Effects of Different Combinations of Halogen Additions to *anti*-$B_{18}H_{22}$ Molecule on Absorption and Emission Wavelength

New Mexico

Supercomputing Challenge

Final Report

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Abstract

Downshifting, the process of absorbing high energy photons and emitting them at lower energies, is promising to improving performance and lifespan of solar panels, especially those in space. With modifications to the structure of fluorescent molecules, the downshifting ability of the molecules can be optimized. One such way is through halogenation, which enhances the ability to absorb and emit light at longer wavelengths. By adding combinations of different halogens onto *anti*-$B_{18}H_{22}$, a naturally fluorescent boron cluster, absorption, emission, and the shift from absorption to emission can be increased. Halogenation of combinations of fluorine or chlorine atoms on the *anti*-$B_{18}H_{22}$ molecule appears to show a positive trend between the size of the halogens and the length of the emission wavelength. Although the effects of halogen combinations on the absorption to emission shift is uncertain, the use of multiple types of halogens was able to widen the shift by more than 30 nm from the original *anti*-$B_{18}H_{22}$ molecule.

Rationale

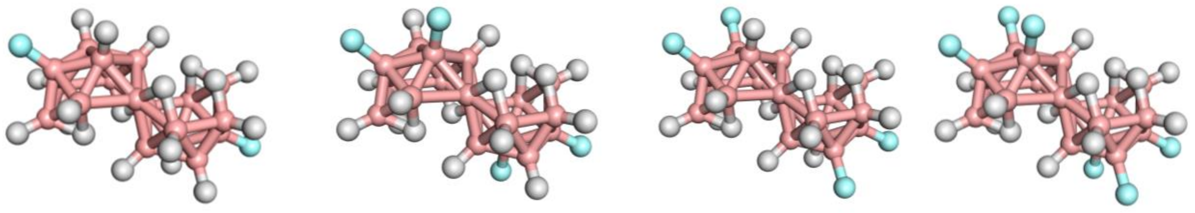
Solar panel cells are a key, renewable source of energy for generating power, especially in space vehicles. The cells in space station solar arrays use the photovoltaic effect to convert light into electricity (Garcia, 2017). Photovoltaic cells mostly utilize visible light with longer wavelengths, such as light in the red or yellow range of the visible spectrum (Pius & Benaiah, 2015). In space, there is a much higher presence of ultraviolet (UV) light than on Earth due to a lack of a shielding atmosphere; however, not only are UV light waves difficult to harvest because of their high energy content, but they also degrade the physical composition of solar panels (National Aeronautics and Space Administration, Science Mission Directorate, 2010; Shamachurn & Betts, 2016). AFRL's various missions largely depend on space vehicles, which has a high reliance on solar panels for power but solar panels are not built to endure the high intensity of UV light, given that their initial intent was to be used in a much more UV-protected environment, Earth. One solution to collecting UV and protecting solar panels in space is to apply the concept of downshifting molecules, which is absorbing high energy photons and emitting them at a lower energy. By downshifting molecules, UV light can be absorbed and emitted as visible light for the solar panels to harness, yet the extent of its efficiency is still uncertain.

Currently, AFRL, the University of California – Los Angeles (UCLA), and the University of New Mexico (UNM) all have combined efforts working in hopes to understand the effects of halogenation on photoluminescent properties and to optimize the geometry of *anti*-$B_{18}H_{22}$ molecules. The reason *anti*-$B_{18}H_{22}$ is chosen is because it has natural fluorescence, high photodegradation resistance, stability to radiation, high quantum yield and can undergo surface modification (Cerdán et al., 2015). In addition, it is important if halogen additions can improve the molecule's downshifting ability, for they are easier to attach to the molecule in lab. By simulating models on computers and synthesizing samples in lab, these three affiliations are working with the goal of using the molecules to develop an application, as simple as a spray, to easily apply onto solar arrays and efficiently utilize the UV light in space. The purpose of this project is to determine how adding different combinations of halogens to the specific molecule, *anti*-$B_{18}H_{22}$, can increase its absorption and emission wavelengths. AFRL, UCLA, and UNM are mainly focused on examining the effects of the types of halogens, the number of halogens, and symmetry so this work is intended to branch upon their efforts to further understand how halogen types affect photoluminescent properties.

Understanding their correlation can narrow down future research scopes and direct further investigations on more favorable configurations for molecules to downshift or even the development of UV dependent panels. The potential impact of these efforts is that they can broaden the range of wavelengths that solar cells can utilize and protect the interior of solar panels from intense UV light waves in space, which will in turn increase their efficiency and reduce frequency or costs of solar array maintenance.

Method

I focused on how combinations of halogens will affect the absorption wavelength, emission wavelength, and shift from absorption to emission in derivatives of *anti*-$B_{18}H_{22}$. To do so, I simulated a total of 19 derivatives, with one *anti*-$B_{18}H_{22}$ molecule without halogenation, 2 with only fluorine or chlorine at 4 and 4’, 4 combinations of fluorine and chlorine at the specific vertices, 1,1’, 4, and 4’, 4 combinations at vertices 3, 3’, 4, and 4’, and 8 combinations at the six specific vertices, 1, 1’, 3, 3’, 4, and 4’.



4 and 4’ 1, 1’, 4, and 4’ 3, 3’, 4, and 4’ 1, 1’, 3, 3’, 4, and 4’

Figure 1. Examples of halogenation at different specified vertices. Halogen additions are shown in blue, borons in pink, and hydrogens in gray

Since it is unclear whether the 1 and 1’ vertices or the 3 and 3’ vertices are a better choice in trying to improve photoluminescence properties, I wanted to test the combinations for both, at 1, 1’, 4, 4’ and 3, 3’, 4, 4’. This way, not only can the data show the effects of combinations of halogens, but it can also show whether the location of the halogens has an impact on absorption or emission. The reason why I wanted to focus on combinations for my project was to see if adding different halogens would increase the advantages of only using one type of halogen, if they would cancel out the favorable properties, or if the atoms affect the molecule's photoluminescence properties independently.

The data collection is dependent on using computer simulations to find absorption and emission wavelengths of the halogenated *anti*-$B_{18}H_{22}$ derivatives. To run the simulations and the data, I primarily use five programs: Discovery Studio Visualizer, PuTTY, Notepad++, WinSCP, and MATLAB. To start off, I simulate the molecular structure of the *anti*-$B_{18}H_{22}$ derivative I am analyzing in Discovery Studio Visualizer and save the XYZ coordinates of all the atoms. Using the software NWChem and the Dunning basis set, I implement the XYZ coordinates of the molecule and run time-dependent density functional theory calculations to find the energies of the most probable excited states. This provides the information for absorption. When doing so, I have to use Notepad++ to create the files and bash scripts to be run, WinSCP to transfer these files from my local computer to a remote supercomputer, and PuTTY to access and run the jobs on the supercomputer. Then, I optimize the geometry of the molecule at its most probable excited state and when the optimization converges, record the total oscillator strength and energy for the most probable excited state in emission. Finally, I graph the data sets in MATLAB to see the absorption and emission spectrum visually. The files used to call the supercomputer, to optimize the geometry of the molecules for absorption and emission, and to graph the data sets were created with the help of my fellow scholar Mariah and secondary mentor Professor Bricker.

Total oscillator strength is directly related to the probability of reaching a particular excited state, so for both absorption and emission, only the highest total oscillator strength is important. Furthermore, in order to find the wavelengths for absorption and emission, I needed to divide 1284 by the energies recorded.

Data/Results

The absorption and emission data for all 19 derivatives of *anti*-$B_{18}H_{22}$ are listed below in the table.

#	Vertex 4/4'	Vertex 3/3'	Vertex 1/1'	Absorption (nm)	Emission (nm)	Shift (nm)
1	-	-	-	332.45	425.31	92.85
2	F			349.40	463.05	113.66
3	Cl			363.66	475.12	111.46
4	F	F		341.93	466.57	124.64
5	F	Cl		347.80	473.54	125.74
6	Cl	F		359.42	474.10	114.68
7	Cl	Cl		364.08	478.60	114.52
8	F		F	351.13	455.97	104.84
9	F		Cl	356.85	459.56	102.71
10	Cl		F	365.42	466.11	100.70
11	Cl		Cl	371.48	472.44	100.96
12	F	F	F	347.86	460.58	112.71
13	F	F	Cl	354.40	462.90	108.50
14	F	Cl	F	354.18	468.60	114.42
15	Cl	F	F	364.21	467.91	103.70
16	Cl	Cl	F	368.93	473.52	104.59
17	Cl	F	Cl	370.28	473.87	103.59
18	F	Cl	Cl	359.92	471.42	111.50
19	Cl	Cl	Cl	374.34	478.00	103.65

When collecting the data, I split all the combinations into 4 groups: group A consisted of combinations at 3, 3’, 4, and 4’; group B consisted of the combinations at 1,1’,4, and 4’; group C consisted of combinations at 1, 1’, 3, 3’, 4, and 4’; group D consisted of all the other simulations. In each of the groups, both the absorption and emission wavelengths increased as chlorines replaced fluorines. In fact, the longest emission wavelengths occurred where there were only chlorine additions, which was consist for all four groups.

When comparing groups A and B, group A had better results in all three dependent variables and had one of the best shifts out of all 19 simulations, showing that vertices 3 and 3’ may be more favorable positions for halogenation. When analyzing the combinations for 6 halides, I also looked more in-depth at the set of having 4 fluorides and 2 chlorides and the set of 2 fluorines and 4 chlorines separately.

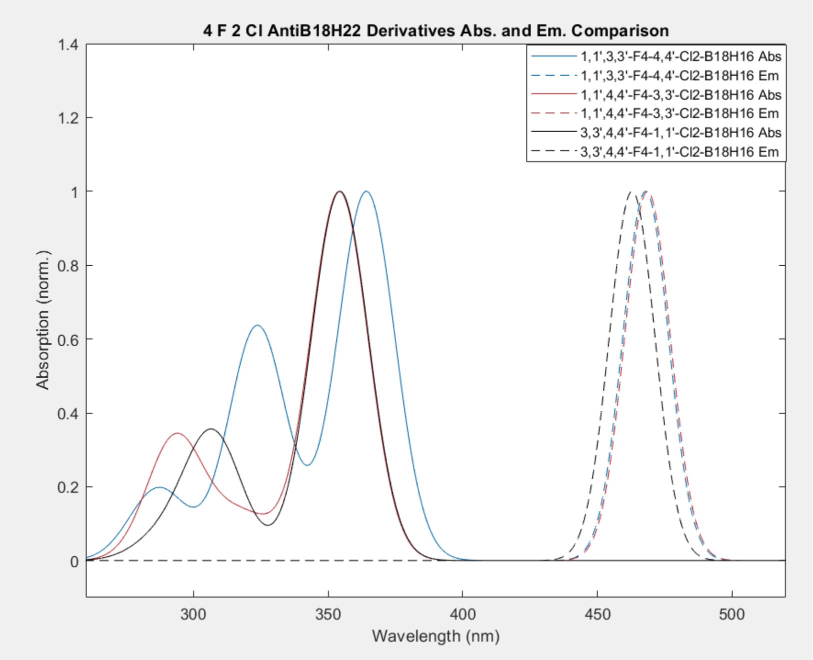


Figure 3. Comparison of the derivatives with 4 fluorines and 2 chlorines. Used Dunning basis

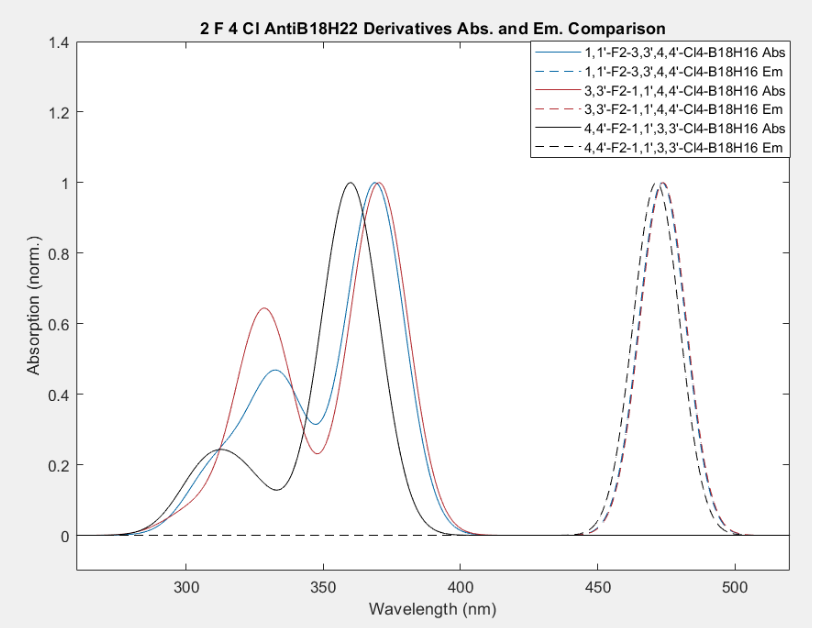


Figure 4. Comparison of the derivatives with 2 fluorines and 4 chlorines. Used Dunning basis.

As the graphs above show, the blue line in Figure 3., which represents 1, 1’, 3, 3’ – F_4 – 4, 4’ – Cl_2 – anti-$B_{18}H_{22}$ and the black line in Figure 4., which represents 4, 4’– F_2 – 1, 1’, 3, 3’ – Cl_4 – anti-$B_{18}H_{22}$, appear to have a greater shift variance than the others. Although it is unclear why that is the case, these two both have the different halogen at vertices 4 and 4’. More data will need to be collected in order to make further conclusions about why the shift is different from others.

Discussion/Conclusion

The optimal result is for the molecule to absorb light at a short wavelength in the UV light spectrum (less than 380 nm) and emit them at a longer wavelength in the visible light spectrum (preferably in the green region at 550 nm). The data shows four things. First, absorption and emission appear to be correlated with the size of the halides added, likely due to the greater electron density of heavier atoms. As more chlorines than fluorines are added, both the absorption and emission wavelength became longer. The only outlier was 4,4'-F_2-1,1',3,3'-Cl_4-*anti*-$B_{18}H_{16}$, which had absorption and emission wavelengths slightly shorter than the other derivatives with 4 chlorines and 2 fluorines and did not follow the relatively linear increase of the data. In addition, the shift from absorption to emission was a lot higher than the other derivatives for 4 chlorines and 2 fluorines. Second, the shift did not appear to be directly related to either the position or the size of the halogen additions. The three greatest shifts were found with 1,1',3,3',4,4'-F_6-*anti*-$B_{18}H_{16}$, 1,1',4,4'-F_4-3,3'-Cl_2-*anti*-$B_{18}H_{16}$, and 4,4'-F_2-1,1',3,3'-Cl_4-*anti*-$B_{18}H_{16}$ but there does not seem to be any clear relationship between these three molecules. Third, halogenation is indeed advantageous to the photoluminescence properties of *anti*-$B_{18}H_{22}$, as it showed an increase in both emission wavelengths and the shift. With halogenation, the absorption increased by at least 10 nm, emission increased by at least 35 nm, and the shift increased by at least 11 nm. Even though a longer absorption wavelength is not ideal, the benefits with emission and shift outweighs that downside. Last, vertices 3 and 3' appear to be more favorable than 1 and 1', given that group A simulations gave the best shifts and longer emissions than group B.

To get a more conclusive and complete set of data regarding halogenation of a combination of fluorines and chlorines, I will need to make simulations for combinations of different sets of halogens, such as bromine and iodine. Vertices 4 and 4' are where the *anti*-$B_{18}H_{22}$ molecules have the most electron position, meaning that halogens are also most likely to go to those vertices. For this reason, it would be most important and feasible to still continue work around or at the vertices 4 and 4'.

In this project, most importantly, I have learned not only the real-world implications of chemistry and computer science, but also an introductory understanding of quantum or computational chemistry. Through the 19 simulations I ran, I learned that the electron density of the different halogens can increase both absorption and emission wavelengths and that halogenation can make *anti*-$B_{18}H_{22}$ photoluminescence properties more favorable for downshifting.

I believe that there is a lot of room to continue further exploration of this topic. It would be interesting and important to see how combinations of a different set of halogens affects absorption and emission wavelength. The halogen additions analyzed can be of an overall larger electron density, two different types of halogens with great electron density differences from each other, or even completely different types of functional groups. Seeing how the groups of halogen additions on different vertices of the *anti*-$B_{18}H_{22}$ molecule can also show effects of position on the photoluminescent properties.

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