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Are Twisted Derivatives of PRODAN More Effective than Planar Derivatives as Detectors of Solvent Acidity in Micellar Solutions?

Zachariah Bach Nealy

College of William and Mary

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Are Twisted Derivatives of PRODAN More Effective than Planar Derivatives as Detectors of Solvent Acidity in Micellar Solutions?

A thesis submitted in partial fulfillment of the requirement
For the degree of Bachelors of Science in Chemistry from
The College of William and Mary

By

Zachariah Bach Nealy

Accepted for________________________________________

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“Once you know what people really want, you can't hate them anymore. You can fear them, but you can't hate them, because you can always find the same desires in your own heart.” ~ Orson Scott Card in Speaker for the Dead

“When I was a child, I talked like a child, I thought like a child, I reasoned like a child. When I became a man, I put childish ways behind me” ~ 1 Corinthian 13:11

“No time is wasted time.” ~ Jim Henson
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Abstract:

Solvent acidity quantifies the hydrogen bond donating ability of a solvent. One of the first measures of solvent acidity was α parameter developed by Kamlet-Taft. Later Catalan and colleagues developed the SA parameter. This study proposes that the emission intensity of several PRODAN derivatives can also be used as a measure of SA. The photophysical properties of PRODAN (1) (6-propionyl-2-(dimethylamino)naphthalene), 3-(dimethylamino)-8,9,10,11-tetrahydro-7H-cyclohepta[a]naphthalene-7-one (2), 6-(2,2-dimethyl-propion-1-yl)-2-(dimethylamino) naphthalene (3), 2,2-dimethyl-1-(4-methyl-1,2,3,4-tetrahydrobenzo[f]quinolin-8-yl)propan-3-one (4) 7-(dimethylamino)-3, and 4-dihydrophanthren-1(2H)-one (5) are reported. These compounds are classified as planar derivatives (1 and 5), which are theorized to be worse at detecting solvent acidity, and twisted derivatives (2, 3, and 4), which are theorized to be better at detecting solvent acidity, based on their geometry. These compounds were used to create correlation curves between solvent acidity and log((E/A)_{max}/(E/A)) values. In this experiment, E is the emission spectra maximum intensity or integrated emission value and A is the absorbance value at 365nm. This correlation curve was used to calculate the apparent solvent acidity that the PRODAN probes sense while in micellar (SDS, CTAB) and reverse micellar (TX-100) solutions. Compound 2 is the most suited as a probe of solvent acidity.
Introduction

The goal of the study was to evaluate the suitability of PRODAN(1) (6-propionyl-2-(dimethylamino)naphthalene) and its derivatives (3-(dimethylamino)-8,9,10,11-tetrahydro-7H-cyclohepta[a]naphthalene-7-one (2), 6-(2,2-dimethyl-propion-1-yl)-2-(dimethylamino)naphthalene (3), 2,2-dimethyl-1-(4-methyl-1,2,3,4-tetrahydrobenzo[f]quinolin-8-yl)propan-3-one (4) 7-(dimethylamino)-3, and 4-dihydrophanthren-1(2H)-one (5)) as detectors of solvent acidity in micellar solutions. The structures and designations can be seen in figure 1.

The molecule, PRODAN, the structural basis of the probes in the study, was originally a detector of polarity to be used in solution. It has fluorescent character as a result of having a naphthalene scaffolding, tertiary amino and propionyl groups. These groups are present in each of the derivatives but the modifications to each of the derivatives are theorized to cause changes in the fluorescent character and absorption of said derivative. 1 is strictly PRODAN. 2 has a seven-membered ring incorporating the carbonyl group of PRODAN and attaches to the 5 position along the naphthalene scaffolding. 3 has a two methyl groups on the 2 position of the propionyl group. 4 has the two methyl groups on the 2 position of the propionyl group as well as a six-membered ring incorporating the tertiary amine group and attaching it to the 10 position on the naphthalene scaffolding. 5 has a six-membered ring incorporating the carbonyl group and attached to the 5 position along the naphthalene structure. Each of these changes will affect the fluorescent character and, as a result, will affect the polarity detection capability, as well as the solvent acidity detection capability, of the probe.

The effect on the detection capabilities is the focus of this study. The main concern is which of the probes would be the best to detect solvent acidity within micelles. Detecting solvent acidity poses an important point of study as detecting the hydrogen bonding ability allows for
better understanding of media that may participate in hydrogen bonding by clarifying the relative amount of hydrogen bonding present. This would allow for the further understanding of chemical processes, interactions and reactions that occur in living and nonliving systems that have potential for hydrogen bonding.

Micelles are a useful media for an experiment such as this as their formation is concentration dependent. This would mean that each of the probes could be used to detect very small concentrations of surfactants and micelle formation itself. This could also be used to detect the polarity and solvent acidity of the environment before, during and after the addition of surfactants and the formation of micelles. This is important as micelles make up a good portion of living systems, such as with fatty acid micelle formation, and interactions with living systems, such as micelle formation with soaps and detergents. Overall, this study provides an important data on the potential of PRODAN and its derivatives as detectors of solvent acidity.

Detection of solvent acidity as well poses an important role to PRODAN itself. PRODAN, originally a polarity probe, often receives interference in detecting polarity from solvent acidity itself. So, in order to clarify polarity data, having a way of detecting solvent acidity with an orthogonal probe would allow to account for possible interference that the planar PRODAN may detect. In finding this, the usefulness of PRODAN itself increases substantially. In particular, this study aims to determine which of PRODAN’s derivatives, if any, are suitable detectors of solvent acidity and whether there is correlation to geometry. Based on the geometry and accepted photophysical properties of the PRODAN and its derivatives, the suitability of the probes as detectors of solvent acidity in micelles is theorized to follow the trend of: \(2 > 3 > 4 > 1 > 5\). Essentially, the theory is that the twisted derivatives are better than planar derivatives at
detecting solvent acidity in micelles as well as other micellar properties. This study aims to test each of these theories and answer questions related to them.
Background

**PRODAN and its derivatives**

PRODAN, 6-propionyl-2-dimethylaminonaphthalene, was first synthesized by Gregorio Weber in 1979 as a solvent polarity probe.² Its structure maximizes the distance between an electron donor and accepter, the tertiary amine and the carbonyl respectively, along an aromatic naphthalene scaffolding. These structures allow for PRODAN’s fluorescent nature.³ PRODAN and its derivatives have been made in the Abelt lab and can be seen below in Figure 1.

![PRODAN and its derivatives](image)

**Figure 1. PRODAN and its derivatives**
PRODAN’s usefulness comes as a result of its solvatochromism. Solvatochromism refers to the change in the intensity and maximum wavelengths of the emission and absorption spectra as a result of a change in the environment’s polarity. Emission in this case is the result of fluorescence, which is luminescence from the excited singlet state from irradiation of the probe by electromagnetic radiation. The solvatochromism stems from the excited state of PRODAN having a larger dipole moment than its ground state. As a result, the excited state will be stabilized more in polar solvents than it would in nonpolar solvents. As the polarity of the solvent changes, the maximum emission wavelength will change. However, a problem of interest that Mennucci and his colleagues discovered is that PRODAN tends to create short wavelength bands in water as a result of hydrogen bonding creating a more polar excited state. The excited state chemistry stabilization can be viewed in figure 2. The problem this poses is that often increasing solvent polarity could be confused with increasing solvent acidity. The reason this problem is interesting is that it means that PRODAN cannot be used as a chemosensor of either property. One of the main focuses of this paper is to determine whether certain derivatives can be used for these properties.

PRODAN’s derivatives are of interest because they possess unique properties. The major distinction between the derivatives is that some are planar while others have the carbonyl group twisted out of plane, and will be referred to as twisted derivatives. All derivatives have been synthesized in lab but 3 has not been reported in the literature. Nevertheless, 3 is predicted to act similarly to the other twisted derivatives. The planar derivatives, 5 and PRODAN, tend to have similar planar intramolecular charge transfer (PICT) excited states and the fluorescence is highly efficient in polar solvents.
Figure 2 – reaction coordinate diagram of the effect of dipole moments and polarity of solvent on the stabilization of the probe.

4, despite the t-butyl group twisting the carbonyl out-of-plane, exhibits similar solvatochromic behavior to PRODAN. The fluorescence intensity of PRODAN and 5 had intensities of an order of magnitude greater than 2 or 4 in protic solvent indicating that they are not sensitive to solvent acidity. The important difference that occurs in 5 but not PRODAN is that the six-membered ring does not twist in the ground or excited state while PRODAN is predicted to change by a few degrees during excitation. Calculations indicate that the 7-membered ring of 2 should significantly twist the carbonyl out-of-plane, and that 4 would twist by 20 degrees. This twisting behavior has led to the belief that the excited state of 2 would be effectively quenched by protic solvents when the carbonyl twists out-of-plane. Overall, the twisted derivatives are all predicted to be very sensitive to protic solvents due to their effective quenching when a solvent’s ability to
hydrogen bond increases, so there is reason to believe that derivatives will be a good indicator of solvent acidity in micellar solutions.\(^7\)

The experimental procedure involves cyclohexane, water and 2-propanol as the main solvents. PRODAN responds by having the extremes in its maximum emission wavelength with 404.6nm in the least polar cyclohexane, 518nm in the most polar solvent water and a signal between these values with the solvent of intermediate polarity, 2-propanol. This wide variation is useful as PRODAN has been found to associate with more polar regions of micelles and bilayers, especially in media that have a high presence of hydrogen bonding. Due to the significant wavelength change related to the hydrogen bonding ability of the media, it might be reasonable that PRODAN can show the existence of hydrogen bonding. However, PRODAN has been found to inhabit hydrophobic environments if it experiences tight packing. This requires that PRODAN can move past the hydrophilic interfaces.\(^8\) Thus, in bilayers, the fortune of using PRODAN and its derivatives is that they’ve been shown to inhabit both the polar and apolar regions of micelles in relatively equal probabilities with a slight favor towards polar environments.

**Refractive indices**

Water, cyclohexane and 2-propanol have different refractive indices. The main concern here is that refractive indices will affect emission intensities. As the concentrations of the micelles in aqueous solution are small, the refractive indices of micellar solutions will not change significantly. The index of refraction needs to be taken into account for mixed solvents for the calibration curve. The values that are used in this experiment to account for mixed solvents and in general come from the experimental values determined in Herraez’s paper and are listed in table 1.\(^9\)
Table 1. list of solvents used, their indices of refraction and their SA values

<table>
<thead>
<tr>
<th>solvent</th>
<th>Index of refraction</th>
<th>SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropanol</td>
<td>1.377</td>
<td>0.283</td>
</tr>
<tr>
<td>Water</td>
<td>1.333</td>
<td>1.062</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.329</td>
<td>0.605</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.36</td>
<td>0.4</td>
</tr>
<tr>
<td>Propanol</td>
<td>1.384</td>
<td>0.357</td>
</tr>
<tr>
<td>Butanol</td>
<td>1.399</td>
<td>0.341</td>
</tr>
<tr>
<td>75/25 water/methanol</td>
<td>1.337228</td>
<td>0.94775</td>
</tr>
<tr>
<td>50/50 water/methanol</td>
<td>1.339486</td>
<td>0.8335</td>
</tr>
<tr>
<td>25/75 water/methanol</td>
<td>1.337683</td>
<td>0.71925</td>
</tr>
<tr>
<td>50/50 methanol/ethanol</td>
<td>1.34276</td>
<td>0.5025</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>1.4262</td>
<td>0</td>
</tr>
</tbody>
</table>

The expression used to adjust for these problems in this study is \((n/n_{\text{ref}})^2 = n^2/n_{\text{ref}}^2\) where \(n\) is the refractive index of the solvent used and \(n_{\text{ref}}\) is the refractive index of a reference solvent.

The expression originates from taking into consideration the medium of refractive index that the intensity is observed in by a detector, \(n\), and the refractive index of the medium it is actually in, \(n_{\text{ref}}\). The reason for squaring the correction is that the correction needs to be taken into account for both light entering and light exiting the medium. The \(n^2/n_{\text{ref}}^2\) expression has been found to work despite being less intuitive. This relation accounts for the possible changes that occur as a result the light moving from media to media. This adjustment almost always results in a value close to 1. Given that the adjustment is so small, it will have little effect on the emission value.\(^{10}\)

**Solvent acidity**

Solvent acidity (SA) can be viewed as the ability of a solvent to undergo hydrogen bonding by means of accepting a pair of electrons by donating the hydrogen.\(^{11}\) The current way of defining SA is as a comparative scale that measures the solvatochromism of as a function of the acidity of the solvent. This scale displays an approximately linear relationship between solvatochromic shifts and hydrogen bonding donor acidity. This property is usually measured
using a fluorophore or dye, a UV/vis spectrophotometer and a fluorimeter. Chemists have attempted to describe this property since the 1800s using a single parameter. However, this has proven to be not very effective due to multiple interacting parameters.\(^1\)

A common measurement system for solvent acidity has become Kamlet-Taft parameters, \(\alpha\) and \(\pi^*\). This method defines the specific interactions, \(\alpha\), and the nonspecific interactions, \(\pi^*\), involved for hydrogen bonding donors. Specifically, \(\alpha\) refers to the ability of a solvent to donate a hydrogen bond and \(\pi^*\) refers to ability to stabilize a charge by means of the solvent’s dielectric effects and its dipole. The \(\alpha\) parameter is more important for protic solvents and the \(\pi^*\) parameter is important for aprotic solvents as \(\alpha\) approaches zero for aprotic solvents.\(^1\) Catalan and his colleagues developed an alternative expression, SA. The parameter that Catalan uses stems from comparison of the probes TBSB (o-tert-butylstilbazolium betaine dye) and DTBSB (o,o-di-tert-butylstilbazolium betaine dye) using the Kamlet-Taft method. The solvatochromism of DTBSB is the zero acidity point. This allowed for the use of one term to detect SA. The values used for the calibration curve in this study come from Catalan’s parameters and are recorded in Table 1.\(^1\)

The measurement of solvent acidity has specific requirements for the probe. It needs to be basic in its electronic ground and excited states so that it can properly characterize its environment’s acidity. In these reagents, PRODAN and its derivatives would fit these requirements quite well.\(^1\)

An important aspect to consider about the solvents is their impact on fluorescence intensity. In a study by Abelt and coworker, PRODAN, 2, 4, and 5 each displayed similar solvent dependence for their fluorescence maxima. Of interest is how cyclohexane produced a very weak fluorescence and water the weakest fluorescence while 2-propanol produced the one of the strongest fluorescence intensity. This occurred with all four probes. Of all the protic solvent
studies, 2-propanol has the lowest hydrogen bonding ability. Isopropanol will function as a good comparison for the relative fluorescence for the other solvents used in the trials.\textsuperscript{16}

\textit{Micelles}

Micelles are composed of a set of surfactant molecules, usually lipid in nature, that aggregate in a when added to a particular solvent.\textsuperscript{17} The lipid molecules that form micelles will consist of a polar head and nonpolar (and hydrophobic) hydrocarbon tail. In a normal micellar solution, the lipids will be in a polar environment, such as water, causing the lipids to be in an energetically less favorable state. Due to the tail’s hydrophobicity, the lipids will usually aggregate together in a spherical formation with the tail facing the inside of the circle and the hydrophilic head facing outside the sphere. In this case, the hydrophobic interactions of the tails and the hydrophilic interactions of the heads and the water will better stabilize the formation of said sphere. A special case of micelles, reverse micelles, are composed of lipids with hydrophobic heads and hydrophilic tails and form inside of hydrophobic environments, such as cyclohexane.\textsuperscript{18} Examples of both types of surfactants are found in Figure 3 with sodium dodecyl sulfate (SDS) and cetylTrimethylammonium bromide (CTAB) being surfactants that form micelles and triton X-100 (TX-100) forming reverse micelles. Figure 4 demonstrates the approximate shape of a formed micelle.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{micelle.png}
\caption{TX-100, SDS, and CTAB (top to bottom)}
\end{figure}
Figure 4- SDS micelle – hydrophobic center that excludes water due to a mixture of hydrophobic interactions and hydrogen bonding.

In general, in low enough concentrations of lipids in the solution, the micelles won’t be able to form in detectable amounts. The critical micelle concentration (CMC) is the
concentration above which micelles form with almost all surfactant molecules in solution and below which no detectable amounts of micelles form. In reference to many of the physical properties of micellar solutions, most will not be present below this concentration. One such physical property is the effect that micelles can have on the fluorescence of organic dyes. This effect is similar to solvent stabilization of excited states of organic dyes. The micelles will depolarize the fluorescence caused by dyes during its relaxation. As well, the organic dyes will be soluble in the aqueous environment due to hydrophobic core of the micelles possessing suitable solvation environment. In reverse micelles, the polar center of the aggregates will possess importance for any polar section of the probe or dye. The polarity and the solvent acidity of the micellar solution will greatly influence the fluorescence of the dye. Out of the three micellar solutions selected for the experiment, CTAB and SDS are normal micelles and TX-100 forms reverse micelles. As such, they should have opposite effects on the fluorescence of the PRODAN and its derivatives as the CMC is reached.
Experimental

Spectrophotometric titrations

Solutions are combined in a quartz non-frosted cuvette and stirred with a micro-stir bar in order to mix the solution and evenly disperse the probe in solution. The data for constructing the absorption spectra are obtained with an Ocean Optics spectrometer using the Spectra Suite Spectroscopy Platform. The absorption spectra requires background scan, which is a scan where light is blocked to detect noise, a reference scan, which is a scan where only the solvent used is present, and finally a sample scan, which is a scan of the solvent and solutes. The emission spectra require only a reference and sample scan. The excitation wavelength is set at 365nm and the slit width normally set to 5nm to excite the PRODAN derivatives in the sample. The fluorescence is measured at a 90 degree angle from the direction of the high intensity Xenon lamp. The emission data are recorded with another Ocean Optics Maya spectrometer using the Spectra Suite Spectroscopy Platform program.

The Spectra Suite Spectroscopy Platform program controls the integration time, boxcar width, and number of scans run for each data set. Each of these parameters will modify the incoming data so that it produces high quality. From here, a clean graph is displayed on the screen that shows the intensity of the emission or absorption versus the wavelength of the emission or absorption. An x, y-list of the data is recorded and then analyzed in Microsoft Excel. The absorption at 365nm, which is the wavelength at which PRODAN and its derivatives is predicted to have its maximum absorption, is determined for each sample. The values for the background (B), reference (R) and sample (S) are used to determine the absorbance value using the expression, \( \log\left(\frac{R-B}{S-B}\right) \). The corresponding emission data is analyzed by extracting the
maximum intensity and wavelength values. The emission intensity is calculated main calculation using the reference (R) and the sample (S) using the value, S – R. Also, all the integrated emission values are determined for each sample; the integrated data is considered more accurate. The measurement determination of the relative integration value is simply the sum of all emission values from 380 nm to 800nm after the emission values were corrected by substituting the lowest value from all other emission values.

Once the emission and absorbance values are measured, the emission value is divided by the absorption value for that particular solvent, and then all values that are measured for that file are divided by the maximum E/A value for all the solvents or solutions used for that trial. From here, the logarithm of the inverse of this value multiplied by the quotient of square of the indices of refraction of the solvent being analyzed divided by the index of refraction of water, or \( \log \left( \frac{1}{(E/A) * (n_{\text{solute}}/n_{\text{reference}})^2} \right) \), is calculated. This computation is done for both the maximum emission and the integrated emission values. Then, the values are plotted versus known solvent acidity values for the solvent acidity calibration plots. For micelles, the \( \log ((E/A)_{\text{max}}/(E/A)) \) is plotted versus micellar concentration. This graph is then used to analyze the probe, solvents involved, micellar solutions involved or any number of parameters related to the experiment. This general procedure was followed for each of the main sections and the specific parameters for each section are listed accordingly.

**Probe solutions**

All probes were synthesized in the Abelt lab. The probe solutions were made by dissolving each of the set amounts of probe in 10mL of methanol. The exact amounts are listed below in Table 2.
mass dissolved in 10mL of methanol

<table>
<thead>
<tr>
<th></th>
<th>PRODAN</th>
<th>derivative 2</th>
<th>derivative 3</th>
<th>derivative 4</th>
<th>derivative 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass dissolved</td>
<td>5.1mg</td>
<td>5.9mg</td>
<td>6.6mg</td>
<td>6.0mg</td>
<td>6.2mg</td>
</tr>
</tbody>
</table>

**Table 2 – amounts of derivative in probe solution**

**Development of SA calibration curves**

Each of the 5 probes with their varying concentrations was run in a series of solvents. The solvents included 2-propanol, water, methanol, ethanol, 1-propanol and 1-butanol. In some of the studies, ethylene glycol and 1,2 propadiol were used but were ultimately removed from use for attainment of enhancement factors. In each of solvent readings, the cuvette was filled with 2mL of solvent and the amount of probe listed below in Table 3. Each of the probes was run under various settings for absorption and emission in Spectra Suite as listed below in Table 3. Once the absorbance data was taken and the graphs of log(I\(_{\text{max}}\)/I) vs. SA were constructed, the graphs were fit linearly and the slope and intercept were determined. The slopes of the line are used to convert the enhancement factors to effective solvent acidities. Several concerns, namely the effect of mixed solvents and aggregation, came up after runs were performed concerning the accuracy of this data, so a few minor studies were performed.

<table>
<thead>
<tr>
<th></th>
<th>absorption (integration time, boxcar width, number of scans)</th>
<th>emission (integration time, boxcar width, number of scans)</th>
<th>slit width (in nm)</th>
<th>volume of probe solution used in each sample (in uL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRODAN (1)</td>
<td>325,8,8</td>
<td>250,4,4</td>
<td>5</td>
<td>5(else)/10(water)</td>
</tr>
<tr>
<td>2</td>
<td>350,8,8</td>
<td>425/4250, 4,4</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>350,8,8</td>
<td>400/4000,4,4</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>325,8,8</td>
<td>300/3000,4,4</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>325,8,8</td>
<td>225,4,4</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

**Table 3 – enhancement factor trial conditions for each probe**
Mixed solvent studies

The basic correction to the absorbance values, \((n_{sample}/n_{reference})^2\), is considered to be adequate to account for the different effects the solvent’s refraction of light has on the absorption and emission values. In the case of mixed solvents, there was some uncertainty as to whether the mixing of solvent would have a large effect on the refractive indices. As well, the calibration curves constructed contained gaps, so using mixed solvents was thought to be a way of filling in those gaps. So, using experimental refractive indices to account for the uncertainties, the mixed solvents were used to make the calibration curves more accurate.

Aggregation studies

The emission graphs showed two main peaks for emission and light-scattering in an ideal graph. However, in some of the twisted derivatives’ graphs, especially 4 and 3 while in water, there was an additional minor peak that was theorized to be caused by aggregation of the derivatives in solutions causing them to show a separate absorption and emission spectrum. In order to confirm this, trials were run on all five of the probes by placing them in water and increasing the concentration to determine at what concentrations of derivative aggregation would occur. The planar derivatives, PRODAN and 5, showed minor, if any, aggregation and that aggregation would not affect their emission data. Generally, the twisted derivatives had some aggregation at high concentrations above 10 μL aliquots of the probe solution. As there is no case where more than 10 μL aliquot was used, this appears to not affect this study.

SDS, CTAB, and TX-100 solution creation

The SDS, CTAB and TX-100 solutions were made from their solid form for SDS and CTAB and from viscous liquid form for TX-100. A 25mL volumetric flask was filled with .72g
of SDS and filled to volume with water to form a 100mM solution. A 100mL volumetric flask was filled with 1.82g of CTAB and filled to volume with water to form a 50mM solution. As TX-100 forms reverse micelles, a 250mL volumetric flask was filled with 1.5g of TX-100 for a 4:1 solution of TX-100 to 1-hexanol and diluted to volume with cyclohexane resulting in a 10mM solution. The solutions were occasionally heated mildly or sonicated in order to remove crystals and to let the surfactants mix evenly in the solution. The solutions were allowed to cool to room temperature before use.

**Micellar solution studies**

The trials for the micelles studies show the effect of the micelle concentration on the E/A values from which the solvent acidity can be calculated. The experiment starts by taking an absorption spectra reading of 2mL of water for SDS and CTAB or 2mL of cyclohexane for TX-100 for the reference and with the probe as a sample at 0M micelle concentration. The reference is used for all of the micelle solutions that contain that solvent in that trial as a reference. Two additional readings were taken at 3 minutes after and then 5 minutes after mixing to see if the micelles formed instantly or not. The conditions for each set of runs are listed in the Table 4. The conditions for some of the solvents or micelle concentrations for emission may have been modified by an order of magnitude when measured but were corrected for when analyzed in Excel.
### Table 4 – conditions for micellar concentration studies

<table>
<thead>
<tr>
<th></th>
<th>absorption (integration time, boxcar width, number of scans)</th>
<th>emission (integration time, boxcar width, number of scans)</th>
<th>slit width (in nm)</th>
<th>volume of probe solution used in each sample (in μL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS runs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PRODAN</td>
<td>500,8,8</td>
<td>200,4,4</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>derivative 2</td>
<td>500,8,8</td>
<td>800,4,4</td>
<td>7.5</td>
<td>7</td>
</tr>
<tr>
<td>derivative 3</td>
<td>500,8,8</td>
<td>1500,4,4</td>
<td>7.5</td>
<td>4</td>
</tr>
<tr>
<td>derivative 4</td>
<td>600,8,8</td>
<td>700,4,4</td>
<td>7.5</td>
<td>7</td>
</tr>
<tr>
<td>derivative 5</td>
<td>450,8,8</td>
<td>30,4,4</td>
<td>7.5</td>
<td>7</td>
</tr>
<tr>
<td>CTAB runs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PRODAN</td>
<td>600,8,8</td>
<td>60,4,4</td>
<td>7.5</td>
<td>7</td>
</tr>
<tr>
<td>derivative 2</td>
<td>600,8,8</td>
<td>350,4,4</td>
<td>7.5</td>
<td>7</td>
</tr>
<tr>
<td>derivative 3</td>
<td>500,8,8</td>
<td>1000,4,4</td>
<td>7.5</td>
<td>7</td>
</tr>
<tr>
<td>derivative 4</td>
<td>600,8,8</td>
<td>1000,4,4</td>
<td>7.5</td>
<td>4</td>
</tr>
<tr>
<td>derivative 5</td>
<td>600,8,8</td>
<td>12,4,4</td>
<td>7.5</td>
<td>7</td>
</tr>
<tr>
<td>TX-100 runs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PRODAN</td>
<td>350,8,8</td>
<td>150,4,4</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>derivative 2</td>
<td>350,8,8</td>
<td>350,4,4</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>derivative 3</td>
<td>500,8,8</td>
<td>1000,4,4</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>derivative 4</td>
<td>500,8,8</td>
<td>350,4,4</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>derivative 5</td>
<td>350,8,8</td>
<td>500,4,4</td>
<td>5</td>
<td>7</td>
</tr>
</tbody>
</table>

The starting concentrations depend on the CMC of the micelle being measured. The trials for SDS with an experimental CMC of 8.3 mM measured 2, 4, 6, 8, 10, 12, 14, 16, and 18 mM with the additional readings at 8mM and 10mM. The trials for CTAB with an experimental CMC of .91mM measured 1, 2, 3, 4, 6, 8, 10, 12, 14, 16, and 18mM with additional readings at 4 and 6 mM. When the CTAB trials originally began, the CMC was predicted to be higher than it was, so there were extra trials ran at 8 and 10mM but a secondary trial was run for the CTAB-PRODAN trial. The trials for TX-100 with an experimental CMC of .15mM was measured at .4, .6, .8, .10, .12, .14, .16, .18, and .20mM with additional readings at .10 and .12mM. The original thought was that the CMC for TX-100 was lower than initially expected so the additional readings were done at 10 and 12 mM.
In addition to these basic sets of conditions, each of the micelle studies were compared with readings in 2-propanol and in mixed solvents. The 2-propanol readings consisted of taking a reference for 2-propanol and then the probe in a sample of 2-propanol. The mixed solvent readings included using 1 mL of water for CTAB and SDS or 1 mL of cyclohexane for TX-100 and 1 mL of 2-propanol for the reference for a 2mL mixed solvent readings. In the two samples, one is the mixture with the probe and one is the mixture, the probe, and micellar solution that will cause the resulting solution to be at the CMC.

After correcting absorbance values so that the lowest point is zero, a graph comparing the absorbance to the micelle concentration of the solution is constructed. This graph indicates the CMC and approximately how the fluorescent enhancement caused by association with the micelle. From this data, the average of emission to absorption ratio values is taken between the plain 2-propanol/probe mixture and the 2-propanol/probe/micelle mixture is taken. This average, A(iPrOH+*), is then divided by the maximum emission to absorption ratio value for that micelle, A(M), which is predicted to be the concentration closest to the CMC without too many or too few surfactants affecting the fluorescence and absorption values, from that trial (equation 1). The logarithm of the inverse of this value is taken and divided by the enhancement factor for that probe, m, which is the slope of the plot of log (I_{max}/I) vs. SA (equation 2). From here, the value is subtracted from the known value of 2-propanol, .283, in order to get the effective SA of the probe in the micelle (equations 3-6). The following set of equations displays the relation between the calculated solvent acidity and the absorbance values.

\[
A(iPrOH+*)/A(M) \tag{1}
\]
\[
m = \log(1/x)/SA(x) \tag{2}
\]
\[ SA(M^*) = SA(iPrOH) - \left( \frac{1}{m} \right) \log \left( \frac{1}{A(iPrOH^*/A(M))} \right) \]

\[ SA(M^*) = SA(iPrOH) - \log(A(M)) - \log(A(iPrOH^*))/m \]

\[ SA(M^*) = SA(iPrOH) + (\log(1/A(M)) - \log(1/A(iPrOH^*))/m \]

\[ SA(M^*) = SA(iPrOH) + SA(M) - SA(iPrOH^*) \]

\[ SA(iPrOH) - SA(iPrOH^*) \approx 0, \]

Thus, \( SA(M^*) = SA(M) \)

In equations 3 through 8, \( SA(M^*) \) is the apparent solvent acidity in the micelle whereas \( SA(M) \) is the experimental solvent acidity as a function of the enhancement factor. The assumption made in equation 7 assumes that the average between the 2-propanol and 2-propanol/micellar solution is as large as \( SA(iPrOH) \). Regardless, the calculation allows to account for both.

All of the analyses follow this formula except for the first PRODAN/SDS trial as the decision to include the 2-propanol solutions had not been made yet. In this case, the same procedures were followed but, instead of averaging 2-propanol’s and a 2-propanol/micellar solution at CMC mixture’s emission to absorption ratio values, the average of water’s and water/micellar solution at CMC mixture’s emission to absorption ratio values are taken. As well, instead of using the solvent acidity value of 2-propanol, .283, the solvent acidity value of water, 1.062, is used for the solvent acidity calculation of the micellar solution. \(^{21}\)
Results and Discussion

Enhancement factors: 1

The absorption of 1 in various polar protic solvents are shown in figure 6. A minor light scattering peak appears at around 365nm. It is largest in 1,2-propanediol. Because the mixed solvent data were added after the initial set of readings, the data figure is the combination of two sets of experiments. The second set of readings with the mixed solvents included a second isopropanol reading so that the second set could be adjusted for a combination with the first set. The two isopropanol data sets differ as a result of the condition of the fluorimeter and Xenon lamp on each of the given days. The corresponding emission spectra are shown in figure 5. The emission intensity is lowest in H\textsubscript{2}O and highest in isopropanol. The absorption values vary between 0.06 and 0.13. Absorption values of less than or equal to 0.1 are typically prescribed to internal filter in effects on emission spectra. The behavior of 1 will serve as a point of comparison to the other compounds as it remains mostly planar in its excited state.

![Figure 5. Emission Spectra of 1 in various protic solvents](image-url)
As polarity and solvent acidity increases, the emission (E) intensity decreases and the peak maxima wavelength shifts to the red. The absorption (A) data follows a similar trend. As solvent acidity increases, absorption decreases. When the E/A data are compared to the solvent acidity, there appears to be an inverse correlation between the two. The E/A ratio will be referred to as I, the absorption adjusted emission intensity. The data were normalized by the maximum I values. A graph of log(1/I) vs. solvent acidity was constructed. Because of how the probe reacted to the di-hydroxyl solvents, these data were excluded on the basis that the second hydroxyl group would change the hydrogen bonding compared to the other solvents. The plot indicates an inverse correlation between I and solvent acidity. The plots of log(I_{max}/I) vs. solvent acidity are shown in figure 7.

The data was fit to a line, and the trendline gave the equation, y = 0.7949x - 0.2324, for the emission maxima data and the equation, y = 0.7256x - 0.2328, for the integrated emission.
data. The enhancement factor, which is the slope of the line, is fairly low for these plots showing that there is relatively little change in the I value as solvent acidity changes. As the enhancement factors are less than one, when solvent acidity changes, this compound would not be a good indicator of solvent acidity.

**Enhancement factors: 2**

The absorption and emission spectra for 2 are shown in figures 8 and 9. The maximum absorbance is centered on 365 nm. The emission peaks are narrower for 2 than for 1. The variation in emission intensity for 2 is similar to 1. The emission values range from 9500 and 59500 counts but decrease in a more pronounced pattern than in 1. The absorption values range between 0.045 and 0.092, but the spectra change more noticeably as solvent acidity increases.

There are multiple readings for isopropanol as the mixed solvent readings were added from a different set of experiments. The correlation between the I values and SA are plotted in figure 10. The maxima trendline produced the equation, \( y = 2.0272x - 0.5635 \), while the
integrated trendline produced the equation, \( y = 1.9617x - 0.5585 \). The enhancement factors are much greater than those of 1 meaning that the I values will noticeably change with solvent acidity. The \( R^2 \)-value is close to one indicating the correlation is strong.

**Figure 8. Emission Spectra of 2 in various protic solvents**

**Figure 9. Absorption spectra of 2 in various protic solvents**
Enhancement factors: 3

The absorption and emission spectra of 3 in a range of polar protic solvents are shown in figure 11 and 12. The absorption spectra vary as seen before: the smallest absorption is in water and it has decreased by 40%. The intensity of the emission spectra of 3 decreases sharply. The problem that occurs with 3 is the occurrence of a secondary emission peak in water and the aqueous mixed solvents. This peak is thought to arise from aggregation of 3. Aggregation would affect both absorption and emission intensity. In this case, the effect isn’t very significant. The twisting in 3 is due to the t-butyl group, and it rotates the carbonyl group out of plane. Interaction of the excited twisted conformation with polar solvents is thought to give rise to efficient non-radiative decay to the ground state.
Figure 11. Emission Spectra of 3 in various protic solvents

Figure 12. Absorption spectra of 3 in various solvents

Given the noticeable difference in the emission intensity as solvent acidity changes, it was suspected that this probe could be useful as a detector of solvent acidity. The relationship between I and solvent acidity is displayed in figure 13. The trendline for the emission maxima data gives the equation, $y = 2.451x - 0.7637$, while the integrated fit gives the equation, $y = 2.2773x - 0.7214$. The enhancement factors are much larger than one meaning that the I values
will noticeably change with solvent acidity. As well, the $R^2$-value is close to one indicating a strong empirical correlation.

![Graph showing the relationship between solvent acidity and log(I_max/I)](image)

**Figure 13. Plot of log(I_{max}/I) vs. SA for 3**

**Enhancement factor: 4**

The absorption and emission spectra of 4 in polar protic solvents are shown in **figures 14 and 15**. The behavior of 4 mimics 3 in that the emission intensity severely decreases as solvent acidity increases. In fact, it falls 98% in water compared to isopropanol. The emission redshift is not as large as with other derivatives. An anomalous peak appears at similar position to that in the emission spectra of 3 indicating significant aggregation in the mixed aqueous solvents and especially in water itself. This peak becomes prominent in the 50:50 water/methanol mixtures. The aggregation peak is dominant in water. Again, the absorption maxima vary between 0.08 and 0.14. The quenching is again attributed to the t-butyl group. The ring prevents the amino
group from rotating at all; in 1, the amino group can rotate freely. The larger extent of aggregation is result of the hydrophobicity of the ring.

Figure 14. Emission spectra of 4 in various protic solvents

Figure 15. absorption spectra of 4 in various protic solvents
Because of the structural similarity with 3, it was hoped that the plot of 4 could be useful as a detector of solvent acidity. The correlations are displayed in figure 16. The maxima fit produced the equation, \( y = 1.4613x - 0.3246 \), while the integrated fit produced the equation, \( y = 1.8641x - 0.459 \). The enhancement factors are greater than one meaning that the I values will change at significantly with solvent acidity. The R\(^2\)-value is not very high but this is likely as a result of aggregation.

**Figure 16. Plot of log(I\(_{\text{max}}/I\)) vs. SA for 4**

**Enhancement factor: 5**

Compound 5 is similar to 1 in its structure. Not surprisingly, it produces similar absorption and emission spectra (figures 17 and 18). The intensities of the emission spectra vary from 17% to 100% while the absorption values run from 0.07 to 0.15. As the polarity and solvent acidity of the solvent increases, the emission intensity decreases. The emission intensity in the two diols are far less than in the alcohol solvents. The emission value for 1-propanol is much
smaller than expected. The peak maximum increases in wavelength. Specifically, all the alcohol solvents showed emission maxima below 500nm and all others showed peaks above 500nm.

Figure 17. emission spectra of 5 in various protic solvents

Figure 18. absorption spectra of 5 in various protic solvents
The absorption values of the alcohol solvents (other than 1-propanol) were around 0.15. The forced planar carbonyl structure of 5 due to its 6-membered ring prevents quenching. Thus, the emission intensities will be similar to that of 1, if not slightly greater.

The plot of \( \log(I_{\text{max}}/I) \) is displayed in **figure 19**. The maxima fit produced the equation, \( y = 0.6261x - 0.1787 \), while the integrated fit produced the equation, \( y = 0.5512x - 0.2067 \). The enhancement factors are lower than one meaning that the I values will not change noticeably with solvent acidity. As well, the \( R^2 \)-value is barely 0.9 indicating marginal correlation. This probe is predicted to be not very good at determining solvent acidity because the slope is so small.

![Figure 19. Plot of \( \log(I_{\text{max}}/I) \) vs. SA for 5](image)

**Enhancement factor: overall**

The result of the developing the calibration curves and extracting the enhancement factors showed that the planar derivatives, 1 and 5, are not well suited for determining solvent acidity.
acidity. This conclusion is because their enhancement factors (Table 5) are less than one indicating that their \( I \) values do not change much with solvent acidity. Among the twisted derivatives, 3 has the highest enhancement factor indicating that it theoretically could be a good probe for solvent acidity. However, 2 has a more sensitive enhancement factor. Compounds 4 and 3 have potential as indicators of solvent acidity, but the t-butyl groups give rise to aggregation peaks. Aggregation in 3 is not as bad as it is in 4, so 3 still holds the possibility of being a good indicator. Overall, the best candidates for probes for solvent acidity at this point in the study are 2 and 3.

<table>
<thead>
<tr>
<th>derivative</th>
<th>m(max)</th>
<th>m(int)</th>
<th>b(max)</th>
<th>b(int)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.79</td>
<td>0.73</td>
<td>-0.23</td>
<td>-0.23</td>
</tr>
<tr>
<td>2</td>
<td>2.02</td>
<td>1.96</td>
<td>-0.56</td>
<td>-0.56</td>
</tr>
<tr>
<td>3</td>
<td>2.45</td>
<td>2.28</td>
<td>-0.76</td>
<td>-0.72</td>
</tr>
<tr>
<td>4</td>
<td>1.46</td>
<td>1.86</td>
<td>-0.32</td>
<td>-0.46</td>
</tr>
<tr>
<td>5</td>
<td>0.63</td>
<td>0.55</td>
<td>-0.18</td>
<td>-0.21</td>
</tr>
</tbody>
</table>

**Table 5. The enhancement factors (m) of derivatives and their y-intercept(b) from peak maxima (max) and integrated (int) intensity data**

**Micellar studies – SDS**

The five probes were used to study three micellar solutions: SDS, CTAB, and TX-100. For each study, the probe was titrated with the micellar components. The absorption and emission spectra from the titration of 1 with SDS is shown in figures 20 and 21. The absorption of 1 decreases until the concentration gets to 4mM SDS, but the shape of the curve doesn’t change until around 8mM SDS when the micelle begins to form. For the 8 and 10 mM SDS data, several spectra were recorded after 3 and 5 minutes to see if micelle formation was instantaneous.
or not. Because emission intensity and absorbance increase with time, micelle formation is not instantaneous. The emission spectra decrease slightly until SDS concentration reaches about 8mM. At 8mM, the intensity begins to increase substantially. At 10 mM, the intensity begins to approach an asymptote. The peak maxima position shifts to lower wavelengths after the CMC has been reached and continues to decrease slightly after the CMC.

The plot of \( \log(I_{\text{max}}/I) \) vs. [SDS] shows an s-shaped curve. This plot shows that 1 responds to micelle formation but not to increasing component concentration. The jump in \( \log(I_{\text{max}}/I) \) is less than one order of magnitude. The plot indicates the CMC is ~7.9mM. This CMC is fairly close to the experimentally accepted value.

**Figure 20.** Emission Spectra of 1 with varying concentrations of SDS ranging from 0mM to 18mM and in isopropanol mixtures. plain is 0mM SDS
Figure 21. Absorption Spectra of 1 with varying concentrations of SDS ranging from 0mM to 18mM and in isopropanol mixtures

Figure 22. Plot of log((E/A)$_{\text{max}}$/E/A) vs. micellar concentration SDS for 1

The absorption and emission titration of 2 with SDS are shown in figures 23 and 24. The absorption spectra for 2 steadily decrease until 4mM SDS. The shape of the absorbance curve stays constant until 6 mM SDS. This point is a somewhat early compared to the experimentally accepted CMC where micellar properties should become evident. Waiting 3 minutes and then 8 minutes at 8mM SDS gives no change indicating complete micelle formation. The emission
intensity decreases slightly until 6mM. The intensity increases substantially at 6mM. At 8 mM, the intensity has nearly reached its maximum. The position of the emission maxima does not shift much when comparing before and after the CMC, and it occurs between the maxima values in isopropanol and water. The peak intensity for isopropanol with and without SDS scaled down by a factor of 100. The peak for isopropanol and water mixed with SDS scaled down by a factor of 10. This adjustment was done in order to display all of the emission data on one graph and still have changes noticeable.

The plot of log(I_{max}/I) vs. [SDS] again shows an s-shaped curve in figure 23. The shape is not as pronounced as with 1. The plot shows that the photophysical behavior of 2 responds to micelle formation and increasing surfactant concentration. The change in log(I_{max}/I) is a 0.75 difference and is fairly large compared to other probes. The plot indicates that the CMC is ~5.5mM. This CMC value is less than the accepted CMC but the complete formation of micelles in solution may be at higher [SDS] based on the fact that the curve doesn’t start to reach an asymptote until 10mM. Because 2 is thought to be fairly sensitive to micelle formation, this makes interpretation sense.
Figure 23. Emission Spectra of 2 with varying concentrations of SDS ranging from 0mM to 18mM and in isopropanol mixtures. Plain is 0mM SDS.

Figure 24. Absorption Spectra of 2 with varying concentrations of SDS ranging from 0 mM to 18mM and in isopropanol mixtures.
Figure 25. Plot of $\log(I_{\text{max}}/I)$ vs. micellar concentration SDS for 2

The titrations for 3 with SDS are shown in figures 26 and 27. The absorption spectra for 3 steadily decrease in until 6mM SDS. The shape of the absorbance curve stays constant until 6 mM SDS. The absorption and emission spectra indicate that the micelles start forming at 6mM. Waiting 3 minutes and 8 minutes at 8mM again showed micelle formation does not occur immediately. The emission intensity decreases until 6mM at which point increases substantially. There is a significant peak corresponding to aggregation around 425nm that is inversely proportional to the size of the peak at 500nm. The aggregation peak increases in size reaching a maximum at 4mM. After this point, as micellar concentration increase, the peak slowly decreases in size. The aggregation peak reaches a minimum at 8mM after 3 minutes have passed. This means that as the micelle forms, the aggregation itself decreases substantially. As well, the emission intensity at 500nm increases beginning at 6mM. At 8 mM, the intensity reaches its maximum. The peak position of micellized 3 does not shift much. The light-scattering peak is much more prominent. Adding isopropanol minimized the aggregation peak indicating that
aggregation is related to water concentration. In the emission spectra, the peaks for isopropanol with and without SDS scaled lower by a factor of 100. The peak for isopropanol and water mixed with and without SDS is lower by a factor of 10.

The plot of $\log(I_{\text{max}}/I)$ vs. [SDS] shows a less defined s-shaped curve in figure 28. This plot shows that the photophysical behavior of 3 responds to micelle formation. The change in $\log(I_{\text{max}}/I)$ is a 0.4 difference for integration and 0.7 for the emission maxima. The plot indicates the CMC is ~4mM from the integrated emission and ~6.2mM from the maxima emission. This CMC value is much less than the accepted CMC but the curve reaches its asymptote at 8mM. The problem with aggregation with 3 could have an affect on the overall absorbance, which could explain the shapes of the plot.

Figure 26. Emission Spectra of 3 with varying concentrations of SDS ranging from 0mM to 18mM and in isopropanol mixtures. Plain is 0mM SDS.
Figure 27. Absorption spectra of 3 with varying concentrations of SDS ranging from 0mM to 18mM and in isopropanol mixtures

Figure 28. Plot of $\log(I_{\text{max}}/I)$ vs. [SDS] for 3

The titrations for 4 are shown in figure 29 and 30. The absorption spectra for 4 steadily decrease in until 8mM SDS. The shape of the absorbance curve stays constant until 8 mM SDS. The absorption and emission spectra indicate that the micelles start forming at 6mM. After 3 minutes and 8 minutes at 8mM, the data taken shows that micelles formation occurs fully. The
emission intensity at 525nm decreases until 6mM. There is a significant peak due to aggregation around 425nm and 450 that are inversely proportional to the size of the peak at 525nm. The aggregation peaks grow until the SDS concentration reaches 6mM. After this point, as micellar concentration increases, the aggregation peaks slowly shrink. The aggregation peaks reach a minimum at 8mM after 3 minutes have passed. The emission intensity at 500nm increases beginning at 6mM. At 8 mM, the intensity at 525nm reaches its maximum. The peak position does not shift much outside of changing the solvent itself. The peaks for isopropanol and the mixed solvents despite being at much lower integration times were still much higher by comparison with this probe and showed minimal aggregation. Thus, the aggregation peaks were most likely a function of the water concentration. The aggregation was still somewhat present even after complete micelle formation, however, showing that 4 has a problem with aggregation. The emission spectra in isopropanol with and without SDS are lower by a factor of 100. The peak for isopropanol and water mixed with and without SDS are scaled down by a factor of 10.

The plot of log(I_{MAX}/I) vs. [SDS] don’t show much of an s-shaped curve in figure 31. The plot begins to level off at the CMC. Again, the photophysical behavior of 4 responds to micelle formation. Due to the aggregation and the weak fluorescence, the derived enhancement factors may not be useful. The change in log(I_{max}/I) is a 0.6 difference. The large, sharp jump in the plot that may be due to the aggregation peaks. According to the plot, the CMC is 7.5~mM, which is close to the accepted value.
Figure 29. Emission Spectra of 4 with varying concentrations of SDS ranging from 0mM to 18mM and in isopropanol mixtures. Plain is 0mM SDS.

Figure 30. Absorption spectra of 4 with varying in concentration of SDS ranging from 0mM to 18mM and in isopropanol mixtures.
Figure 31. Plot of log(I\textsubscript{max}/I) vs. [SDS] for 4

The titration plots for 5 with SDS appear in figures 32 and 33. The absorption spectra of 5 decrease until 6mM SDS. The shape of the absorbance curve doesn’t change until 8mM SDS. The absorption spectra are nearly constant changing only slightly as micelle concentration increases. The absorption and emission spectra indicate that micelle formation occurs at 8mM SDS after 3 minutes passed and compound 5 exhibits similar behavior to 1. The emission intensity decreases until 6mM. At 6mM, the intensity begins to increase substantially. At 8 mM, the intensity begins to approach an asymptote. The wavelength of the emission maxima does not change much with increasing [SDS]. The mixed solvent and isopropanol spectra are intense but only the isopropanol peak maximum changes position indicating that water affects the position while isopropanol affects the emission intensity. In the plot of emission intensity, the spectra for isopropanol without SDS are scaled down by a factor of 5.

The plot of log(I\textsubscript{MAX}/I) vs. [SDS] shows an s-shaped curve (figure 34). This plot shows that the photophysical behavior of 5 responds to micelle formation but not increasing surfactant
concentration. The change in $\log(I_{\text{max}}/I)$ is a 0.6 difference and the plot shows a CMC value of ~7mM. This CMC is fairly close to the experimentally accepted value.

Figure 32. Emission Spectra of 5 with varying concentrations of SDS ranging from 0mM to 18mM and in isopropanol mixtures - plain is 0mM SDS.

Figure 33. Absorption spectra of 5 in water in varying concentrations of SDS ranging from 0mM to 18mM and in isopropanol mixtures
Micellar studies: CTAB

Titration plots for 1 with CTAB are shown in figures 35 and 36. The absorption spectra for 1 increase very slightly as [CTAB] increases. The shape of the absorption spectra doesn’t change until around 3mM CTAB. According to the absorption and emission spectra, the micelles form at 3mM CTAB. After 3 minutes at 4mM CTAB, the micelles formation is evident and the emission spectra increase dramatically in intensity. At 6 mM, the intensity approaches an asymptote. The maxima position blue shifts by approximately 30 nm when the micelle is completely formed. The peaks for isopropanol with and without CTAB are scaled down by a factor of 100. The peak for isopropanol and water mixed with CTAB scaled down by a factor of 10.

The plot of log(I_{max}/I) vs. [CTAB] for 1 shows a reasonably s-shaped curve (figure 37). This plot shows that the photophysical behavior of 1 responds to micelle formation, that the
change in \( \log(I_{\text{max}}/I) \) is 0.55, and that the CMC is \( \sim 3.5 \text{mM} \). The CMC value is far off from the accepted value. At this concentration, 1 becomes insensitive to further increases in CTAB.

**Figure 35.** Emission Spectra of 1 with varying concentrations of CTAB and in isopropanol mixtures. Plain is 0mM CTAB.
Compound 2 is very dynamic absorption and emission spectra (figure 38 and 39). As concentration increases, the absorbance seems to increase steadily. The emission intensities drastically increase between 2 and 3 mM CTAB. At 4mM, the micelles form after several minutes. The emission maximum blue shifts from 535 nm to 515 nm after 2mM CTAB. The isopropanol and mixed solvent emission intensities are very large compared to the values in 4.5mM CTAB. Multiple trials were done in order to ascertain data around the CMC.

The plot of log(I_max/I) versus [CTAB] for 2 show a very sharp change in the I-values as the CTAB concentration increases from 2 to 3mM (figure 40). The micelle forms around 3mM, and the curve begins to reach its asymptote at 3mM. There is a slight S-shape to the curve. The change in log(I_max/I) values is 1.4, a very large number. The plot shows the CMC value is about ~2.2mM CTAB. This CMC is also far off the accepted value but closer than the CMC indicated by 1.
Figure 38. Emission Spectra of 2 with varying concentrations of CTAB and in isopropanol mixtures. Plain is 0mM CTAB.
Figure 39. Absorption spectra of 2 in various solvents in varying concentrations of CTAB and in isopropanol mixtures

Figure 40. plot of log(I_{max}/I) vs. [CTAB] for 2
Titration curves for 3 are shown in figure 41 and 42. The absorption spectra of 3 are much lower in aqueous solutions than in isopropanol. The shape of the absorption spectra change around 3mM. The emission spectra show a definite aggregation peaks around 430nm but there is minor shifting of the maximum peak from 505 nm before the CMC to 495 nm above the CMC. The intensity of 3 in aqueous solution was relatively small even when the integration time was increased by a factor of 10 in the plot. Lower integration times were needed to keep the light scattering peaks on scale. They were almost two to three times as larger than the strongest probe emission. The emission spectra intensities increase around 4mM CTAB but steadily increase even at the maximum [CTAB]. The aggregation peak starts to decrease in size at 4mM but doesn’t reach its minima until 10mM. The problem with aggregation still exists with this probe in aqueous solution. Again, multiple trials were done in order to fully characterize the behavior around the CMC. The peaks for concentrations 0 through 4mM CTAB were rescaled by a factor of 10 in order to be visible on the graph.

The plot of log(I$_{\text{max}}$/I) vs. [CTAB] for 3 shows a slight s-shaped curve (figure 43). The log(I$_{\text{max}}$/I) values change well before the CMC values indicated by the other probes. The aggregation peaks again interfered with the plots. The log(I$_{\text{max}}$/I) value for Compound 3 changes by 1.5 as concentration increased. The CMC value according to this plot is approximately 2mM. The aggregation peaks may have interfered with this determination.
Figure 41. Emission Spectra of 3 with varying concentrations of CTAB and in isopropanol mixtures. Plain is 0mM CTAB.

Figure 42. Absorption spectra of 3 in varying concentrations of CTAB and in isopropanol mixtures
Figure 44. Plot of log(I$_{\text{max}}$/I) vs. [CTAB] for 3

The titration curves for 4 were as prevalent as with 3 (figure 44 and 45). The absorption spectra of 4 increased in magnitude and changed in shape as CTAB concentration increased. The most notable change occurs at 6mM CTAB where the shape of the absorption spectra becomes more rounded at 365nm. After 10mM CTAB, the absorption spectra decrease. The emission spectra show aggregation problems similar to 3. The emission of 4 blue shifts from 510 nm to 500nm after micellization. The aggregation emission peak is larger than the non-aggregated emission peak until 8mM CTAB. Again, non-aggregated emission peak intensity is inversely proportional to the aggregation peak intensity. The aggregation emission maximum occurs at 3mM, but it quickly decreases at higher CTAB concentrations. The emission spectra show that the aggregation of 4 occurs even after micelles have formed. Multiple trials were done in order to refine the behavior around the CMC. The peaks for concentrations 0 through 4mM CTAB and 9mM CTAB H$_2$O/iPrOH solution were rescaled lower by a factor of 10 in order to be noticeable on the plot.
Figure 44. Emission Spectra of 4 with varying concentrations of CTAB and in isopropanol mixtures. Plain is 0mM CTAB.

Figure 45. Absorption spectra of 4 in various solvents in varying concentrations of CTAB and in isopropanol mixtures

The plot of $\log(I_{max}/I)$ vs. [CTAB] for 4 shows more of s-shaped curve than with 3 (figure 46). The initial change in $\log(I_{max}/I)$ occurs at 2mM CTAB and reaches its asymptote at 8 minutes after adding 6mM CTAB. The aggregation does have a large effect here. Thus, the CMC is difficult to discern from the plot, but indicates that the CMC value is ~4mM CTAB. This
CMC is again different from the accepted CMC value, but the log(I\textsubscript{max}/I) values for 4 are responsive to the formation of CTAB micelles.

![Figure 46](image)

**Figure 46. Plot of log(I\textsubscript{max}/I) vs. [CTAB] for 4**

Finally the titration curves for 5 are relatively well behaved (figures 47 and 48). The maximum absorption values of 5 are between 0.16 and 0.21. The spectra change shape slightly after 6mM and increase to the range maximum absorption at 8mM. The emission and absorption spectra begin to change around 6mM CTAB. This behavior is similar to 1 in that the absorption stays relatively constant and the emission changes fairly concretely. The emission intensity decreases as the CTAB concentration increases from 1mM until about 4mM. At 6mM, the intensity begins to increase substantially. At 8 mM, the intensity begins to approach an asymptote. The peak maximum shifts from 510nm to 490nm as concentration increases from 0mM to 14mM. The peaks for 0mM to 4mM CTAB have been rescaled larger by a factor of 1.5 in order to properly show them on the graph.
Figure 47. Emission Spectra of 5 in various solvents with varying concentrations of CTAB and in isopropanol mixtures. Plain is 0mM CTAB.

Figure 48. Absorption spectra of 5 in water in varying concentrations of CTAB and in isopropanol mixtures.

The plot of log(I_{max}/I) vs. [CTAB] for 5 forms an s-shaped curve (figure 49). The curve does not reach an asymptote after the micelle properties are apparent. However, there is a point
where the log(I_{\text{max}}/I) values would have begun to level off in a normal s-curve. After 6mM, the plot appears to be linearly decreasing in a different manner than it was before the CMC. This behavior does not occur with any other planar derivatives in this study. All other graphs eventually reach an asymptote. This may be due to unknown complications that could’ve occurred during the study; however, while this aspect could bring up further research topics, it is not the concern of the study. This behavior further underscores that 5 would not be a good probe for solvent acidity. There is a jump in log(I_{\text{max}}/I) from roughly 0.65 to 0.25. The overall range is fairly large, but, considering the linearity of the log(I_{\text{max}}/I) values vs. concentration at the end, this range is too large. The plot indicates that the CMC is ~5mM, again far from the experimentally accepted value.

![Figure 49. Plot of log(I_{\text{max}}/I) vs. [CTAB] for 5](image)

**Micelle Studies: TX-100**

TX-100 forms reverse micelles inside of nonpolar media. As a result, it will display properties that seem opposite of normal micelle formation. The inner core of the reverse micelle is polar so, when the reverse micelle forms, the PRODAN derivative should orient the carbonyl
group near the polar center. Because the overall polarity of these micelles is much less than SDS and CTAB micelles, the emission maxima will appear at lower wavelengths and at lower intensities.

PRODAN (1) shows this behavior. As concentration of TX-100 increases, the emission intensity decreased steadily and the absorption spectra decreased sharply and then leveled off (figure 50). The absorption spectra is visible in figure 51. The spectra shows a sudden jump at 0.4mM TX-100. After 0.4mM, as concentration increased, the absorption steadily decreased reaching an asymptote. The shape of the absorption spectra did not change much. In the emission spectra, as concentration of TX-100 increases, the emission intensity steadily decreases and blue shifts. These changes occur even before the CMC is reached. From the absorption spectra or the emission spectra alone, there is no indication of an asymptote. However, these values are combined and an asymptote becomes apparent. All emission peaks have the same relative width to height ratio.

The plot of log($I_{\text{max}}/I$) vs. [TX-100] for 1 shows an s-curve, but it is in the opposite direction of SDS and CTAB micelles. At 0mM and 0.04mM, the log($I_{\text{max}}/I$) increases slightly and then drops at 0.06mM. From 0.06mM, it begins to follow the s-shaped pattern implying that the probe is sensitive to the formation of micelles. The change in log($I_{\text{max}}/I$) is approximately 0.18, and the plot shows that the CMC value is approximately 0.14mM. This is fairly close to the accepted value of 0.15mM. As the S-shape is not very distinct and the 0mM and 0.04mM points are only an order of magnitude greater than the 0.06mM point. Compound 1 is not responsive to formation of TX-100 micelles. These properties are shown in figure 52.
Figure 50. Emission Spectra of 1 with varying concentrations of TX-100 ranging from 0mM to 2.0mM and in isopropanol mixtures. Plain is 0mM TX-100 in cyclohexane.

Figure 51. Absorption spectra of 1 in varying concentrations of TX-100 ranging from 0mM to 2.0mM and in isopropanol mixtures.
Figure 52. Plot of log(I_{max}/I) vs. [TX-100] for 1

Titration of 2 with TX-100 gives similar results. The absorption of 2 decreases immediately after the addition of TX-100 (figure 54) and continues to drop even after the formation of micelles. The emission spectra begin to decrease steadily as [TX-100] increases (figure 53). With greater wait times at 0.10mM and at 0.12mM, the emission intensity decreases showing that micelle formation for TX-100 has not occurred. As [TX-100] increases, the emission maxima blue shifts by a few nanometers.
Figure 53. Emission Spectra of 2 with varying concentrations of TX-100 ranging from 0mM to 2.0mM and in isopropanol mixtures. Plain is 0mM TX-100 in cyclohexane.

Figure 54. Absorption spectra of 2 in varying concentrations of TX-100 ranging from 0mM to 2.0mM and in isopropanol mixtures.
Figure 55. Plot of log(I\textsubscript{max}/I) vs. [TX-100] for 2

The plot of log(I\textsubscript{max}/I) vs. [TX-100] for 2 shows a distinct s-shaped curve. The drop in log((E/A)\textsubscript{max}/(E/A)) after the addition of 0.04mM TX-100 occurs in this sample as well but 2 responds to the immediate addition of surfactant. Also, because of the comparative sharpness of the s-curve, 2 is sensitive to micelle formation. The plot shows that micelles completely form by 0.14mM TX-100. The log(I\textsubscript{max}/I) values change by 0.23 and shows a predicted CMC value of about 0.14mM TX-100. This value is fairly close to the accepted CMC value. The plot can be seen in figure 55.

The absorption spectra of 3 decrease substantially after the initial addition of TX-100 as shown in figure 57. The absorption spectra decrease as [TX-100] increases. The absorbance maxima in isopropanol and the mixed isopropanol solvents shift to the red by several nanometers. The emission spectra steadily decrease in intensity as [TX-100] increases as seen in figure 56. The positions of the maxima shift to the blue as [TX-100] increases. As time passes at 0.10mM and 0.12mM TX-100, the emission intensity decreases indicating that micelle formation
is not complete until at least 0.16mM. The isopropanol and mixed solvents emission maxima are shifted almost 100nm to the red and shift to the blue after the addition of 0.105mM TX-100.

Figure 56. Emission Spectra of 3 with varying concentrations of TX-100 ranging from 0mM to 2.0mM and in isopropanol mixtures. Plain is 0mM TX-100 in cyclohexane.

Figure 57. Absorption spectra of 3 in varying concentrations of TX-100 ranging from 0mM to 2.0mM and in isopropanol mixtures.
The plot of $\log(I_{\text{max}}/I)$ vs. [TX-100] for 3 does not show an s-shaped curve (figure 58). The plot shows a slight curve at 0.14mM and the point at 0.16mM seems erroneous. When those two points are excluded, the curve is just a line. While 3 is usually sensitive to SDS and CTAB micelle formation, this graph shows that it is not sensitive to TX-100 micelle formation. The overall change in $\log(I_{\text{max}}/I)$ is roughly 0.2. If the slight change at 0.14mM and 0.16mM are indicators of micelle formation, then the plot indicates that the CMC value is approximately 0.15mM. This is very close to the accepted CMC value of TX-100.

![Figure 58. Plot of $\log(I_{\text{max}}/I)$ vs. [TX-100] for 3](image)

The absorption spectra of 4 slowly decrease from 0mM until 0.20mM as seen in figure 60. The shape of the absorbance curve changes in isopropanol and mixed isopropanol solvent compared to the rest. The emission spectra decreases steadily from 0mM to 0.10mM as seen in figure 59. After 3 and 8 minutes at 0.10mM, the emission spectra increases in intensity indicating that the micelle has not formed. From 0.10mM to 0.12mM, the intensity decreases significantly and, after 3 and 8 minutes, the emission maxima intensity decreases indicating the micelle are beginning to form. This compound shows two maxima after micelle formation. There
are two possible explanations for this behavior: 1) duel probe locations in the micelle or 2) dual emission from the local excited (LE) and the charge transfer (ICT) states.

Figure 59. Emission Spectra of 4 with varying concentrations of TX-100 ranging from 0mM to 2.0mM and in isopropanol mixtures. Plain is 0mM TX-100 in cyclohexane

Figure 60. Absorption spectra of 4 in varying concentrations of TX-100 ranging from 0mM to 2.0mM and in isopropanol mixtures
The plot of $\log(I_{\text{max}}/I)$ vs. [TX-100] for 4 show a small s-shaped curve (figure 61). Due to the changing absorptions at 6mM and 12mM after 3 minutes, the titration curve is skewed. The change in $\log(I_{\text{max}}/I)$ is approximately 0.2 which is a fairly large gap compared to the other probes in TX-100 micelles. This probe is still somewhat sensitive to micelle formation as the s-shape can still be discerned. There is little change in the height of the points until the CMC is reached. This plot indicates that the CMC is approximately 0.11mM. This is far lower than the accepted.

![Figure 61. Plot of log(I_max/I) vs. [TX-100] for 4](image)

Finally, the absorption spectra of 5 slowly and steadily decrease as [TX-100] increases as is shown in figure 63. The shape of the spectra do not change as concentration increases. As expected, 5 behaves similarly to 1 in the absorption and emission titrations. The emission spectra (figure 62) decrease from 0mM to 0.10mM. After 3 minutes, the emission intensity increases but then decreases after 8 minutes. The changes are small and can be due to inherent experimental
error. After 0.10mM, the emission spectra intensities slowly decrease until 0.14mM and then make a sudden decrease between 0.14mM and 0.16mM. The spectra again decrease until 0.20mM. The emission maxima shifts to the blue as [TX-100] increases. As with 4, another peak begins to appear on the blue side of the main emission maxima. Again this can be ascribed to different probe location or dual emission from different electronic states.

Figure 62. Emission Spectra of 5 with varying concentrations of TX-100 ranging from 0mM to 2.0mM and in isopropanol mixtures. Plain is 0mM TX-100 in cyclohexane

Figure 63. Absorption spectra of 5 in various solvents in varying concentrations of TX-100 ranging from 0mM to 2.0mM and in isopropanol mixtures
The plot of log(I_{max}/I) vs. [TX-100] for 5 shows an ill-defined s-shaped curve (figure 64). The curve begins to reach an asymptote near 0.20mM but it is not as clear as it is with 2 and 4 titration curves. The sudden drop from 0mM to 0.04mM in log(I_{max}/I) values occurs again. The spread in the points at 0.10mM and 0.12mM show that micelle formation is not immediate. The large spread that occurs in 5 indicates that it would not be a good probe. The change in log(I_{max}/I) values is approximately 0.16 and, according to the plot, the CMC is approximately 0.14mM, close to the accepted CMC value.

![Figure 64. Plot of log(I_{max}/I) vs. [TX-100] for 5](image)

**Micellar Study: overall**

Apparent solvent acidities are calculated for each of the micelles from the titration plots for each of the five probes in each of the 3 micellar solutions using the emission maxima intensity and the integrated emission (table 6). Also, the experimental CMC and the changes in the log(I_{max}/I) are listed in table 7. Determining the apparent solvent acidity of probes in various micelles is the main interest of this study.
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<td>SDS (charge= -1)</td>
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Table 6. Apparent solvent acidity values for each micelle based change in $\log(I_{\text{max}}/I)$ values as micelles form from emission maxima or integrated emission data

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<tr>
<td>SDS (charge= -1)</td>
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<td>0.7</td>
<td>.4(maxima)</td>
<td>.58(integrated)</td>
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<td>1.4</td>
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<td>-0.2</td>
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<td><strong>CMC (in mM)</strong></td>
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Table 7. Micelle properties from titrations

**Evaluation of the probes**

The negative solvent acidity values are a clear sign that the probe was not effective at determining solvent acidity and that this method failed. As there are no accepted Solvent Acidity values for these micelles, there is no validation for this method. The solvent acidity experience by the probes for each of the three micelles should follow the trend: $\text{SA}_{\text{SDS}} > \text{SA}_{\text{CTAB}} > \text{SA}_{\text{TX-100}}$. This is reasonable based on the overall polarity of the micelles which follows the same pattern: $p_{\text{SDS}} > p_{\text{CTAB}} > p_{\text{TX-100}}$. This is also reasonable based their structures. TX-100 only contains
hydrogen bonding at its hydroxyl group tail, so it should have the lowest SA. SDS would have a
greater SA than CTAB as the sulfonates on SDS require more water in the interfacial region
compared to CTAB. A good detector of solvent acidity, based on these micelles, would follow
this basic solvent acidity trend.

From this parameter, compounds 5 and 4 are would not be as effective of a probe of
solvent acidity as each lists at least one surfactant’s solvent acidity as negative. Assuming that
the agreement of multiple probes’ solvent acidity values is the standard for solvent acidity
values, the values that 1, 2, and 3 produce for SDS and TX-100 are fairly close. However, 3
produces a very low value for CTAB. 1, 2, and 4 all produce similar values for the solvent
acidity of for CTAB. So, 3’s value for solvent acidity of CTAB is most likely incorrect. 4’s
integrated effective solvent acidity value is close to 1, 2, and 3 for SDS and its CTAB value is
close to that of 1 and 2. Although, 4 produced a negative solvent acidity value for TX-100, which
makes it not useful. 5 consistently gives very low solvent acidity values; however, the value it
produced for TX-100 was close enough for agreement with the values probes 1, 2, and 3
produced. The problem with all of the TX-100 titrations is that the solvent acidity values they
gave were below the scale that used for their enhancement factors. The experimental SA scale
that was made with PRODAN and its derivatives ran from 0.283 to 1.064. PRODAN (1)
produced values similar to those of 2 and they even tended to agree with many of the other
probes’ values. The main difference between 1 and 2 was that 1 gave values that were
consistently higher than those of 2. It was that 1 would be a poor probe, so more studies need to
be done with 1 to confirm its status as a good probe of solvent acidity. The values of 2 are
considered to be the most reliable.
Individually, each of the probes has their individual problems and praises. Looking at the probes as indicators of micelle formation and CMC, 2 responded the best to micelle formation and showed the largest change in the log($I_{\text{max}}/I$) values. The CMC values shown by 2 were too low on occasion for SDS and TX-100 and slightly high for CTAB. With the exception of SDS, it was often the probe that produced the closest results to the accepted values for CMC. Also, the log($I_{\text{max}}/I$) values were always the highest indicating that 2 showed the most sensitivity out of the probes to micelle formation. The t-butyl probes 3 and 4 produced large change in log($I_{\text{max}}/I$) values and 3 always produced relatively accurate CMC values. Compound 4 produced a correct CMC value for SDS but was not accurate with CTAB and TX-100. Compounds 1 and 5 had relatively small changes in log($I_{\text{max}}/I$) values and produced correct CMC values for SDS but not for the other micellar solutions.

The shape of the titration curves was indicative of the sensitivity of the probe to the micelle formation. If the probe produced an s-shaped curve, it was most likely sensitive to micelle formation and would give a good measure of the micelle’s solvent acidity. Compound 1 produced clean s-curve for SDS and CTAB but not for TX-100. Compound 2 produced cleaner s-curves for all the micelles. Compound 3 showed a slight s-curve for SDS, a clean s-curve for CTAB, and no curve for TX-100. It was estimated that the aggregation had affected the log($\log((E/A)_{\text{max}}/(E/A))$) values for 3. Aggregation effects were seen with 3 and they varied from micelle to micelle. The aggregation was only an issue in water and aqueous solutions before the CMC. The fact that aggregation occurred means that the probe position might be variable based on aggregation.

Aggregation was not an issue in CTAB compared SDS and not a problem in TX-100. As 4 contains a 6 membered ring, it will tend to locate in a more nonpolar environment deeper
inside of the micelle or at the surface of the reverse micelle. Compound 4 appears to be sensitive to the micelle formation in water but even more so for reverse micelles. Compound 5 showed a light s-curve for SDS, a partial s-curve that turned into a line for CTAB, and a very rough s-curve for TX-100. In general, 5 is not a well-behaved probe.
Conclusion:

Among the probes, 5 and 4 were considered the least suitable as probes for solvent acidity in micelles. 5 produced a negative SA value for CTAB and did not show the theoretical trend of SA values for the micelles. 4 had problems with aggregation that complicated the determination of solvent acidity. While 4 followed the trend of SA values for the micelles, it gave a negative value for TX-100. Both of these probes also showed bad emission.

Compounds 1, 2, and 3 gave fairly consistent results. None produced negative SA values. PRODAN (1), despite being planar, showed smaller changes in the log(I_{max}/I) but despite having a smaller enhancement factors, gave solvent acidity values that agreed were in agreement with the other probes. This result may be due to the fact that the enhancement factor calibration curve had a very high R^2-value. More studies on the use of 1 as a probe of solvent acidity need to be done in order to confirm its utility. Compound 3 produced reasonable values for solvent acidity except for CTAB. The change in the log(I_{max}/I) values were large and the CMC values were fairly accurate. Problems with aggregation affected SA determination. 2 produced a large change in the log(I_{max}/I) values as a result of micelle formation and give reliable CMC value. Overall, 2 produced the highest quality data in the study and is the most suited for detecting solvent acidity in micelles.

Compounds 1, 4, and 2 all followed the proper trend of solvent acidity while 3 and 5 did not. The study showed that 2 was the best probe available. The initial belief that 1 would not be as good of a probe and that 3 would be one of the better suited probes still needs to be confirmed with further research. The belief that 4 and 5 would not be as good of probes was confirmed; however, the theoretical order of which the probes would be best suited was slightly different.
from $2 > 3 > 4 > 1 > 5$. The results of this study show that, from best to worst detectors of solvent acidity in micelles, the probes follow this trend: $2 > 1 > 3 > 4 > 5$. Based on the resulting trend, there is no clear definition as to whether or not the planar or twisted derivatives are better detectors of solvent acidity in micelles. As detectors of solvent acidity, the twisted derivatives have the most sensitive $\log((E/A)_{\text{max}}/(E/A))$ values relative to changes in solvent acidity; however, the twisted geometry was not definitive as to which probes produced the best solvent acidity values. $2$ is overall the best detector among the probes studied. Overall, the study was successful in its elucidation of the properties of PRODAN and its derivatives as probes of solvent acidity in micelles.
References

   <http://www.elmhurst.edu/~chm/vchembook/558micelle.html>


Vita

**Zachariah Bach Nealy**

Zachariah Bach Nealy attended high school in Virginia Beach, VA, at Princess Anne High School’s International Baccalaureate Program. When not performing chemistry, he enjoys teaching and learning Kung Fu, rock climbing, parkour, tai chi and mediation as well as listening to ska music and reading science fiction novels. If there is a problem too big, hold no doubt that he caused it and created a solution for it. He went on to attend the College of William and Mary in Williamsburg, VA from 2008 to 2012 and will receive a Bachelors of Science in Chemistry in May 2012.