Electronic Supplementary Information

Synthesis of Li-Encapsulated PCBM: n-Dopant for Fullerene Derivatives

Hiroshi Ueno,[a,b]* Daiki Kitabatake,[a] Hao-Sheng Lin,[c] Yue Ma,[d] Il Jeon,[e] Seiichiro Izawa,[f,g] Masahiro Hiramoto,[f,g] Fuminori Misaizu,[b] Shigeo Maruyama,[h] Yutaka Matsuo[b,c,h]*

[a] Creative Interdisciplinary Research Division, Frontier Research Institute for Interdisciplinary Sciences (FRIS), Tohoku University, 6-3 Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan;

[b] Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan;

[c] Department of Chemical Systems Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan;

[d] Hefei National Laboratory for Physical Science at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China;

[e] Department of Nano Engineering, SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University (SKKU), Seobu-ro 2066, Jangan-gu, Suwon-si, Gyeonggi-do 16419, Republic of Korea;

[f] Division of Molecular Nanoscience, Research Center for Molecular Scale Nanoscience, Institute for Molecular Science, Okazaki, Aichi 444-8787, Janan;

[g] SOKENDAI (The Graduate University for Advanced Studies), Okazaki, Aichi 444-8787, Japan;

[h] Department of Mechanical Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan;

E-mail: hiroshi.ueno.d5@tohoku.ac.jp (HU), yutaka.matsuo@chem.material.nagoya-u.ac.jp (YM)

General Procedure

Unless otherwise noted, all chemicals, including anhydrous solvents, were obtained from commercial suppliers and used as received without further purification. ITO substrates (15 × 15 mm with sheet resistance of 6 Ω $sq.^{-1}$) were purchased from Techno Print Co., Ltd. The substrates were sequentially cleaned with detergent, distilled water, acetone, and 2-propanol in an ultrasonic bath for 15 min each, and were subjected to ultraviolet/ozone treatment for 15 min just before use. $Li^+@C_{60}$ $TFSI^-$ and Li^+@PCBM $TFSI^-$ were prepared according to reported procedures.[S1] ESR spectra were recorded on a JEOL JES-X330 system. The Fermi level was measured using a Kelvin probe (FAC-1, Riken-Keiki). DLS measurements were performed with a Malvern Zetasizer Nano ZS.

Ref S1: Y. Ma, H. Ueno, H. Okada, S. Manzhos and Y. Matsuo, *Org. Lett.* 2020, **22**, 7239–7243.

Synthesis of neutral Li@PCBM

A DCM/MeCN (1/1, v/v) solution (2.0 mL) containing Fc* (1.0 mg, 3.0 μmol) was slowly added to a DCM/MeCN (1/1, v/v) solution (2.0 mL) containing Li^+@PCBM $TFSI^-$ (3.6 mg, 3.0 μmol). Stirring for 10 min afforded a greenish-black dispersion. The obtained solid was collected by filtration and washed with DCM/MeCN (1/1, v/v) 3 times using an ultrasonicator. After filtration, drying of the residue under vacuum at ambient temperature resulted in the isolation of Li@PCBM as a black powder (2.4 mg, 2.7 μmol, 90%).

Fermi level measurement

A PCBM solution (30 mg mL^{-1}) and the same PCBM solution mixed with 0.5−5.0% of neutral Li@PCBM were spin-coated onto ITO substrates at 3000 rpm for 30 s. The Fermi levels of the films were measured using a Kelvin probe without exposure to air. The Kelvin probe was installed in a glovebox under a N_2 atmosphere (H_2O <1 ppm, O_2 <1 ppm).

Device fabrication and characterization

PEDOT:PSS (30 μL) was spin-coated onto ITO substrates at 3000 rpm for 30 s, followed by annealing at 105 °C for 5 min. The perovskite precursor was prepared by mixing CH_3NH_3I, PbI_2, and anhydrous dimethyl sulfoxide (molar ratio 1:1:1) in anhydrous *N*,*N*-dimethylformamide at a concentration of 50 wt %. The solution was filtered through a 0.45 μm poly(tetrafluoroethylene) filter before use. The perovskite precursor solution (25 μL) was spin-coated onto the PEDOT:PSS layer at 4000 rpm for 30 s, and 0.5 mL of anhydrous diethyl ether was slowly dropped onto the substrate 5 s after the start of the spin-coating process. This was followed by annealing at 65 °C for 1 min and then 100 °C for 5 min to obtain a dense brown $MAPbI_3$ film. For deposition of the electron transport layer, a PCBM solution (10 mg mL^{-1}) and the same PCBM solution mixed with 1.0%, 2.0%, 3.0%, or 4.0% of Li@PCBM were spin-coated at 1000 rpm

for 30 s. Finally, a 5-nm-thick bathocuproine (BCP) layer and 70-nm-thick Ag electrode were fabricated by thermal deposition at a constant evaporation rate of 0.05 nm s^{-1} under a pressure of 10^{-6} Torr. The *J*–*V* characteristics were measured using a software-controlled source meter (2400 SourceMeter, Keithley) in the dark and under simulated sunlight irradiation of 1 sun (AM 1.5G; 100 mW cm^{-2}) using a solar simulator (EMS-35AAA, Ushio Spax Inc.) with an Ushio Xe short arc lamp 500. The source meter was calibrated using a silicon diode (BS-520BK, Bunkokeiki)

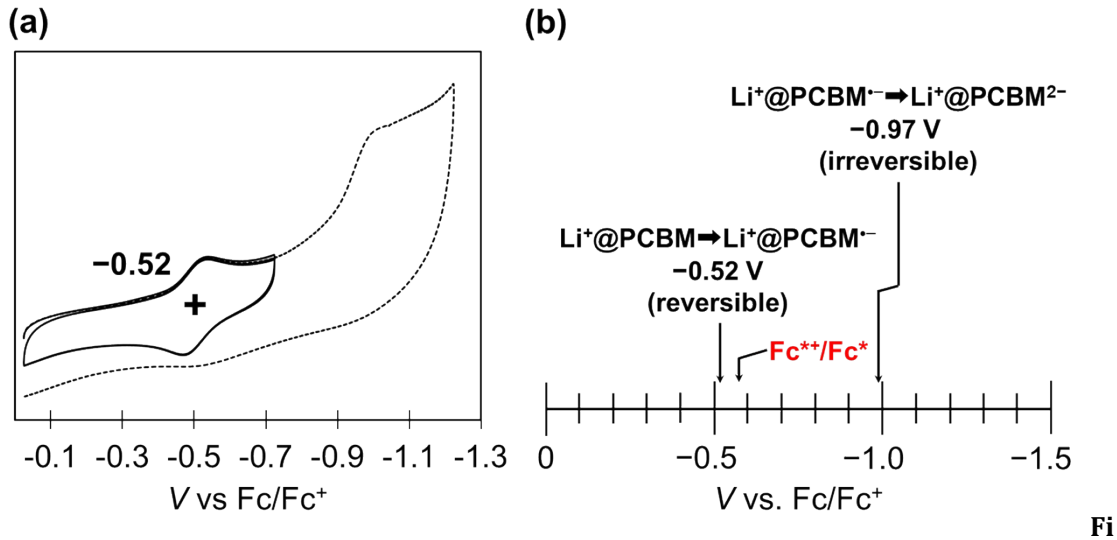

Fig. S1. (a) Cyclic voltammogram of Li^+@PCBM $TFSI^-$ in CH_2Cl_2/MeCN (1/1, v/v) containing 0.1 M tetrabutylammonium $TFSI^-$. (b) List of first and second reduction potentials of Li^+@PCBM $TFSI^-$ along with the oxidation potential of Fc*.

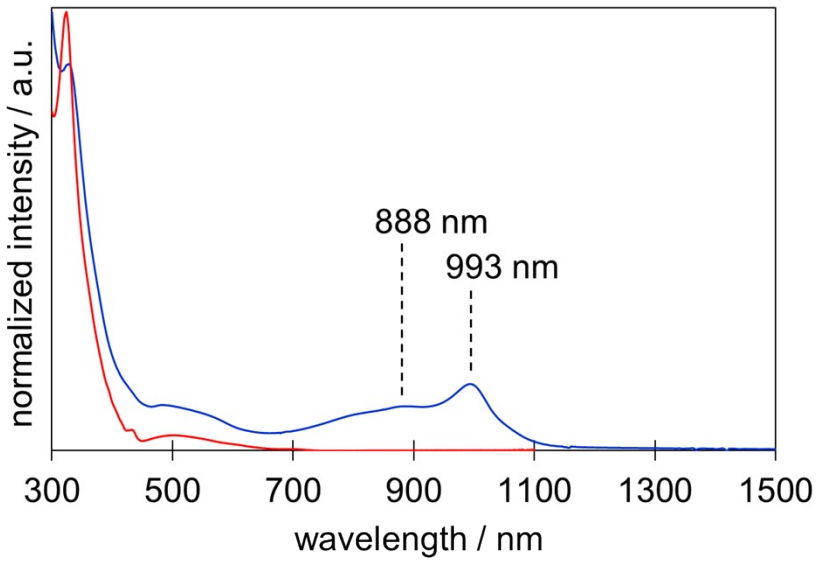

Fig. S2. UV-vis-NIR absorption spectrum of Li@PCBM measured in dichloromethane at room temperature (blue line). The spectrum of Li^+@PCBM $TFSI^-$ is also shown as a reference (red line).

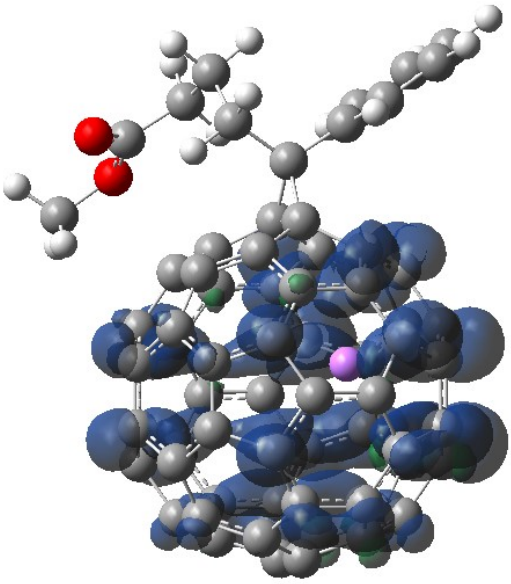

Fig. S3. Calculated spin density distribution of Li@PCBM in the optimized structure at (U)M062X/6-31G(d) level. Blue and green surfaces represent a and b spin density, respectively.

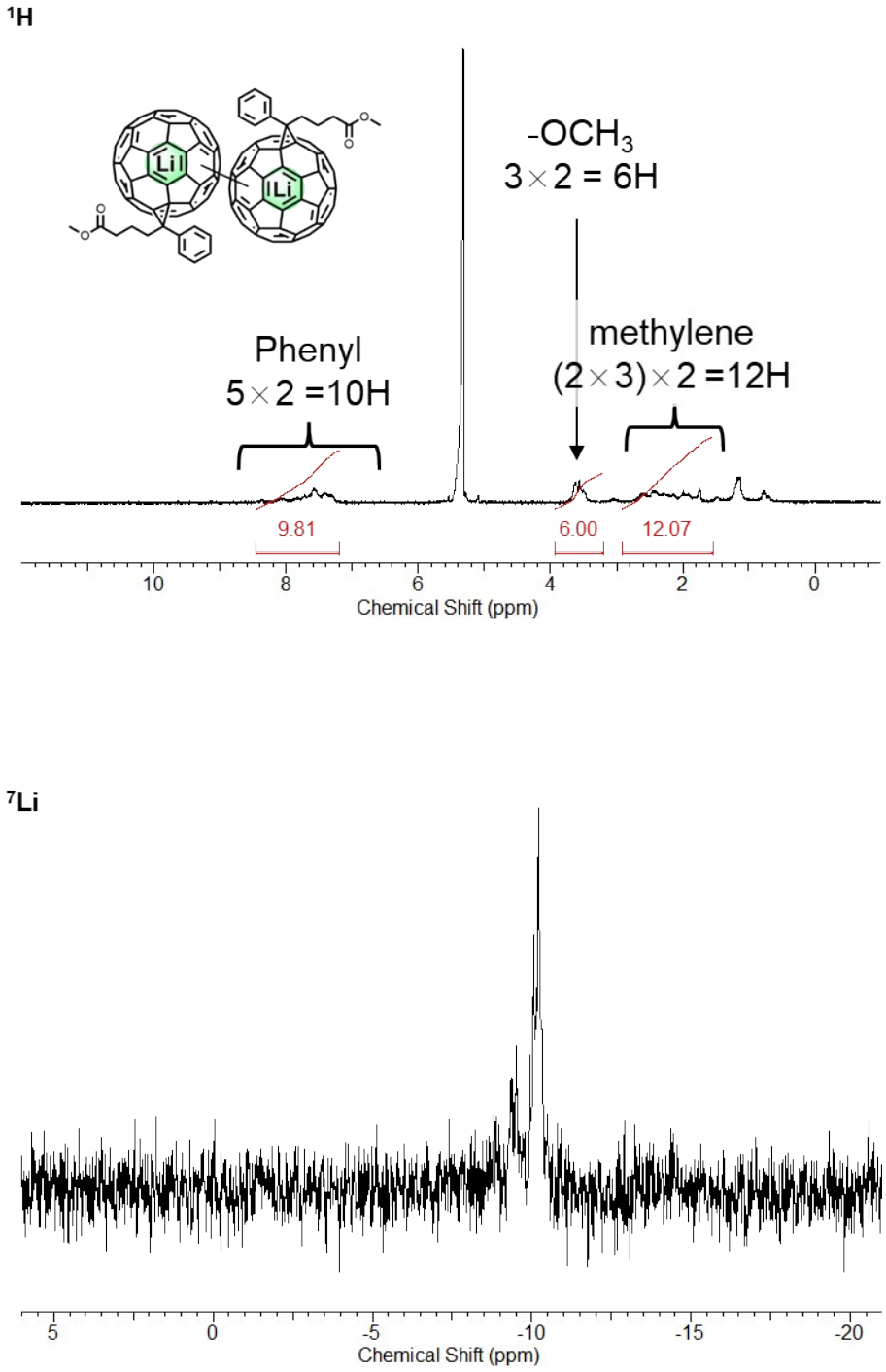

Fig. S4. ^{1}H and ^{7}Li NMR spectrum of Li@PCBM in CD_2Cl_2 at 193 K. $LiCl/D_2O$ at ambient temperature was used as an external standard for ^{7}Li NMR measurement.

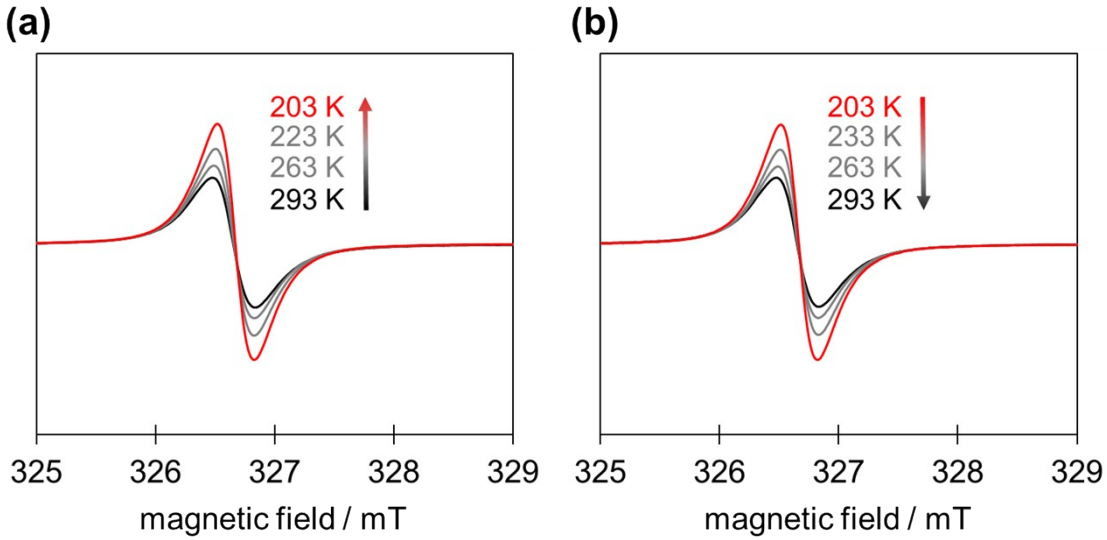

Fig. S5. VT-ESR spectra of Li@PCBM solid. (a) On cooling process and (b) heating process.

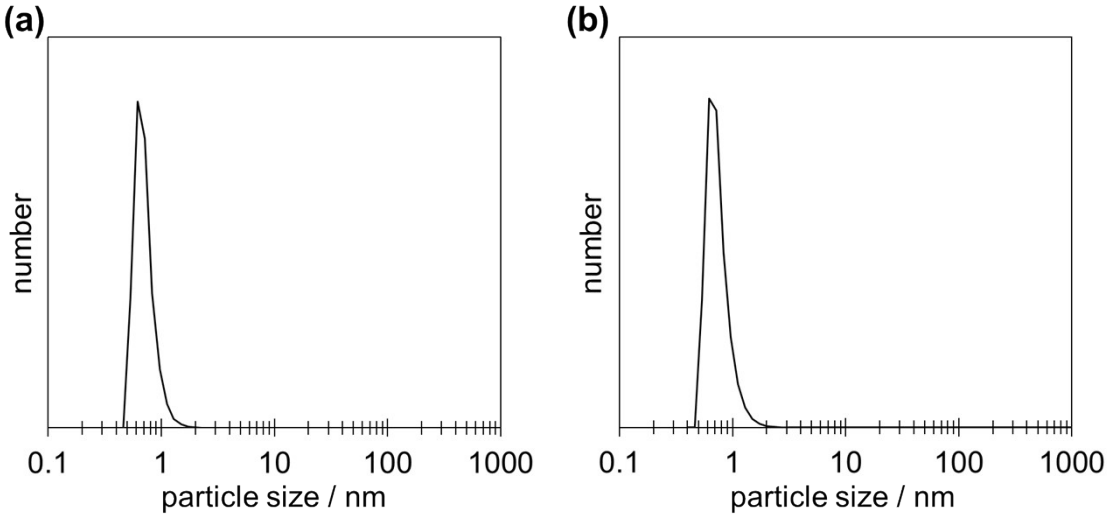

Fig. S6. Particle size distribution of (a) Li@PCBM (0.1 mg/mL) and (b) 0.1 mg/mL of empty PCBM with 1wt% Li@PCBM in chlorobenzene.

Table S1. Dopant-ratio dependence of the Fermi levels of Li@PCBM:PCBM binary film measured by Kelvin probe.

Li@PCBM conc./wt% (mg/mL^{-1}))	Fermi level (eV)
0 (0)	−4.65 ± 0.1
0.5 (0.15)	−4.52 ± 0.1
1 (0.3)	−4.52 ± 0.1
2 (0.6)	−4.52 ± 0.1
3 (0.9)	−4.52 ± 0.1
4 (1.2)	−4.52 ± 0.1
5 (1.5)	−4.52 ± 0.1

Computational Results

Full geometry optimizations followed by frequency calculations have been carried out by using Gaussian 16 program at the M06-2X/6-31G(d) level. All frequency calculations showed no imaginary frequency. Full citation is as follows:

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16, Revision C.01*, Gaussian, Inc., Wallingford CT, 2016.

Geometrical coordinates

Li^{+}@$PCBM^{\bullet -}$ by (U)M06-2x/6-31G(d)

E= −2908.921927 au

O	2.172159	7.214977	5.132162	C	8.307187	3.796185	4.983177
O	0.863123	5.595762	5.974024	C	7.999014	4.447108	6.224595
C	3.629933	3.348821	4.039488	C	6.733351	5.001181	6.418018
C	5.051537	3.580375	3.352668	C	6.062696	4.838576	7.688276
C	6.047473	4.343647	4.160500	C	4.651952	4.662113	7.432135
C	5.743658	4.946354	5.362553	C	3.905683	3.782475	8.217421
C	4.429995	4.730270	6.001560	C	2.932306	2.926617	7.599168
C	3.480961	3.924297	5.410127	C	2.973282	1.635816	8.278909
C	2.747041	2.980940	6.219219	C	2.808550	0.463695	7.554202
C	2.571316	1.762351	5.459756	C	2.596523	0.517837	6.119187
C	3.202399	1.926570	4.188026	C	3.301331	-0.579129	5.527836
C	3.893858	0.864816	3.605945	C	3.943640	-0.423919	4.287038
C	5.197559	1.076954	2.970294	C	5.245416	-1.021264	4.063025
C	5.776653	2.345485	2.933074	C	6.023727	-0.085957	3.273786
C	7.166936	2.506577	3.222833	C	7.394405	0.084142	3.534349
C	7.339316	3.725721	3.983587	C	7.979206	1.390311	3.498481

C	8.976476	1.462933	4.551244	C	8.124800	-0.135530	8.669739
C	9.138917	2.634185	5.277181	C	3.776367	4.105897	2.744967
C	9.353241	2.584075	6.706041	C	3.319214	3.435339	1.477026
C	8.638110	3.697057	7.294682	C	4.143370	3.484943	0.350070
C	7.988664	3.544007	8.513360	C	3.722252	2.938725	-0.857554
C	6.679775	4.126530	8.719658	C	2.469577	2.335746	-0.950238
C	5.906849	3.206542	9.526203	C	1.642905	2.282090	0.168191
C	4.549132	3.034060	9.285215	C	2.066221	2.829712	1.376922
C	3.962915	1.711063	9.330010	C	3.573090	5.619794	2.757493
C	4.763345	0.599513	9.612619	C	2.121150	6.055116	2.538217
C	4.595372	-0.620632	8.862108	C	1.162129	5.602043	3.636311
C	3.634419	-0.693842	7.849135	C	1.474658	6.243001	4.970798
C	3.944361	-1.339945	6.597126	C	1.141975	6.104219	7.278382
C	5.207355	-1.894941	6.384373	Li	5.529293	0.791672	5.262620
C	5.873602	-1.746533	5.111610	H	5.124326	3.948544	0.428593
C	7.281624	-1.558989	5.374373	H	4.373595	2.979306	-1.724882
C	8.038938	-0.676587	4.602963	H	2.140947	1.905567	-1.890999
C	9.019570	0.178351	5.227023	H	0.667465	1.810418	0.103526
C	9.221446	0.128530	6.609446	H	1.422500	2.775884	2.251385
C	9.389185	1.348964	7.360371	H	4.195235	6.034705	1.955317
C	8.711708	1.192485	8.632453	H	3.939535	6.046441	3.695681
C	8.028837	2.262027	9.196969	H	2.101699	7.148165	2.491984
C	6.739003	2.053063	9.824924	H	1.762706	5.679794	1.573980
C	6.179356	0.782487	9.865055	H	0.131517	5.876606	3.380004
C	6.890848	-0.335514	9.270616	H	1.158971	4.515230	3.774015
C	5.907182	-1.200692	8.643136	H	0.748921	7.117958	7.384326
C	6.206913	-1.828194	7.440772	H	2.220876	6.121038	7.452085
C	7.496069	-1.619369	6.813082	H	0.651904	5.424028	7.973282
C	8.436774	-0.791122	7.411609				

Li^+@PCBM cation by M06-2x/6-31G(d)

E= −2908.727905 au

O	2.306984	7.083232	5.187626	C	6.084479	4.309278	4.146374
O	0.823068	5.568142	5.925861	C	5.785746	4.908040	5.359150
C	3.609405	3.348611	4.036303	C	4.470309	4.708260	6.003793
C	5.079928	3.566558	3.322708	C	3.494667	3.920577	5.416508

C	2.758727	2.986572	6.241138	C	3.909006	-1.342614	6.609701
C	2.571468	1.760089	5.489202	C	5.158658	-1.907664	6.403332
C	3.188709	1.920265	4.191094	C	5.827677	-1.744209	5.123966
C	3.880208	0.856496	3.636315	C	7.250500	-1.596933	5.376997
C	5.195698	1.052613	2.988912	C	8.006941	-0.733106	4.599168
C	5.779252	2.306877	2.919830	C	9.005456	0.117176	5.222907
C	7.185946	2.446358	3.226255	C	9.197812	0.067362	6.596524
C	7.373299	3.673011	3.978359	C	9.385150	1.294795	7.350508
C	8.339695	3.731350	4.976365	C	8.711652	1.143878	8.626581
C	8.039983	4.395863	6.221051	C	8.050410	2.223902	9.194157
C	6.782609	4.959580	6.410622	C	6.757624	2.031644	9.828222
C	6.111559	4.807130	7.687663	C	6.184444	0.768218	9.865934
C	4.692694	4.646237	7.435561	C	6.875494	-0.360266	9.269014
C	3.943214	3.784661	8.230021	C	5.881645	-1.216428	8.647219
C	2.954020	2.931214	7.616779	C	6.165321	-1.848858	7.444790
C	2.970769	1.649803	8.301889	C	7.457997	-1.656534	6.810621
C	2.791652	0.477679	7.583281	C	8.408691	-0.840686	7.407667
C	2.590104	0.534035	6.145896	C	8.109517	-0.176572	8.663472
C	3.274922	-0.584676	5.546275	C	3.795325	4.099345	2.745271
C	3.917936	-0.419658	4.323310	C	3.326698	3.430949	1.478051
C	5.222044	-1.017973	4.109122	C	4.146145	3.487808	0.348074
C	6.008216	-0.108643	3.296644	C	3.715144	2.950609	-0.859975
C	7.372497	0.024796	3.535799	C	2.459462	2.352573	-0.947598
C	7.974160	1.335086	3.505005	C	1.637835	2.295355	0.174403
C	8.986520	1.399250	4.544800	C	2.069863	2.833231	1.384616
C	9.164729	2.570791	5.264361	C	3.621511	5.618705	2.760122
C	9.371990	2.520382	6.699124	C	2.181121	6.084014	2.527707
C	8.676290	3.649060	7.291196	C	1.191857	5.634801	3.599829
C	8.029059	3.501254	8.508947	C	1.519701	6.195223	4.965974
C	6.719411	4.096510	8.712187	C	1.046955	6.053125	7.251540
C	5.937007	3.189786	9.534348	Li	5.265497	2.330792	5.216745
C	4.578001	3.038796	9.300851	H	5.125787	3.956453	0.417064
C	3.976881	1.717999	9.344724	H	4.358548	2.998749	-1.732313
C	4.764127	0.607615	9.616882	H	2.122421	1.932717	-1.889577
C	4.576842	-0.619953	8.863307	H	0.658332	1.832990	0.110371
C	3.610256	-0.685014	7.869406	H	1.423630	2.783080	2.257606

H	4.258450	6.014565	1.960680	H	1.125677	4.544021	3.686693
H	3.986973	6.042129	3.699943	H	0.737973	7.097141	7.331452
H	2.190454	7.177437	2.498935	H	2.107794	5.979844	7.506980
H	1.831055	5.735617	1.550929	H	0.446510	5.422129	7.904503
H	0.179581	5.971213	3.346378				

Empty PCBM by M06-2x/6-31G(d)

E= −2901.380081 au

O	2.198910	7.197585	5.139641	C	5.234743	-1.016062	4.104773
O	0.871074	5.580565	5.955445	C	6.017333	-0.103684	3.292349
C	3.640896	3.326347	4.040661	C	7.380787	0.034896	3.533559
C	5.063622	3.545234	3.353443	C	7.973870	1.347528	3.505287
C	6.064403	4.300129	4.160845	C	8.981323	1.418021	4.548829
C	5.765856	4.913291	5.359174	C	9.152394	2.590007	5.269052
C	4.451677	4.708556	5.998944	C	9.355715	2.538488	6.703919
C	3.499185	3.903985	5.410220	C	8.654149	3.664347	7.294367
C	2.761111	2.972179	6.226390	C	8.007232	3.514254	8.512395
C	2.582143	1.746812	5.474314	C	6.695159	4.103378	8.713157
C	3.209053	1.906417	4.187520	C	5.914455	3.192651	9.531467
C	3.886618	0.846289	3.625287	C	4.557085	3.034834	9.291086
C	5.199778	1.048638	2.983186	C	3.962820	1.710837	9.331871
C	5.772662	2.301488	2.936973	C	4.753160	0.603547	9.609629
C	7.173668	2.451690	3.236549	C	4.573830	-0.624145	8.855573
C	7.353175	3.677494	3.988647	C	3.612113	-0.690801	7.856490
C	8.324218	3.747496	4.980174	C	3.916292	-1.347546	6.597564
C	8.020330	4.410308	6.223226	C	5.168405	-1.909388	6.395561
C	6.758899	4.966378	6.409271	C	5.840253	-1.743870	5.118517
C	6.086239	4.807354	7.684473	C	7.260978	-1.588630	5.375422
C	4.668676	4.643333	7.428555	C	8.013327	-0.718341	4.600300
C	3.920269	3.779089	8.221381	C	9.005132	0.136913	5.227900
C	2.938885	2.921829	7.603753	C	9.197697	0.085611	6.601865
C	2.959857	1.639818	8.286687	C	9.376999	1.313124	7.356335
C	2.788769	0.467312	7.566963	C	8.701010	1.158989	8.630246
C	2.590153	0.520783	6.129492	C	8.032285	2.236207	9.195386
C	3.279441	-0.594837	5.533043	C	6.738647	2.037639	9.825866
C	3.926349	-0.425019	4.312640	C	6.171581	0.770963	9.862770

C	6.869598	-0.353783	9.267341	C	1.495971	6.232315	4.962756
C	5.881537	-1.214405	8.642931	C	1.144985	6.074353	7.265950
C	6.171147	-1.843776	7.439820	H	5.132089	3.940023	0.426908
C	7.464691	-1.645314	6.809311	H	4.367331	2.998342	-1.733677
C	8.410846	-0.826259	7.410140	H	2.128032	1.938371	-1.901848
C	8.104779	-0.163990	8.665019	H	0.663417	1.828869	0.098492
C	3.793895	4.086486	2.748434	H	1.433690	2.765997	2.253104
C	3.328890	3.426766	1.477624	H	4.240605	6.013360	1.967684
C	4.148336	3.482696	0.347615	H	3.972202	6.022167	3.705779
C	3.719394	2.951941	-0.864034	H	2.155883	7.150146	2.495805
C	2.463137	2.356567	-0.957918	H	1.808972	5.691547	1.564889
C	1.641501	2.295081	0.163697	H	0.163836	5.893647	3.357145
C	2.073187	2.827424	1.376351	H	1.174116	4.518433	3.748916
C	3.607749	5.602450	2.763646	H	0.763052	7.091688	7.378101
C	2.163129	6.056606	2.534634	H	2.222687	6.077416	7.448330
C	1.189166	5.606005	3.620403	H	0.641467	5.394109	7.951246