Fluorescence-Based Characterizations of the First Two Polycyclic Aromatic Hydrocarbons Observed in Interstellar Space

By

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Abstract

The first two polycyclic aromatic hydrocarbons (PAHs) ever to be identified in interstellar space, 1- and 2-naphthonitrile, were spectroscopically analyzed in this project with an emphasis on their fluorescence properties. By providing spectroscopic quantities and spectral analyses, the further discovery of these two PAHs elsewhere in the universe can be facilitated. This is especially the case if either are present in the solar system, specifically in areas where future space missions plan to probe. This is because one experimental technique that was utilized in this research, synchronous fluorescence, is a useful, and established identification technique. However, it has recently been proposed to also be a potential complementary astrochemical identification technique that could be utilized in missions to planets or other satellites in the solar system. This is because spectra produced from this technique are identifiable, and significantly narrower than typical fluorescence emission spectra. Stemming from this logic, synchronous fluorescence spectra were measured for the two naphthonitrile isomers of interest, with the idea that the technique will be taken advantage of by the space industry in the future.

To further investigate their spectroscopic properties, both molecules were thoroughly analyzed while dissolved in various solvents. Such analyses included absorption and fluorescence spectra, quantum yields, and fluorescence lifetimes. Each of these experiments were conducted in four solvents, namely water, acetonitrile, methanol, and cyclohexane. Fluorescence sensitivity to both polarity and oxygen were also explored via comparing emission intensities for solutions of ethanol and water, before and after being purged with Argon. These results highlight the dependence of a given fluorescence spectrum of 1- or 2-CN on its environment, in this case the solvent or its exposure to

molecular oxygen. These results have implications on their emission properties in space. Additionally, the measured spectra have applicability for reference with optical telescope observations (direct collection of fluorescence emission), which are arguably even more significant than the collection of synchronous fluorescence spectra.

Effects on the fluorescence of 1- and 2-CN were also explored by the use of host-guest chemistry. Host-guest experimentation was implemented in this research due to the convenient size and shape of 1- and 2-CN, as this indicated that they could possibly be incorporated within larger host molecules. Consequently, two host molecules were attempted for 1-CN, and one for 2-CN, where one displayed significant binding to 1-CN. These hosts were cucurbit(7)uril (CB[7]), and (2-hydroxypropyl)-β-cyclodextrin (β-CD), with CB[7] successfully suppressing the fluorescence of 1-CN. CB[7] inclusion was also attempted with 2-CN, however a negligible impact on its fluorescence was observed.

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1-CN: 1-cyanonaphthalene or 1-naphthonitrile

2-CN: 2-cyanonaphthalene or 2-naphthonitrile

PAH: polycyclic aromatic hydrocarbon

UIRs: unidentified infrared bands

CB[7]: cucurbit(7)uril

β-CD: (2-Hydroxypropyl)-β-cyclodextrin

ISC: intersystem crossing

IC: internal conversion

VR: vibrational relaxation

PSF: polarity sensitivity factor

OSF: oxygen sensitivity factor

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Chapter 1 Introduction

The field of astrochemistry is relatively new to science. Sitting as the in-between for chemistry and astronomy, astrochemistry gained its footing conjointly with the advancement of radio telescopes in the last half century.[1] A large portion of the field's resources are devoted to the identification and explanation of extrasolar molecules. Most of these molecules, especially smaller ones, are identified in outer space via their unique rotational fingerprints that are caused by their interaction with radio waves which originate from nearby stars.[1] Larger molecules however, like polycyclic aromatic hydrocarbons (PAHs), are best for study through the use of infrared or optical light.[2] Over time, numerous molecules have been identified in interstellar space, some being incapable of forming naturally on Earth, and others being quite prevalent here. As knowledge and techniques within the field rise, more and more molecules are hoped to be added to the catalogue of molecules identified in space, as well as what places in the universe they are prevalent.

The two molecules that this research is centered around are two naphthalene derivatives, 1- and 2-naphthonitrile (1- and 2-CN). Naphthalene is the smallest PAH there is, therefore, these molecules sit right in the middle of small and large astrochemicals, making them applicable to both radio and optical identification. Their identification was found through their radio rotation spectra. However, a search of the literature revealed that very little is known about their UV and optical spectra. Consequently, there is a necessity for the enlightenment of this knowledge gap through experimental measurement and analysis.

1.1 PAH Astrochemistry

Out of the molecules sought to be found, organics are of particular importance, as they hold within them the potential to help explain the origins of life. For decades it has been suspected that PAHs are the culprits for a large portion of the previously unidentified infrared bands (UIRs) that are especially present in the Milky Way, as well as many other extragalactic sources.[1] The reasoning behind this idea is due to the presence of C – C and C – H bond bends and stretches that are typically observed in PAHs.[1] It was not until the recent discovery of benzonitrile within the pre-stellar, dark molecular cloud of TMC-1 that evidence was finally found to support this long-hypothesized theory.[3,4] Although benzonitrile is not a PAH, it does give good insight towards the idea that aromatic chemistry is not only possible in space but is also likely to be ubiquitous throughout the universe, especially if it can be found in a dark molecular cloud like TMC-1.[3] Soon after this discovery, further evidence was found in the same area supporting the same theory. This evidence was the discovery of two pairs of isomers that were found in rapid succession. The first pair being 1-cyano-1,3-cyclopentadiene, as well as 2-cyano-1,3-cyclopentadiene, and the second pair being 1- and 2-CN.[3,5,6] The rotational spectra which allowed for the discovery of 1- and 2-CN can be seen below in Figure 1.1.

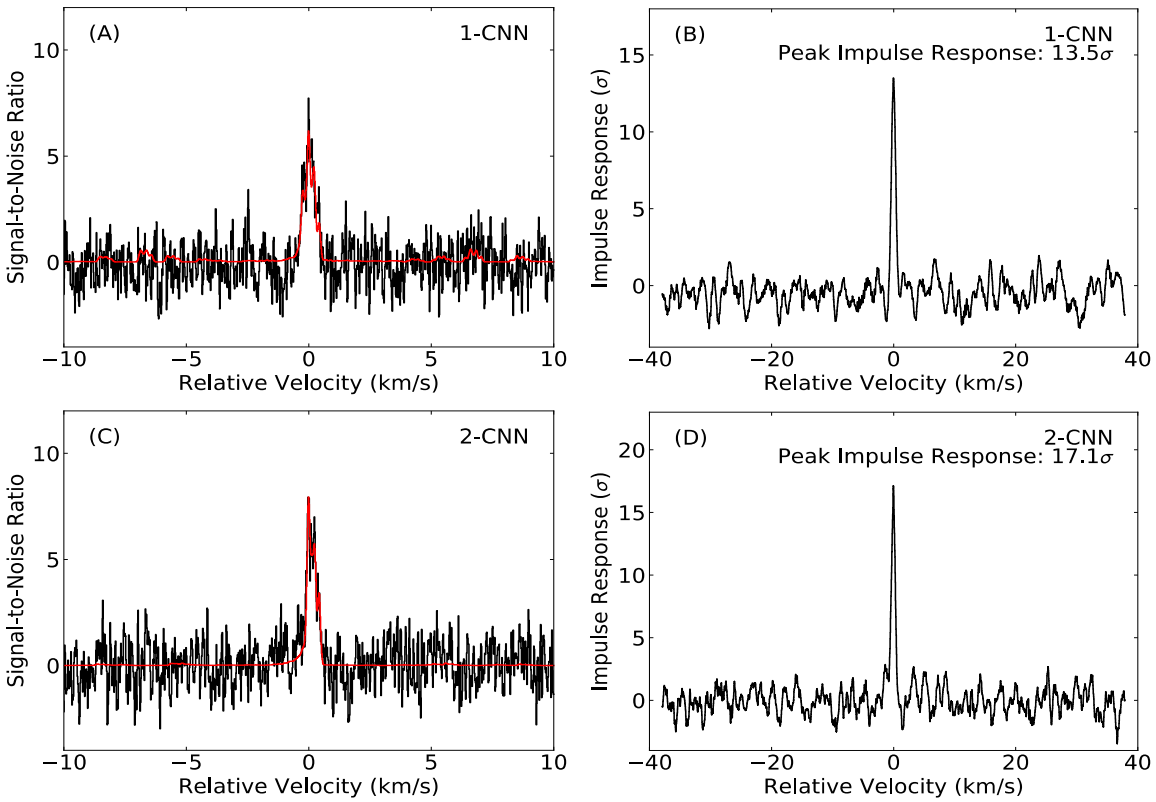

Figure 1.1: Stacked spectra (A and C) of observed GOTHAM DR2 data (black) with line profiles overlaid (red), along with impulse response functions of the stacked spectra (B and D) (used without permission from reference 3).

Of these five molecules, 1- and 2-CN are especially important astrochemical discoveries as they are the first PAHs whose existences have been confirmed within interstellar space.[3] This discovery thereby adds further support to the idea that UIRs are caused by the presence of PAHs throughout the universe. It also adds noteworthy importance to said molecules, as they are the first of their kind to be identified. Numerous experimental studies have provided detailed explanations regarding PAH formation and development in similar environments to TMC-1. Based on information gathered from such sources, it has been estimated that 10-25% of all carbon contained within interstellar

media exist as PAHs.[7] Therefore, it is highly likely that 1- and 2-CN, are among the first of many PAH discoveries, and are thus forerunners for what is to come. For these reasons, further spectroscopic analyses of these molecules could prove to be helpful in providing resources to refer to when seeking them or other PAHs like them elsewhere in the universe. In this project, detailed studies of the UV-Visible absorption and fluorescence properties of these two fascinating astrochemical molecules will be conducted to add to the understanding of their photophysical properties, and their potential for optical spectroscopic detection. In addition, as they are of a convenient size and shape for host inclusion, their host-guest chemistry will also be explored.

1.2 Cyanonaphthalenes

Of the previously mentioned astrochemical discoveries, all of them have a single cyano functional group present in their structure. This similarity is of no coincidence. These cyano functionalized derivatives of their parent hydrocarbons house permanent, and significant dipole moments due to their functionalization and as a result allow for easier detection via their unique radio fingerprints.[3] These rotational fingerprints are illustrated best by the experimentally determined rotational spectra, for 1- and 2-CN as seen below in Figure 1.2.[3] It would be more desirable to have detected these derivative's parent hydrocarbons instead, however they possess no dipole moments, and therefore have no rotational radio spectra to be observed.[3] Fortunately, these cyano functionalized derivatives are good indications for the presence as well as the suspected abundances of their parent hydrocarbons.[3] This is true because the cyano radical is copious in most

molecular clouds and is said to not be the limiting reagent for the synthesis of these cyano derivatives.[3] When these radicals come into contact with any of the previously discussed parent hydrocarbons, the formation of the cyano functionalized derivatives are exothermic and face no activation energy barrier to overcome.[3] With TMC-1 being as cold and diffuse as it is, the presence of any activation energy barrier would likely prevent the existence of such molecules from forming within it. Consequently, these reactions are spontaneous.

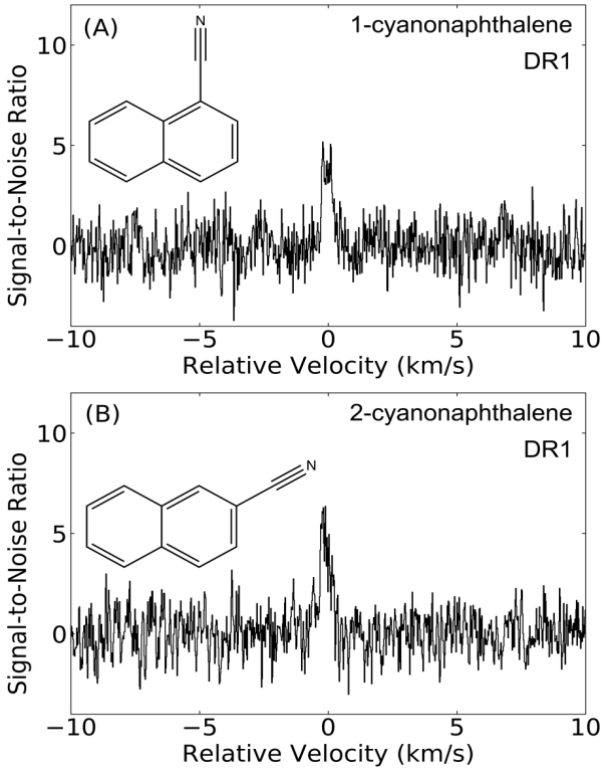

Figure 1.2: A display of the experimentally proven permanent dipole moments of 1-CN (A) and 2-CN (B), detailing the necessity of their cyano functional groups for astrochemical observation (used without permission from reference 3).

Currently, the mechanisms for interstellar PAH formation are uncertain.[3] However, one of two pathways are the generally expected methods of synthesis, or a combination thereof. They are referred to as the 'top-down' and 'bottom-up' approaches.[3] Unsurprisingly, both occur exactly as most would assume, given their names. The top-down approach requires the intervention of stars, particularly their emissions of UV radiation. Upon absorption of UV light, larger carbon containing species can be broken down to form a multitude of PAHs.[3] Such carbon containing species can include carbon soot or carbon clusters.[3] The bottom-up approach, however, involves the presence of smaller molecules that are employed as building blocks to form the final PAH product.[3] There are many reaction pathways in which both processes are capable of occurring. However, the top-down approach requires a star supplying UV radiation to those larger carbon-containing molecules that are usually contained within the stellar envelope. The resulting PAHs are spewed out into space, eventually reaching interstellar space, and populating molecular clouds such as TMC-1.[3] This implies that the detected 1- and 2-CN in TMC-1 could have been formed via the top-down approach. However, there is no star relatively close to TMC-1, and small PAHs like naphthonitriles are not capable of traversing long distances after being formed by the top-down approach. This is because the constant bombardment of UV radiation from the star they are formed from causes their destruction. Therefore, due to the absence of a star being relatively nearby to TMC-1, the bottom-up approach is expected to be the main or only cause for the 1- and 2-CN abundances that have been observed in this molecular cloud.[3]

1.3 Fluorescence

Luminescence is an umbrella term which describes the emission of radiation via a molecule that has been promoted to an excited electronic state.[8] For the most part, these promoted electrons exist in their excited state for a very short period of time, and soon after return to their ground state. The reason that luminescence is an umbrella term, is due to the fact that there are multiple types of luminescence. Relevant types of luminescence to this research are fluorescence and phosphorescence, with fluorescence being especially significant. Both types involve the absorption of radiation to promote an electron in a molecule to an excited electronic state, however once promoted to an excited state, phosphorescence involves an extra step.[8] This extra step is known as intersystem crossing (ISC), which requires an electron to change its spin from one spin state to another (i.e. +1/2 to -1/2, or vice versa).[8] When this occurs, the molecule enters into what is known as a triplet state, as there are now two electrons that are not spin-paired.[8] Normally, organic molecules such as the two being studied, exist as having all of their electrons being spin-paired, and as a result are in what is called a singlet state.[8] This remains the case during fluorescence, when one of these electrons is promoted to an excited state. These two electronic states are illustrated in Figure 1.3 below.

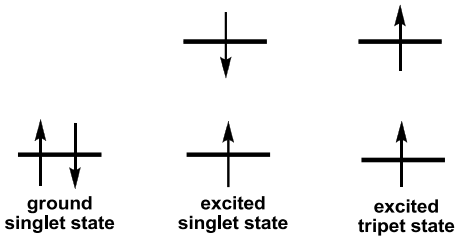

Figure 1.3: Illustration of relevant excited electronic states compared to their ground state (used without permission from reference 8).

The reasoning behind the names of singlet and triplet stem from the number of split energy levels that are produced when a magnetic field is applied.[8] These designations are shown in Table 1.1 below.[8]

Table 1.1: Designations for the number of spin-unpaired electrons in a molecule.

Number of spin-unpaired electrons	0	1	2	3
Designation	Singlet	Doublet	Triplet	Quartet

Doublets usually require the presence of a radical, and thus the triplet state is more relevant to this project as it is associated with phosphorescence, which decreases the amount of fluorescence that a molecule is capable of.[8] Phosphorescence typically occurs on a much longer time scale as opposed to fluorescence though. As a result, it does not significantly contribute to the total emission of a molecule when compared to the total amount of fluorescence, or other occurring processes. The reason that phosphorescence occurs for as long as it does is because of the requirement of a spin change, which is spin

forbidden.[8] Just by contemplating the Pauli Exclusion Principle, one can distill why it would make phosphorescence a less desirable process for the electron to move through. The Pauli Exclusion Principle states that no two fermions can have the same quantum number. Distilling this into terms more practical to chemistry, this means that no two electrons of the same spin can occupy the same orbital. Therefore, to go through the process of phosphorescence, the already switched spin of the excited electron would have to revert back to the same spin in order to reoccupy the ground state with its electron pair. Since the excited electron naturally wants to reoccupy its ground state, phosphorescence makes this much more complicated than fluorescence, which involves no spin change. Besides phosphorescence, there are also other processes which subtract from the amount of total fluorescence that a molecule is capable of producing. Such processes include transferring the previously absorbed energy to another molecule, and internal conversion (IC) which also involves vibrational relaxation (VR), where the molecule relaxes to its ground state via the release of heat.[8] This occurs by the excited electron passing through successive vibrational states, until it reaches the ground state.[8] A useful visualization of all these possible processes that an excited electron can go through can be seen below in the Jablonski diagram in Figure 1.4.

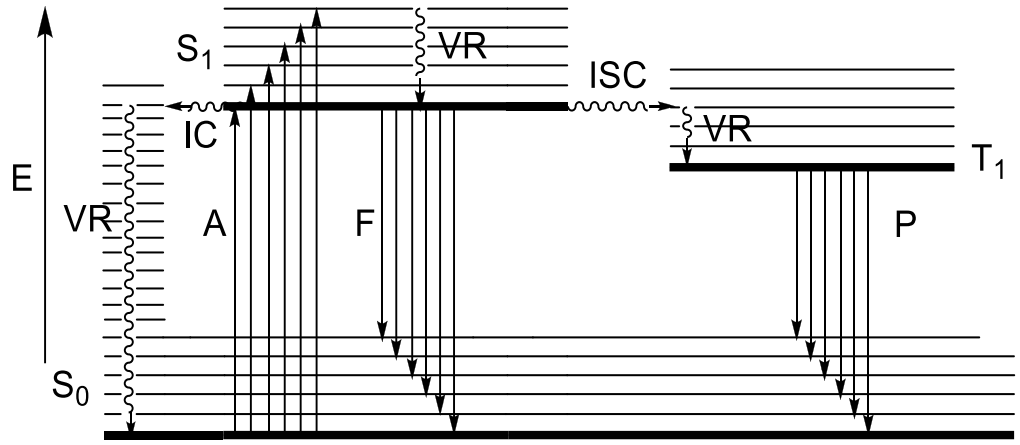

Figure 1.4: A Jablonski diagram, where F stands for fluorescence, P for phosphorescence, and A for Absorbance.

All straight arrows outline transitions that involve radiative transfer, while wavey arrows are nonradiative processes. It should be noted that, as seen in Figure 1.4, the energy of the absorbed photon that excites the molecule, is always of higher energy than the photon that is emitted by the molecule. This is true whether the photon is emitted through fluorescence, or phosphorescence. This happens because the excited molecule passes down through subsequent vibrational states before fluorescence or phosphorescence can occur, thus losing some of the initially absorbed energy.[8] This has great significance in fluorescence or phosphorescence-based studies, such as this one, because the wavelength of the photon required to excite a molecule is always different, and higher in energy than the one that is detected via its emittance. This phenomenon is commonly referred to as the Stokes shift.

A helpful measurement that explains the amount of absorbed light that fluoresces from a given molecule is its quantum yield. It is denoted on a scale of 0 to 1; 0 being no

observed fluorescence, and 1 indicating that all the absorbed light is emitted through fluorescence. A molecule's quantum yield is dependent on different characteristics of its environment, these characteristics include its solvent, temperature, and pressure.[9] The quantum yield can be found from the rate constants of the various decay processes shown below in Equation 1.1. Here, k_R refers to the radiative decay rate constant (fluorescence), and k_{NR} to the nonradiative decay rate constant (IC). Together, they encapsulate all relevant decay pathways of the excited molecule. Thus, when k_R is divided by the sum of the two, the relative fraction of radiative decay can be established.

$$\phi_F = \frac{k_R}{k_R + k_{NR}} \qquad \textbf{Equation 1.1}$$

In this research various solvents are utilized for both naphthonitrile isomers to see their effect on quantum yield, and fluorescence lifetimes. Fluorescence lifetime is the amount of time that a molecule remains in its excited state. Fluorescence is an extremely fast process, with lifetime values being found in the nanoseconds. Measuring this quantity is valuable because it provides information on multiple properties that effect a fluorophore's fluorescence, such as solvent polarity, quenching effects, and its ability to transfer its absorbed energy to another molecule.[9] These values are typically measured through an experimental technique called Time-Resolved Fluorescence. Fluorescence lifetime is defined by Equation 1.2 below, where k_R and k_{NR} are the radiative and nonradiative rate constants for the molecule.

$$\tau_F = \frac{1}{k_R + k_{NR}}$$ **Equation 1.2**

The effect that solvent polarity has on a dissolved fluorophore can be measured through the use of another experimental technique as well. An understanding of this effect can be determined through the quantification of the fluorophore's polarity sensitivity factor (PSF), after performing the required experimentation.[10] The process of performing this experiment is detailed in Section 2.5. A PSF value greater than one indicates that a molecule fluoresces most intensely when in a non-polar environment. This is the most common scenario; however the opposite is also possible.[10] The opposite being when a PSF value less than one is observed. This implies that a fluorophore fluoresces most intensely when in a polar environment, a fluorophore of this nature is referred to as having "reverse polarity dependence".[10] Fluorescence dependence on molecular oxygen can be found while PSF is being determined as well. The oxygen sensitivity factor (OSF) involves the fluorescence measurement of a fluorophore before and after it has been purged of molecular oxygen, making clear the effect of oxygen on its fluorescence. This effect arises because molecular oxygen has a ground triplet state, which can readily quench the excited state of other molecules via energy transfer. A value greater than one indicates that when molecular oxygen is present in solution, it is capable of quenching the fluorescence of the fluorophore, and therefore decreasing the total amount of fluorescence. Typically, longer fluorescence lifetimes are indicative of a molecule being likely to be sensitive to the presence of oxygen, as oxygen has the necessary time to

quench it. Equations for the determination of both PSF and OSF can be found in Equations 2.3, 2.4, and 2.5.

1.4 Host – Guest Inclusion Chemistry

Another method of determining what impacts the fluorescence of the molecules of interest to this research was by employing host-guest chemistry. The two cyano naphthalene molecules that were studied provide the opportunity to investigate the effects of their inclusion into molecular hosts on their spectroscopic properties. This interest is based on our research group's overall interest in supramolecular chemistry, more so than in its implications for astrochemistry. Host – Guest inclusion is a supramolecular, chemical phenomenon in which two or more molecules interact in a non-covalent fashion.[11] The interaction requires one molecule (the host) encapsulating the other, creating a completely different environment for the encapsulated molecule (the guest). This has significant impacts on the guest's properties, and sometimes even the host's.[11] Such properties include physical properties like stability, reactivity, and solubility, while also impacting spectroscopic properties like infrared spectra, UV-Visible absorption, and subsequent emission after absorption.[11] Emission is particularly significant to this research, due to the fluorescent focus on the naphthonitrile isomers' interaction with host molecules.

No covalent chemical bonds are formed or destroyed in the process of the host-guest interaction, meaning that the process is completely reversible. This is due to the fact that the spontaneous formation of the host-guest system is purely caused by

intermolecular forces such as London dispersion, dipole-dipole, hydrogen bonding, and the hydrophobic effect.[11] The hydrophobic effect is clearly only prevalent in aqueous solutions though. Only aqueous solutions were used in any host guest involving experiments in this research, and therefore the hydrophobic effect is quite relevant to the driving forces which caused the reported host-guest interactions. A simple depiction of host guest inclusion is illustrated in Figure 1.5, notice the equilibrium arrow, which indicates the reversibility of the process.

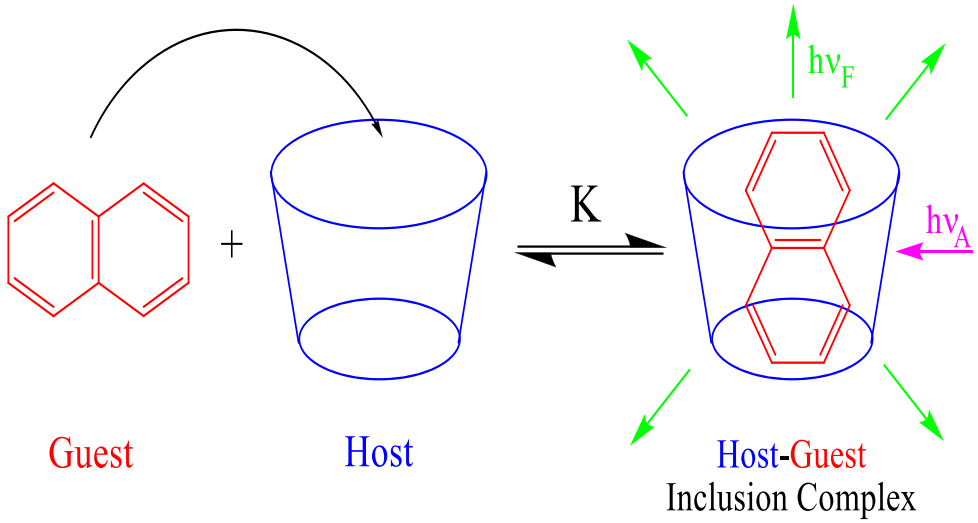

Figure 1.5: A basic illustration of a 1:1 host-guest inclusion complex.

Solvent is an important parameter to consider in these interactions. Generally, guest molecules will actually compete with solvent molecules to occupy the host's cavity.[11] When contemplating whether a process is spontaneous, one must consider enthalpic, as well as entropic consequences caused by the chemical process. Host-guest interactions are no different, and therefore when guests displace solvent molecules within the host cavity, entropy increases.[11] The host-guest interactions produce a negative

enthalpy change, due to the stabilization of one another. As seen in Equation 1.3, a solvated host-guest system is therefore generally spontaneous, as ΔG will be negative when enthalpy is negative, and entropy is positive.

$$\Delta G = \Delta H - T\Delta S \qquad \textbf{Equation 1.3}$$

For this reason, all that is necessary to prepare solvated host-guest inclusion is to dissolve the host and guest molecules in a solvent. This is because the process is spontaneous, and therefore the inclusion is self-assembled. Gas phase host-guest inclusion is also possible; however, its spontaneity is typically less favourable due to the formation of the complex always causing a negative entropy change.[11] The reason for this being due to the fact that there are no solvent molecules located within the cavity for the guest to displace.[11] Thus, the stabilization of both molecules through forming the complex must produce a significantly negative enthalpic change to drive its spontaneous formation.[11]

An indication of the stability of an inclusion complex can be obtained by analyzing its binding constant, K. The larger the value of K, the more stable the complex.[11] The formula for K is shown below in Equation 1.4, where it is equal to the concentration of host-guest inclusions, divided by the concentration of the individual host and guest molecules, multiplied by one another.

$$K = \frac{[H:G]}{[H][G]} \qquad \textbf{Equation 1.4}$$

Stoichiometry also comes into play when studying hosts and how they bind to their guests.[11] The simplest form of host-guest chemistry involves one host molecule engulfing one guest molecule. However, there are multiple combinations for the host to guest ratio in an inclusion complex. The most common being 1:1, however combinations such as 2:1, 1:2, and 2:2 are all possible as well.[11] Shown below in Figure 1.6 is an illustration of different possible ratios of host-guest inclusion.

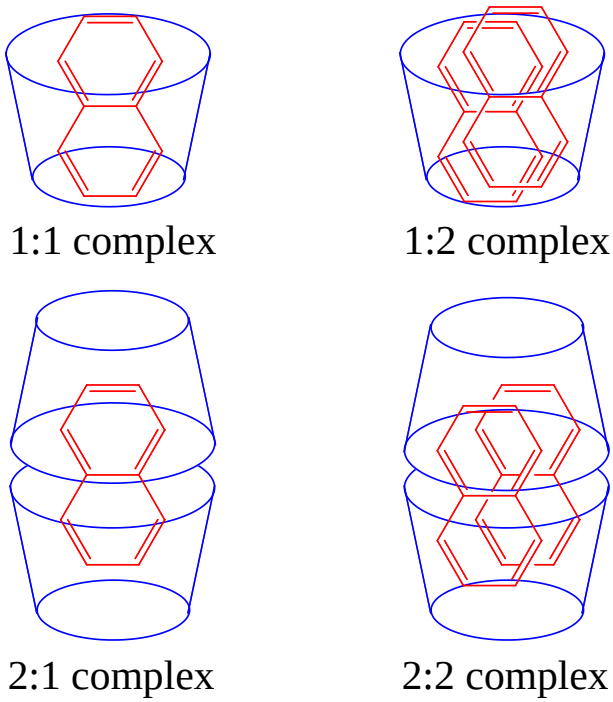

Figure 1.6: An illustration of some of the different stoichiometric proportions that a host-guest inclusion complex is capable of existing as.

For reasons explained in Section 3.5, the significant host to guest ratio for this research project is 1:1. A total of two host molecules were utilized in host-guest experiments within this research. Those hosts were cucurbit(7)uril (CB[7]), and (2-hydroxypropyl)-β-cyclodextrin (β-CD). Like most hosts, CB[7] and β-CD's host cavities

are relatively non-polar. The two molecular cavities differ in shape slightly. The shape of β-CD is toroidal in nature, while CB[7]'s is more similar to the shape of a pumpkin, hence the name cucurbituril.[12] Both hosts contain polar attributes as well though. CB[7] contains carbonyl groups that surround the outskirts of its cavity. These can help in the stabilization of a guest that has both polar and non-polar properties. This is typically the nature of most guests that it binds well with.[12] Due to the oxygen atoms on these ketones being negative, CB[7] binds guests that contain positive, or partial positive charges. Specifically, positively charged aromatic compounds.[12] It is already known that CB[7] binds well to naphthalene.[12] From these points alone, it makes sense that CB[7] could bind to 1- and 2-CN as both are not much larger than naphthalene, and the cyano group is partially positive, as it is electron withdrawing. The visualization of the binding of a guest molecule to the cavity of CB[7] is most easily apparent when considering the structure of CB[7] from the side, as shown below in Figure 1.7.

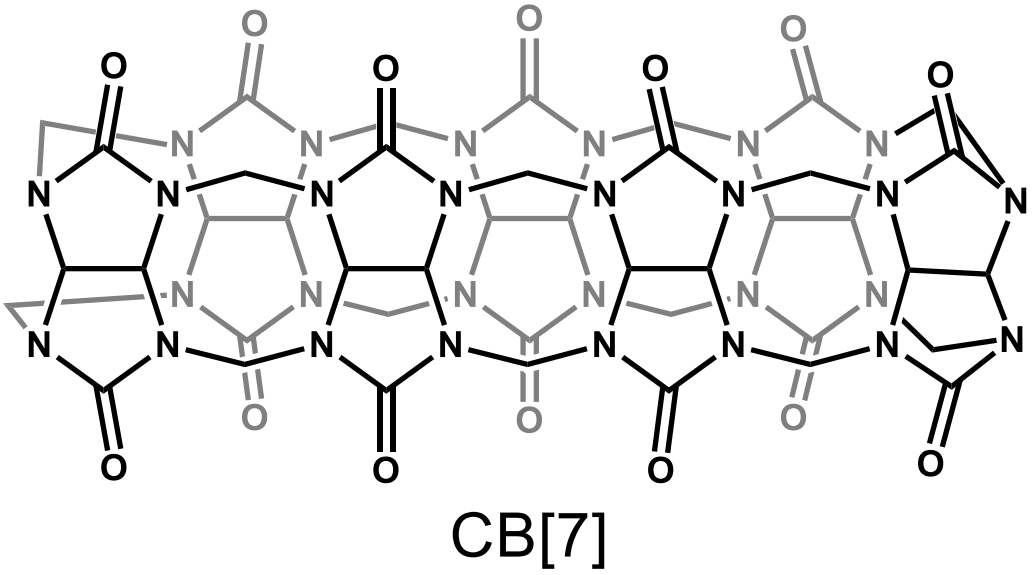

Figure 1.7: Structure of the host molecule CB[7].

In terms of 1- or 2-CN binding to β-CD, however, its cavity is slightly less voluminous, where CB[7] is just large enough to contain the molecule naphthalene.[12,13] Since 1- and 2-CN are slightly larger than naphthalene, they may face issues binding to the cavity of β-CD because of their size. That being said, β-CD also has polar attributes on the outskirts of its cavity as well. These are located on the hydroxyl groups located around the macrocycle. It should be noted however, that hydroxyl groups are less polar than carbonyl groups, so β-CD's ability to stabilize positively charged guest molecules is reduced. The structure of β-CD can be seen below in Figure 1.8, where its host cavity, and surrounding hydroxyl groups are illustrated.

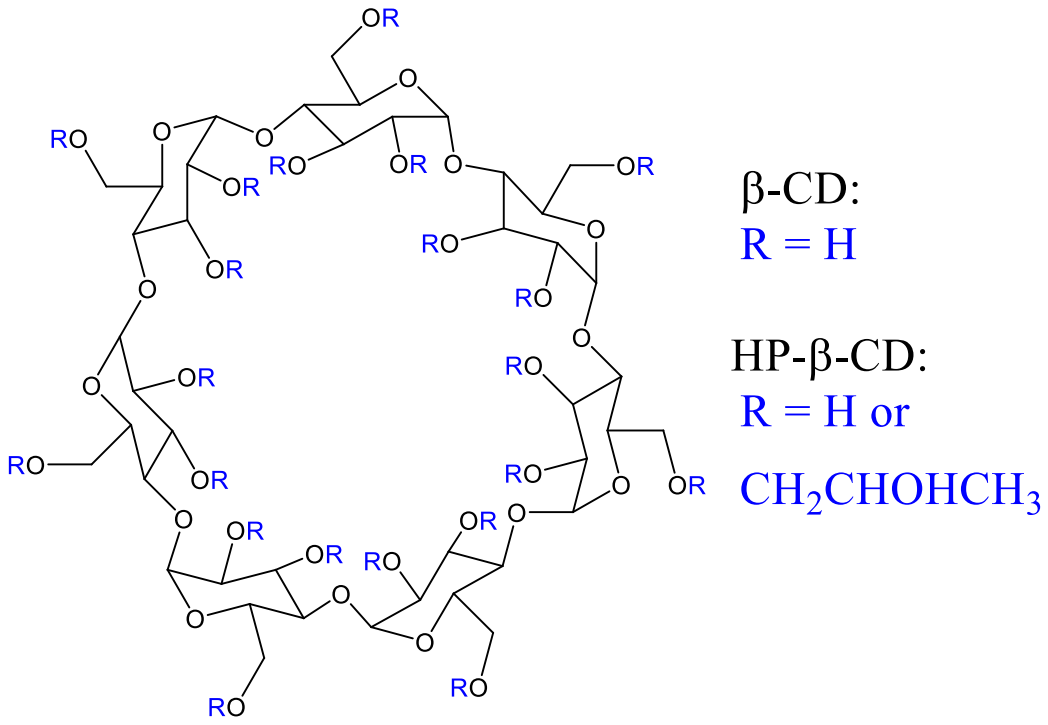

Figure1.8: A Structural representation of β-CD, where the R-groups are hydrogens.

1.5 Project Goals

The motive behind this research was to advance the current knowledge and available reference spectra of two recently identified astrochemicals. These astrochemicals are 1- and 2-cyanonaphthalene, the first two PAHs discovered in interstellar space. If their existence has been proven in a cold, dark, diffuse region of space such as TMC-1, it is not illogical to deduce that they are likely prominent in many other places in the universe with similar environments, such as the outskirts of our solar system. A likely place to find these molecules within the solar system are in comets.[14] The molecule toluene has been discovered by the Philae lander on comet 67P/Churyumov-Gerasimenko.[14] Although toluene is not technically a PAH, analogous to the discovery of benzonitrile in TMC-1, it is a good indication that such molecules exist within comets. To expand on this logic, Cyanide and hydrogen cyanide have also been identified during cometary outgassing via a ground based optical telescope.[15] Thus all of the ingredients for the formation of 1- and 2-CN are present within comets.

By providing reference spectra and measuring spectroscopic properties of PAHs such as 1- and 2-CN, further astrochemical discoveries could be facilitated. To do this, fluorescent characteristics would be a good aid in doing so, especially through the employment of the identification technique known as synchronous fluorescence.[16] Synchronous fluorescence both simultaneously scans the excitation and emission wavelengths with a constant difference between them, where that difference is equal to the Stokes shift of the molecule of interest. The result is a unique and identifiable spectrum that is typically significantly narrower than that of traditional fluorescence spectroscopy. It has been proposed that synchronous fluorescence would be a good

complementary technique for the identification of fluorescent compounds from samples of comets, or even utilized within future missions to other planetary bodies within the solar system.[16] To do this a fluorescence instrument with a tunable laser source would have to be implemented within a rover, where a robotic arm would be useful to aid it being pointed toward the ground beneath the rover.[16] The potential also remains for flyby missions as well, where probes or satellites would be utilized.[16] With that said, receiving emission spectra in this case is much more realistic, as satellites typically travel very fast relative to the object they orbit. Emission spectra would be more likely to be received here, as light directly from the satellite is not necessary to excite the desired area, whereas in synchronous fluorescence it would be, thus requiring more time that the instrument may not have.

The fluorescence spectra of both cyanonaphthalenes are the most relevant outcomes of this research in terms of their further identification in space. Synchronous fluorescence is a technique that would have to be utilized on site, such as on probes, or rovers, whereas the traditional fluorescence emission spectra that was gathered in this research is applicable to optical telescope observations, that can be done while on Earth or in space.[2] It was mentioned earlier that comets are a likely place to find 1- and 2-CN, this could be done so optically from Earth as well. It is not necessarily required to visit one through the use of a lander, satellite, or probe. This is because when one passes in front of the sun, a cometary tail is produced, where gaseous molecules are released from the nuclei.[15] This light can cause released fluorophores to fluoresce, then this light can be analyzed via optical telescopes.[15] Such telescopes have to be partially capable of capturing ultraviolet light though, this being due to 1- and 2-CN emitting at longer

ultraviolet wavelengths. It should also be noted that all of the obtained fluorescence spectra was done so while 1- and 2-CN were present in solution, however it is much more likely that they would be in a gaseous state in space. That being said, the obtained data regarding the two compounds is still very relevant to the emission spectra that would be observed. Not only this, but other experiments that were performed, such as PSF and OSF determinations, should be good indications to how much atmospheric and solvent effects impacted their observed emission peaks that are reported in Chapters 3 and 4.

Other helpful quantities such as quantum yields, and fluorescence lifetimes were recorded for both cyanonaphthalene isomers while dissolved in various solvents as well. These solvents included water, methanol, acetonitrile, and cyclohexane. Fluorescence emission spectra were produced for each compound in each solution. Polarity and oxygen sensitivity experiments were also performed, in the hope of determining the impact of polarity and oxygen on the fluorescence of 1-CN and 2-CN. Although the presence of host-guest chemistry within this research may be deceiving, it is completely unrelated to astrochemistry, as well as the locating of 1- and 2-CN in space. However, due to the combination of the accessibility for performing the experiments, the available expertise on the matter, and the convenient size and shape of these molecules as guests; the effect on the absorption and fluorescence of aqueous solutions of 1- and 2-CN while in the presence of a host molecule were also explored. Both successful and unsuccessful binding studies were obtained.

Chapter 2 Experimental

2.1 Materials

Table 2.1: A list of materials that were used during experimentation. All were used as received.

Chemicals	Manufacturer
Ethanol - 95%	Commercial Alcohols
Methanol - 99.9%	BDH
Acetonitrile	Fisher Chemical
Cyclohexane - 99.5%	Aldrich
(2-Hydroxypropyl)-β-cyclodextrin	Aldrich
Cucurbit(7)uril	Aldrich
1-Naphthonitrile	TCI
2-Naphthonitrile	Thermo scientific

2.2 Solution Preparation

The preparation for all 1- or 2-CN containing solutions followed the same procedure. This was true for all experiments that were performed after the spontaneous, unaided solidification of 1-CN, which occurred relatively soon into the experimental analysis of this research. The only difference of preparation being the need to pipette the originally liquid 1-CN. This process begun with the dissolving of either solute in one of the five solvents, where solvents of choice depended on the experiment being performed. This was done in volumetric flasks. The concentrations of either solute was not necessary for the preparation of these solutions, and therefore was not measured. Solutions that were found to have absorbances between 0.2 and 0.45, for the appropriate wavelength, were considered to have appropriate solute concentration to allow for further experimental analysis. If a solution was found to be below this range, more solute was added, and if it was found to be above, a dilution was performed.

Titration experiments required the addition of a host to the previously prepared solutions. In these cases, host weights were accurately measured inside glass vials to obtain masses required to produce the desired concentration. All weighing was performed on an analytical balance. Host-guest solutions were prepared by the addition of three milliliters of the 1- or 2-CN containing solution, via a volumetric pipette to the vial containing the weighed-out host. Dilutions were then performed on higher concentrated host solutions to yield lower concentrated ones, which were necessary for titrations. Absorbances were measured for every differently concentrated host solution during these titration experiments, as hosts can occasionally affect the guest molecule's absorbance.

Absorbance determination was accomplished through the utilization of UV-Visible spectroscopy, specifically using a Cary Bio UV-Vis spectrophotometer. To obtain this measurement, a glass pipette was used to draw roughly three to four milliliters of the prepared solution and was subsequently released into a $1cm^2$, quartz cuvette. From there, the cuvette was wiped clean with a Kimwipe to limit obstruction to absorption measurements by unforeseen contaminants. The cleaned cuvette was then placed in the sample holder of the spectrophotometer, and the instrument was zeroed according to the sample. Each solution's absorbance was measured from 250-500nm, using the medium scan rate. If it was intended for the solution to be subsequently purged, some of the cuvettes that were used were too tall to fit within the sample chamber, and therefore a black cloth was used to cover the sample chamber, as it could not be closed.

2.3 Fluorescence Measurements

All solutions that had their fluorescence measured were prepared as outlined in Section 2.2. Aside from fluorescence lifetime experiments, all fluorescence data was acquired through the use of a Photon Technology International (PTI) RF-M2004 Luminescence Spectrometer. The Felix application allowed for the setting of experimental parameters, as well as the running and evaluating of fluorescence measurements. One of these parameters is temperature, which was kept constant at 25ºC. Other parameters chosen were the excitation and emission wavelengths, which varied for both naphthonitrile isomers. For the 1- and 2-CN isomers, excitation wavelengths of 300nm, and 290nm were used, respectively. In terms of emission wavelength ranges, 1-CN's fluorescence emission was measured from 310nm to 510nm, and 2-CN's was measured from 300nm to 500nm. Slit widths of 0.38mm were chosen, yielding monochromator band passes of 1.0nm. These parameters were constant for all but synchronous fluorescence measurements. Appropriate solvent blanks were also run for all fluorescence measurements performed on the PTI RF-M2004 Luminescence Spectrometer.

2.3 Synchronous Fluorescence

The majority of fluorescence scans performed on the Photon Technology International RF-M2004 Luminescence Spectrometer were done as emission scans, however the synchronous fluorescence spectra were acquired through synchronous scans, which required different parameters. Synchronous fluorescence scans were also measured

at a constant temperature of 25 ºC, however water was the only solvent utilized in this experiment. Due to the fact that the experimental technique of synchronous fluorescence excites a sample over a range of wavelengths, while simultaneously measuring its emission at another range, a different type and set of parameters were required for both the excitation and emission of the isomers being studied. When choosing the excitation and emission wavelength ranges for either isomer, it was necessary to use their Stokes shifts. Both the measured excitation and emission ranges were varied over a 100nm range. For 1-CN, the absorbance maximum was found to be 297nm, and the emission maximum was 354nm, therefore having a Stokes shift of 57nm. Thus, the excitation range was from 247nm to 347nm, and the emission range was 304nm to 404nm. This way, the difference between the excitation wavelength being scanned, and the emission wavelengths being measured, was always 57nm throughout the measurement. For 2-CN, the absorbance maximum was 281nm, and had an emission maximum of 356nm, producing a Stokes shift of 75nm. Given these values, the excitation range was performed from 231nm to 331nm, and the emission range was 306nm to 406nm. Therefore in this case, the difference between the excitation wavelength being scanned, and the emission wavelengths being measured was always 75nm. As previously mentioned, slit widths of 0.38mm were used for emission scans. For synchronous scans however, 0.19mm was the chosen parameter, and a range of 0.5nm of light was allowed to pass into the chamber where the sample was held. By scanning both the excitation and emission wavelengths simultaneously, narrower spectra can be obtained compared to traditional emission scans (in which the excitation wavelength is fixed).

2.4 Fluorescence Titrations

In terms of titration experiments, naphthonitrile solutions and host-guest solutions were prepared as outlined in Section 2.1. A total of two hosts were utilized, and water was the only solvent used. The two host molecules were CB[7], and β-CD. Host containing solutions were never any more concentrated than 1.5mM for the CB[7] titrations. Higher concentrations of β-CD were used, however this experiment proved to be unsuccessful. Dilutions were then performed to obtain less concentrated CB[7]-containing solutions, due to the required host concentration being so small. The Felix program was employed to extract integrated areas of solution emission spectra after emission measurements were carried out. From there, Equation 2.1 was used to calculate $\frac{\mathrm{F}}{\mathrm{F_0}}$ values.

$$\frac{F}{F_0} = \frac{(\int \text{Host and Guest Solution Emission}) - (\int \text{Water Blank Emission})}{(\int \text{Guest Solution Emission}) - (\int \text{Water Blank Emission})} \qquad \textbf{Equation 2.1}$$

Titration curves were constructed as a plot of $\frac{\mathrm{F}}{\mathrm{F_0}}$ versus host concentration. The Cyclodextrin Equilibrium Constant for Windows (CDEQWIN) program was then used to find the fit of the function produced by these points and allow for the successive calculation of the binding constant. Since the complex that was studied was 1:1, Equation 2.2 was used to find the binding constant K.

$$\frac{F}{F_0} = 1 + \left(\frac{F_\infty}{F_0} - 1\right) \frac{[host]_0 K}{1 + [host]_0} \qquad \textbf{Equation 2.2}$$

2.5 Polarity and Oxygen Sensitivity Factors

To determine the polarity sensitivity factors (PSF) and oxygen sensitivity factors (OSF) for the two naphthonitrile molecules of interest to this research, two solutions for both compounds were prepared using the process outlined in Section 2.2. These solutions were prepared with nanowater and ethanol as the solvents. Both PSF and OSF experiments were able to be conducted together, as they required very similar data. Each molecule underwent three trials, and in each trial, six emission scans were performed. Two of these scans were solvent blanks, two were unpurged solutions of each solution, and two were solutions that were purged with Argon, to eliminate oxygen dissolution. The equation to determine PSF is shown in equation 2.3, where A is equal to the absorbance at the excitation wavelength. OSF was calculated for both the water and ethanol solutions. The equations to determine the OSF for both water and ethanol can be found below in equation 2.4, and 2.5, respectively.

$$\mathrm{PSF} = \frac{(\int \text{EtOH Solution Emission}_{(\text{Purged})}) - (\int \text{EtOH Blank Emission})}{(\int \text{Water Solution Emission}_{(\text{Purged})}) - (\int \text{Water Blank Emission})} \times \frac{A_{H_2O}}{A_{EtOH}} \qquad \textbf{Equation 2.3}$$

$$\mathrm{OSF}_{\mathrm{Water}} = \frac{\int \text{Water Solution Emission}_{(\text{Purged})} - \int \text{Water Blank Emission}}{\int \text{Water Solution Emission}_{(\text{Unpurged})} - \int \text{Water Blank Emission}} \qquad \textbf{Equation 2.4}$$

$$\mathrm{OSF}_{\mathrm{EtOH}} = \frac{\int \text{Ethanol Solution Emission}_{(\text{Purged})} - \int \text{Ethanol Blank Emission}}{\int \text{Ethanol Solution Emission}_{(\text{Unpurged})} - \int \text{Ethanol Blank Emission}} \qquad \textbf{Equation 2.5}$$

2.6 Quantum Yields

Just like the PSF and OSF determinations, the naphthonitrile containing solutions that were used for quantum yield analysis were prepared as outlined in Section 2.2. In this experiment however, all of the solutions used were purged prior to fluorescence emission scans. Purged solutions of naphthonitrile were compared against a standard solution. This standard solution was 9,10-diphenylanthracene, dissolved in cyclohexane. The reason that this standard was chosen was due to the fact that the quantum yield for it is known, large, and that it absorbs light at a similar region of the electromagnetic spectrum as compared to 1- and 2-CN. This solution was prepared analogously to the purged naphthonitrile solutions, with the difference being that 9,10-diphenylanthracene was used instead of one of the naphthonitrile isomers. The equation used to calculate the reported quantum yield values is shown in Equation 2.6, where ϕ_F is the quantum yield of the naphthonitrile solution, $\phi_{F,S}$ is the quantum yield of the standard, A refers to absorbance, and n is the refractive index of the appropriate solvent.[17]

$$\phi_F = \phi_{F,S} \times \frac{\int \text{Solution Emission}_{(\text{Purged})} - \int \text{Solution Blank}}{\int \text{Standard Emission}_{(\text{Purged})} - \int \text{Cyclohexane Blank}} \times \frac{A_S}{A} \times \left(\frac{n}{n_S}\right)^2 \qquad \textbf{Equation 2.6}$$

2.7 Fluorescence Lifetimes

Unlike all other fluorescence measurements, fluorescence lifetime values were obtained through the use of a time resolved spectrometer. The specific time resolved spectrometer used was a Photon Technology Timemaster. The same process was carried out for solution preparation as outlined in Section 2.2, and just like quantum yield determinations, all measured solutions were purged. A reference scattering solution was

used during measurements, where the fluorescence decay curves of the sample solutions were compared with a scattering solution to measure the lamp profile. This was done by the Timemaster program, where it compared the known decay curve of the scattering solution with the fit of the curve for the sample solution, thus allowing for the lifetime of the fluorophore in the solution to be calculated by the program. After the lifetime and quantum yield values were found for a given solution, their k_R and k_{NR} values could then be calculated. These values were calculated by employing Equations 2.7 and 2.8, respectively, where ϕ_F is quantum yield, and τ_F is fluorescence lifetime.

$$k_R = \frac{\phi_F}{\tau_F} \qquad \textbf{Equation 2.7}$$

$$k_{NR} = \left(\frac{1}{\tau_F}\right) - k_R \qquad \textbf{Equation 2.8}$$

Chapter 3 1-naphthonitrile

As a result of the fact that this research focuses mainly on the spectroscopic properties of two molecules in particular, the focus of this chapter is on the first isomer, 1-naphthonitrile or as it has been referred to previously, 1-cyanonaphthalene (1-CN). Chapter 4 discusses the spectroscopic properties of 2-naphthonitrile, or 2-cyanonaphthalene (2-CN), and Chapter 5 focuses on the comparison of the findings from both. Specifically, this section will report and discuss all of the experimentally determined quantities and spectra for 1-CN. These findings include the effect on absorption and emission of 1-CN being dissolved in various solvents, its quantum yields and fluorescence lifetimes in various solvents, the sensitivity of the compound's fluorescence to oxygen and polarity, its synchronous fluorescence spectra, its photophysical parameters, and the effect on its fluorescence when dissolved with host molecules, which were CB[7] and β-CD.

3.1 Spectroscopic Effects of Dissolution in Various Solvents

Interestingly, there was little to no effect on the absorption of 1-CN when it was dissolved in various solvents. For the most part, its maximum absorption wavelength did not exceed or fall below the range of 295-298nm for all measured absorption spectra via UV-Visible spectroscopy. All solvents that 1-CN were dissolved in were water, methanol, acetonitrile, and cyclohexane. The emission spectra of each were compared and plotted on a graph with one another and normalized as a means of comparing the effect on

emission. This plot can be seen below in Figure 3.3. The absorption spectra of 1-CN in both water and cyclohexane can also be seen below in Figure 3.1 and 3.2, respectively.

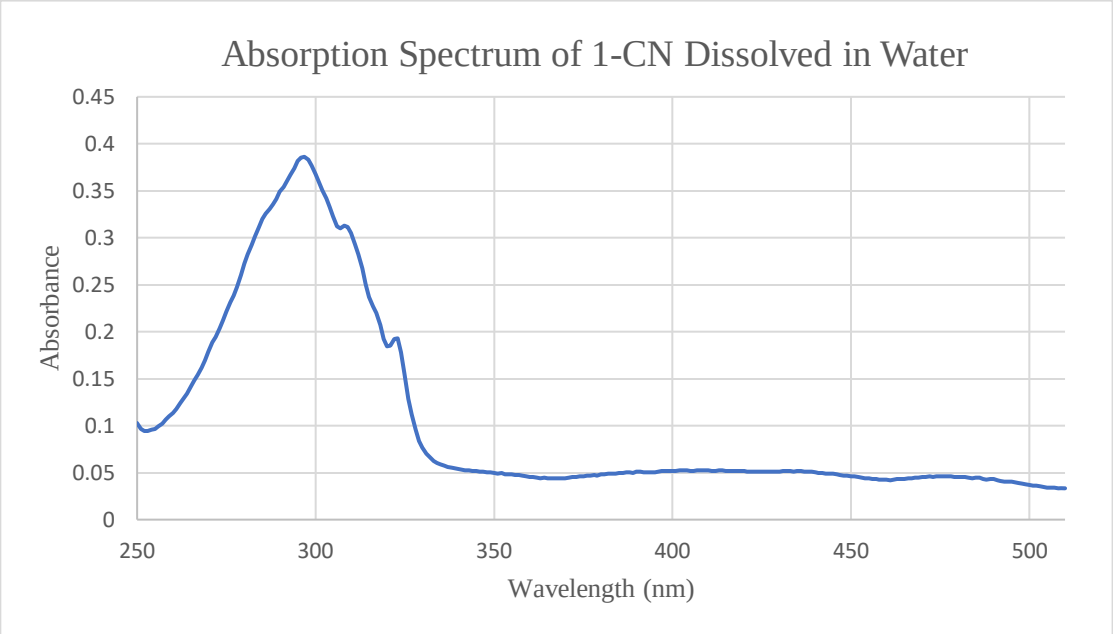

Figure 3.1: The absorption spectrum of 1-CN dissolved in water.

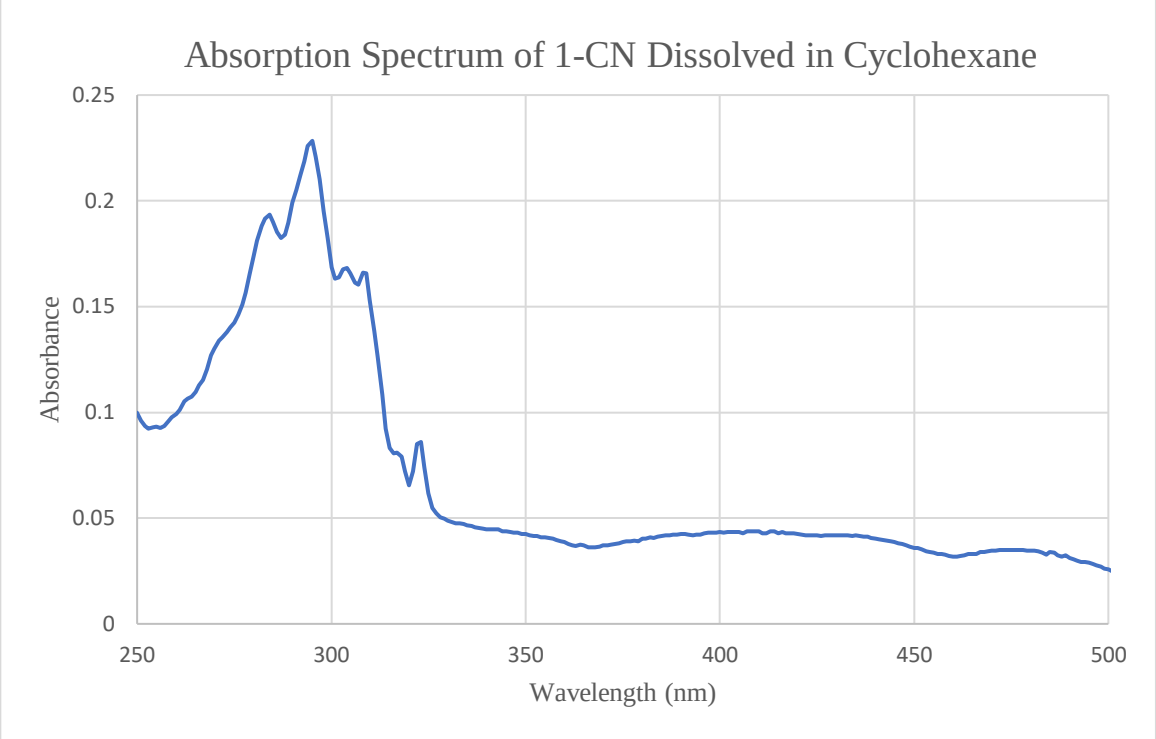

Figure 3.2: The absorption spectrum of 1-CN dissolved in cyclohexane.

Immediately after looking at the two absorption spectra above, it is quite apparent that when 1-CN is dissolved in cyclohexane, the least polar solvent utilized, it produces the most detailed absorption spectra. This is no coincidence, as non-polar solvents typically allow for more vibronic resolution, as solvent interactions do not "wash out" these peaks as much as in the case of polar solvents. The absorption spectra were not shown for acetonitrile and methanol, however as one would likely expect, solutions where less polar solvents were employed display the most detailed spectra. Thus, water had the least detailed, and cyclohexane the most, with acetonitrile and methanol in between. There is very little polarity associated with cyclohexane, and therefore when 1-CN is dissolved in it, this is the most similar to the environment that 1-CN would experience in space, in terms of polarity. As a result, it can be assumed that the absorption spectrum of

1-CN while dissolved in cyclohexane would be the most usable, and similar spectrum measured to what would actually be observed from 1-CN in space.

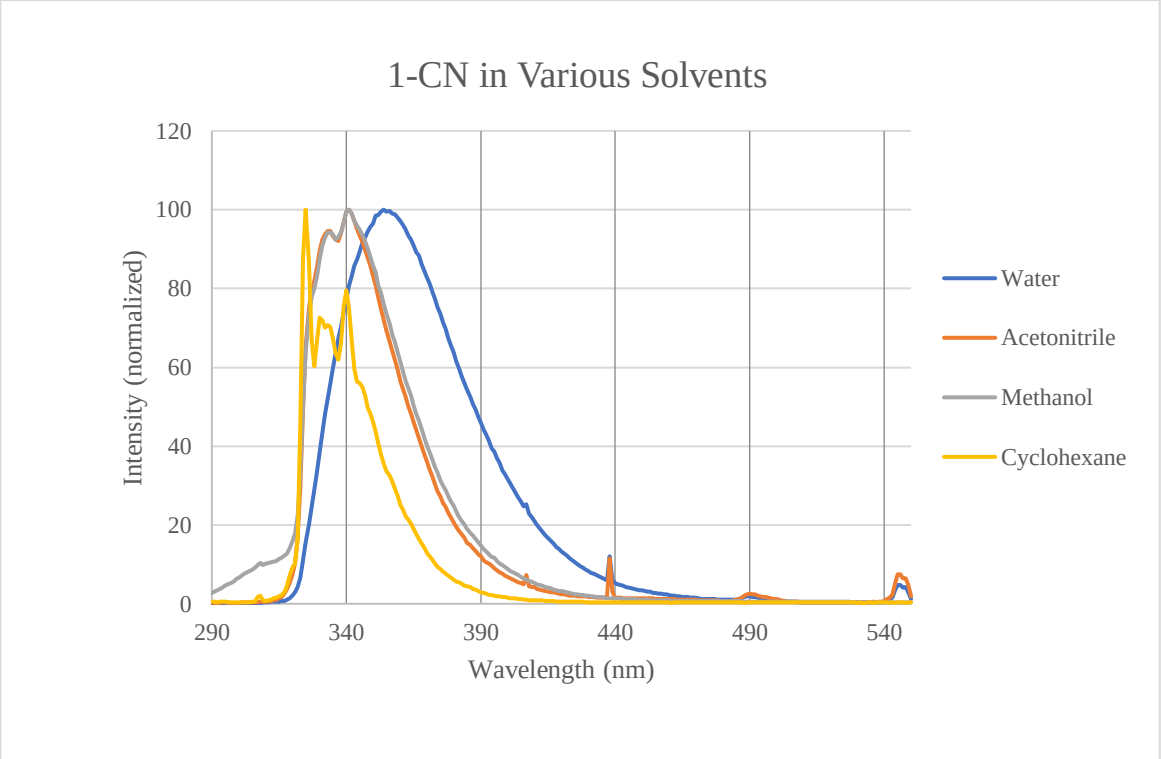

Figure 3.3: Emission spectra of 1-CN in various solvents, where the intensity has been normalized.

Clearly, when 1-CN is dissolved in water, it produces the broadest emission spectrum. Acetonitrile then has the next broadest, closely followed by methanol, and cyclohexane being the least broad. This makes sense, as water is the most polar. Acetonitrile and methanol have very similar polarities; however, acetonitrile is slightly more polar. This shows good agreement with theory and experiment, as acetonitrile has the slightly broader peak here. Last in terms of polarity is cyclohexane which contains the shortest peak. Cyclohexane shows the most detailed, and distinguishable peak among the

rest. This was expected, as non-polar solvents typically interact with fluorophores the least, and therefore do not "wash out" vibronic resolution within the peak. As mentioned previously, due to it interacting the least with the solute, the cyclohexane solution would provide spectra most similar to the gas phase, which is the state that 1-CN exists as in the vacuum of space. Also notable, is the fact that as the solvents become less polar, the emission maxima become blue-shifted.

3.2 Quantum Yields and Fluorescence Lifetimes

Quantum Yield and fluorescence lifetime values were found for the four previously discussed solvents in Section 3.1. Each number reported for each value are the average of three trials, with quantum yields having no units, and lifetimes being measured in nanoseconds. After the determination of these values, their subsequent k_R and k_{NR} values were determined via the use of the averages. These were calculated through the use of the quantum yields and lifetimes. Shown below in Table 3.1 are all of the values that were experimentally determined, along with the subsequently calculated k_R and k_{NR} values. The equations for determining k_R and k_{NR} can be seen above in Equations 2.7, and 2.8, respectively. Quantum yield and fluorescence lifetime are denoted as ϕ_F and τ_F, respectively, and were previously defined in Section 1.3.

Table 3.1: The experimentally determined quantum yield, and fluorescence lifetimes, as well as the calculated values of k_R and k_{NR} for all four solvents.

Solvent	τ_F (ns)	ϕ_F	k_R	k_{NR}
Water	5.2 ± 0.2	0.41 ± 0.02	0.078 ± 0.004	0.11 ± 0.01
Acetonitrile	8.1 ± 1.0	0.27 ± 0.04	0.034 ± 0.006	0.089 ± 0.015
Methanol	8.0 ± 0.3	0.28 ± 0.03	0.034 ± 0.005	0.090 ± 0.013
Cyclohexane	13.2 ± 0.6	0.22 ± 0.02	0.017 ± 0.002	0.059 ± 0.007

As in Section 3.1, the experimental data in Table 3.1 follows trends that are associated with solvent polarity. Having water as the solvent, produces the highest quantum yield, then methanol, acetonitrile, and cyclohexane having the smallest. This makes sense, as will be seen in the next section, the PSF of 1-CN is found to be less than one, indicating that it fluoresces better in more polar solvents. More detail on the PSF of 1-CN can be found in Section 3.3. It is slightly irregular that methanol has a higher quantum yield than acetonitrile, however due to the fact that the two solvents have such similar dielectric constants, it is not alarming that methanol produced a slightly higher quantum yield average. The standard deviations of both are also a sufficient explanation for this on its own. In terms of fluorescence lifetimes, it was found for 1-CN, that the more polar the solvent the shorter the fluorescence lifetime. This was because water had the shortest, then methanol, acetonitrile, and cyclohexane had the longest. Again,

acetonitrile should in theory have the shorter lifetime here, when compared to methanol. However, this is easily explained through the same reasoning as their quantum yields were. Although, it is interesting that this trend was found for both experiments, when completely different solutions were prepared for each experiment. Stemming from these two experiments, the k_R and k_{NR} values were subsequently determined and utilized in the preparation of plots against the dielectric constants for their associated solvents. For this purpose, solvent dielectric constant, ε, was chosen as a good measure of solvent polarity. These plots were made for k_R versus dielectric constant, and k_{NR} versus dielectric constant, both can be seen below in Figure 3.4, and Figure 3.5, respectively.

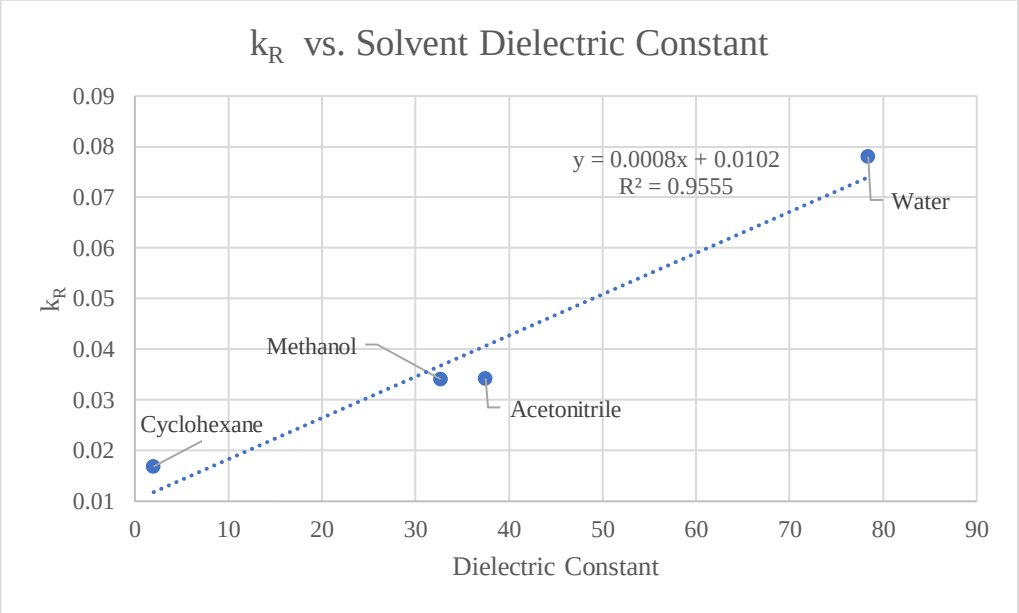

Figure 3.4: A plot of k_R versus solvent dielectric constants, where k_R was calculated via quantum yield, and fluorescence lifetime averages.

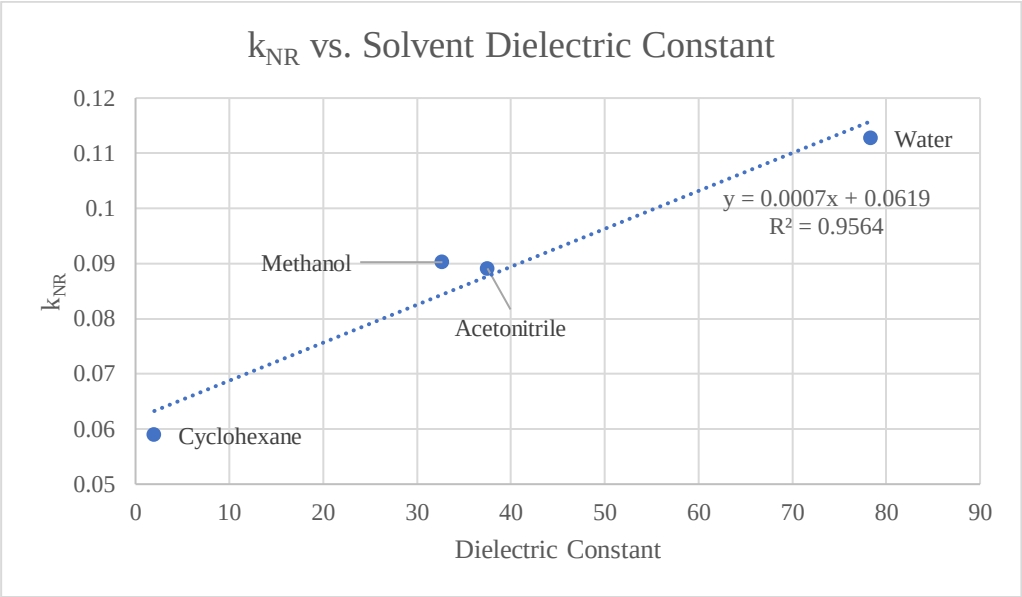

Figure 3.5: A plot of k_{NR} versus solvent dielectric constants, where k_{NR} was calculated via quantum yield and fluorescence lifetime averages.

In the above plots, it is quite obvious that both display a reasonably linear trend. Only having four data points does limit the ability to comment on this trend though. Unfortunately, methanol and acetonitrile having as similar dielectric values as they do also contribute to the limited ability for any mentions of linearity. A R^2 value of 0.9555, and 0.9564 for Figures 3.4 and 3.5 respectively, does indicate linear character though. It would be beneficial to include two more solvents in future work, with one having a dielectric constant between water and acetonitrile, and the other between methanol and cyclohexane, so that comments on linearity of both graphs would hold more weight than they do currently.

3.3 Polarity and Oxygen Sensitivity

1-CN's sensitivity to solvent polarity and oxygen were determined through comparisons of the fluorescence emission of sample solutions where the solvent was either ethanol or water. Their emission spectra were measured before and after being purged with argon for five minutes. These values were obtained by taking the average of three experimental trials. It was found that 1-CN is sensitive to polarity, as it produced a PSF value of 0.79 ± 0.06. This value indicates that the molecule will fluoresce more when dissolved in a more polar solvent, such as water, meaning that 1-CN has "reverse polarity dependence", which is not as common amongst fluorophores.[10] This trend was also observed in the previous section, where quantum yield decreased as a less polar solvent was used. In regard to oxygen sensitivity, it was found that the fluorescence of 1-CN is insensitive to oxygen quenching while dissolved in water. This was because an OSF value of 1.02 ± 0.03 was found for the water solution, where a value of 1 indicates no sensitivity whatsoever. However, it was found that 1-CN is much more sensitive to oxygen quenching while it is dissolved in ethanol. For ethanol, an OSF of 1.37 ± 0.07 was reported. This indicates that to minimize molecular oxygen quenching and maximize fluorescence while 1-CN is dissolved in ethanol, the solution should be purged of oxygen. However, this is not necessary when 1-CN is dissolved in water. This is most easily seen in the fluorescence emission spectrum that was recorded for this experiment. This spectrum can be seen below in Figure 3.6. It should be noted that while present in the vacuum of space, polarity and oxygen sensitivity will not impact the fluorescence of 1-CN. However, by providing values for the PSF and OSF of the molecule, the bias associated with measuring its spectra on Earth, and in solution are more understood.

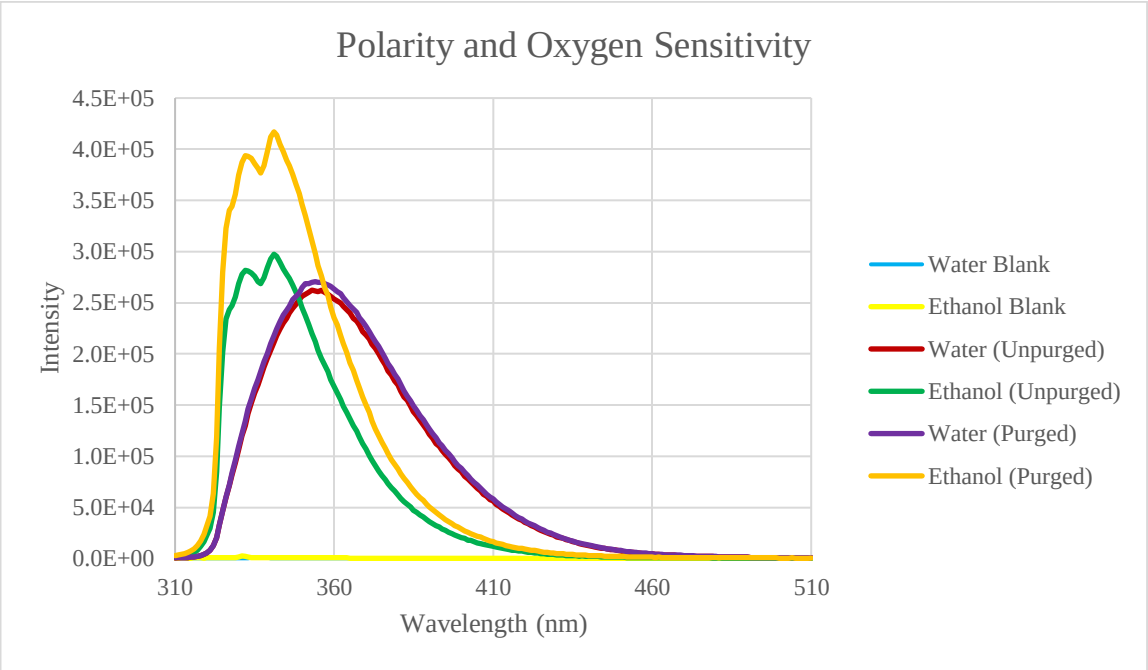

Figure 3.6: Fluorescence spectra of 1-CN dissolved in ethanol and water, before and after being purged, producing good indications of the molecule's sensitivity to polarity and molecular oxygen.

3.4 Synchronous Fluorescence

A synchronous scan of 1-CN, dissolved in water was conducted, and an emission scan was also performed over the same range of wavelengths to compare the resolution and peak breadth of the synchronous spectrum. Due to the use of smaller slit widths for the synchronous scan, the synchronous spectrum was much less intense than the emission spectrum, and therefore to compare the two, the intensities had to be normalized. The compared spectra can be seen below in Figure 3.7.

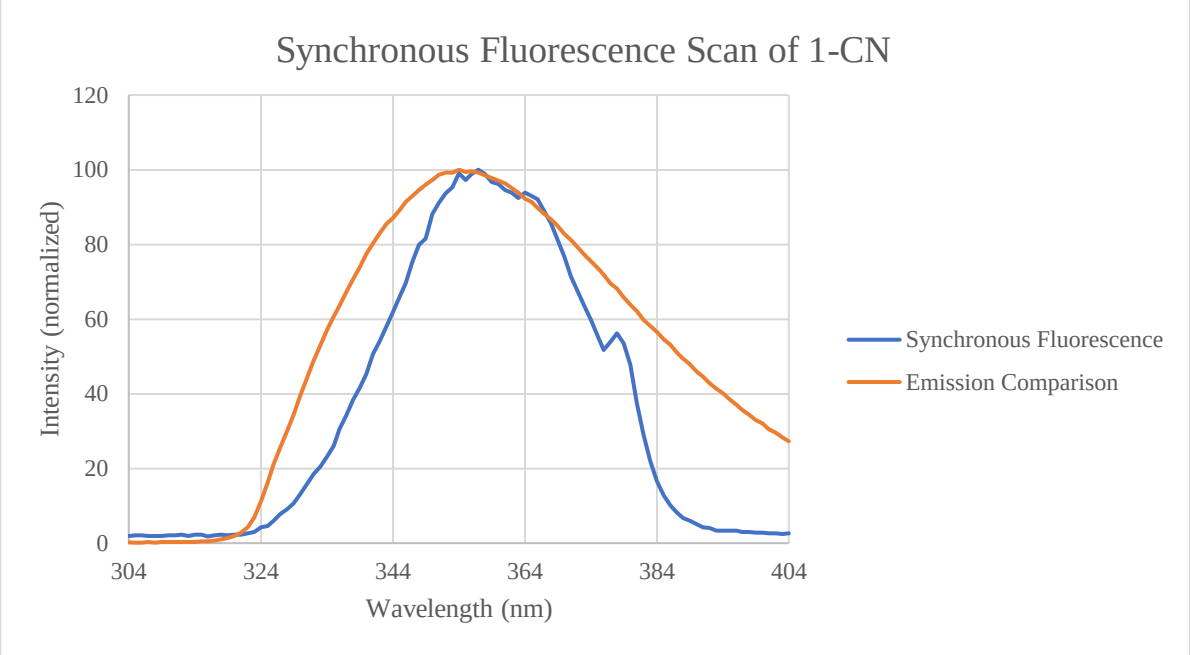

Figure 3.7: A synchronous fluorescence spectrum overlaid with the fluorescence emission spectrum of 1-CN over the same range of wavelengths.

It is clear that the synchronous spectrum is significantly narrower than the emission spectrum. In the emission spectrum, all minor peaks that are present in the synchronous spectrum are completely lost. In the synchronous spectrum however, there is a small peak that is very apparent, centering near 376nm, and the very top of the peak has very noticeable smaller peaks. It is also defined over a smaller range of wavelengths as well, making it more distinguishable when attempting to identify 1-CN. As a result, the synchronous spectrum contains many more identifiable peaks, and is refined over a smaller range of wavelengths, allowing for more confident and swift identification of the molecule. The solvent used in this measurement was water, which was the most polar of the solvents utilized in this research. To produce a spectrum most relevant to what would be observed in practice, cyclohexane should be used instead. With that said, this

technique is very new to the field of astrochemistry, and this study was more so meant to determine its viability for being used on 1-CN. Nonetheless, the produced spectrum remains relevant, and helpful to what would be observed in practice. Overall the experiment was a success because a usable, identifiable spectrum was obtained. The amount of time that it took to obtain the spectrum is also notable. The scan did not occur in a matter of seconds, but rather over a minute. This has implications to flyby missions, as time is a limited resource in these. Therefore, the length of time required to perform this scan is indicative that synchronous fluorescence would be most usable in space missions where a rover or lander is utilized instead. This being because more time is available to perform the scan.

3.5 Host-Guest Studies

1-CN was dissolved in aqueous solutions which contained one of two different hosts. It was found that only one host produced a significant impact on its fluorescence. The host that was found to not affect the fluorescence of 1-CN was β-CD. A titration with this host was performed. However, the most significant $\frac{F}{F_0}$ value obtained from the titration was 0.91 which was when the highest concentration of β-CD (20mM) was used. This indicates that very little host-guest inclusion was occurring; or, if significant binding was occurring then the host cavity was not non-polar enough to allow for a different enough environment to significantly impact the fluorescence of 1-CN. Despite this, one thing notable about this titration was that it had a minor suppressive effect on fluorescence. This is in agreeance with the PSF value of 0.79 for 1-CN, indicating that 1-

CN is fluoresces more in polar environments. Given that the host cavity of β-CD is relatively non-polar, it makes sense that suppression of fluorescence was observed. This titration can be seen below in Figure 3.8.

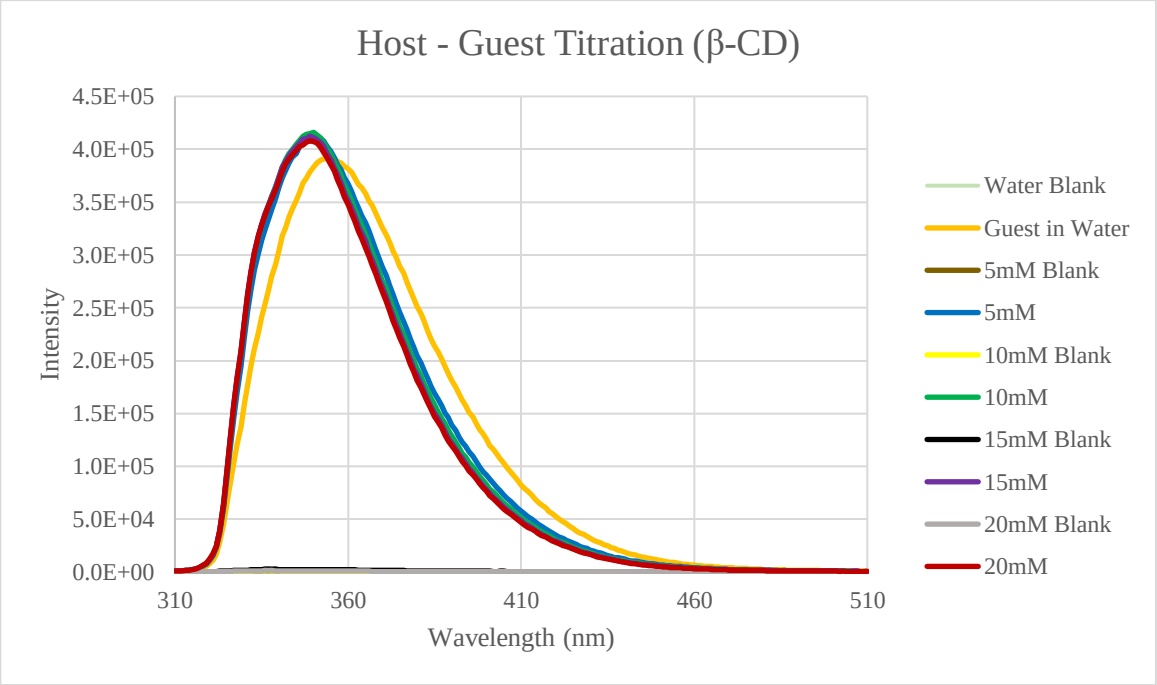

Figure 3.8: A host-guest titration where β-CD was used as the host molecule, and 1-CN was intended to be the guest.

After the titration of 1-CN with β-CD was found to be unsuccessful in terms of impacting the fluorescence of 1-CN, another host was utilized. This host was CB[7]. Similarly to β-CD, CB[7] also displayed fluorescence suppression. This is also in agreement with the obtained value for the PSF of 1-CN. Differing from β-CD though, CB[7] displayed more significant suppression of fluorescence. Thus, either more significant binding was occurring, or the cavity was more non-polar. Due to this, four

titrations were performed for this host-guest system, to obtain binding constants. With that said, only two produced useable binding constants, and therefore the other two were omitted. The two successful titrations can be seen below in Figures 3.9 and 3.10, where the first trial was found to be the best out of the two.

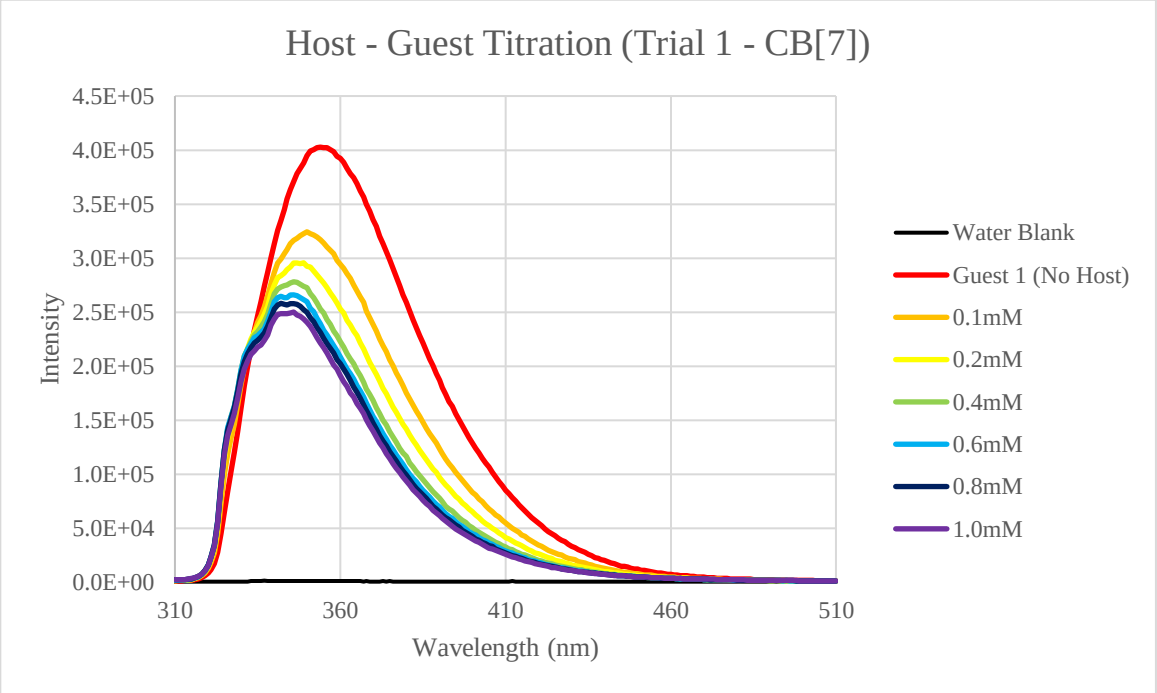

Figure 3.9: A host-guest titration where CB[7] was utilized as the host molecule, and 1-CN was the guest molecule. This is the first of two successful trials.

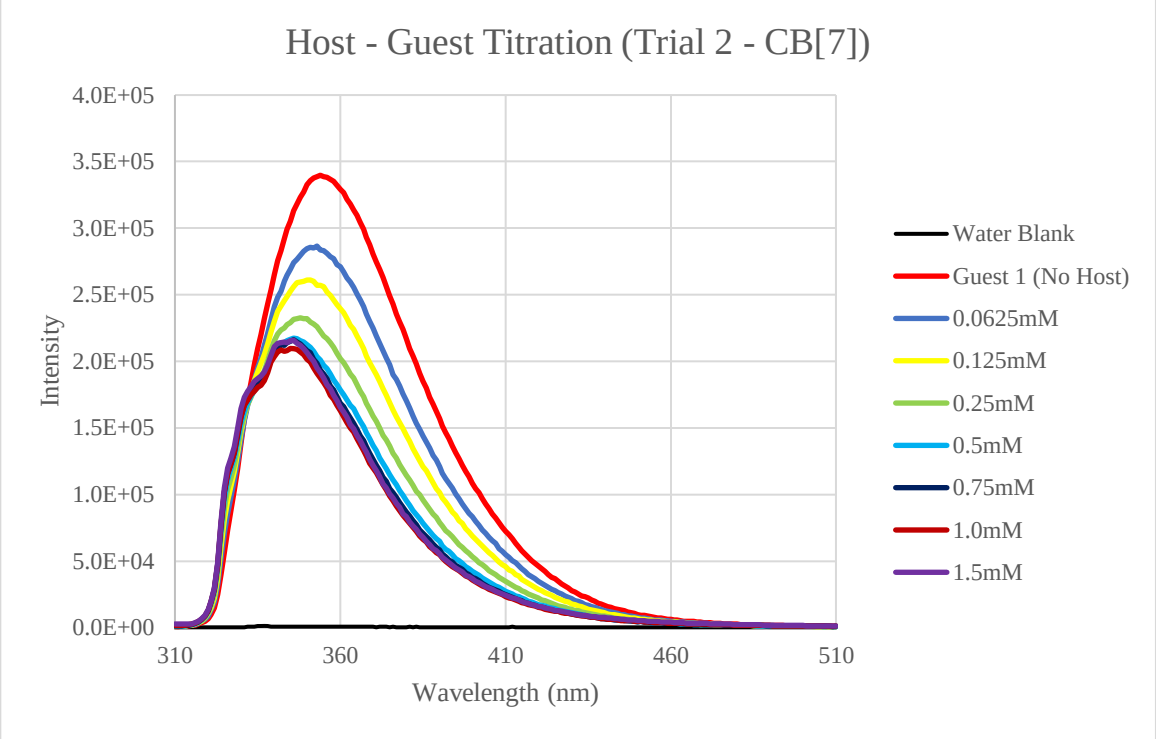

Figure 3.10: A host-guest titration where CB[7] was utilized as the host molecule, and 1-CN was the guest molecule. This is the second of two successful trials.

Both Figures 3.9 and 3.10 display clear evidence of binding of 1-CN to CB[7]. This inclusion complex was found to be 1:1 in nature and demonstrates significant suppression of fluorescence. For the first titration, a binding constant of $7500M^{-1}$ was calculated. For the second titration that was performed, a binding constant of $8700M^{-1}$ was produced. The binding constants for the two titrations are in reasonably good agreement. They are within 20% error, which is typical experimental error for binding constants, indicating precision. Along with this, the calculated binding constants were very high, indicating that very significant binding of 1-CN to the host cavity of CB[7] was occurring. The binding constant for the two shown titrations produced excellent fits

for $\frac{F}{F_0}$ versus host concentration, as they display very distinguishable plateaus. These plots can be seen below in Figures 3.11 and 3.12.

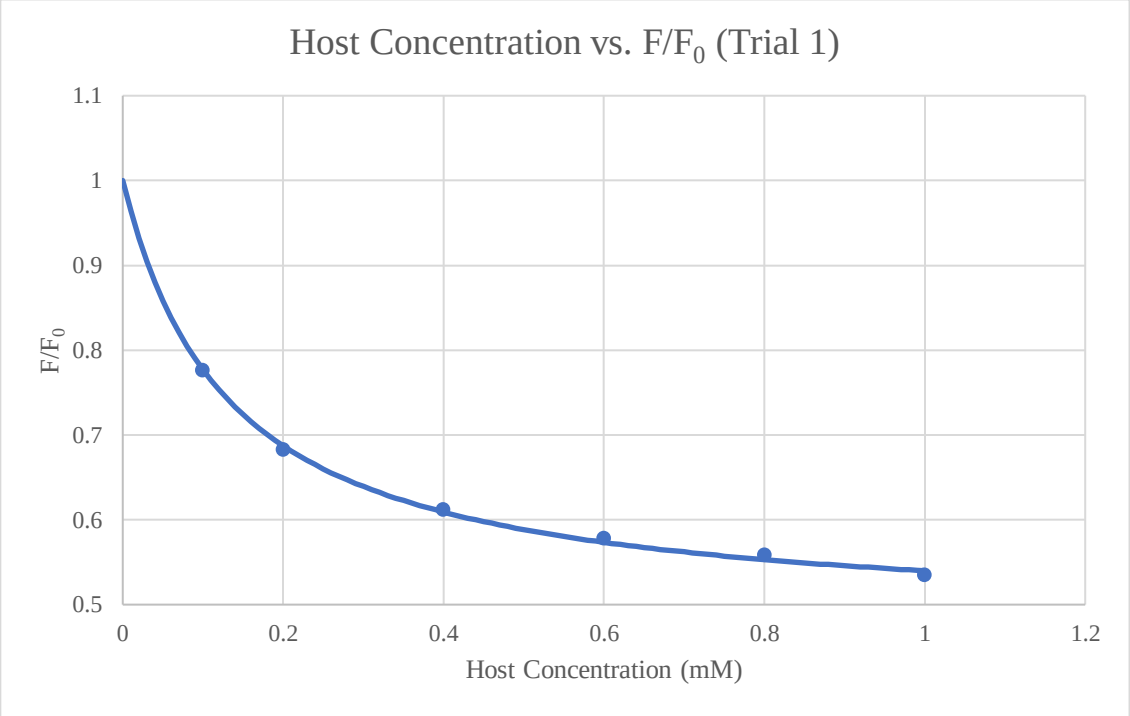

Figure 3.11: A plot of $\frac{F}{F_0}$ versus host concentration, for the titration of CB[7] with 1-CN in water for trial 1.

It was previously mentioned that this titration was the best out of the two useable ones. The reason for this is rooted in the results from the double reciprocal plot shown below in Figure 3.13.

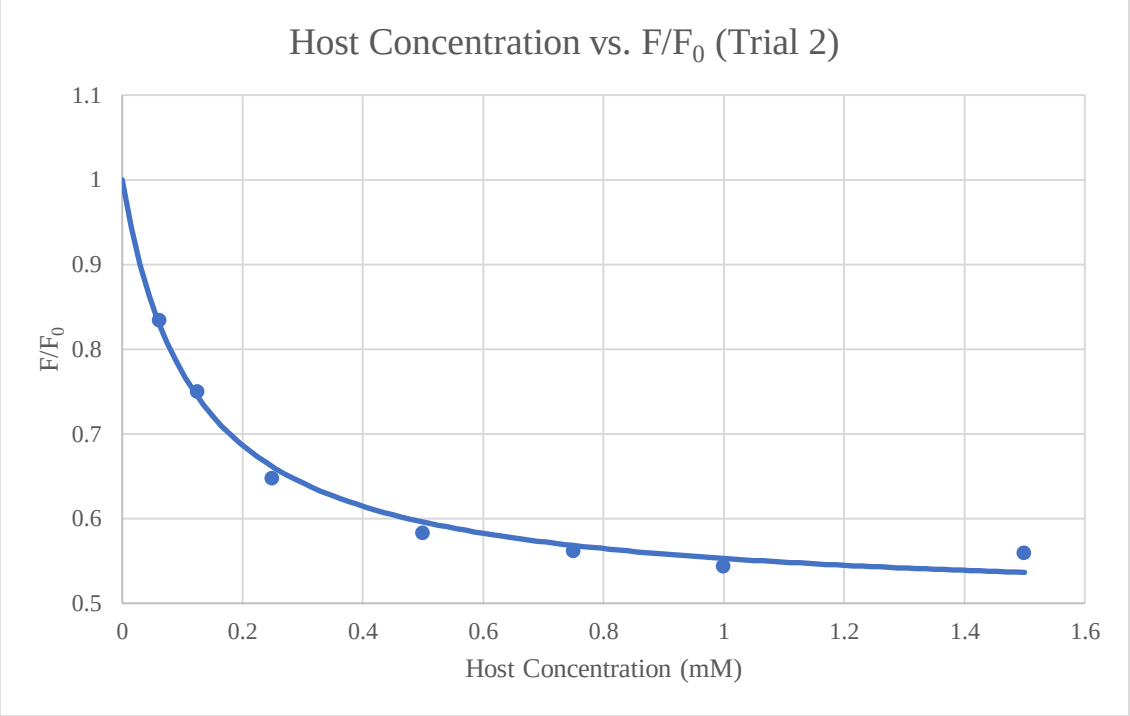

Figure 3.12: A plot of $\frac{F}{F_0}$ versus host concentration, for the titration of CB[7] with 1-CN in water for trial 2.

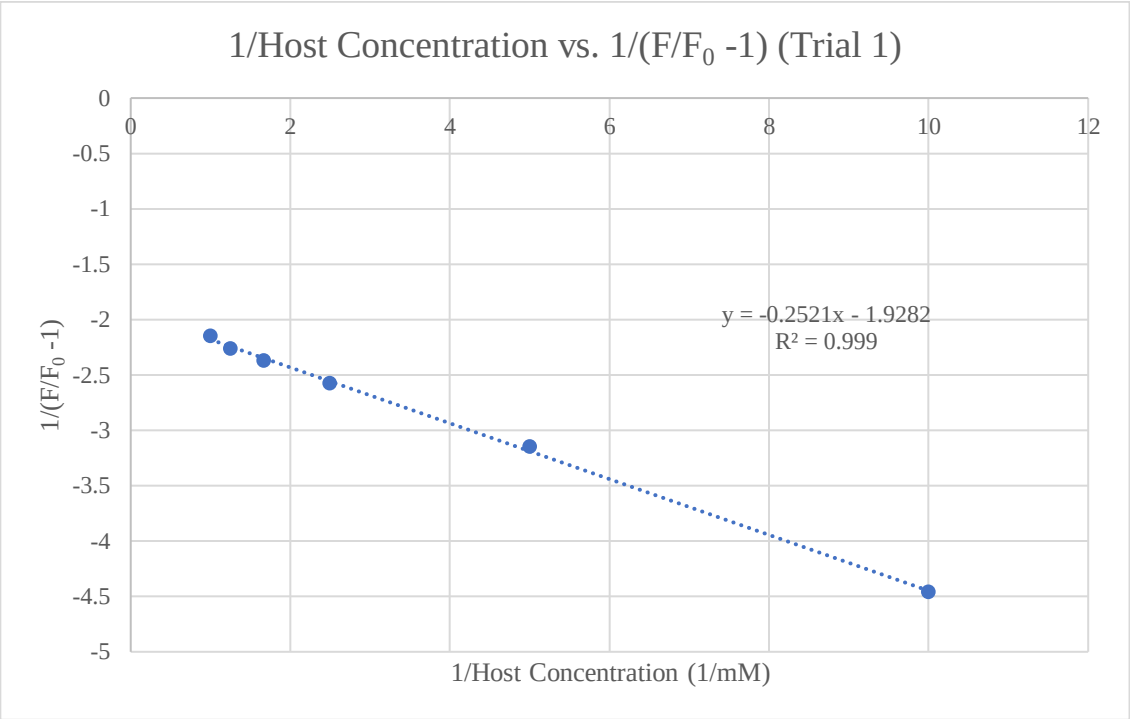

Figure 3.13: A double reciprocal plot of CB[7] with 1-CN in water for trial 1.

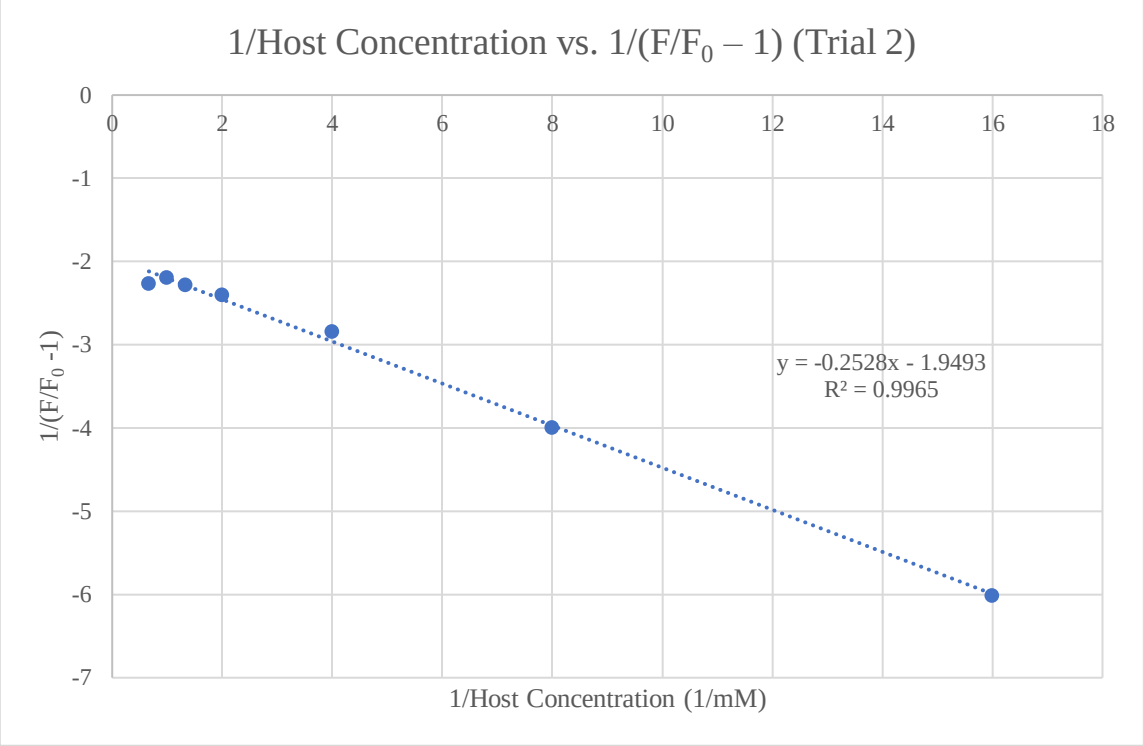

Figure 3.14: A double reciprocal plot of CB[7] with 1-CN in water for trial 2.

The double reciprocal plot for trial 1 produced an extremely linear trend, as it gave a R^2 value of 0.999. A perfectly linear trend in a plot like this one indicates 1:1 complexation. For this reason, it can be said with great confidence that 1-CN bound to CB[7] in a 1:1 fashion. The second titration's double reciprocal plot produced a R^2 value of 0.9965, and thus was also extremely linear. Therefore, it can be deduced that 1-CN binds to CB[7] as a 1:1 host-guest complex.

Like most hosts, CB[7]'s host cavity is non-polar. However, it also contains carbonyl groups that surround the outskirts of its cavity, allowing for the stabilization of a guest that has both polar and non-polar properties. Naphthonitrile fits this description well, as the naphthalene portion of the molecule is non-polar and thus interacts well with

the inside of the host cavity. Meanwhile, the cyano group is quite polar, likely allowing for interactions with the ketones of the host cavity. This is likely how the inclusion of 1-CN within CB[7] occurred, and 1-CN being more fluorescent in polar environments resulted in the sensical suppression of its fluorescence.

Chapter 4 2-naphthonitrile

The focus of this chapter is on the spectroscopic analyses of the second isomer, 2-naphthonitrile, or previously referred to in this thesis as 2-cyanonaphthalene (2-CN). This chapter will discuss and present the experimentally determined quantities and obtained spectra for 2-CN. Relevant talking points include the effect on absorption and emission of separately dissolving 2-CN in four different solvents, determined quantum yields and the fluorescence lifetime found for 2-CN in water, 2-CN's polarity and oxygen sensitivity, its synchronous fluorescence spectrum, as well as the host-guest titration that was performed with it.

4.1 Spectroscopic Effects of Dissolution in Various Solvents

There was little effect on the absorption spectra and maximum of 2-CN. It never varied more than a nanometer, in any experiment. The absorption maximum ranged from 281 to 282nm, never deviating any further. Spectra can be seen below in Figures 4.1 and 4.2 for 2-CN dissolved in water and cyclohexane, respectively. Due to the lamp available in the fluorimeter that was used, 290nm was used as its excitation wavelength. The solvents that 2-CN was dissolved in were the same as listed in Section 3.1 for 1-CN, which were water, methanol, acetonitrile, and cyclohexane. Just like 1-CN ethanol was also used in PSF and OSF experiments, however it was not for other experiments, as methanol was used instead. The emission spectra of 2-CN in its various solvents can be seen below in Figure 4.3.

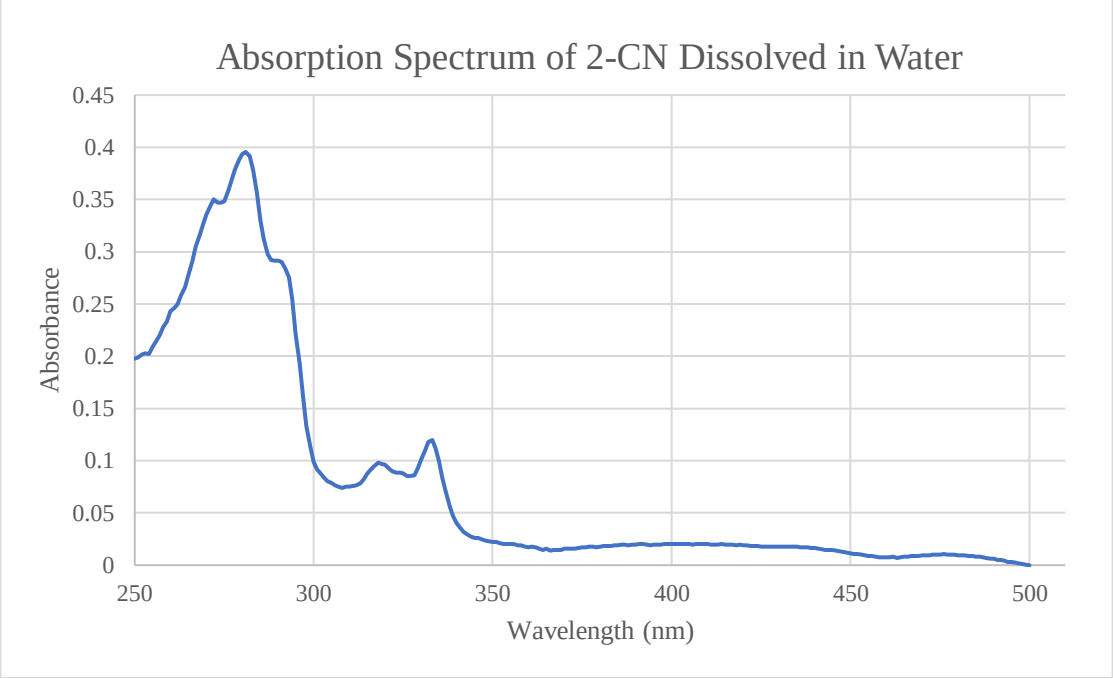

Figure 4.1: The absorption spectrum of 2-CN dissolved in water.

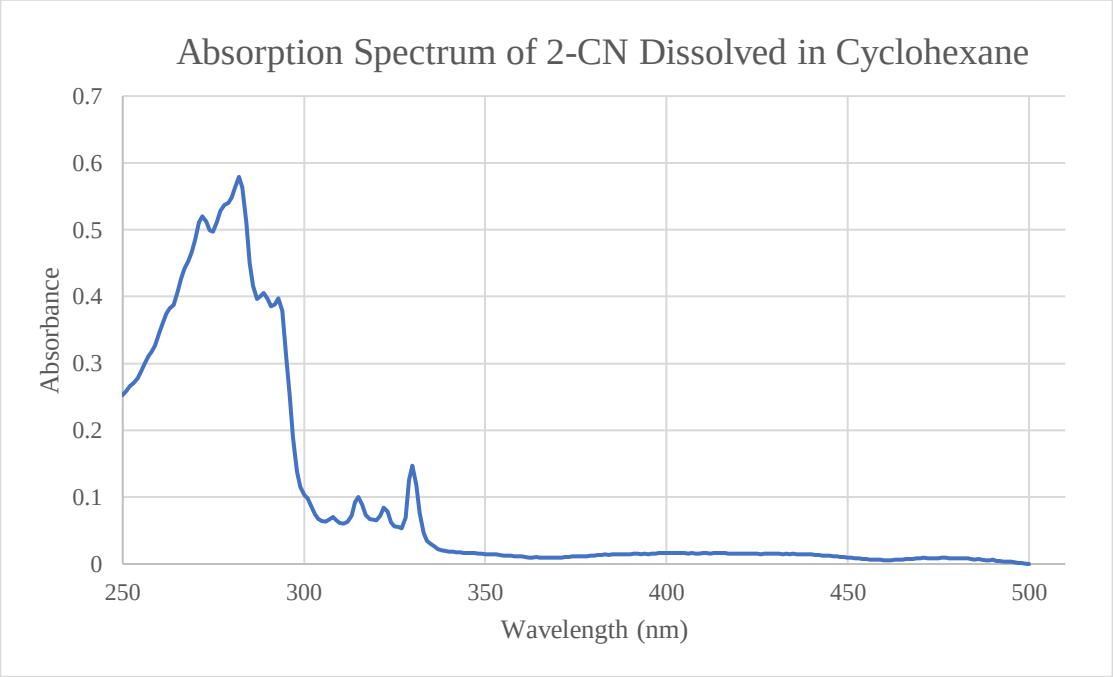

Figure 4.2: The absorption spectrum of 2-CN dissolved in cyclohexane.

Just like in Section 3.1, it is immediately apparent that when cyclohexane was used as a solvent, it produced a much more detailed spectrum. All peaks are much clearer, and identifiable. The same reasoning that was described previously is also the cause of the extra detail here. As in Section 3.1, absorption spectra for 2-CN dissolved in acetonitrile or methanol are also not shown in this section. However, more detailed spectra are associated with less polar solvents, so the spectrum in methanol is slightly less detailed than that in cyclohexane, then acetonitrile, then water. Since cyclohexane is the least polar solvent, its absorption spectrum is most indicative of what would be seen in reality, if 2-CN's absorption were to be measured in space

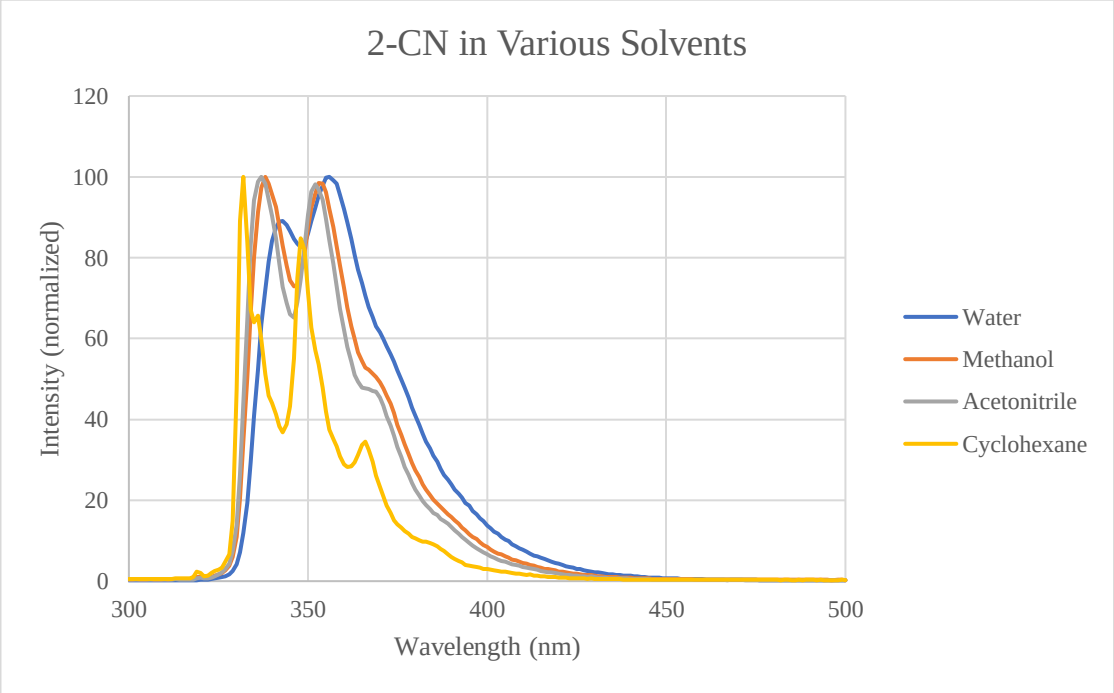

Figure 4.3: Emission spectra of 2-CN dissolved in various solvents, where the intensity has been normalized.

2-CN produced very similar peak breadth while dissolved in the different solvents that were utilized. The molecule also produced very distinguishable spectra, where cyclohexane was the most resolvable by far here as well. As was mentioned in Section 3.1, less polar solvents having more peak resolution here is in good agreeance with theory, as polar solvents typically "wash out" the vibronic resolution that would normally be apparent in their spectra. The emission maxima also moved to smaller wavelengths as less polar solvents were used, however only very slightly.

4.2 Quantum Yields and Fluorescence Lifetimes

Quantum Yields for 2-CN were found for all four solvents. However, only when 2-CN was dissolved in water was it possible to measure its fluorescence lifetime. This was a result of the fact that 2-CN's maximum wavelength was actually 281nm, but 290nm had to be used instead for its excitation (due to limitations in the instrument's excitation lamp range). Therefore it did not produce an emission that was intense enough to allow for accurate, consistent fluorescent decay curve fitting. Each experimentally determined value (quantum yields and fluorescence lifetime for water) are the average of three trials. Due to lifetimes not being measurable for the three other solvents, k_R and k_{NR} values could not be calculated for them, and only for water. Consequently, plots of k_R versus solvent dielectric constant, as well as k_{NR} versus solvent dielectric constant could not be constructed for 2-CN. All experimentally determined quantum yields, the fluorescence lifetime for water, and the subsequently calculated k_R and k_{NR} values for water are shown below in Table 4.1.

Table 4.1: The experimentally determined quantum yields in the four solvents, as well as fluorescence lifetime, and the calculated values of k_R and k_{NR} for water.

Solvent	τ_F (ns)	ϕ_F	k_R	k_{NR}
Water	11 ± 2	0.37 ± 0.01	0.034 ± 0.007	0.058 ± 0.012
Acetonitrile	-	0.38 ± 0.08	-	-
Methanol	-	0.41 ± 0.01	-	-
Cyclohexane	-	0.42 ± 0.08	-	-

The formulas for calculating k_R and k_{NR} can be found in Section 3.2. For 2-CN it was found that quantum yield decreased as the solvent became more polar. However, the differences between solvents are much smaller than in the case of 1-CN discussed in the last chapter, indicating that 2-CN is less polarity-sensitive than 1-CN. When dissolved in water, a lifetime of 11 ± 2ns was found. This value had a relatively high standard deviation; however, it was due to the fact that the solution had to be excited at 290nm, causing less intense fluorescence, and therefore making it difficult for curve fitting the fluorescent decay.

4.3 Polarity and Oxygen Sensitivity

Polarity and oxygen sensitivity for 2-CN was found through its separate dissolution in both water and ethanol, producing solutions whose fluorescence were measured before and after being purged with argon. By eliminating any molecular oxygen

dissolved in both solutions, and subsequently comparing their emission spectra with unpurged spectra, the sensitivity to oxygen was able to be found. Additionally, by comparing the purged solutions of ethanol and water, the fluorescence sensitivity of 2-CN was determined. Both OSF, and PSF values were found by taking the average of three trials. In terms of polarity, 2-CN appeared to not be very sensitive to it when having its fluorescence measured. A PSF value of 1.12 ± 0.07 was calculated via the measured fluorescence spectra. There is some sensitivity present here, what is most notable though is that 2-CN appears to fluoresce more intensely in non-polar solvents, as opposed to more polar ones. This is most common in fluorophores; however it is interesting that the opposite was observed for 1-CN.[10] It was found that 2-CN is insensitive to oxygen quenching while it is dissolved in water, however it is quite sensitive to it while dissolved in ethanol. This is because the OSF for 2-CN in water was found to be 1.01 ± 0.02, while the OSF for 2-CN in ethanol was 1.76 ± 0.03. Therefore indicating that for maximal fluorescence, a solution of 2-CN in ethanol should be purged of molecular oxygen prior to excitation. If 2-CN is dissolved in water however, purging is not necessary. Polarity and oxygen sensitivity of 2-CN is illustrated best in Figure 4.4 below.

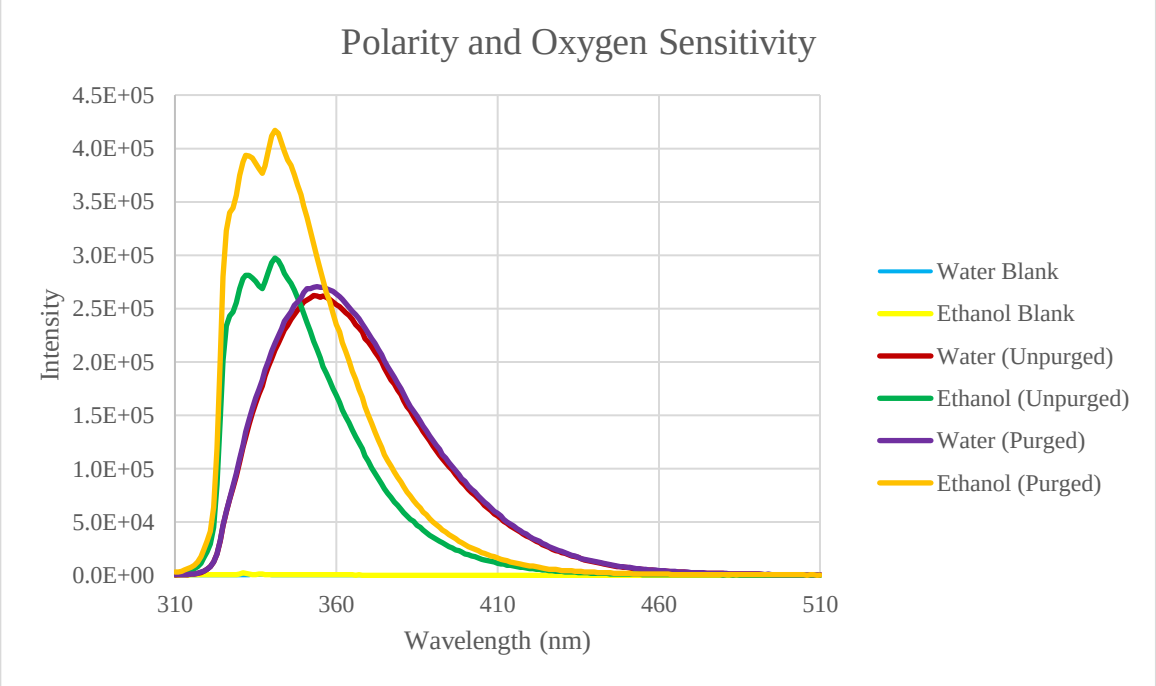

Figure 4.4: Fluorescence spectra of 2-CN dissolved in ethanol and water, before and after being purged, showing the molecule's fluorescence sensitivity to both polarity and oxygen.

4.4 Synchronous Fluorescence

A synchronous fluorescence spectrum was measured for 2-CN in an aqueous solution. An emission scan of the same solution was also produced over the same range of wavelengths, as a means for understanding how much more identifiable the synchronous scan was. The intensities were normalized due to the fact that the synchronous scan emitted light of much lower intensities when compared to the emission spectrum. However, this was expected as smaller slit widths had to be utilized for the synchronous scan, as they were required to distill the range of light that was exciting the molecule at

each moment throughout the scan. The synchronous fluorescence spectrum and emission comparison spectrum can be seen below in Figure 4.5.

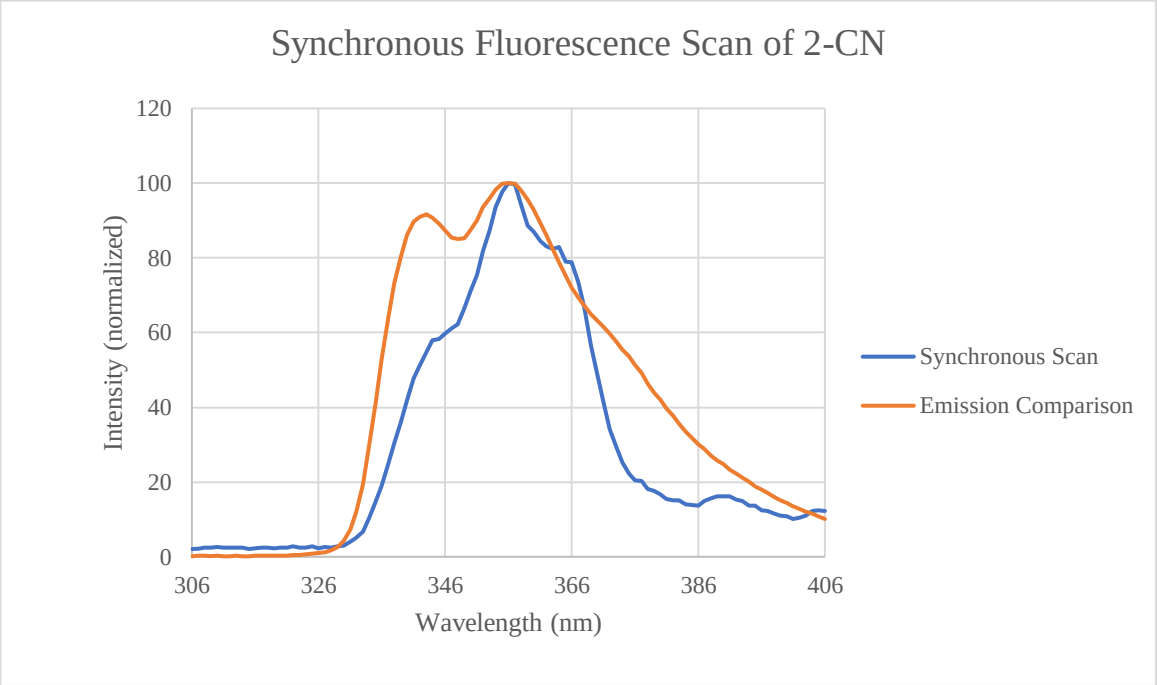

Figure 4.5: A synchronous fluorescence spectrum overlaid with an emission spectrum over the same range of wavelengths, for a solution of 2-CN in water.

As seen above, the synchronous fluorescence spectrum of 2-CN is much more identifiable and narrower as compared to its emission comparison. Both sides of the spectrum house identifiable traits, with smaller peaks centering near 346 and 364nm, and the largest at 351nm. As a result, the produced synchronous spectrum is a more distinguishable spectrum as opposed to its emission counterpart, allowing for more likely identification of the molecule. As mentioned in Section 3.4, a cyclohexane solution would be much more indicative of the actual environment that 2-CN would experience in space.

With that said, the viability of this experimental technique in terms of producing a useable, identifiable spectrum of 2-CN was determined. The spectrum is considered usable, and therefore the experiment was a success. Also as mentioned in Section 3.4 was the length of time taken for this measurement. Since the experiment was performed over the same magnitude of wavelengths, the measurement took the same amount of time, and therefore the same conclusion can be drawn for its usability. This conclusion is that this technique is most useful being implemented on a rover or lander, rather than a satellite, or probe.

4.5 Host-Guest Titration

For 2-CN, one host-guest titration was performed, where the host that was used was CB[7]. This host was chosen because 1-CN showed considerable binding to its cavity which resulted in notable suppression of fluorescence. For the titration with 2-CN, the same concentrations of CB[7] were used for the experiment. Unfortunately however, 2-CN showed insignificant binding to the host cavity of CB[7]. The highest $\frac{F}{F_0}$ value obtained from the titration was 0.97, which was when the highest host concentration (1.0mM) was used. It should be noted that fluorescence suppression was also noticed here, however only negligibly. For this reason, a binding constant was not able to be extracted from the titration. It should also be noted that due to the host cavity of CB[7] being nonpolar, and 2-CN having a PSF above 1, that fluorescence enhancement should have been observed. With that said, very minor suppression was noticed, even less so

than when 1-CN was present with β-CD. Therefore, this suppression can be attributed to experimental error.

There are two possible reasons as to why fluorescence enhancement was not observed in this experiment. The first being due to insignificant binding of 2-CN to CB[7]'s cavity, which could be caused by the difference in configuration of 2-CN, as compared to 1-CN. This difference in structure could cause the cyano-carbonyl, and naphthalene-cavity interactions to not be possible at the same time, and therefore causing one to constantly be destabilized. The other possible reason is that 2-CN had a PSF whose difference from 1 was not as great as 1-CN's. Thus, 2-CN is less polarity sensitive than 1-CN. 1-CN's was 0.79, where 2-CN's was 1.12. A PSF of 1 means that polarity of the fluorophore's environment has no effect on its fluorescence.[10] Therefore, 2-CN's difference being less, implies that the host cavity will always have less of an impact on its fluorescence, when binding to the same cavity as 1-CN. It is likely that both factors contributed to the minor impact on the fluorescence of 2-CN.

Chapter 5 Comparison of Naphthonitrile Isomers

The focus of this chapter is largely based on comparing and contrasting the experimental data and spectra that was previously reported and discussed in Chapters 3 and 4 regarding 1-CN and 2-CN, respectively.

5.1 Spectroscopic Effects of Dissolution in Various Solvents

In terms of absorption, both molecules' absorption maxima did not deviate much at all, no matter the experiment being performed. 1-CN's absorbance maximum stayed within the small range of 295-298nm, while 2-CN's maximum did not deviate any further than the even smaller range of 281-282nm. When looking at Figures 3.1 and 4.1, it is quite obvious that the peaks for 1-CN vary much more over a range of wavelengths, as compared to 2-CN. 2-CN has its peaks much more localized over the same range of wavelengths. These peaks do deviate a bit, however, not as much as what is observed by 1-CN in Figure 3.1. For both spectra, when either isomer was present in a solution where cyclohexane was the solvent, the emission spectra was much more resolved, as it shows very detailed peaks and troughs within either spectrum. It was also observed that the water containing solutions were the least detailed peaks for both spectra. The solutions where acetonitrile and methanol were used also showed very similar spectra for both, as theorized. Overall, 2-CN produced spectra that were more detailed than 1-CN in all cases.

5.2 Quantum Yields and Fluorescence Lifetimes

Obviously only so much can be compared for 1-CN and 2-CN here, due to 2-CN not having measurable lifetimes while it was dissolved in methanol, acetonitrile, or cyclohexane. With that said, all quantum yields, and lifetimes for the two aqueous solutions can be compared. In terms of quantum yield, an opposite trend was found for both 1-CN and 2-CN. For 1-CN, quantum yields increased as more polar solvents were used, but for 2-CN, quantum yields decreased as more polar solvents were used. This trend is consistent with the PSF values that were found for both molecules. The PSF for 1-CN was less than one, which indicates that it is more fluorescent in more polar molecules, and thus agrees with its quantum yield trend. Meanwhile, 2-CN had a PSF greater than one, indicating that it is more fluorescent in non-polar solvents, and therefore agrees with its trend of quantum yields as well. Again, this was likely due to the structures of 1- and 2-CN. 2-CN is a much more linear molecule, as its cyano functional group is in line with its two rings, while 1-CN is less linear, as its cyano group protrudes in the opposite direction of its two rings. Along with this, the position of the cyano substitution as ortho or meta would have a significant impact on the distribution of pi electrons within the naphthalene ring, which would also have a significant impact on fluorescence properties, thus contributing to the differences that were observed. The only possible comparison in terms of lifetimes were the lifetimes of the aqueous solutions of both isomers. 2-CN was found to have the longer lifetime, with a lifetime of 11 ± 2ns, while 1-CN had a lifetime of 5.2 ± 0.2ns. k_R and k_{NR} values were also both higher for the aqueous solution of 1-CN.

5.3 Polarity and Oxygen Sensitivity

Both isomers were found to have very similar OSF values when dissolved in water, as both proved to be insensitive to oxygen quenching, with 1-CN having a calculated value of 1.02 ± 0.03, and 2-CN's being 1.01 ± 0.02. It can be said from these results that the presence of molecular oxygen in an aqueous solution of either isomer will have little to no effect on fluorescence. Similarly to this, 1- and 2-CN were both sensitive to oxygen quenching when they were dissolved in ethanol. This is because when dissolved in ethanol, OSF values of 1.37 ± 0.07 , and 1.76 ± 0.03 were found for 1- and 2-CN, respectively. Clearly, 2-CN being the more sensitive isomer of the two.

In terms of polarity, it was found that 1-CN fluoresces better in polar solvents, while 2-CN fluoresces better in less polar solvents. This is the case because PSF values of 0.79 ± 0.06, and 1.12 ± 0.07 were found for 1- and 2-CN, respectively. Both isomers proved to be somewhat sensitive to polarity, but not extremely sensitive. With that said, 1-CN is more polarity-sensitive than 2-CN. The most interesting piece of information gathered from these experiments stemmed from the obtained PSF values. 2-CN has a higher affinity to fluoresce in less polar solvents, while 1-CN has a higher affinity to fluoresce in more polar solvents. This explains the previously reported phenomenon regarding the reversed trends in quantum yields for the two isomers. This reasoning is also a likely explanation as to why 1-CN's fluorescence was impacted in the presence of CB[7], while 2-CN's was not, as it was less sensitive to solvent polarity.

5.4 Synchronous Fluorescence

In terms of the measured synchronous fluorescence spectra, 2-CN proved to have the much more resolvable spectrum, as it was the most differentiated from its emission comparison. With that said, both synchronous scans were successful in producing peaks that were narrower and more resolved than their emission spectra, and thus could be utilized to aid in the identification of either molecule. The length of time required to perform each measurement was the same, however the fact that the measurement required over a minute to be performed is an indication to some of the drawbacks of synchronous fluorescence as an astrochemical identification technique. With this amount of time required to perform the experiment, it was deduced that the technique would most realistically be used on a rover, or lander, rather than a probe or satellite. It also should be known that due to the polarity of water, there would be peaks present in either spectrum that did not show up for the ones reported. Therefore, in the future, solutions should be measured in cyclohexane.

5.5 Host-Guest Titration

Interestingly, a viable host was able to be found for 1-CN which was CB[7]. This host was then attempted for its isomer, but significant fluorescence impacts were not observed. As a result, it is likely that 2-CN could not successfully bind to CB[7], unlike its isomer counterpart. This was likely another consequence of the structural difference between both molecules. In Figure 1.7, it can be seen from the structure of CB[7] that the outskirts of the host cavity are polarized by the carbonyl groups circulating the cavity,

while the very middle of the cavity is relatively non-polar. It is likely that 1-CN was able to align within the host cavity in such a way that allowed for the non-polar naphthalene portion of the molecule to sit in the very middle of the cavity, while the polarized cyano group was stabilized by the polarized carbonyls. One can see how this alignment would be less likely for 2-CN as it is much more linear, and thus a longer molecule. CB[7] has a relatively small cavity as well and is just barely capable of fitting naphthalene within it. This likely would have also contributed to the possibly insignificant binding of 2-CN, in which the cyano group would be pointing outwards, well away from the host carbonyls. In addition, the position of the cyano group on the naphthalene ring would have significant electronic effects on the molecule. This means that if binding could not occur, it was likely a combination of differences in steric and electronic factors between the two isomers. If significant binding was occurring however, the reason that an impact on fluorescence was not observed was due to the differences in PSF of both molecules. As previously mentioned, the magnitude of the difference between the PSF of 1-CN and a PSF value where polarity has no effect on fluorescence (1) was greater than what was found for 2-CN. Indicating, that 2-CN is less polarity sensitive, and thus is less affected by changes in polarity.

Chapter 6 Conclusions and Future Work

Spectroscopic studies which revealed useful quantities and spectra relating to the recently identified astrochemical PAHs known as 1- and 2-CN were conducted. In doing so, the two naphthalene derivatives' spectroscopic properties, mainly relating to fluorescence, were able to be compared with one another, and explanations were drawn to explain the observed differences between the two. The spectra and quantities that were gathered for the two molecules include the following: absorption and emission effects caused by being dissolved separately in various solvents, PSF, OSF, quantum yield, and fluorescence lifetime determinations, synchronous fluorescence emission spectra, as well as host guest titrations.

The effects on fluorescence when dissolved in various solvents were explored for both molecules. It was found that 1-CN produced emission peaks that varied over a larger range of wavelengths, and 2-CN showed more resolvable spectra overall. Various solvents were also utilized during quantum yield, and fluorescence lifetime determinations. 1-CN allowed for the development of a complete table filled with fluorescence lifetimes, quantum yields, and the subsequently calculated k_R and k_{NR} values. This table can be seen in Table 3.1. It was found that quantum yields were highest for solvents that were most polar. The opposite trend was observed for 2-CN. These differences in trends were further illustrated through the use of the PSF values of the two molecules, where 1-CN was found to have "reverse polarity dependence", and 2-CN was found to have the opposite dependence, that is much more typical of fluorophores.[10] As a result of the construction of this table, the dielectric constants of all the solvents that were used were able to be plotted against the calculated k_R and k_{NR} values in separate graphs. A

relationship with notable linearity was produced; however it would be ideal to have two more solvents added to these graphs to be able to comment more on its trend. One of these having a dielectric constant between acetonitrile's and water's, and the other having a dielectric constant, between methanol's and cyclohexane's. This could be accomplished in future work. Although experimental determination of fluorescence lifetimes for 2-CN were attempted, only the aqueous solution's was found to be usable due to the low fluorescence intensities. This was caused by having to excite the solutions at 290nm, instead of closer to its maximal absorption wavelength, which is 281nm. If possible, it would be of great significance to be able to produce usable fluorescence lifetimes in the future for the three other solvents. This would have to be attempted with a different lamp, or fluorimeter altogether, as the lamp that was used excited best within the range of 290-350nm. If this were possible, then k_R and k_{NR} values could be calculated for each solvent, and then plotted against their associated solvent dielectric constants. This would also allow for more comparisons to be made between the two isomers, as the lifetimes, k_R and k_{NR} values, as well as the trends of the four plots could be compared.

PSF and OSF values were also obtained for each molecule from them being dissolved in either water or ethanol. Both molecules were found to be negligibly sensitive to oxygen quenching, as values of 1.02 ± 0.03, and 1.01 ± 0.02 were reported for 1-CN and 2-CN, respectively. However, this was not the case for both molecules while they were present in solutions where ethanol was the solvent. Significant oxygen quenching was observed for these solutions as OSF values of 1.37 ± 0.07, and 1.76 ± 0.03 were found for 1-CN and 2-CN, respectively. The most interesting conclusion from this experiment was that 1-CN was found to be more fluorescent in polar solvents, while 2-

CN is more fluorescent in non-polar solvents. Thus 1-CN has "reverse polarity dependence", while 2-CN has the more common dependence on polarity, where its fluorescence is most intense while in non-polar solvents. This was concluded because PSF values of 0.79 ± 0.06, and 1.12 ± 0.07 were found for 1-CN and 2-CN, respectively. This also helped explain the observed trend for how quantum yields of 1-CN became higher as the polarity of its solvent increased, and how the opposite was observed for 2-CN. It also gave possible reasoning as to why impacts on fluorescence were observed for 1-CN while in the presence of CB[7], while there was no impact on the fluorescence of 2-CN when the same was attempted for it.

Synchronous fluorescence spectra were measured for both isomers in an aqueous solution during this research as a means for aided astrochemical identification. This was successfully accomplished, with both spectra indicating resolvable peaks, and identifiable spectra. They were also normalized and overlaid with emission spectra over the same range of wavelengths, which was intended for comparison. The comparison proved to be worthwhile, as what was observed, was a more refined, resolvable spectrum compared to the two compound's associated emission spectra. To date, synchronous fluorescence spectroscopy has never been attempted for astrochemical identification. However, after gathering spectra via this experimental technique, its complementary potential for identifying molecules such as PAHs on other planetary bodies within the solar system remains.

The final fluorescence experiment performed was the employment of host guest titrations. Two hosts were employed for 1-CN, however only one was able to showcase significant binding. The host that was successful at this was CB[7], while the

unsuccessful host was β-CD. CB[7] was found to bind to 1-CN in a 1:1 complexation ratio of host to guest. This finding is quite confident as the both of the two double reciprocal plots that were constructed from the two successful titrations produced a line with R^2 values very close to 1 (0.999 and 0.996), where a value of 1.0 indicates a perfectly 1:1 host-guest inclusion complex. CB[7] was also utilized as the host during a titration with 2-CN, however either very little binding occurred, or if significant binding did occur, fluorescence was not impacted because 2-CN was found to be less sensitive to polarity when compared to 1-CN. If binding was insufficient, it was believed to be caused by the difference in structure of this isomer compared to its structural isomer. In terms of future work, finding a host that binds well to 2-CN is desirable. This is because, if one were to be found, the environment within this host's cavity could be compared to CB[7]'s, thus allowing for more comparisons to be made between the two naphthonitrile isomers, specifically on how their structures impact their ability to bind to different host molecules. Given more time, β-CD would be a great starting point, as it was attempted with 1-CN and failed to show significant impacts on fluorescence, so if it were to bind well to 2-CN, then it would allow for an interesting comparison.

In conclusion, this research proved that the positions of the cyano functional group on the parent hydrocarbon (naphthalene) of 1- and 2-naphthonitrile had significant impacts on the fluorescence of either molecule. The two possible positions of the cyano group led the two molecules to having completely reversed trends in quantum yield, as well as their sensitivity to solvent polarity. Stemming from solvent polarity sensitivity, this also caused significant suppression of fluorescence for 1-CN, while it was bound to CB[7]. Likely due to its PSF as well, significant impacts on fluorescence were prevented

from occurring when the same was attempted for 2-CN. All in all, emission spectra were found for 1- and 2-CN, allowing for their facilitated optical identification in space. Not only this, but synchronous fluorescence spectra were also obtained for both compounds, allowing for reference if the technique is ever taken advantage of in future space missions where probes or rovers are utilized.

Chapter 7 References

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