Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Tunable Single-Molecule Electronic Conductance of C_{60} by Encapsulation

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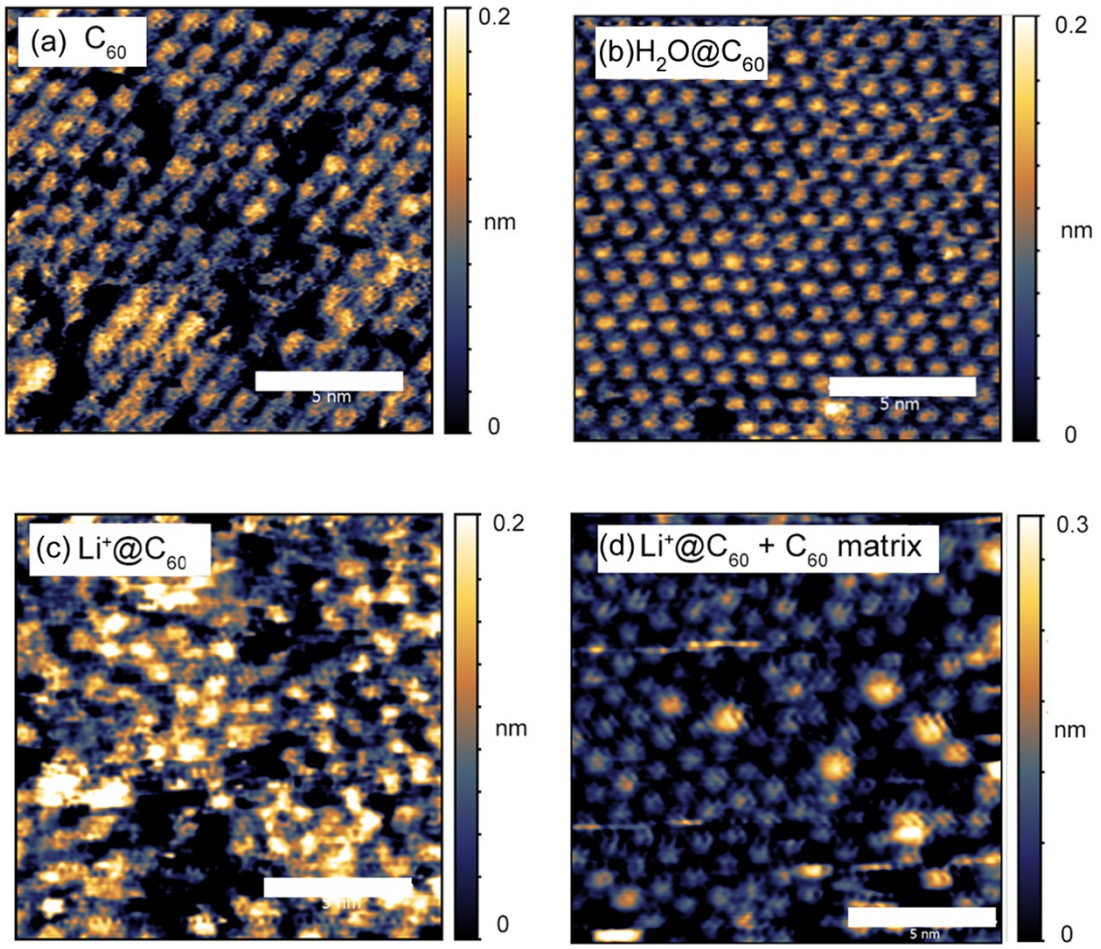


Figure S1. STM images of (a) C_{60}, (b) $H_2O@C_{60}$, (c) $Li^+@C_{60}$, and (d) $Li^+@C_{60}$ + C_{60} matrix on Au(111) under ultrahigh vacuum conditions at room temperature using Au-STM tips — imaging condition: (a) tunnelling current (I_t) = 0.3 nA and sample bias voltage (V_s) = −0.1 V, (b) I_t = 0.2 nA and V_s = +0.2 V, (c) I_t = 0.3 nA and V_s = +0.1 V, and (d) I_t = 0.6 nA and V_s = −0.1 V

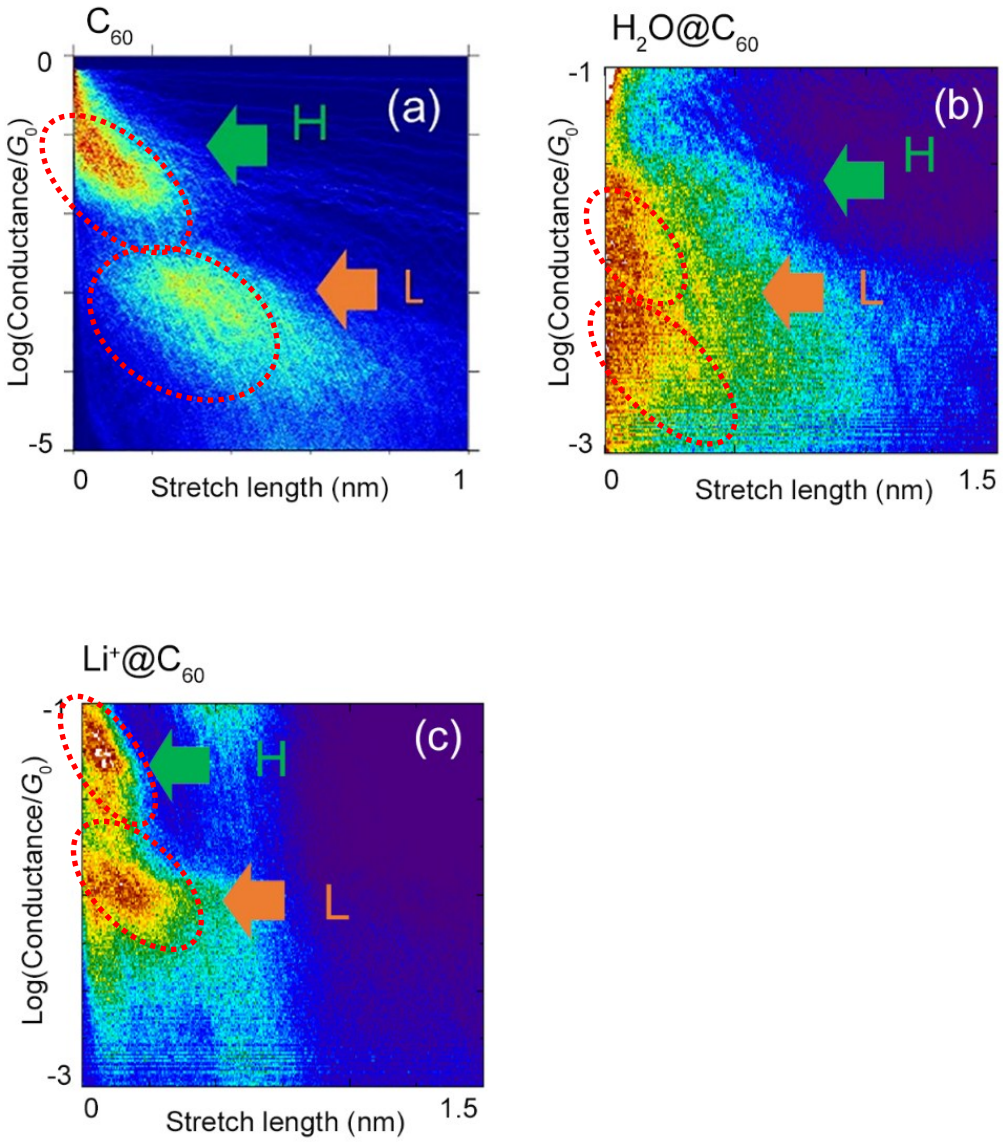


Fig. S2 Two-dimensional (2D) histograms of conductance vs. stretch length traces for SMJs of (a) C_{60}, (b) $H_2O@C_{60}$ and (c) $Li^+@C_{60}$. The histograms are made from the same data set used for the conductance histogram in Fig. 2. The histograms are constructed by identifying the first data point that has a conductance value lower than 0.5 G_0, assigning it as a relative zero length L = 0 for each trace, and then overlapping all of the individual traces in 2D space — the histogram of C_{60} in (a) was from a previous result[1] Dotted circles are guildes for the eye, indicating the H and L distribution.

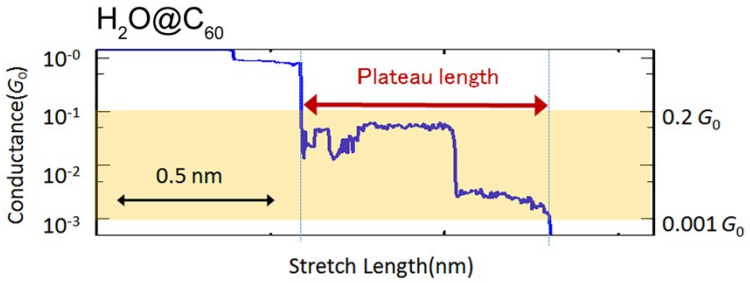


Fig. S3 An example of the conductance *versus* stretch length trace for $H_2O@C_{60}$. The length of the junction is defined by the length of the condcutance plateau within the conductance window from 0.001 G_0 to 0.2 G_0.

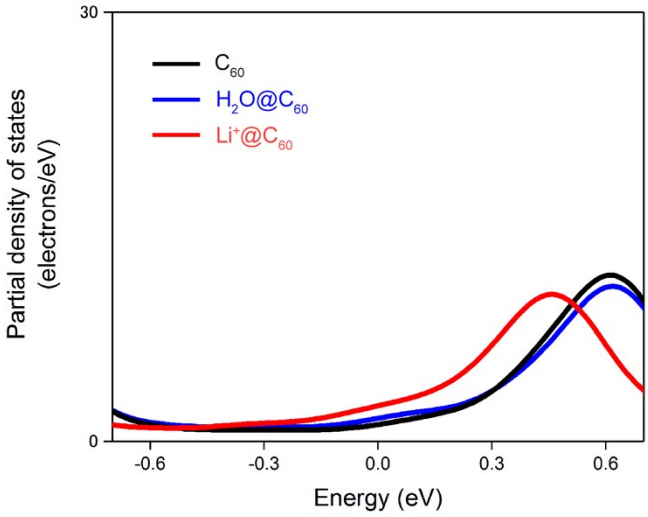
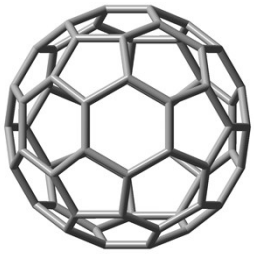


Fig. S4 The calculated density of states projected onto atomic orbitals of the C_{60} molecule for C_{60} (black), $H_2O@C_{60}$ (blue), and $Li^+@C_{60}$ (red) on Au(111). DFT calculations were performed using the CASTEP program [2] and the Perdew–Burke–Ernzerhof (PBE) XC functional [3] with van der Waals corrections [4]. The Au(111) is modelled by a slab of five layers of (4×4) Au-hexagonal lattice on which each molecule is deposited. The layers are separated by vacuum of > 1 nm along the z-direction. The bottom two layers of the slabs are kept fixed, while all upper layers including the adlayers are fully relaxed. The electronic wave functions were expanded in a plane-wave basis set with a cutoff kinetic energy of 40 Ry. Brillouin-zone integration was performed using a uniform 2×2×1 Monkhorst-type k-point grid [5].

Table S1. Optimized structure of C_{60} (B3LYP-D3/6-31G(d,p))

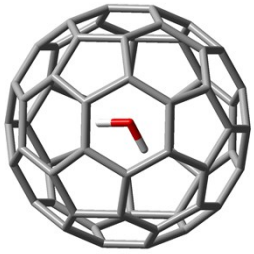


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.407680	-0.728179	-0.679370
2	6	0	2.790905	-0.954231	-1.976325
3	6	0	1.937872	-2.042302	-2.162857
4	6	0	1.665687	-2.949649	-1.060103
5	6	0	2.257844	-2.733147	0.184234
6	6	0	3.146518	-1.599405	0.378594
7	6	0	2.452230	0.340379	-2.544381
8	6	0	0.710425	-1.881642	-2.925261
9	6	0	0.270799	-3.350135	-1.141506
10	6	0	1.480034	-2.908081	1.400018
11	6	0	2.917504	-1.072669	1.713985
12	6	0	3.450101	0.706106	-0.446173
13	6	0	0.141035	-3.291933	1.321732
14	6	0	-0.475958	-3.518146	0.024928
15	6	0	-0.846390	-2.666099	2.185797
16	6	0	-1.844387	-3.031553	0.087692
17	6	0	1.274553	0.494540	-3.275986
18	6	0	-0.319859	-2.689986	-2.294028
19	6	0	-2.073715	-2.505391	1.423320
20	6	0	-1.633457	-2.223925	-2.234081
21	6	0	0.385814	-0.639352	-3.470610
22	6	0	1.887635	-1.881298	2.345064
23	6	0	2.958829	0.303656	1.937891
24	6	0	0.455066	1.681231	-3.093060
25	6	0	3.230481	1.211428	0.835463
26	6	0	2.860205	1.366533	-1.598956
27	6	0	1.971575	0.929258	2.802391
28	6	0	2.411518	2.398406	1.018544
29	6	0	2.073715	2.505391	-1.423320
30	6	0	-2.411518	-2.398406	-1.018544
31	6	0	0.940040	-1.280893	3.174404
32	6	0	-0.982777	-0.153355	-3.407458
33	6	0	1.633457	2.223925	2.234081
34	6	0	1.844387	3.031553	-0.087692
35	6	0	0.846390	2.666099	-2.185797
36	6	0	-0.141035	3.291933	-1.321732
37	6	0	-0.940040	1.280893	-3.174404
38	6	0	-1.971575	-0.929258	-2.802391
39	6	0	-2.958829	-0.303656	-1.937891
40	6	0	0.475958	3.518146	-0.024928
41	6	0	-0.270799	3.350135	1.141506
42	6	0	-1.665687	2.949649	1.060103
43	6	0	0.319859	2.689986	2.294028
44	6	0	-0.455066	-1.681231	3.093060
45	6	0	-2.917504	1.072669	-1.713985
46	6	0	0.982777	0.153355	3.407458
47	6	0	-0.385814	0.639352	3.470610
48	6	0	-1.887635	1.881298	-2.345064
49	6	0	-3.230481	-1.211428	-0.835463
50	6	0	-3.450101	-0.706106	0.446173
51	6	0	-1.480034	2.908081	-1.400018
52	6	0	-2.257844	2.733147	-0.184234
53	6	0	-0.710425	1.881642	2.925261
54	6	0	-1.937872	2.042302	2.162857
55	6	0	-3.146518	1.599405	-0.378594
56	6	0	-1.274553	-0.494540	3.275986
57	6	0	-2.860205	-1.366533	1.598956
58	6	0	-3.407680	0.728179	0.679370
59	6	0	-2.452230	-0.340379	2.544381
60	6	0	-2.790905	0.954231	1.976325

The total electronic energy was calculated to be –2286.2863809 Hartree.

Table S2. Optimized structure of $H_2O@C_{60}$ (B3LYP-D3/6-31G(d,p))



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	3.043165	0.411547	-1.778341
5	6	0	2.609362	1.734042	-1.673663
6	6	0	1.437381	2.174261	-2.412439
7	6	0	0.030326	-0.956210	-3.416975
8	6	0	2.325762	-1.819529	-1.969089
9	6	0	3.485379	-0.305618	-0.593629
10	6	0	2.597112	2.393537	-0.377667
11	6	0	0.700831	3.105658	-1.574246
12	6	0	-0.704521	1.269425	-3.236972
13	6	0	3.021060	1.704335	0.760800
14	6	0	3.475977	0.327291	0.650525
15	6	0	2.283166	1.834934	2.007248
16	6	0	3.019134	-0.392044	1.828193
17	6	0	0.029111	-2.197602	-2.782668
18	6	0	3.041424	-1.684376	-0.711985
19	6	0	2.282362	0.539155	2.666140
20	6	0	2.602003	-2.373413	0.418109
21	6	0	1.199657	-2.638033	-2.044103
22	6	0	1.416975	3.241328	-0.316212
23	6	0	-0.694691	3.101323	-1.585372
24	6	0	-1.150326	-2.645099	-2.062792
25	6	0	-1.411953	2.165462	-2.435203
26	6	0	-1.147981	-0.109084	-3.355206
27	6	0	-1.431700	3.232554	-0.339016
28	6	0	-2.592944	1.718001	-1.715261
29	6	0	-2.280708	-0.538871	-2.664766
30	6	0	2.589639	-1.714219	1.712746
31	6	0	0.709539	3.366485	0.880678
32	6	0	0.743548	-3.357246	-0.867610
33	6	0	-2.605447	2.377530	-0.419299
34	6	0	-3.016901	0.392865	-1.826851
35	6	0	-2.282669	-1.833730	-2.005980
36	6	0	-3.019198	-1.703082	-0.760490
37	6	0	-0.708741	-3.361658	-0.879217
38	6	0	1.430321	-3.228347	0.338546
39	6	0	0.693787	-3.097567	1.583447
40	6	0	-3.473594	-0.327110	-0.649306
41	6	0	-3.487993	0.305786	0.594861
42	6	0	-3.045563	-0.410771	1.779699
43	6	0	-3.043338	1.685647	0.712304
44	6	0	1.151276	2.649474	2.065725
45	6	0	-0.699933	-3.101925	1.572313
46	6	0	-0.744352	3.362021	0.869045
47	6	0	-1.200588	2.642306	2.046976
48	6	0	-1.415600	-3.237159	0.315761
49	6	0	1.409915	-2.161822	2.432732
50	6	0	0.704339	-1.268935	3.238046
51	6	0	-2.593749	-2.389552	0.376535
52	6	0	-2.606125	-1.730277	1.671169
53	6	0	-2.326343	1.820755	1.970398
54	6	0	-2.328042	0.524959	2.629283
55	6	0	-1.435341	-2.170650	2.409979
56	6	0	-0.029120	2.201852	2.786105
57	6	0	1.148255	0.109192	3.355009
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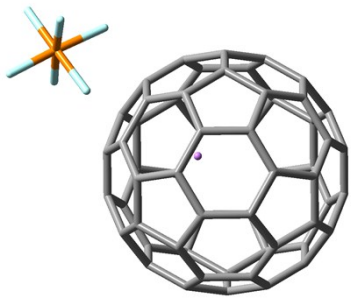
59	6	0	-0.030294	0.956895	3.415510
60	6	0	-1.202442	0.101943	3.336177
61	8	0	0.002014	-0.160655	-0.012679
62	1	0	-0.766644	0.420978	0.023430
63	1	0	0.754628	0.440345	0.039942

The total electronic energy was calculated to be –2362.7374868 Hartree.

Table S3. Optimized structure of $[Li^+@C_{60}](PF_6^-)$ (B3LYP-D3/6-31G(d,p))



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	6	0	0.653631	-2.424524	-2.561427
3	6	0	-0.401519	-2.786119	-1.629109
4	6	0	-1.451215	-1.783530	-1.727511
5	6	0	-1.044826	-0.803456	-2.727328
6	6	0	-2.281082	0.332446	1.032502
7	6	0	-2.427064	0.035249	-0.383416
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12	6	0	3.939801	-1.567801	-1.436955
13	6	0	3.532733	-2.546882	-0.442384
14	6	0	2.327870	-3.202178	-0.924269
15	6	0	1.990229	-2.628410	-2.216355
16	6	0	-0.417303	0.435188	3.188607
17	6	0	-0.975706	-0.843356	2.765011
18	6	0	0.074661	-1.846159	2.864096
19	6	0	1.279143	-1.188719	3.343466
20	6	0	0.975938	0.220128	3.542733
21	6	0	-0.797806	1.614578	2.542807
22	6	0	0.198448	2.626283	2.224114
23	6	0	-0.138317	3.201438	0.928571
24	6	0	-1.348411	2.546386	0.445687
25	6	0	-1.754209	1.561273	1.441948
26	6	0	1.214765	-0.228928	-3.544252
27	6	0	0.911991	1.178804	-3.346428
28	6	0	2.116346	1.835066	-2.861571
29	6	0	3.164219	0.831738	-2.762278
30	6	0	2.607221	-0.443347	-3.183765
31	6	0	-0.077794	-3.336309	-0.387582
32	6	0	1.314757	-3.547210	-0.028555
33	6	0	1.464943	-3.250596	1.387097
34	6	0	0.165373	-2.855394	1.904239
35	6	0	-0.789823	-2.908226	0.807116
36	6	0	-1.335850	0.550078	-2.539021
37	6	0	-2.047140	0.978067	-1.340571
38	6	0	-1.491665	2.257838	-0.919924
39	6	0	-0.432163	2.617735	-1.855934
40	6	0	-0.339016	1.562083	-2.855848
41	6	0	0.875882	3.544001	0.028485
42	6	0	2.268866	3.327372	0.387289
43	6	0	2.979093	2.898349	-0.807195
44	6	0	2.026699	2.848155	-1.905046
45	6	0	0.726041	3.247095	-1.389235
46	6	0	4.233789	-0.987305	1.336480
47	6	0	3.522958	-0.558014	2.529993
48	6	0	2.526680	-1.568594	2.846725
49	6	0	2.621820	-2.621492	1.849318
50	6	0	3.677191	-2.262862	0.916129
51	6	0	3.982693	1.933781	-0.711424
52	6	0	4.320400	1.359863	0.581048
53	6	0	4.624417	-0.047825	0.381840
54	6	0	4.474898	-0.344060	-1.033231
55	6	0	4.078025	0.880400	-1.709080
56	6	0	1.933126	1.190776	3.238414
57	6	0	3.233021	0.793060	2.722185
58	6	0	3.640053	1.771937	1.727343
59	6	0	2.591845	2.775017	1.628140
60	6	0	1.537598	2.415921	2.563656
61	3	0	-0.232391	0.572936	-0.001334
62	15	0	-5.735905	-0.001978	0.000574
63	9	0	-4.801035	-0.391329	-1.316303
64	9	0	-6.636094	-1.322550	-0.251042
65	9	0	-6.578255	0.385797	1.326382
66	9	0	-6.692156	0.898524	-0.943143
67	9	0	-4.692132	-0.904329	0.935923
68	9	0	-4.748339	1.311492	0.249780

The total electronic energy was calculated to be –3234.3902244 Hartree.

Reference

[1] Y. Isshiki, S. Fujii, T. Nishino and M. Kiguchi, *J. Am. Chem. Soc.*, 2018, **140**, 3760.
[2] M. D. Segall, J. D. L. Philip, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J Clark. *et al. J. Phys. Cond. Matter.*, 2002, **14**, 2717–2744.
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[4] A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.*, 2009, **102**, 073005.
[5] H. J. Monkhorst, *Phys. Rev. B*, 1976, **13**, 5188–5192.