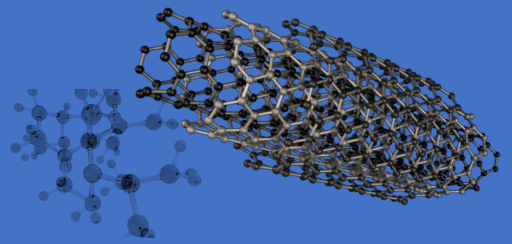
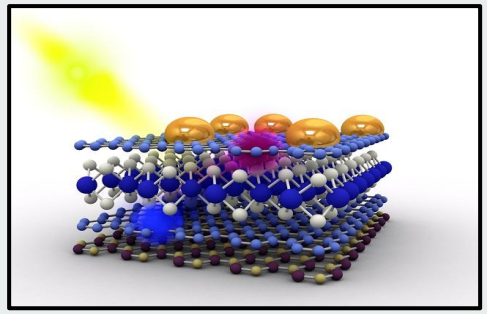


Study on the Organic Nanoparticles for Sustainable Energy Using Computational Simulations

Daniel Sung

Purpose and Objective



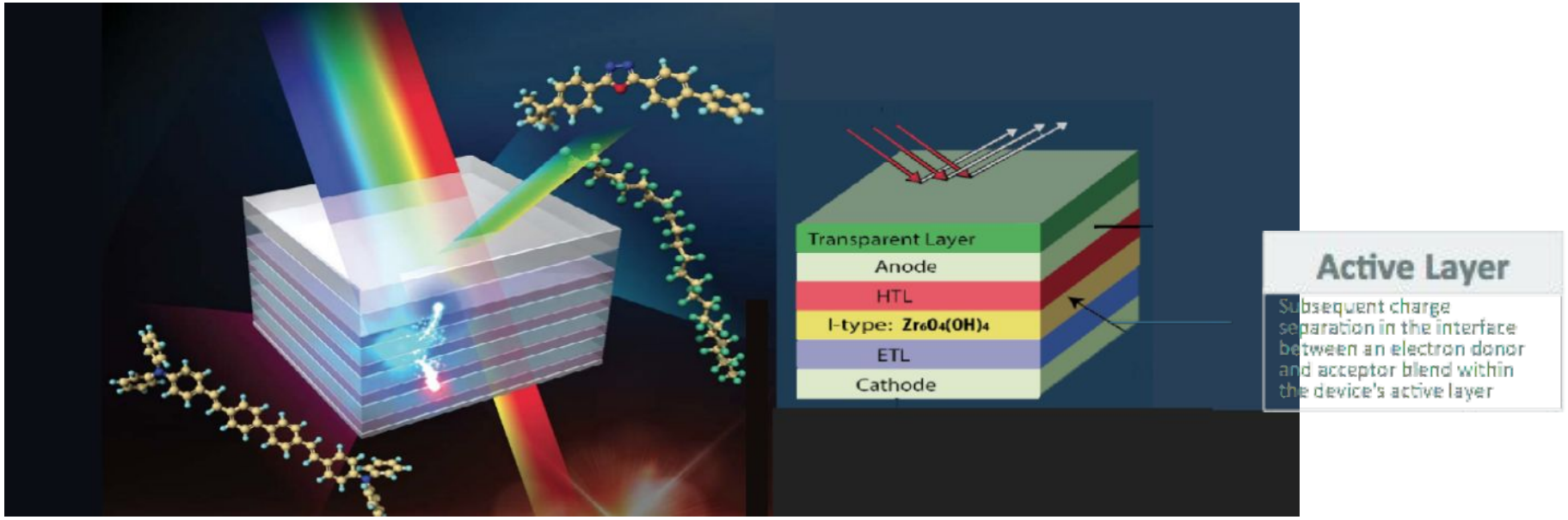
- **Examine current photovoltaic cells**

→ In the contemporary fuel cell technology, carbon-based nanomaterials display great potential to improve fuel efficiency and reduce the cost. However, their relatively low activity limits the development and application of photovoltaic cells.

- **Investigate possible nano composites using computational analysis**

→ Study capacitors and computationally construct CNT(carbon nanotube) with MOFs(metal–organic frameworks) composites to evaluate their thermodynamic and electrical efficiencies.

Photovoltaic Cell



Subsequent charge separation in the interface between an electron donor and acceptor blend within the device's active layer (Google image)

Electrical Potential of CNTs

(Past Research by Yakobson)

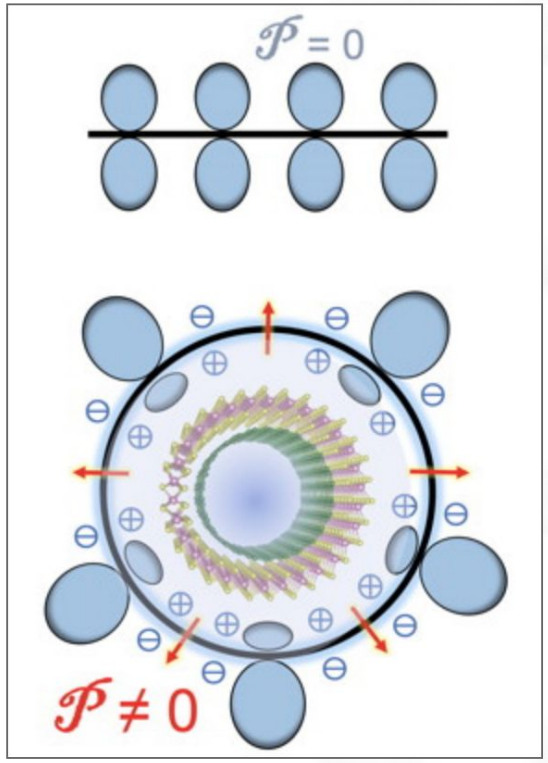
- Rice University theorists have calculated flexoelectric effects in double-walled carbon nanotubes.

→ The electrical potential (P) of atoms on either side of a graphene sheet (top) are identical, but not when the sheet is curved into a nanotube. Double-walled nanotubes (bottom) show unique effects as band gaps in inner and outer tubes are staggered. (Credit: Yakobson Research Group/Rice University)

- Double-walled carbon nanotubes(CNTs) have electro-optical advantages

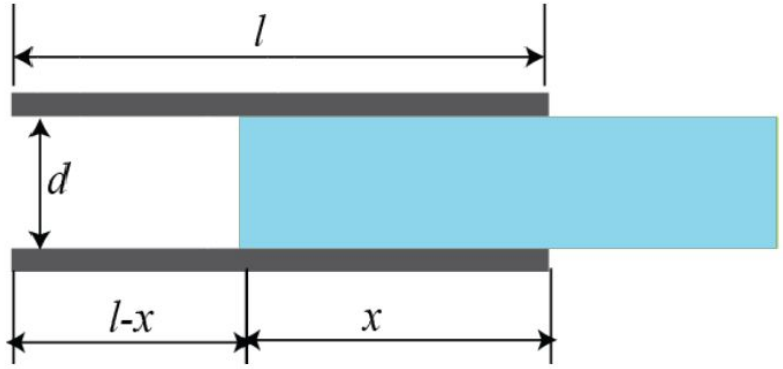
→ Rice University calculations show they could be highly useful for solar panels

(Houston, TX | Posted on March 27th, 2020)



(Houston, TX | Posted on March 27th, 2020)

A Plate Capacitor Filled with a Dielectric



A slab of width *d* and dielectric constant *K* is inserted at a distance *x* between the square parallel plates (of side *l*) of a capacitor as shown in Figure. Let's determine the capacitance and the energy stored as a function of *x*.

A Plate Capacitor Filled with a Dielectric

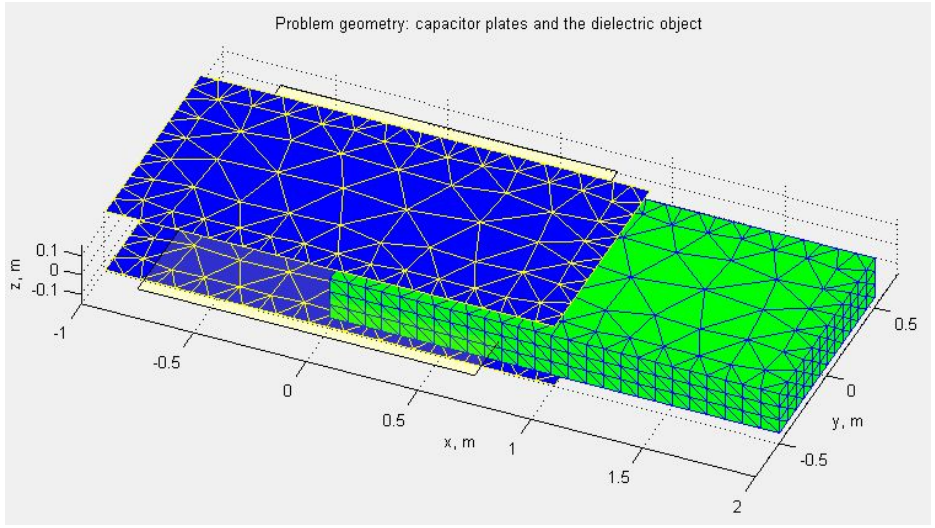
$$C = C_{air} + C_{dielectric}$$

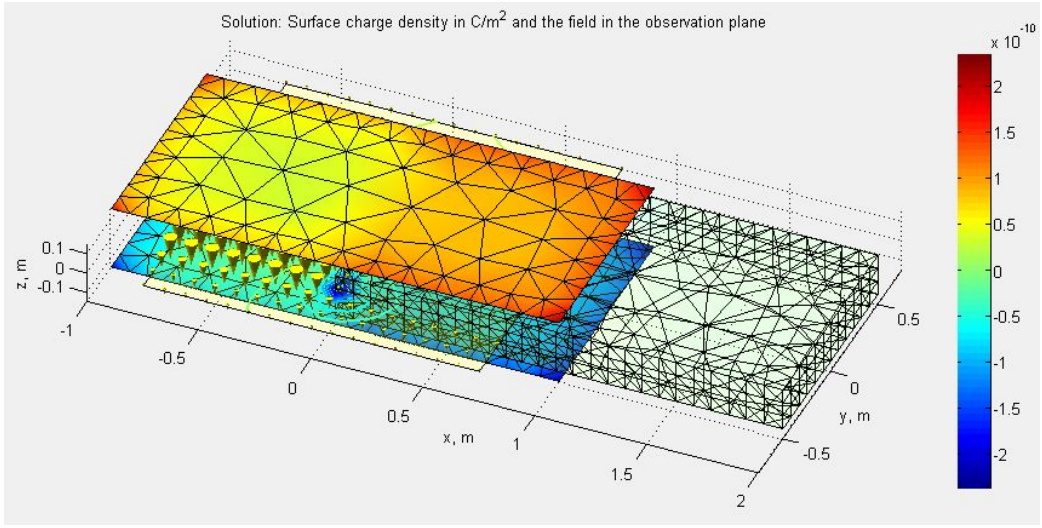
$$= \frac{\epsilon_0 l(l-x)}{d} + \frac{K\epsilon_0 l x}{d}$$

$$U = \frac{1}{2}CV_0^2 = (\frac{\epsilon_0 l^2 V_0^2}{2d})(1 + (K-1)(\frac{x}{l}))$$

A slab of width *d* and dielectric constant *K* is inserted at a distance *x* between the square parallel plates (of side *l*) of a capacitor as shown in Figure. Let's determine the capacitance and the energy stored as a function of *x.*

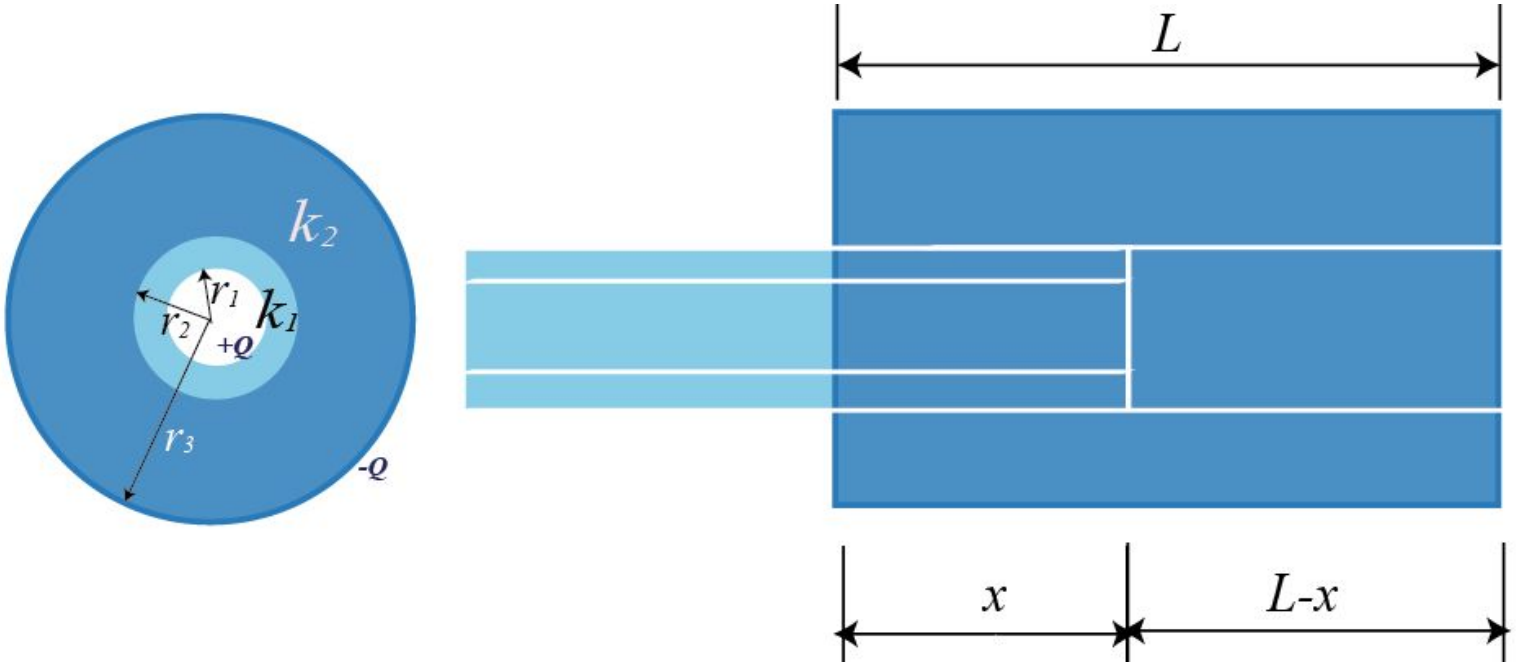
A Plate Capacitor Filled with a Dielectric





A capacitor inserted with a dielectric - Calculation of dC and dE of the capacitors as the distance inserted in the system changes

Cylindrical Shell Capacitor



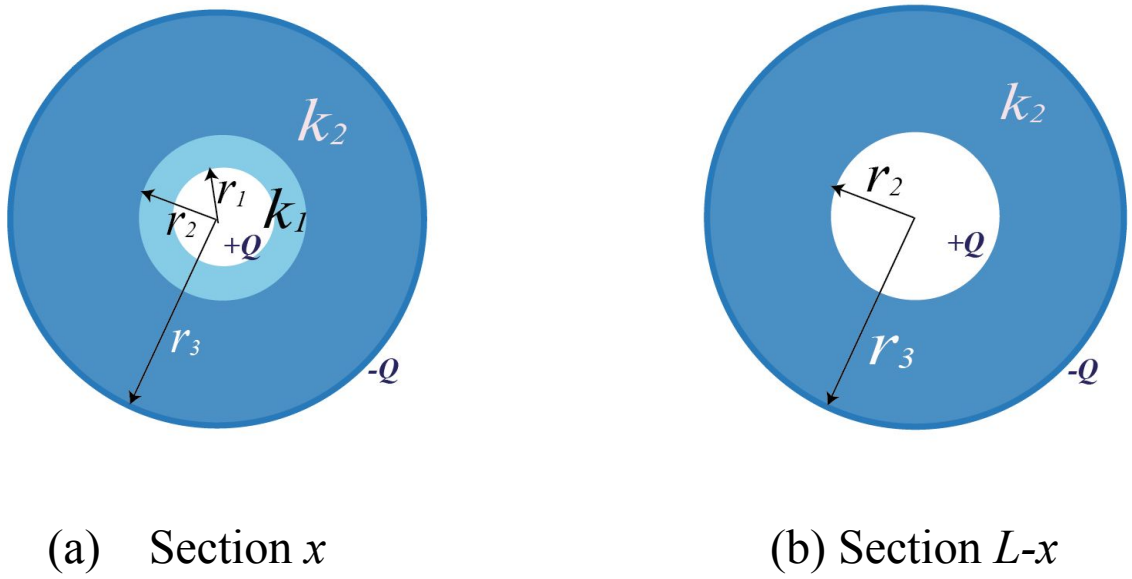
A thin-walled hollow cylinder capacitor filled with 2 dielectrics with concentric shells of radii r1, r2 and r3 respectively

A thin-walled hollow cylinder(k1) is concentric with a solid cylinder(k2) with radius ra<rb. Each has length L.

By changing the insertion distance x, the capacitance and the amount of charge stored in the system can be adjusted.

Let's find the capacitance as a function of x. expressing the capacitance in terms of r1, r2, r3 , k, L, x, epsilon and pi.

Cylindrical Shell Capacitor



(a) Section x (b) Section L-x

A thin-walled hollow cylinder capacitor filled with 2 dielectrics with concentric shells of radii r1, r2 and r3 respectively

Cylindrical Shell Capacitor

$$C = C_A + C_B$$

$$C = [\frac{k_2 ln\frac{r_2}{r_1} + k_1 ln\frac{r_3}{r_2}}{2\pi\epsilon_0 k_1 k_2}](\frac{1}{x}) + (L - x)(\frac{2\pi\epsilon_0 k_2}{ln\frac{r_3}{r_2}})$$

$$U = \frac{1}{2}CV_0^2 = \frac{1}{2}[\frac{k_2 ln\frac{r_2}{r_1} + k_1 ln\frac{r_3}{r_2}}{2\pi\epsilon_0 k_1 k_2 x} + (L - x)(\frac{2\pi\epsilon_0 k_2}{ln\frac{r_3}{r_2}})]V_0^2$$

A thin-walled hollow cylinder capacitor filled with 2 dielectrics with concentric shells of radii r1, r2 and r3 respectively

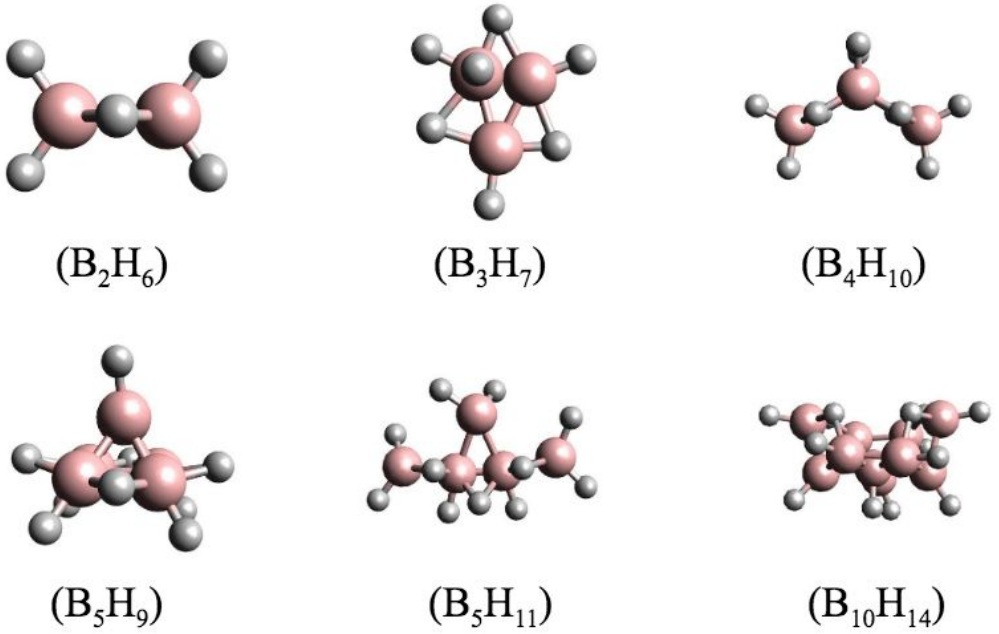
Borane Complexes

Fullerene and Single-walled carbon nanotubes (SWCNTs) or MWCNTs hold vast potential for future electronic devices due to their outstanding properties, however C-C covalent bonds often limit their full potential.

Here, we demonstrate the fabrication of a functionalized complexes to enhance potential V.

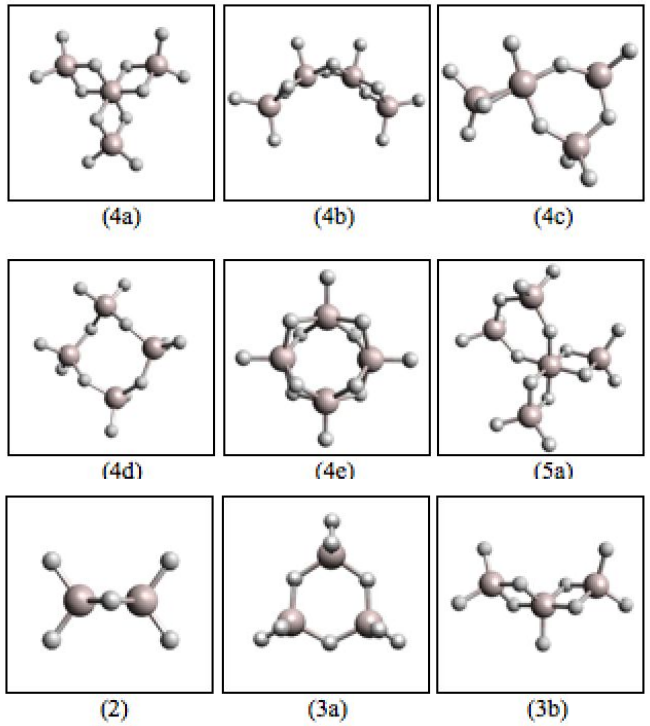
Borane

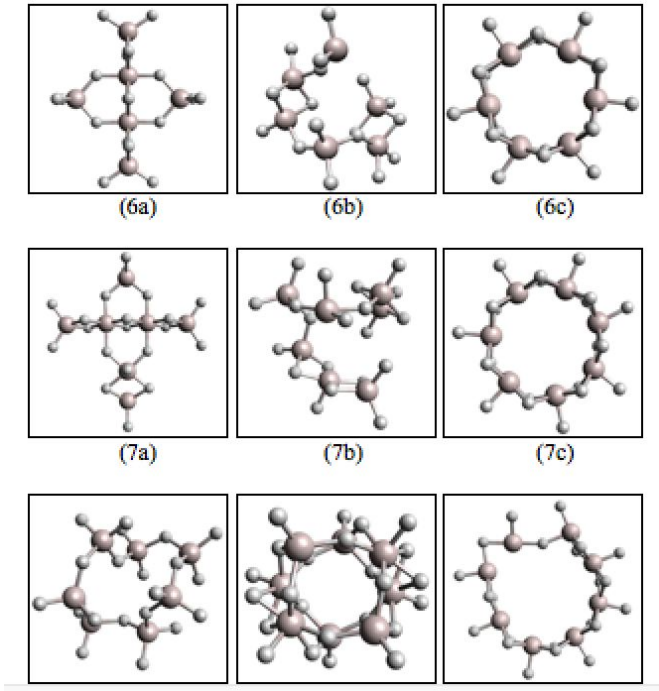
Structures of $(BH_3)_n$ (n=2, 3, 4, 5, 10)

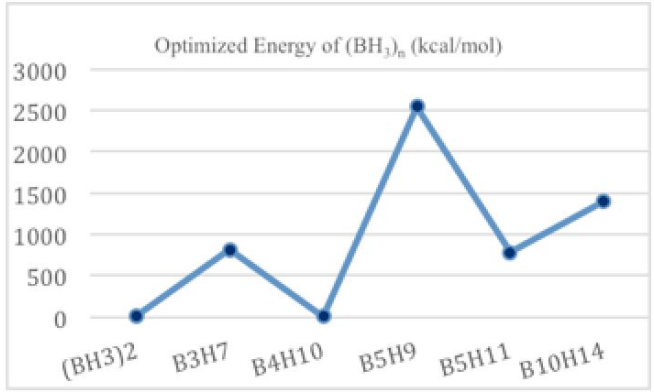


Due to a stronger attraction between B and H, the distance between B and H are shorter than that for Al and H, which probably means stronger repulsion between the H atoms on borane clusters. This will lead to a greater torsional strain, and hence greater energy.

Borane







More structures of $(BH_3)_n$

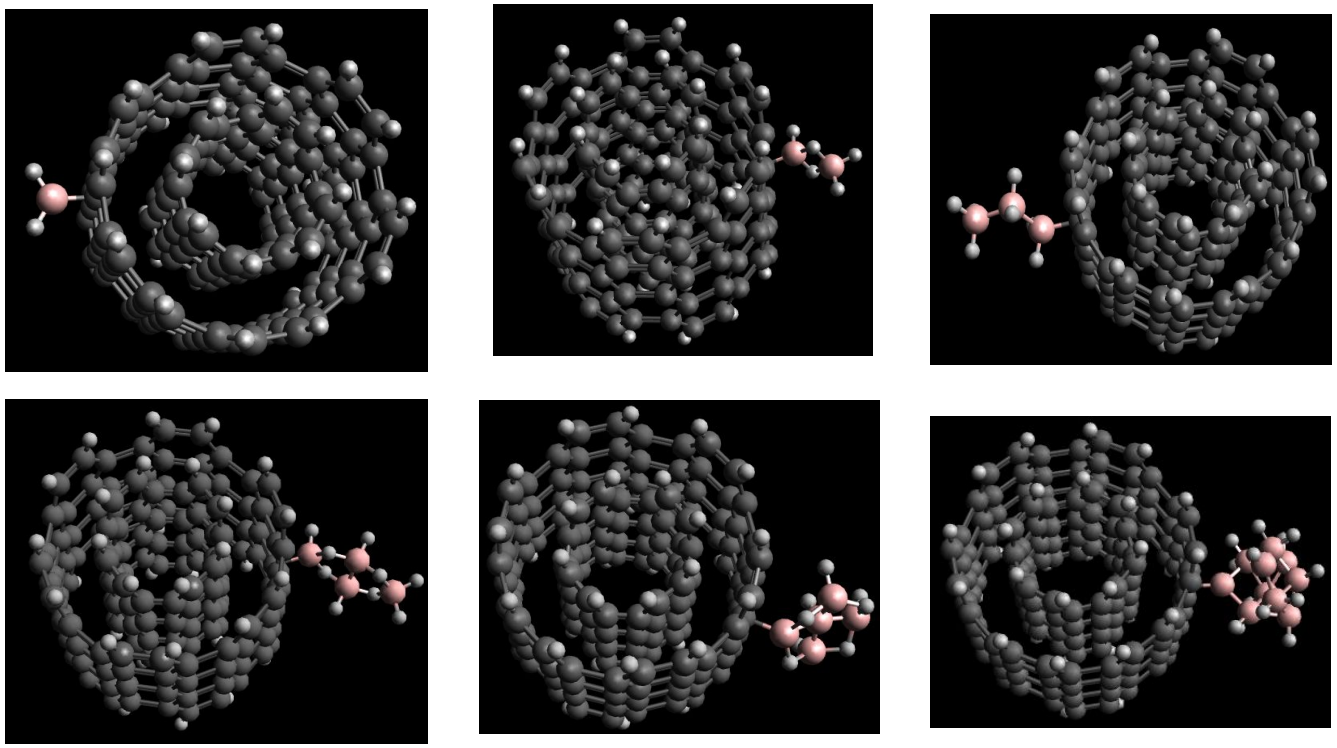
Borane

Structures of $(BH_3)_n$ (n=2, 3, 4, 5, 10, 12)

Molecule's Name		Chemical Formula	Molecular Weight (g/mol)	Energy (kJ/mol)	Estimated Dipole Moment
A	Borane	BH_3	13.835	0	0.000
B	Diborane	B_2H_6	27.670	34.841	0.000
C	Octahydrotriborate	$B_3H_8^-$	40.497	0	0.000
D	Tetra-borane	B_4H_{10}	53.323	92.658	0.000
E	Penta-borane	B_5H_9	63.126	1071.584	0.000
F	Decaborane	$B_{10}H_{14}$	122.221	16526.544	0.000
G	Dodecaborate	$B_{12}H_{12}^{2-}$	141.827	44321.501	0.000

As referenced in our previous study on alane and borane clusters, this may be due to boron's higher electronegativity; due to a stronger attraction between B and H, the distance between B and H are shorter than that for Al and H, which probably means stronger repulsion between the H atoms on borane clusters. This will lead to a greater torsional strain, and hence greater energy.

Borane+CNT



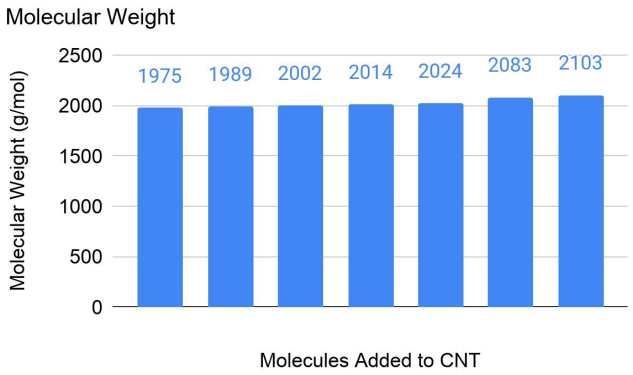
A thin-walled hollow CNT with the of $(BH_3)_n$ (n=2, 3, 4, 5, 10, 12)

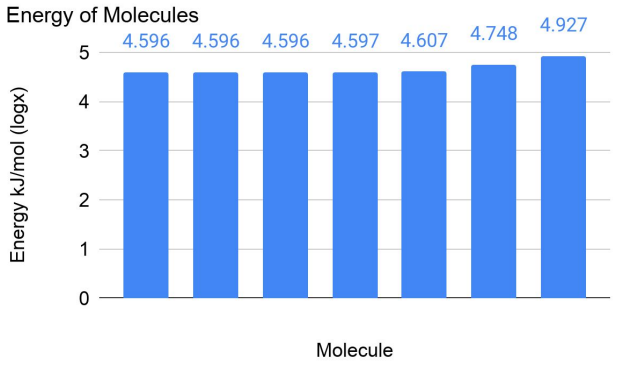
Borane+CNT

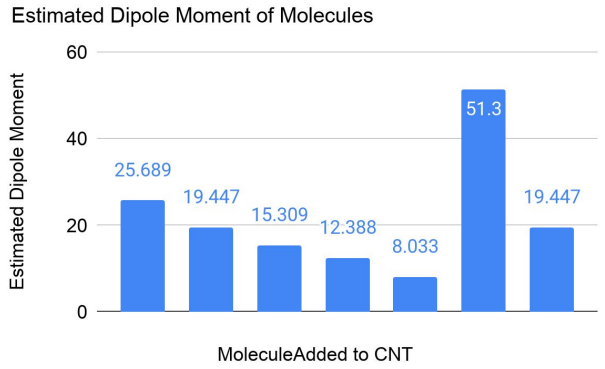
Molecule Added to CNT		Chemical Formula	Molecular Weight (g/mol)	Energy (kJ/mol)	Estimated Dipole Moment
A	Borane	$C_{160}H_{12}B$	19748.596	39485.233	25.689
B	Diborane	$C_{160}H_{47}B_2$	1988.691	39450.839	19.447
C	Octahydrotriborate	$C_{160}H_{47}B_3$	2001.518	39453.228	15.309
D	Tetra-borane	$C_{160}H_{53}B_4$	2014.345	39502.392	12.388
E	Penta-borane	$C_{160}H_{52}B_5$	2024.148	40421.933	8.033
F	Decaborane	$C_{160}H_{53}B_{10}$	2083.243	55980.195	51.300
G	Dodeca-borate	$C_{160}H_{51}B_{12}$	2102.849	84527.859	19.447

A thin-walled hollow CNT with the of $(BH_3)_n$ (n=2, 3, 4, 5, 10, 12)

Borane+CNT

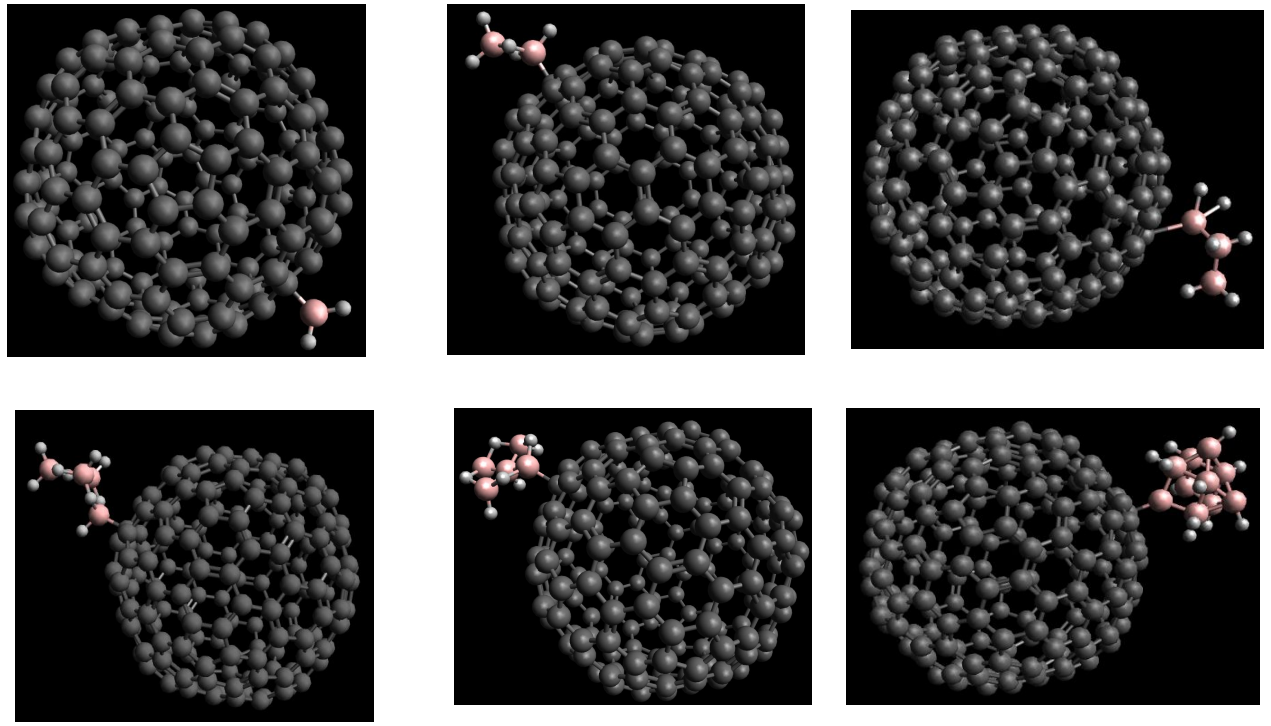






A thin-walled hollow CNT with the of $(BH_3)_n$ (n=2, 3, 4, 5, 10, 12)

Borane+Fullerene



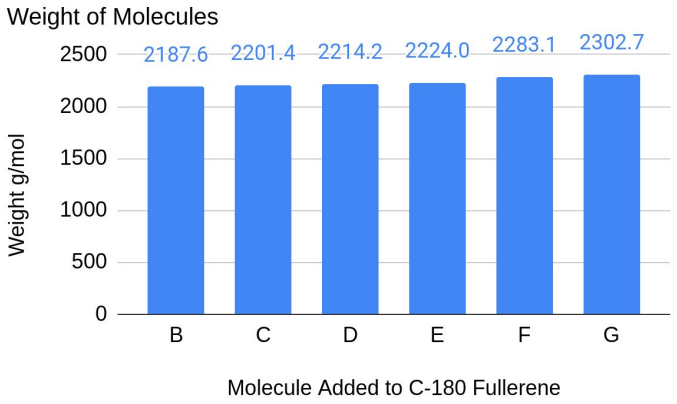
Structures C130 with $(BH_3)_n$ (n=2, 3, 4, 5, 10)

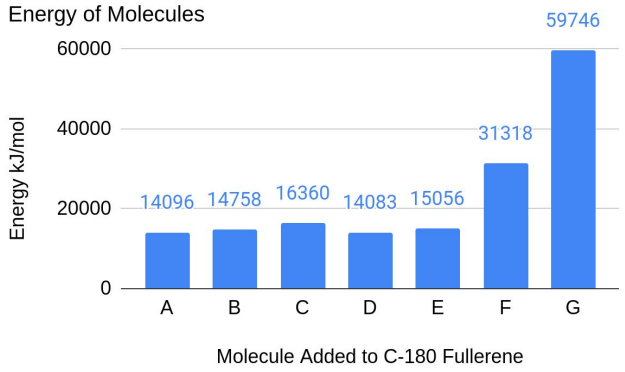
Borane+Fullerene

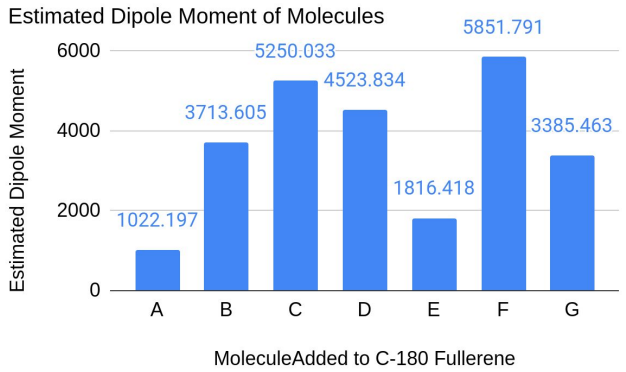
MoleculeAdded to C-180 Fullerene		Chemical Formula	Molecular Weight (g/mol)	Energy (kJ/mol)	Estimated Dipole Moment
A	Borane	$C_{180}H_2B$	2174.753	14095.548	1022.197
B	Diborane	$C_{180}H_7B_2$	2187.580	14757.857	3713.605
C	Octahydrotriborate	$C_{190}H_7B_3$	2201.415	16360.233	5250.033
D	Tetra-borane	$C_{180}H_{13}B_4$	2214.241	14083.428	4523.834
E	Penta-borane	$C_{180}H_{12}B_5$	2224.045	15055.775	1816.418
F	Decaborane	$C_{180}H_{13}B_{10}$	2283.139	31318.186	5851.791
G	Dodecaborate	$C_{180}H_{11}B_{12}$	2302.745	59745.627	3385.463

Optimized energy of C130 with $(BH_3)_n$ (n=2, 3, 4, 5, 10)

Borane+Fullerene

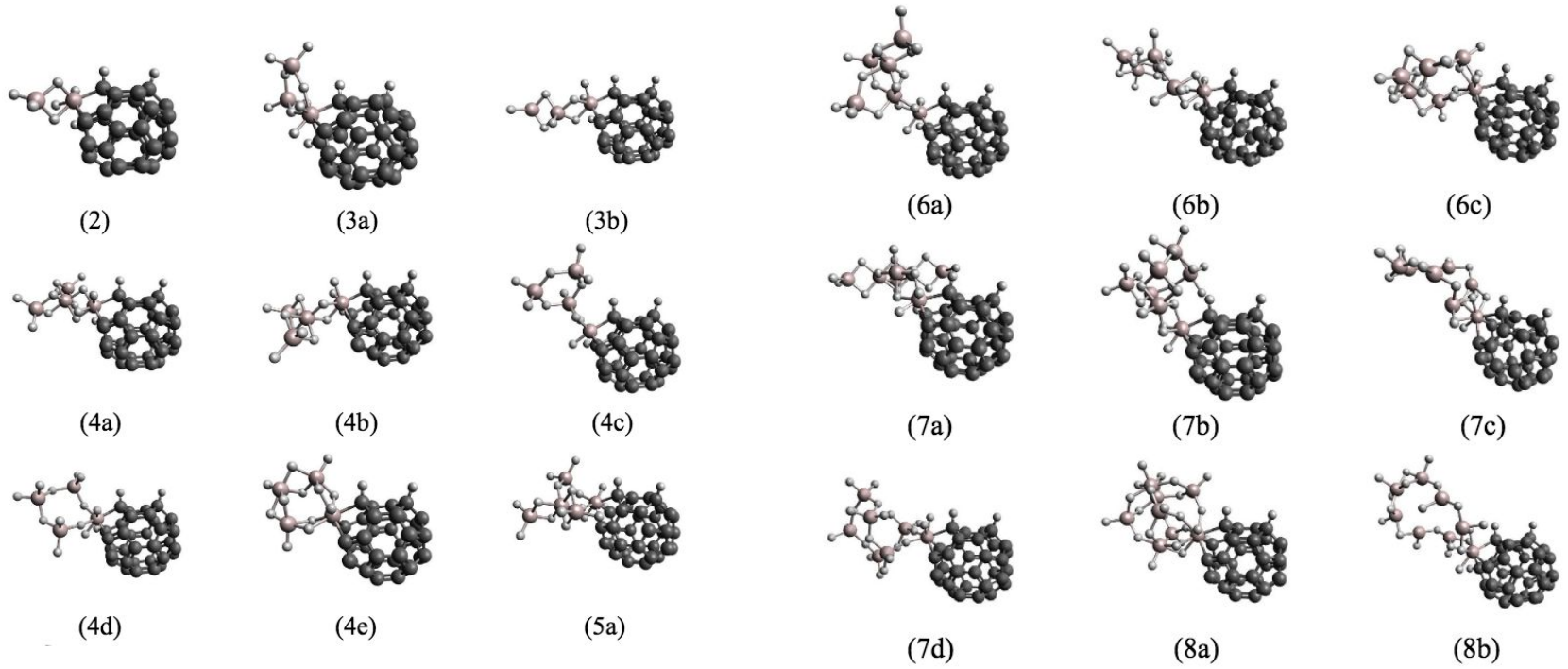






Optimized energy of C130 with $(BH_3)_n$ (n=2, 3, 4, 5, 10)

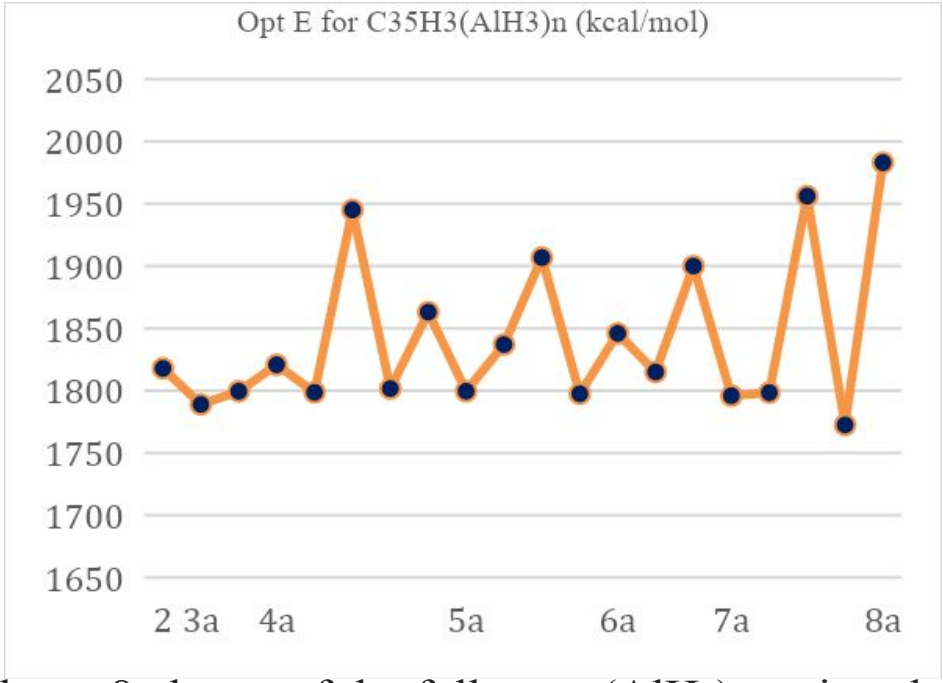
Alane+Fullerene



For n > 4, the $(AlH_3)_n$ series has higher standard deviation than the fullerene-$(AlH_3)_n$ series. The n=2 is not shown since this cluster does not have any isomers. Interestingly, the $(AlH_3)_n$-doped $C_{36}H_2$ has lower molecular energy than $C_{36}H_2$ alone (2121.107 kcal/mol)

Alane+Fullerene

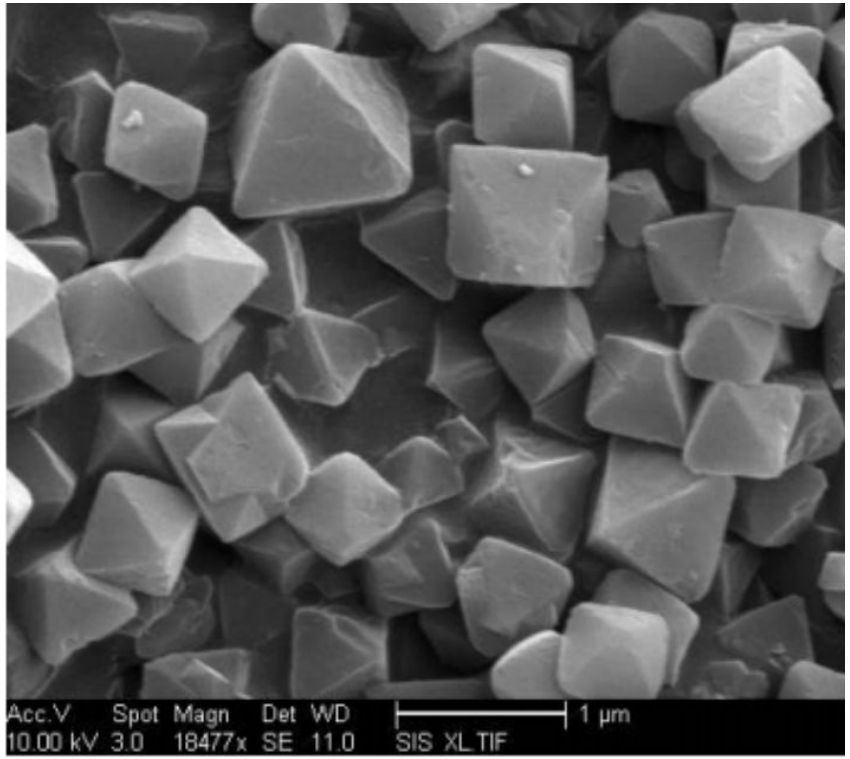
Optimized Energy of $C_{35}H_2(AlH_3)_n$

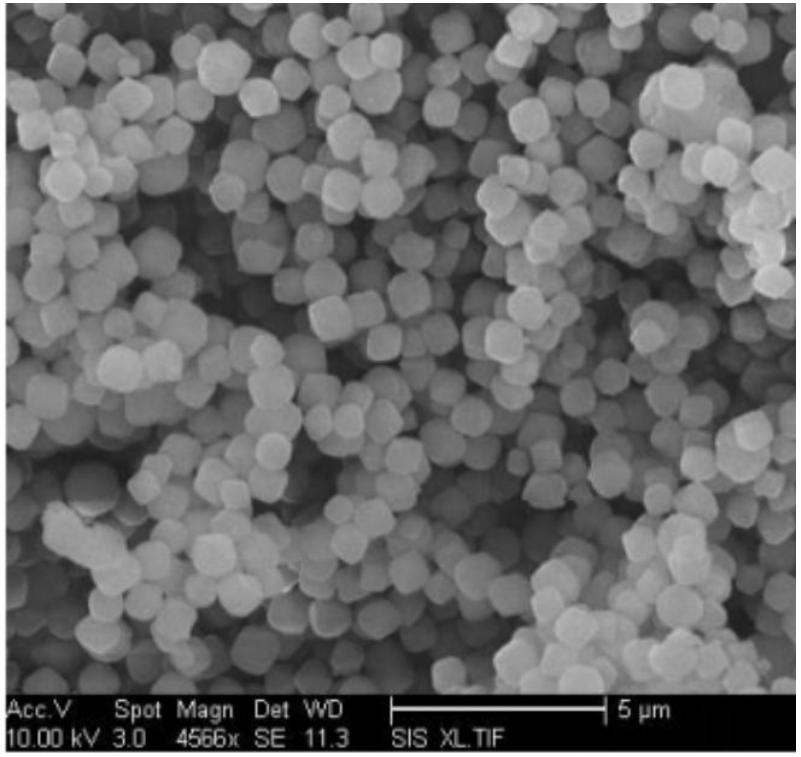


Especially in the n=8 cluster of the fullerene-$(AlH_3)_n$ series, the three isomers 8a, 8b, and 8c virtually the same energy, despite their standard deviation being about 10 times greater in the $(AlH_3)_n$ series.

CNT+MOFs

CNT+MOFs



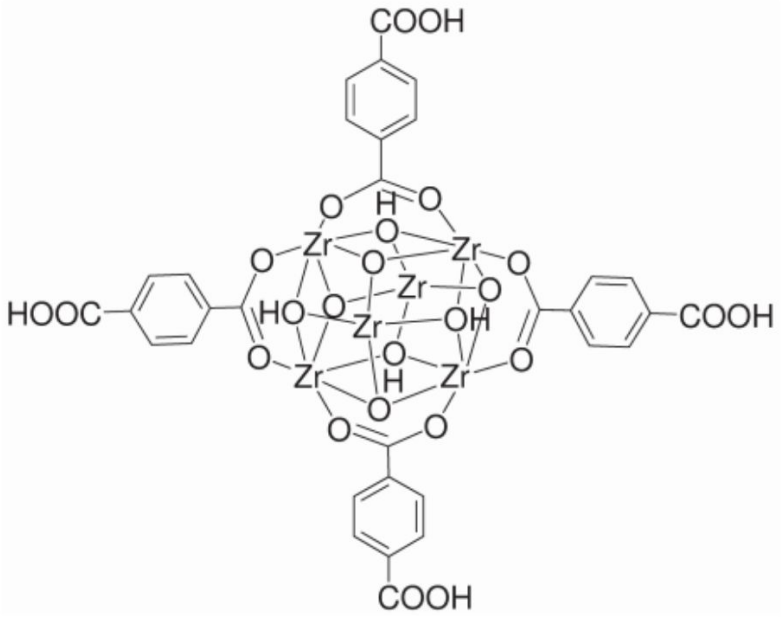


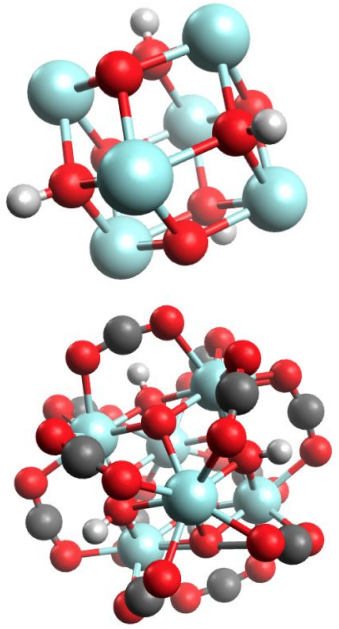
SEM of UiO-66 - Scale bar is 1 µm on the left, and 5 µm on the right.

(https://www.cell.com/cms/10.1016/j.chempr.2017.02.005/attachment/11a3c484-b032-47a8-b9f1-065e0cac5f51/mmc1)

CNT+MOF(UIO-66)

- MOF (UiO-66-BDC)-Zirconium benzenedicarboylate
- Particle size: 0.2-0.5 micron
- Thermal stability: good
- New zirconium-based inorganic building brick that allows the synthesis of very high surface area MOF's with unprecedented stability

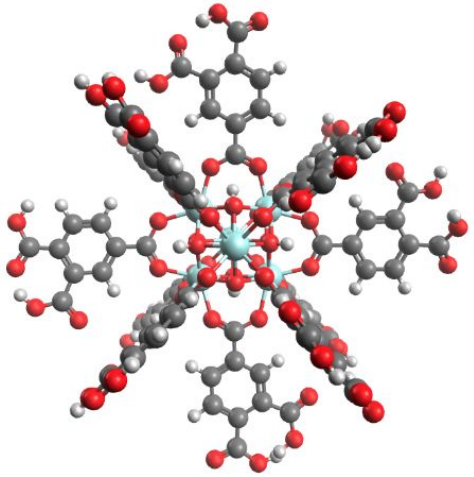


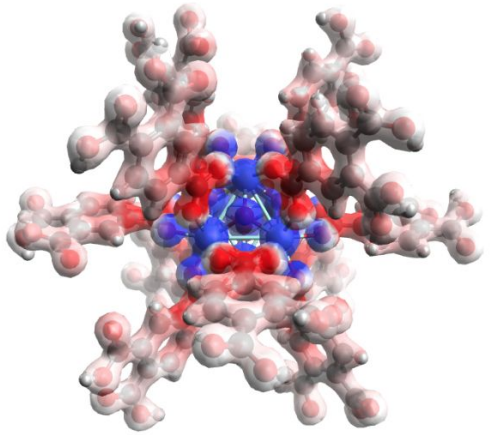


UiO-66-BDC-COOH: Zirconium trimellitate - $[Zr_6O_4(OH)_4]^{+12}$

CNT+MOF

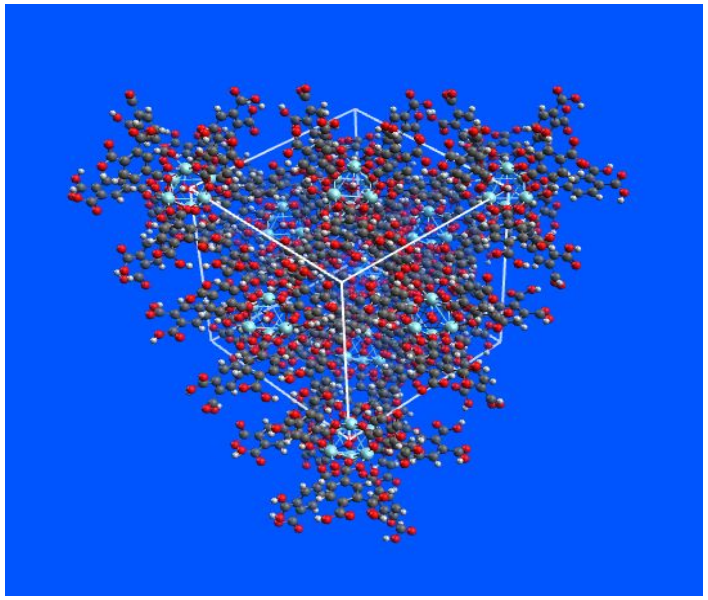
UiO-66-BDC-COOH: Zirconium trimellitate - $[Zr_6O_4(OH)_4]^{+12}$

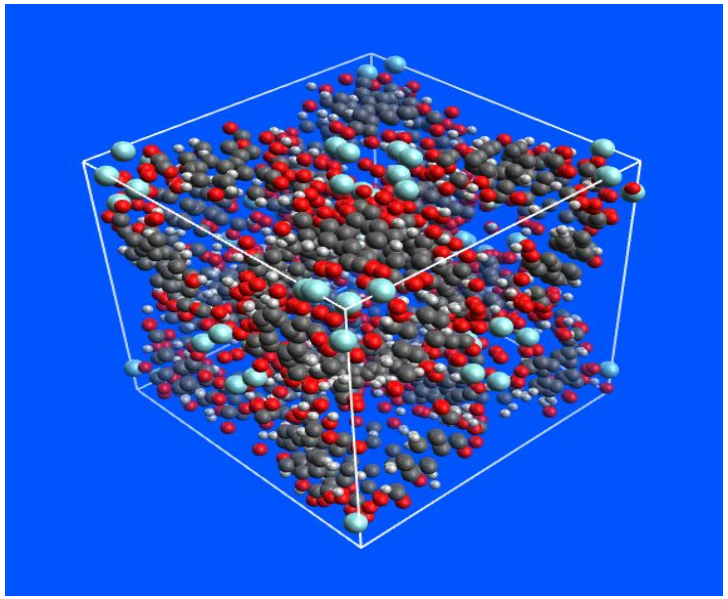


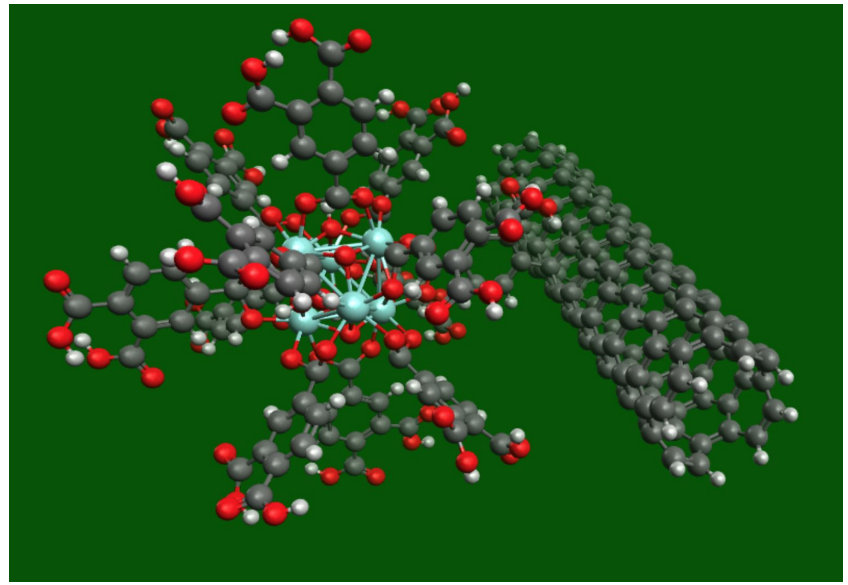


Computational modeling: EPM
Metal–organic frameworks and carbon nanotube composites
Activity is high due to high DM(Dipole Moment)
Stable due to very low optimized energy

CNT+MOFs - Unit Cell

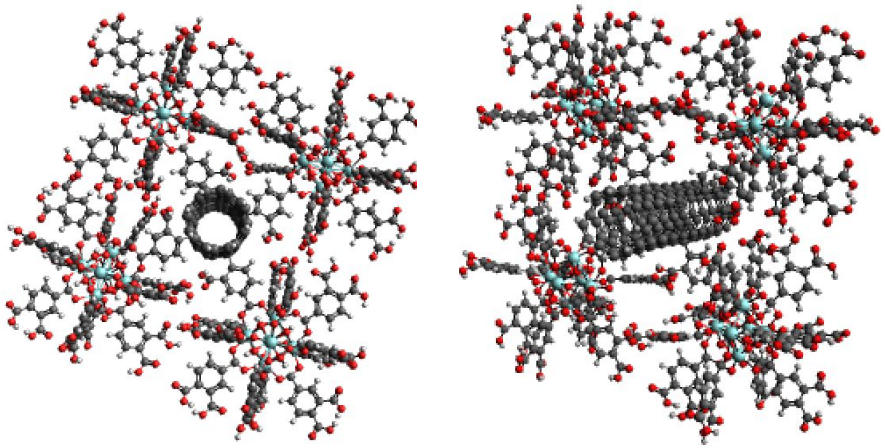






UiO-66-BDC-COOH: Zirconium trimellitate - $[Zr_6O_4(OH)_4]^{+12}$

CNT+MOFs



IUPAC Molecule Name:	unknown
Molecular Weight (g/mol):	14,513.608
Chemical Formula:	$C_{588}H_{268}O_{312}Zr_{24}$----
Energy (kJ/mol):	0.000
Estimated Dipole Moment (D):	1,811.036
Number of Atoms:	1,192
Number of Bonds:	1,452

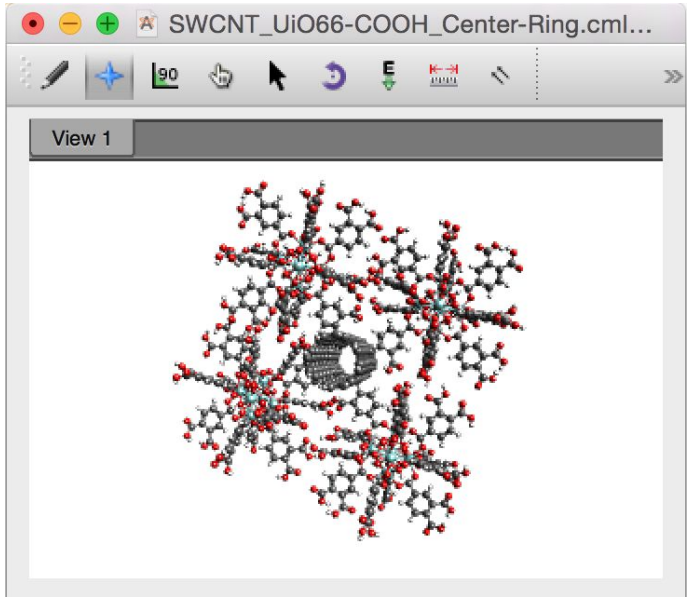
Computational modeling:

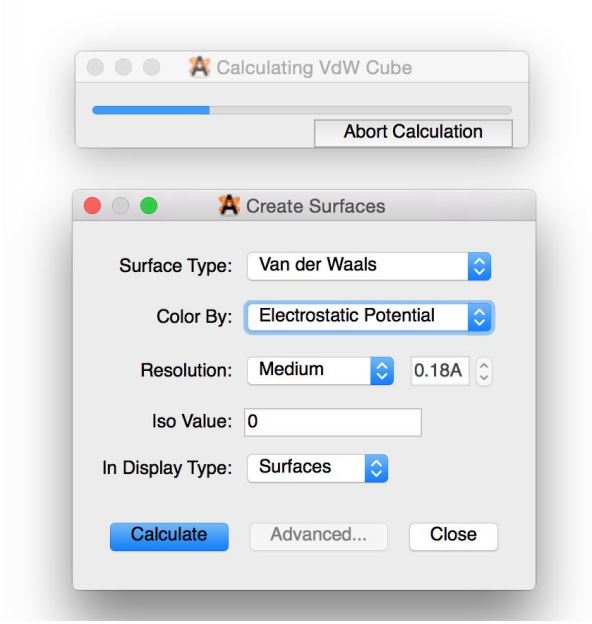
Metal–organic frameworks and carbon nanotube composites

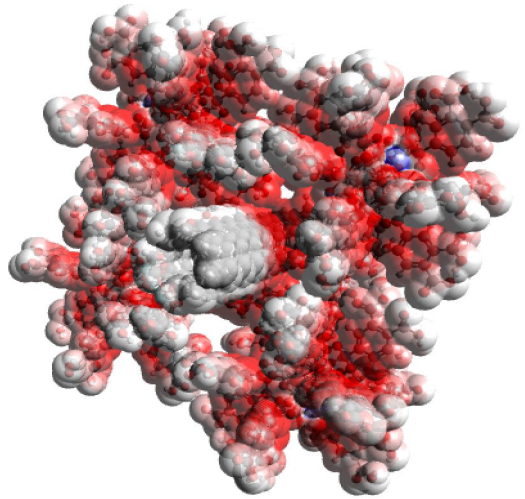
- Activity is high due to high DM(Dipole Moment)
- Stable due to very low optimized energy

CNT+MOFs - EPM

UiO-66-BDC-COOH: Zirconium trimellitate - $[Zr_6O_4(OH)_4]^{+12}$







Computational modeling: EPM
Metal–organic frameworks and carbon nanotube composites
Activity is high due to high EN(Electronegativity) differences
Polar due to high EN(Electronegativity) differences

Conclusions

- **Compared Borane and Aland complexes**

  → Our assumption of the feasibility of this doping and the different chemical composition of $(AlH_3)_n$ and $(BH_3)_n$ further complicates the interpretation of the optimized energy.

- **Compared Opt. E/DM/EPM of** $(AlH_3)_n$-doped fullerene and $BH_3)_n$-doped fullerene

  → Consistent with our previous study, we have found that the $(BH_3)_n$-doped fullerene tends to have higher optimized energy than the $(AlH_3)_n$-doped fullerene, possibly due to boron's higher electronegativity and sometimes rigid structure. The $(AlH_3)_n$-doped fullerene exhibited both smaller within-cluster variation than $(AlH_3)_n$ alone and lower molecular energy than the $(BH_3)_n$-doped fullerene. The latter may be an indication that $(AlH_3)_n$ is a better choice for doping fullerenes than $(BH_3)_n$, but it is difficult to say until more analyses are done with fullerenes with lower and higher complexities.

Conclusions

- **Examined thermodynamic and electrical efficiencies of CNT complexes**

Porous metal-organic frameworks with CNTs representing a diversity of structure types and metrics, sizes and functionalities studied for their thermodynamic and electrical efficiencies using computational analysis.

- **Checked Opt. E/DM/EPM of UIO 66 + CNT for potential use as ED/EA (Electron Donor and Acceptor) in the photovoltaic dells.**

⟶ It is observed that the pore environment produced by functional groups on MOF clearly influences the enthalpies in the CNT with MOF-66s.

→ Members of a new class of chemically and thermally stable MOFs based on Zn show progressively better performance.

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