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

Comparative Density Functional Theory – Density Functional Tight Binding Study of fullerene derivatives: effects due to fullerene size, addends, and crystallinity on bandstructure, charge transport and optical properties

Amrita Pal[a], Lai Kai Wen[b], Chia Yao Jun[b], Il Jeon[c], Yutaka Matsuo[c] and Sergei Manzhos[a]

[a]Department of Mechanical Engineering, National University of Singapore, Block EA #07-08, 9 Engineering Drive 1, Singapore 117576.

[b]NUS High School of Mathematics and Science, 20 Clementi Avenue 1,Singapore 129957

[c] Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Supporting Information

1. Frontier orbitals and oxidation potentials.

Table S1: HOMO-LUMO values for all the C60 and C70 fullerene molecules computed by Gaussian program with B3LYP functional and 6-31+g(d,p) basis set.

Molecule	HOMO, eV	LUMO, eV
C60	-6.40	-3.68
C70	-6.33	-3.67
C60QM	-6.02	-3.52
C70QM	-5.94	-3.46
$C60CH_2QM$	-5.84	-3.35
$C70CH_2QM$	-5.77	-3.34
$C60QM_2$	-5.79	-3.38
$C70QM_2$	-5.69	-3.28
C60IND	-6.01	-3.51
C70IND	-5.94	-3.44
$C60CH_2IND$	-5.88	-3.41
$C70CH_2IND$	-5.76	-3.33
$C60IND_2$	-5.76	-3.35
$C70IND_2$	-5.68	-3.24
C60SIMEF	-6.00	-3.48
C70SIMEF	-5.66	-3.46
$C60CH_2(CH_2Ar)_2$	-5.87	-3.35
$C70CH_2(CH_2Ar)_2$	-6.03	-3.43
$C60(CH2Ar)_2$	-6.02	-3.50
$C70(CH2Ar)_2$	-5.75	-3.66
C60PCBM	-6.05	-3.53
C70PCBM	-5.99	-3.49
$C60PCBMCH_2$	-5.87	-3.44
C70PCBM CH_2	-5.80	-3.37
C60BISPCBM	-5.83	-3.39
C70BISPCBM	-5.75	-3.33

Table S2: The oxidation and reduction potential of all the C60 and C70 fullerene molecules computed by Gaussian program with ωB97XD functional and 6-31+g(d,p) basis set.

Molecule	Oxidation potential, eV	Reduction potential, eV
C60	7.89	2.35
C70	7.58	2.44
C60QM	7.44	2.26
C70QM	7.15	2.45
$C60CH_2QM$	7.20	2.09
$C70CH_2QM$	6.95	2.37
$C60QM_2$	7.20	2.17
$C70QM_2$	6.84	2.33
C60IND	7.42	2.25
C70IND	7.14	2.43
$C60CH_2IND$	7.28	2.16
$C70CH_2IND$	6.94	2.36
$C60IND_2$	7.15	2.16
$C70IND_2$	6.82	
$C60CH_2(CH_2Ar)_2$	7.20	2.10
$C70CH_2(CH_2Ar)_2$	7.09	2.31
$C60(CH2Ar)_2$	7.36	2.32
$C70(CH2Ar)_2$	6.90	2.69
C60SIMEF	7.26	2.31
C70SIMEF	6.89	2.36
C60PCBM	7.07	2.50
C70PCBM	7.17	2.48
$C60PCBMCH_2$	6.90	2.43
C70PCBM CH_2	6.97	2.41
C60BISPCBM	7.20	2.22
C70BISPCBM	6.87	2.41

2. PDOS obtained by Gaussian.

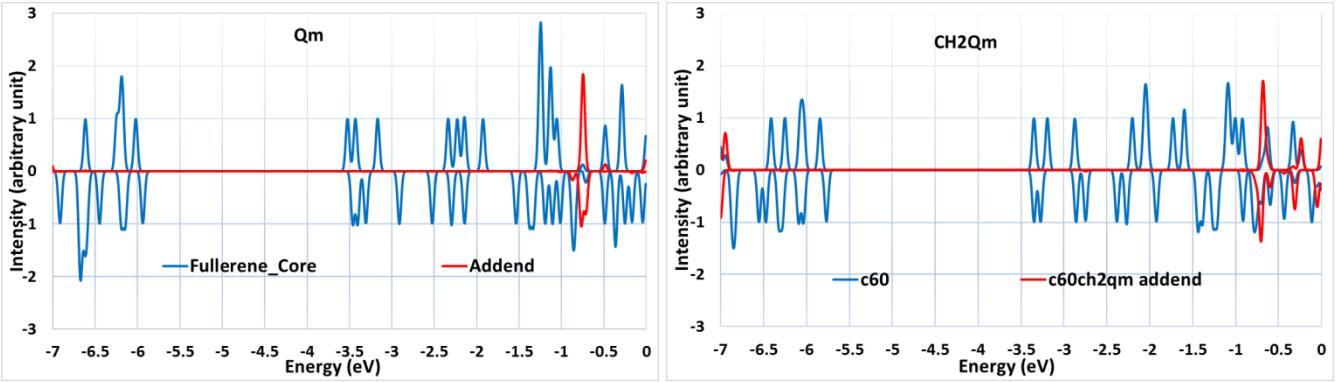


Figure S1. The The partial density of states (PDOS) of C60/70QM and CH_2QM obtained by Gaussian calculation. The contribution due to the C60/70 part and the addend part for each C60 and C70 derivatives are shown in blue and red colour, respectively. The upper and the lower parts are plotted for C60 and C70 accordingly. The presentation for PDOS for other systems in this study are similar.

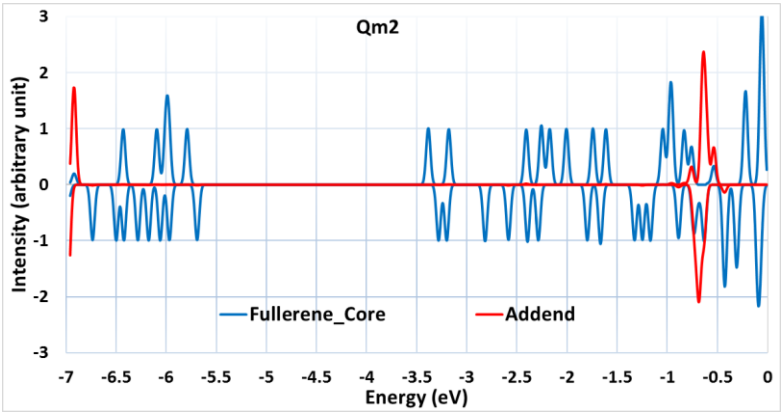


Figure S2. The partial density of states (PDOS) of C60/70QM_2 obtained by Gaussian calculation.

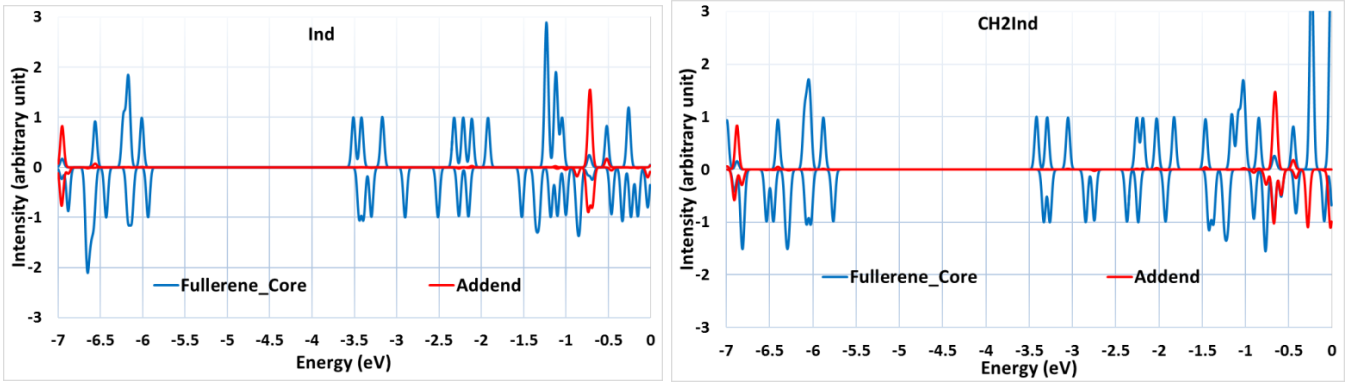


Figure S3. The partial density of states (PDOS) of C60/70IND and CH_2IND obtained by Gaussian calculation.

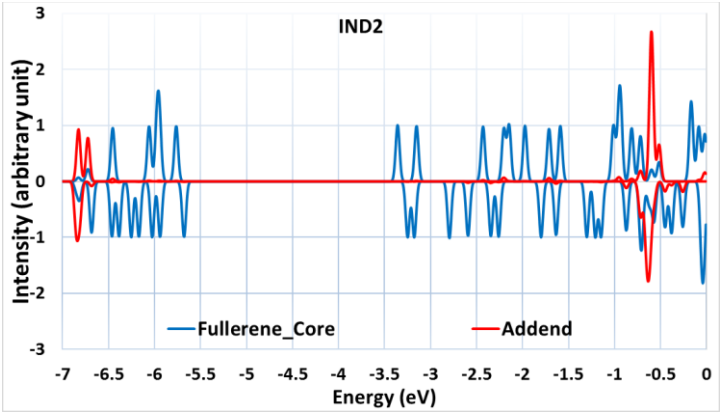


Figure S4. The partial density of states (PDOS) of C60/70IND_2 obtained by Gaussian calculation.

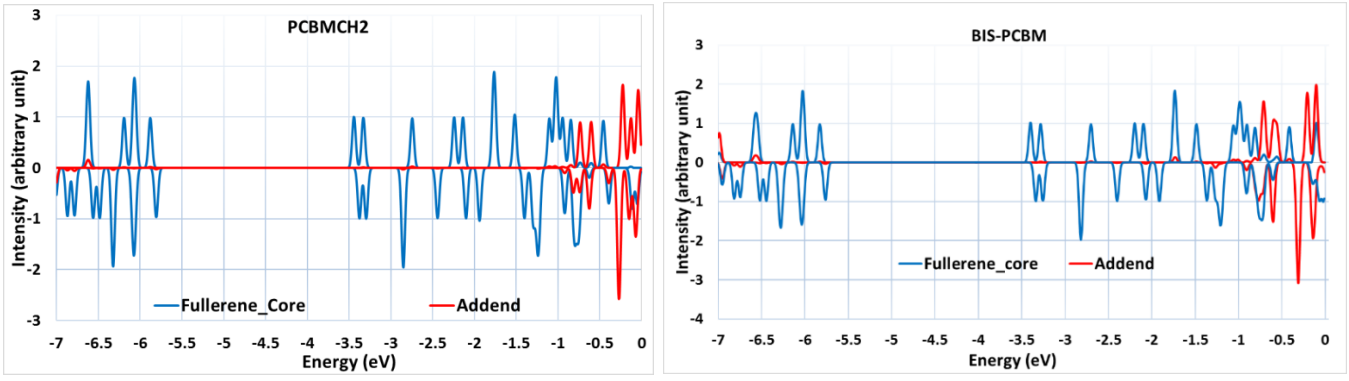


Figure S5. The partial density of states (PDOS) of C60/70PCBMCH_2 obtained by Gaussian calculation.

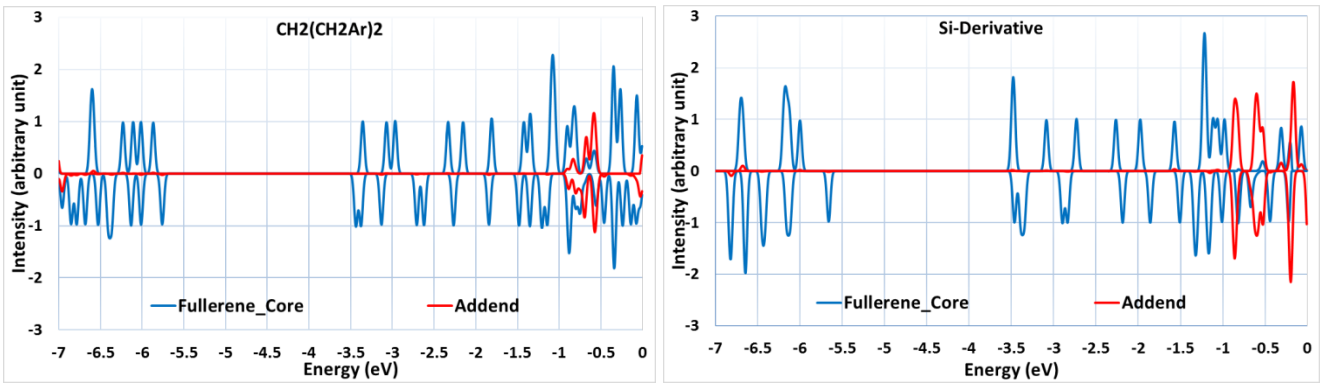


Figure S6. The partial density of states (PDOS) of C60/70$CH_2(CH_2Ar_2)$ and SIMEF obtained by Gaussian calculation.

3. Orbitals having addend states, which are involved in solar absorption as shown in Table 3 in the manuscript.

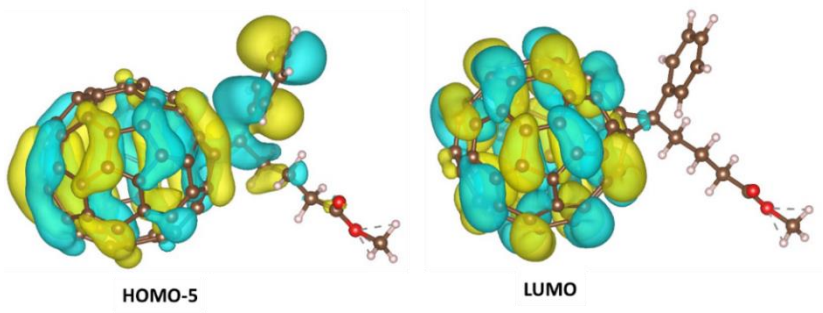


Figure S7. The HOMO-5 and the LUMO of C60PCBM.

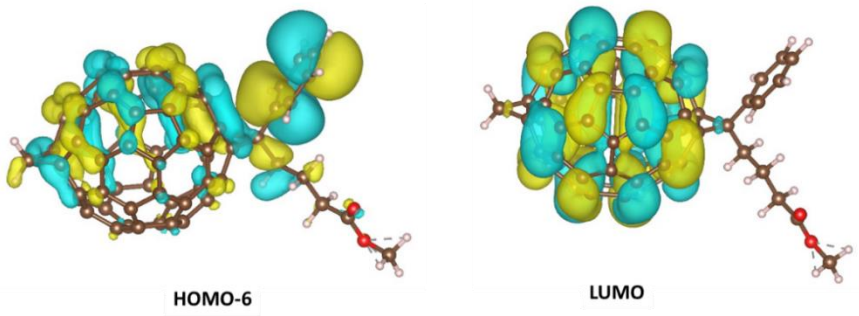


Figure S8. The HOMO-6 and the LUMO of $C60CH_2PCBM$.

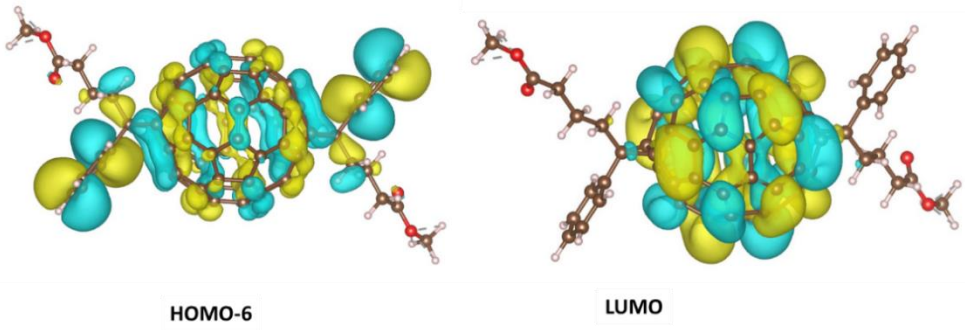


Figure S9. The HOMO-6 and the LUMO of C60BISPCBM.

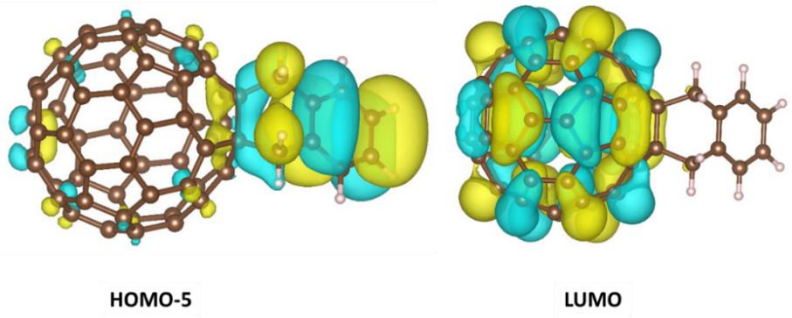


Figure S10. The HOMO-5 and the LUMO of C60QM.

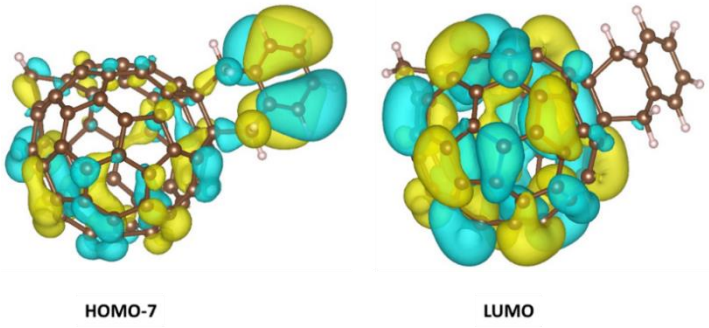


Figure S11. The HOMO-7 and the LUMO of $C60CH_2QM$.

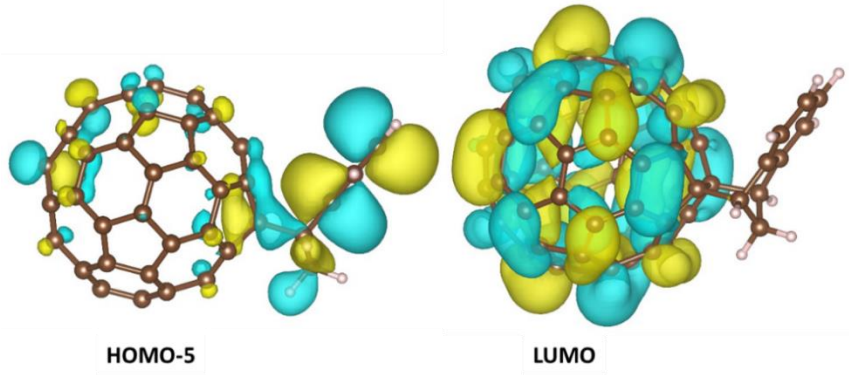


Figure S12. The HOMO-5 and the LUMO of C60IND.

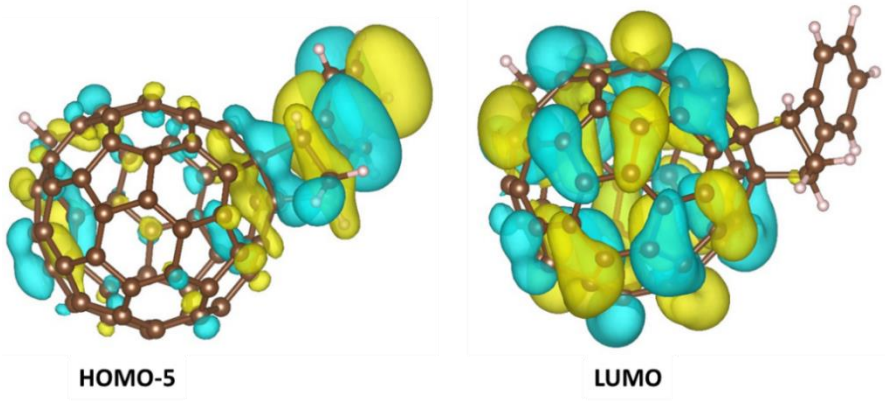


Figure S13. The HOMO-5 and the LUMO of $C60CH_2IND$.

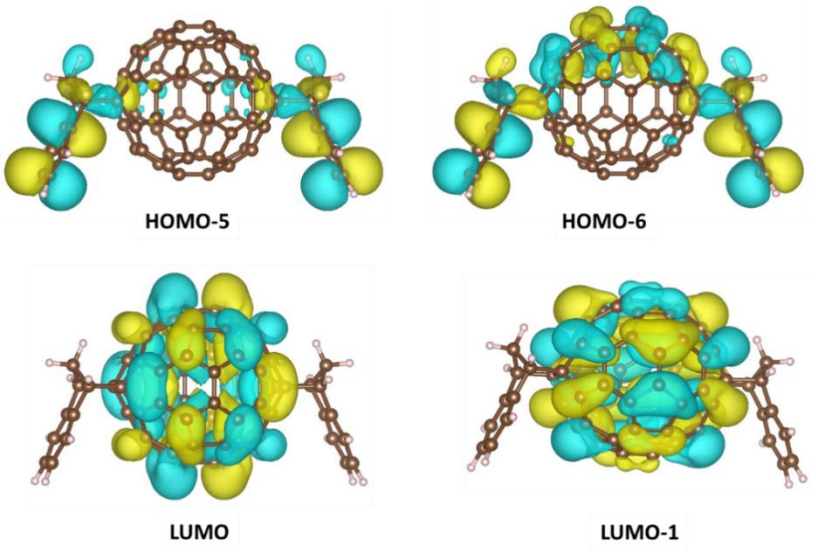


Figure S14. The HOMO and the LUMO of IND_2 as shown in Table3.

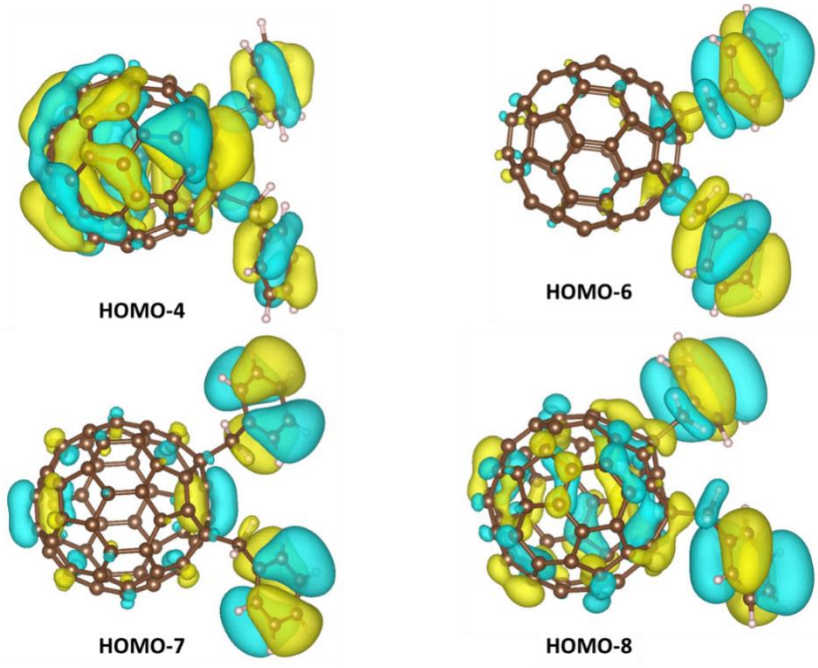


Figure S15. The HOMO and other bonding orbitals of CH_2Ar_2 that are having addend state, which can take part in solar absorption.

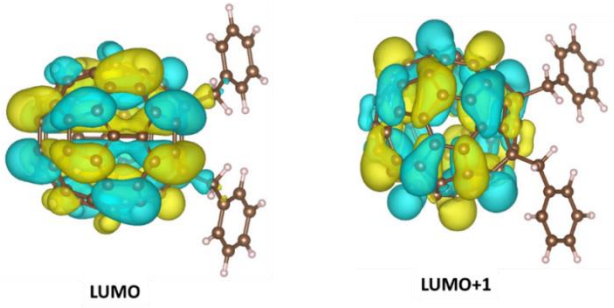


Figure S16. The LUMO of CH_2Ar_2.

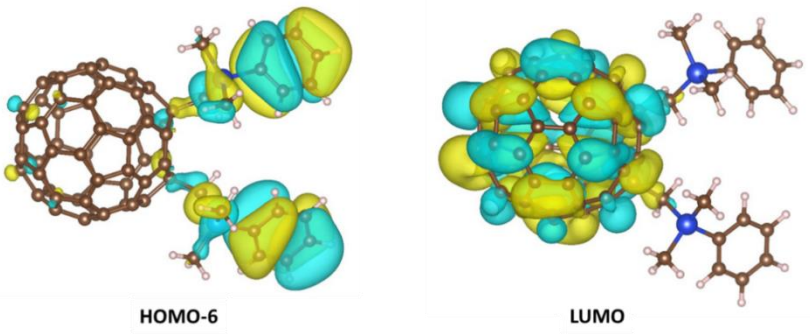


Figure S17. The HOMO-6 and the LUMO of SIMEF.

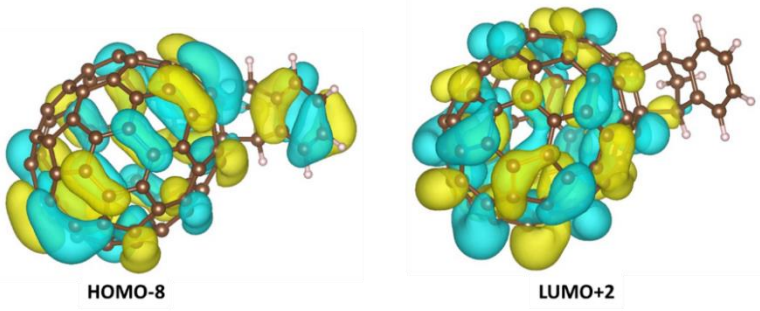


Figure S18. The HOMO-8 and the LUMO+2 of C70IND.

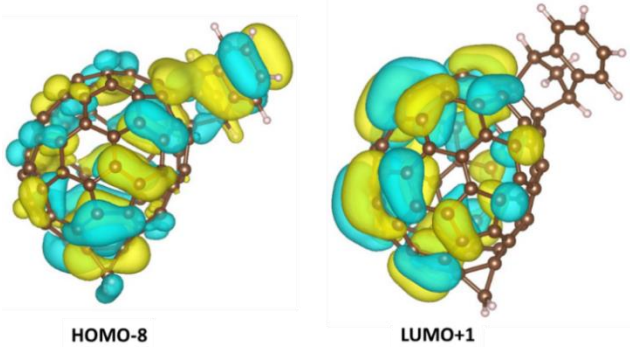


Figure S19. The HOMO-8 and the LUMO+1 of $C70CH_2IND$.

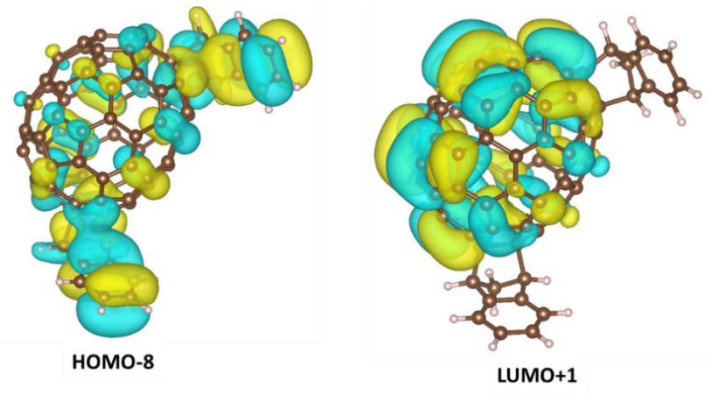


Figure S20. The HOMO-8 and the LUMO+1 of C70IND.

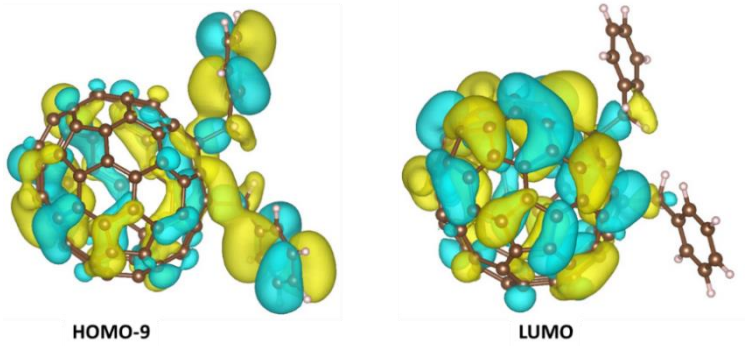


Figure S21. The HOMO-9 and the LUMO of $C70CH_2Ar_2$.

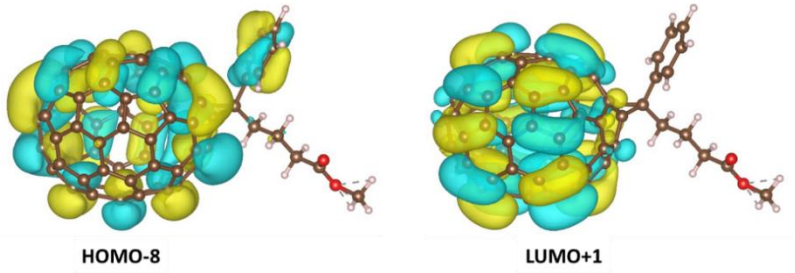


Figure S22. The HOMO-8 and the LUMO+1 of C70PCBM.

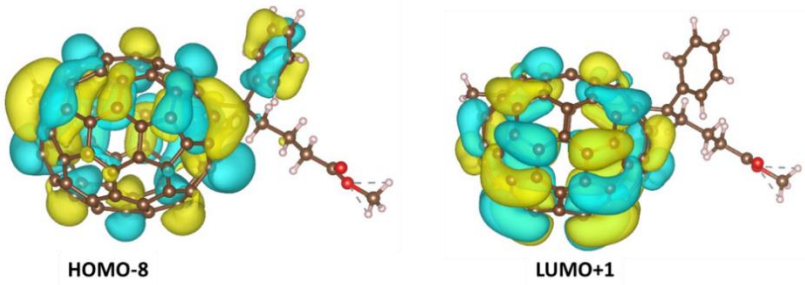


Figure S23. The HOMO-8 and the LUMO+1 of CH_2PCBM.

4. The PDOS obtained with DFTB.

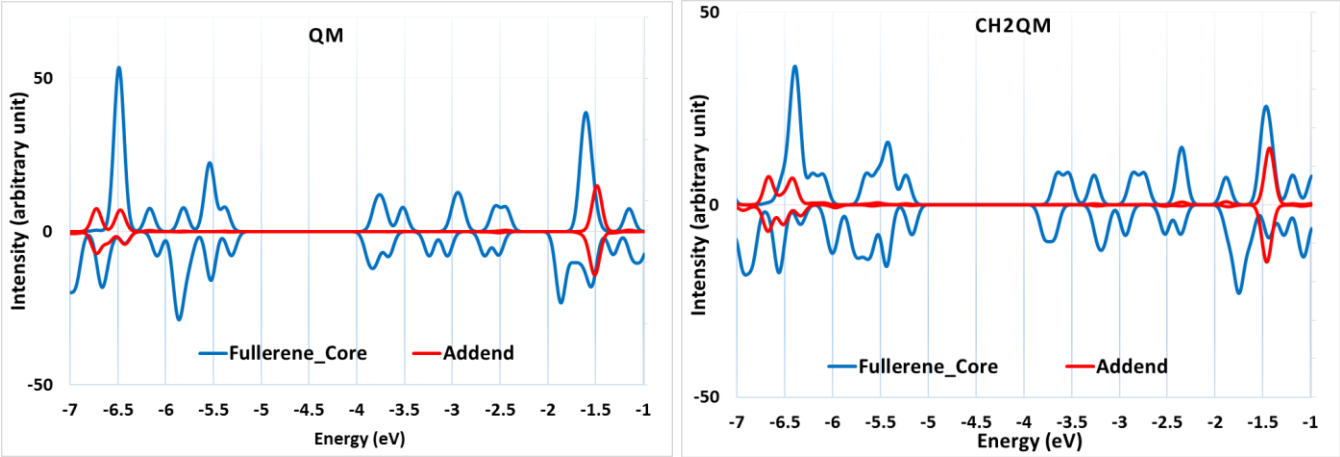


Figure S24. The partial density of states (PDOS) of C60/70QM and CH_2QM obtained by DFTB calculation.

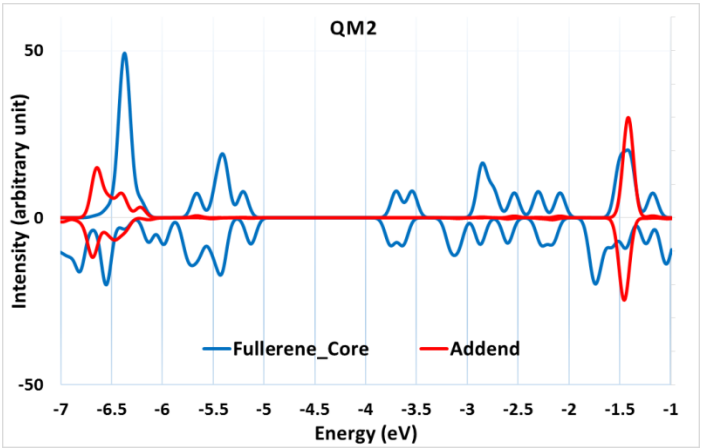


Figure S25. The partial density of states (PDOS) of C60/70QM_2 obtained by DFTB calculation.

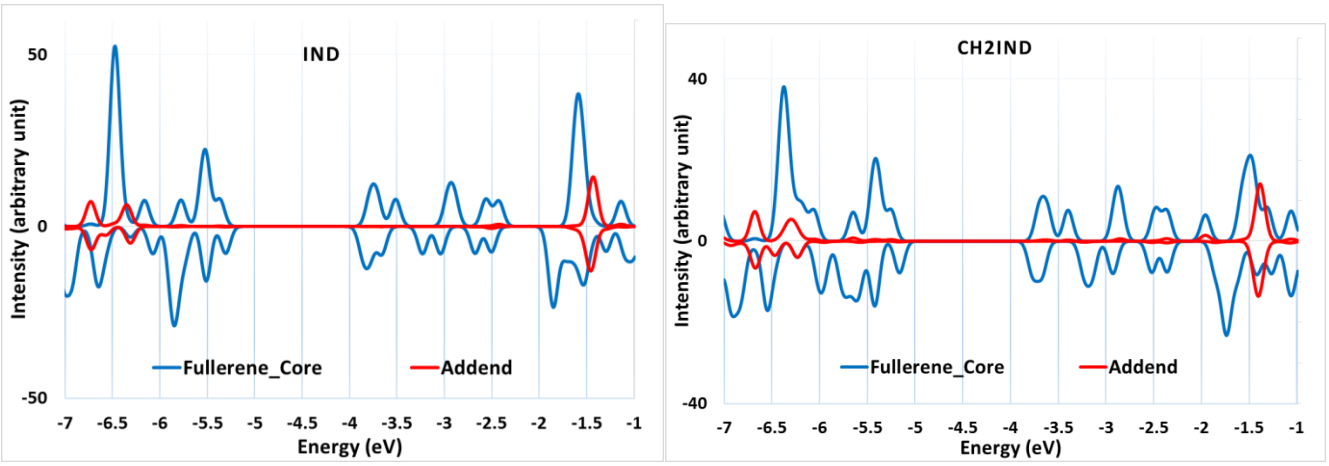


Figure S26. The partial density of states (PDOS) of C60/70IND and CH_2IND obtained by DFTB calculation.

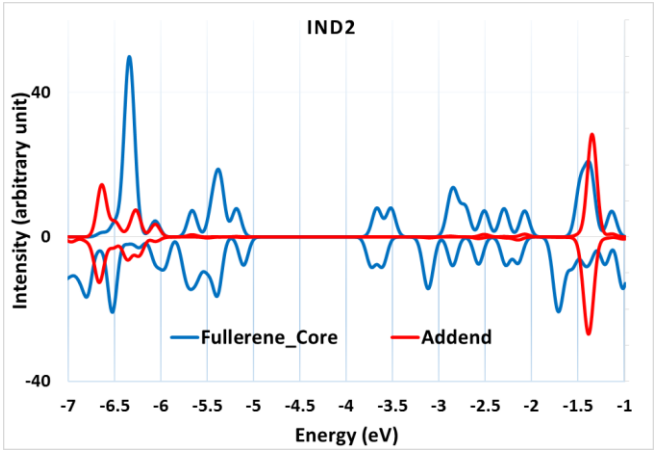


Figure S27. The partial density of states (PDOS) of C60/70IND_2 obtained by DFTB calculation.

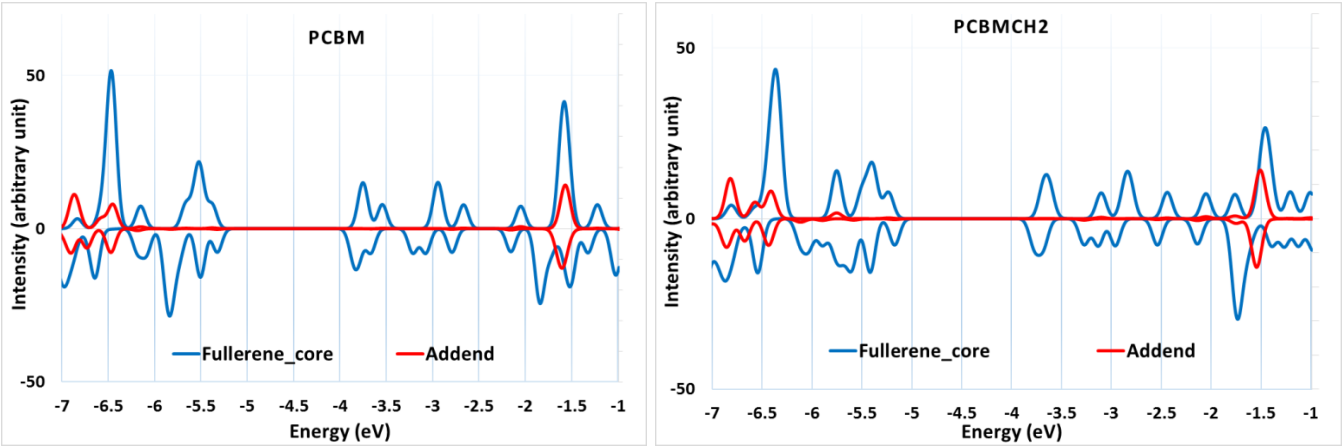


Figure S28. The partial density of states (PDOS) of C60/70PCBM and CH_2PCBM obtained by DFTB calculation.

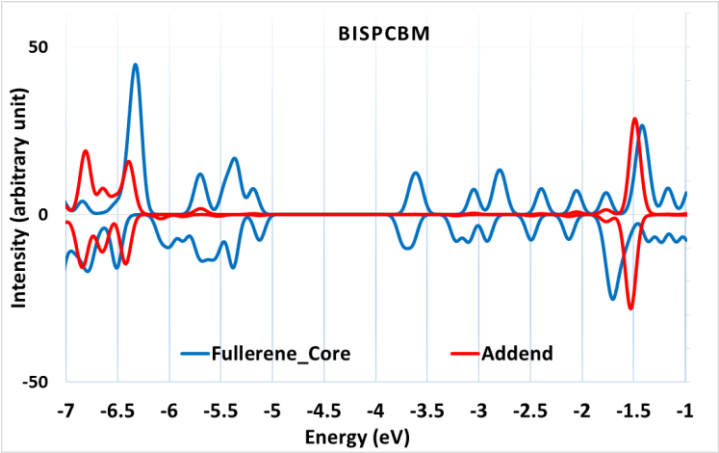


Figure S29. The partial density of states (PDOS) of C60/70BISPCBM obtained by DFTB calculation.

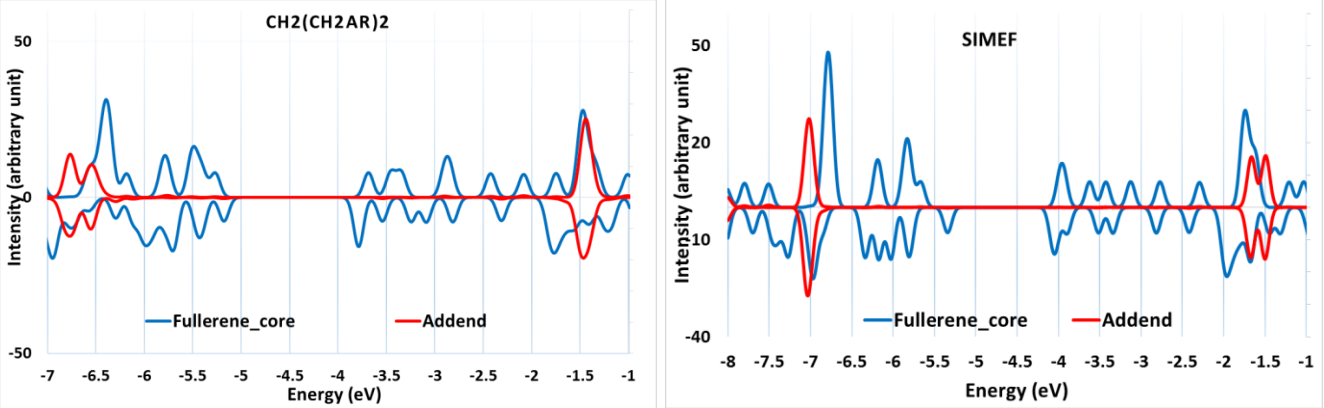


Figure S30. The partial density of states (PDOS) of C60/70CH_2(CH_2Ar_2) and C60/70SIMEF obtained by DFTB calculation.

5. Comparison of DFTB to DFT and effect of crystallinity

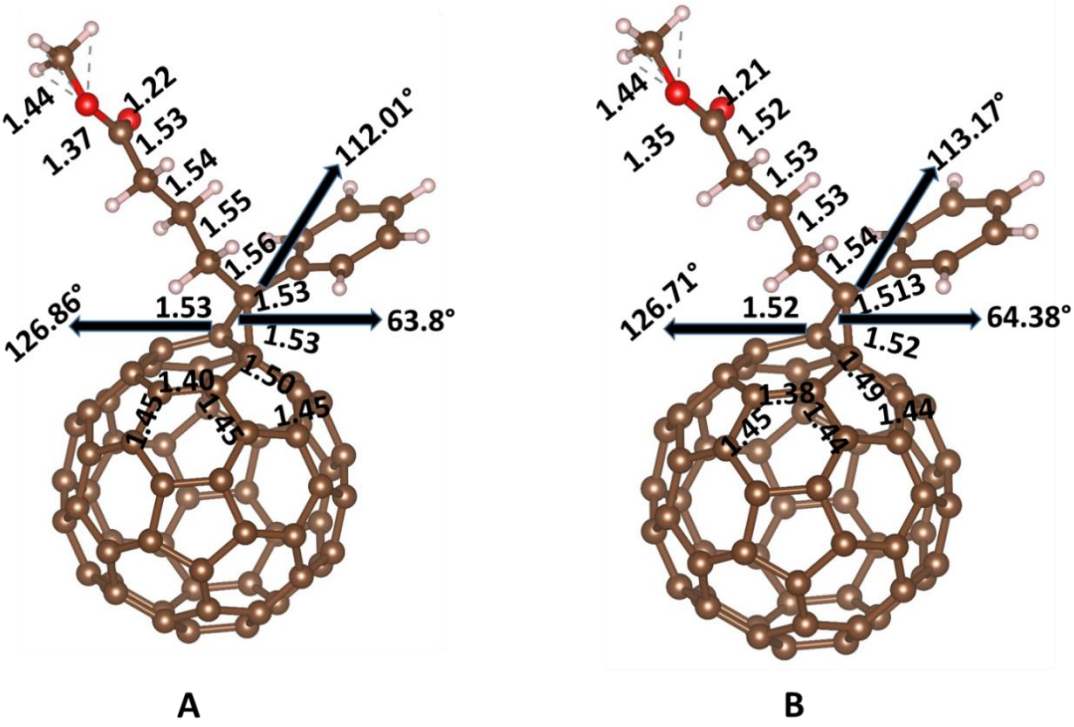
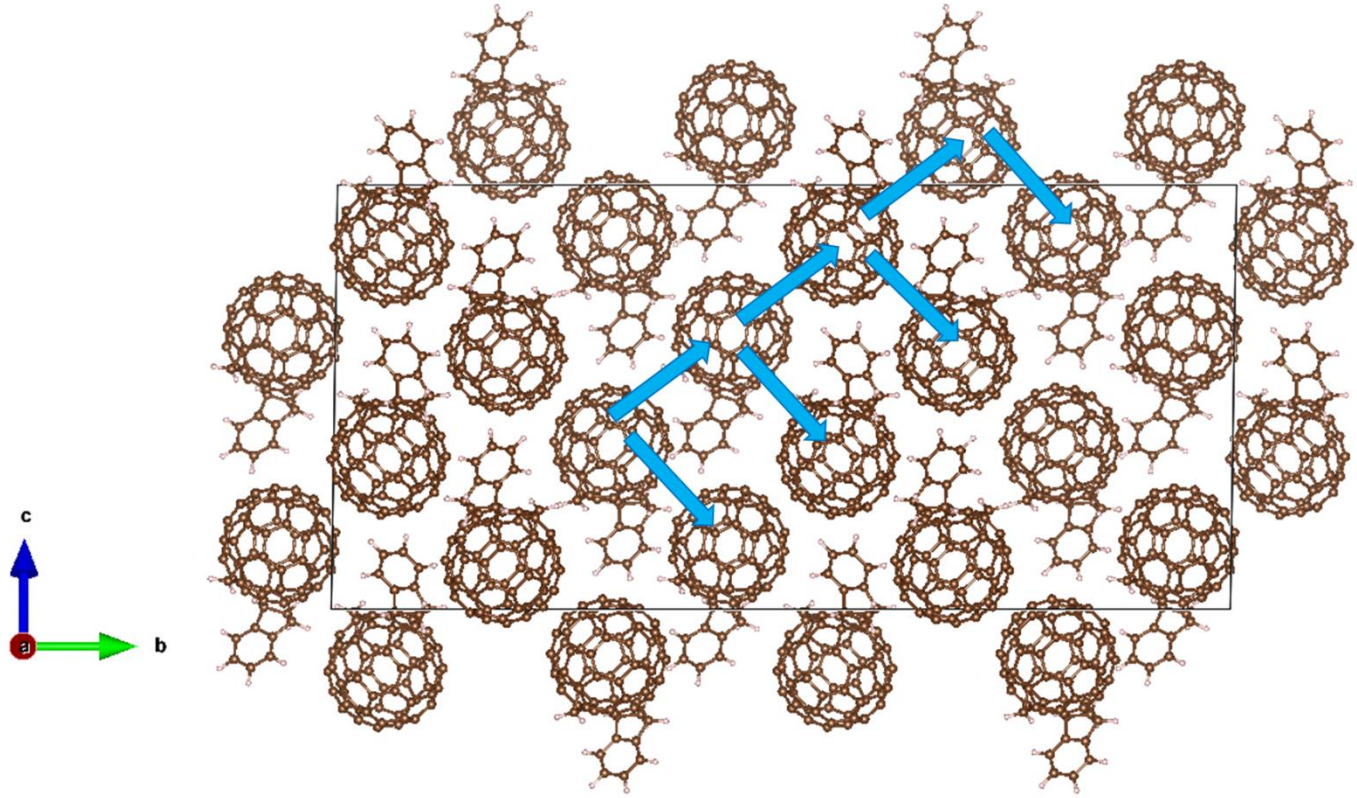


Figure S31. The Comparison between the $PC_{60}BM$ geometries obtained from DFTB (A) and DFT (B3LYP functional) (B) program.

Table S3. The stabilization of the HOMO, LUMO energies due to crystallinity. All the values are obtained by DFTB and are in eV. The (M) and (C) represent the molecular and crystalline energy (for the lowest energy structures) values, respectively.

Name of the molecules	HOMO (M)	LUMO (M)	HOMO (C)	LUMO (C)	BAND GAP (M)	BAND GAP (C)
C60	-5.67479	-3.90898	-5.4941	-4.01017	1.76581	1.48393
C70	-5.60887	-3.99776	-5.52551	-4.05799	1.61111	1.46752
C60QM	-5.37855	-3.79816	-5.32892	-4.04733	1.58039	1.28159
C70QM	-5.31202	-3.873	-5.34802	-4.03201	1.43902	1.31601
$C60(CH_2)QM$	-5.23331	-3.64985	-5.36222	-3.99951	1.58346	1.36271
$C70(CH_2)QM$	-5.17049	-3.78286	-5.21576	-3.96589	1.38763	1.24987
$C60(QM)_2$	-5.20523	-3.70009	-5.27461	-3.92718	1.50514	1.34743
$C70(QM)_2$	-5.12845	-3.7565	-5.21576	-3.94977	1.37195	1.26599
C60IND	-5.36814	-3.78186	-5.43184	-3.98858	1.58628	1.44326
C70IND	-5.30695	-3.8559	-5.35061	-4.02893	1.45105	1.32168
$C60(CH_2)IND$	-5.25026	-3.6985	-5.38604	-3.8557	1.55176	1.53034
$C70(CH_2)IND$	-5.16339	-3.7675	-5.24229	-4.01124	1.39589	1.23105
$C60(IND)_2$	-5.18351	-3.6692	-5.25838	-3.89351	1.51431	1.36487
$C70(IND)_2$	-5.1075	-3.7311	-5.20591	-3.99828	1.3764	1.20763
$C60CH_2(CH_2Ar)_2$	-5.26719	-3.68497	-5.26029	-3.81901	1.58222	1.44128
$C70CH_2(CH_2Ar)_2$	-5.1773	-3.7932	-5.25317	-3.97875	1.3841	1.27442
$C60(CH_2Ar)_2$	-5.36149	-3.83554	-5.42798	-3.98756	1.52595	1.44042
$C70(CH_2Ar)_2$	-5.14639	-4.01131	-5.17913	-4.10381	1.13508	1.07532
C60SIMEF	-5.6656	-3.98486	-5.63541	-4.06259	1.68074	1.57282
C70SIMEF	-5.34129	-4.07099	-5.33364	-4.13168	1.2703	1.20196
C60PCBM	-5.37948	-3.76921	-5.45667	-3.99655	1.61027	1.46012
C70PCBM	-5.3236	-3.85649	-5.38791	-4.03339	1.46711	1.35452
$C60(CH_2)PCBM$	-5.23428	-3.68361	-5.201	-4.06494	1.55067	1.13606
$C70(CH_2)PCBM$	-5.17214	-3.77149	-5.23253	-3.94271	1.40065	1.28982
C60BISPCBM	-5.18621	-3.64777	-5.22518	-3.8006	1.53844	1.42458
C70BISPCBM	-5.12521	-3.73856	-5.25874	-3.97565	1.38665	1.28309

6. The highlighted dimer positions for C60CH_2IND crystal structure that was used to calculate the transfer integral. Similar approach was used for all the derivatives in this study.



7. The HOMO and LUMO of all the fullerene derivatives studied in this work.

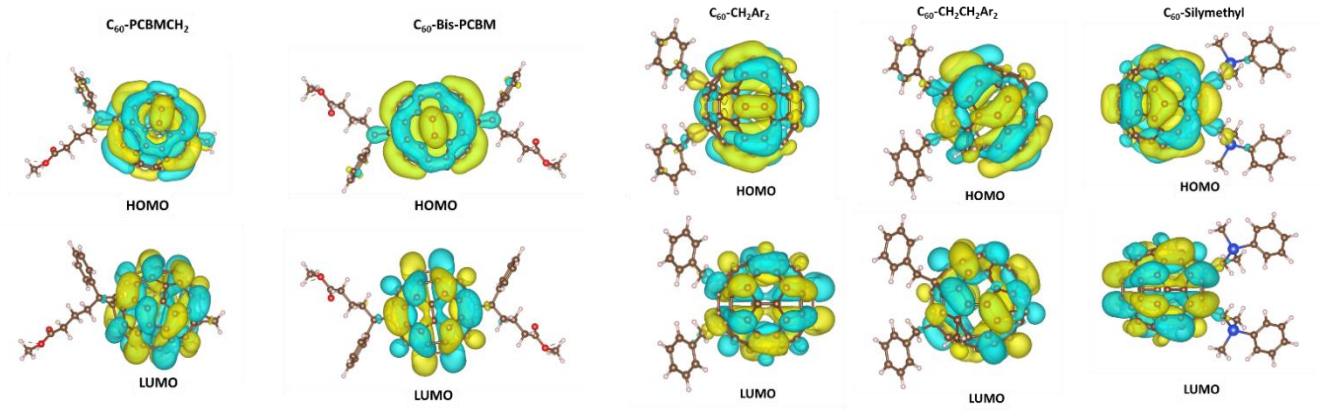


Figure S32. The HOMO and LUMO of PCBMCH$_2$, Bis-PCBM, CH$_2$Ar$_2$, CH$_2$CH$_2$Ar$_2$ and Silymethyl addends with C60 core.

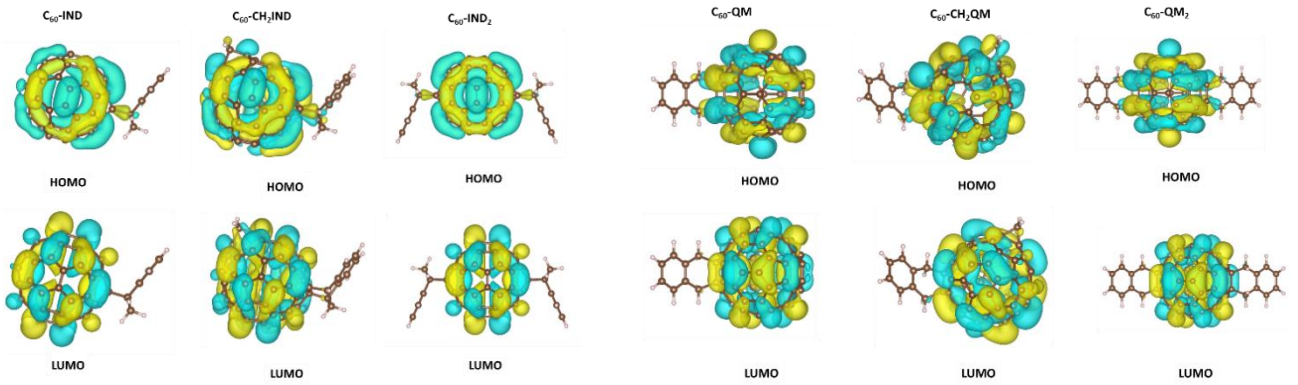


Figure S33. The HOMO and LUMO of IND, CH_2IND, IND_2, QM, CH_2QM and QM_2 addends with C60 core.

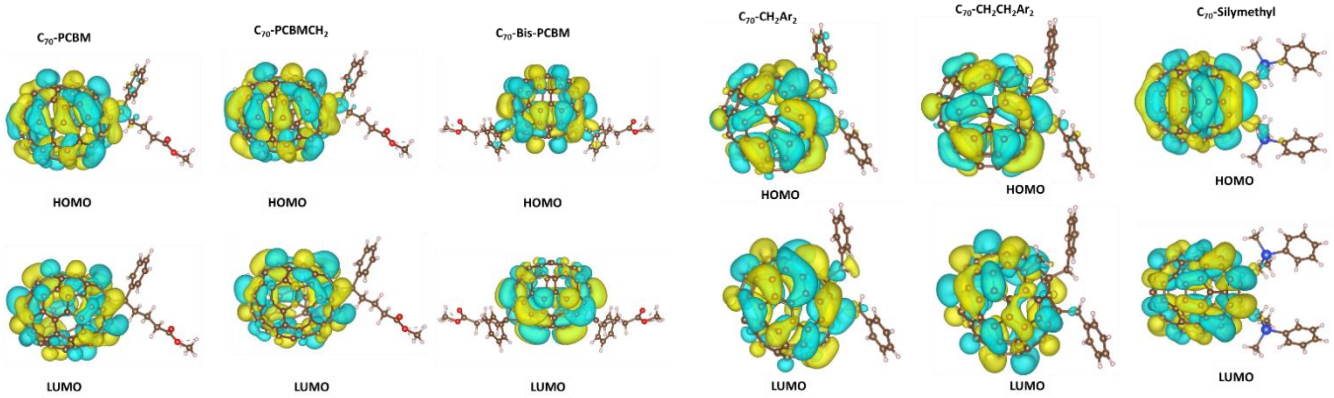


Figure S34. The HOMO and LUMO of PCBM, $PCBMCH_2$, Bis-PCBM, CH_2Ar_2, $CH_2CH_2Ar_2$ and Silymethyl addends with C70 core.

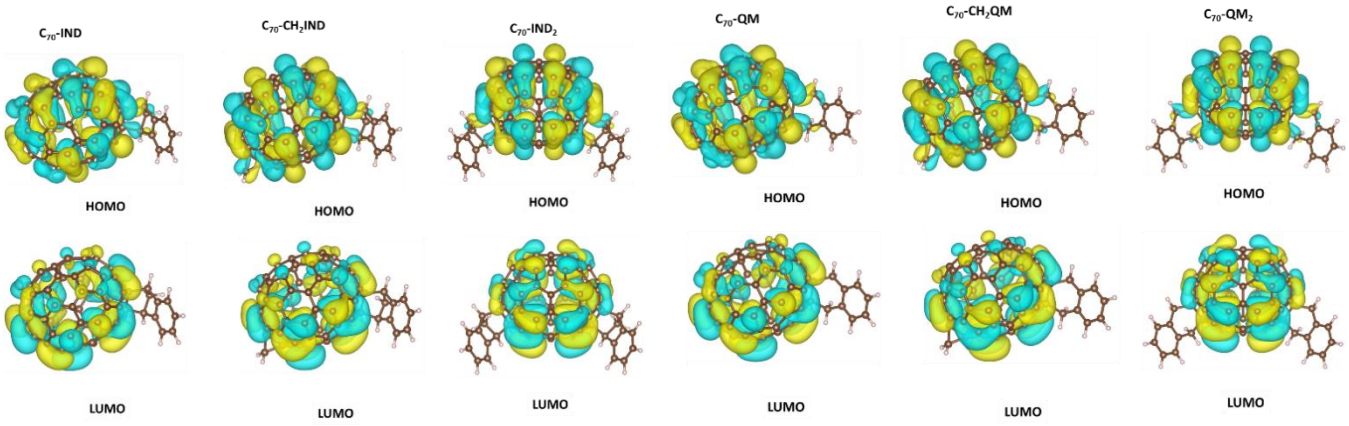


Figure S35. The HOMO and LUMO of IND, CH_2IND, IND_2, QM, CH_2QM and QM_2 addends with C70 core.

8. The crystal structure and the lattice constants of all the fullerene derivatives studied in the manuscript.

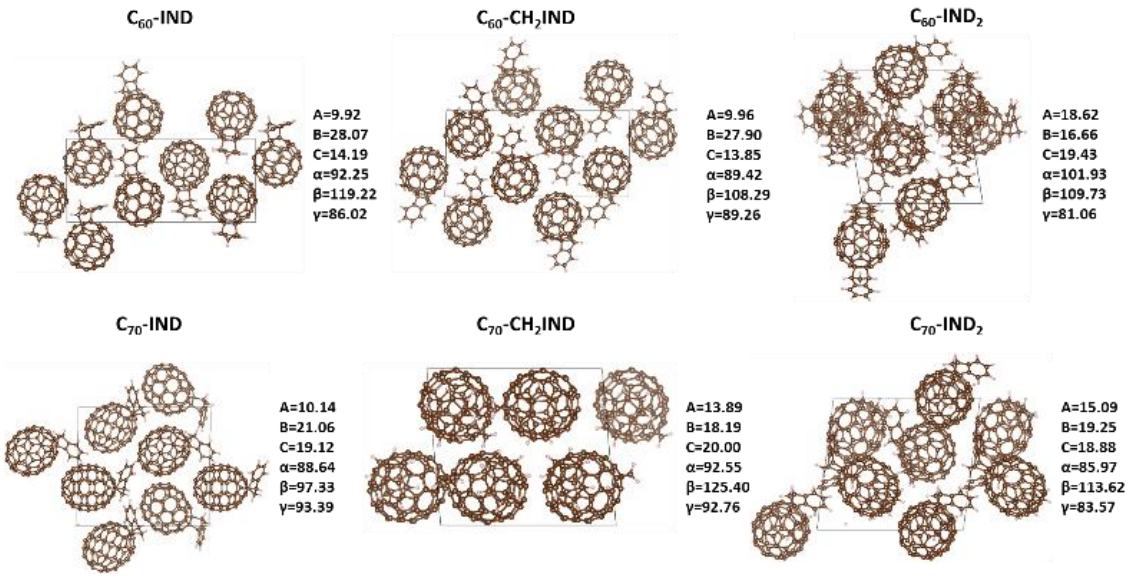


Figure S36. The crystal (unit cell) structure and the lattice constants for IND, CH_2IND and IND_2 addends with both the C60 and C70 core.

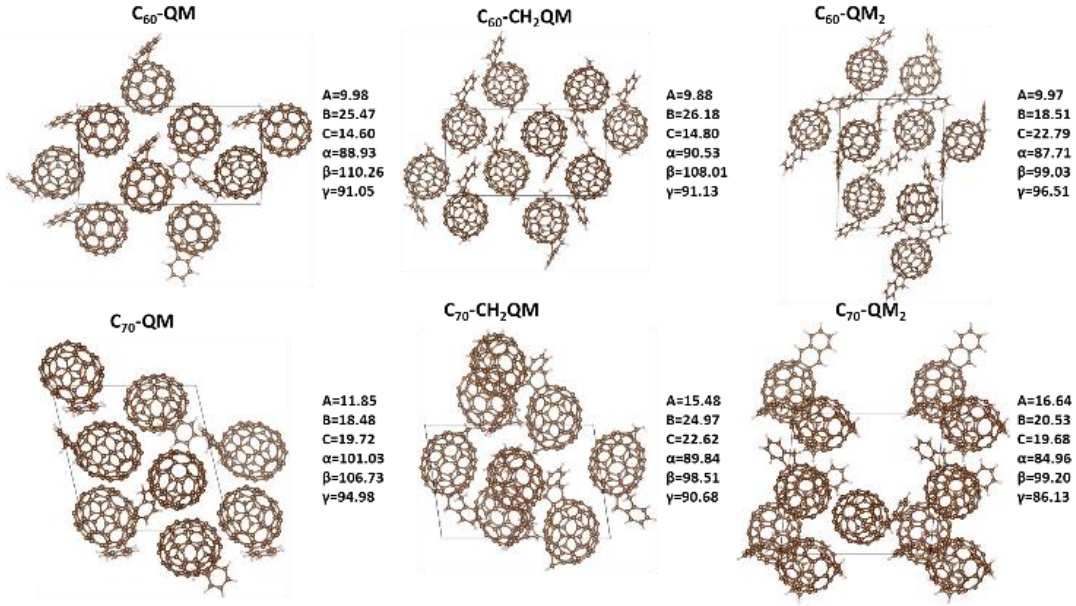


Figure S37. The crystal (unit cell) structure and the lattice constants for QM, CH_2QM and QM_2 addends with both the C60 and C70 core.

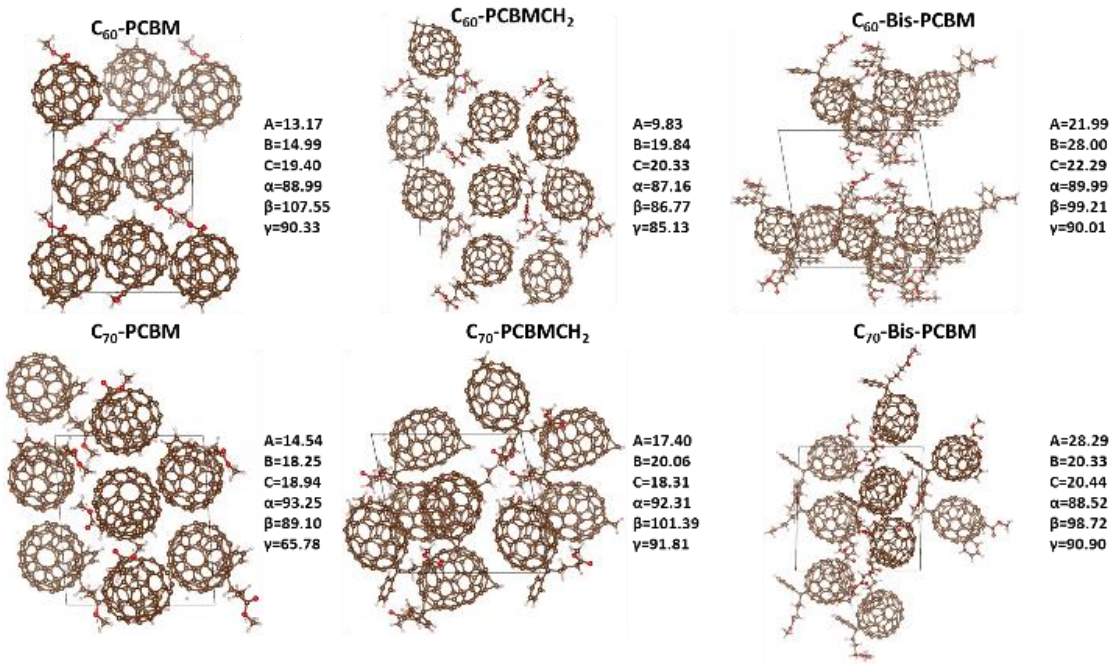


Figure S38. The crystal (unit cell) structure and the lattice constants for PCBM, CH_2PCBM and Bis-PCBM addends with both the C60 and C70 core.

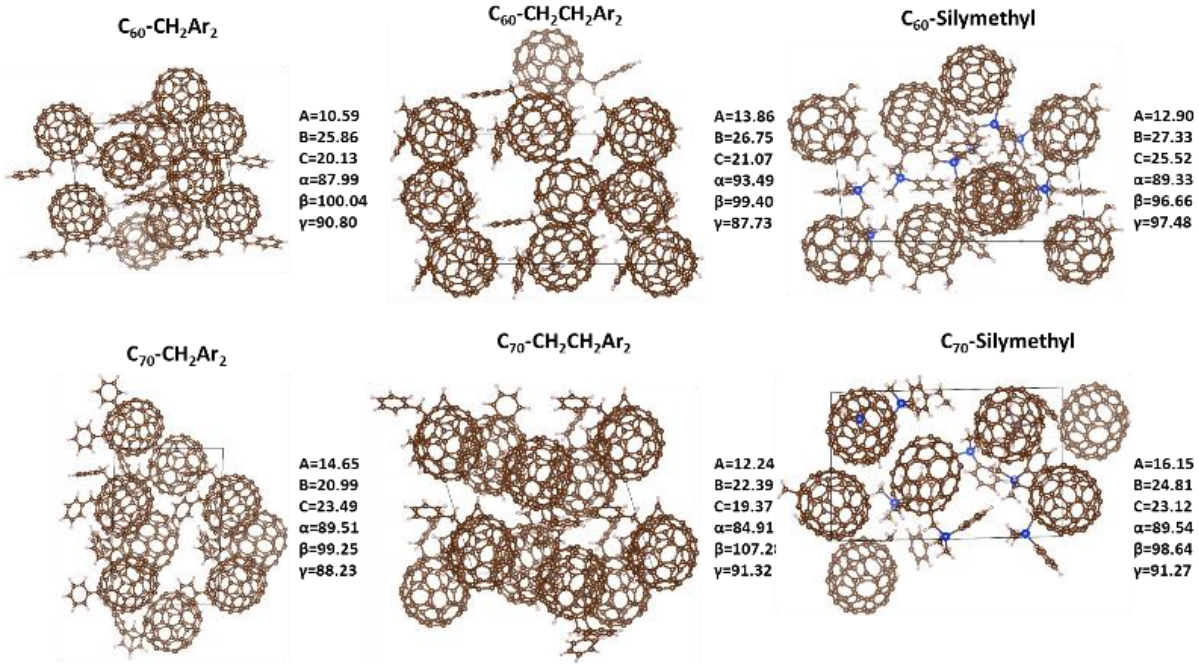


Figure S39. The crystal (unit cell) structure and the lattice constants for CH_2Ar_2, $CH_2CH_2Ar_2$ and silymethyl addends with both the C60 and C70 core.

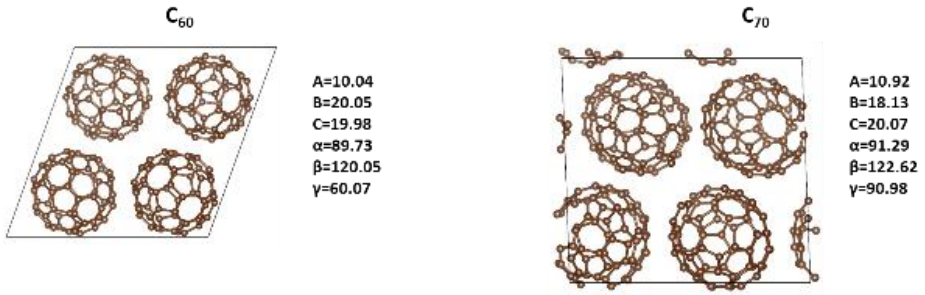


Figure S40. The crystal (unit cell) structure and the lattice constants for C60 and C70 fullerene.