Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary Information

Electronic structure of $Li^+@C_{60}$ adsorbed on methyl-ammonium lead iodide perovskite $CH_3NH_3PbI_3$ surfaces

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From Figs. S4-S11 (Table 2), the $MAPbI_3/Li^+$(bottom)@C_{60} system with the aboveC geometry is stabilized by two C···H(-C) (in the ranges 2.612Å- 2.660Å), two C···C(-H) (in the ranges 3.538Å – 3.544Å) and one C···I(-Pb) (~3.787 Å) vdWs interactions. On the other hand, there are four vdWs interactions in the $MAPbI_3/Li^+$(top)@C_{60} system with the aboveC geometry: two C···H(-C) in the ranges 2.619Å- 2.665Å, one C···C(-H) ~ 3.544 Å and one C···I(-Pb) ~3.787 Å. This could be one of the factors that contributes to the total energy difference of ~0.031 eV (and the biding energy difference of ~0.031 eV) from the most stable structure (the $MAPbI_3/Li^+$(bottom)@C_{60} system with the aboveC geometry). It is interesting to see that the $MAPbI_3/Li$@C_{60} system with the aboveC geometry has more atomic distances within the sum of their vdW radii than the $MAPbI_3/Li^+$@C_{60} system. There are six C···I(-Pb) bond distances within the vdWs interactions (in the ranges of 3.411Å - 3.762Å) in both the $MAPbI_3/Li^+$(top)@C_{60} and $MAPbI_3/Li^+$(bottom)@C_{60} system with the aboveI geometry. For the $MAPbI_3/Li^+$@C_{60} system with the bridge geometry, they have six potential vdW interactions: two C···H(-C) in the ranges 2.791Å – 2.990Å, two C···C(-H) in the ranges 3.443Å – 3.465Å and two C···I(-Pb) in the ranges 3.519Å – 3.741Å.

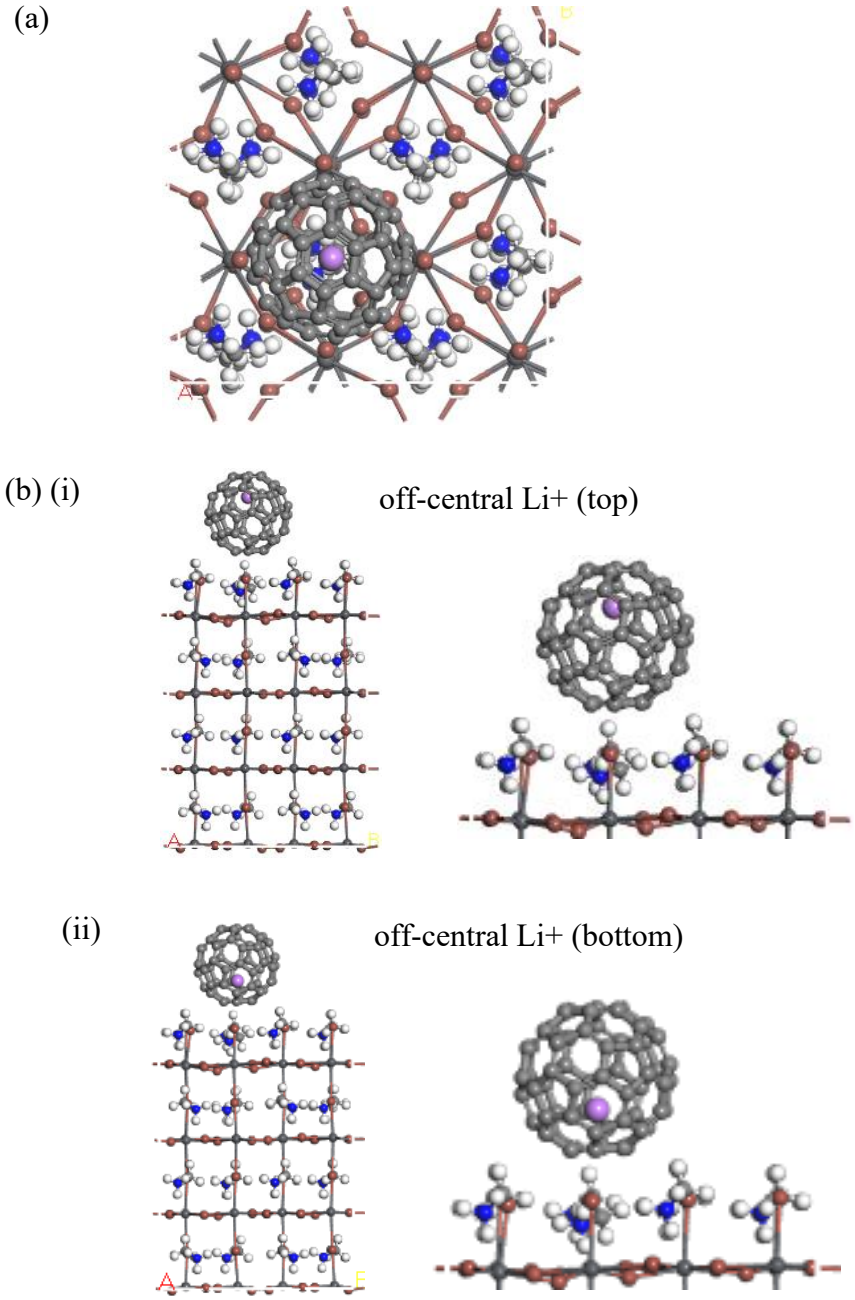


Figure S1. Optimized structures of a $MAPbI_3/Li^+@C_{60}$ heterojunction with tetragonal-phase perovskites: (a) top and (b) side views. The perovskite has a topC orientation with a lithium endohedral fullerene $Li^+@C_{60}$ on the aboveC geometry. (b) Side views represent the Li^+ located at the off-central (i) top and (ii) bottom inside the C_{60} cage. H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively.

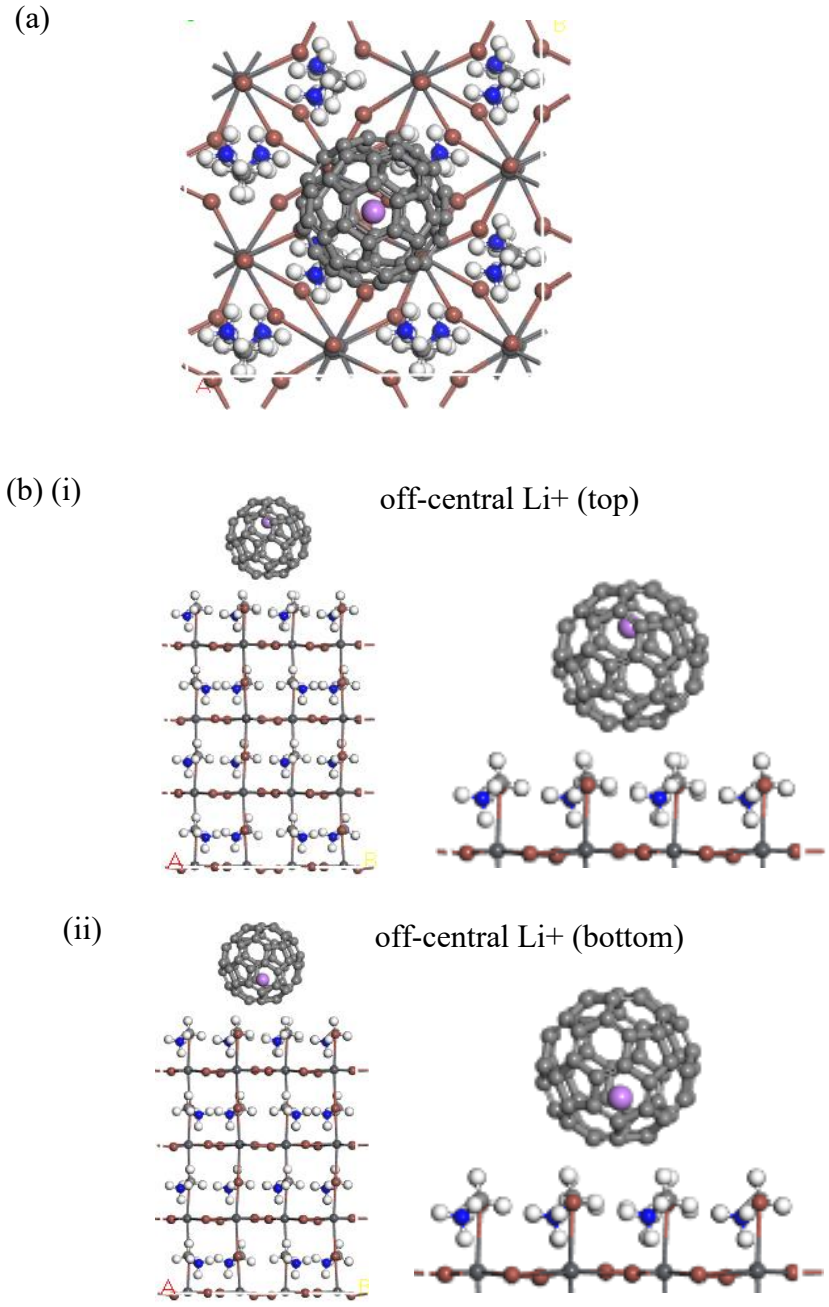


Figure S2. Optimized structures of a $MAPbI_3/Li^+@C_{60}$ heterojunction with tetragonal-phase perovskites: (a) top and (b) side views. The perovskite has a topC orientation with a lithium endohedral fullerene $Li^+@C_{60}$ on the aboveI position. (b) Side views represent the Li^+ located at the off-central (i) top and (ii) bottom inside the C_{60} cage. H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively.

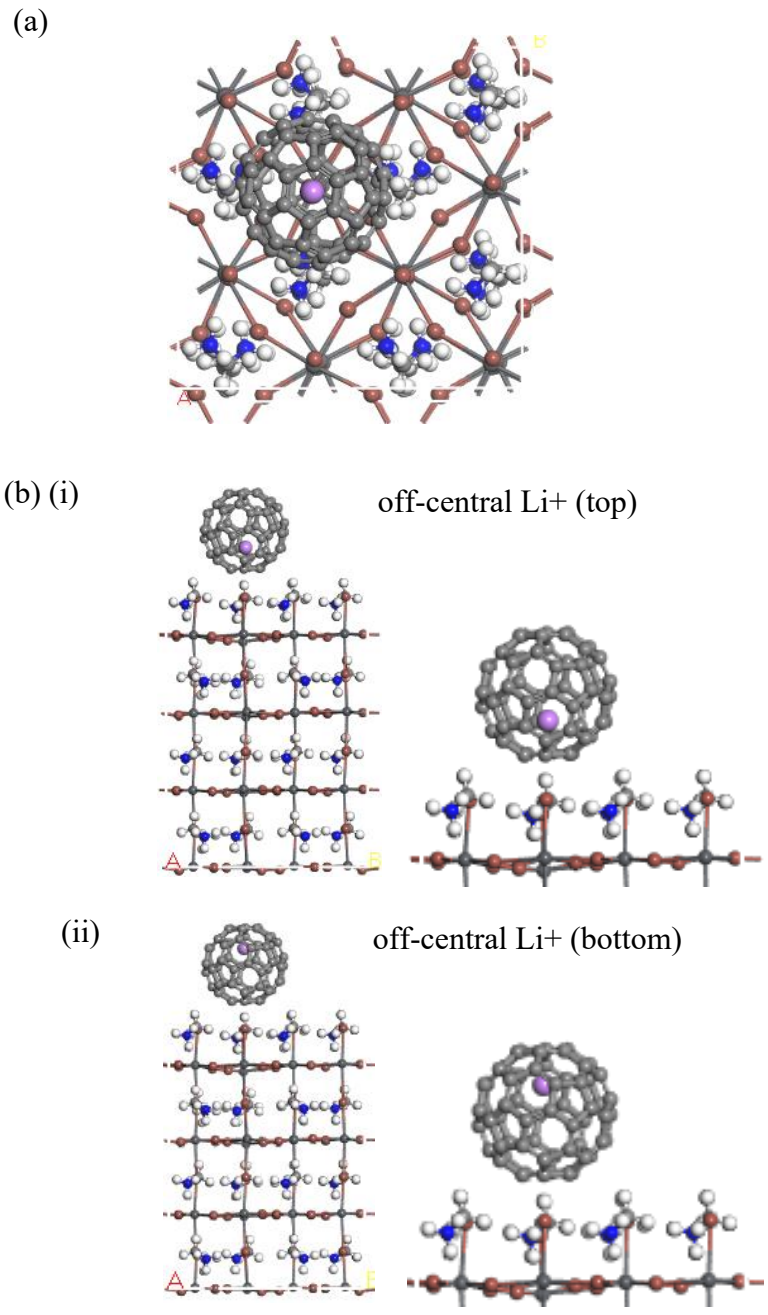
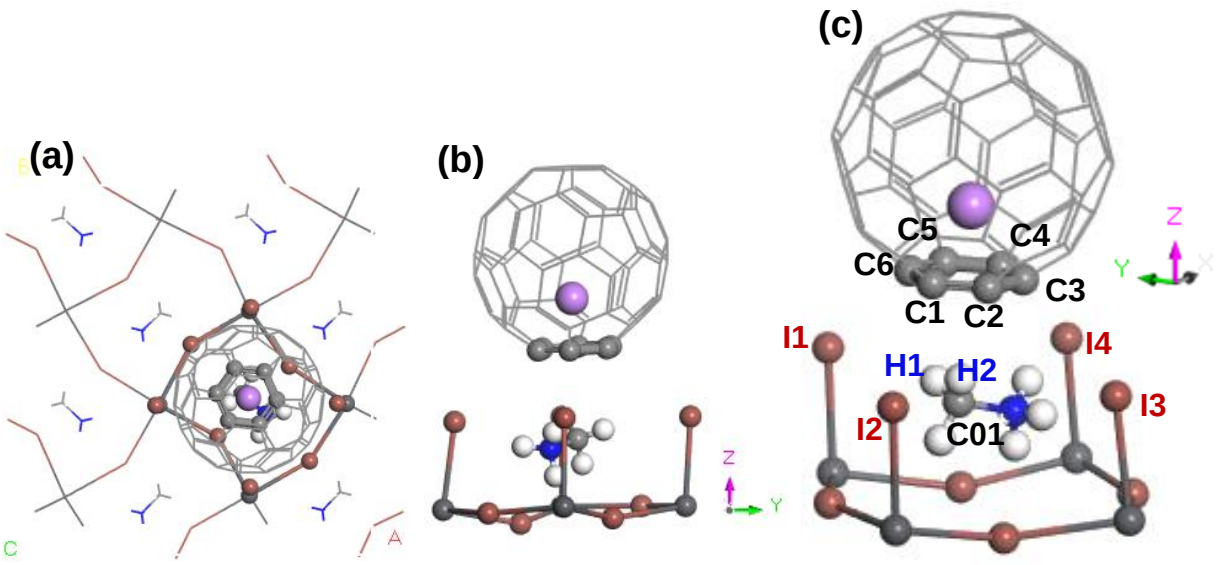
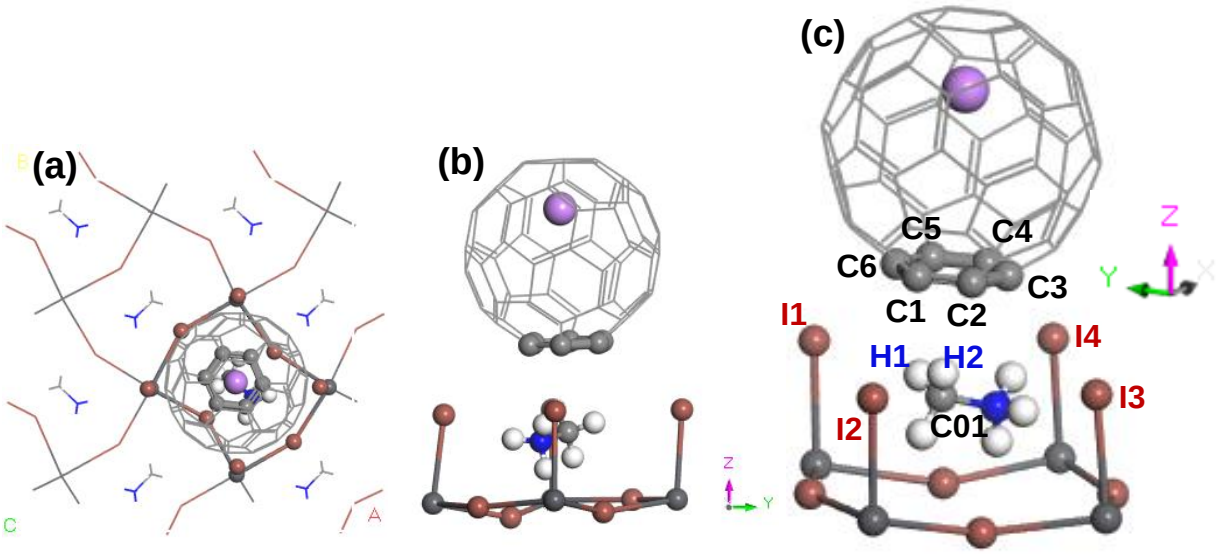


Figure S3. Optimized structures of a $MAPbI_3/Li^+@C_{60}$ heterojunction with tetragonal-phase perovskites: (a) top and (b) side views. The perovskite has a topC orientation with a lithium endohedral fullerene $Li^+@C_{60}$ on the bridge position. (b) Side views represent the Li^+ located at the off-central (i) top and (ii) bottom inside the C_{60} cage. H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively.



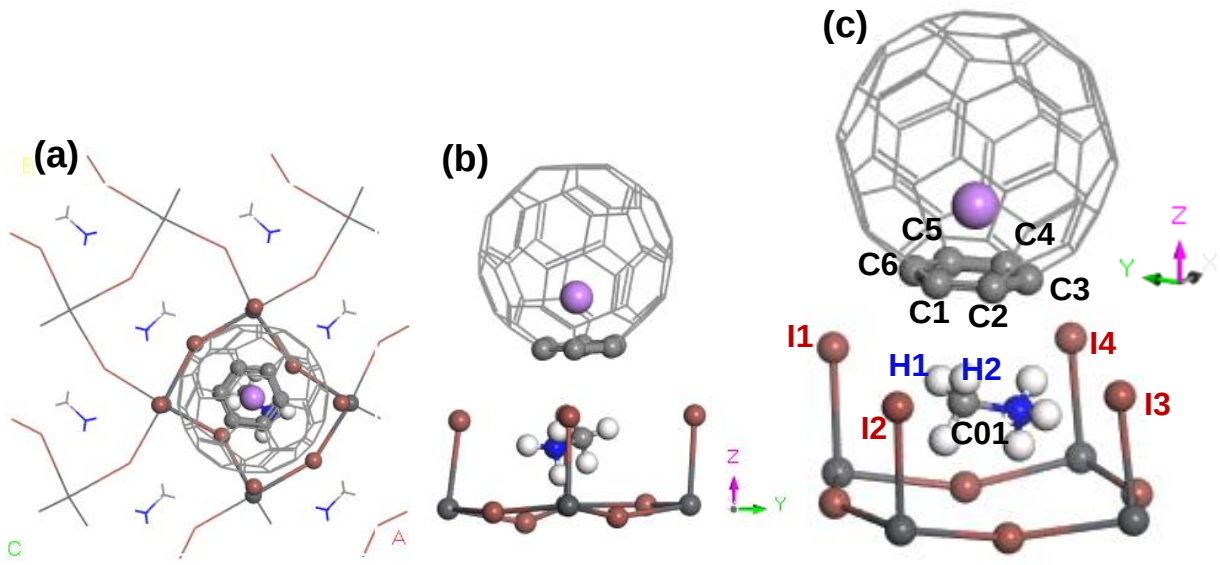
C···H distance [Å] [vdWs radius < 2.97Å]		C···C distance [Å] [vdWs radius < 3.54Å]		C···I distance [Å] [vdWs radius < 3.81Å]	
C1···H1	3.499	C1···C01	3.530	C5···I1	3.934
C2··· H1	3.792	C2···C01	3.546	C6···I1	3.887
C3··· H1	3.699	C3···C01	3,572	C1···I1	5.043
C4··· H1	3.301	C4···C01	3.580	C6···I2	4.792
C5··· H1	2.944	C5···C01	3.558	C1···I2	3.833
C6··· H1	3.057	C6···C01	3.532	C2···I2	4.265
C1···H2	2.667			C2···I3	4.213
C2··· H2	2.618			C3···I3	3.931
C3··· H2	2.977			C4···I3	4.983
C4··· H2	3.321			C3···I4	4.518
C5··· H2	3.359			C4···I4	3.729
C6··· H2	3.058			C5···I4	4.457

Figure S4. (a) Top view of topC-oriented $MAPbI_3$ with a neutral lithium endohedral fullerene $Li@C_{60}$ on the aboveC position. The Li located at the off-central bottom inside the C_{60} cage. (b) Side and (c) perspective views are the selected area (ball and sticks in $MAPbI_3$) from top view (a). H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively. Atoms located at the interface between $MAPbI_3$ and C_{60} are labelled, and their atomic distance are summarized in table. Atomic distances that falls within the vdWs atomic radius are represented in red color.



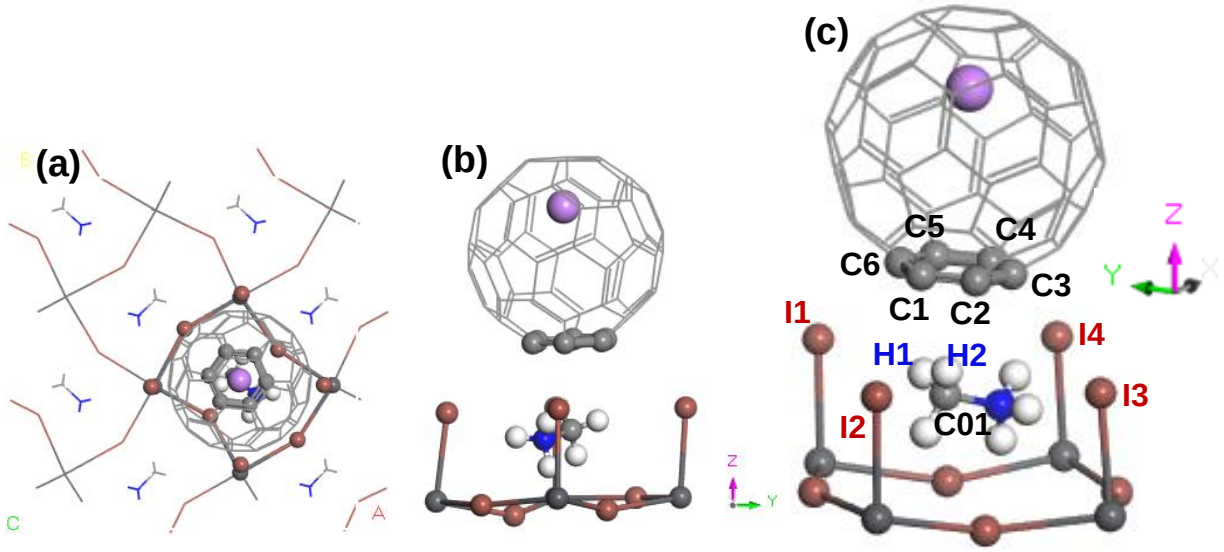
C···H distance [Å] [vdWs radius < 2.97Å]		C···C distance [Å] [vdWs radius < 3.54Å]		C···I distance [Å] [vdWs radius < 3.81Å]	
C1···H1	3.527	C1···C01	3.547	C5···I1	3.950
C2··· H1	3.796	C2···C01	3.545	C6···I1	3.919
C3··· H1	3.692	C3···C01	3.562	C1···I1	5.061
C4··· H1	3.304	C4···C01	3.581	C6···I2	4.829
C5··· H1	2.982	C5···C01	3.584	C1···I2	3.886
C6··· H1	3.103	C6···C01	3.565	C2···I2	4.304
C1···H2	2.672			C2···I3	4.264
C2··· H2	2.621			C3···I3	3.991
C3··· H2	2.973			C4···I3	5.043
C4··· H2	3.320			C3···I4	4.541
C5··· H2	3.367			C4···I4	3.782
C6··· H2	3.069			C5···I4	4.540

Figure S5. (a) Top view of topC-oriented $MAPbI_3$ with a neutral lithium endohedral fullerene $Li@C_{60}$ on the aboveC position. The Li located at the off-central top inside the C_{60} cage. (b) Side and (c) perspective views are the selected area (ball and sticks in $MAPbI_3$) from top view (a). H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively. Atoms located at the interface between $MAPbI_3$ and C_{60} are labelled, and their atomic distance are summarized in table. Atomic distances that falls within the vdWs atomic radius are represented in red color.



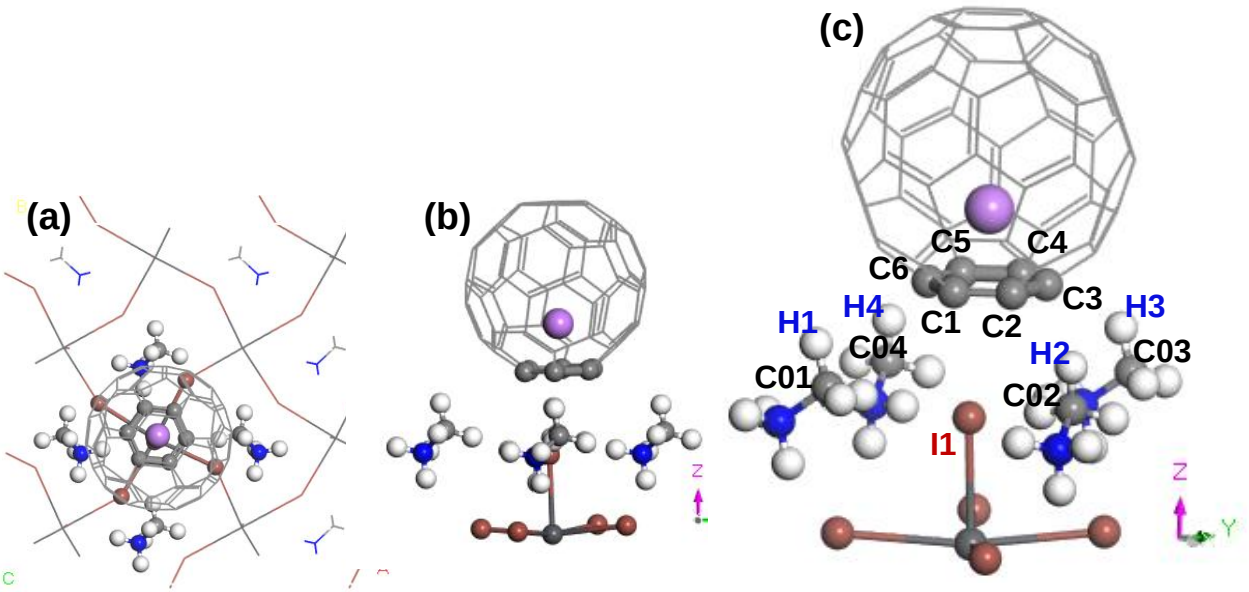
C···H distance [Å] [vdWs radius < 2.97Å]		C···C distance [Å] [vdWs radius < 3.54Å]		C···I distance [Å] [vdWs radius < 3.81Å]	
C1···H1	3.529	C1···C01	3.538	C5···I1	3.943
C2··· H1	3.804	C2···C01	3.544	C6···I1	3.888
C3··· H1	3.710	C3···C01	3,578	C1···I1	5.021
C4··· H1	3.326	C4···C01	3.604	C6···I2	4.851
C5··· H1	2.998	C5···C01	3.597	C1···I2	3. 884
C6··· H1	3.108	C6···C01	3.563	C2···I2	4.296
C1···H2	2.660			C2···I3	4.226
C2··· H2	2.612			C3···I3	3.974
C3··· H2	2.977			C4···I3	5.044
C4··· H2	3.330			C3···I4	4.501
C5··· H2	3.369			C4···I4	3.744
C6··· H2	3.059			C5···I4	4.507

Figure S6. (a) Top view of topC-oriented $MAPbI_3$ with a lithium endohedral fullerene $Li^+@C_{60}$ on the aboveC position. The Li^+ located at the off-central bottom inside the C_{60} cage. (b) Side and (c) perspective views are the selected area (ball and sticks in $MAPbI_3$) from top view (a). H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively. Atoms located at the interface between $MAPbI_3$ and C_{60} are labelled, and their atomic distance are summarized in table. Atomic distances that falls within the vdWs atomic radius are represented in red color.



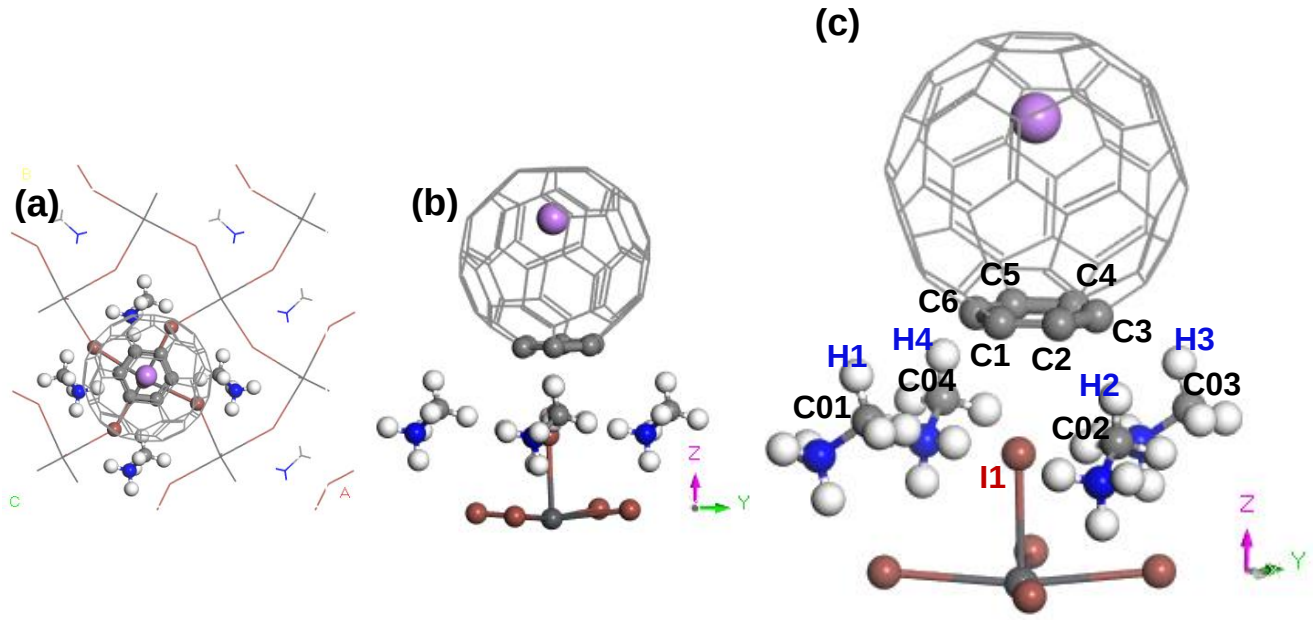
C···H distance [Å] [vdWs radius < 2.97Å]		C···C distance [Å] [vdWs radius < 3.54Å]		C···I distance [Å] [vdWs radius < 3.81Å]	
C1···H1	3.534	C1···C01	3.544	C5···I1	3.972
C2··· H1	3.806	C2···C01	3.549	C6···I1	3.918
C3··· H1	3.714	C3···C01	3.583	C1···I1	5.044
C4··· H1	3.335	C4···C01	3.610	C6···I2	4.877
C5··· H1	3.009	C5···C01	3.604	C1···I2	3.918
C6··· H1	3.117	C6···C01	3.570	C2···I2	4.324
C1···H2	2.665			C2···I3	4.259
C2··· H2	2.619			C3···I3	4.009
C3··· H2	2.983			C4···I3	5.067
C4··· H2	3.333			C3···I4	4.537
C5··· H2	3.370			C4···I4	3.787
C6··· H2	3.062			C5···I4	4.543

Figure S7. (a) Top view of topC-oriented $MAPbI_3$ with a lithium endohedral fullerene $Li^+@C_{60}$ on the aboveC position. The Li^+ located at the off-central top inside the C_{60} cage. (b) Side and (c) perspective views are the selected area (ball and sticks in $MAPbI_3$) from top view (a). H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively. Atoms located at the interface between $MAPbI_3$ and C_{60} are labelled, and their atomic distance are summarized in table. Atomic distances that falls within the vdWs atomic radius are represented in red color.



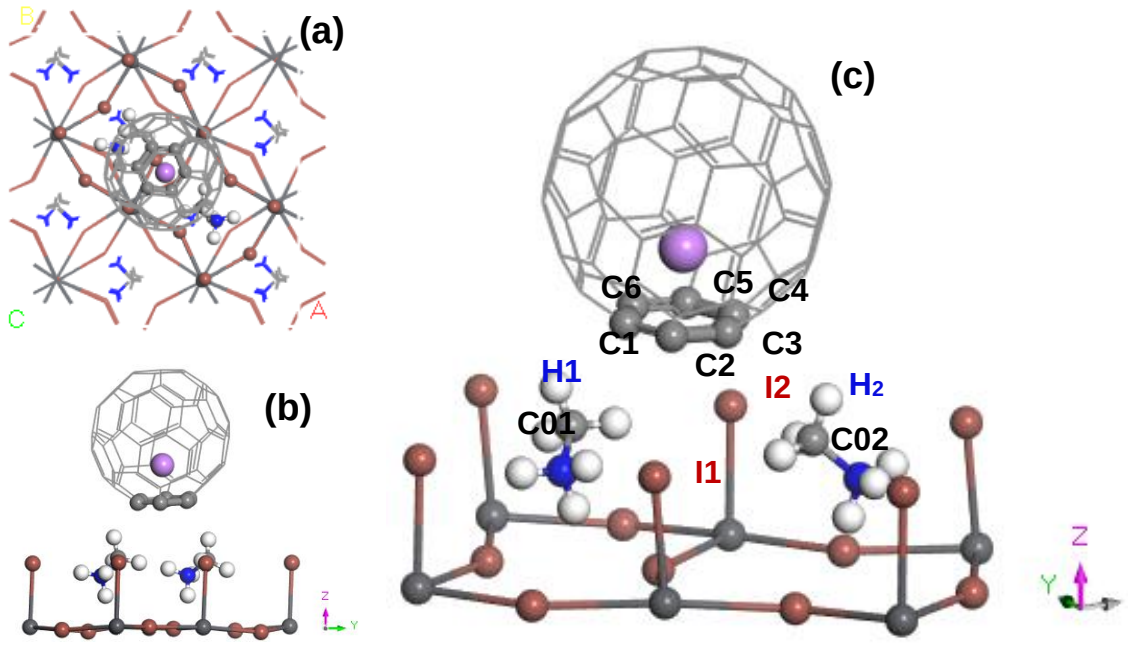
C···H distance [Å] [vdWs radius < 2.97Å]		C···C distance [Å] [vdWs radius < 3.54Å]		C···I distance [Å] [vdWs radius < 3.81Å]	
C6 ···H1	3.677	C6···C01	4.058	C1···I1	3.428
C1··· H1	3.619	C1···C01	3.887	C2···I1	3.580
C2··· H1	4. 917	C2···C01	5.032	C3···I1	3.742
C1··· H2	4.083	C1···C02	4.431	C4···I1	3.751
C2··· H2	3. 169	C2···C02	3.606	C5···I1	3.604
C3··· H2	3.958	C3···C02	4.247	C6···I1	3.442
C2···H3	4.631	C2···C03	5.037		
C3··· H3	3.286	C3···C03	3.856		
C4··· H3	3.014	C4···C03	3.752		
C5··· H4	3.200	C5···C04	4.011		
C6··· H4	3.800	C6···C04	4.572		
C1··· H4	5.143	C1···C04	5.803		

Figure S8. (a) Top view of topC-oriented $MAPbI_3$ with a lithium endohedral fullerene $Li^+@C_{60}$ on the aboveI position. The Li^+ located at the off-central bottom inside the C_{60} cage. (b) Side and (c) perspective views are the selected area (ball and sticks in $MAPbI_3$) from top view (a). H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively. Atoms located at the interface between $MAPbI_3$ and C_{60} are labelled, and their atomic distance are summarized in table. Atomic distances that falls within the vdWs atomic radius are represented in red color.



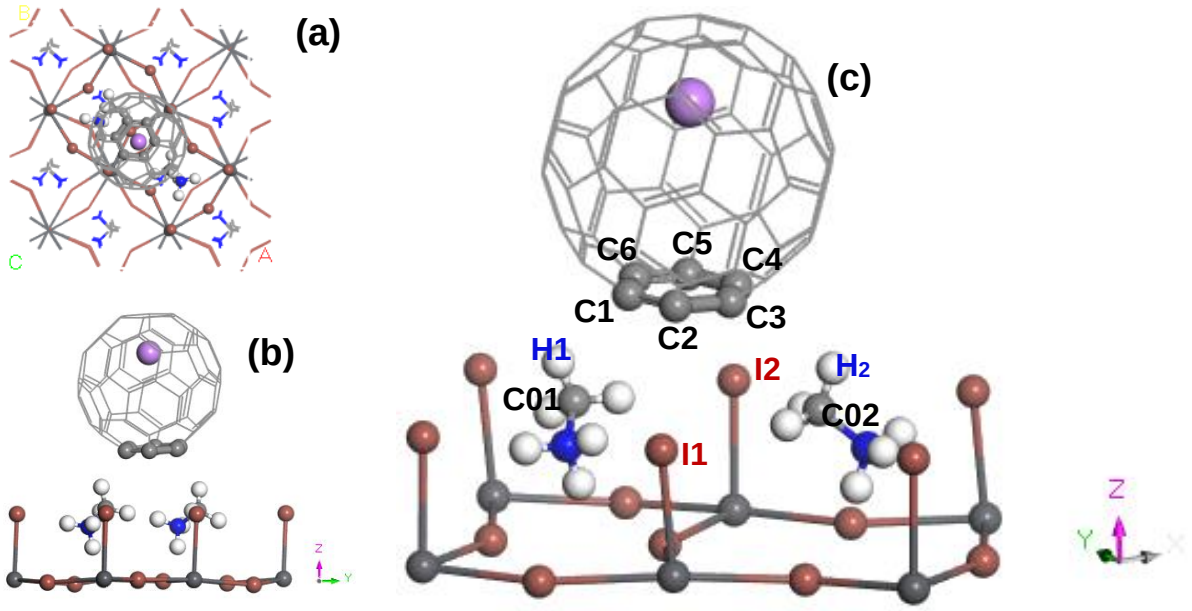
C···H distance [Å] [vdWs radius < 2.97Å]		C···C distance [Å] [vdWs radius < 3.54Å]		C···I distance [Å] [vdWs radius < 3.81Å]	
C6 ···H1	3/686	C6···C01	4.084	C1···I1	3.411
C1··· H1	3.624	C1···C01	3.908	C2···I1	3.566
C2··· H1	4.911	C2···C01	5.045	C3···I1	3.742
C1··· H2	4.080	C1···C02	4.429	C4···I1	3.762
C2··· H2	3.173	C2···C02	3.617	C5···I1	3.613
C3··· H2	3.956	C3···C02	4.266	C6···I1	3.438
C2···H3	4.625	C2···C03	5.002		
C3··· H3	3.255	C3···C03	3.831		
C4··· H3	2.998	C4···C03	3.736		
C5··· H4	3.193	C5···C04	3.999		
C6··· H4	3.782	C6···C04	4.548		
C1··· H4	5.120	C1···C04	5.733		

Figure S9. (a) Top view of topC-oriented $MAPbI_3$ with a lithium endohedral fullerene $Li^+@C_{60}$ on the aboveI position. The Li^+ located at the off-central bottom inside the C_{60} cage. (b) Side and (c) perspective views are the selected area (ball and sticks in $MAPbI_3$) from top view (a). H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively. Atoms located at the interface between $MAPbI_3$ and C_{60} are labelled, and their atomic distance are summarized in table. Atomic distances that falls within the vdWs atomic radius are represented in red color.



C···H distance [Å] [vdWs radius < 2.97Å]		C···C distance [Å] [vdWs radius < 3.54Å]		C···I distance [Å] [vdWs radius < 3.81Å]	
C1···H1	3.055	C1···C01	3.732	C1···I1	4.074
C2··· H1	4.162	C2···C01	4. 602	C2···I1	3.519
C3··· H1	4.902	C3···C01	5.519	C3···I1	4.125
C4··· H1	4.747	C4···C01	4.959	C4···I1	5.064
C5··· H1	3.780	C5···C01	4.135	C5···I1	5.476
C6··· H1	2.791	C6···C01	3.443	C6···I1	5.062
C1···H2	5.243	C1···C02	5.399	C1···I2	5.496
C2··· H2	4.203	C2···C02	4.473	C2···I2	5.674
C3··· H2	2.974	C3···C02	3.451	C3···I2	4.978
C4··· H2	3.177	C4···C02	3.629	C4···I2	3.969
C5··· H2	4.499	C5···C02	4.765	C5···I2	3.703
C6··· H2	5.365	C6···C02	5.521	C6···I2	4.564

Figure S10. (a) Top view of topC-oriented $MAPbI_3$ with a lithium endohedral fullerene $Li^+@C_{60}$ on the bridge position. The Li^+ located at the off-central bottom inside the C_{60} cage. (b) Side and (c) perspective views are the selected area (ball and sticks in $MAPbI_3$) from top view (a). H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively. Atoms located at the interface between $MAPbI_3$ and C_{60} are labelled, and their atomic distance are summarized in table. Atomic distances that falls within the vdWs atomic radius are represented in red color.



C···H distance [Å] [vdWs radius < 2.97Å]		C···C distance [Å] [vdWs radius < 3.54Å]		C···I distance [Å] [vdWs radius < 3.81Å]	
C1···H1	3.065	C1···C01	3.744	C1···I1	4.122
C2··· H1	4.161	C2···C01	4.605	C2···I1	3.568
C3··· H1	4.895	C3···C01	5.156	C3···I1	4.159
C4··· H1	4.740	C4···C01	4.958	C4···I1	5.092
C5··· H1	3.778	C5···C01	4.140	C5···I1	5.508
C6··· H1	2.801	C6···C01	3.457	C6···I1	5.092
C1···H2	5.247	C1···C02	5.406	C1···I2	5.518
C2··· H2	4.215	C2···C02	4.485	C2···I2	5.692
C3··· H2	2.990	C3···C02	3.465	C3···I2	5.006
C4··· H2	3.191	C4···C02	3.643	C4···I2	4.001
C5··· H2	4.507	C5···C02	4.766	C5···I2	3.741
C6··· H2	5.369	C6···C02	5.526	C6···I2	4.593

Figure S11. (a) Top view of topC-oriented $MAPbI_3$ with a lithium endohedral fullerene $Li^+@C_{60}$ on the bridge position. The Li^+ located at the off-central top inside the C_{60} cage. (b) Side and (c) perspective views are the selected area (ball and sticks in $MAPbI_3$) from top view (a). H, C, N, I, Pb and Li atoms are represented by the white, light grey, blue, brown, dark grey and purple spheres, respectively. Atoms located at the interface between $MAPbI_3$ and C_{60} are labelled, and their atomic distance are summarized in table. Atomic distances that falls within the vdWs atomic radius are represented in red color.

Table S1. Highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), band gap and the total energies of the $MAPbI_3/Li^+@C_{60}$ heterojunctions relative to the aboveC position with a Li+ (Li) at the off-central bottom inside the C_{60} cage. The calculated values in bracket are for a $MAPbI_3$ with a neutral lithium endohedral fullerene $Li@C_{60}$ on the topC position.

Position of Li^+ (Li) in C_{60} cage	**Surface geometry**	**HOMO [eV]**	**LUMO [eV]**	**band gap [eV]**	**total relative energy [eV]**
off-central top	aboveC	-6.309 (-5.190)	-5.706 (-5.065)	0.603 (0.125)	0.031 (0.008)
	aboveI	-6.282	-5.719	0.563	0.267
	bridge	-6.260	-5.672	0.589	0.173
off-central bottom	aboveC	-6.369 (-5.127)	-5.743 (-5.002)	0.626 (0.125)	0 (0)
	aboveI	-6.338	-5.763	0.575	0.250
	bridge	-6.322	-5.708	0.614	0.163

Table S2. Hirshfeld atomic charges of fragments [CH_3], [1], [Li], [Li^+] and [C] at the $MAPbI_3$ /$Li^+@C_{60}$ interface with the $Li^+@C_{60}$ on the aboveC, aboveI and bridge positions. The Li^+ located at the off-central top inside the C_{60} cage. Values in bracket denote the atomic distance for the Li^+ located at the off-central bottom inside the C_{60} cage. Fragments are labelled in according to Fig. S4-S11.

fragments	**$MAPbI_3$ /$Li@C_{60}$**	**$MAPbI_3$ /$Li^+@C_{60}$**		
	aboveC [e] (neutral Li)	**aboveC [e]**	**aboveI [e]**	**bridge [e]**
[C01H$_3$]	-0.006 (-0.007)	-0.004 (-0.007)	0.057 (0.058)	0.058 (0.057)
[C02H$_3$]			0.048 (0.046)	0.062 (0.060)
[C03H$_3$]			0.067 (0.066)	
[C04H$_3$]			0.071 (0.069)	
[I1]	-0.212 (-0.211)	-0.205 (-0.211)	-0.169 (-0.177)	-0.213 (-0.218)
[I2]	-0.222 (-0.221)	-0.215 (-0.220)		-0.213 (-0.219)
[I3]	-0.222 (-0.221)	-0.216 (-0.220)		
[I4]	-0.216 (-0.212)	-0.209 (-0.210)		
[Li^+]/[Li]	0.361 (0.359)	0.360 (0.362)	0.360 (0.363)	0.358 (0.362)
[C1]	0.000 (-0.010)	-0.001 (-0.009)	-0.003 (-0.010)	-0.007 (-0.015)
[C2]	-0.003 (-0.012)	-0.003 (-0.011)	-0.002 (-0.010)	-0.005 (-0.013)
[C3]	-0.06 (-0.014)	-0.007 (-0.016)	-0.005 (-0.014)	0.000 (-0.007)
[C4]	-0.07 (-0.016)	-0.009 (-0.018)	-0.010 (-0.020)	-0.001 (-0.009)
[C5]	-0.012 (-0.027)	-0.007 (-0.015)	-0.010 (-0.019)	-0.004 (-0.012)
[C6]	-0.007 (-0.023)	-0.002 (-0.009)	-0.008 (-0.008)	-0.001 (-0.009)