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

Site and chirality selective chemical modifications of boron nitride nanotubes (BNNTs) via Lewis acid/base interactions

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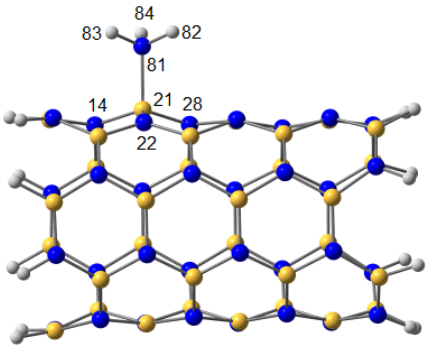
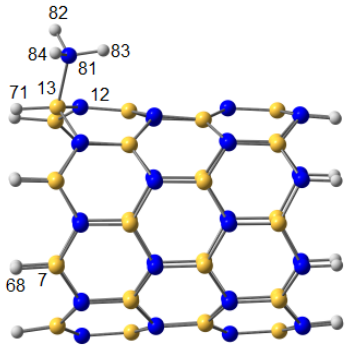
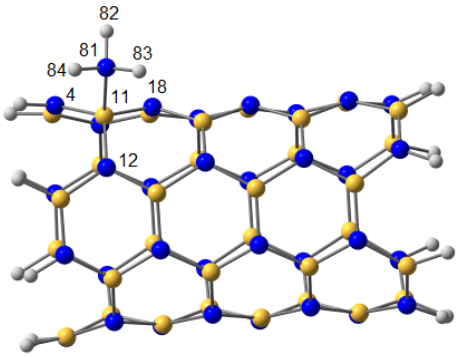
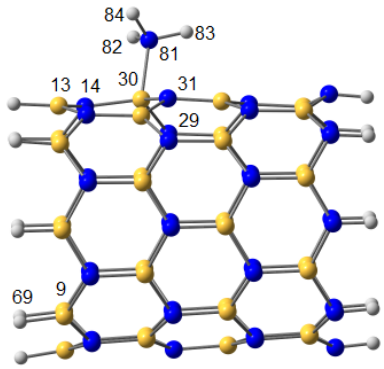
Table S1. Comparison of B3LYP/6-31G* and B3LYP/6-31+G* adsorption energies of BNNT-NH_3 and BNNT-BH_3 (see Figure 1-4 for structures). All energies are in kcal/mol.

	E_{ad}	
(4,4)-BNNT-NH_3	6-31G*	6-31+G*
1A	9.86	7.58
1B	9.70	7.64
1C	9.65	7.49
1D	9.34	7.20
(8,0)-BNNT-NH_3		
2A	16.60	14.03
2B	10.18	7.68
2C	9.72	7.28
2D	3.25	1.29
(4,4)-BNNT-BH_3		
3A	22.96	21.05
3B	10.57	9.28
3C	10.04	8.39
3D	9.20	7.85
(8,0)-BNNT-BH_3		
4A	17.06	15.80
4B	17.01	15.53
4C	9.71	8.04
4D	9.25	7.71

Table S2. Bond distances and changes in distances (δR) of BH_3 adsorbed BN-nanotubes at the adsorption sites as well as at their neighbors. All distances are in Å.

Bond distance (R)							
Name of the System	6-31+G* (BSSE)	6-31+G* (δR)	6-31G* (δR)	Name of the System	6-31+G* (BSSE)	6-31+G* (δR)	6-31G* (δR)
(4,4)-BNNT-NH_3(1A) 				(8,0)-BNNT-NH_3(2A) 			
N81-H84	1.021	-0.001	0.000	N81-H84	1.020	-0.001	-0.001
N81-H83	1.021	-0.001	-0.001	N81-H83	1.023	-0.001	-0.001
N81-H82	1.021	-0.001	-0.001	N81-H82	1.020	0.001	0.002
B21-N81	1.724	0.006	0.000	N81-B13	1.691	0.007	0.005
B21-N14	1.526	0.000	0.003	B13-N12	1.534	0.000	0.001
B21-N28	1.518	0.000	0.002	B13-H71	1.204	0.001	0.001
B21-N22	1.530	0.000	0.002	H68-B7	1.192	0.000	0.000
(4,4)-BNNT-NH_3(1B) 				(8,0)-BNNT-NH_3(2B) 			
N81-H84	1.021	-0.001	-0.001	N81-H84	1.021	0.000	0.000
N81-H83	1.022	-0.001	0.000	N81-H83	1.023	0.000	0.000
N81-H82	1.021	-0.001	0.000	N81-H82	1.021	-0.001	0.000
B11-N81	1.727	0.010	0.001	N81-B30	1.725	0.009	0.005
B11-N4	1.510	0.000	0.004	B30-N31	1.525	0.000	0.001
B11-N18	1.517	0.000	0.001	B30-N14	1.513	0.000	0.002
B11-N12	1.535	-0.001	0.002	H69-B9	1.193	0.001	0.000

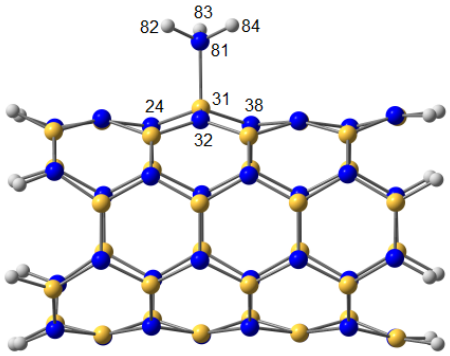
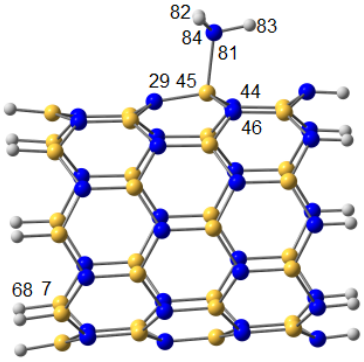
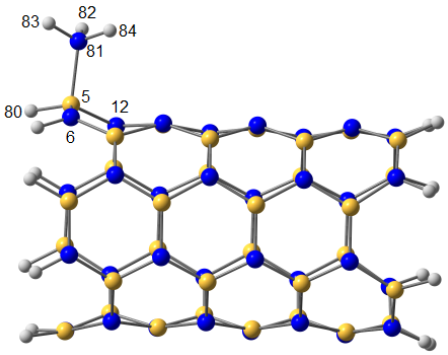
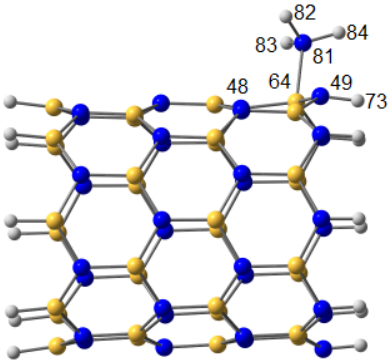
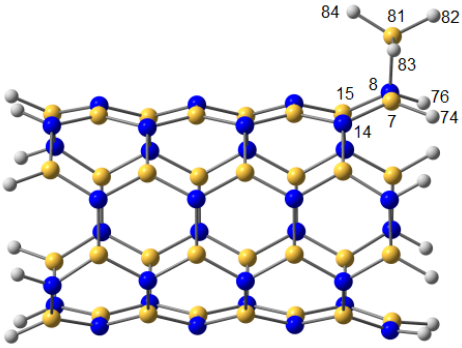
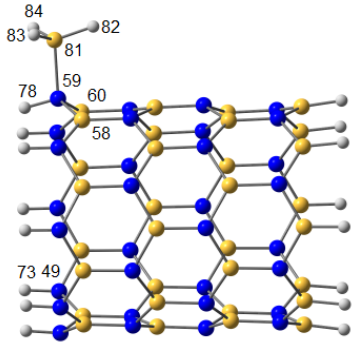
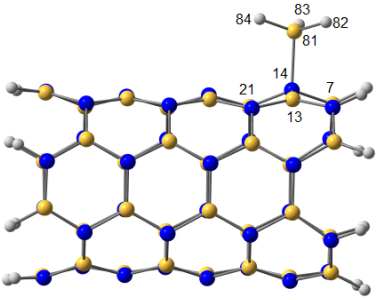
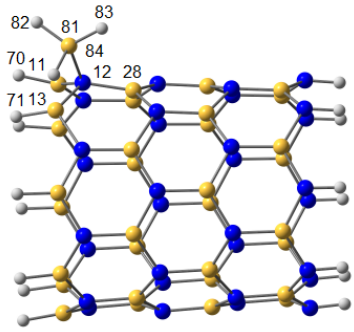
(4,4)-BNNT-NH_3(1C)				(8,0)-BNNT-NH_3(2C)			
							
N81-H84	1.021	-0.001	-0.001	N81-H84	1.020	-0.001	-0.001
N81-H83	1.021	-0.001	0.000	N81-H83	1.024	-0.001	-0.001
N81-H82	1.021	-0.001	-0.001	N81-H82	1.020	-0.001	-0.001
B31-N81	1.733	0.010	0.003	N81-B45	1.724	0.009	0.006
B31-N24	1.516	-0.001	0.001	B45-N46	1.527	-0.001	0.001
B31-N38	1.516	0.000	0.002	B45-N29	1.508	0.000	0.002
B31-N32	1.526	0.000	0.002	H68-B7	1.193	0.001	0.000
(4,4)-BNNT-NH_3(1D)				(8,0)-BNNT-NH_3(2D)			
							
N81-H84	1.022	-0.001	-0.001	N81-H84	1.021	0.000	0.000
N81-H83	1.020	-0.001	0.000	N81-H83	1.020	0.001	0.001
N81-H82	1.021	-0.001	0.000	N81-H82	1.020	-0.001	-0.001
B5-N81	1.724	0.010	0.004	N81-B64	1.789	0.056	0.003
B5-N80	1.213	0.000	0.000	B64-N48	1.506	-0.001	0.001
B5-N12	1.524	-0.001	0.001	B64-N80	1.513	-0.001	0.007
B5-N6	1.510	0.000	0.003	N80-H73	1.016	0.000	0.000

Table S3. Bond distances and changes in distances (δR) of BH_3 adsorbed BN-nanotubes at the adsorption sites as well as at their neighbors. All distances are in Å.

Bond distance(R)							
Name of the System	6-31+G* (BSSE)	6-31+G* (δR)	6-31G* (δR)	Name of the System	6-31+G* (BSSE)	6-31+G* (δR)	6-31G* (δR)
(4,4)-BNNT-BH_3(3A) 				(8,0)-BNNT-BH_3(4A) 			
B81-H84	1.194	0.001	0.001	B81-H84	1.212	0.000	0.001
B81-H83	1.197	0.001	0.001	B81-H83	1.212	0.000	0.001
B81-H82	1.326	-0.001	-0.001	B81-H82	1.207	0.000	0.001
N8-B81	1.585	0.002	0.003	N59-B81	1.740	0.004	0.002
B7-H74	1.196	0.000	0.000	N59-B60	1.503	0.000	0.001
B7-B14	1.493	0.000	0.001	N59-B58	1.503	0.000	0.001
N8-H76	1.015	0.000	0.000	N59-H78	1.019	0.000	0.001
N8-B15	1.484	0.000	0.000	N49-H73	1.015	0.000	0.001
B7-N8	1.590	0.002	0.002	-	-	-	-
(4,4)-BNNT-BH_3(3B) 				(8,0)-BNNT-BH_3(4B) 			
B81-H84	1.204	0.003	0.002	B81-H84	1.315	-0.001	-0.001
B81-H83	1.210	0.000	0.000	B81-H83	1.196	0.000	0.001
B81-H82	1.208	0.000	-0.001	B81-H82	1.195	0.001	0.001
N14-B81	1.804	0.008	0.010	N12-B81	1.610	0.002	0.004
N14-B7	1.500	0.000	0.002	N12-B11	1.610	0.003	0.004
N14-B21	1.501	0.000	0.002	H71-B13	1.192	0.000	0.000
N14-B13	1.501	0.000	0.002	N12-B28	1.488	0.000	0.000
-	-	-	-	H70-B11	1.187	0.000	0.000
-	-	-	-	N12-B13	1.606	0.000	0.000

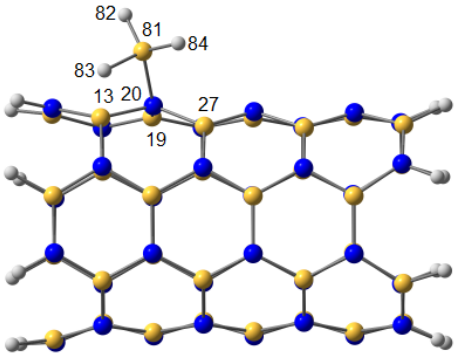
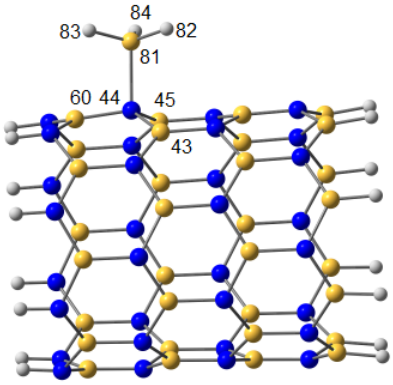
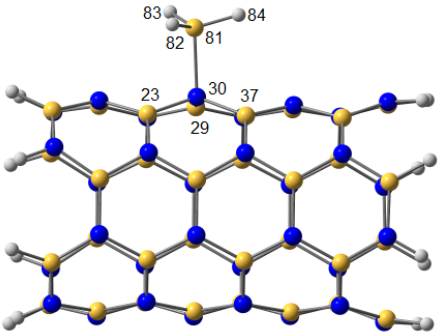
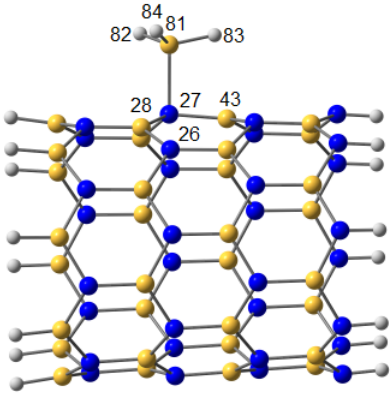
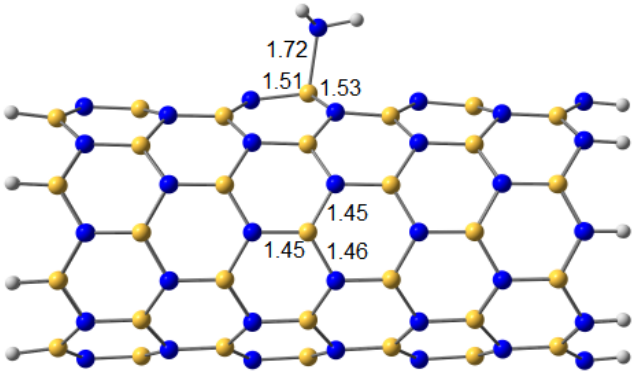
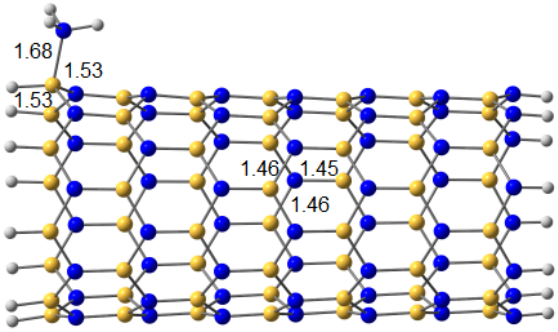
(4,4)-BNNT-BH_3(3C)				(8,0)-BNNT-BH_3(4C)			
							
B81-H84	1.201	0.000	0.001	B81-H84	1.209	0.000	0.000
B81-H83	1.299	0.000	0.001	B81-H83	1.209	0.000	0.000
B81-H82	1.195	0.001	0.001	B81-H82	1.204	0.001	0.001
N20-B81	1.629	0.002	0.004	N44-B81	1.808	0.008	0.014
N20-B13	1.557	0.000	0.001	N44-B60	1.490	0.000	0.002
N20-B27	1.501	0.000	0.0	N44-B43	1.499	-0.001	0.002
N20-B19	1.506	0.000	0.001	N44-B45	1.499	0.000	0.001
(4,4)-BNNT-BH_3(3D)				(8,0)-BNNT-BH_3(4D)			
							
B81-H84	1.202	0.000	0.000	B81-H84	1.205	0.002	0.002
B81-H83	1.206	0.000	0.000	B81-H83	1.216	0.003	0.002
B81-H82	1.209	0.000	0.000	B81-H82	1.204	-0.002	-0.002
N30-B81	1.828	0.008	0.015	N27-B81	1.783	-0.004	0.002
N30-B37	1.494	-0.001	-0.002	N27-B26	1.495	0.000	0.001
N30-B23	1.497	-0.001	0.004	N27-B43	1.489	0.001	0.001
N30-B29	1.498	0.000	-0.001	N27-B28	1.495	0.000	0.001

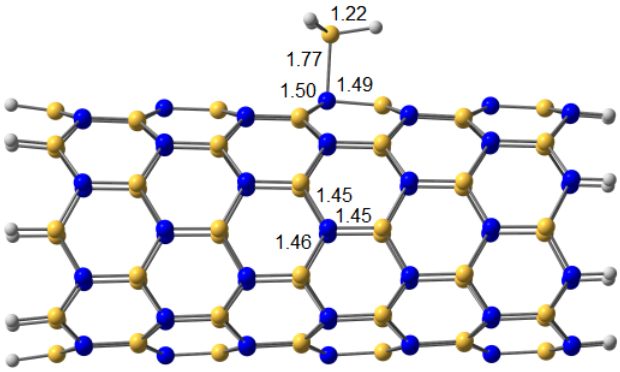
Fig. S4. B3LYP/6-31+G* optimized structures of L-(8, 0)-BNNT-NH_3/BH_3. Blue, yellow and grey colors represent N, B and H atoms, respectively. m and e stand for middle and edge site respectively. Bond lengths are in Å. BSSE corrected adsorption energies (in kcal/mol) are given in parenthesis and a positive value indicates attractive interaction between two units,



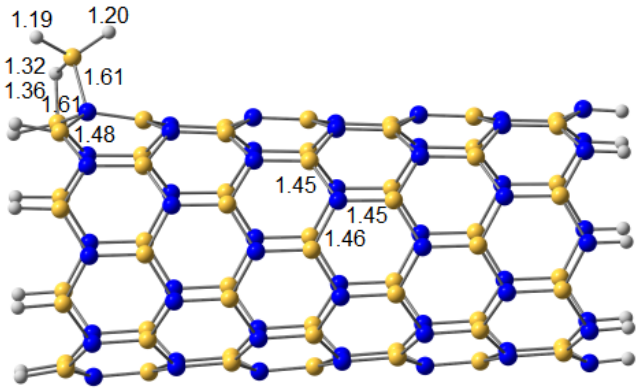
L-(8,0)-BNNT-NH3-m (**4.2**)



L-(8,0)-BNNT-NH3-e (**11.9**)

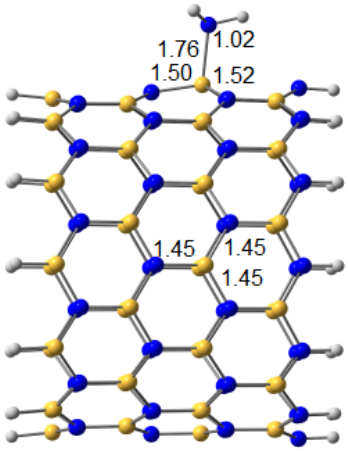


L-(8,0)-BNNT-BH3-m (**6.9**)

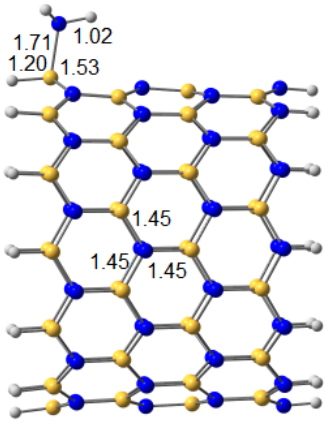


L-(8,0)-BNNT-BH3-e (**14.2**)

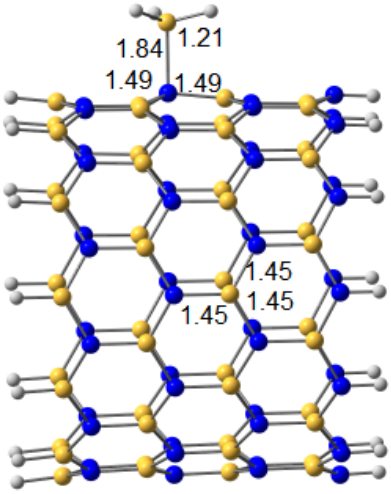
Fig. S5. B3LYP/6-31+G* optimized structures of (12, 0)-BNNT-NH_3/BH_3. Blue, yellow and grey colors represent N, B and H atoms, respectively. m and e stand for middle and edge site respectively. Bond lengths are in Å. BSSE corrected adsorption energies (in kcal/mol) are given in parenthesis and a positive value indicates attractive interaction between two units,



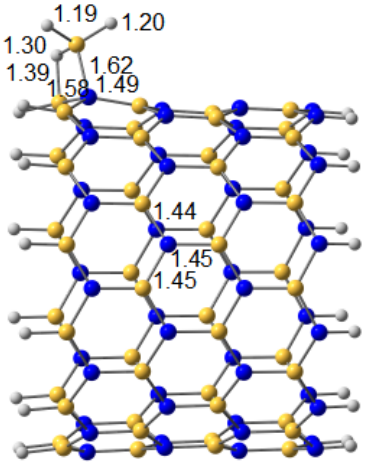
(12,0) BNNT-NH3-m (**1.3**)



(12,0) BNNT-NH3-e (**6.9**)



(12,0) BNNT-BH3-m (**4.4**)



(12,0) BNNT-BH3-e (**9.7**)

Fig. S6. Hybridization angle (ϕ in degree) of BH_3 (sp^2), NH_3 (sp^3) and H_3BNH_3.(sp^3). The dummy atom (pink) is used to show angles.

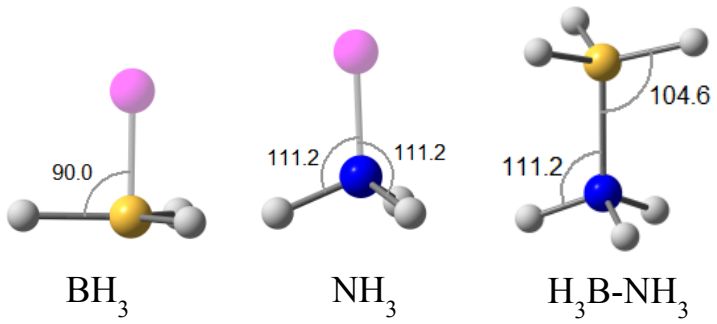


Fig. S7. Approximate hybridization angles (ϕ in degree) of B (Lewis acid centers) and N (Lewis base centers) sites in (4,4) and (8,0) BNNTs, The dummy atom (pink) is used to show angles.

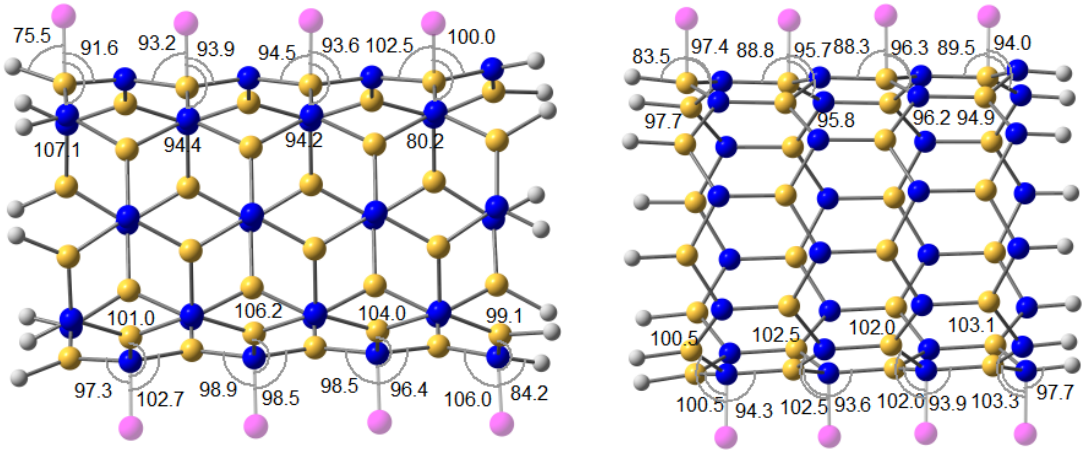
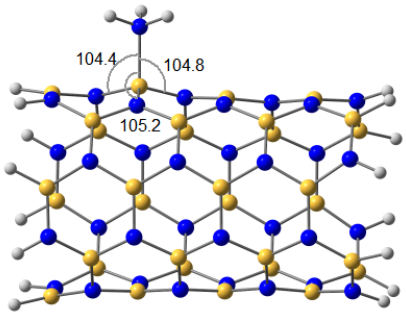
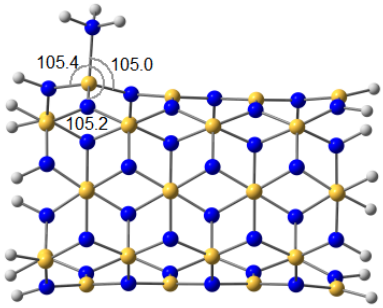


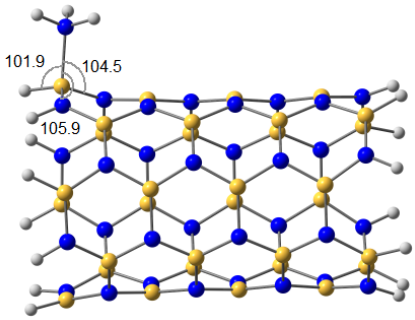
Fig. S8. Hybridization angles (ϕ in degree) of BNNT-NH_3 complexes.



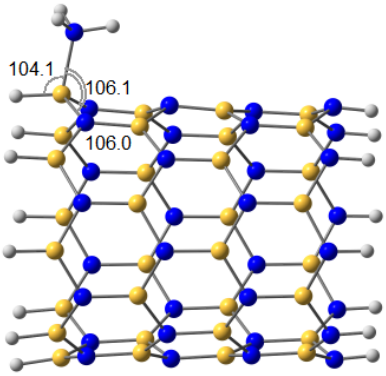
(4,4)-BNNT-NH_3 (1A)
Middle site



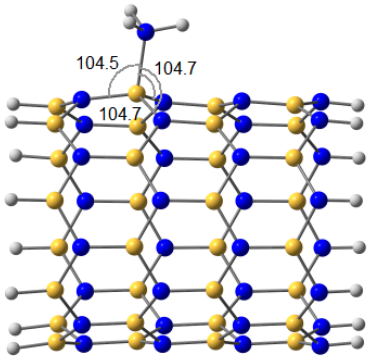
(4,4)-BNNT-NH_3 (1B)
Near the edge site



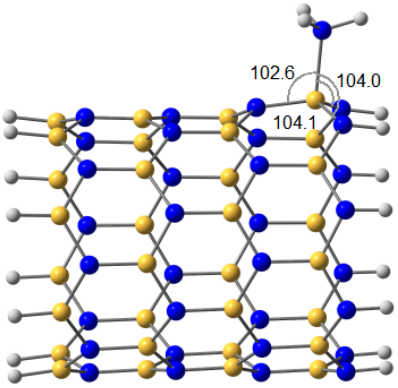
(4,4)-BNNT-NH_3 (1D)
Edge site



(8,0)-BNNT-NH_3 (2A)
Edge site

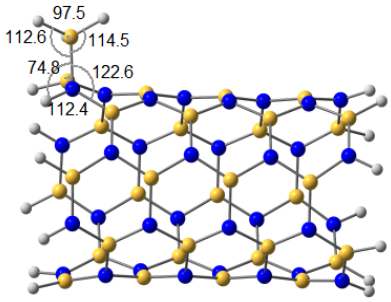


(8,0)-BNNT-NH_3 (2B)
Middle site

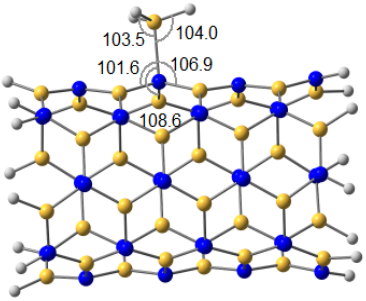


(8,0)-BNNT-NH_3 (2D)
Near the edge site

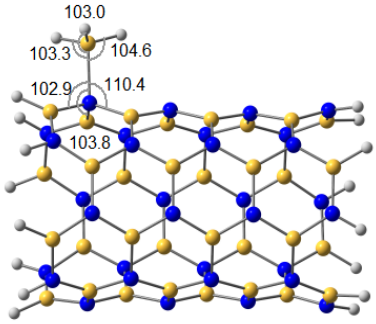
Fig. S9. Hybridization angles (ϕ in degree) of BNNT-BH_3 complexes.



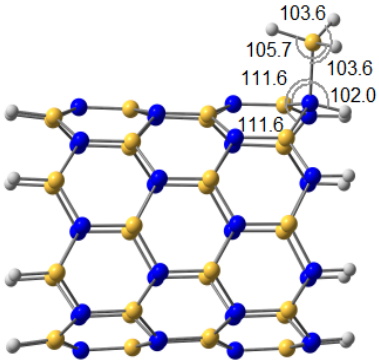
(4,4)-BNNT-BH_3
(3A)



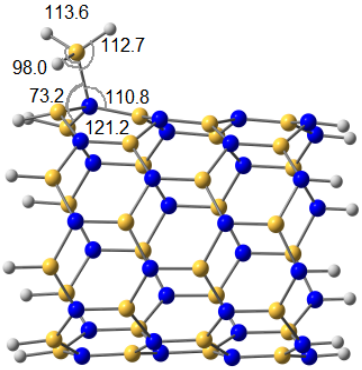
(4,4)-BNNT-BH_3
(3B)



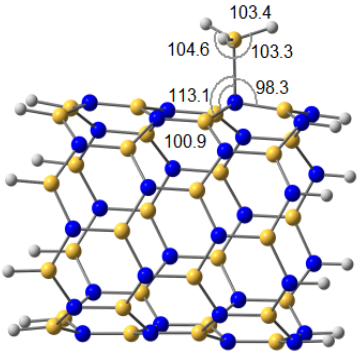
(4,4)-BNNT-BH_3
(3D)



(8,0)-BNNT-BH_3
(4A)



(8,0)-BNNT-BH_3
(4B)



(8,0)-BNNT-BH_3
(4C)

Fig. S10. Natural bond orbitals (NBO) of B-N and B-H-B 3c-2e bonds of most stable BNNT-NH_3/BH_3 complexes. NBO representing multi-center B-H-B bond of B_2H_6 are shown in the last diagram.

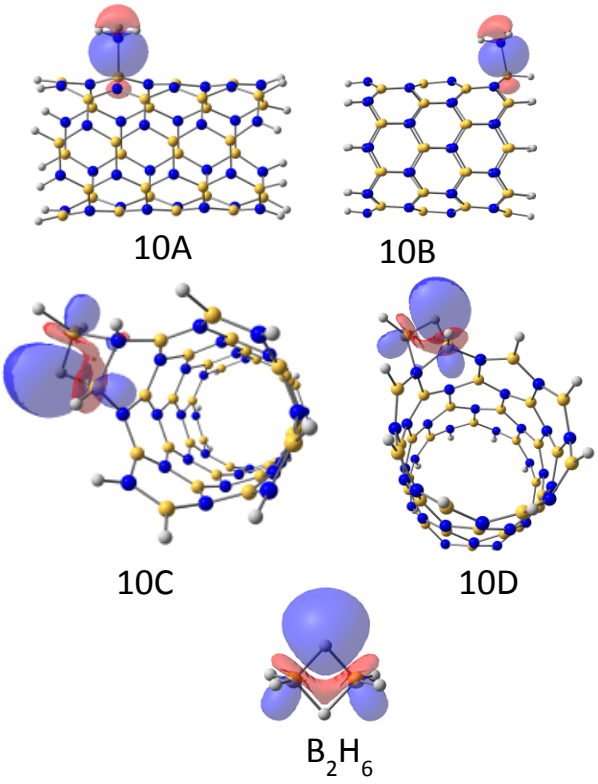
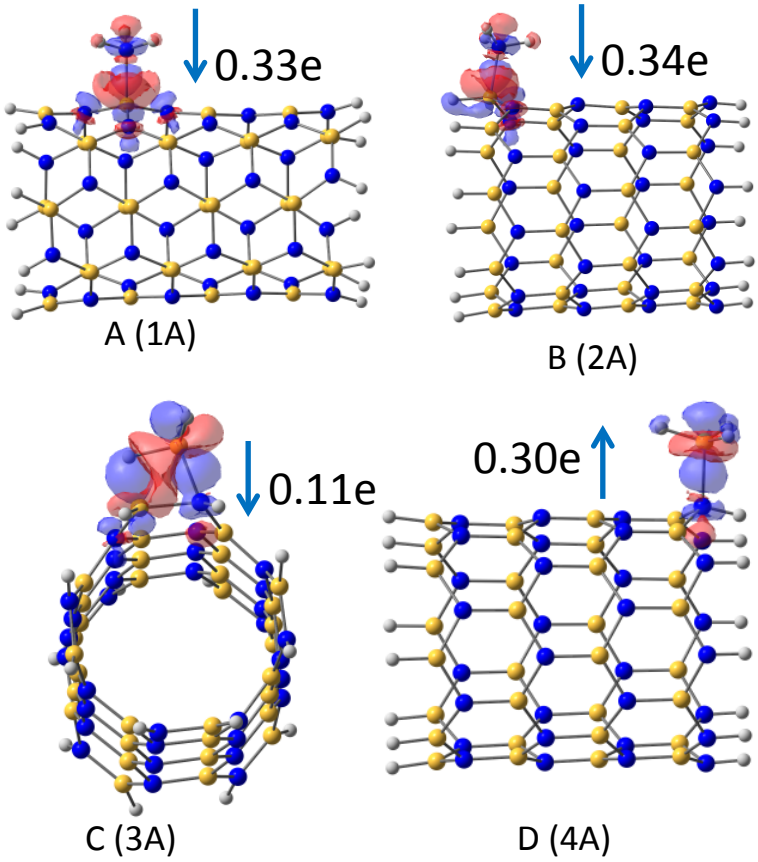


Fig. S11. Density difference plots of most stable BNNT-NH_3/BH_3 structures. Blue and red regions indicate gain and loss of electron density, respectively, upon complex formation. Contour value is 0.005 au. Electron transfer from or to BNNTs are shown by arrow with number of electron.



Density difference plots clearly indicate charge gain (blue) or loss (red) is localized in the vicinity of the active site only. In all complexes, electron density builds between B and N atoms of host and guest, indicated by blue region and some gain is also noted on nitrogen of NH_3 in 1A and 2A. However, boron of BH_3 in 3A and 4A loses some density. Formation of 3c-2e bond in 3A (also in 4B, not shown) causes gain in density between H(BH_3) and B(NT), while weakening of H_2B-H bond is reflected by the loss of density.

Table S12. Electron exchange between BN-nanotubes and NH_3/BH_3 in complexes. Natural (NPA) group charges are obtained from B3LYP/6-31G* calculations.

(4,4)-BNNT-NH_3		(8,0)-BNNT-NH_3	
1A	$NH_3 \xrightarrow{0.33\,e}$ (4,4) BNNT	2A.	$NH_3 \xrightarrow{0.34\,e}$ (8,0)BNNT
1B	$NH_3 \xrightarrow{0.32\,e}$ (4,4) BNNT	2B	$NH_3 \xrightarrow{0.33\,e}$ (8,0)BNNT
1C	$NH_3 \xrightarrow{0.33\,e}$ (4,4)BNNT	2C	$NH_3 \xrightarrow{0.33\,e}$ (8,0)BNNT
1D	$NH_3 \xrightarrow{0.33\,e}$ (4,4)BNNT	2D	$NH_3 \xrightarrow{0.33\,e}$ (8,0)BNNT
(4,4)-BNNT-BH_3		(8,0)-BNNT-BH_3	
3A	$BH_3 \xleftarrow{0.11e}$ (4,4) BNNT	4A	$BH_3 \xrightarrow{0.30\,e}$ (8,0)*BNNT*
3B	$BH_3 \xrightarrow{0.26\,e}$ (4,4) BNNT	4B	$BH_3 \xleftarrow{0.14\,e}$ (8,0)BNNT
3C	$BH_3 \xleftarrow{0.10\,e}$ (4,4) BNNT	4C	$BH_3 \xrightarrow{0.22\,e}$ (8,0)*BNNT*
3D	$BH_3 \xrightarrow{0.23\,e}$ (4,4) BNNT	4D	$BH_3 \xrightarrow{0.19\,e}$ (8,0)*BNNT*

Fig. S13. B3LYP/6-31+G* optimized structures of H_3N-AlH_3 and corresponding BNNT-AlH_3. Bond lengths are in Å and angles are in degree. e and m stand for edge and middle adsorption sites of the tube, respectively. BSSE corrected adsorption energies (in kcal/mol) are given in bold and a positive value indicates attractive interaction between two units, otherwise interaction is repulsive. Electron transfer from or to BNNTs are shown by arrow with number of electron.

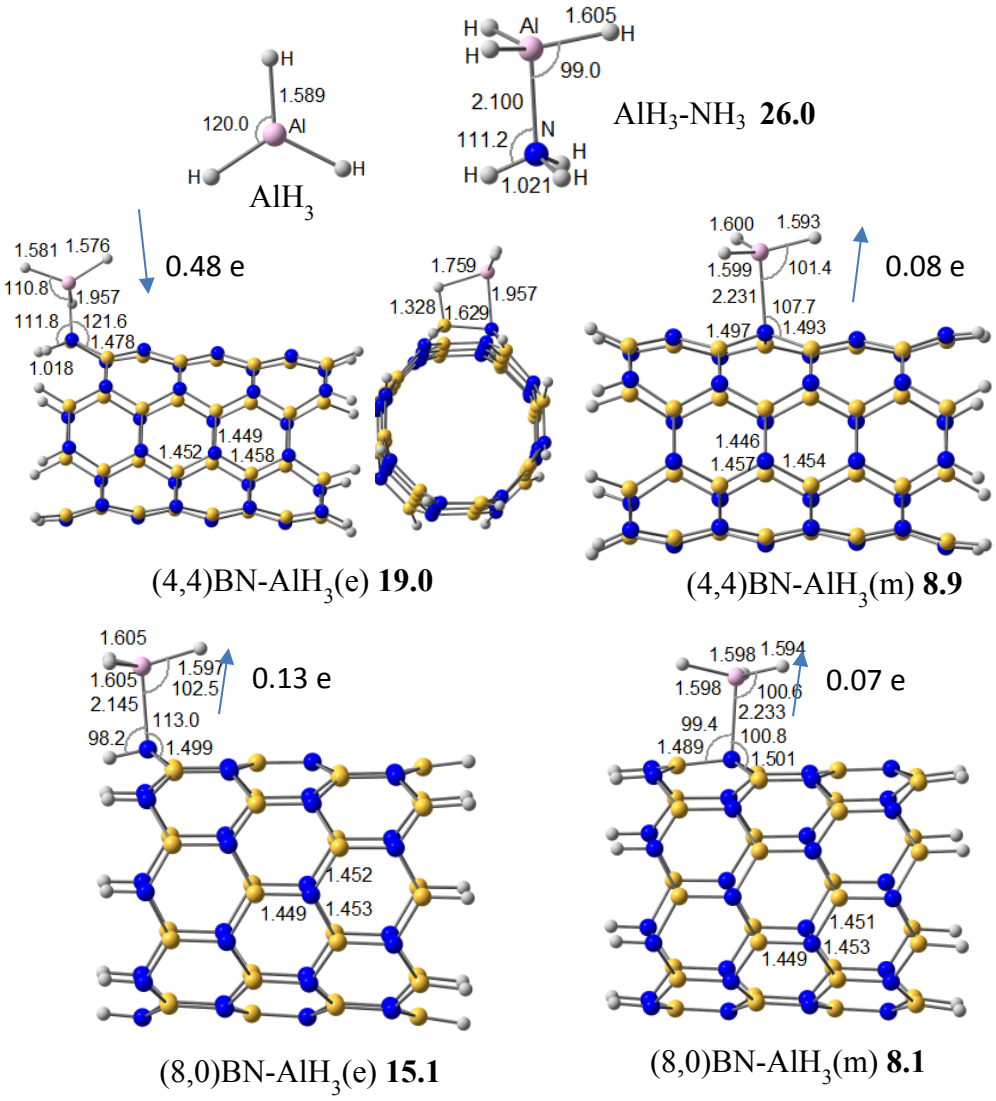


Fig. S14. B3LYP/6-31+G* optimized structures of H_3N-BF_3 and corresponding BNNT- BF_3. Bond lengths are in Å and angles are in degree. e and m stand for edge and middle adsorption sites of the tube, respectively. BSSE corrected adsorption energies (in kcal/mol) are given in bold and a positive value indicates attractive interaction between two units, otherwise interaction is repulsive. Electron transfer from or to BNNTs are shown by arrow with number of electron.

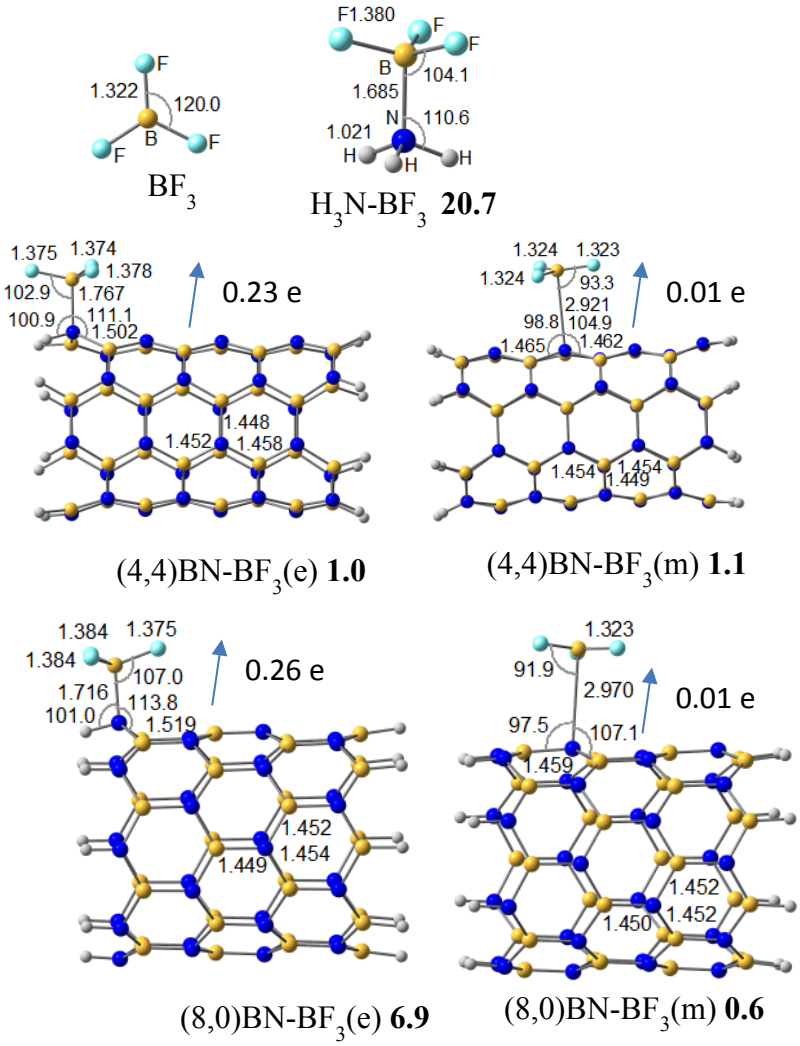


Fig. S15. B3LYP/6-31+G* optimized structures of H_3N- BCl_3 and corresponding BNNT- BCl_3. Bond lengths are in Å and angles are in degree. e and m stand for edge and middle adsorption sites of the tube, respectively. BSSE corrected adsorption energies (in kcal/mol) are given in bold and a positive value indicates attractive interaction between two units, otherwise interaction is repulsive. Electron transfer from or to BNNTs are shown by arrow with number of electron.

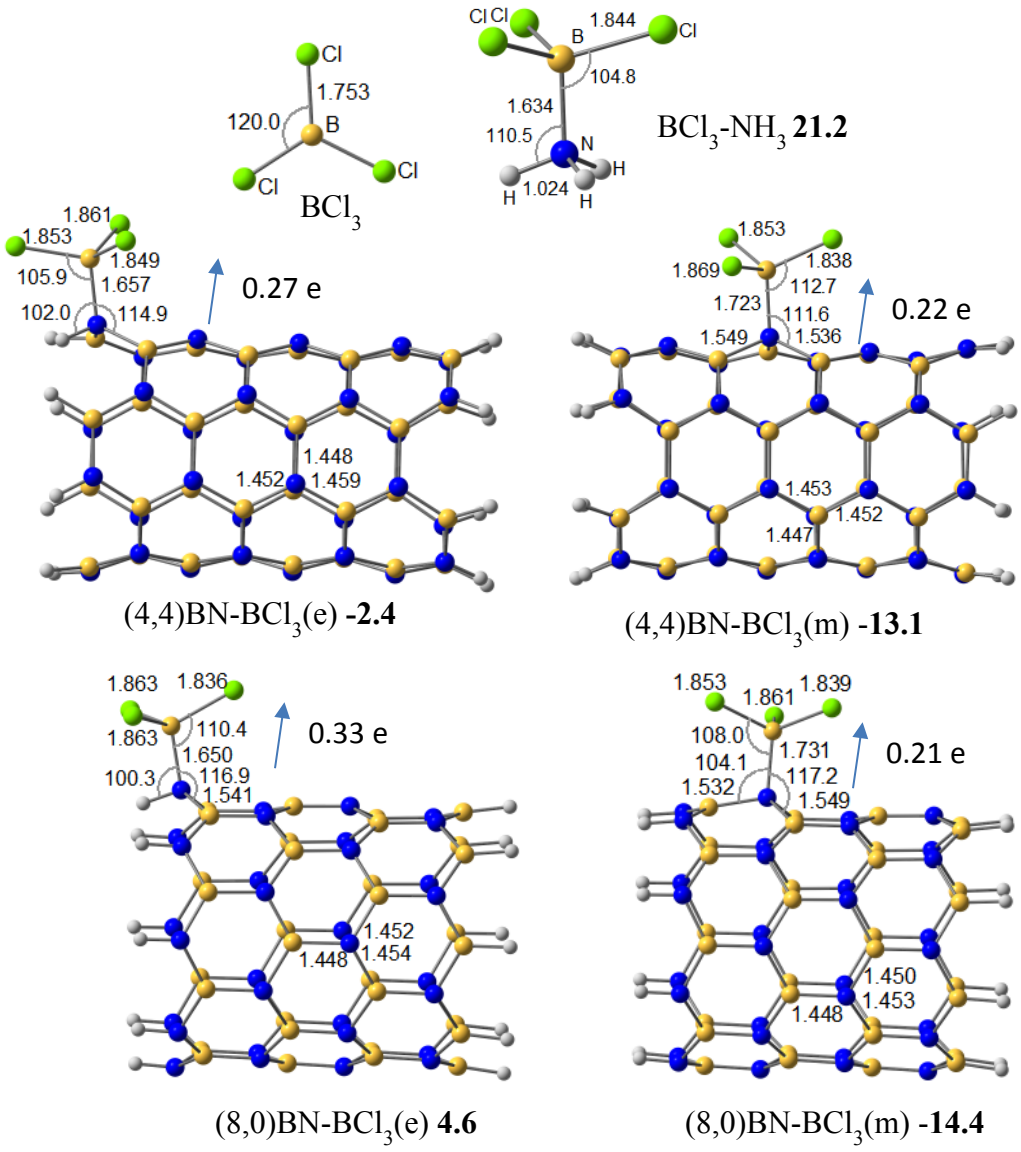
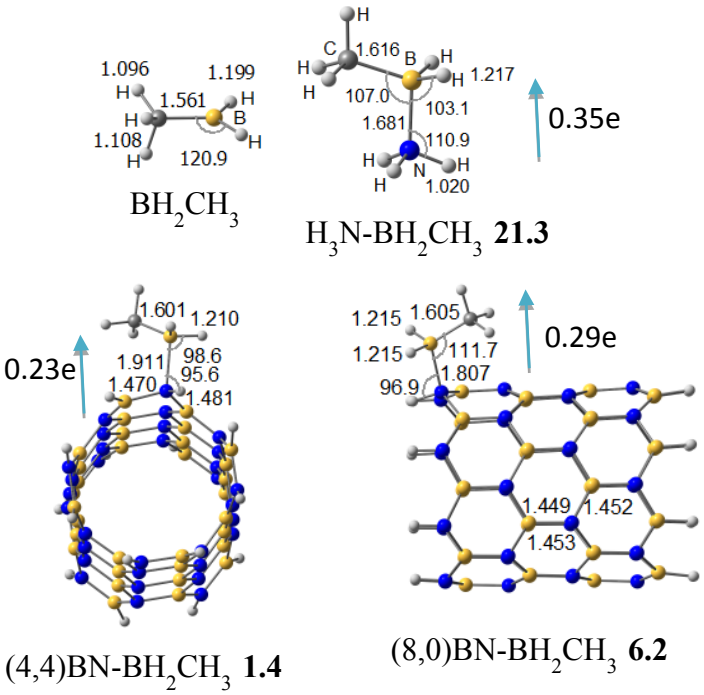


Fig. S16. B3LYP/6-31+G* optimized structures of H_3N-BH_2CH_3 and corresponding BNNT- BH_2CH_3. Bond lengths are in Å and angles are in degree. e and m stand for edge and middle adsorption sites of the tube, respectively. BSSE corrected adsorption energies (in kcal/mol) are given in bold and a positive value indicates attractive interaction between two units, otherwise interaction is repulsive. Electron transfer from or to BNNTs are shown by arrow with number of electron.



BH_2CH_3

H_3N-BH_2CH_3 **21.3**

(4,4)BN-BH_2CH_3 **1.4**

(8,0)BN-BH_2CH_3 **6.2**

Table-S17. Effects of BSSE correction on adsorption energies; non-corrected energy (E_{ad}) and CP-corrected adsorption energies ($E_{ad(CP)}$). All energies are in kcal/mol.

	BNNT as Lewis Base (LB)				Models	
	(4,4)		(8,0)		NH_3 as LB	
Lewis acids	E_{ad}	$E_{ad(CP)}$	E_{ad}	$E_{ad(CP)}$	E_{ad}	$E_{ad(CP)}$
BH_3 (e)	21.1	20.0	15.8	14.7	30.1	28.3
BH_3 (m)	9.3	8.3	8.0	7.0		
BF_3 (e)	3.9	1.0	10.1	6.9	23.6	20.7
BF_3 (m)	3.3	1.1	2.6	0.6		
BCl_3 (e)	0.8	2.4	8.2	4.6	24.3	21.2
BCl_3 (m)	-8.9	-13.1	-10.4	-14.4		
BH_2CH_3 (e)	2.7	1.4	7.7	6.2	23.3	21.3
AlH_3 (e)	20.7	19.0	16.8	15.1	27.7	26.0
AlH_3 (m)	10.8	8.9	9.9	8.1		
CH_3^+ (e)	110.5	109.2	115.4	113.8	112.2	109.8
CH_3^+ (m)	112.0	110.6	108.7	107.3		
Lewis base	BNNT as Lewis Acid (LA)				BH_3 as LA	
NH_3 (e)	7.2	4.6	14.0	11.4	30.1	28.3
NH_3 (m)	7.6	4.6	7.7	4.7		
NH_2CH_3 (e)	8.9	6.6	13.9	11.5	33.8	32.4
NH_2CH_3 (m)	9.6	6.7	10.0	7.1		
NH_2COOH					13.4	12.2
H-Bond						
NH_2COOH (e)	5.0	2.8	8.9	7.8	12.8	11.2
NH_2COOH (m)	5.0	4.1	4.0	2.0		
NH_2COOH (m1)			2.4	0.9		