Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Modification of σ-framework of [60]fullerene for bulk-heterojunction solar cells

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1. General

The glass substrates covered with indium tin oxide (ITO) (5 Ω sq^{-1}) were purchased from GEOMATEC Co., Ltd. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) (Denatron PT-100) was purchased from Nagase ChemteX Co. (6,6)-Phenyl C_{61}-butyric acid methyl ester (PCBM) was purchased from Nano-C, Inc. Poly(3-hexylthiophene) (P3HT) was purchased from Sigma-Aldrich Co. Titanium tetraisopropoxide was purchased from Wako Pure Chemical Industries, Ltd. The ITO/glass substrate was cleaned with a UV/ozone cleaner (UV-253) (Filgen, Inc.). Photocurrent-voltage characteristics were measured by using a CEP 2000 (BUNKOUKEIKI Co., Ltd.). The light intensity of the illumination source was adjusted by using a standard silicon photodiode (BS520) (BUNKOUKEIKI Co., Ltd.). The thicknesses of the films were determined with an Alpha-Step IQ Surface Profiler (KLA-Tencor Co.). The skeletally-modified fullerenes (SMFs) were prepared by following the procedure reported previously.[1]

2. CV of 1, C_{60} and PCBM

The results on cyclic voltammerty (CV) for **2** and **3** were reported earlier.[1]

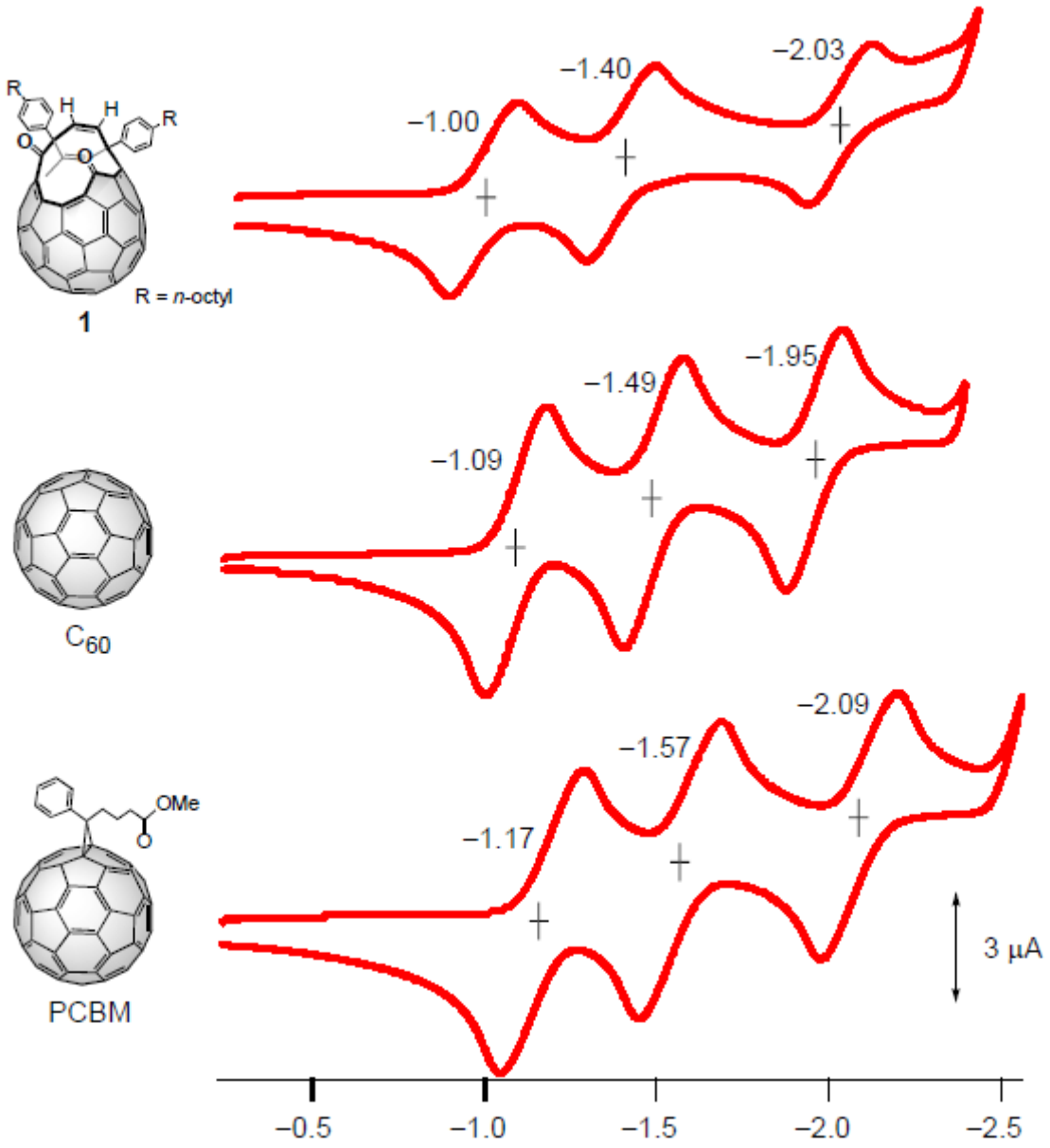


Fig. S1 CV (in 1,2-$Cl_2C_6H_4$ with 0.1 M Bu_4NBF_4, scan rate 20 mV s^{-1}) of **1**, C_{60}, and PCBM.

3. Procedure for fabrication of the BHJ solar cells

The photovoltaic devices with a layered structure of glass/ITO/PEDOT:PSS/**1**:P3HT/TiO_x/Al were fabricated as follows. The ITO-coated glass substrate (5 Ω sq^{-1}, 2.5 cm × 2.5 cm) was washed carefully under ultrasonic irradiation using water, acetone, and ethanol. The substrate was further cleaned with a UV/ozone cleaner. A thin layer (~40 nm) of PEDOT:PSS was prepared onto the ITO surface by spin-coating the solution (Denatron PT-100) at 5000 rpm for 1 min. The resulting substrate was heated at 200 °C for 10 min under ambient conditions. Then, an active layer (77 nm) was prepared onto the PEDOT:PSS layer by spin-coating a solution (50 μL) containing SMF derivative **1** and P3HT (weight ratio of 1 : 1.6) in dry chlorobenzene with a concentration of 24 mg/mL at 1000 rpm for 40 seconds under argon. The substrate was annealed at 150 °C for 6 min under argon. After cooling to room temperature, a thin layer (~10 nm) of TiO_x was immediately prepared on the active layer by spin-coating a solution of titanium tetraisopropoxide in ethanol (50 μL) at 4000 rpm for ~20 seconds and by being hydrolyzed for 20 min under ambient conditions. Finally, aluminum electrodes were thermally deposited under vacuum (3.8×10^{-5} Torr).

The devices based on SMF derivatives **2**, **3**, and PCBM were prepared in a manner similar to that described above. The thicknesses of the active layers of **2**:P3HT and **3**:P3HT were 84 nm and 95 nm, respectively.

4. IPCE of 3:P3HT-based device

(IPCE: Incident Photon to Current Conversion Efficiency)

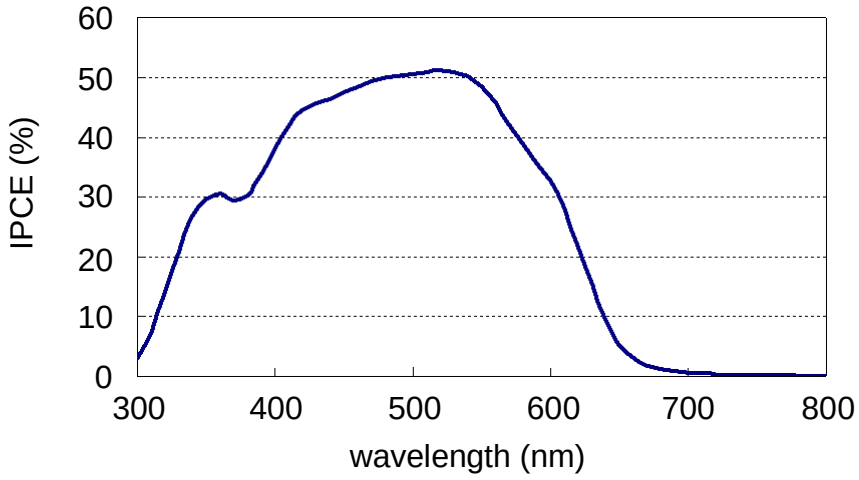
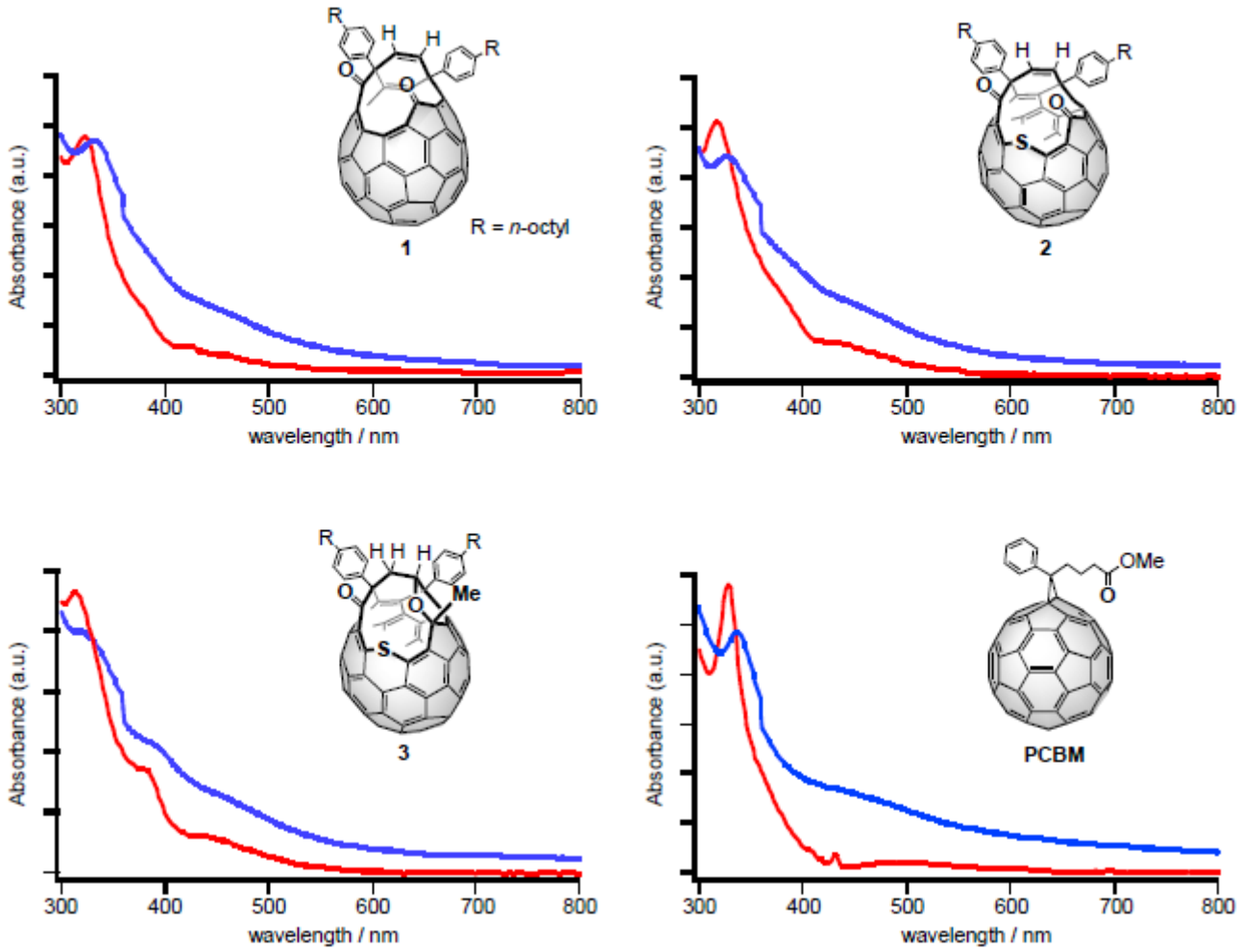


Fig. S2 IPCE spectrum of the BHJ solar cell composed of **3** and P3HT.

5. UV-vis absorption spectra

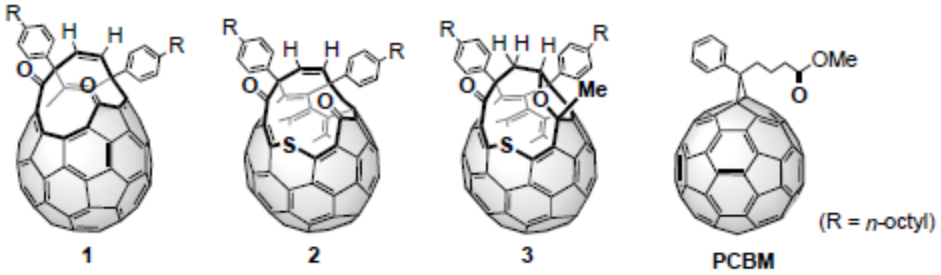
The spectra of **1-3** and PCBM in cyclohexane (red line) and as the film on a quartz glass (blue line).

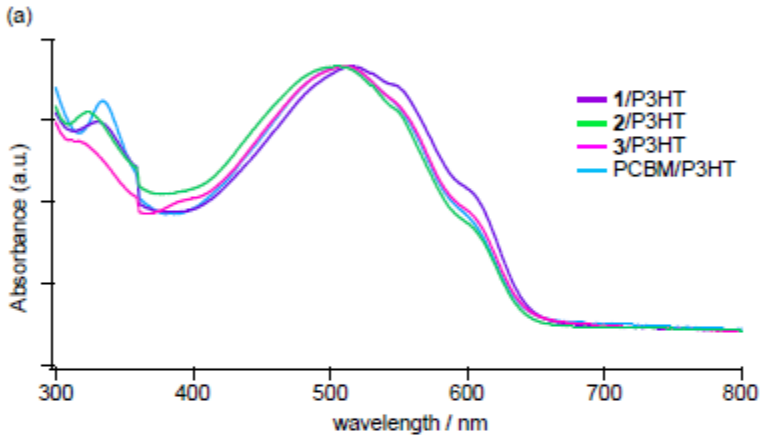
The films were prepared by spin-coating (1000 rpm, 40 seconds) the chlorobenzene solution of each C_{60} derivatives (9 mg/mL) on a quartz glass.

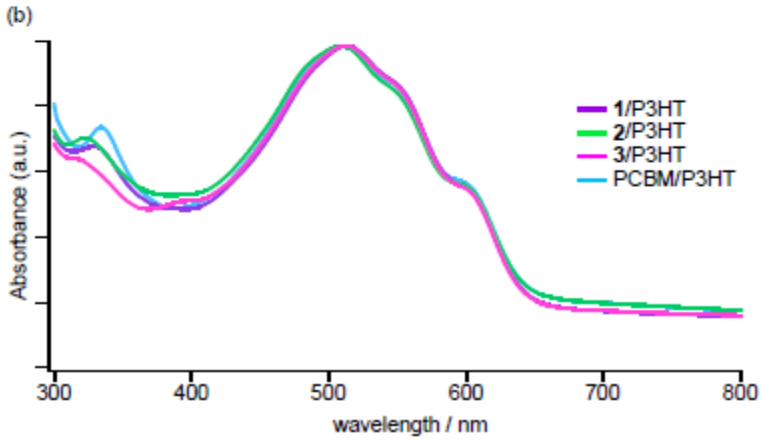


6. UV-vis absorption spectra of the blend films

Normalized absorption spectra of the blend films consisting of the fullerene derivative (**1-3** or PCBM) and P3HT. These films were prepared by spin-coating (1000 rpm, 40 s) the chlorobenzene solution containing each fullerene derivative and P3HT at weight ratio of 1 : 1.6 with a concentration of 24 mg/mL. The spectra were recorded (a) before and (b) after annealing at 150 °C for 6 min under ambient conditions.







7. Optimized geometry of 1

Electron energies (*E* in hartrees) and Cartesian coordinates for compounds **1** (the two n-octyl groups were replaced by methyl groups) calculated at the B3LYP/6-31G* level. Optimized geometries of **2** and **3** were reported previously.[1]

1 (*E* = – 3132.1507247)

0 1

C	2.555039	1.607224	-3.069388
C	1.111008	1.721020	-2.987533
C	0.319103	0.614981	-3.254586
C	0.926883	-0.663705	-3.571138
C	2.313731	-0.789967	-3.604217
C	3.147032	0.373734	-3.356836
C	0.769220	2.601999	-1.883863
C	-0.855794	0.384566	-2.455750
C	0.114957	-1.683478	-2.940473
C	2.947687	-1.941045	-2.979749
C	4.309399	-0.059320	-2.600654
C	3.122323	2.466798	-2.050017
C	2.161096	-2.908817	-2.346971
C	0.716850	-2.775836	-2.331365
C	2.565790	-3.439288	-1.057772
C	0.228476	-3.207999	-1.036796
C	-0.351210	2.359146	-1.059324
C	-1.006060	-1.047231	-2.290095
C	1.367224	-3.592189	-0.251776
C	-1.578541	-1.542537	-1.120062
C	-1.228159	1.240041	-1.411428
C	4.178124	-1.487282	-2.358350
C	4.857770	0.770492	-1.620795
C	-0.258035	2.696253	0.371834
C	4.264782	2.068513	-1.350224
C	2.022269	3.097420	-1.346218
C	5.302495	0.210812	-0.354655
C	4.366757	2.321433	0.075850
C	2.128341	3.357004	0.010755
C	-0.882773	-2.621540	-0.414297
C	4.582253	-2.022362	-1.131212
C	-2.157138	0.719754	-0.430919
C	5.006751	1.170507	0.693855
C	3.328386	2.976341	0.738841
C	0.980046	3.152755	0.858926
C	1.475392	2.696708	2.137172
C	-1.186095	2.032802	1.293797
C	-2.379482	-0.637258	-0.329195
C	-2.239312	-2.155472	1.635979
C	2.914340	2.541081	2.054937
C	3.523778	1.433662	2.647478

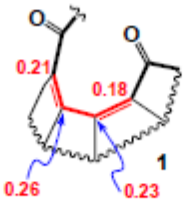
C	2.702187	0.442189	3.319686
C	4.579466	0.727461	1.950038
C	3.752045	-3.007261	-0.467119
C	5.157416	-1.157677	-0.111606
C	4.686914	-1.613772	1.181968
C	-0.657175	1.511836	2.467819
C	-0.928649	-2.536784	1.040010
C	0.266186	-2.655571	1.766112
C	0.706820	1.777322	2.826150
C	1.327500	0.599454	3.405012
C	4.399511	-0.697541	2.191793
C	3.211121	-0.864499	3.010474
C	0.390802	-0.493787	3.281198
C	3.795288	-2.736153	0.960612
C	1.392305	-3.264017	1.105492
C	0.848623	-1.733411	2.833673
C	2.629232	-2.846213	1.714981
C	2.303502	-1.898799	2.750096
C	-2.564474	1.682179	0.682093
C	-3.208950	-1.283442	0.760867
C	-3.844742	-0.253263	1.665389
C	-3.529211	1.038928	1.652897
C	-3.266621	2.949454	0.145268
C	-4.119012	2.874384	-0.961732
C	-4.820487	3.995486	-1.401902
C	-4.707329	5.227388	-0.745558
C	-3.863772	5.294344	0.369973
C	-3.158206	4.175613	0.811811
C	-5.489786	6.434221	-1.207886
C	-4.325718	-2.187607	0.168626
C	-4.915323	-3.204431	0.932054
C	-5.961007	-3.968087	0.415152
C	-6.464290	-3.743563	-0.871784
O	-2.563681	-2.565424	2.734515
O	-1.948995	-0.089352	3.876456
C	-0.969808	0.225502	3.251682
C	-5.878503	-2.720347	-1.625650
C	-4.831685	-1.953074	-1.116278
C	-7.615908	-4.556833	-1.414298
H	-4.543250	-0.638015	2.400702
H	-3.990152	1.712244	2.370105
H	-4.235930	1.931527	-1.488683
H	-5.467415	3.909976	-2.272310
H	-3.752234	6.236930	0.901478
H	-2.511695	4.265498	1.680682
H	-6.460648	6.497936	-0.698286
H	-5.690446	6.393794	-2.283737
H	-4.952478	7.365336	-0.998460
H	-4.554534	-3.405825	1.934763
H	-6.391381	-4.757055	1.028205
H	-6.244616	-2.517267	-2.629768
H	-4.407721	-1.166486	-1.732424
H	-8.581611	-4.114226	-1.135210
H	-7.603960	-5.579564	-1.022413
H	-7.588293	-4.612721	-2.507672

8. LUMO Coefficients

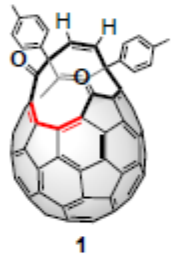
(The DFT calculations were performed at the B3LYP/STO-3G//B3LYP/6-31G(d) level.)

The molecular orbital coefficients of the selected atoms were obtained by an equation:

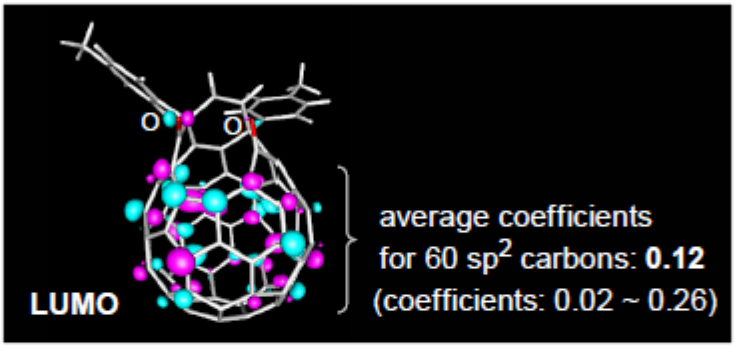
$$C = (C_{2px}^{2} + C_{2px}^{2} + C_{2px}^{2})^{0.5}.$$

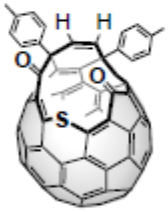


large coefficients in the conjugated butadiene unit



1





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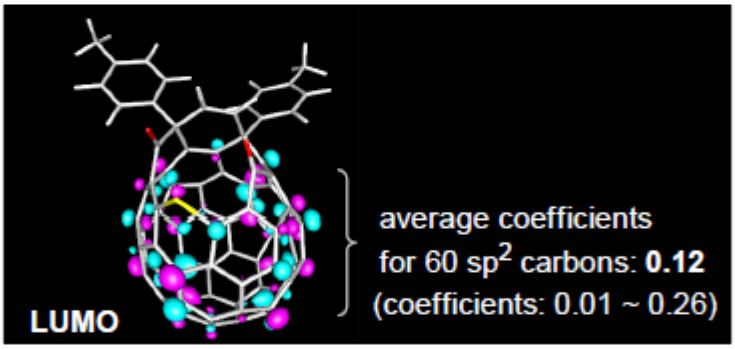

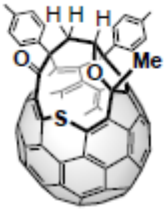

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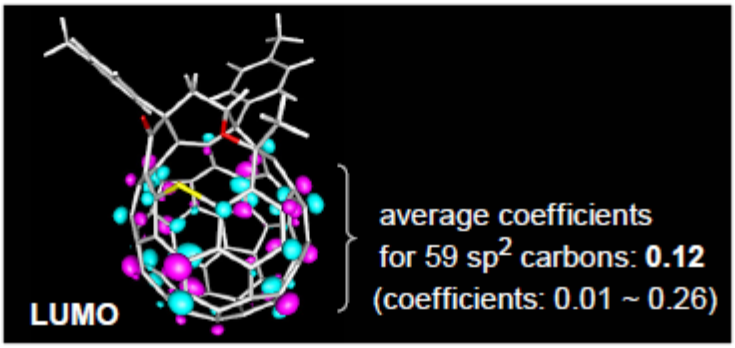

9. Complete reference 13

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10. Reference

1) Murata, M.; Morinaka, Y.; Kurotobi, K.; Komatsu, K.; Murata, Y. *Chem. Lett*, **2010**, *39*, 298.