

Spectroscopic Analysis to Distinguish Two Cucurbitur[n]urils In a Mixture

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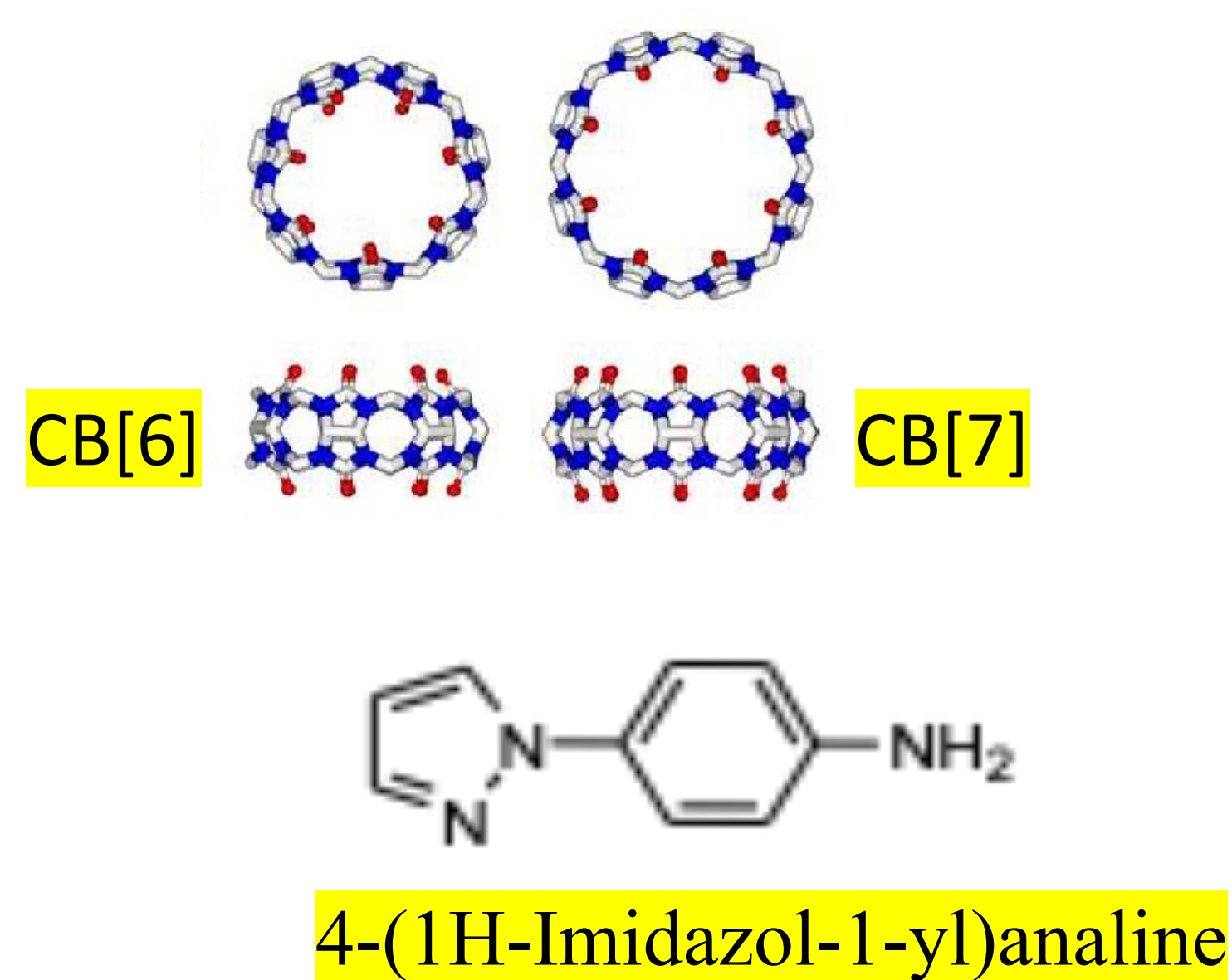
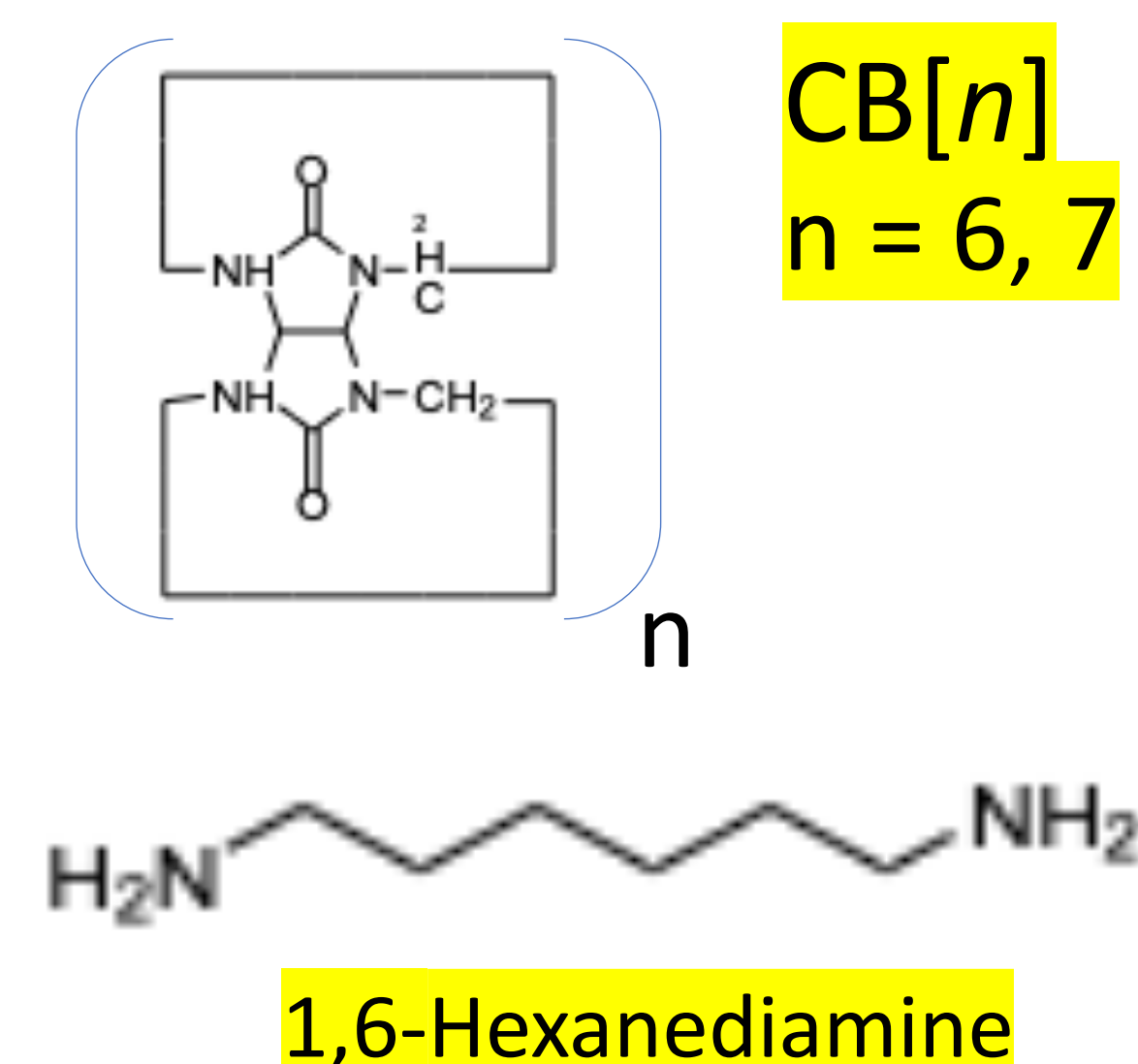
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Introduction

- A macrocycle is a cyclic molecule that consists of 12 or more atoms and is shaped to encapsulate molecules called guests.
- Cucurbit[6]uril (CB[6]) and Cucurbit[7]uril (CB[7]) are types of macrocycles that exhibit hydrogen bonds, ionic bonds, Van der Waal's forces or hydrophobic interactions with guest molecules.
- Cucurbit[n]urils are size-complimentary to hold guests, such as 4-(1H-Imidazol-1-yl) aniline (IMA) and 1,6 – hexanediamine dihydrochloride (DAH). Portal, cavity and outer diameter increase from CB[6] to CB[7]. However, height stays the same throughout.

Objectives

The objectives of my research is to distinguish between CB[6] and CB[7] using fluorescence spectroscopy and detect a minimum amount of CB[6] when mixed with CB[7]. As well, find out if changing the total concentration of CB affects fluorescence.



Methods

- Steady-state fluorescence
- Experiments were done at 20 °C with a 10 mm x 10 mm fluorescence cuvette and using a gastight syringe for insertion of DAH.

Results

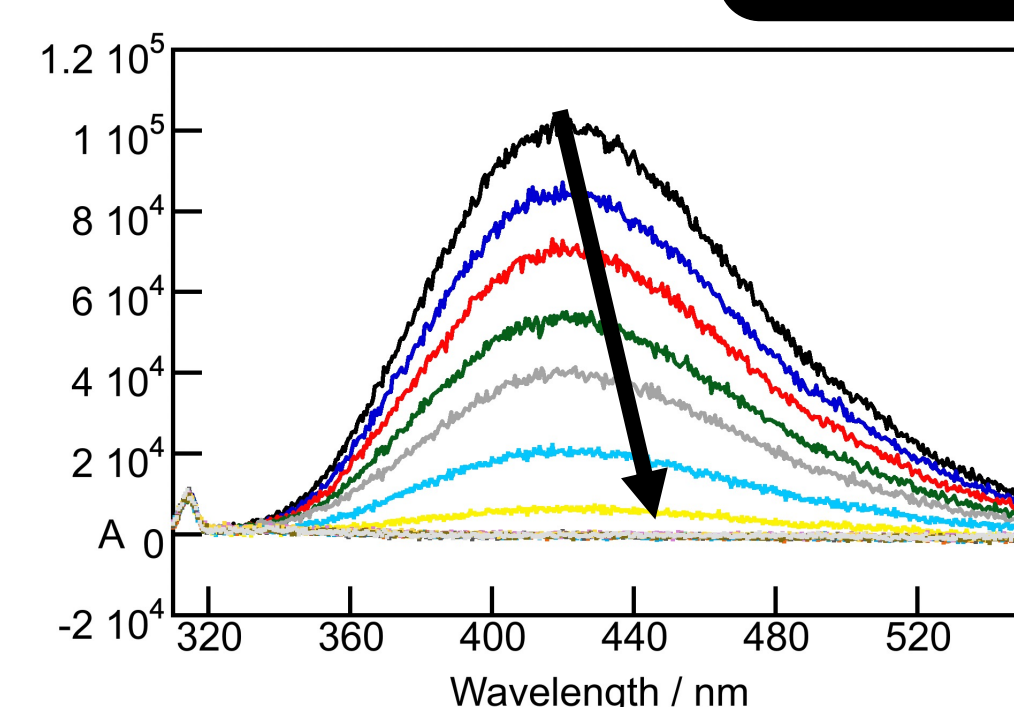


Figure 1. Titration between IMA, HCl and CB[6] in water with the addition of DAH. 3 mL increments of 1 mM DAH were added to 20 μ M IMA, 1 mM HCl and 10 μ M CB[6]. IMA competed for the cavity of CB[6] with DAH. Intensity decreases until it disappears indicating that all the fluorescent guest has been displaced. Absorbance and fluorescence decrease as you add DAH due to competition and inhibition of IMA complex.

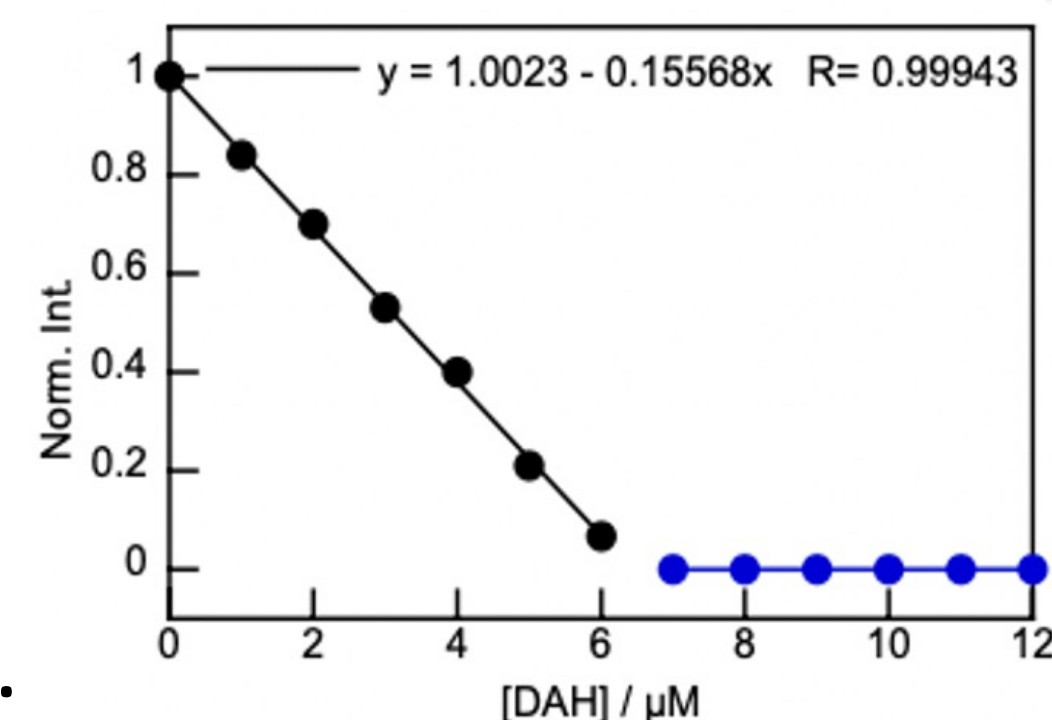


Figure 2. The area under the fluorescence spectrum vs [DAH] in μ M from the titration involving IMA, HCl and CB[6] in water. Data was calculated by finding the area of fluorescence intensities. This graph is normalized. The percentage of CB[6] purity was calculated to be 66% from this graph.

References

1. W. L. Mock, N. Y. Shih, *J. Org. Chem.* 1986, 51, 4440–4446.
2. Cong, H. et al *Org. Biomol. Chem.*, 2016, 14, 4335-4364
3. Yi, S.; A.E. *J Org Chem* 2011, 76, 10275

Results

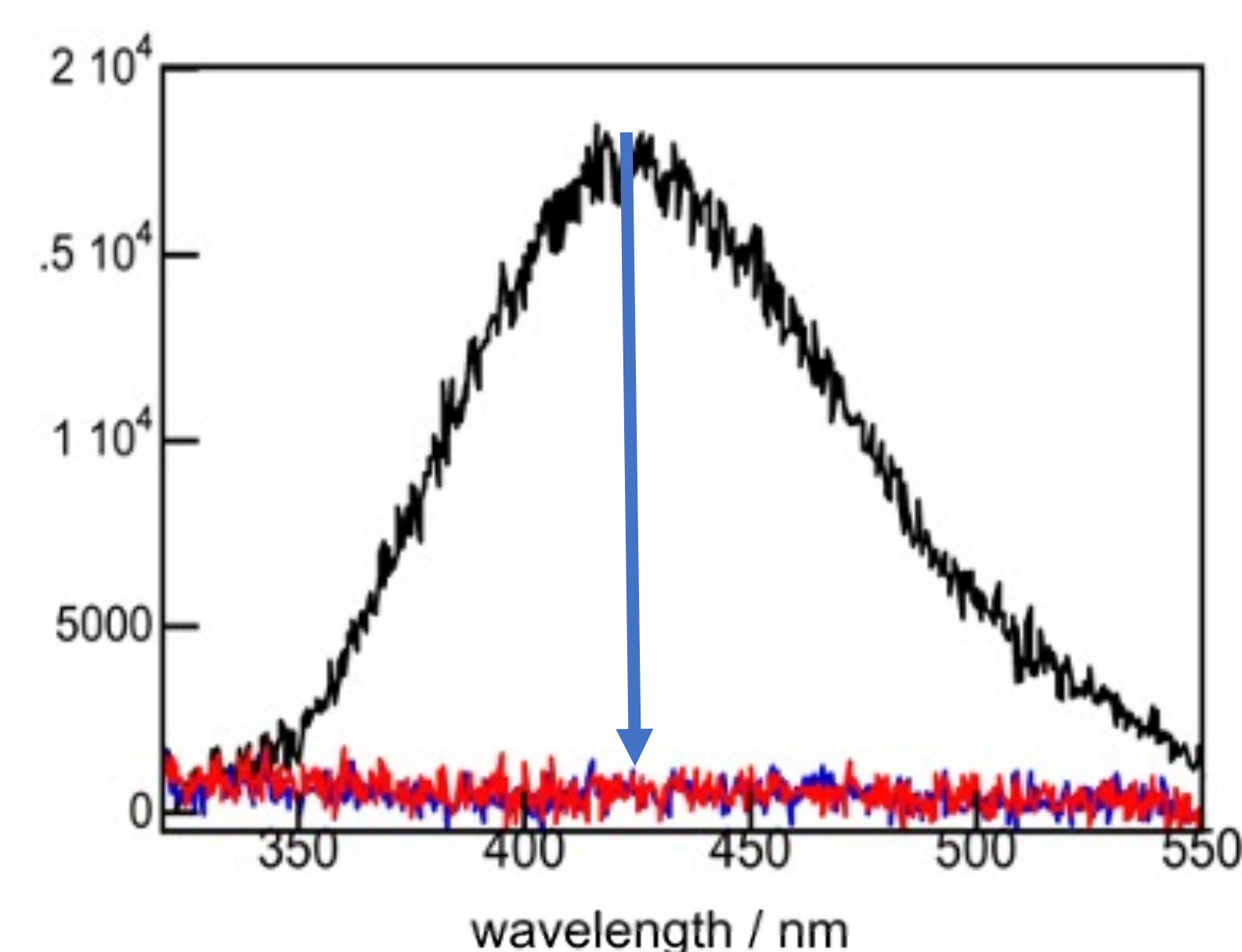


Figure 3. 10 μ M CB[6]/10 μ M CB[7] was titrated with 1 mM DAH. 3 μ L additions of DAH to the CB[7]/CB[6] solution were performed. 3 μ L of DAH were added in total to reach a saturation point when the intensity is 0.

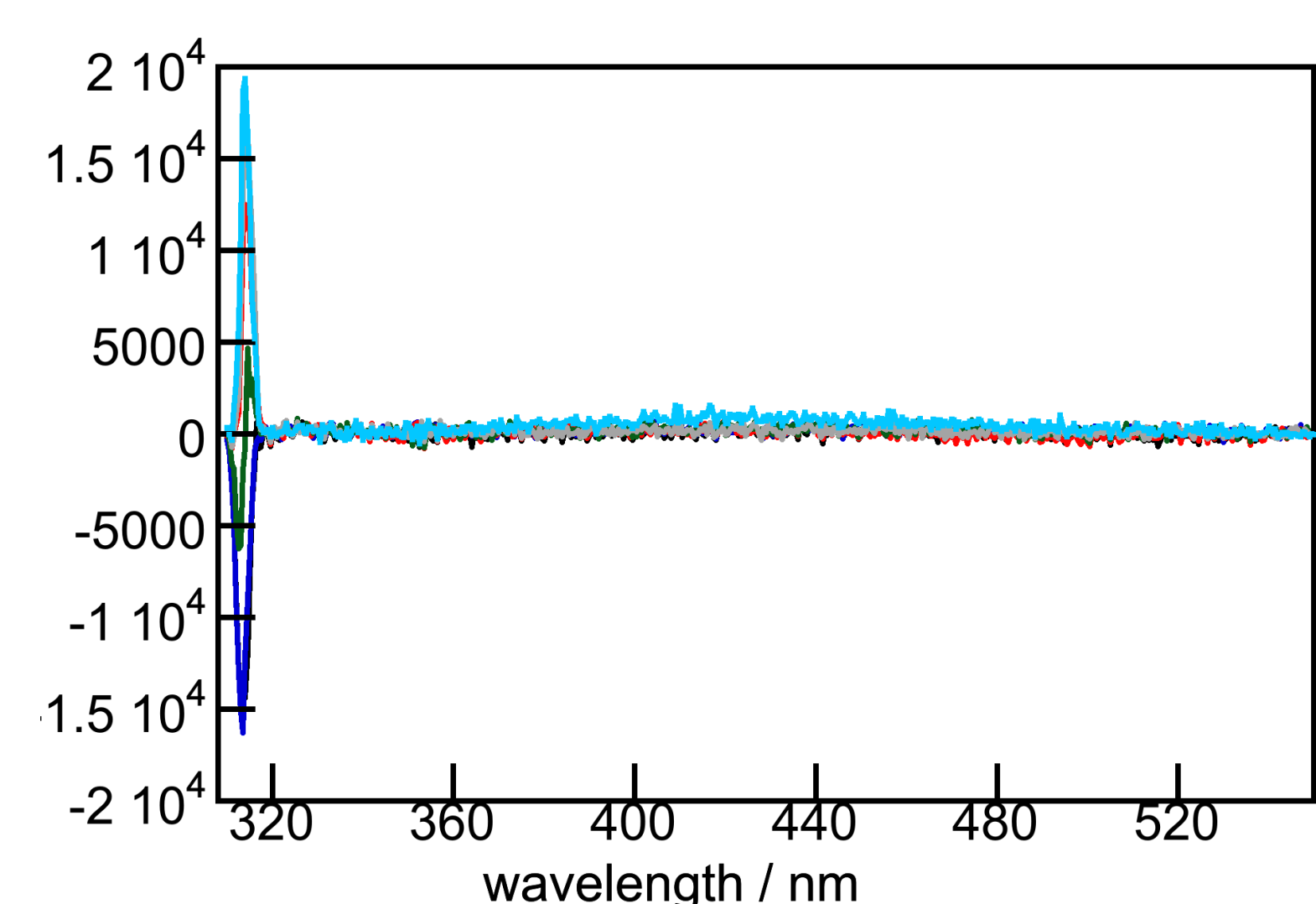


Figure 5. 3 μ L additions of 1 mM DAH to 10 μ M CB[7]. No fluorescence was measured from a wavelength of 320 nm to 560 nm. The scan was measured from 300 nm to 560 nm. The peak occurs at around 310 nm due to Raman scattering where incoming light is scattered by the sample.

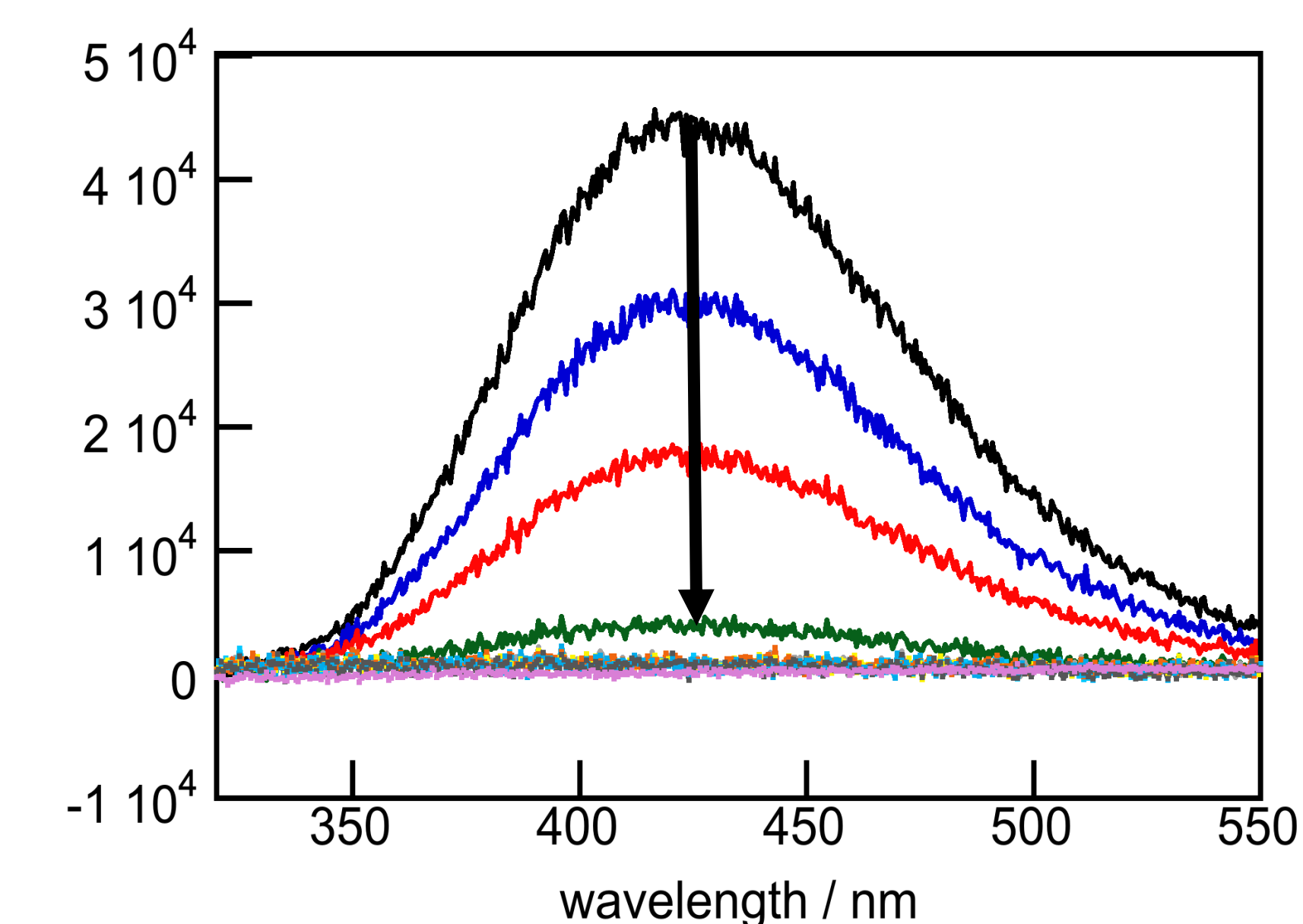


Figure 4. 5 μ M CB[6]/5 μ M CB[7] was titrated with 1 mM DAH. 3 μ L additions of DAH to the CB[7]/CB[6] were performed. A total of 15 μ L of DAH were added to the sample before saturation was reached.

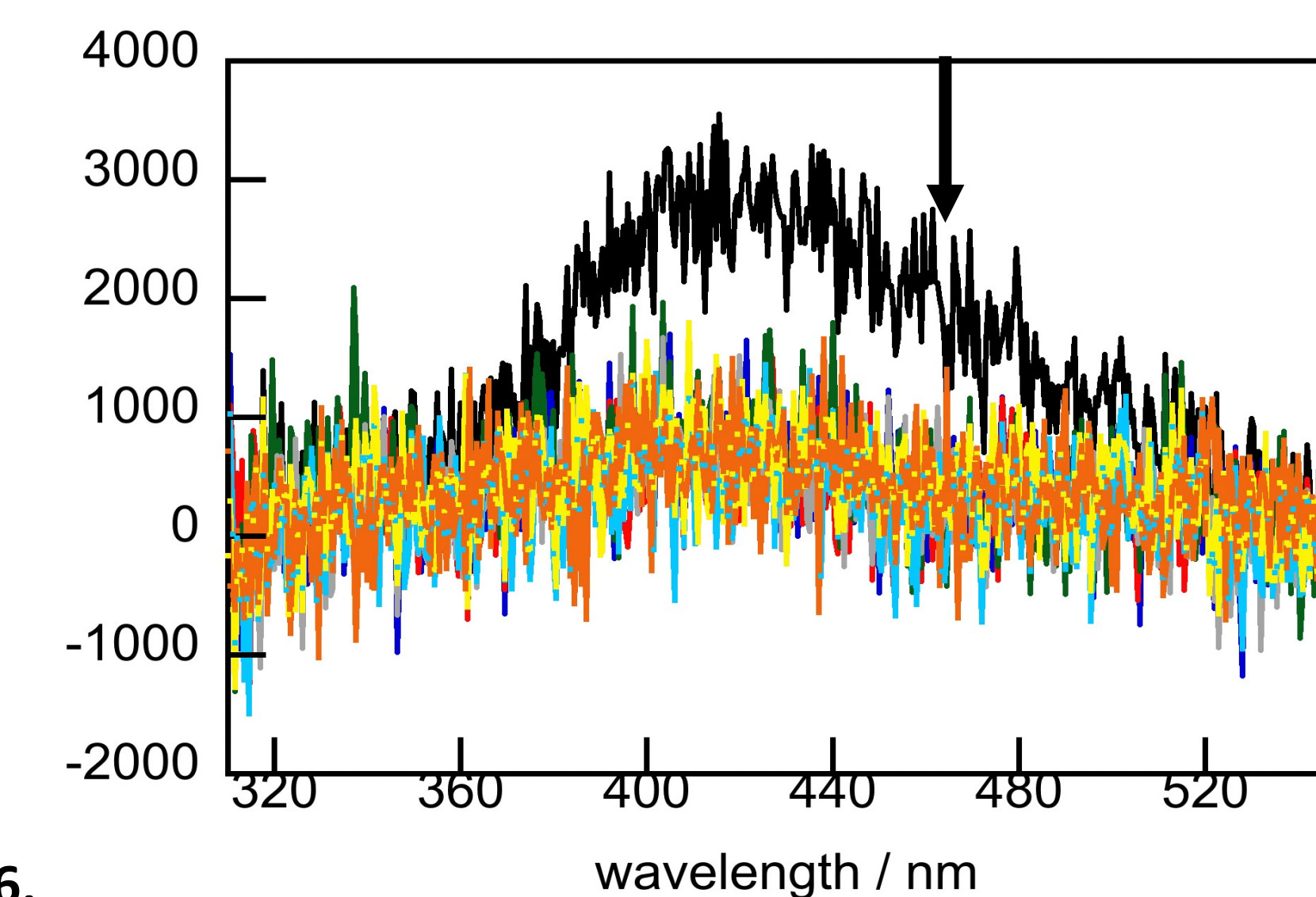


Figure 6. 0.01 μ M CB[6]/10 μ M CB[7] was able to be detected at the very minimum. 3 μ L of DAH was enough to reach a fluorescence value of 0 and saturate the system. The lower the percentage of CB[6] to CB[7] the lower the peak fluorescence is, and saturation is easier to achieve. 0.1% CB[6] in this case had a maximum peak..

- CB[7] is non-selective and exhibits no fluorescence because when figure 5 is compared with figures 3 and 4 a different trend is shown and there appears to be not a lot of fluorescence detected. A complex with CB[7], if it is being formed, is not emissive.
- CB[6] is selective and its guest (IMA) exhibits fluorescence upon encapsulation. When figure 1 is compared with figures 3 and 4 the same trend of decreasing fluorescence occurs due to the displacement of the guest from its cavity.
- As the total concentration of CB changes, so does fluorescence trends. In figures 3 and 4, 20 μ M of CB requires only 1 addition of DAH to fully saturate, while 10 μ M of CB required 4 additions to reach a saturation point.

Conclusions

- Overall, we answered our objectives and future work can be built on my research. Host-inclusion complexes can be used in real-life applications and more steps can be taken to fully understand Cucurbitur[n]urils complexes.
- We found that CB[6] interferes with the detection of CB[7] using its specific titration procedure. However, CB[7] cannot interfere with the CB[6] titration because it either forms a non-emissive complex or, more likely, forms an unstable complex with low equilibrium constant.
- Detection as low as 0.1% CB[6] to a 99.9% CB[7] ratio was analyzed through titration

Acknowledgements



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