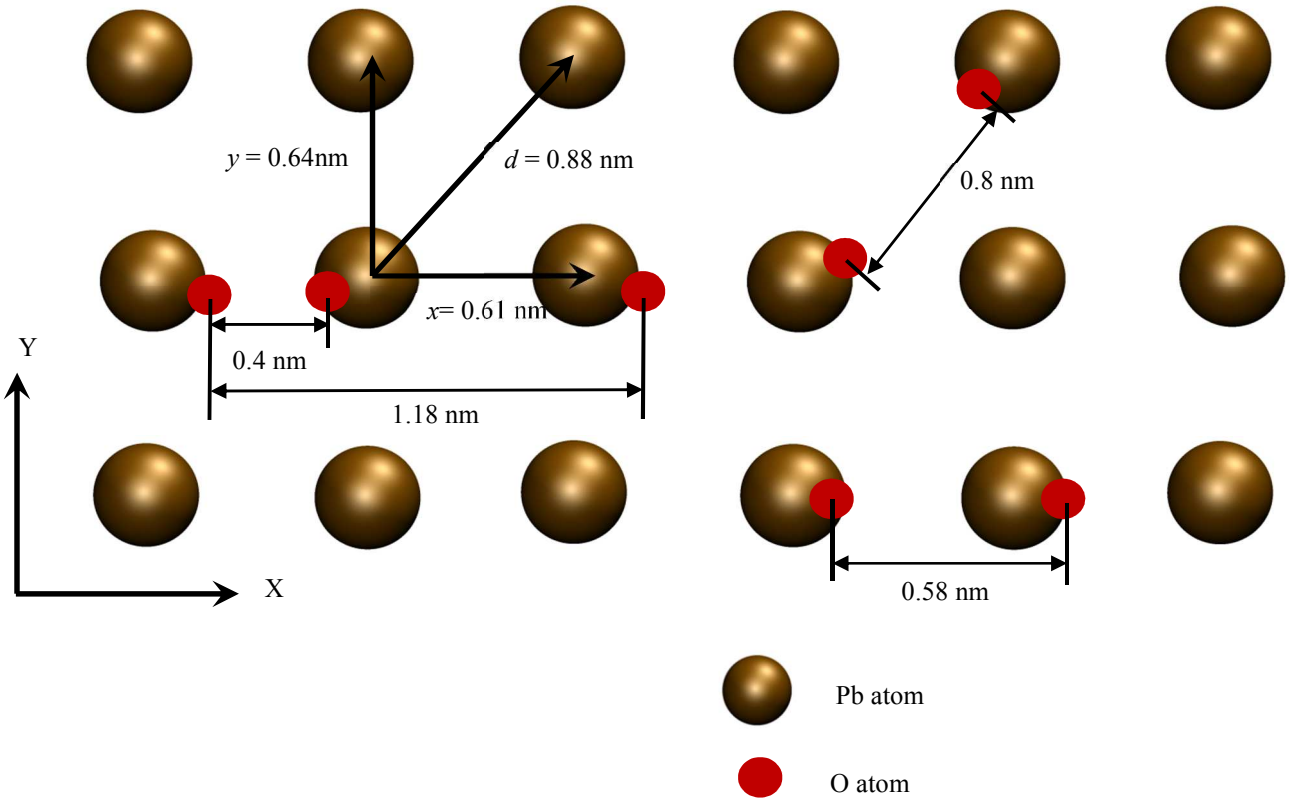

Figure S2: Inter-atomic arrangements of Pb and O atoms in the *x*-*y* plane of (110) perovskite crystal face are shown. Here, *x*, *y* and *d* represents the distance between Pb atoms, which are along *x*-axis, *y*-axis and diagonal-direction, respectively. The corresponding radius of Pb and O atoms are not in actual scale.

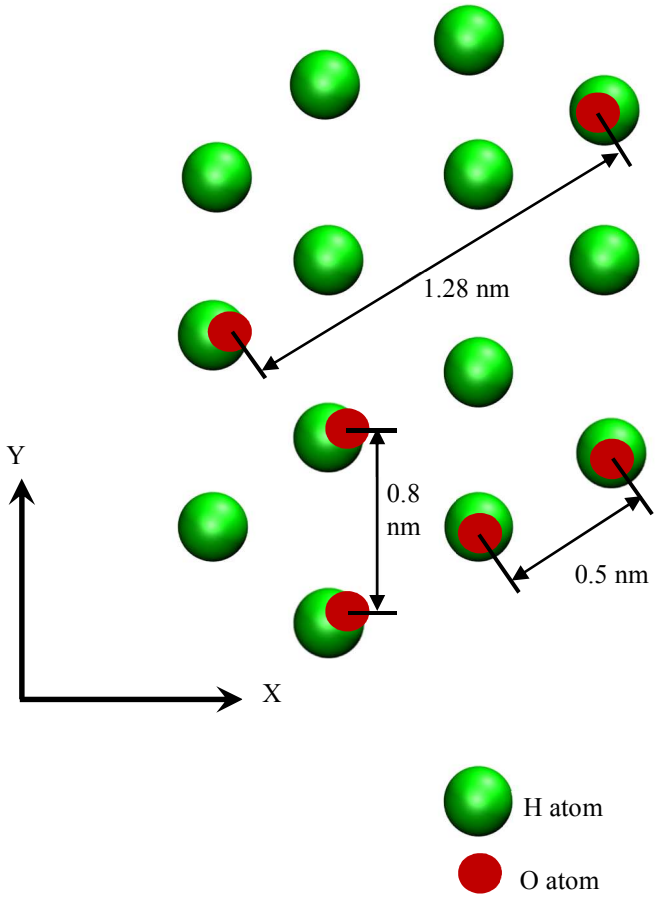

Figure S3: Inter-atomic arrangements of H and O atoms in the x-y plane of (100) perovskite crystal face are shown. The corresponding radius of H and O atoms are not in actual scale.

Supplementary references

1. Markov, I. V., *Crystal Growth for Beginners: Fundamentals of Nucleation, Crystal Growth and Epitaxy*. 2nd ed.; World Scientific: New Jersey, USA, 2003.
2. Ohring, M., *Material Science of Thin Films*. 2nd ed.; Academic Press: Orlando, USA, 2001.
3. Gupta, V. K.; Abbott, N. L., Using droplets of nematic liquid crystal to probe the microscopic and mesoscopic structure of organic surfaces. *Langmuir* **1999,** *15* (21), 7213-7223.