

Photophysical Properties of Bis-DMAC

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Abstract

Two symmetrically substituted 2,5-diarylidene cyclopentanone compounds have been synthesized and their solvent dependent photophysics investigated. Specifically the compounds were (2E,5E)-2,5-bis(p-dimethylaminobenzylidene)-cyclopentanone (Bis-DMAB) and (2E,5E)-2,5-bis(p-dimethylaminocinnamylidene)-cyclopentanone (Bis-DMAC). UV-Vis absorption spectra, fluorescence emission spectra and fluorescence quantum yields were measured in acetone (Ac), isopropanol (IP) and toluene (Tol). The relative polarities of these solvents, as given by the solvent polarity function (Δf) are 0.2843, 0.2769 and 0.0131 respectively. The absorption maxima showed little solvent dependence with Bis-DMAB changing by 22 nm (Ac 460 nm, IP 474 nm, Tol 452 nm) and Bis-DMAC by 26 nm (Ac 492 nm, IP 518 nm, Tol 494 nm). However, the fluorescence maxima were significantly more solvent dependent with Bis-DMAB changing by 78 nm (Ac 546 nm, IP 565 nm, Tol 487 nm) and Bis-DMAC by 85 nm (Ac 611 nm, IP 635 nm, Tol 550 nm). The quantum yields (Φ_F) and fluorescence lifetimes were also found to be solvent dependent and trended differently for the two materials. For Bis-DMAC Φ_F went from 0.11 in Tol to 0.24 in IP while for Bis-DMAB Φ_F was 0.43 in Tol and 0.27 in Ac. The lifetimes were all less than 1 ns with 0.2 ns for Bis-DMAB in Tol and 0.93 in IP and for Bis-DMAC 0.86 ns in Tol and 0.36 in IP. The reasons for the excited state solvent dependence but limited ground state dependence is not yet clearly understood but a preliminary mechanism based on the experimental results and molecular orbital calculations suggests greater solvent interactions with the first excited state.

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Introduction

Symmetrically substituted 2,5-diarylidene cyclopentanones are a class of compounds studied for their “push-pull” electronic structure. Molecules with “push-pull” structures contain electron donating groups and electron accepting groups, connected by a conjugated π system.¹ In this class of compounds, a D-A-D system may be formed from electron donor moieties (D) on the extremities and the central carbonyl acting as an electron acceptor (A). Upon photoinduced excitation, this system readily lends itself to internal charge transfer (ICT) in which electron density is “pushed” from the electron donors and “pulled” towards the electron acceptor, causing a change in the polarity of the molecule. This phenomenon gives these compounds applications as fluorescent solvent polarity probes.² Other applications for these compounds include uses as photosensitizers for electronic energy transfer processes³ and non-linear optical materials.⁴

The photophysical properties and internal charge transfer states of a variety of symmetric and asymmetric 2,5-diarylidene cyclopentanone compounds have been investigated.⁵ Two compounds investigated previously, (2E,5E)-2,5-bis(p-dimethylaminobenzylidene)-cyclopentanone (Bis-DMAB) (Figure 1) and (2E,5E)-2,5-bis(p-dimethylaminocinnamylidene)-cyclopentanone (Bis-DMAC) (Figure 2), were the subject of this research.

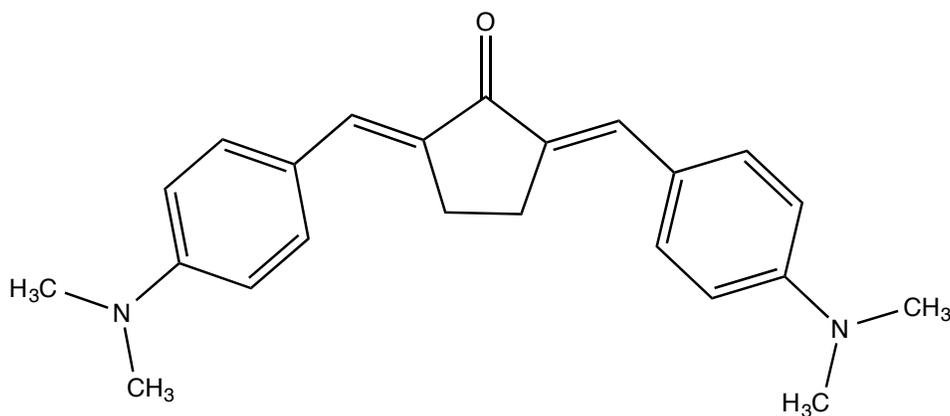


Figure 1: Structure of bis-DMAB

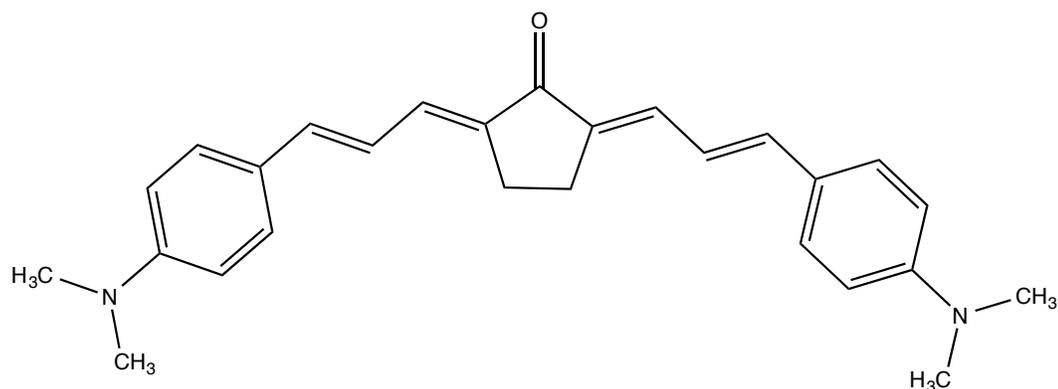


Figure 2: Structure of bis-DMAC

Both bis-DMAB and bis-DMAC are symmetrically substituted with dimethyl amino groups attached to the phenyl rings in the para-substituted position. The structural difference between these compounds is that the conjugated pi system in bis-DMAC is two carbons longer than the one in bis-DMAB. Both compounds share the C_{2v} point group. Computed gas phase optimized geometries for Bis-DMAC can be seen in Figure 3 and an X-ray crystal structure of bis-DMAB is shown in Figure 4.⁵ These figures show the 3-dimensional structure of the molecules in the ground state which can be used to show its conformation.

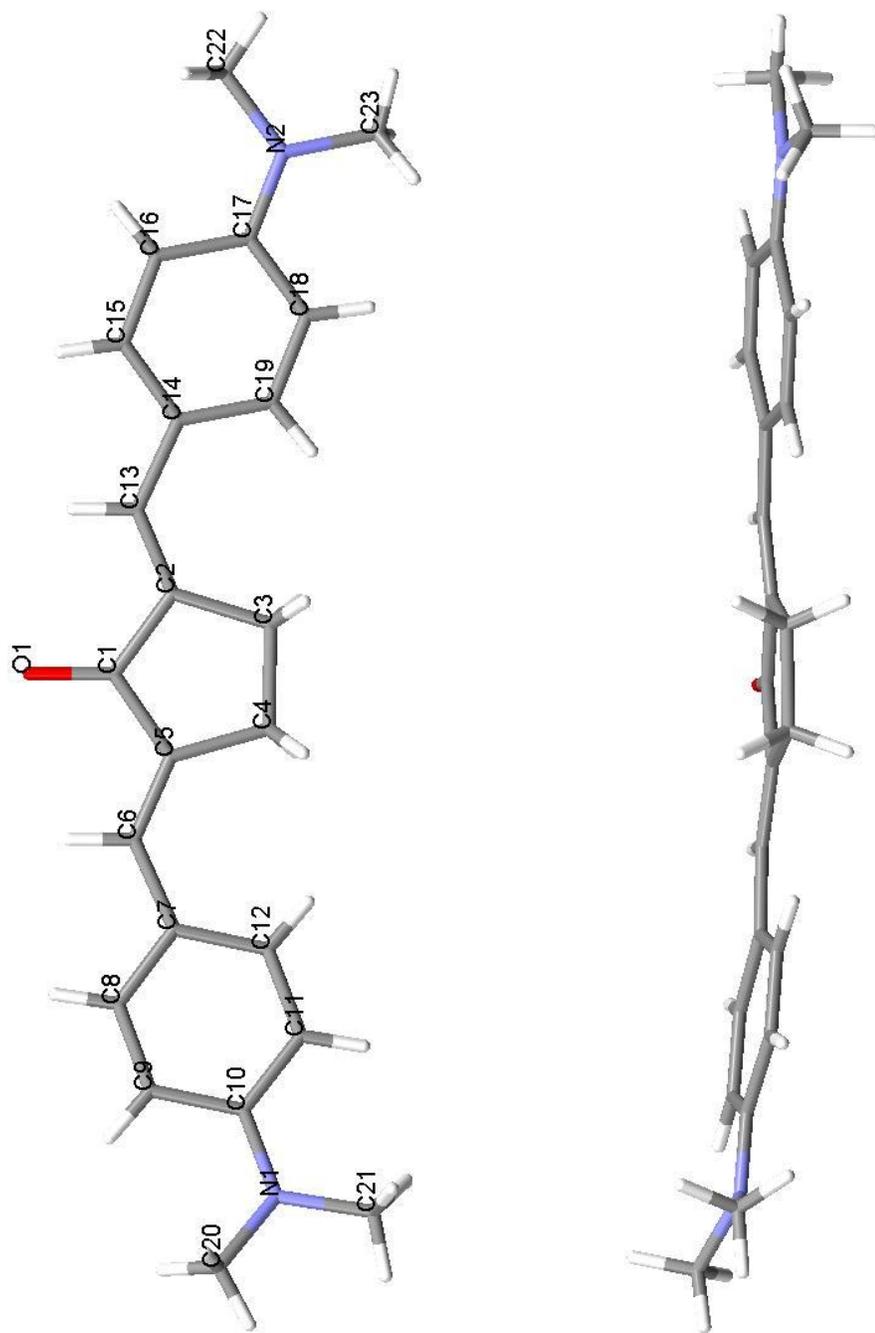


Figure 3: X-ray crystal structure of bis-DMAB⁵

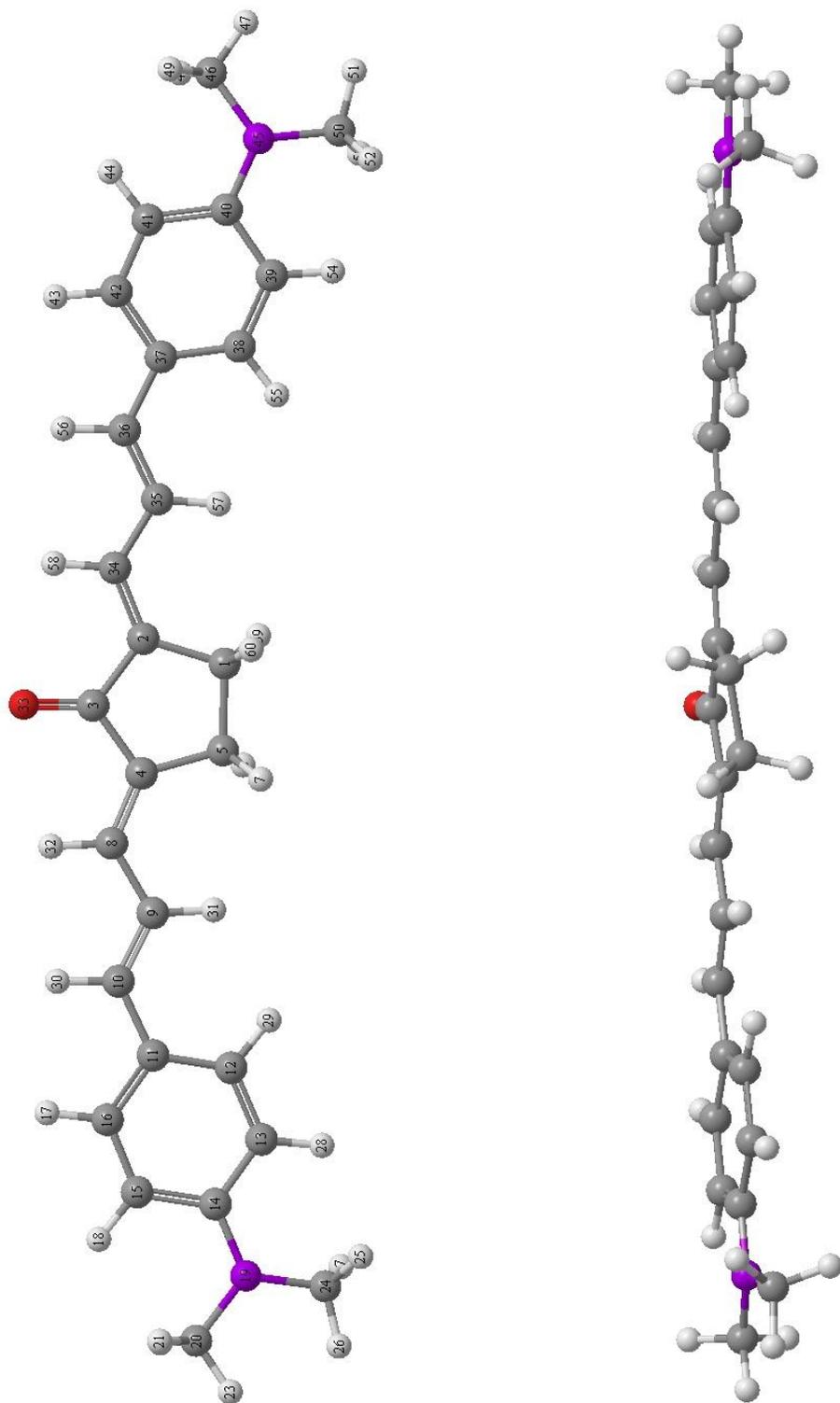


Figure 4: Optimized geometry of bis-DMAC⁵

Molecules absorb different wavelengths of light depending on their structure and environment. Once absorbed, if the molecule has a transition that is resonant with the wavelength of energy, those photons will excite the molecule and will promote electrons from the S_0 (HOMO) to the S_1 electronic state (LUMO). Electrons may be further excited to higher energy levels by additional photons or higher energy photons. As shown in the Jablonski diagram in Figure 5, the excited electron will first undergo internal conversion to the lowest excited vibrational state. From there a number of things may occur. The electron may relax down to the S_0 state through non-radiative processes such as release of heat, through the emission of light (fluorescence) or may go through intersystem crossing into the triplet (T_1) state. From the T_1 state the electron will relax slowly to the ground state while giving off light through a process called phosphorescence or through non-radiative decay.

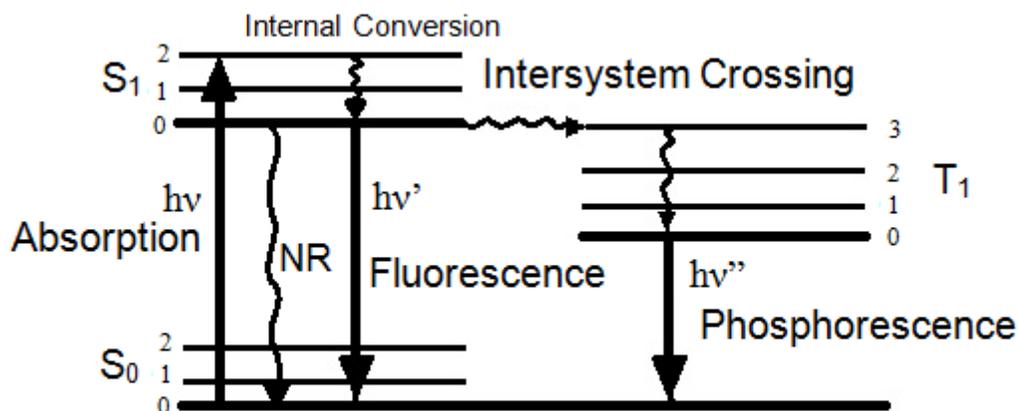


Figure 5: Jablonski diagram displaying typical modes of absorption and radiative decay⁶

The absorption and fluorescence of bis-DMAB and bis-DMAC have been studied in a wide range of solvents.⁵ It was found that both of these compounds undergo bathochromic shifts, absorbance and emission moving to a longer wavelength, when changing between aprotic and protic solvents. Consequently, the change in fluorescence when changing solvents was found to correlate to the polarity of the solvents.

One of the ways polarity can be measured is using the solvent polarity function (Δf). This function measures the orientation polarization of the solvent which is the polarity of a molecule that is the result of the dipole arising from an uneven charge distribution. The Δf parameter also is a measurement of the ability of a solvent to orient itself about a charge. The solvent polarity function is defined in equation 1 in which ϵ is the dielectric constant and n is the refractive index

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (1)$$

of the solvent. Three solvents were chosen to determine how different solvents affected photochemical properties. The solvents used were Acetone (C_3H_6O , $\Delta f = 0.2843$), Isopropanol (C_3H_8O , $\Delta f = 0.2769$) and Toluene (C_7H_8 , $\Delta f = 0.0131$) and were chosen to encompass a range of polar and hydrophobic properties.

This research sought to further characterize bis-DMAB and bis-DMAC by determining their photochemical properties as a function of solvent. The properties sought are absorbance and emission maxima, stokes shifts, molar extinction coefficients, fluorescence quantum yield and fluorescence lifetimes. Characterization of the compounds utilized UV-Vis spectroscopy, fluorescence spectroscopy, time resolved fluorescence, and ultimately laser flash photolysis.

Methods

Synthesis of Bis-DMAB

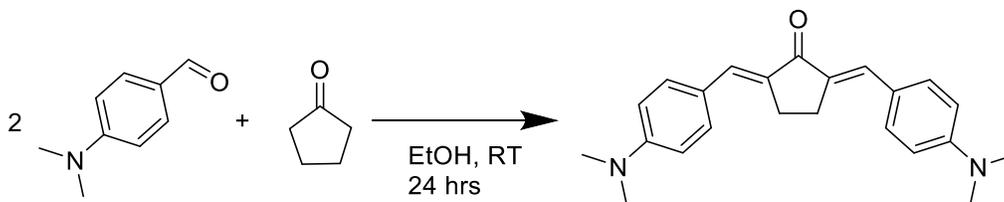


Figure 6: Reaction scheme of bis-DMAB

Bis-DMAB was synthesized by adding 2mL of 20% sodium hydroxide to a solution of cyclopentanone (0.44mL, 5mmol) in 50mL of ethanol. 4-dimethylaminobenzaldehyde (1.5g, 10mmol) was then added to the solution which immediately turned orange. The mixture was left to stir overnight at room temperature. The bright orange product was collected via filtration, washed 3 times with ethanol and then recrystallized twice from hot toluene. 1.24 g, 71.7%, ^1H NMR (500MHz, CDCl_3) δ 7.57 (6H, d), 6.76 (4H, d), 3.11 (4H, s), 3.07 (12H, s). Figure 7 shows ^1H NMR of bis-DMAB in chloroform-D. Peaks are labeled by color and letter in the figure with expanded peaks shown to the right. The peak at 7.3ppm is the solvent peak for chloroform-D. The peak at 1.59ppm is thought to be an impurity in the solvent due to water.

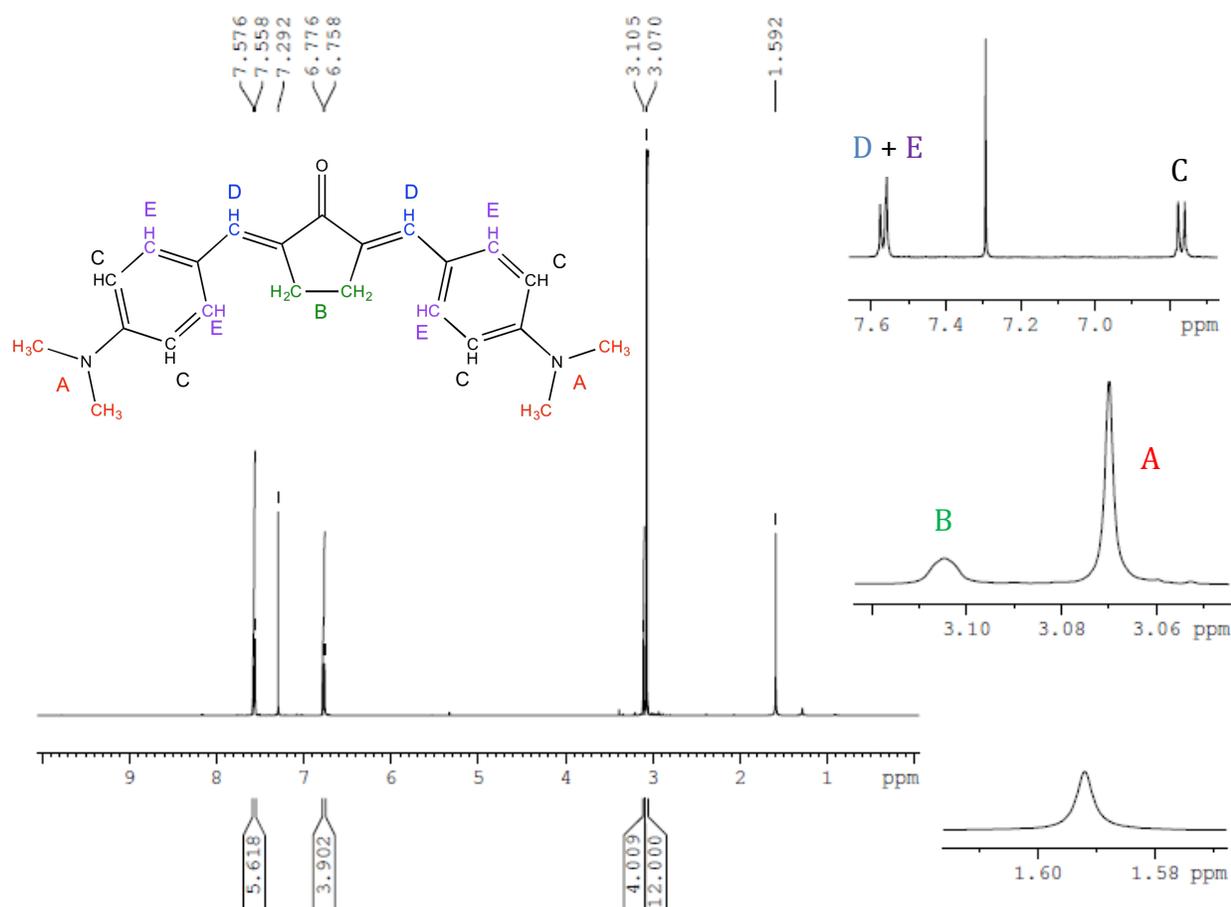


Figure 7: ¹H NMR of bis-DMAB with peaks labeled

Synthesis of Bis-DMAC

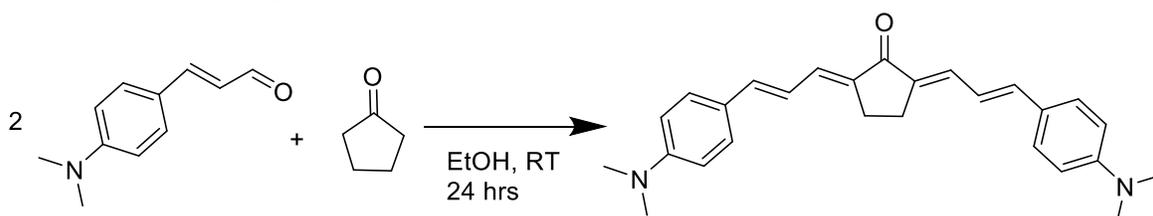


Figure 8: Reaction scheme of bis-DMAC

Bis-DMAC was synthesized by adding 2mL of 20% sodium hydroxide to a solution of cyclopentanone (0.44mL, 5mmol) in 50mL of ethanol. 4-dimethylaminocinnamaldehyde (1.75g, 10mmol) was then added to the solution which immediately turned a dark red. The mixture was left to stir overnight at room temperature. The dark purple product was collected via filtration, washed 3 times with ethanol and then recrystallized twice from hot toluene. 1.96 g, 98.5% ¹H

NMR (500MHz, CDCl₃) δ 7.43 (4H, d), 7.27 (2H, d), 6.93 (2H, d), 6.81 (2H, q), 6.71 (4H, d), 3.04 (12H, s), 2.89 (4H, s). Figure 9 shows ¹H NMR of bis-DMAC in chloroform-D. Peaks are labeled by color and letter in the figure with expanded peaks shown to the right. The peak at 7.3ppm is the solvent peak for chloroform-D. The peak at 1.65ppm is thought to be an impurity in the solvent due to water.

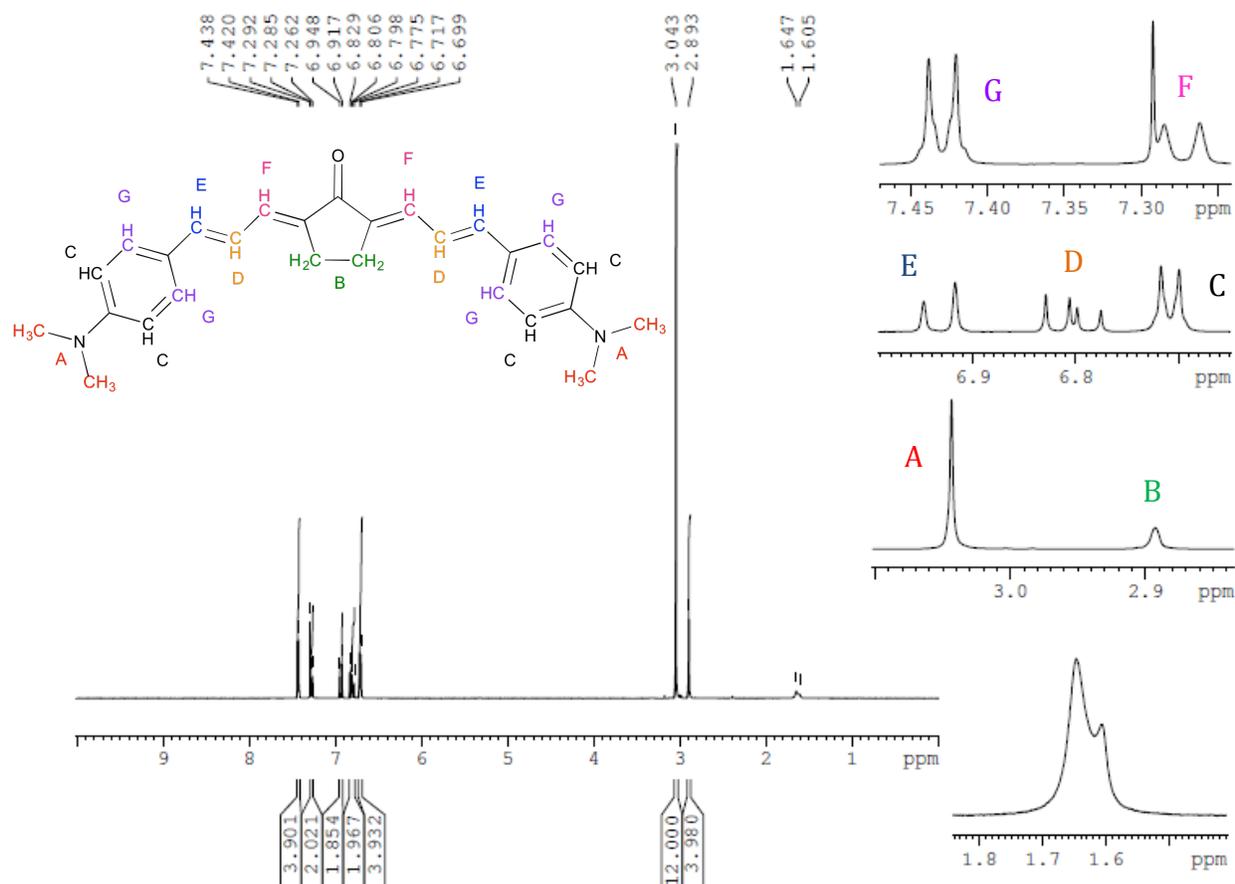


Figure 9: ¹H NMR of bis-DMAC with peaks labeled

Molar Extinction Coefficient Calculation

Molar extinction coefficients were calculated using the Beer-Lambert law given in equation 2. This law states that a compound's absorbance (A) is proportional to its concentration (c), path length ($l = 1\text{ cm}$) and molar extinction coefficient (ϵ).

$$A = \epsilon cl \quad (2)$$

The value of the coefficient was calculated by weighing out a known amount of solute on a filter and pouring acetone through the filter into a volumetric flask. The filter and solute were dried in *vacuo* and weighed to determine the mass in solution and from that, the concentration. The stock solutions in acetone were diluted 8 fold in each solution and UV-vis spectra were obtained on the Thermo Scientific Evolution 300 Spectrometer. Figure 10 shows that the mixture of solvents at this ratio retains the characteristics of the solute in the dominant solvent.

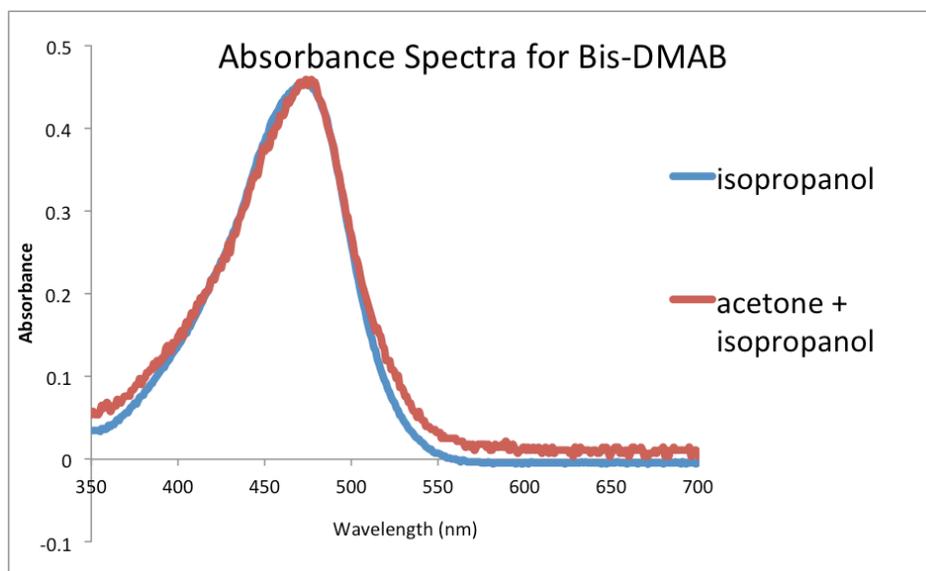


Figure 10: Bis-DMAB in isopropanol vs. bis-DMAB in mixture of 7:1 isopropanol:acetone

Fluorescence Quantum Yield Determination

Quantum yield is defined as the number of photons of light emitted per photons of light absorbed by a compound. Quantum Yield is calculated according to equation 3 in which Φ is the

$$\Phi = \Phi_{std} * \frac{OD_{std}}{OD} * \frac{n^2}{n^2_{std}} * \frac{D}{D_{std}} \quad (3)$$

quantum yield, OD is the optical density obtained at 450nm, n is the refractive index of the solvent and D is the area under the corrected curve of the fluorescence emission spectrum. This spectrum was obtained on the Hitachi F-4500 FL Spectrophotometer equipped with an R928 photomultiplier with slit widths of 2.5nm. Optical density and area under the corrected emission was likewise calculated for a solution of fluorescein in 0.1 M NaOH with known quantum yield ($\Phi = 0.95^7$) to be used as a standard. In order to reduce the possible discrepancies in the calculation of quantum yield, solutions were matched to have optical densities of approximately 0.1 at 450nm.

To correct fluorescence emission spectra, the spectrum of 10^{-4} M N, N-DMANB (N, N-dimethyl-3-nitro-aniline) in 30% benzene, 70% n-hexane was obtained. This spectra was compared to the relative emission spectra for the same compound found in “Principles of Fluorescence Spectroscopy”.⁷ Correction factors were calculated by first dividing the reference by the experimental results. In MathCad these values were fitted using a cubic spline function and then, using the software, other data points in the range were interpolated to obtain the correction factors at each wavelength. The factors were applied multiplicatively to the emission spectra at each corresponding wavelength to correct them. The correction factors obtained using this method range from 460-800 nm and are shown in Figure 11.

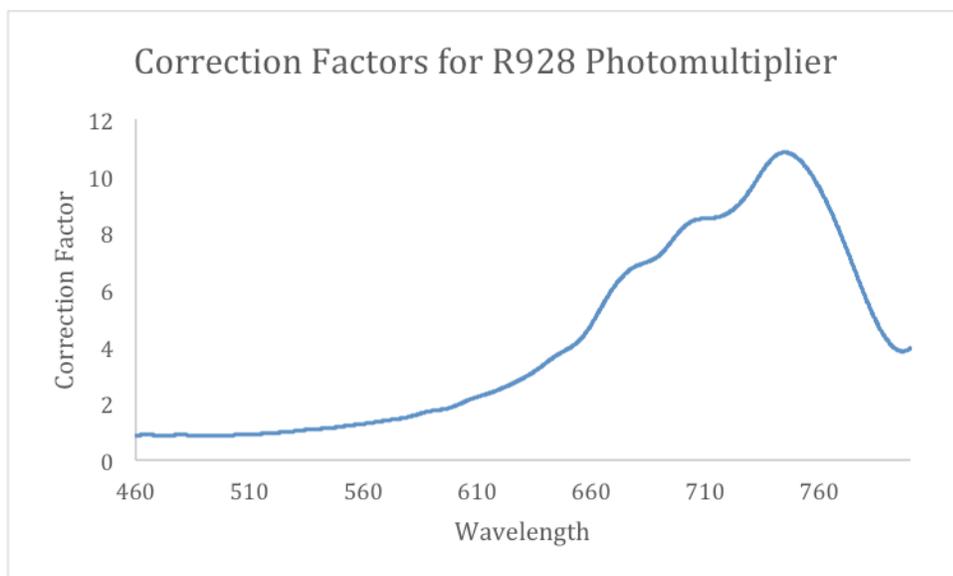


Figure 11: Correction factors for emission spectra at the given wavelengths

Fluorescence Lifetime Measurements

To determine fluorescence lifetimes, dilute solutions (Optical Densities < 0.1) were made of bis-DMAB and bis-DMAC in the three solvents. This was found to be the optimal optical density for the instrument to measure because higher optical densities went off the recordable scale of the instrument. The solutions were sealed in a quartz cuvette and purged with nitrogen so that oxygen would not quench the fluorescence. The solutions were excited using a GL-3300 Nitrogen Laser by Photon Technology International. The laser works by exciting the molecules at their absorbance maxima many times and records the time it takes for the electrons to return to the ground state. The computer calculates the average of these and reports it as the fluorescence decay curve. In order for the laser to emit light of the appropriate wavelength to excite the samples, laser dyes were utilized. The dye used as the medium for the laser was a 10^{-2} M solution of coumarin 481 in para-dioxane. Additionally a plot of scattered light was obtained using non-dairy coffee creamer suspended in water excited at the same wavelengths as the samples. The plot was normalized to the decay curve, thus creating the instrument response function (IRF) which was used to correct for the light that is scattered rather than absorbed by our compounds in solution. Using the FELIX 32 program, the fluorescence decay curves were deconvoluted and a fitted decay curve was obtained. Along with the decay curve lifetime values and X^2 values were reported by the software. Chi squared values are a measure of the accuracy of the decay fit. Values between 0.8-1.2 are considered to be acceptable fits for the X^2 parameter.

Results

Absorbance and Emission Maxima

Both compounds show smooth absorbance peaks in both acetone and isopropanol. However in toluene bis-DMAB exhibits a second, smaller peak at approximately 430nm and bis-DMAC exhibits a plateau as a maximum spanning from approximately 470-500nm. Absorbance spectra for bis-DMAB are shown in Figure 12 and those for bis-DMAC are shown in Figure 13.

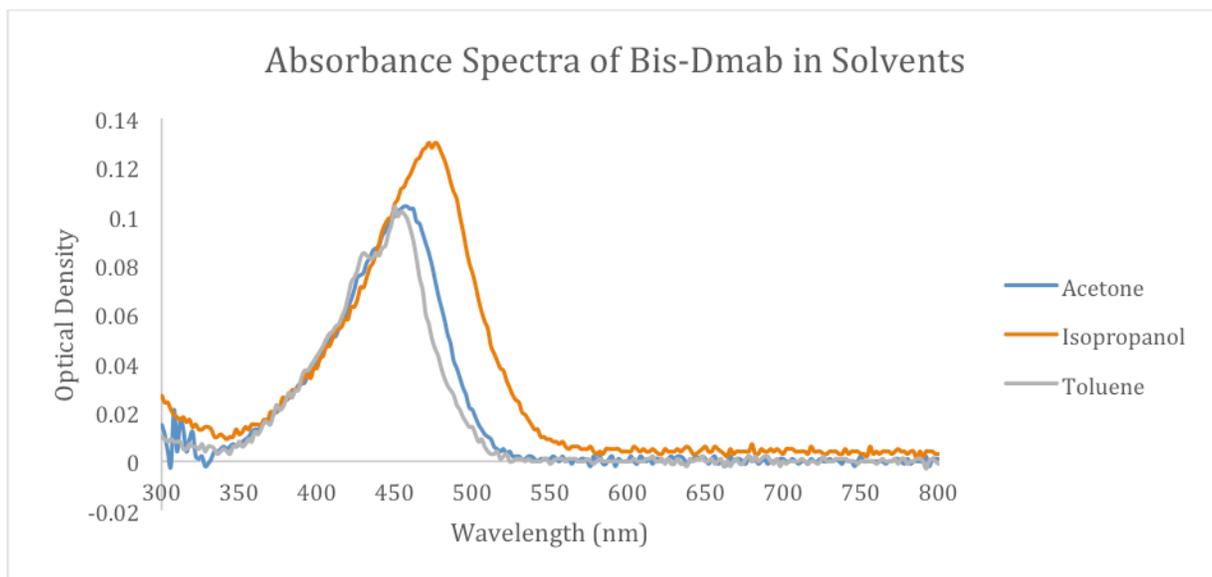


Figure 12: Absorbance spectra of bis-DMAB in all 3 solvents

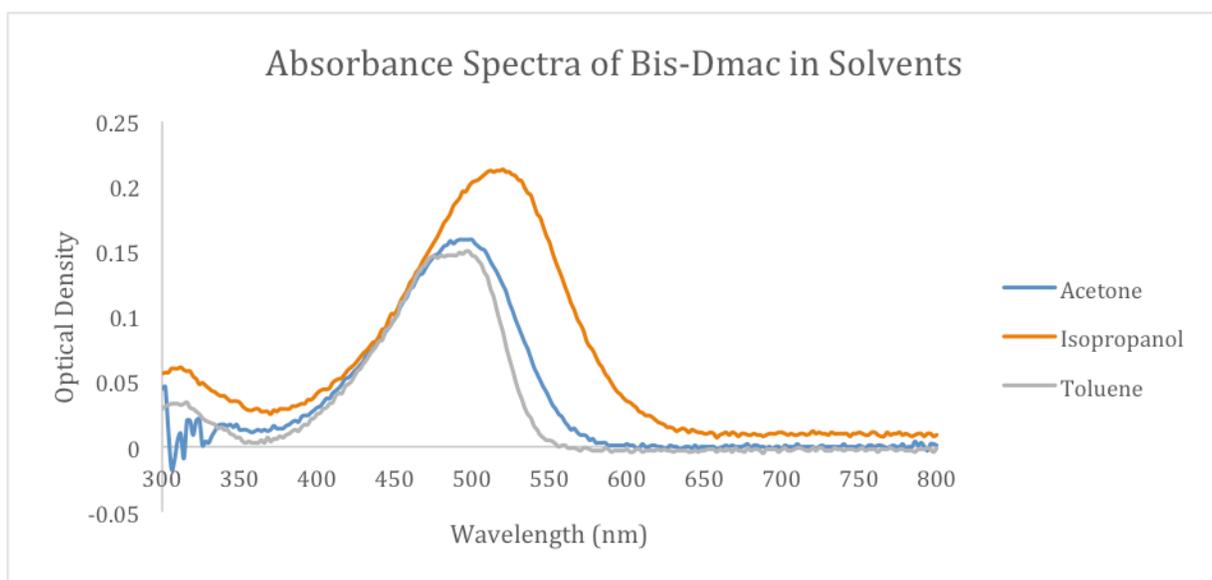


Figure 13: Absorbance spectra of bis-DMAC in all 3 solvents

Emission spectra of bis-DMAB were smooth curves for in all solvents except in toluene where a shoulder at 520nm was apparent. Bis-DMAC in isopropanol had a smaller secondary peak at 700 nm and showed slight shoulders on both sides of the peak. In toluene, bis-DMAC exhibited a prominent secondary peak at 580nm. These additional peaks are likely due to vibronic structures within the S_1 state. Emission spectra for bis-DMAB are shown in Figure 14 and those for bis-DMAC are shown in Figure 15. Individual absorbance and emission spectra used to calculate quantum yields can be found in Appendix 1. Both absorbance and emission maxima, as well as stokes shifts, the difference between absorbance and emission maxima, are reported in Table 1. The data suggests that stokes shifts are correlated to Δf with larger stokes shifts corresponding to greater Δf values.

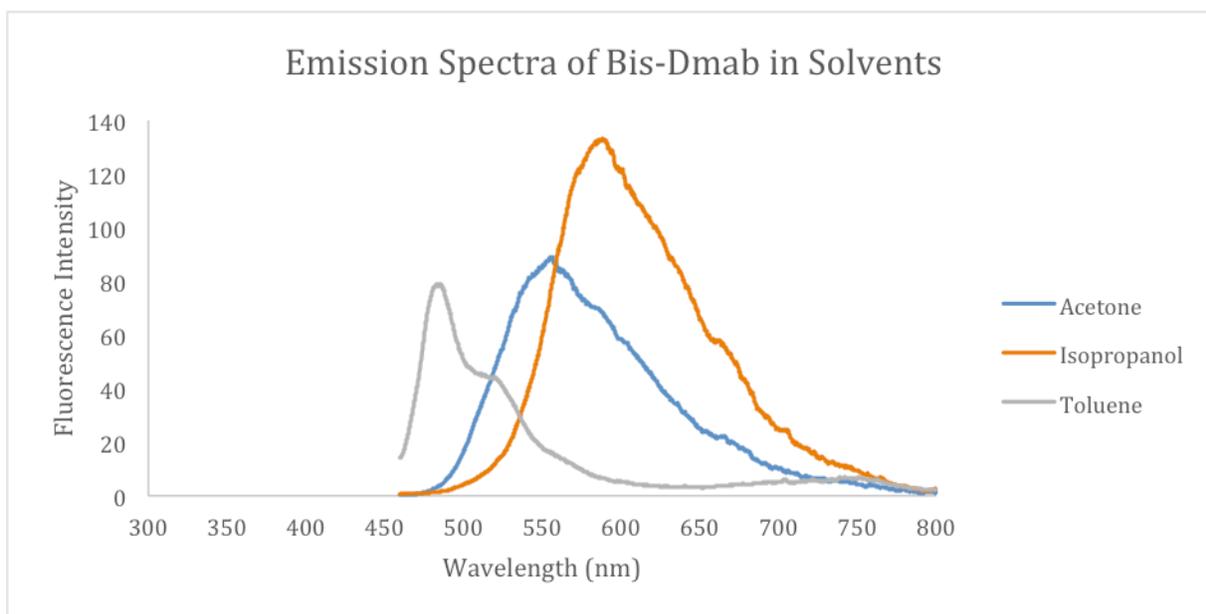


Figure 14: Corrected fluorescence emission spectra of bis-DMAB in all 3 solvents

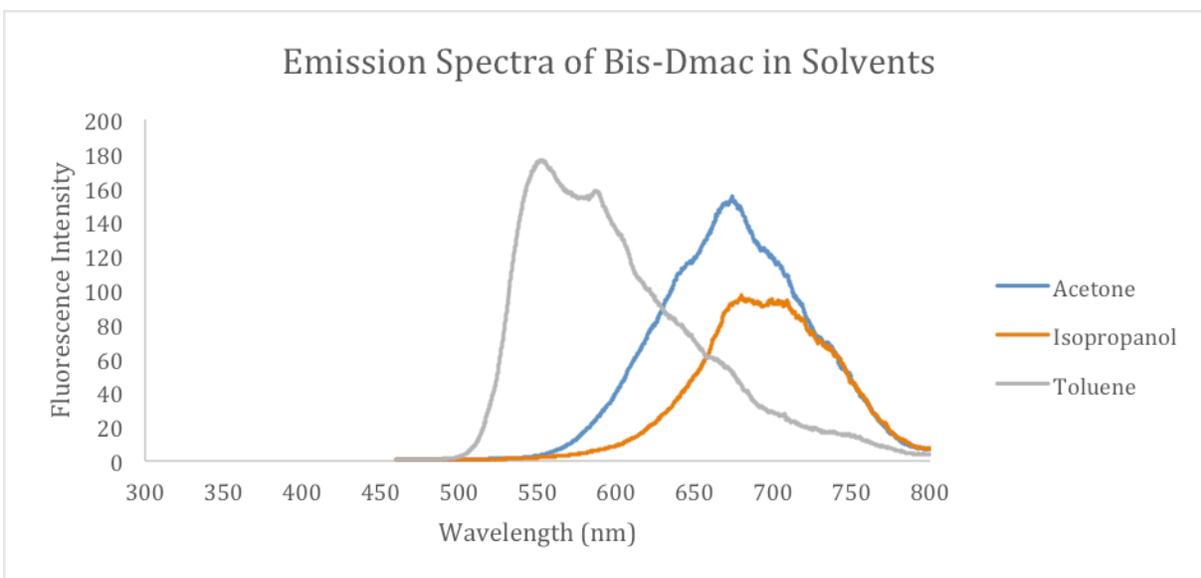


Figure 15: Corrected fluorescence emission spectra of bis-DMAC in all 3 solvents

Table 1: Excitation and Emission maxima and Stokes shifts of compounds in solvents

Solute	Solvent	$\lambda_{\text{Absorbance Max}}$ (nm)	$\lambda_{\text{Emission Max}}$ (nm)	Stokes Shift (nm)	Stokes Shift (cm^{-1})
Bis-DMAB	Acetone	460	546	86	3424
Bis-DMAB	Isopropanol	474	565	91	3398
Bis-DMAB	Toluene	452	487	35	1590
Bis-DMAC	Acetone	493	609	116	3959
Bis-DMAC	Isopropanol	518	633	115	3557
Bis-DMAC	Toluene	495	551	56	2061

Molar Extinction Coefficient Calculation

Absorbance spectra were obtained of both compounds in order to find their molar extinction coefficient in each solvent as well as the wavelength at which the compounds absorbed most. The extinction coefficients as well as the data required to calculate them are reported in Table 2. With the concentrations, absorbance maxima and path length (1cm), equation 2 could be used to calculate the extinction coefficient. It appears that the molar

extinction coefficient is not solvent dependent. The value obtained in acetone for bis-DMAB is presumed to be an outlier. All spectra used for the determination of the molar extinction coefficient may be found in Appendix 2. Results for the Acetone were based on one measurement while the results for isopropanol and toluene were based on two measurements.

Table 2: Molar extinction coefficients and related data

Solution	Concentration (M)	Absorbance at λ_{Max}	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)
Bis-DMAB Acetone	$6.24 \cdot 10^{-6}$	0.327	52404
Bis-DMAB Isopropanol	$6.5 \cdot 10^{-6}$	0.558	70000
Bis-DMAB Toluene	$6.5 \cdot 10^{-6}$	0.455	66615
Bis-DMAC Acetone	$6.66 \cdot 10^{-6}$	0.566	84545
Bis-DMAC Isopropanol	$6.88 \cdot 10^{-6}$	0.433	82267
Bis-DMAC Toluene	$6.88 \cdot 10^{-6}$	0.552	80233

Fluorescence Quantum Yield Determination

Fluorescence quantum yields were calculated over three trials and the final value was calculated as the average over all the runs. Table 3 reports the quantum yields of each compound in the three solvents as well as the values obtained during each trial. The quantum yields were calculated using equation 3 with the relevant data given in Table 3. Bis-DMAB has the greatest quantum yield in isopropanol and the least in toluene. Interestingly bis-DMAC shows the exact opposite with its highest yield in toluene and lowest in isopropanol. Because of the discrepancy between the quantum yields of the two compounds the data does not suggest any trend corresponding to solvent polarity.

Table 3: Fluorescence quantum yield calculations for each sample

Solvent	Solute	Optical Density (450nm)	n ²	D	Φ _F	Φ _F average
Acetone	Bis-DMAB	0.100	1.8458	10080	0.173	0.163
		0.097		9030	0.160	
		0.099		9035	0.157	
Isopropanol	Bis-DMAB	0.105	1.8967	14781	0.249	0.237
		0.104		14159	0.241	
		0.103		12873	0.221	
Toluene	Bis-DMAB	0.104	2.2380	5451	0.109	0.111
		0.105		6289	0.125	
		0.102		4868	0.099	
Acetone	Bis-DMAC	0.098	1.8458	16896	0.297	0.273
		0.103		16544	0.276	
		0.099		14098	0.245	
Isopropanol	Bis-DMAC	0.102	1.8967	10465	0.181	0.161
		0.096		9032	0.166	
		0.102		7918	0.137	
Toluene	Bis-DMAC	0.099	2.2380	20296	0.428	0.433
		0.100		23244	0.485	
		0.098		18201	0.387	
0.1M NaOH	Fluorescein Standard	0.102	1.7769	58520	0.95 ⁷	
		0.102		57760		
		0.100		56530		

Fluorescence Lifetime Determination

The fluorescence lifetimes of our compounds and the X² values are reported in Table 4. The decay curves and instrument responses for each sample can be found in Appendix 3. Similar to quantum yields, the fluorescence lifetimes do not trend according to solvent polarity and show opposite trends between bis-DMAB and bis-DMAC. While bis-DMAB had the longest lifetime in isopropanol and shortest in toluene, bis-DMAC has the longest lifetime in toluene and the shortest in isopropanol.

Table 4: Fluorescence lifetime data with X^2 values and optical density

Solute	Solvent	Optical Density	τ_F	X^2
Bis-DMAB	Acetone	0.0508	0.6115	0.9188
Bis-DMAB	Isopropanol	0.0564	0.9264	0.9771
Bis-DMAB	Toluene	0.0539	0.1997	1.105
Bis-DMAC	Acetone	0.0543	0.7573	1.165
Bis-DMAC	Isopropanol	0.1369	0.3627	1.002
Bis-DMAC	Toluene	0.0451	0.8623	1.199

Discussion

Neither compound shows a strong change in their absorbance between solvents (the greatest is 22nm for bis-DMAB and 26nm for bis-DMAC). The small difference in energy means that Δf does not greatly impact the $S_0 \rightarrow S_1$ transition. No appreciable difference is observed because neither bis-DMAB nor bis-DMAC are very polar in the ground state and therefore solvent polarity would not have a large effect on their properties. Since for each compound the absorbance maxima and molar extinction coefficient does not change between solvents the compound in both cases is absorbing similar amounts of energy. Therefore it must be that any difference in photochemical properties of either compound is largely the result of differing interactions between solvent and the excited state molecule. In the reported stokes shifts, both compounds in acetone and isopropanol show nearly equivalent shifts between absorbance and emission maxima. However in toluene, the compound with a significantly lower polarity (0.0131 versus 0.2843 and 0.2769), stokes shifts are nearly half of those in acetone (1590 cm^{-1} versus 3424 cm^{-1} for bis-DMAB and 2061 cm^{-1} versus 3959 cm^{-1} in bis-DMAC). Based on this trend it appears that solvent polarity has an effect on the energy of light being emitted with greater polarity of solvent leading to a longer wavelength of emission.

As seen in Figure 16 and Figure 17 upon photoexcitation of bis-DMAB and bis-DMAC, electron density shifts from the outer regions of high electron density in the S_0 state (HOMO) containing the two nitrogen atoms and the aromatic rings to the carbonyl and vinyl carbons of high electron density in the S_1 state (LUMO). This increased polarity causes the molecule to interact differently with the solvent once in the excited state. More polar solvents are better able to stabilize the excited state leading to a lowering of energy in the S_1 state.

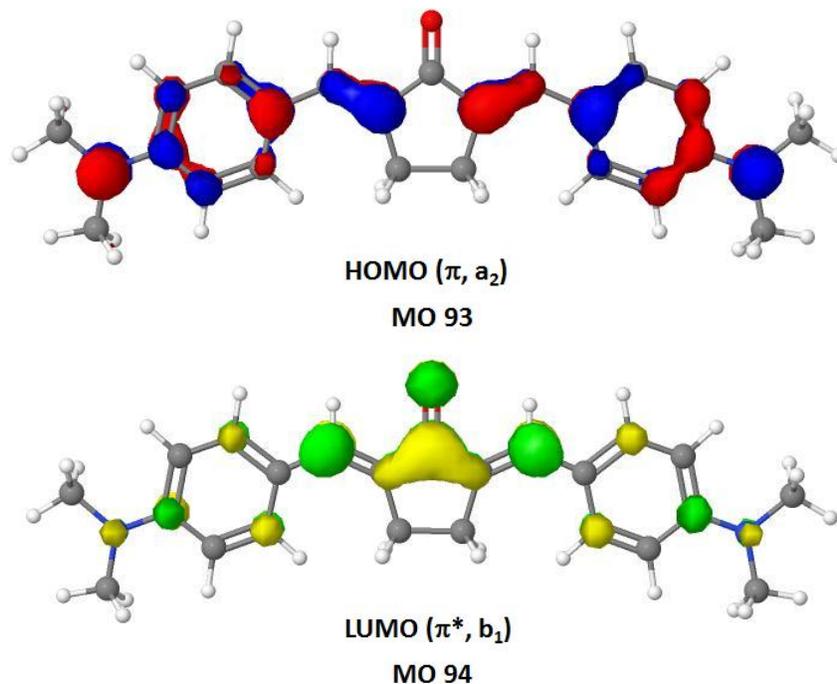


Figure 16: Ground state (top) and excited state (bottom) of bis-DMAB

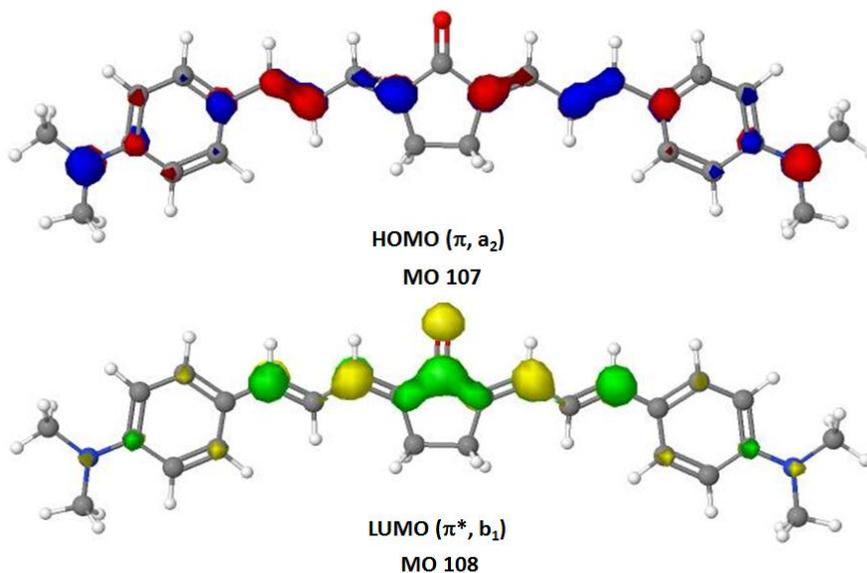


Figure 17: Ground state (top) and excited state (bottom) of bis-DMAC

This solvent-solute interaction arises from a ground state arrangement of solvent around the non-polar solute. When the transition from the S_0 to S_1 state is made, the solvent cage undergoes reorientation in a process known as solvent relaxation. Solvent relaxation occurs so that the solvent dipole may better accommodate the change in charge distribution. The

reorientation requires energy that is drawn from the S_1 state, lowering the overall energy. Solvents with lower orientation polarizations (Δf) do not have as stabilizing an effect because reorientation of the solvent dipole does not occur to as great an extent. Because the electrons start out at lower energy, when they relax, photons of lower energy, and as a result longer wavelengths, are emitted.

A slightly expanded explanation hypothesized is that electrons move through different vibrational levels than those on a normal absorbance-emission path. In this hypothesis, electrons are promoted to the S_1 state and undergo internal conversion. Solvent relaxation occurs during internal conversion and creates an alternate lower energy excited vibrational level. When the electron fluoresces, the molecule is no longer in the excited state however, because the change in electronic and vibrational levels is simultaneous and instantaneous in accordance with the Franck-Condon principle, the solvent would not have had time to reorient itself around the less-polar state. This leads to an artificially higher ground state before the solvent cage can reorient to accommodate the ground state of the molecule. For solvents with lower Δf values, the interaction between themselves and the excited state should be minimal. The path is represented in the Jablonski diagram in Figure 18. This interaction would be observed as a vibrationally excited ground state of lower energy than that of a solvent with higher Δf . Once the solvent cage relaxes, the electron can return to the S_0 state through radiationless decay.

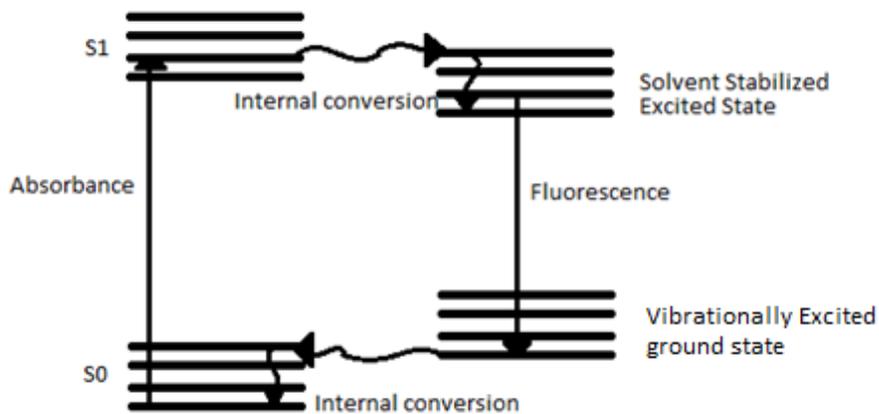


Figure 18: Jablonski diagram fully accounting for solvent stabilization

In solvents in which the compounds have short lifetimes there is less time for solvent relaxation. This leads to a lower energy vibrationally excited ground state and therefore lower

energy emitted. There is a limitation to this. After enough time has passed for solvent relaxation to take place, no additional changes will occur because the solvent will have reached an optimal orientation. According to Figure 19, which compares stokes shift to lifetime, this limit is reached at its' latest at around 0.36 ns. This is seen on the graph as the near plateau in data points around 3500 cm^{-1} . The time limit would also be shorter in more polar solvents because they interact more strongly with the excited state. Additionally it may be the case that for a larger molecule such as bis-DMAC, solvent relaxation takes longer to reach the lowest energy artificial ground state because there is more solvent to reorient.

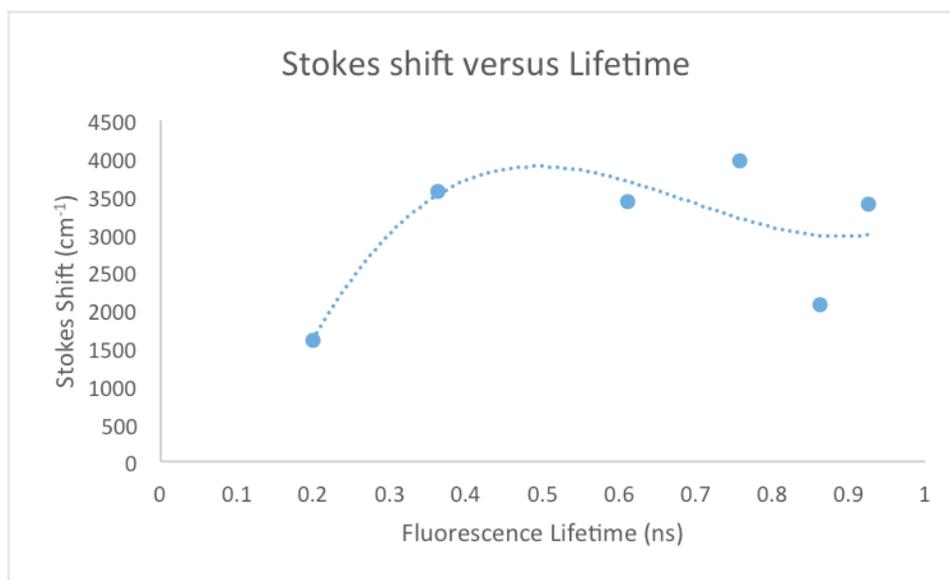


Figure 19: Stokes shift versus fluorescence lifetime trend

While stability of the excited state does explain trends observed for the stokes shifts, it does not explain either the trend of fluorescent lifetimes nor that of the fluorescent quantum yields. Even more interesting is that these two properties seem to be exactly opposite between bis-DMAB and bis-DMAC. This must be due to differences between the two compounds. A possible source of the discrepancy could be how each compound interacts with solvents of differing viscosities. Bis-DMAC for instance would be expected to interact more with a viscous solvent as it is a larger, more flexible molecule and therefore have a longer lifetime. While the data is inconclusive about this idea, it may be that viscosity of solvent does have some effect on the fluorescence properties of the compounds. An alternative explanation is that the change in polarity of the S_1 state causes the molecule to alter its' geometry to an optimal orientation. This

phenomena is known as twisting internal charge transfer.⁷ If this were the case, the two compounds could re-optimize their geometries in different ways. This could cause the compounds to interact with the solvents differently and might explain the opposite trends in lifetimes and quantum yields.

Conclusions

This research has successfully been able to characterize many of the photophysical properties of both bis-DMAB and bis-DMAC in three solvents: acetone, isopropanol, and toluene. These properties included absorption and fluorescence maxima, Stokes shifts, molar extinction coefficients, fluorescence quantum yields, and fluorescence lifetimes. Upon photoexcitation, internal charge transfer occurs as electrons are promoted from the HOMO to the LUMO. While in the HOMO, charge is more evenly spread across the π system but in the LUMO, charge density shifts drastically to the center of the molecule and is highest around the carbonyl. The increase in charge density around the carbonyl would naturally lead to an increase in the overall polarity of the molecule. Solvent relaxation is greatest in solvents with high orientation polarizations as they are most capable of reorienting themselves about the new charge distribution in the excited state. It is hypothesized that this is responsible for the lowering of energy in the S_1 state. As the energy that the electrons possess is lowered, when they relax, the photons that they emit will be of lower energy and therefore longer wavelengths.

Future Work

Future research will seek to further characterize the excited state properties of both bis-DMAB and bis-DMAC by calculating the quantum yield of the triplet state. This could give a more complete understanding of how these compounds, when excited, relax down to the ground state. Preliminary work has been carried out to investigate the photophysics of bis-DMAC further using laser flash photolysis. The apparatus for this work has been constructed by Z. Blais⁸ and A. Salerni⁶ and described in two previous MQP reports. Briefly the apparatus uses an Nd:YAG laser that generates an eight nanosecond pulse of 532 nm light. The time resolved absorbance changes are monitored using a fast photomultiplier and digital oscilloscope. The apparatus is controlled with a LabView program written in house and based on software originally written by R.W. Redmond.⁹

Bis-DMAC was dissolved in isopropanol at a concentration that gave an absorbance of ~ 0.5 at the laser excitation wavelength (532 nm). The sample was deoxygenated by bubbling with nitrogen for 20 minutes. A triplet – triplet difference spectrum was acquired every 20 nm from 370 nm to 710 nm and is shown in Figure 20.

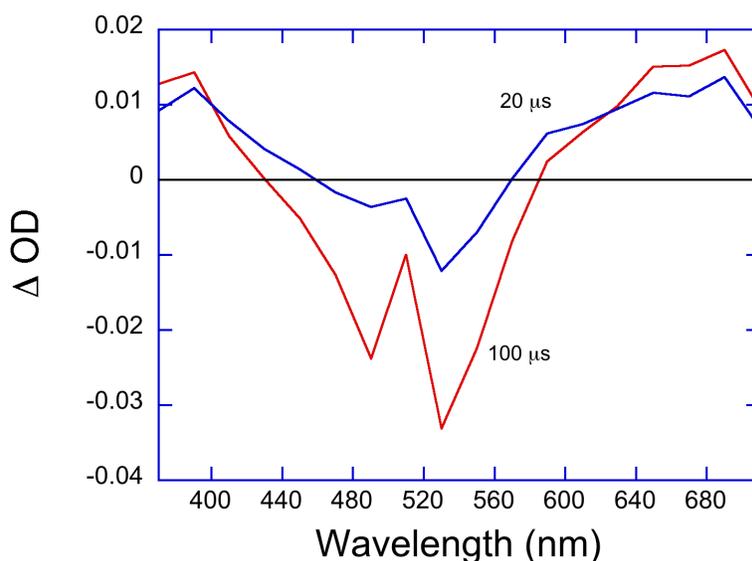


Figure 20: Triplet-triplet difference absorbance spectra obtained by 532nm excitation of bis-DMAC in isopropanol

The difference spectrum is noisy and this is likely to be because the data has not been corrected for variations in pulse to pulse energy of the laser. However it can be clearly seen that the triplet state absorbs less than the ground state at ~ 500 nm but continues to absorb above 600 nm.

The sample was replaced after 20 shots and was shaken between shots to minimize photobleaching. The effect of saturating the sample with air was determined by observing the transient absorption at 470 nm and the result is shown in Figure 21. The apparent lifetime of this species is about 30 microseconds in a nitrogen saturated solution.

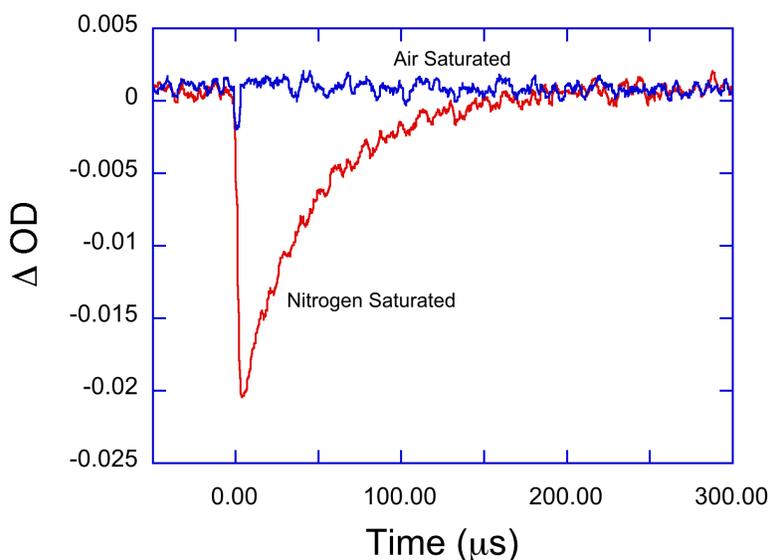


Figure 21: Effect of air saturation upon transient absorption by bis-DMAC at 470nm

The most likely interpretation of these results is that bis-DMAC undergoes intersystem crossing upon irradiation as evidenced by the oxygen quenching. It is possible that at 470nm this species could also be a radical anion but no evidence was seen for a solvated electron or radical cation that might be expected to be formed if this species was a radical.

It is important, for a complete picture of the photophysics of bis-DMAB and bis-DMAC that the yield of the triplet be quantified as a function of solvent. It will be interesting to see if the solvent dependent quantum yields of fluorescence formation determined for bis-DMAB and bis-DMAC are a consequence of increased internal conversion or a change in the yield of triplet state caused by a change in the rate of intersystem crossing.

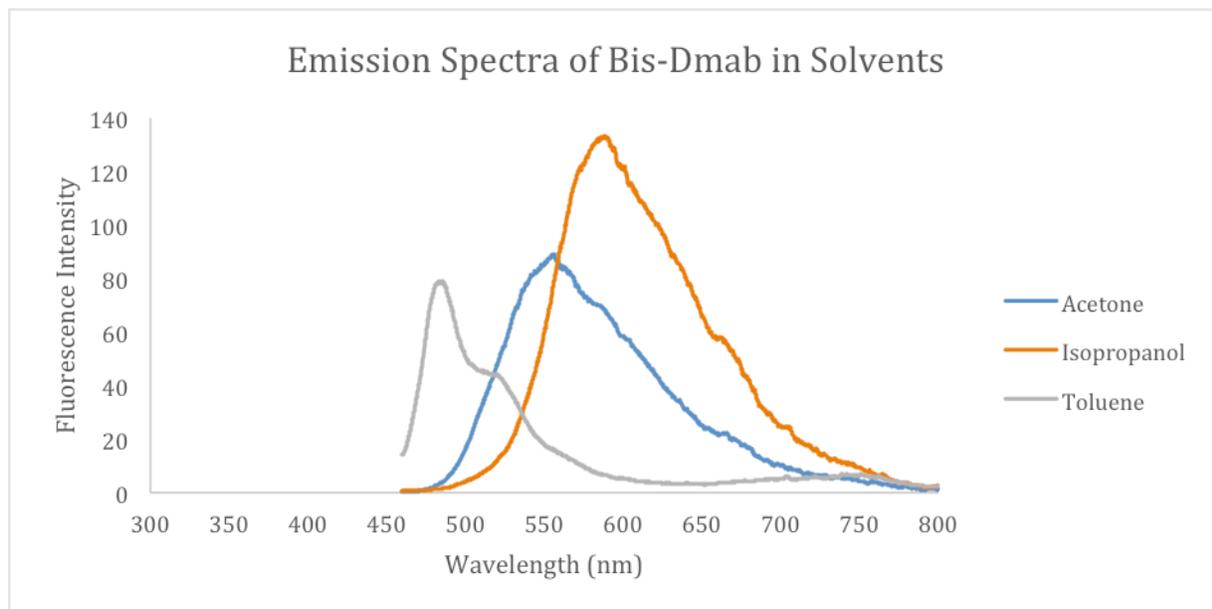
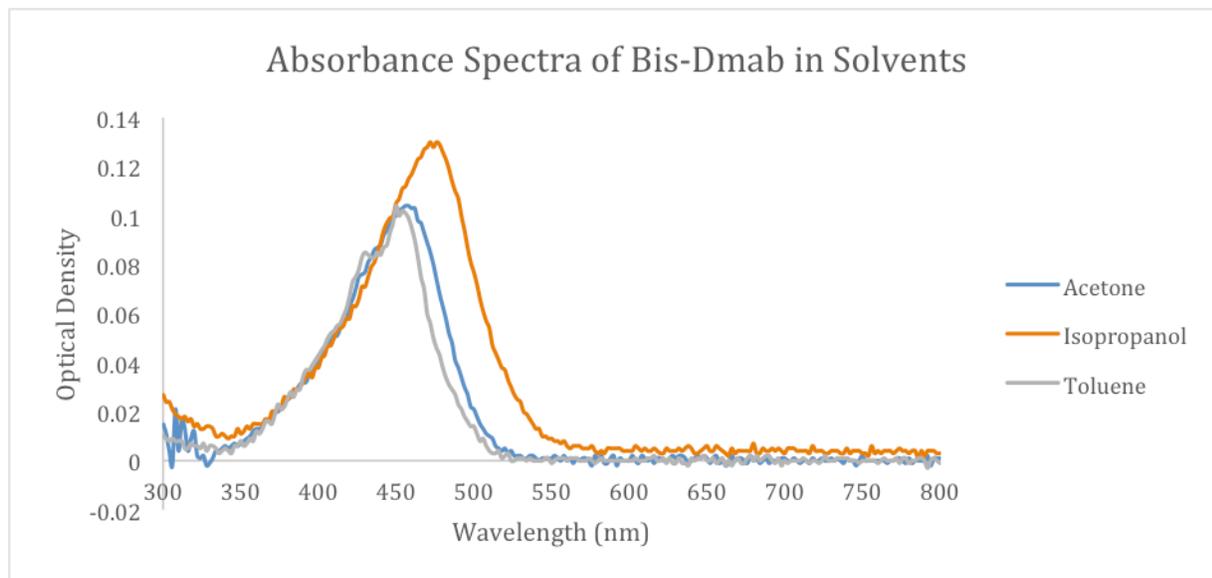
Changes in solvent polarity did not fully explain the trends in lifetimes of both compounds so other factors must influence them. One such factor could be solvent viscosity and its' effects on the stability of the excited molecule. A very important tool to aid in future investigation would be to create 3D models of the compounds in different solutions so it could be determined if the conformation of the excited state is different than that of the ground state and if the conformation varies based on solvent.

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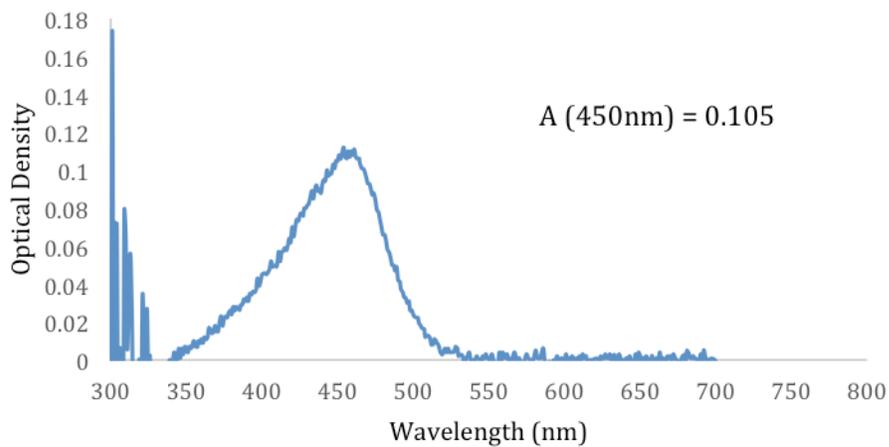
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Appendix

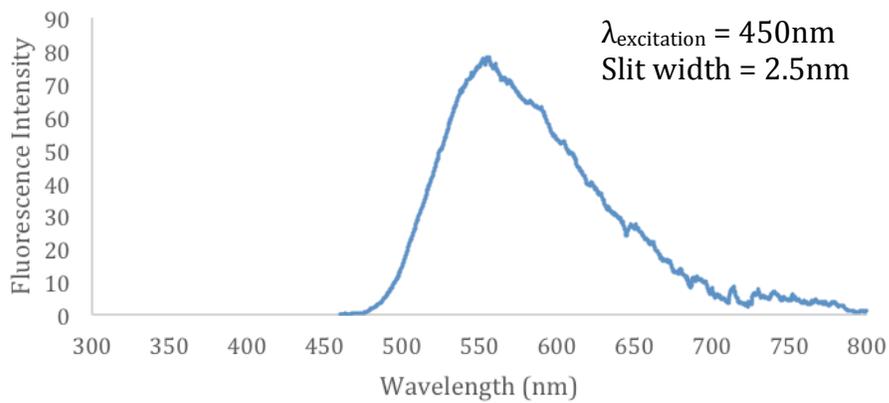
Appendix 1. Spectra for calculation of quantum yield



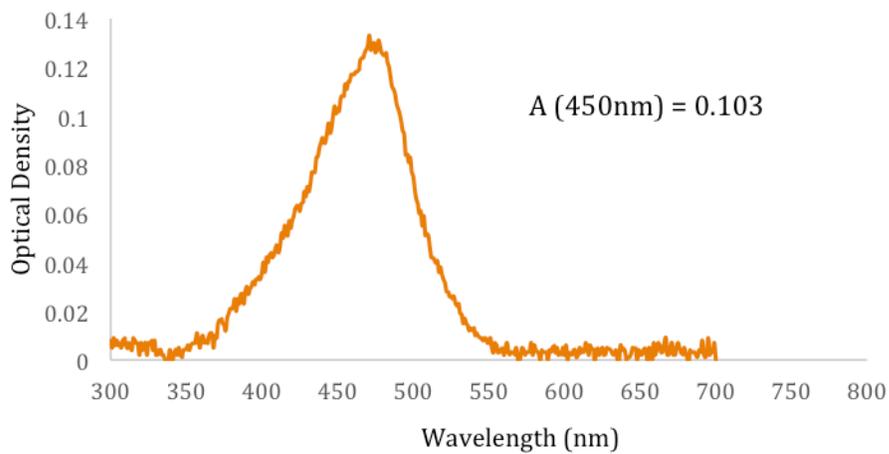
Absorbance of Bis-Dmab in Acetone



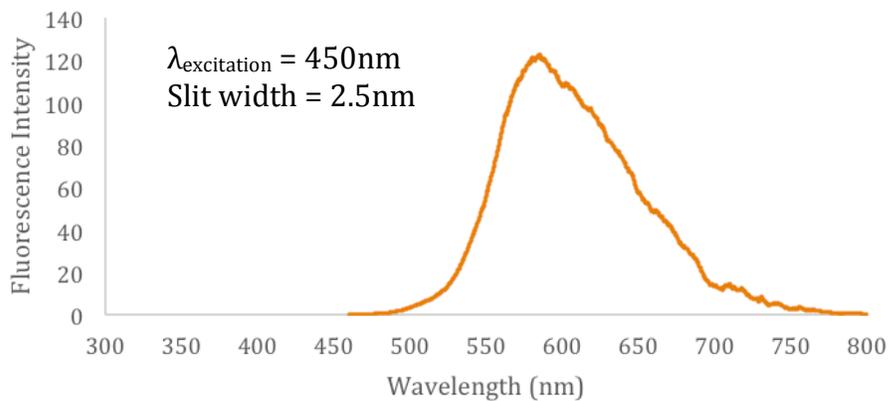
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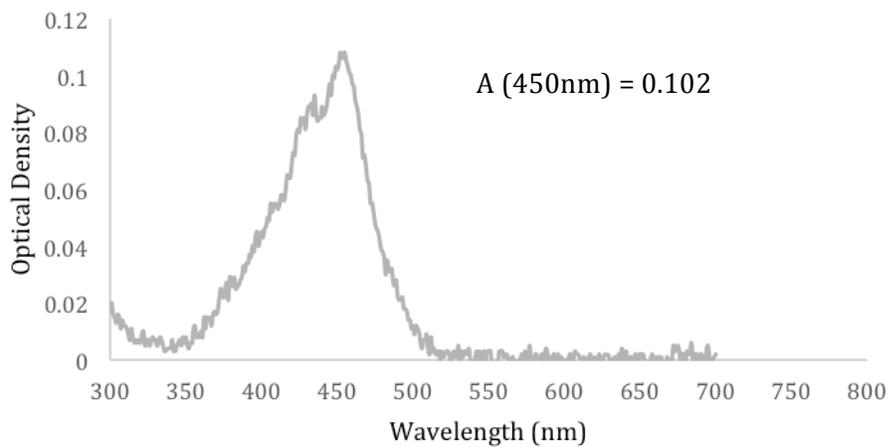
Absorbance of Bis-Dmab in Isopropanol



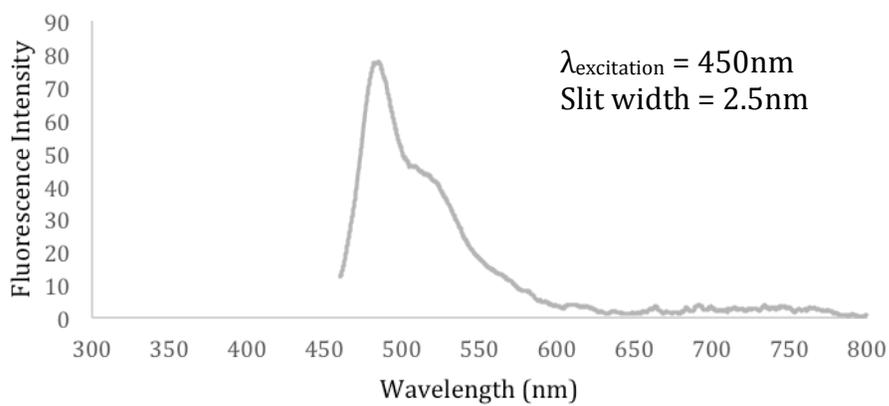
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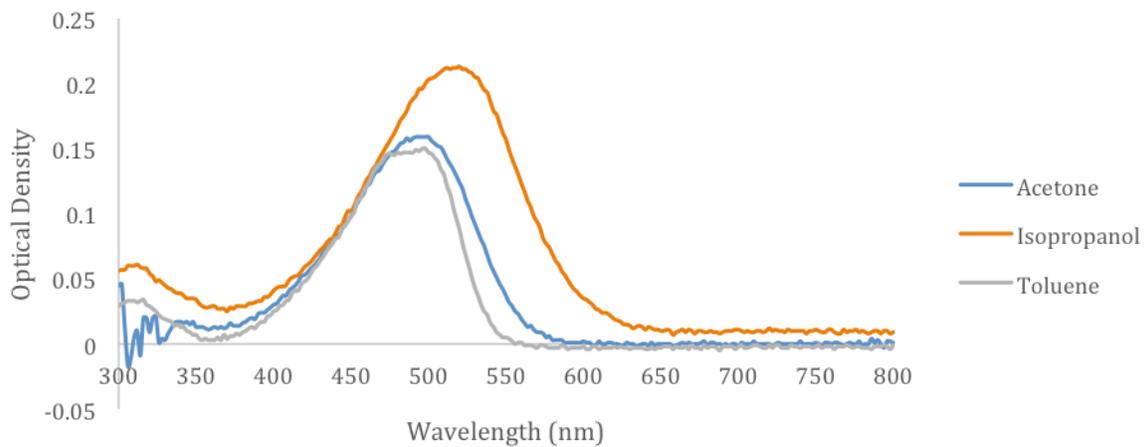
Absorbance of Bis-Dmab in Toluene



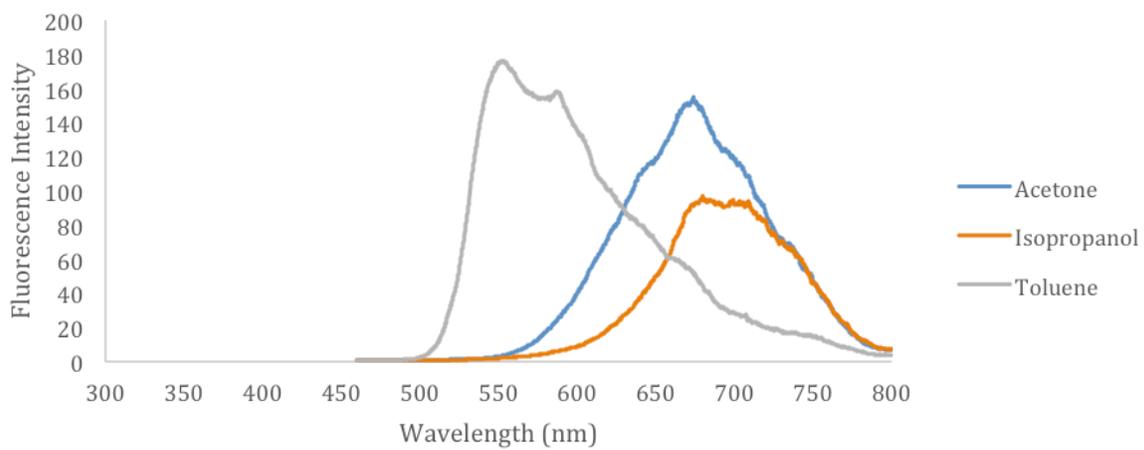
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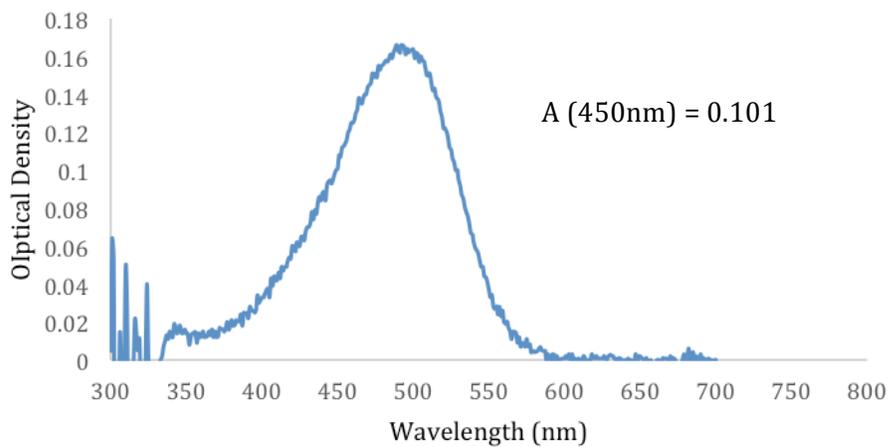
Absorbance Spectra of Bis-Dmac in Solvents



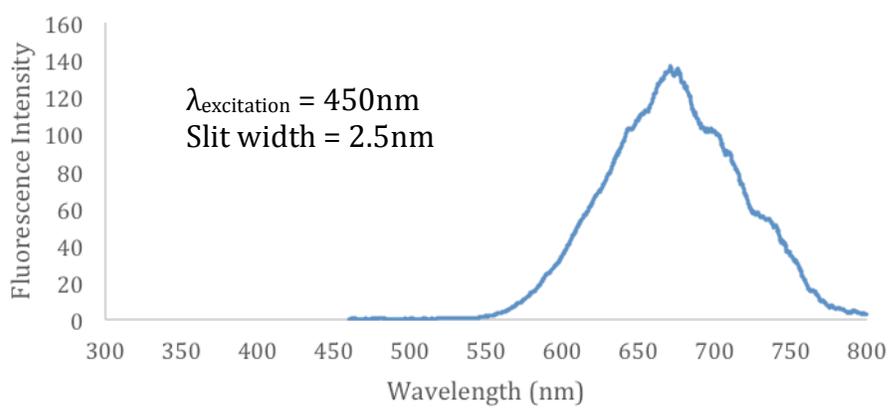
Emission Spectra of Bis-Dmac in Solvents



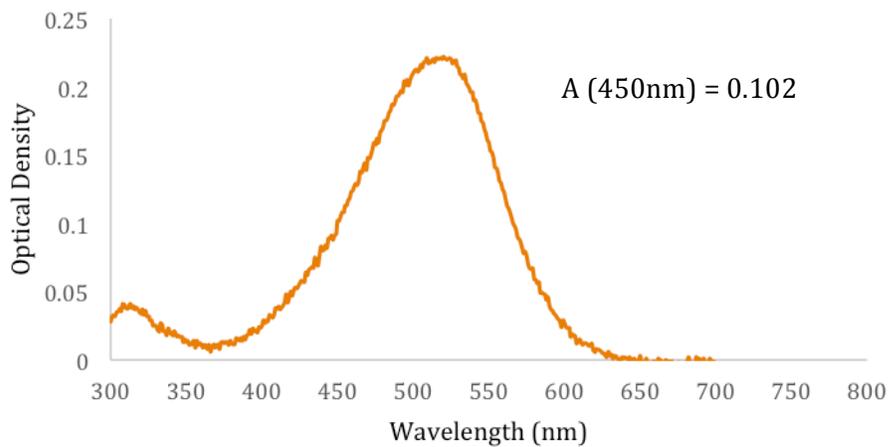
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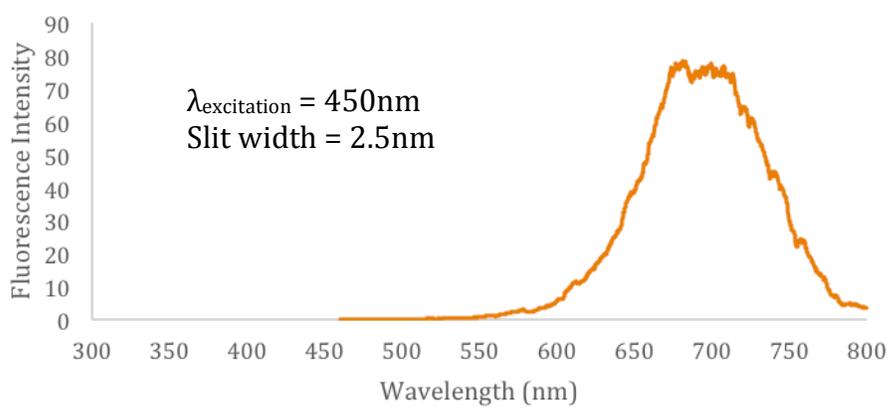
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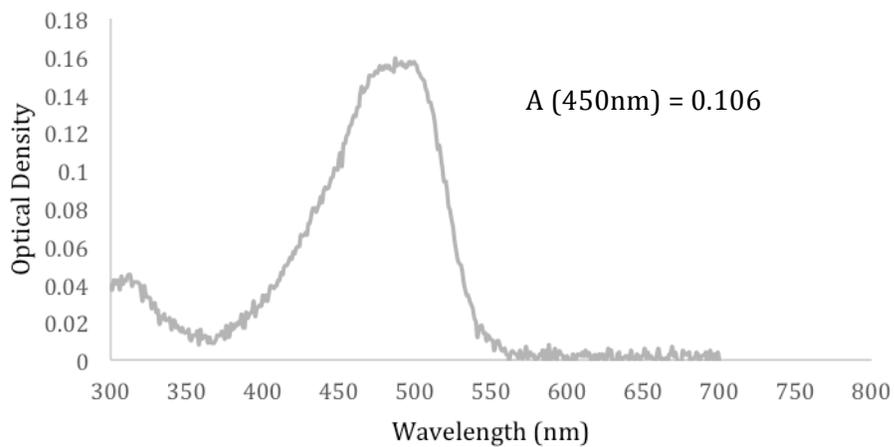
Absorbance of Bis-Dmac in Isopropanol



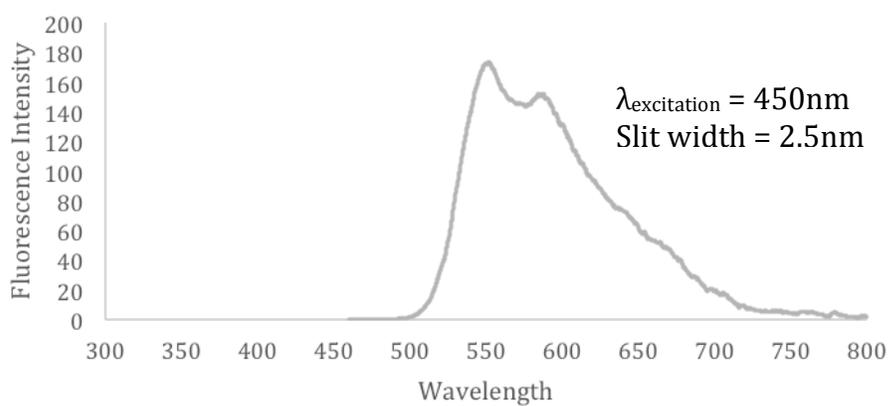
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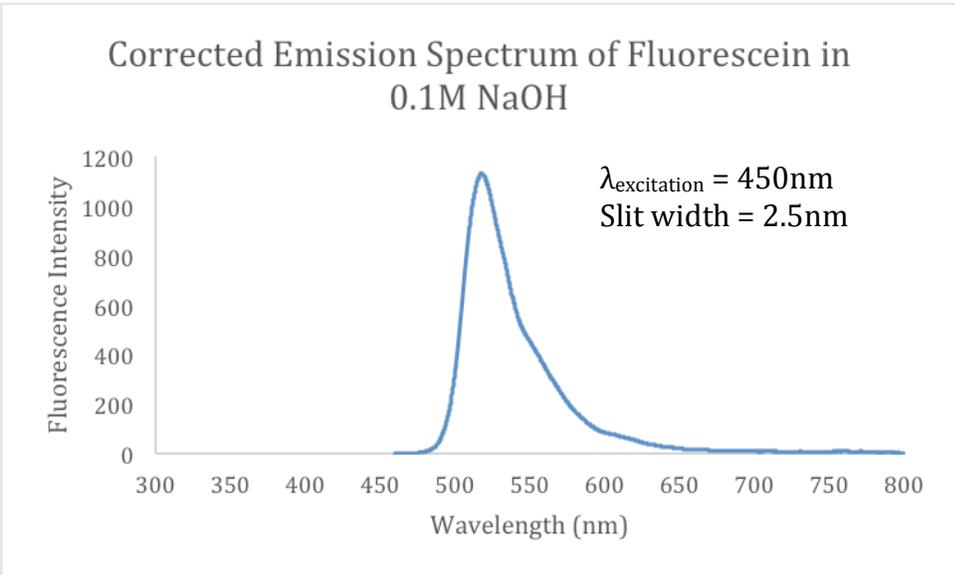
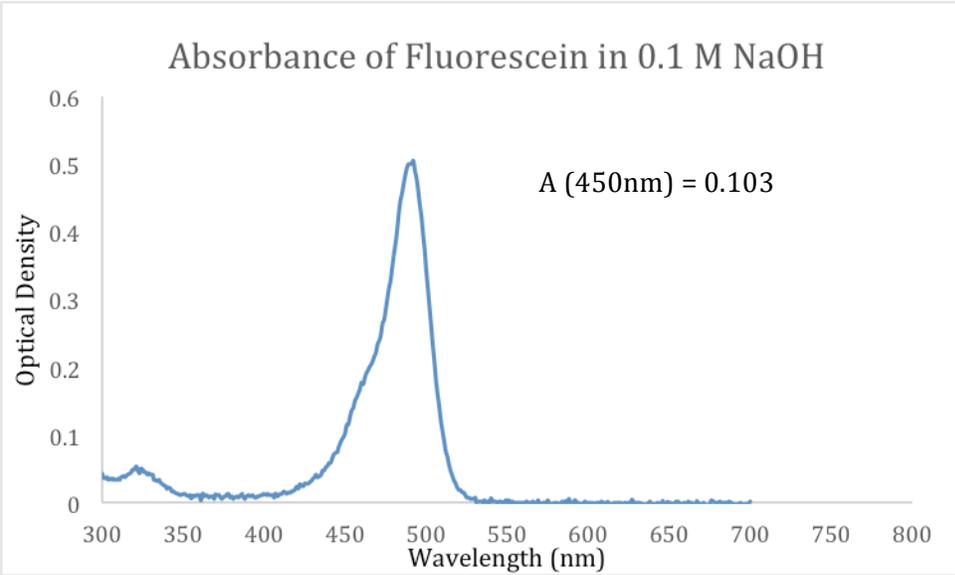


Absorbance of Bis-Dmac in Toluene

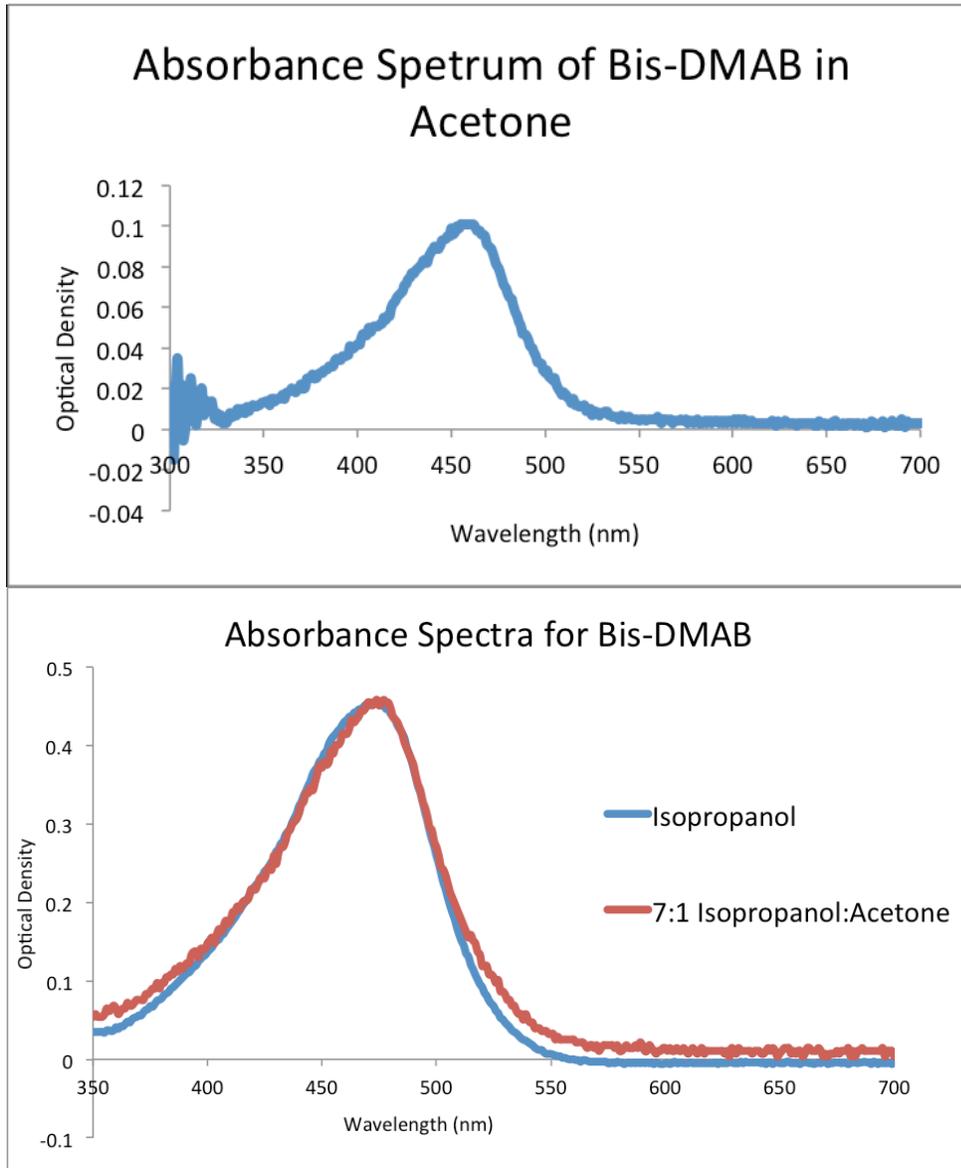


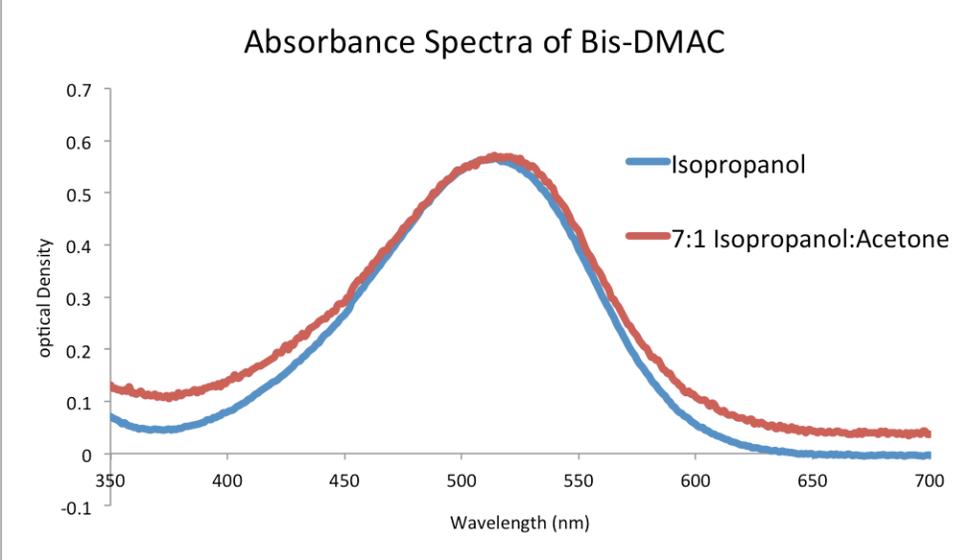
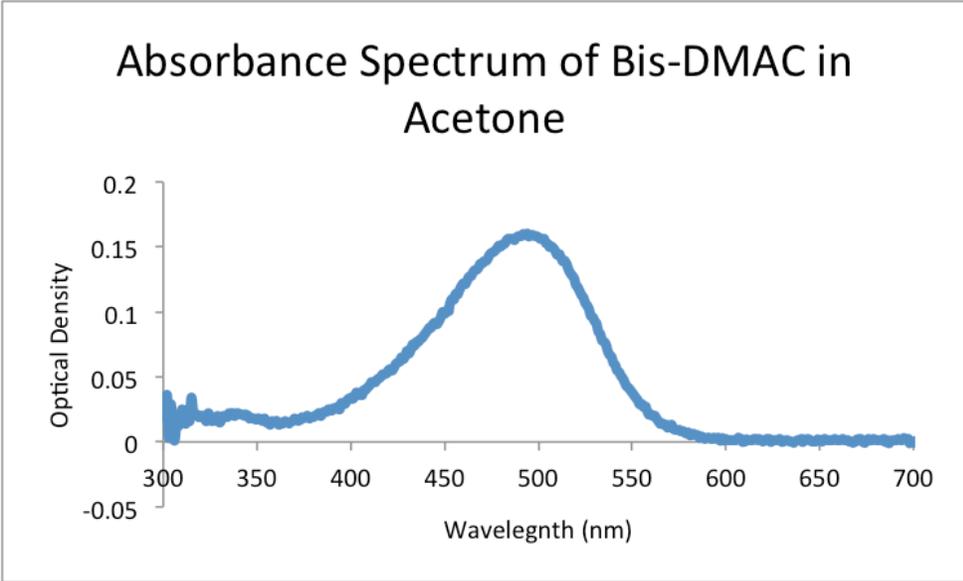
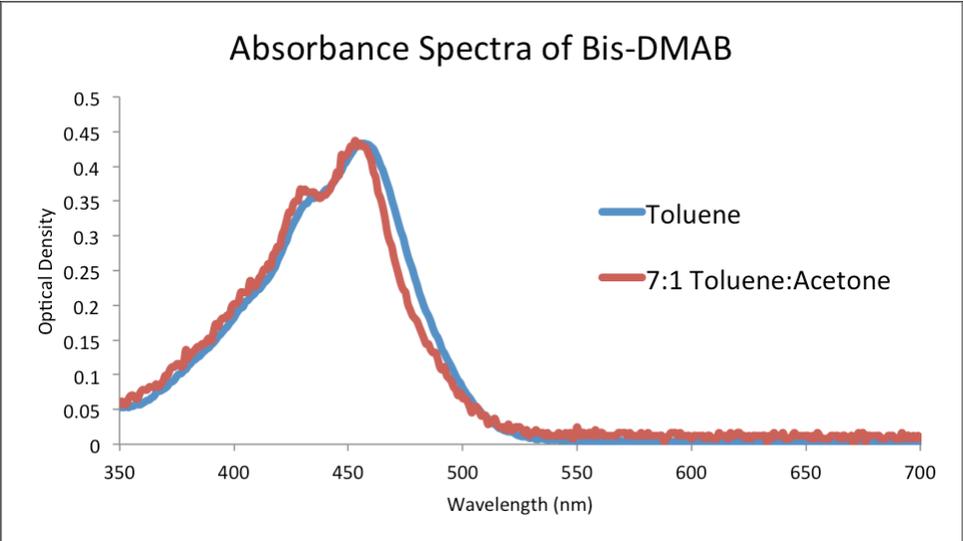
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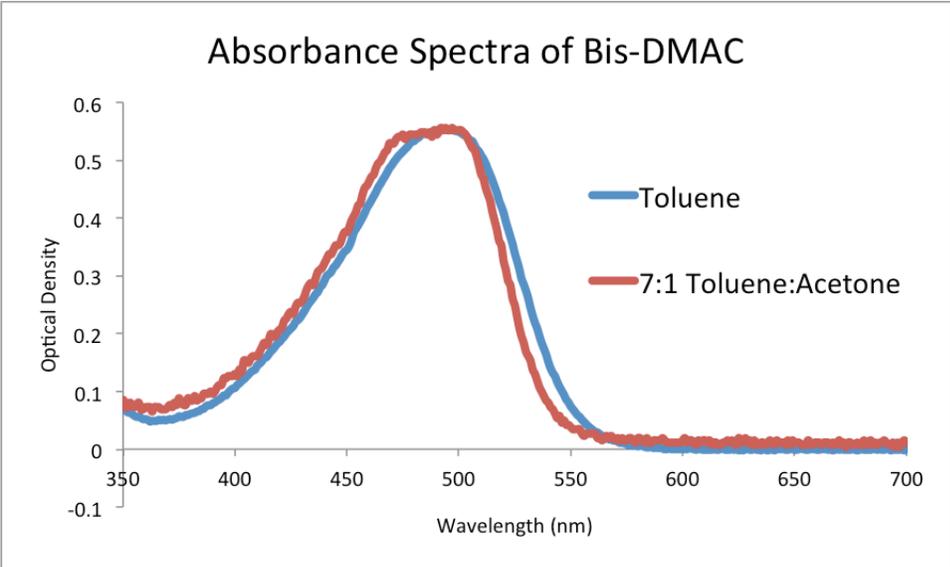




Appendix 2: Absorbance spectra for calculation of molar extinction coefficient







Appendix 3: Decay curves for calculation of fluorescence lifetime

