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Amino Acid Methyl Ester Chiral Ionic Liquids: A Concentration Study

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Christopher J. Brown
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Abstract

This project will investigate novel amino acid methyl ester chiral ionic liquids and determine how increased concentration of lanthanide solute and changes in size of counter ions tetramethylammonium and tetrabutylammonium affects interaction between the ionic liquid and the fluorescent lanthanide solute. Both concentration dependence and temperature dependence were discovered. The chiral ionic liquid [L-prolineC1][Tf2N] reacted uniquely to the change in concentration.
1 Introduction

1.1 Background

A chiral molecule, in its most basic terms, is a species with a non-superimposable mirror image. Human hands are an example of this as they are mirror images of one another but not stackable (i.e. not super imposable). The left hand and right hands are chiral enantiomers of one another. Chiral molecules are important to many areas of chemistry, one being biochemistry. This importance is seen by the overwhelming abundance of a single enantiomer in nature. Floudas et al. searched the protein database and revealed that over 99% of proteins are made of a single amino acid enantiomer. This finding is synonymous to saying that in nature everyone has only his or her left hand, and the right hand is less important or even detrimental. Chirality also plays an important role in drug formulation. The metabolism of certain drugs can be affected by a single chiral difference, as noted by Pham-Huy et al. Because of lowered potency or detrimental health outcomes associated with some chiral molecules separation of the enantiomers is often crucial. One way to effectively separate or influence chirality may be through the use of chiral ionic liquids.

Chiral ionic liquids (CILs) have many purposes both in analytical chemistry and catalyst chemistry. They have useful properties in analytical chromatography such as being thermally stable, homogeneous and reusable. CILs have also been used in electrochemical techniques to study complex samples. Other chemists have found CILs useful in enantioselective or asymmetric reactions, allowing a single chiral enantiomer to be
formed. It is the purpose of this thesis to investigate how CIL solvents influence solutes chiral equilibrium, forming asymmetric solutions.

Chiral amino acid methyl ester derived chiral ionic liquids were used in this study. The CILs are composed of the cations and anion shown in Figure 1.1.1 below. The cations are based on amino acids, which are the building blocks of life and chiral. We used the methylated monomer in these CILs with a common ionic liquid anion bis(trifluoromethanesulfonimide), [Tf2N]. Using the methyl ester form allowed for the amino acids to have a positive charge for a larger pH region. The cationic nature of the amino acid methyl esters is important as it allows for the amino acid methyl ester to be attracted and surrounded by negatively charged anions. These amino acid methyl esters when combined with [Tf2N] provide a CIL that can be used as the solvent for different solutes.
Figure 1.1.1: Amino acid methyl ester cation’s (left), anion bis(trifluoromethanesulfonylimide) on the right. Displayed using ChemDraw.

1.2 Europium Complex

To study how the CIL affects solutes dissolved in it we employed a fluorescent europium complex, \([\text{Eu}(\text{dpa})_3]^{3-}\) (dpa = 2,6-pyridinecarboxilate dianion), shown below in Figure 1.2.1. \([\text{Eu}(\text{dpa})_3]^{3-}\) is a lanthanide metal complex having a propeller blade like configuration. The direction of the propeller blades determines the handedness or chirality of the complex. Three dimensionally this is recognized as a right or left hand rotation. The right and left hand conformations are enantiomers of one another. Figure 1.2.3 shows both of these conformations connected with a racemization double arrow.
Racemization process occurs through the labile rotation of the ligands around the europium metal core. The left complex shows a propeller blade that would follow the left hand rule, where the leading wedge bonds follow a clockwise rotation making that complex lambdaoid chirality and \([\Lambda - \text{Eu(dpa)}_3]\)^3. Lanthanide metal complexes have strong emission bands and therefore can often be employed for spectroscopic measurements. The complex uses the dpa’s conjugated system as excitation antennae to absorb more radiation and allow for europium electronic transition. Following this electronic transition the europium center is left in an excited state. The relaxation process often involves the emission of a photon of light defined by a certain chiral rotation, and deemed circularly polarized. Circular polarized light is shown in Figure 1.2.2, where the emission from the different enantiomers causes the two different light rotations. The circular polarization is determined by the chiral conformation, or handedness, of \([\text{Eu(dpa)}_3]^3\).

![Figure 1.2.1 [Eu(dpa)_3]^3 shown in flat skeletal structure using ChemDraw.](image-url)
The CIL can have interact with the large \([\text{Eu(dpa)}_3]^{3-}\) molecule forming many different transitory structures. Of these many different structures or orientations, there are some more probable than others. Some of these probable interaction points are the symmetry axis found in the europium complex. A symmetry axis is an axis that can be rotated \(n\) times at \(360/n\) degrees yielding an identical image at each step in the rotation. These symmetry axes are seen in both conformations of the chiral complexes. Figure 1.2.4 shows both of the symmetry axis in the \([\Delta - \text{Eu(dpa)}_3]^{3-}\) complex. The left image shows a \(C_3\) symmetry axis, where the molecule can be rotated \(120^\circ\) three times, yielding the
identical structure at each step, while the left structure shows a C$_2$ axis (two 180° rotations).

Figure 1.2.4: [$\Delta$ -Eu(dpa)$_3$]$^{3-}$ shown aligned with the symmetry axes present in the molecule. Left structure shows the C$_3$ axis and the right structure shows the C$_2$ axis.

The molecules that surround the europium complex, such as the CILs, can influence the chiral conformation of the complex. Because lanthanide complexes form labile but constant connections with their ligands, chiral changes can occur through rotation of the ligands, changing the configuration of the propeller blades. The propeller blades rotate at the europium metal center forming each enantiomer.

Further, Huskowska et al. used chiral sugars to influence a similar lanthanide probe, [Tb(dpa)$_3$]$^{3-}$. They argue the racemization process occurs rapidly in non-viscous solutions. Yoneda et al. showed how sugars with differing chiral centers affected the chiral equilibrium of the two enantiomers presented in Figure 1.2.3. Viscosity and chirality seem to both be playing an important role in the racemization of lanthanide complexes.

Kroupa et al. found that the CIL solvent, both viscous and singularly chiral, imposes a perturbation on the the racemization of [Eu(dpa)$_3$]$^{3-}$. Kroupa also found [D-
alanineCl][Tf_2N] causes the conformation and thus emission of the europium complex to be opposite that of the emission seen by the complex in [L-alanineCl][Tf_2N]. The changes in conformation seen while using the europium complex can be considered an equal but opposite equilibrium perturbation imposed by each of the CIL solvents. They determined the CIL solvents increased either the amount of left-handed (\( \Lambda \)) or the right-handed (\( \Delta \)) europium complex in equilibrium.

One way to study these changes in the chiral equilibrium is to measure the relative amounts of rotated light. This can be accomplished through measuring circular dichroism\(^{11} \) (CD) or circular polarized luminescence (CPL)\(^{12} \). Both techniques allow measure of the population of circularly polarized light. CD uses circular polarized light absorbance, and relates an increase in absorbance to the amount to the increase of a particular chiral center. CD, however, often suffers from poor sensitivity. CPL uses a probe, like \([\text{Eu(dpa)}_3]^{2+}\), to emit circular polarized light. CPL measurements relate the population of rotated light to the amount of each chiral conformation, or enantiomer, in the solution. As the amount of the measured light changes between liquids it is important to develop a means to compare them. In CPL spectroscopy\(^{13} \) this comparison factor is termed a dissymmetry factor, known as \( g_{\text{em}} \).

Using CPL spectroscopy the difference in the polarized light must be measured, designated \( \Delta I (\lambda) \). The difference in polarized light is then related to the dissymmetry factor through equation 1.1 where differences of each samples total emission are
accounted for. The total light intensity is noted as \( I(\lambda) \). The dissymmetry factor can be calculated as follows:

\[
g_{em}(\lambda) = \frac{2[I_L(\lambda) - I_R(\lambda)]}{I_L(\lambda) + I_R(\lambda)} = \frac{2\Delta I(\lambda)}{I(\lambda)}
\]

Again, the dissymmetry factor is used to find the perturbation of the chiral equilibrium when using CPL spectroscopy.

Finding the ratio of the chiral enantiomers involves relating the dissymmetry factor to the enantiomeric excess, termed \( \eta \). The enantiomeric excess is the concentration and is found by dividing the polarized light observed, \( g_{em}(\lambda) \), by the total possible polarized light, \( g_{em}^A(\lambda) \), as shown in equation 1.2. Kroupa et al.\(^{14}\) provided the total possible polarized light as \( g_{em}^A(\lambda) = 0.29 \). The enantiomeric excess is the ratio of measured dissymmetry factor to the total possible dissymmetry factor. The enantiomeric excess can be related to the population of each enantiomer in solution.

\[
\eta = \frac{g_{em}(\lambda)}{g_{em}^A(\lambda)}
\]

The enantiomeric excess allows for further calculation of the racemization equilibrium constant \( K_{rac} \). An equilibrium constant can be calculated for reaction 1.3 where the equilibrium constant is effectively the ratio of enantiomers. The equilibrium constant from equation 1.3 is represented as the equilibrium constant, \( K_{rac} \), and is defined in equation 1.4.

\[
\Delta = [Eu(dpAc)\text{]}_{3}^{-3} = A - [Eu(dpAc)\text{]}_{3}^{-3}
\]
Calculation of $K_{rac}$ is completed using the enantiomeric excess values determined in equation 1.2. The enantiomeric excess is used to give the $K_{rac}$ in equation 1.5:

$$K_{rac} = \frac{\Lambda - [Eu(dpa)_3]^{3-}}{\Delta - [Eu(dpa)_3]^{3-}} = \frac{1 + \eta}{1 - \eta}$$  

Following the determination of the $K_{rac}$ it is also possible to determine the enthalpy of the racemization reaction, $\Delta H_{rac}$. The $\Delta H_{rac}$ is the energy released or required for the proposed racemization to occur. A negative $\Delta H_{rac}$ means it is an exothermic process and a positive means that the process is endothermic. This value is calculated using a Van't Hoff plot, with the natural log of the equilibrium constant as the vertical axis and the inverse temperature as the horizontal axis. The slope of this line is the $\Delta H$ divided by the gas constant, $R$, as shown in equation 1.6.

$$\ln K_{rac} = -\frac{\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R}$$  

1.3 Pfeiffer Effect of Chiral Discrimination

If chiral compounds are synthetically formed without any sort of favored chiral conformation they will be made racemic, 50:50 mixtures. That racemic formation is seen for $[Eu(dpa)_3]^{3-}$ when originally formed. That racemization mechanism forms equal amounts of CPL emitted from $[Eu(dpa)_3]^{3-}$ in an achiral solution, a solution lacking a chiral influence. However, if a molecule in the solution has a fixed chiral influence we find that the originally 50:50 equilibrium of enantiomers is perturbed. The induced shift in a chiral equilibrium, Figure 1.2.3, is known as the Pfeiffer effect$^{15,16}$. 

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The Pfeiffer effect is the formation of a non-racemic mixture by the influence of a
environment of molecules that is chiral. Adding a chiral environment can induce optical
activity, or perturb equilibrium. Within the Pfeiffer effect literature\textsuperscript{17} there are two
proposed mechanism for this dissymmetry, associative and dissociative. The associative
mechanism proposes that the chiral environment is totally associated with the influence
molecule that is being monitored. This would propose a static complex of $[\text{Eu(dpa)}_3]^{3-}$
with CIL molecules locked in a specific formation. The dissociative mechanism proposes
that the chiral environment is not directly associated with the influenced molecule that is
being monitored. A dynamic fluid movement of chiral environment around the
$[\text{Eu(dpa)}_3]^{3-}$ is proposed, where the chiral environment-europium complexes do not form.
Wu \textit{et al.}\textsuperscript{18} gives evidence supporting the dissociative model when using L-histidine with
$[\text{Tb(dpa)}_3]^{3-}$.

An associative mechanism would involve the CILs forming a stabilizing structure around
the ligands of the europium complex. The ligands would be more stabilized in one
conformation, and perturb the equilibrium in that direction. Brittain \textit{et al.}\textsuperscript{19} shows
different chiral phenylalkylamines, phenylalkylamino alcohols and phenylalkylamino
acids could form stabilizing interactions, through an associative Pfeiffer effect using a
similar lanthanide complex, $[\text{Tb(dpa)}_3]^{3-}$. Crucially different between the previous study
and the current work is the identity of the chiral effector. The chiral effector in the
previous study was a co-solute while in the current thesis is the solvent. Brittain similar
study focuses on using only micro amounts of the chiral effector. The effect of a chiral
solvent on the $[\text{Eu(dpa)}_3]^{3-}$ probe is the focus of this work.
1.4 Summary:

CILs have many uses throughout a diverse range of chemistry fields, one being their ability to impose chiral perturbation. This study looks at the chiral perturbation of \([\text{Eu(dpa)}_3]^{3-}\) racemic equilibrium using circular polarized luminescence spectroscopy. It will investigate how changes to \([\text{Eu(dpa)}_3]^{3-}\) concentration effect the degree of equilibrium perturbation, with hopes to draw conclusions on how the CIL interacts with the emitting complex (Pfeiffer effect). Finally, using van't Hoff plots the heat of reaction will be investigated.

2 Method and Materials

2.1 Preparation of Chiral Ionic Liquids

L-Alanine methyl ester hydrochloride (MW: 139.58 g/mol, L-alanineCl), D-Alanine methyl ester hydrochloride (MW: 139.58, D-alanineCl), L-Proline methyl ester hydrochloride (MW: 165.62 g/mol, L-prolineCl), L-Leucine methyl ester hydrochloride (MW: 181.66 g/mol, L-leucineCl), and Bis(trifluoromethane) sulfonamide lithium ([Tf$_2$N]Li) salt (MW:287.09 g/mol, [Tf$_2$N]) were all purchased from Sigma Aldrich and used without further purification. Molar equivalents of a single amino acid methyl ester hydrochloride and [Tf$_2$N]Li were stirred in separate beakers using approximately 3mL deionized water. After dissolving each of the solids, the solutions were mixed and allowed to stir for approximately 10 minutes or until micelles of chiral ionic liquid (CIL) began to form. This solution is then transferred to a separatory funnel for separation of the CIL layer from aqueous layer. The mixture is allowed to sit for two to three days before collection of CIL. After collection the CIL layer is dried in a vacuum desiccator for three or more days.

2.2 Preparation of \([\text{Europium}(2.6\text{-pyridinedicarboxylate dianion})_3]X_3\) (X=[TMA]$^+$ or [TBA]$^+$):

Europium (III) chloride hexahydrate (EuCl$_3$$\cdot$6H$_2$O, MW: 366.41 g/mol), 2,6-pyridinedicarboxylic acid (dpa, MW: 167.12 g/mol), tetramethylammonium hydroxide solution ([TMA]$^+$, MW: 91.15), and tetrabutylammonium hydroxide solution ([TBA]$^+$, MW:259.47 g/mol) were all purchased from Sigma Aldrich and used without further purification. EuCl$_3$$\cdot$6H$_2$O, 1 equivalent, is dissolved in water, and later 3 equivalents of NaOH was used to precipitate Eu(OH)$_3$. The solid is filtered. 2,6-pyridinedicarboxylic acid (dpaH$_2$) is added drop wise to the filtered Eu(OH)$_3$ to reach a neutral pH, roughly 3
molar equivalents. To the \([\text{Eu(dpa)}_3]^{2+}\) solution 3 molar equivalents of \([X][\text{OH}]\) is added, precipitating \([Xh][\text{Eu(dpa)}_3]\). Solvent was removed by heating (<60°C) under vacuum for approximately 2 hours leaving a white crystalline and amorphous solid for \([\text{TMAh}]_3[\text{Eu(dpa)}_3]\) (856.86 g/mol) and \([\text{TBAh}]_3[\text{Eu(dpa)}_3]\) (1374.68 g/mol), respectively.

2.3 Sample Preparation

Concentration dependence was determined by separately adding each complex to each CIL so that the final millimolality was 0.1 mm, 0.2 mm, 0.3 mm, 0.4 mm, 0.5 mm, and 0.6 mm. Mass by difference was completed using Mettler-Toledo analytical balance. For example if making 0.4 mm concentration of \([\text{TMAh}]_3[\text{Eu(dpa)}_3]\) 0.00051 g of the europium complex would be added to a glass vial. Following this approximately 1.5 g of a CIL is added allowing for the correct final concentration. Mass measurements are taken at every step in the combination allowing for accurate concentration determination.

2.4 Circular Polarized Luminescence (CPL) Measurement

The measurement were completed using a custom-built CPL spectrometer, which consists of a 450W Xenon arc lamp, monochromator, photoelastic modulator (Hinds PEM-80), a linear polarizer, a high-resolution monochromator (Horiba John Yvon iHR320), and red-sensitive photomultiplier tube (PMT, Hamamatsu R928). White light from the Xenon arc lamp was passed through a time resolving chopper an initial filtering monochromator, isolating 280nm light. This light was directed towards the sample cuvette that is 90° from the following spectrographic components. Following sample excitation and emission, light was filtered allowing for selective passage of uniquely rotated light through the PEM and is then passed to the high-resolution monochromator for selection and subsequent detection over the 585-600nm wavelength range. The signal output from the PMT was processed by a lock-in amplifier, which reduces background electrical noise. Electrically resolved data is collected using LabView® software and stored on laboratory computer. Data was stored in the form of chiral resolved intensity and the total intensity for chiral influence determination. Variable temperature dependence studies were also completed on the varied concentration samples. Temperature control was completed using a heated/cooled water bath that cycles through the sample housing.

2.5 Lifetime Measurement

Luminescence lifetime decay measurements were completed on previously described instrument. Time resolving chopper modulated light at 90 Hz and selected 280 nm monochromatic light was focused onto the sample. Lifetime measurements were collected using PEM-80 linearized light and the high-resolution monochromator measuring emission at 614 nm. Linear polarization from PEM-80 was optimized for monochromator detection allowing high signal sensitivity. Signal averaging was completed using approximately 1000 scans processed by the oscilloscope, collected using LabView® designed software, and was stored on laboratory computer.
2.6 Emission Spectra

Sample emission spectra were obtained using a Perkin Elmer LS55 spectrophotometer in both fluorescent and phosphorescent scan mode. Fluorescent scan mode measured the immediate emission of light caused by fast relaxation of the excited europium complex. Phosphorescent scan mode collected emission spectra after a brief delay allowing for the forbidden relaxation events to be measured, and was used. Excitation wavelength was set at 280nm. Emission was measured over 500-650 nm wavelength range.

2.7 Karl-Fischer Titration

Karl-Fischer titration was used to measure water content of the CIL's prior to addition of the europium complex and the CPL measurement. A small amount (~0.010 g) of CIL was drawn into a syringe and then dispensed into the electrolytic cell. Mass by difference using the syringe allowed calculation of mass that was used in the Karl-Fischer titration analysis of water content.

3 Results and Discussion

3.1 Experimental Interpretation

Emission spectra of the europium complex were measured in each CIL before further tests were completed. The spectra allowed confirmation that the [Eu(dpa)3][TMA]3 complex had not decomposed as it was heated and mixed with the CIL. The emission scan has two clear peaks at ~595 nm and 615 nm, caused by the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ electronic transitions, see Figure 3.1.1 and 3.1.2. The 595 nm peak should contain a weak shoulder at 588 nm, which is descriptive of the lanthanide in complex with the three-dpa ligands. If the lanthanide complex decomposed then the emission scan would not have shown the shoulder at approximately 590 nm.
Figure 3.1.1: Fluorescence emission spectra taken using the Perkin-Elmer LS55 on 0.4 mm [Eu(dpa)_3][TMA]_3 in [D-alanineC1][Tf_2N].

Figure 3.1.2: Phosphorescent emission spectra taken using the Perkin-Elmer LS55 of 0.4 mm [Eu(dpa)_3][TMA]_3 in [D-alanineC1][Tf_2N].
A phosphorescence spectrum, not a fluorescence spectrum, was used for structural confirmation. The fluorescence spectrum, shown in Figure 3.1.1, had a sloping baseline and high background signals. The increased background noise was influenced, most likely, by the purity of the ionic liquid. The phosphorescent scan mode on the Perkin-Elmer LS-55 conditioned the signal by running an optimizing phototube dark current and capturing the spectra after a short time delay, Figure 3.1.2. The delay resolved the phosphorescence spectrum from the noise present in the fluorescence spectrum.

Fluorescence scans occur directly following the excitation and contain many radiative relaxations. A short delay postpones measurement until the non-descriptive radiative relaxations had occurred and only the descriptive lanthanide radiative decays remained. Descriptive lanthanides electronic transitions were selectively measured by the LS50 in the phosphorescence scan mode. The phosphorescent spectra allowed us to conclude that the europium complex is still intact in the CIL.
Figure 3.1.3: Fluorescent lifetime measurement for the [Eu(dpa)₃][TMA]₃ probe in [L-alanineC1][Tf₂N] CIL.

Lifetime measurements were completed for the europium complex in each CIL. A lifetime measurement, see Figure 3.1.3, was used to check the local environment of the lanthanide complex. In each sample the lanthanide complex was closely interacting with solvent molecules. These molecules were primarily the CILs and trace amounts of H₂O. The interaction makes it possible for energy to be transferred to the solvent molecules surrounding the complex. The energy transferred to those molecules was then allowed to decay on its own, often through non-radiative decays. The monitoring of the excited state lifetime can be used to search for differences in the water content, solvation, and other microenvironment changes around the lanthanide complex in each sample. The lifetime emission could also be characterized to the europium complex in H₂O, allowing further structural conformation.
The lifetime scans allowed for the actual lifetimes to be calculated by fitting the raw data to an exponential decay. The lifetimes varied between 1.5 ms and 2.1 ms, but did not seem to be correlated to the concentration of the europium complex. Trends would have ideally indicated differences in the microenvironments surrounding the europium complex. Water concentrations were determined throughout the study using a Carl-Fisher titration apparatus, and no correlations between lifetime and percent H₂O were found. All water content was kept low by storing the samples in a vacuum desiccator up to analysis.

Figure 3.1.4: TL (black) and CPL (red) scans for 0.3 mm [Eu(dpa)₃][TMA]₃ in [L-alanineC1][Tf₂N] CIL.
Prior to calculating the dissymmetry both a total luminescence (TL) and circular polarized luminescence (CPL) scan must be measured, examples of 0.3 mm [Eu(dpa)₃][TMA]₃ in [L-alanineC1][Tf₂N] were overlaid in Figure 3.1.4. Following this the resulting dissymmetry factor was calculated using equation 3.1.

\[ g_{em}(\lambda) = \frac{2[I_L(\lambda) - I_R(\lambda)]}{I_L(\lambda) + I_R(\lambda)} = \frac{2\Delta I(\lambda)}{I(\lambda)} \tag{3.1} \]

The circular polarized luminescence magnitude was measured as the difference in left and right rotated light intensity, \( I_L(\lambda) - I_R(\lambda) \). The total luminescence (TL) from the europium sample effectively sum of the polarized intensities, \( I_L(\lambda) + I_R(\lambda) \). Using these measurements the dissymmetry factor or \( g_{em}(\lambda) \) is calculated. The dissymmetry factor allows for the CPL output to be related with varying TL. The dissymmetry factor equalizes the difference in the scale of emission that is observed in each CIL, and was a better metric of the chiral emission composition than the CPL magnitude alone. The dissymmetry factor allowed measurement of differences in the chiral influence of the racemization equilibrium in each CIL.

Analysis of the TL and CPL scans in both Figure 3.1.4, of 0.3 mm [Eu(dpa)₃][TMA]₃ in [L-alanineC1][Tf₂N], and Figure 3.1.5, of 0.3 mm [Eu(dpa)₃][TMA]₃ in [D-alanineC1][Tf₂N], indicated small signatures of the europium complex’s lanthanide electronic transitions. Europium emits at wavelengths 588 and 595 nm (as well as 615nm, but not shown here). The TL scan, in Figure 3.1.4, had a small shoulder coming directly before the main emission. The general spectra form was consistent with spectra measured for the europium complex in other solutions. The previously discussed peaks merge together, and only one \( g_{em} \) calculation was made corresponding to the main 593 nm peak.
Figure 3.1.5: TL (black) and CPL (red) scans for 0.3 mm [Eu(dpa)$_3$][TMA]$_3$ in [D-alanineC1][Tf$_2$N] CIL.

Changes in the chiral influence by the CIL on the europium complex were seen in the CPL scan through changes in magnitude and sign. Figure 3.1.5 shows how the [D-alanineC1][Tf$_2$N] CIL affected the europium complex with the same magnitude but with opposite sign as [L-alanineC1][Tf$_2$N] in Figure 3.1.4. Also, the same europium signature was measured in Figure 3.1.5 immediately prior to the main peak. Again, changes were seen in the magnitude of both the CPL and TL scans allowing for inferences to be drawn about how the CIL changes the chirality of the europium complex in the system.
3.2 Discussing Dissymmetry Factor

Table 3.2.1 and 3.2.2 present numerical data of the CIL dissymmetry factors at changing concentration of the europium complex as shown.

Table 3.2.1: Concentration dependent $g_{em}$ values for $[\text{Eu(dpa)}_3][\text{TMA}]_3$ in each CIL.

<table>
<thead>
<tr>
<th>Concentration (mm)</th>
<th>[L-alanineC1]$^+$</th>
<th>[D-alanineC1]$^+$</th>
<th>[L-leucineC1]$^+$</th>
<th>[L-prolineC1]$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.006</td>
<td>-0.005</td>
<td>-0.003</td>
<td>0.011</td>
</tr>
<tr>
<td>0.21</td>
<td>0.01</td>
<td>-0.016</td>
<td>0.004</td>
<td>0.01</td>
</tr>
<tr>
<td>0.3</td>
<td>0.011</td>
<td>-0.016</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>0.017</td>
<td>-0.022</td>
<td>0.013</td>
<td>0.005</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0.016</td>
<td>-0.013</td>
<td></td>
<td>0.006</td>
</tr>
<tr>
<td>0.96</td>
<td>0.015</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2.2: Concentration Dependent $g_{em}$ values for $[\text{Eu(dpa)}_3][\text{TBA}]_3$ in each CIL.

<table>
<thead>
<tr>
<th>Concentration (mm)</th>
<th>[L-alanineC1]$^+$</th>
<th>[D-alanineC1]$^+$</th>
<th>[L-leucineC1]$^+$</th>
<th>[L-prolineC1]$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.004</td>
<td>-0.01</td>
<td>-0.01</td>
<td>0.016</td>
</tr>
<tr>
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<td></td>
<td>0.0025</td>
<td></td>
</tr>
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<td>0.3</td>
<td>0.008</td>
<td>-0.015</td>
<td></td>
<td>0.006</td>
</tr>
<tr>
<td>0.4</td>
<td>0.012</td>
<td>-0.007</td>
<td>0.008</td>
<td>0.011</td>
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<tr>
<td>0.5</td>
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<td></td>
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<tr>
<td>0.6</td>
<td></td>
<td></td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
[L-alanineC1]+ and [D-alanineC1]+ at varying concentration of [Eu(dpa)3][TMA]3

As shown in Figure 3.2.1, when using [L-alanineC1][Tf2N] and [D-alanineC1][Tf2N] the [Eu(dpa)3][TMA]3 dissymmetry values followed similar magnitude trends with opposite sign. The opposite sign was due to [L-alanineC1][Tf2N] and [D-alanineC1][Tf2N], the chiral influencing agent, favoring the opposite handedness. The europium complex sensed a different chirality in each CIL, which was imposed at carbon-2 of the amino acid cation (see Figure 1.1.1). The influence of the CIL solvent selectively stabilized one enantiomer of europium over the other. By stabilizing one enantiomer the 50:50 typical equilibrium ratio was perturbed and the equilibrium shifted away from an equal, racemic mixture.
Figure 3.2.1 also presented dissymmetry values at 0.4 \( \text{mm} \), showed a possible change in the interaction of the europium complex with the chiral solvent. Figure 1.2.3 showed two different symmetry axes for the europium complex. The two symmetry axes provide two possible locations for the CIL to orient. Those orientations would likely have different ability to chirally resolve the solute by the solvent. Changing the concentration of the europium complex could have changed the ordering of the CIL that surrounded the europium complex, and changed the ability for chiral perturbation. This peak in dissymmetry may suggest a change in the chiral sense mechanism seen when concentration was varied and possibly linked with the degree of chiral resolve by a specific orientations of CILs at each symmetry axes.
Figure 3.2.2: Observed dissymmetry values at varying concentration of \([\text{Eu(dpa)}_3][\text{X}]_3\) (where \([\text{X}]^+ = [\text{TMA}]^+\) (black) or \([\text{TBA}]^+\) (red)) in \([\text{L-alanineC1}][\text{Tf2N}]\).

The observed dissymmetry values increased as both concentration of \([\text{Eu(dpa)}_3][\text{TMA}]_3\) and \([\text{Eu(dpa)}_3][\text{TBA}]_3\) increased, Figure 3.2.2. Concentrations above 0.4 \(mm\) for the \([\text{Eu(dpa)}_3][\text{TBA}]_3\) solute was not measured because loss of solubility with the \([\text{TBA}]^+\) counter ion. \([\text{Eu(dpa)}_3][\text{TMA}]_3\) was still soluble after 0.4 \(mm\) concentrations. It was proposed that the difference in solubility was based on the size difference in the ammonium counter ion. \([\text{TBA}]^+\) was significantly larger than the \([\text{TMA}]^+\) cation, and may be the cause for the difference in solubility. Insolubility was visually seen and could be determined with both lifetime and phosphorescence scans.
Figure 3.2.2 showed that [Eu(dpa)$_3$][TMA]$_3$ constantly gives a larger magnitude dissymmetry factor than [Eu(dpa)$_3$][TBA]$_3$. The difference between these magnitude was possibly reflected by the size difference between [TMA]$^+$ and [TBA]$^+$. The [TMA]$^+$ counter ion was much smaller and would be less likely to ‘interrupt’ interaction of the CIL with the europium complex. With a more constant, smaller counter ion disturbance, it was assumed that there was more stabilization and therefore an increased dissymmetry factor.

The dissymmetry factor shown for [Eu(dpa)$_3$][TBA]$_3$ and [Eu(dpa)$_3$][TMA]$_3$ both were initially increasing with increasing concentration. The increase is observed for both europium complexes up to 0.4 mm. Only the [Eu(dpa)$_3$][TMA]$_3$ complex can be considered past that concentration. Following the 0.4 mm inflection point the dissymmetry factor of [Eu(dpa)$_3$][TMA]$_3$ begins to decrease. The decreasing dissymmetry value continued for the rest of the concentrations studied.
Figure 3.2.3: Dissymmetry values at varying concentrations (mm) of [Eu(dpa)$_3$][TMA]$_3$ in [L-leucineCl][Tf$_2$N] CIL.

When [L-leucineCl][Tf$_2$N] was employed as the CIL and [Eu(dpa)$_3$][TMA]$_3$ as the solute (Figure 3.2.3) the dissymmetry value trend first observed in the [L-alanineCl]$^+$ and [D-alanineCl]$^+$ CIL was observed. An increasing magnitude of the dissymmetry to 0.4 mm, and then a subsequent decrease in dissymmetry was observed at concentrations greater than 0.4 mm. In [L-leucineCl][Tf$_2$N] the [Eu(dpa)$_3$][TMA]$_3$ dissymmetry values began in the negative region when at low concentrations.

Because the dissymmetry factor changes from a negative to a positive value it is theorized that there was a change in chiral stabilization of the solution. At 0.1 mm the
CIL molecules stabilized one enantiomer of the complex, while at 0.2 mm the other was stabilized. It was concluded that the enantiomer stabilized in the CIL had changed but the actual chiral solvent had not. The same phenomenon was replicated by using the chiral enantiomers: [D-alanineC1]⁺ and [L-alanineC1]⁺. Therefore it is interesting to find that a single ionic liquid oriented itself in a manner that changed the stabilization mechanism.

![Graph](image)

**Figure 3.2.4: Dissymmetry values at varying concentrations (mm) of [Eu(dpa)₃][TBA]₃ in [L-leucineC1][Tf₂N] CIL.**

In Figure 3.2.4 [L-leucineC1][Tf₂N] CIL and [Eu(dpa)₃][TBA]₃ shows again an increase in dissymmetry was observed to a maximum concentration at 0.4 mm and then a subsequent decrease was observed. A similar trend was seen for the europium complexes in [L-leucineC1][Tf₂N], [L-alanineC1][Tf₂N] and [D-alanineC1][Tf₂N]. The
dissymmetry factor began at a negative value and moved to a positive value indicating a change in the europium enantiomer stabilized, observed with $[\text{Eu(dpa)}_3][\text{TMA}]_3$ in $[\text{L-leucineC1}][\text{Tf}_2\text{N}]$ (Figure 3.2.3).

![Graph showing dissymmetry values at varying concentrations](image)

Figure 3.2.5: Dissymmetry values at varying concentrations (mm) of $[\text{Eu(dpa)}_3][\text{TMA}]_3$ in $[\text{L-prolineC1}][\text{Tf}_2\text{N}]$ CIL.

$[\text{L-prolineC1}][\text{Tf}_2\text{N}]$ dissymmetry trends (Figure 3.2.5) were different than those observed with $[\text{L-alanineC1}][\text{Tf}_2\text{N}]$, $[\text{D-alanineC1}][\text{Tf}_2\text{N}]$, and $[\text{L-leucineC1}][\text{Tf}_2\text{N}]$. The dissymmetry value decreased until 0.4 mm and then continued to increase at higher concentrations. As the concentration of the europium complex, or the chiral effector, increased we saw a decrease in the amount of chiral influence, as proposed by Pfeiffer.
effect literature\textsuperscript{22}. The unique behavior seen by [L-prolineCl][Tf\textsubscript{2}N] could be due to structural differences compared to the other CILs. [L-prolineCl][Tf\textsubscript{2}N] has a rigid, ring structure. It may be possible for this structure to allow a unique interaction with the europium complex, unseen in the interactions with the chain alkyl groups of the other CILs.

Figure 3.2.6: Dissymmetry values at varying concentrations (mm) of [Eu(dpa)\textsubscript{3}][TBA]\textsubscript{3} in [L-prolineCl][Tf\textsubscript{2}N] CIL.

When using [L-prolineCl][Tf\textsubscript{2}N] with [Eu(dpa)\textsubscript{3}][TBA]\textsubscript{3} (Figure 3.2.6) the observed trend in the dissymmetry matched that of [Eu(dpa)\textsubscript{3}][TMA]\textsubscript{3} in [L-prolineCl][Tf\textsubscript{2}N]. Again, the dissymmetry decreased until it reached 0.3 mm, and then increased. We were unable to reach the same concentration range using [Eu(dpa)\textsubscript{3}][TBA]\textsubscript{3} as with the other
europium complex, because of decreased solubility. With the limited concentration range we were still able to measure the same general form shown by the [Eu(dpa)$_3$][TMA]$_3$ complex. Again it was possible that the difference in [L-prolineCl][Tf$_2$N] was that the amino acid methyl ester possessed a rigid structure. This may have caused the unique and different dissymmetry trend not observed in the other CILs.
3.3 Temperature Dependence

Figure 3.3.1: Total luminescence (TL) scan taken at variable temperature, indicated in the legend (given in °C), of the [Eu(dpa)₃][TMA]₃ in [L-proCl][Tf₂N].

Temperature dependence studies were completed in the consecutive order of TL scan followed by a CPL scan. The direction of temperature change was varied to investigate possible photobleaching occurrences over the long periods of exposure light. No photobleaching was observed in the samples studied. The TL scans shown in Figure 3.3.1 of [Eu(dpa)₃][TMA]₃ in [L-proCl][Tf₂N], showed a decrease in the TL with increasing temperature. It appeared that the magnitude of absolute difference between consecutive temperature changes decreased at higher temperatures. This was also observed in the CPL scan shown in Figure 3.3.2.
Figure 3.3.2: Circular polarized luminescence scans at variable temperature, indicated in the legend (given at °C), of the \([\text{Eu(dpa)}_3][\text{TMA}]_3\) in [L-proCl][Tf₂N].

CPL scans of \([\text{Eu(dpa)}_3][\text{TMA}]_3\) in [L-proCl][Tf₂N] at variable temperature were collected and results shown in Figure 3.3.2. It appeared that as the temperature increased the chiral luminescence measured by the CPL scan decreased. The change in magnitude of this decrease in CPL seemed again to slow as the temperature was increased. This same trend was shown in the TL scan in Figure 3.3.1. In both cases the decreasing emission with increasing temperature may have been due to an increase in non-radiative decay. The lifetime of initial intensity of \([\text{Eu(dpa)}_3][\text{TBA}]_3\) in [D-alanineCl][Tf₂N] (Figure 3.3.3) decreased as the temperature increased, while the lifetime was nearly
constant. Likewise, there was no observable pattern in any of the lifetime of any other CILs.

Figure 3.3.3: Lifetime spectra taken of $[\text{Eu(dpa)}_3][\text{TBA}]_3$ in $[\text{D-alanineC}1][\text{Tf}_2\text{N}]$ at variable temperature: 10°C (black), 20°C (red), 30°C (green), 40°C (blue), and 50°C (purple).
Figure 3.3.4 Dissymmetry ($g_{em}$) values at varying temperature for $[Eu(dpda)_{3}][TMA]_{3}$ in $[L$-proC1]$	ext{[Tf}_2\text{N}]$.

For all of the temperature dependent CPL and TL scans of $[Eu(dpda)_{3}][TMA]_{3}$ in $[L$-proC1]$	ext{[Tf}_2\text{N}]$, dissymmetry factors were determined (Figure 3.3.4). These dissymmetry factors have been transformed into equilibrium constants shown in equation 3.2:

$$\Delta - [Eu(dpda)_{3}]^{-3} \approx \Lambda - [Eu(dpda)_{3}]^{-3}$$

This equation can be further understood by converting the measured $g_{em}$ to enantiomeric excess values, $\eta$. The enantiomeric excess was calculated by dividing the $g_{em}$ value
\(g_{em}(\lambda)\) by the maximum possible dissymmetry for \([\text{Eu(dpa)}]_{3}^{-}\), which was \(g_{em}^\lambda(\lambda) = 0.29\).\(^{23}\) The enantiomeric excess was defined in equation 3.3:

\[
\eta = \frac{g_{em}(\lambda)}{g_{em}^\lambda(\lambda)} \tag{3.3}
\]

The value of the enantiomeric excess can be transformed into a racemization equilibrium constant, \(K_{\text{rac}}\), for \([\text{Eu(dpa)}]_{3}^{-}\), as shown in equation 3.4:

\[
K_{\text{rac}} = \frac{1 + \eta}{1 - \eta} \tag{3.4}
\]

The van't Hoff equation (equation 3.5) was used to determine the heat of reaction (\(\Delta H\)) for the racemization. A plot of the natural log of the equilibrium term, \(K_{\text{rac}}\), against the inverse temperature (\(T\)) formed the van't Hoff plot (Figure 3.3.5). The slope of the line is defined as the heat of reaction divided by the gas law constant. This same procedure was carried out for the other CIL's containing \([\text{Eu(dpa)}]_{3}^{-}[\text{TMA}]_{3}\) and were summarized in a table 3.3.

\[
\ln K_{\text{rac}} = -\frac{\Delta H}{R \frac{1}{T}} + \frac{\Delta S}{R} \tag{3.5}
\]
Figure 3.3.5: Van’t Hoff plots for [Eu(dpa)₃][TMA]₃ in labeled CIL. Note CIL labeling is reduced for legend, therefore “LprolineC1”=[L-prolineC₁][Tf₂N].

Table 3.3.1: Van’t Hoff equation for all [Eu(dpa)₃][TMA] sample in CIL, followed by the extrapolated ΔHₘₑ values.

<table>
<thead>
<tr>
<th>[Eu(dpa)₃][X]:[CIL][Tf₂N]</th>
<th>Van’t hoff equation</th>
<th>ΔHₘₑ</th>
<th>Error:</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Eu(dpa)₃][TMA]:[L-alanineC₁][Tf₂N]</td>
<td>Y=-0.23973 + (102.20684) (1/T) (R²=0.9)</td>
<td>0.85 kJ/mol</td>
<td>0.116 kJ/mol</td>
</tr>
<tr>
<td>[Eu(dpa)₃][TMA]:[D-alanineC₁][Tf₂N]</td>
<td>Y=0.15222+ (-69.62299) (1/T) (R²=0.8)</td>
<td>-0.58 kJ/mol</td>
<td>0.1010 kJ/mol</td>
</tr>
<tr>
<td>[Eu(dpa)₃][TMA]:[L-leucineC₁][Tf₂N]</td>
<td>Y=0.15055 + (-34.7148) (1/T) (R²=0.6)</td>
<td>~0 kJ/mol</td>
<td>0.1001 kJ/mol</td>
</tr>
<tr>
<td>[Eu(dpa)₃][TMA]:[L-prolineC₁][Tf₂N]</td>
<td>Y=-0.45052 + (163.44847) (1/T) (R²=0.9)</td>
<td>1.36 kJ/mol</td>
<td>0.18 kJ/mol</td>
</tr>
<tr>
<td>[Eu(dpa)₃][TBA]:[L-alanineC₁][Tf₂N]</td>
<td>0.7 kJ/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Eu(dpa)₃][TBA]:[D-alanineC₁][Tf₂N]</td>
<td>-0.7 kJ/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Eu(dpa)₃][TBA]:[L-leucineC₁][Tf₂N]</td>
<td>0.0 kJ/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Eu(dpa)₃][TBA]:[L-prolineC₁][Tf₂N]</td>
<td>0.7 kJ/mol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The $\Delta H_{\text{rac}}$ of [L-prolineC1][Tf$_2$N] was an order of magnitude greater than the other heat of reaction values. The large heat of reaction could be attributed to [L-prolineC1]$^+$ rigid ring structure. The ligand arms of the europium complex could be wedged or locked in place with the rigid ring, similar to the hydrophobic interactions hypothesized by Brittain$^{24}$. That “lock” could have provided a barrier to racemization. [L-prolineC1][Tf$_2$N] appeared to provide resistance to the racemization of europium, giving a positive $\Delta H$.

Another interesting finding was the $\Delta H$ of the europium complex when in [L-leucineC1][Tf$_2$N]. Kroupa et al. cited the unique environment that [L-leucineC1][Tf$_2$N] created for the europium racemization, as the temperature didn’t effect the [Eu(dpa)$_3$][TBA]$_3$ racemization equilibrium constant. Within the error the [L-leucineC1][Tf$_2$N] CIL showed a $\Delta H_{\text{rac}} = 0$ kJ/mol. This thesis reassures that [L-leucineC1][Tf$_2$N] does not enthalpically favor one enantiomer of [Eu(dpa)$_3$][TMA]$_3$ over the other, as the slope of the van’t Hoff plot was 0.

It should be noted that the coefficient of determination ($R^2$), shown in Table 3.3.1, for these van’t Hoff plots were poor except for [Eu(dpa)$_3$][TMA]$_3$ in [L-prolineC1][Tf$_2$N]. The data should be collected in smaller temperature intervals to ensure the temperature dependence.
Because of this future studies should also look into how the counter ion ([TMA]$^+$ and [TBA]$^+$) effect the perturbation of the europium probe. It may be possible to use some computer modeling to answer the role of the counter ion. Additional chiral environment molecules may create a tailored chiral sense in the europium complex? If this is the case it may be possible to create tailored chiral affecting liquids.

3.4 Conclusion

CILs have the ability to influence the racemization equilibrium of lanthanide complexes, [Eu(dpa)$_3$][TMA]$_3$ and [Eu(dpa)$_3$][TBA]$_3$. Previously it was found that these influences were temperature dependent, showing an enthalpic effect. In this work it was determined that there was also a concentration dependence. The concentration dependence of the europium complex in [L-prolineCl][Tf$_2$N] and [L-leucineCl][Tf$_2$N] were unique when compared to the other CILs, and it was proposed that structural differences may be the cause of this difference.

Van’t Hoff determination of $\Delta H_{\text{rac}} = 1.141$ kJ/mol and 0.0 kJ/mol for [Eu(dpa)$_3$][TMA]$_3$ in [L-prolineCl][Tf$_2$N] and [L-leucineCl][Tf$_2$N] respectively. The large heat of racemization observed for the solute in [L-prolineCl][Tf$_2$N] may be due to the rigid ring structure. The structure may allow intermolecular bonds strong enough to influence the chirality of the solute. That strong enthalpic motivation may explain the unique concentration dependence observed in the dissymmetries. The weak intermolecular enthalpic motivation seen for the solute in [L-leucineCl][Tf$_2$N] could describe the unique concentration dependence also. For [L-leucineCl][Tf$_2$N], it was proposed that the $\Delta H_{\text{rac}} =$
0 kJ/mol, meaning that the intermolecular bonding between one enantiomer and the CIL molecules was no stronger than the CIL with the other enantiomer. This proposes that any change in the racemization is enacted from the change in entropy based on the concentration.
4 Appendix

4.1 Emission Spectra

Figure 4.1.1: Fluorescence scan of 0.4 mm [Eu(dpa)₃][TMA]₃ in [D-alanineCl][Tf₂N]. Slit width: 5.
Figure 4.1.2: Phosphorescence scan of 0.6 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-alanineC1][Tf$_2$N]. Slit width: 2.5.

Figure 4.1.3: Phosphorescence scan of 0.6 mm [Eu(dpa)$_3$][TMA]$_3$ in [D-alanineC1][Tf$_2$N]. Slit width: 5.
Figure 4.1.3: Phosphorescence scan of 0.4 mm [Eu(dpa)_3][TMA]_3 in [D-alanineCl][Tf_2N]. Slit width: 5.

Figure 4.1.4: Phosphorescence scan of 0.3 mm [Eu(dpa)_3][TBA]_3 in [L-leucineCl][Tf_2N]. Slit width: 2.5.
Figure 4.1.5: Phosphorescence scan of 0.6 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-leucineCl][Tf$_2$N]. Slit width: 2.5.

Figure 4.1.6: Phosphorescence scan of 0.1 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-prolineCl][Tf$_2$N]. Slit width: 2.5.
Figure 4.1.7: Phosphorescence scan of 0.2 mm [Eu(dpa)₃][TMA]₃ in [L-prolineC1][Tf₂N]. Slit width: 2.5.
Figure 4.1.8: Phosphorescence scan of 0.3 mm $[\text{Eu(dpa)}_3][\text{TMA}]_3$ in $[\text{L-prolineCl}][\text{Tf}_2\text{N}]$. Slit width: 2.5.

Figure 4.1.9: Phosphorescence scan of 0.4 mm $[\text{Eu(dpa)}_3][\text{TMA}]_3$ in $[\text{L-prolineC1}][\text{Tf}_2\text{N}]$. Slit width: 2.5.
4.2 Lifetime Spectra

Figure 4.2.1: Lifetime scan of 0.1 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-alanineC1][Tf$_2$N].

Figure 4.2.2: Lifetime scan of 0.2 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-alanineC1][Tf$_2$N].
Figure 4.2.3: Lifetime scan of 0.3 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-alanineCl][Tf$_2$N].

Figure 4.2.4: Lifetime scan of 0.4 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-alanineCl][Tf$_2$N].
Figure 4.2.5: Lifetime scan of 0.4 mm [Eu(dpa)$_3$][TBA]$_3$ in [L-alanineCl][Tf$_2$N].

Figure 4.2.6: Lifetime scan of 0.2 mm [Eu(dpa)$_3$][TMA]$_3$ in [D-alanineCl][Tf$_2$N].
Figure 4.2.7: Lifetime scan of 0.3 mm [Eu(dpa)$_3$][TMA]$_3$ in [D-alanineCl][Tf$_2$N].

Figure 4.2.8: Lifetime scan of 0.4 mm [Eu(dpa)$_3$][TMA]$_3$ in [D-alanineCl][Tf$_2$N].
Figure 4.2.9: Lifetime scan of 0.6 mm [Eu(dpa)$_3$][TMA]$_3$ in [D-alanineCl][Tf$_2$N].

Figure 4.2.10: Lifetime scan of 0.1 mm [Eu(dpa)$_3$][TBA]$_3$ in [D-alanineCl][Tf$_2$N].
Figure 4.2.11: Lifetime scan of 0.1 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-prolineC1][Tf$_2$N].

Figure 4.2.12: Lifetime scan of 0.2 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-prolineC1][Tf$_2$N].
Figure 4.2.13: Lifetime scan of 0.3 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-prolineCl][Tf$_2$N].

Figure 4.2.14: Lifetime scan of 0.4 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-prolineCl][Tf$_2$N].
Figure 4.2.15: Lifetime scan of 0.1 mm [Eu(dpa)₃][TBA]₃ in [L-prolineCl][Tf₂N].

Figure 4.2.16: Lifetime scan of 0.3 mm [Eu(dpa)₃][TBA]₃ in [L-prolineCl][Tf₂N].
Figure 4.2.17: Lifetime scan of 0.2 mm $[\text{Eu(dpa)₃}][\text{TMA}]_3$ in [L-leucineCl][Tf₂N].

Figure 4.2.18: Lifetime scan of 0.2 mm $[\text{Eu(dpa)₃}][\text{TBA}]_3$ in [L-leucineC1][Tf₂N].
Figure 4.2.19: Lifetime scan of 0.6 mm [Eu(dpa)$_3$][TBA]$_3$ in [L-leucineC1][Tf$_2$N].
4.3 Total Luminescence and Circular Polarized Luminescence Spectra

Figure 4.3.1: TL/CPL overlay of 0.1 mm [Eu(dpa)_3][TMA]_3 in [L-alanineC1][Tf_2N].

Figure 4.3.2: TL/CPL overlay of 0.2 mm [Eu(dpa)_3][TMA]_3 in [L-alanineC1][Tf_2N].
Figure 4.3.3: TL/CPL overlay of 0.3 mm [Eu(dpa)₃][TMA]₃ in [L-alanineC1][Tf₂N].

Figure 4.3.4: TL/CPL overlay of 0.4 mm [Eu(dpa)₃][TMA]₃ in [L-alanineC1][Tf₂N].
Figure 4.3.5: TL/CPL overlay of 0.6 mm [Eu(dpa)₃][TMA]₃ in [L-alanineC1][Tf₂N].

Figure 4.3.6: TL/CPL overlay of 0.1 mm [Eu(dpa)₃][TBA]₃ in [L-alanineC1][Tf₂N].
Figure 4.3.7: TL/CPL overlay of 0.2 mm [Eu(dpa)$_3$][TBA]$_3$ in [L-alanineC1][Tf$_2$N].

Figure 4.3.8: TL/CPL overlay of 0.3 mm [Eu(dpa)$_3$][TBA]$_3$ in [L-alanineC1][Tf$_2$N].
Figure 4.3.9: TL/CPL overlay of 0.4 mm [Eu(dpa)_3][TBA]_3 in [L-alanineC1][Tf_2N].

Figure 4.3.10: TL/CPL overlay of 0.2 mm [Eu(dpa)_3][TMA]_3 in [D-alanineC1][Tf_2N].
Figure 4.3.11: TL/CPL overlay of 0.3 mm [Eu(dpa)_3][TMA]_3 in [D-alanineC1][Tf_2N].

Figure 4.3.12: TL/CPL overlay of 0.4 mm [Eu(dpa)_3][TMA]_3 in [D-alanineC1][Tf_2N].
Figure 4.3.13: TL/CPL overlay of 0.5 mm [Eu(dpa)₃][TMA]₃ in [D-alanineCl][Tf₂N].

Figure 4.3.14: TL/CPL overlay of 0.6 mm [Eu(dpa)₃][TMA]₃ in [D-alanineCl][Tf₂N].
Figure 4.3.15: TL/CPL overlay of 0.1 mm $\text{Eu(dpa)}_3\text{TBA}_3$ in $\text{D-alanineC}[\text{Tf}_2\text{N}]$.

Figure 4.3.16: TL/CPL overlay of 0.1 mm $\text{Eu(dpa)}_3\text{TMA}_3$ in $\text{L-prolineC}[\text{Tf}_2\text{N}]$. 
Figure 4.3.17: TL/CPL overlay of 0.2 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-prolineC1][Tf$_2$N].

Figure 4.3.18: TL/CPL overlay of 0.3 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-prolineC1][Tf$_2$N].
Figure 4.3.19: TL/CPL overlay of 0.4 mm [Eu(dpa)₃][TMA]₃ in [L-prolineCl][Tf₂N].

Figure 4.3.20: TL/CPL overlay of 0.6 mm [Eu(dpa)₃][TMA]₃ in [L-prolineCl][Tf₂N].
Figure 4.3.21: TL/CPL overlay of 0.1 mm [Eu(dpa)$_3$][TBA]$_3$ in [L-prolineC1][Tf$_2$N].

Figure 4.3.22: TL/CPL overlay of 0.3 mm [Eu(dpa)$_3$][TBA]$_3$ in [L-prolineC1][Tf$_2$N].
Figure 4.3.23: TL/CPL overlay of 0.4 mm [Eu(dpa)₃][TBA]₃ in [L-prolineC₁][Tf₂N].

Figure 4.3.24: TL/CPL overlay of 0.1 mm [Eu(dpa)₃][TMA]₃ in [L-leucineC₁][Tf₂N].
Figure 4.3.25: TL/CPL overlay of 0.2 mm [Eu(dpa)_3][TMA]_3 in [L-leucineCl][Tf_2N].

Figure 4.3.26: TL/CPL overlay of 0.4 mm [Eu(dpa)_3][TMA]_3 in [L-leucineCl][Tf_2N].
Figure 4.3.27: TL/CPL overlay of 0.6 mm [Eu(dpa)$_3$][TMA]$_3$ in [L-leucineC1][Tf$_2$N].

Figure 4.3.28: TL/CPL overlay of 0.2 mm [Eu(dpa)$_3$][TBA]$_3$ in [L-leucineC1][Tf$_2$N].
Figure 4.3.29: TL/CPL overlay of 0.3 mm [Eu(dpa)₃][TBA]₃ in [L-leucineC1][Tf₂N].

Figure 4.3.30: TL/CPL overlay of 0.4 mm [Eu(dpa)₃][TBA]₃ in [L-leucineC1][Tf₂N].
Figure 4.3.31: TL/CPL overlay of 0.6 mm [Eu(dpa)$_3$][TBA]$_3$ in [L-leucineC1][Tf$_2$N].
4.4 Temperature Dependent Data

Figure 4.4.1: CPL scan of [Eu(dpa)₃][TMA]₃ in [L-alanineC1][Tf₂N] at variable temperature

Figure 4.4.2: CPL scan of [Eu(dpa)₃][TMA]₃ in [D-alanineC1][Tf₂N] at variable temperature
Figure 4.4.3: CPL scan of [Eu(dpa)$_3$][TMA]$_3$ in [L-prolineC1][Tf$_2$N] at variable temperature.

Figure 4.4.4: CPL scan of [Eu(dpa)$_3$][TMA]$_3$ in [L-leucineC1][Tf$_2$N] at variable temperature.
Figure 4.4.5: TL scan of [Eu(dpa)$_3$][TMA]$_3$ in [L-alanineCl][Tf$_2$N] at variable temperature.

Figure 4.4.6: TL scan of [Eu(dpa)$_3$][TMA]$_3$ in [D-alanineC1][Tf$_2$N] at variable temperature.
Figure 4.4.7: TL scan of [Eu(dpa)₃][TMA]₃ in [L-prolineCl][Tf₂N] at variable temperature.

Figure 4.4.8: TL scan of [Eu(dpa)₃][TMA]₃ in [L-leucineCl][Tf₂N] at variable temperature.
Figure 4.4.9: \( g_{em} \) plot of \([\text{Eu(dpa)}_3][\text{TBA}]_3\) in \([\text{L-alanineCl}][\text{Tf}_2\text{N}]\) at variable temperature.

Figure 4.4.10: \( g_{em} \) plot of \([\text{Eu(dpa)}_3][\text{TBA}]_3\) in \([\text{D-alanineCl}][\text{Tf}_2\text{N}]\) at variable temperature.
Figure 4.4.11: $g_{em}$ plot of [Eu(dpa)$_3$][TBA]$_3$ in [L-prolineCl][Tf$_2$N] at variable temperature.

Figure 4.4.12: $g_{em}$ plot of [Eu(dpa)$_3$][TBA]$_3$ in [L-leucineCl][Tf$_2$N] at variable temperature.
Figure 4.4.13: van’t Hoff plot of \([\text{Eu}(dpa)_3][\text{TBA}]_3\) in \([\text{L-alanineCl}][\text{ Tf}_2\text{N}]\).

Figure 4.4.14: van’t Hoff plot of \([\text{Eu}(dpa)_3][\text{TBA}]_3\) in \([\text{D-alanineCl}][\text{Tf}_2\text{N}]\).
Figure 4.4.15: van't Hoff plot of [Eu(dpa)₃][TBA]₃ in [L-prolineCl][Tf₂N].

Figure 4.4.16: van't Hoff plot of [Eu(dpa)₃][TBA]₃ in [L-leucineCl][Tf₂N].
References