Electronic Supplementary Information (ESI) of

Superhalogen inside fullerenes X@C_{2n} (X = BO_2, BeF_3; 2n = 60, 70)

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Content

Table S1 The encapsulation energies (kcal/mol) of $X@C_{60}$ and $X@C_{70}$ (X = BO_2, BeF_3, BF_4, LiF_2, NO_3) calculated at PBE-D3(zero) level.

	BO_2	BeF_3	BF_4	LiF_2	NO_3
C_{60}	**-7.0**	**-56.8**	12.8	17.9	--
C_{70}	**-45.3**	**-52.4**	-48.1	-48.9	8.3

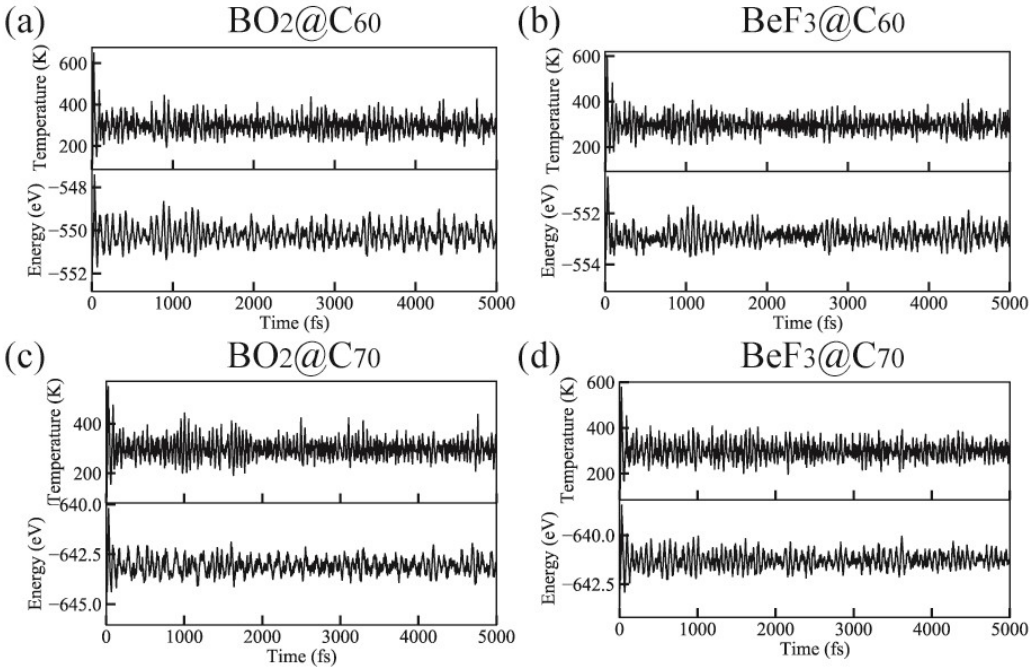

Fig. S1 Fluctuation of total potential energy and temperature of (a) $BO_2@C_{60}$, (b) $BeF_3@C_{60}$, (c) $BO_2@C_{70}$, and (d) $BeF_3@C_{70}$ complex during the AIMD simulation at 300 K.

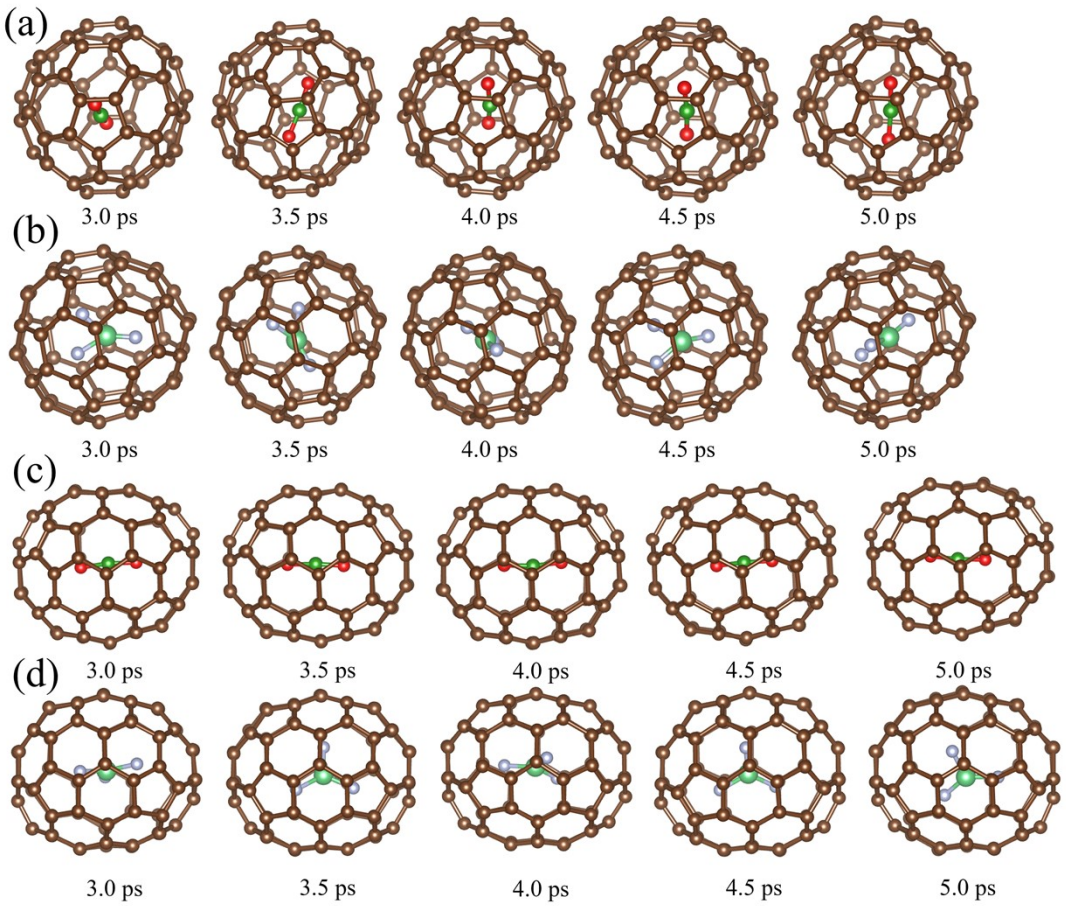

Fig. S2 The snapshot structure at 3.0 ps ~ 5.0 ps for (a) $BO_2@C_{60}$, (b) $BeF_3@C_{60}$, (c) $BO_2@C_{70}$ and (d) $BeF_3@C_{70}$ during the AIMD simulation at 300 K.

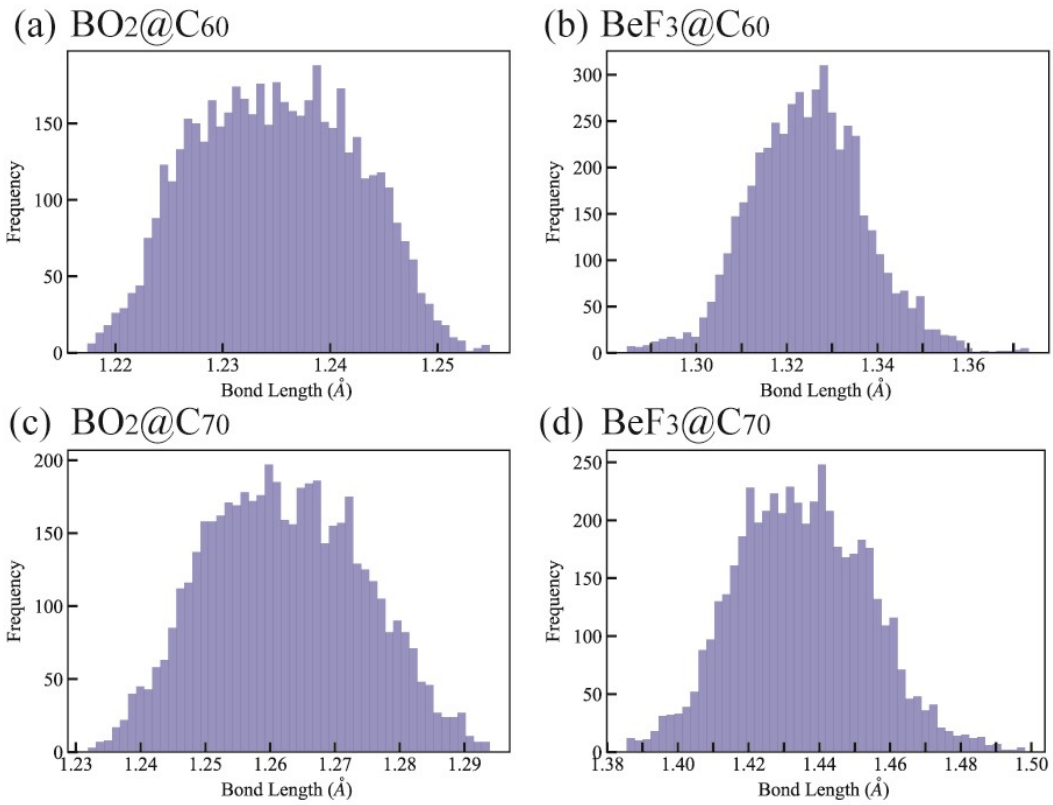

Fig. S3 (a) The B–O bond length distributions for $BO_2@C_{60}$, (b) the Be–F bond length distributions for $BeF_3@C_{60}$, (c) the B–O bond length distributions for $BO_2@C_{70}$, and (d) the Be–F bond length distributions for $BeF_3@C_{70}$ complex during the AIMD simulation at 300 K.

Table S2 The NBO and QTAIM charges ($|e^{-}|$) of superhalogen in the complexes, the Wiberg bond order *P* and the bond length *d* (Å) for B–O and Be–F bond obtained at the ωB97XD/TZ2P//ωB97XD/def2-TZVP level.

Complexes	Atom	Q(X)NPA	Q(X)AIM	P(B–O)	*P*(Be–F)	*d*(B–O)	*d*(Be–F)
BO_2	B	1.11	2.29	1.45		*1.258*	
	O	−0.56	−1.15	1.45		*1.258*	
	O	−0.56	−1.15				
BeF_3	Be	1.73	1.76		0.23		*1.389*
	F	−0.86	−0.86		0.14		*1.530*
	F	−0.44	−0.45		0.14		*1.530*
	F	−0.44	−0.45				
BO_2^-	B	1.11	2.30	1.45		*1.259*	
	O	−1.05	−1.65	1.45		*1.259*	
	O	−1.05	−1.65				
BeF_3^-	Be	1.72	1.76		0.17		*1.483*
	F	−0.91	−0.92		0.17		*1.483*
	F	−0.91	−0.92		0.17		*1.483*
	F	−0.91	−0.92				
$BO_2@C_{60}$	B	1.56	2.30	1.16		*1.221*	
	O	−1.29	−1.60	1.16		*1.221*	
	O	−1.29	−1.60				
$BeF_3@C_{60}$	Be	1.78	1.74		0.10		*1.365*
	F	−0.95	−0.91		0.10		*1.368*
	F	−0.95	−0.89		0.10		*1.368*
	F	−0.95	−0.90				
$BO_2@C_{70}$	B	1.30	2.32	1.34		*1.251*	
	O	−1.15	−1.61	1.34		*1.251*	
	O	−1.15	−1.60				
$BeF_3@C_{70}$	Be	1.76	1.75		0.13		*1.411*
	F	−0.93	−0.90		0.12		*1.429*
	F	−0.93	−0.90		0.13		*1.429*
	F	−0.93	−0.89				

Table S3 Calculated Electron Density and its Laplacian at the Bond Critical Point of the superhalogens. (All the Quantities are in a.u.)

	Isolated		**In C_{60}**		**In C_{70}**	
Superhalogen	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$\rho(r_c)$	$\nabla^2\rho(r_c)$
BO_2	0.2879486	1.182678	0.3120965	1.411586	0.2904327	1.201068
	0.2879485	1.182679	0.3121055	1.411697	0.290401	1.200747
BeF_3	0.1458025	1.166818	0.1510395	1.308987	0.1246373	1.009768
	0.08939327	0.6823115	0.149979	1.295308	0.13173	1.090542
	0.08939327	0.6823115	0.1500051	1.293365	0.1245666	1.008866
BO_2^-	0.2831167	1.147832				
	0.2831167	1.147832				
BeF_3^-	0.1066436	0.8128306				
	0.1064915	0.8113143				
	0.1064915	0.8113143				

Table S4 Calculated Electron Density and Laplacian of Electron Densities for BO_2 and BeF_3 encapsulated C_{60} and C_{70} at Bond Critical Point (BCP)**.**

BCP	**BO_2@C_{60}**			**BeF_3@C_{60}**	
	$\rho(r_c)$	$\nabla^2\rho(r_c)$		$\rho(r_c)$	$\nabla^2\rho(r_c)$
1	0.02730935	0.1261491	1	0.03262463	0.1650219
2	0.02686009	0.1243469	2	0.03260767	0.1649477
3	0.02687295	0.124393	3	0.03455546	0.1718149
4	0.02733373	0.1262457	4	0.0246587	0.1194284
			5	0.03059264	0.1533274
			6	0.03055286	0.1531621

	BO_2@C_{70}			**BeF_3@C_{70}**	
	$\rho(r_c)$	$\nabla^2\rho(r_c)$		$\rho(r_c)$	$\nabla^2\rho(r_c)$
1	0.0103137	0.04534308	1	0.0181594	0.0894681
2	0.01040412	0.04576176	2	0.01914713	0.09109866
3	0.01035883	0.04577179	3	0.01958082	0.09327319
4	0.0104441	0.04592899	4	0.01773343	0.08434358
5	0.01030795	0.04532053	5	0.02729897	0.1335843
6	0.01020926	0.04510525			
7	0.01041595	0.04581569			
8	0.01041299	0.04580288			
9	0.01047702	0.04611701			
10	0.01045374	0.0460203			

Table S5 EDA results at the ωB97XD/TZ2P//ωB97XD/def2-TZVP level level of $X@C_{2n}$ ($X = BO_2$, BeF_3; 2n = 60, 70) using different fragments with various electronic states (S = Singlet, D = Doublet). Energies are in kcal/mol. The best bonding model is given by the smallest absolute ΔE_{orb} value in bold format.

Complex	Model	Fragments	ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{disp}	ΔE_{orb}
$BO_2@C_{60}$	A	BO_2^- (S) + C_{60}^+ (D)	−105.3	136.7	−172.0	−32.4	−**37.6**
	B	BO_2 (D) + C_{60} (S)	−73.6	102.8	−45.3	−32.4	−98.8
$BeF_3@C_{60}$	A	BeF_3^- (S) + C_{60}^+ (D)	−74.3	203.9	−195.5	−35.5	−**47.2**
	B	BeF_3 (D) + C_{60} (S)	−66.8	171.6	−68.1	−35.5	−134.8
$BO_2@C_{70}$	A	BO_2^- (S) + C_{70}^+ (D)	−136.5	40.4	−119.6	-30.7	−**26.7**
	B	BO_2 (D) + C_{70} (S)	−104.4	27.31	−15.3	−30.7	−85.7
$BeF_3@C_{70}$	A	BeF_3^- (S) + C_{70}^+ (D)	−111.2	98.2	−143.1	−34.5	−**32.9**
	B	BeF_3 (D) + C_{70} (S)	−114.4	80.9	−34.8	−34.5	−126.0

Table S6 Bader charges (|e⁻|) of X and C_{60} in X@C_{60} calculated at PBE-D3(zero) level via VASP software.

	Q(Li)	Q(C_{60})	Q(BO_2)	Q(C_{60})	Q(BeF_3)	Q(C_{60})
Li@C_{60}	+0.88	−0.88				
BO_2@C_{60}			−0.84	+0.84		
BeF_3@C_{60}					−0.97	+0.97
BO_2@C_{60}-Li@C_{60}	+0.87	−0.49	−0.81	+0.43		
BeF_3@C_{60}-Li@C_{60}	+0.84	−0.28			−1.01	+0.45

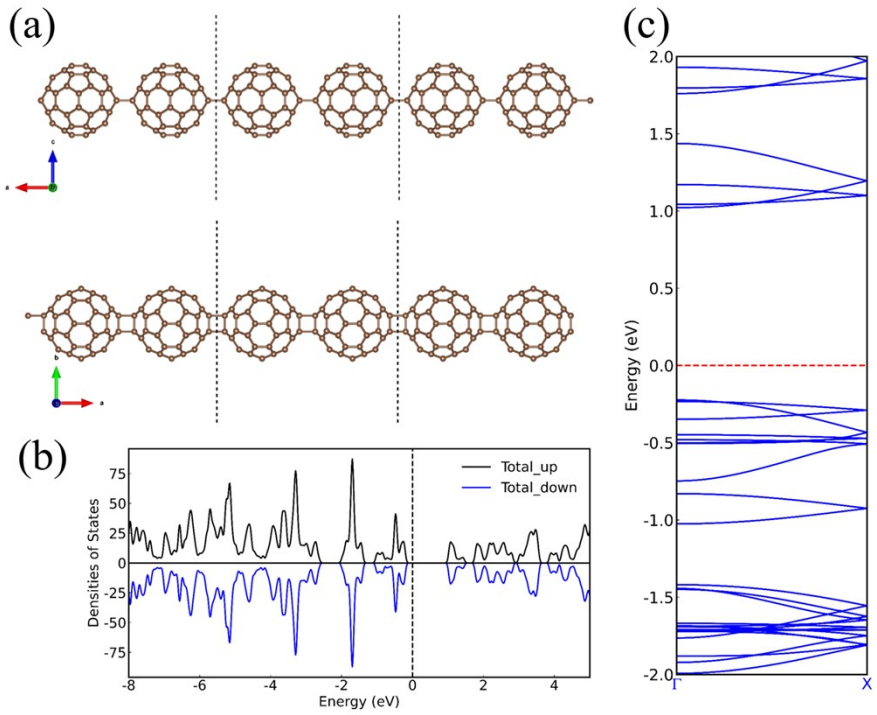

Fig. S4 (a) Geometry structure (side and top view), (b) the total densities of states, and (c) band structure of 1D C_{60} nanowire.