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LIGHT-ACTIVATED RARE EARTH CATION INTERPHASE
TRANSPORT

By

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ABSTRACT OF THE THESIS

Light-activated Rare Earth Cation interphase transport

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We design a method to achieve rare earth cation interphase transport under the control of external light. Photoisomerizable molecules (PMs) obtained via a one-step synthesis routine are used to capture rare earth cations utilizing cavity-size-fit theory and transport the ion between the two different phases. Under the influence of light, the PMs are capable of switching between “*trans*-” and “*cis*-” isomers, resulting in a change of chemical polarity. Meanwhile, the size-fit crown ether on the PMs can capture desired rare earth elements to transport the cations between two different phases. In our research, we used benzo-15-crown-5 ether (B15C5) as PMs to manipulate the distribution of trivalent Europium cations (Eu^{3+}) in different phases. The complex formed by *trans*-PMs and Eu^{3+} went to different solvent with the

configuration changing to the “*cis*-” one under the control of externally applied ultraviolet (UV) light. Concentration distribution is measured by photoluminescence (PL) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The transport efficiency of PMs to the desired Eu^{3+} cations reaches 30% after the process reaches equilibrium within 100 min; *cis*-PMs have greater affinity to aqueous solutions after UV light exposure. PL intensity is linearly proportional ($R^2 > 0.999$) to low concentrations of Eu^{3+} . This work used a simple synthesis method to demonstrate PMs has the capability to capture and transport rare earth ion between different phases. It provided the theoretical basis for further research on rare earth elements recovery from the industrial wastes.

Acknowledgements

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Chapter 1: Introduction

1.1 Background on Rare Earths

There are 17 elements that are defined as rare earth elements by the IUPAC in the periodic table: the fifteen lanthanides as well as yttrium and scandium¹. Rare earth elements are distributed all over the world in low concentrations because of their geochemical properties². In 1787, the first rare earth mineral was discovered as the black mineral “Ytterbite” in the village of Ytterby in Sweden³. Rare earth elements were found to have many applications in technology such as superconductors, lasers, and even cancer treatment. Because of their high demand in many fields, the exploitation of rare earth elements has risen sharply since the 1950s. From the 1950s till the 1980s, India, Brazil, South Africa, and USA were the world’s leading producers⁴. China began to dominate the market beginning in the 1980s with almost 95% of the production of rare earth metals coming from Inner Mongolia⁵. However, the Chinese government announced quotas on rare earth exports in 2009 and global prices of rare earths increased beyond that of gold⁶.

1.2 Background on Ion Transport

The growing demand of rare earth elements raises concerns of their supply. Scientists began to develop methods to recover rare earth cations from alternative sources. Besides the excavation of raw minerals, some rare earth elements also exist in the waste streams of industrial operations and mining. These waste streams are overlooked as useful sources for the extraction of precious metals. The concentration

of cations in these streams varies from hundreds of parts per million (ppm) to several weight percent. Using precipitation methods to extract the desired cations from aqueous solutions is difficult. We have to avoid the precipitation of undesirable cations and eliminate the adsorption of other species onto the surface of the precipitate. Meanwhile, precipitating the desired cations from the aqueous solutions must be subjected to unit operations such as centrifugation or filtration followed by washing the precipitate of the adsorbed species. This process discharges lots of valuable chemical species into the waste stream resulting in low recovery. Ion exchange resins could provide an alternative method since they can be fine-tuned to extract the ion of interest from solution by passing the solution over a resin bed⁷. The trapped ion in the bed can be isolated by a second washing step where a concentrated solution of a different ion displaces the ion captured by the resin into the washing solution. However, the lifetime of the resin will degrade due to multiple washing steps and contaminating by undesired ions. A more efficient method which can continuously recover the valuable metals from the solutions needs to be developed, especially for waste streams derived from mining or other industrial operations.

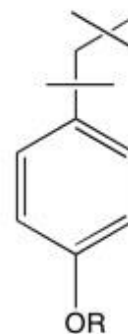
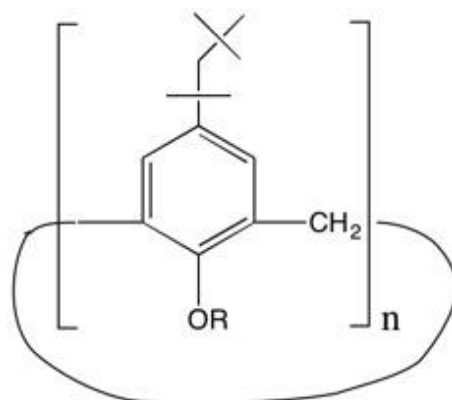
Cations are known to be transported through membranes with the aid of antibiotics or synthesized macrocyclic polyesters⁸. In the 1970s, Kobuke⁹, Kirch, and Lehn¹⁰ reported that the best way to transport the ion through a liquid membrane is to use a ligand that has a moderately stable structure rather than forming a stable complex. This is because a stable complex captures the ion and will not release the ion.

In the 1980s, Shinkai *et al.*⁸ demonstrated the extraction and transport of alkali metals across a liquid membrane under light irradiation. In their system, the crown ether was used as carriers for ion extraction and the transport process was fulfilled by the structure switch of the complex. The crown ether formed the stable complex with the large alkali metal cation with the order of $\text{Rb}^+ > \text{Cs}^+ > \text{K}^+ > \text{Na}^+$. **Table 1** shows the stability and isomer rate of the complex. They demonstrated that the thermal reaction from the “*cis*-” isomer to “*trans*-” was suppressed.

Then, a novel molecule called calixarenepolyol and its derivatives attracted attention since they could serve as a stable structure in the complex^{11, 11b, 12}. These compounds were considered ion specific extractants due to their recognition ability by introducing the ion-exchange functional group¹³. Izatt *et al.*¹⁴, Yoshida *et al.*¹⁵, and Nagasaki *et al.*¹⁶ reported the extraction of transition metal ions. However, those calixarene derivatives had poor solubility in organic diluents due to the *t*-butyl groups¹³. So, in 1995, Seiji Shinkai¹³ reported another class of the calixarene derivatives with longer branched alkyl chains to improve lipophilicity. **Figure 1** shows the designed structures of the novel extractants. The new synthesized compounds had a higher solubility than earlier ones and the extractability and solubility were not dependent on the pH of the organic diluent. Meanwhile, the structural difference of the cyclic extractants influenced the extractability by giving a higher strain than the acyclic one, which led to a contraction of the extractability. So for rare earth extraction, the order of the extractability among these designed compounds is $\mathbf{3_6} > \mathbf{3_3} > \mathbf{3_4} > \mathbf{3_1}$ ¹³, while the

ring size of the calixarene did not affect the selectivity of the rare earth in this system.

However, the synthesis of these compounds took a long time, ranging from 9 to 23 h under stringent conditions of a nitrogen atmosphere and high temperature, in addition to a complicated post-treatment process.



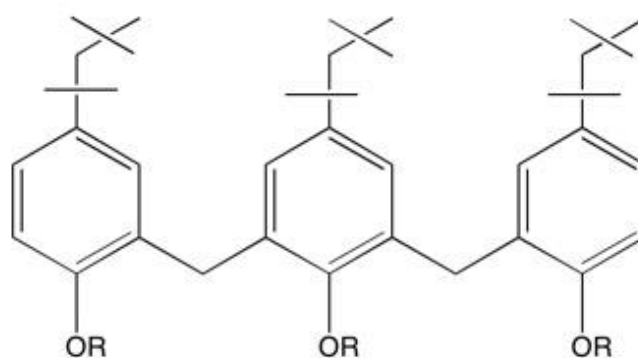
1_n: R=H

2_n: R=CH₂COOCH₂CH₃

3_n: R=CH₂COOH

(n=4, 6)

3₁=CH₂COOH



1₃: R=H

2₃: R=CH₂COOCH₂CH₃

3₃: R=CH₂COOH

Figure 1. Chemical structures of the extractants

Table 1. Stability and isomer rate of the cation complex

Cation	cis/trans	k_{rel}
none	52/48	1.00
Na+	58/42	0.96
K+	64/36	0.41
Rb+	98/2	0.13
Cs+	89/11	0.18

1.3 Brief Summary of Photoisomerizable Molecules

Photoisomerization is a property of molecules where the molecular structure changes under the influence of light, resulting in the change of macroscopic properties of the molecules, such as aggregation, conductance, and chemical polarity. In 1867, Fritzsche, Russew, and Hecht¹⁷ discovered a phenomenon in which the bleaching of an orange colored tetracene solution in daylight re-colored at night. Since then, a family of compounds have been synthesized that change color under light^{17,18}. However, it was not until the 1950s that Hirshberg and Fischer¹⁷ reported comprehensive mechanistic and synthetic studies. Research on photoisomerizable molecules had a rapid growth in the 1980s when scientists overcame the problem of photodegradation by developing fatigue-resistant spiropyrans and diarylethenes. One of the early applications of photochromes was colored sunglasses and was later expanded to optical switches, memory, and variable electrical currents to meet the requirements for an all-optical computer¹⁷. They also fabricated photoresponsive polymers and other materials with external properties that can be controlled by light. **Figure 2**¹⁷ shows some of the most popular classes.

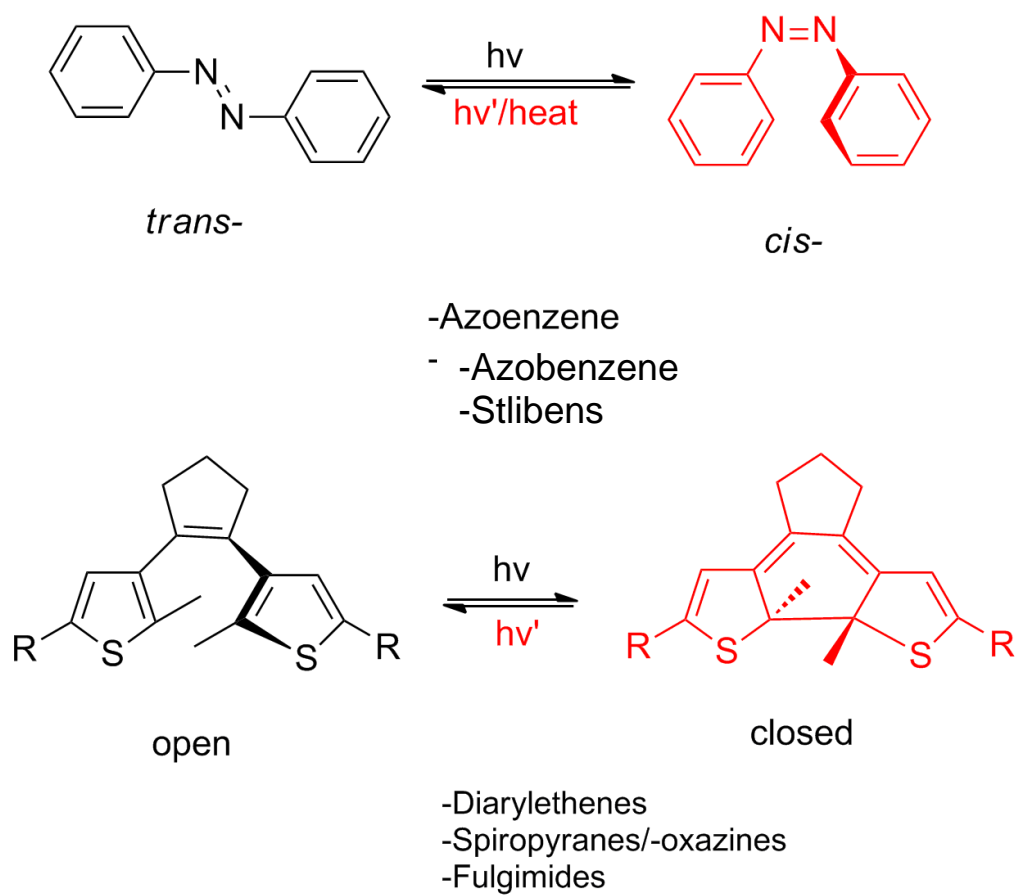


Figure 2. Photoswitch molecules: the structures switch between two independently reversible states, which affect the macroscopic properties (shape, aggregation, and conductance)

One aspect of the research is to use the photoisomerizable host molecules to achieve the transport of ions between two different phases. These molecules comprise a photoisomerizable moiety and a host moiety, where the photoisomerizable moiety has two states: the first state has an affinity for one phase while the other state is more stable in the second phase. The light-induced transformation between the two states lead to property changes such as chemical polarity and solubility¹⁹. Molecules that have photoisomerizable moieties contain at least one double-bonded functional group that let molecules switch between the corresponding “*cis*-” and “*trans*-” isomers. For a variety of reasons, the “*trans*-” isomer is much more stable than the “*cis*-” isomer, since the “*cis*-” isomer has a distorted configuration and its electron density is less delocalized than that of the “*trans*-” configuration²⁰.

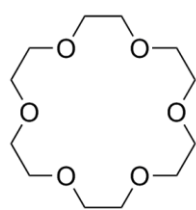
Azobenzene is photoisomerizable between the “*trans*-” and “*cis*-” isomers. The configuration switch can be achieved by using ultraviolet light, which corresponds to the energy gap of the $\pi - \pi^*$ (S2 state) transition, for *trans*- to *cis*- conversion. Irradiation with blue light, which is equivalent to that of the $n - \pi^*$ (S1 state) transition, is used for the “*cis*-” to “*trans*-” isomerization²¹. The “*trans*-” isomer is approximately 50 kJ/mol more stable than the “*cis*-” isomer, with a 200 kJ/mol energy barrier to the photoisomerization between the “*trans*-” and “*cis*-”. Thus, the “*cis*-” isomer will convert back to the “*trans*-” configuration with heating. The “*cis-trans*” isomerization of the azobenzene moiety represents a model photochemical process in which one stereoisomer is thermodynamically favored and the other stereoisomer is

photochemically favored^{21b}.

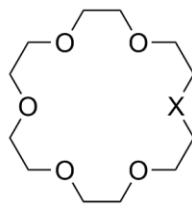
1.4 Characteristic(s) of Captured Metals

The “size-fit” principle was first reported by Pedersen in 1968²². It presented a relationship between the host molecules and the captured cations. Photoisomerizable host molecules had a special selectivity to the cations, which was determined by the cavity size and shape of host molecules. The thermodynamic stability is decided by the interaction between the cavity and the ion. The largest stability constant is achieved if the size of ion approaches but does not exceed the size of the host cavity. If the cations are either too large or too small to fit within a cavity, complexes may still form. In this case, other factors such as cation charge, cation type, ligand donor atom type, and solvent are important²².

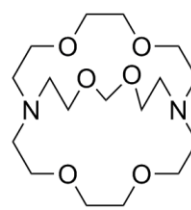
The host moiety is selected from macrocyclic molecules, chelating agents, complexing agents, and/or metal organic frameworks. Macrocyclic molecules can be independently selected from crown ethers, cryptates, cryptands, and cyclodextrins²³ due to their varying cavity sizes. **Figure 3** shows the typical macrocyclic molecules. Chelating agents can also be carboxylates (e.g., acetate, stearate, acrylates, etc.).



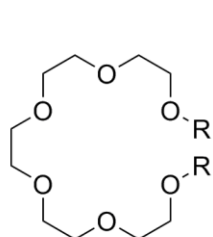
Crown ether



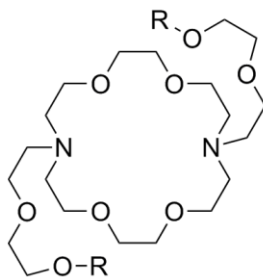
Coronand



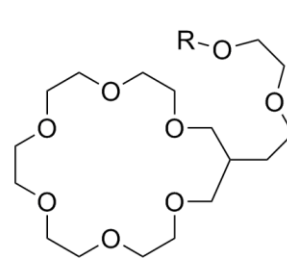
Crytand



Podand



N-Pivot Lariat



C-Pivot Lariat

Figure 3. Typical macrocyclic molecules²³

Examples²⁴ have shown that specific crown ethers fit specific alkali metals. For example, a crown-4 host selectively binds Li^+ while a 15-crown-5 host selectively binds Na^+ and forms a 1:1 cation/crown complex. Further, a crown-6 system complexes selectively with K^+ forming a 1:2 cation/crown complex²⁵. **Tables 2 and 3** show cation diameters with corresponding host cavity sizes²⁴. The ionic diameter of the rare earth cation Eu^{3+} is around 2.00 Å. 15-crown-5 is of suitable cavity size and can be used to capture Eu^{3+} .

Table 2. Group I and II metal cation diameters²⁶

Group I	Ionic diameter (Å)	Group II	Ionic diameter (Å)
Li	1.20	Be	0.62
Na	1.90	Mg	1.30
K	2.66	Ca	1.98
Rb	2.96	Sr	2.26
Cs	3.34	Ba	2.70

Table 3. Host cavity sizes of some crown ether and cryptands

Crown ether	Cavity Diameter (Å)²⁷	Crown ether	Cavity Diameter (Å)²⁸
14-crown-4	1.2-1.5	[1.1.1] cryptand	1.0
15-crown-5	1.7-2.2	[2.1.1] cryptand	1.6
18-crown-6	2.6-3.2	[2.2.1] cryptand	2.2
21-crown-7	3.4-4.3	[2.2.2] cryptand	2.8
		[3.3.2] cryptand	4.2
		[3.3.3] cryptand	4.8

1.4 Overview of Research Plan

An azobenzene crown ether will be used as the photoisomerizable molecule (PM) formed via a one-step synthesis route. A functional group with an optical response property is created in the process. Compared to previous works, this synthesis method does not require complicated and stringent reaction conditions. We also select a rare earth element that also optically responds to the excitation light used to isomerize the PM in order to simultaneously conduct photoluminescence spectroscopy. We will observe how rare earth concentration changes between the two different solvent phases with the aid of the PMs under the influence of external high-power UV light. Optically active Europium was chosen along with 15-crown-5 ether as the cation host moiety to investigate the transport properties of the PM, and assess whether the photoisomerization method has potential as an effective method to recovery rare earths from industrial waste. **Figure 4** shows the transport process of PMs under the control of high power UV light.

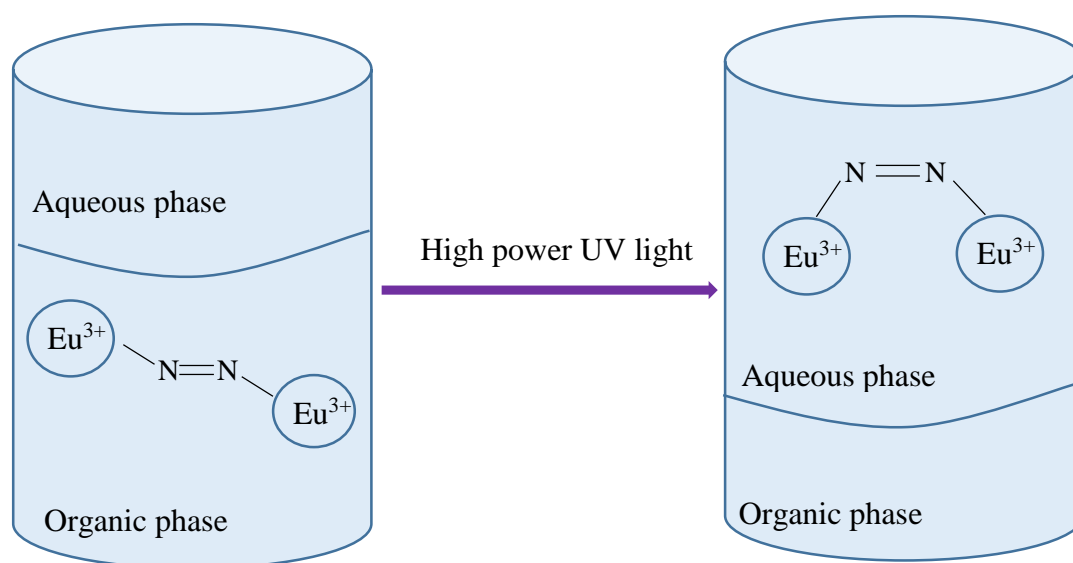


Figure 4. Cation transport process

Chapter 2: Experimental Methods

In the experiment, the photoisomerizable molecules (PMs) were synthesized and characterized by using nuclear magnetic resonance (NMR). The ability of PMs to manipulate the distribution of Eu^{3+} in different phases under external UV light was investigated by determining changes in concentration. Concentration changes were verified by the photoluminescence spectroscopy and inductively coupled plasma optical emission spectroscopy (ICP-OES).

2.1 Synthesize the PMs: Benzo-15-crown-5 (compound 1)

Chemicals: 4'-nitrobenzo-15-crown-5 (99%), Sodium hydroxide (NaOH, 98%), Potassium hydroxide (KOH, 85%), Chloroform (CHCl_3 , HPLC grade), hydrochloric acid (HCl, aqueous 36%), and Acetic acid (CH_3COOH , glacial) were purchased from Alfa Aesar (Ward Hill, MA, USA). Zinc powder (99%) was purchased from Sigma Aldrich (St. Louis, MO, USA).

Instruments: Handle UV lamp UVG-54, 254 nm was purchased from VWR International (Radnor, PA, USA)

Method: 4'-nitrobenzo-15-crown-5 (4 g) was dissolved in toluene (30 mL) and NaOH (1 g) was dissolved in water (1 mL). Aforementioned solutions were mixed and heated to 80 °C under vigorous stirring; solutions became yellow during this process. Then, Zinc powder (4 g) and KOH (16 g) were added into the heated, 80 °C solution; the solution turned black. The hot black solution was filtered after 5 h.

Methanol (30 mL) was used to wash the residual. Air was introduced into the filtrate by exposing the solution to the ambient in a hood for 4 hours. The reaction was quenched and neutralized by adding concentrated HCl. The resultant filtrate was separated and purified by column chromatography and thin layer chromatography (TLC). The mobile phase was a 9:1 mixture of CHCl_3 and CH_3COOH . The developing solvent was a 2:1 mixture of CHCl_3 and CH_3COOH . A low power portable UV lamp was used to trace the TLC process. **Figure 5** shows the synthesis procedure.

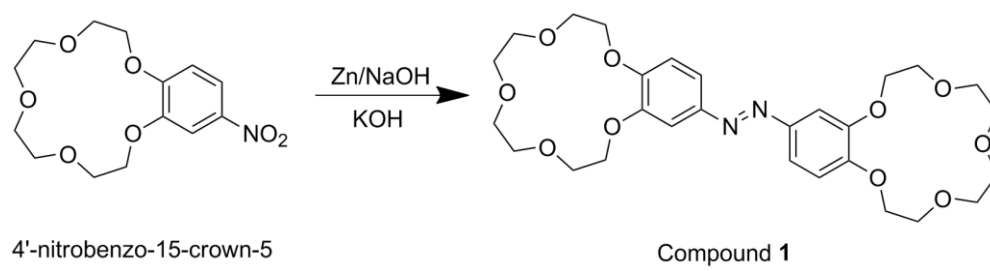


Figure 5. Synthesis routine of the benzo-15-crown-5

2.2 Solvent Extraction

Chemicals: Europium (III) nitrate ($\text{Eu}(\text{NO}_3)_3$, 99.9%) and *o*-dichlorobenzene (99%) were purchased from Alfa Aesar (Ward Hill, MA).

Instruments: Four-sided transparent standard cuvette, 12×12×45 mm (Fisher Scientific, Pittsburgh, PA, USA)

$\text{Eu}(\text{NO}_3)_3$ was used as the source of Eu^{3+} . Eu^{3+} solutions (0.001 M) were prepared and mixed with the organic solvent *o*-dichlorobenzene (DCB) (5 mL) in equal volumes. Mixed solutions were kept stirring at room temperature for 10, 40, 100 min, and one sample was left overnight; all mixed solutions were turbid. Solutions separated into two phases once stirring was removed. The upper aqueous solution (3 mL) was withdrawn and placed into standard cuvette for photoluminescence (PL) measurement.

2.3 Photoluminescence Measurement

Instruments: Edinburgh Instruments FLS 920 Photospectrometer fitted with Hamamatsu R928 photomultiplier tube, 450 Watt Xe lamp (Livingston, UK). 100 watt Black Ray B-100A High intensity UV lamp (Los Angeles, CA, USA)

2.3.1 Emission Intensity vs. Eu^{3+} Concentration

Eu^{3+} solutions were prepared with concentrations varying from 10^{-2} to 10^{-4} M. Each solution (3 mL) was placed into a standard cuvette. The photoluminescence spectra of

Eu^{3+} were measured under the following conditions: excitation wavelength $\lambda = 393$ nm, dwell time $t = 0.50$ s, the emission spectrum region was from 550.00 to 720.00 nm, excitation band width was 4.00 nm and emission band width was 2.00 nm.

2.3.2 Procedure Blank Calibration

Equal volumes of *o*-dichlorobenzene and Eu^{3+} (0.001 M) solutions were mixed, and kept stirring at room temperature for 10, 40, 100, and 1200 min. After stopping stirring, the solution separated into two phases and the upper aqueous solution (3 mL) was withdrawn into the standard cuvette and used above PL conditions to record the emission spectrum of Eu^{3+} .

2.3.3 Eu^{3+} Ion Extraction and Transfer

Control:

Compound **1** was dissolved in *o*-dichlorobenzene to prepare the organic ligand extraction solution (3.50×10^{-4} M). The equal volumes of *o*-dichlorobenzene containing **1** (3.50×10^{-4} M) and the ionic solution containing Eu^{3+} (0.001 M, 5 mL) were mixed and kept stirring at room temperature for 10, 40, 100, and 1200 min. The mixed solutions separated into two phases after stopping stirring. The upper aqueous solution (3 mL) was transferred into a standard cuvette and used above PL conditions to record the emission spectrum of Eu^{3+} .

Photoisomerization:

The aforementioned solution was placed into a cuvette and irradiated with a 100 watt mercury UV lamp at a distance of 10 cm. The mixture was kept stirring at room temperature for 10, 40, 100, and 1200 min. After stopping stirring, the solution

separated into two phases. The upper aqueous solution (3 mL) was withdrawn into the standard cuvette and used above PL conditions to record the emission spectrum of Eu^{3+} at each time point.

2.4 Inductively Coupled Plasma Measurement

Instruments: Perkin Elmer Optima 7300 DV Inductively Coupled Plasma Optical Emission Spectrometer (Waltham, MA, USA)

Chemicals: Europium (III) nitrate ($\text{Eu}(\text{NO}_3)_3$, 99.9%) was purchased from Alfa Aesar (Ward Hill, MA, USA)

$\text{Eu}(\text{NO}_3)_3$ hexahydrate (0.5 g) was dissolved in water (50 mL) to prepare the 10,000 ppm Eu^{3+} standard solution. 1,000 ppm of the Eu^{3+} standard solution was prepared by withdrawing 5 mL of the 10,000 ppm standard and diluting it to 50 mL. The other Eu^{3+} standard solutions with concentration varying from 1 to 100 ppm were prepared by this dilution method. All of the standard solutions were transparent.

The upper aqueous phase (2 mL) was withdrawn from the above mixed solution, which was exposed under the high power UV light and this solution (2 mL) was diluted by three times. Then the concentrations of the diluted solution and the Eu^{3+} solution (0.001 M) were measured using ICP.

Chapter 3: Results and Discussions

3.1 Characterization of Benzo-15-crown-5 (Compound 1)

Compound **1** was characterized by ^1H -NMR, using TMS as the internal standard and CDCl_3 as solvent: ^1H -NMR (CDCl_3): 3.65, 3.95, 4.34 (m, 35H); 6.87 (s, 2H); 7.81 (m, 4H). Due to the structure of the Compound **1** being symmetric, the protons have been labeled as in **Figure 6**. The two protons at chemical shift around 7.8 belong to the H on the benzene ring near the $-\text{N}=\text{N}-$ group at position 1. Two protons at chemical shift 7.6 belong to the H on the benzene ring at position 3. Two protons at chemical shift 6.8 belong to the H at position 2. Eight protons at chemical shift 4.3 belong to position 4 and 11. Eight protons at chemical position 3.9 belong to position 5 and 10. The residual 16 protons belong to the position at 6, 7, 8 and 9. **Figure 6** shows the structure of compound **1** and **Figure 7** shows the characterization of the synthesis of the bi-crown ether. The yield is 7%. The product appeared as a dark yellow grease.

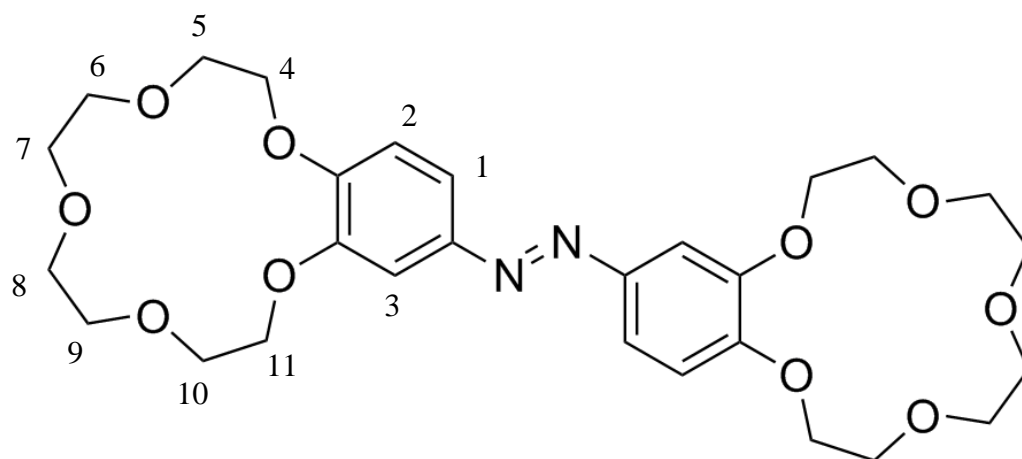


Figure 6. Structure of the compound 1

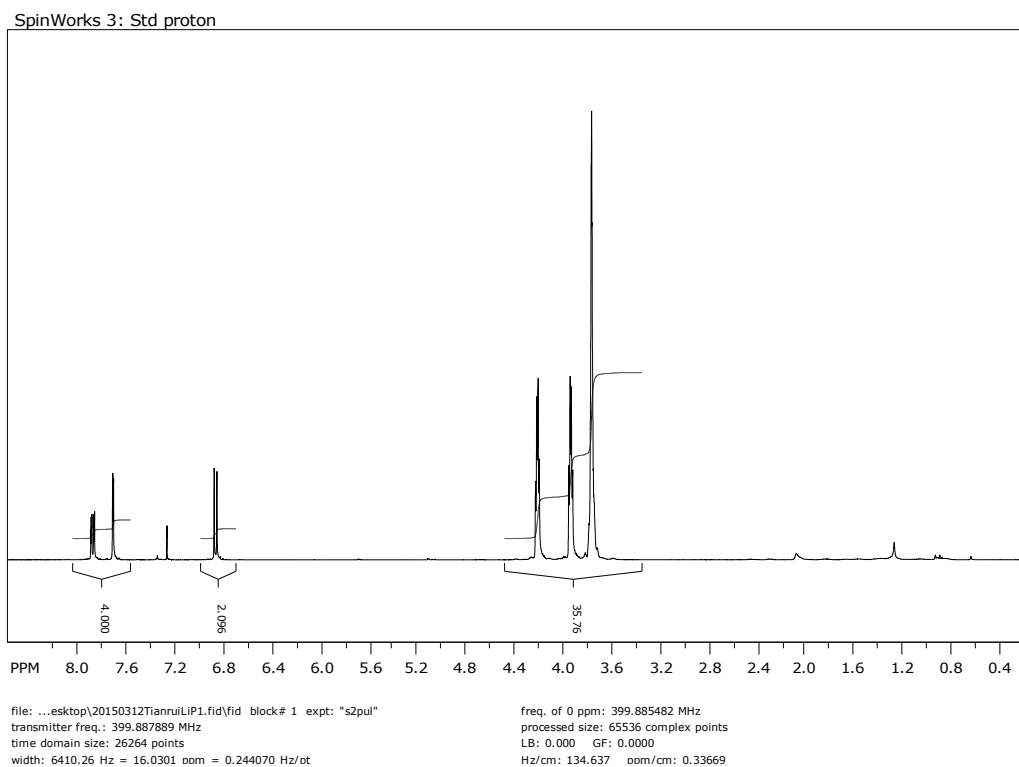


Figure 7. ^1H -NMR of Compound **1**

3.2 Rare Earth Extraction

3.2.1 Emission Profile of Eu^{3+} and the Standard Calibration Curve

Emission intensities of the characteristic peaks of Eu^{3+} increased as a function of solution concentration. A quantitative method to determine the concentration of Eu^{3+} from the area of emission peak was utilized. **Figure 8** shows the emission profiles of different solutions and **Table 4** shows relative intensities and corresponding concentrations. According to the orbital configuration of Eu^{3+} , the emission peaks are generated by electronic transitions: peak 1 is the $^5\text{D}_0$ - $^7\text{F}_1$ transition, peak 2 is the $^5\text{D}_0$ - $^7\text{F}_2$ transition, and peak 3 is the $^5\text{D}_0$ - $^7\text{F}_4$ transition.

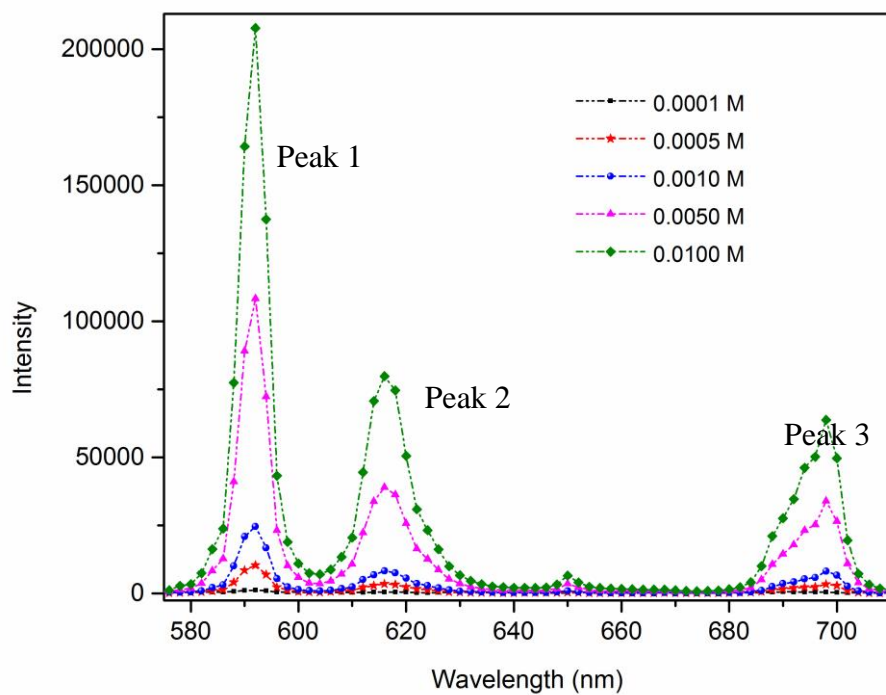


Figure 8. Emission profile of different concentrations of Eu^{3+}

Table 4. Photoluminescence intensities with corresponding concentrations

Sample	0.0100 M	0.0050 M	0.0010 M	0.0005 M	0.0001 M
Peak1	2.79×10^6 (± 8408)	1.42×10^6 (± 2102)	3.05×10^5 (± 792.0)	1.33×10^5 (± 7420)	3.00×10^4 (± 35.00)
Peak2	1.53×10^6 (± 8558)	7.60×10^5 (± 925.0)	1.46×10^5 (± 155.0)	6.09×10^4 (± 19.79)	4.04×10^3 (± 14.80)
Peak3	1.19×10^6 (± 2620)	6.07×10^5 (± 1266)	1.36×10^5 (± 902.0)	6.20×10^4 (± 312.0)	6.82×10^3 (± 133.0)

Based on the absolute area of the intensity for the concentrations, **Figures 9-11** show the calibration curves of the three peaks. We determined that in low Eu^{3+} concentrations of emission intensity is linear ($R^2 > 0.999$) with concentration. In addition, peak 1 has a higher standard error $R^2 = 0.99939$ and its emission profile shows dramatic changes with respect to changing concentrations (**Figure 8**). Hence, the emission intensity vs peak area calibration curve for peak 1 was chosen as the standard against which the following work was quantified.

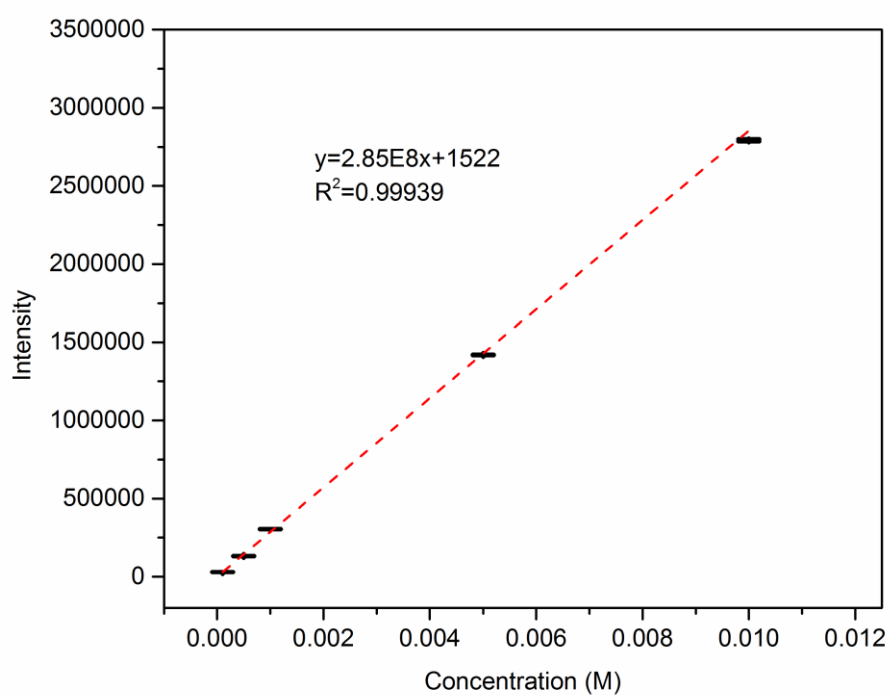


Figure 9. Calibration curve for peak 1

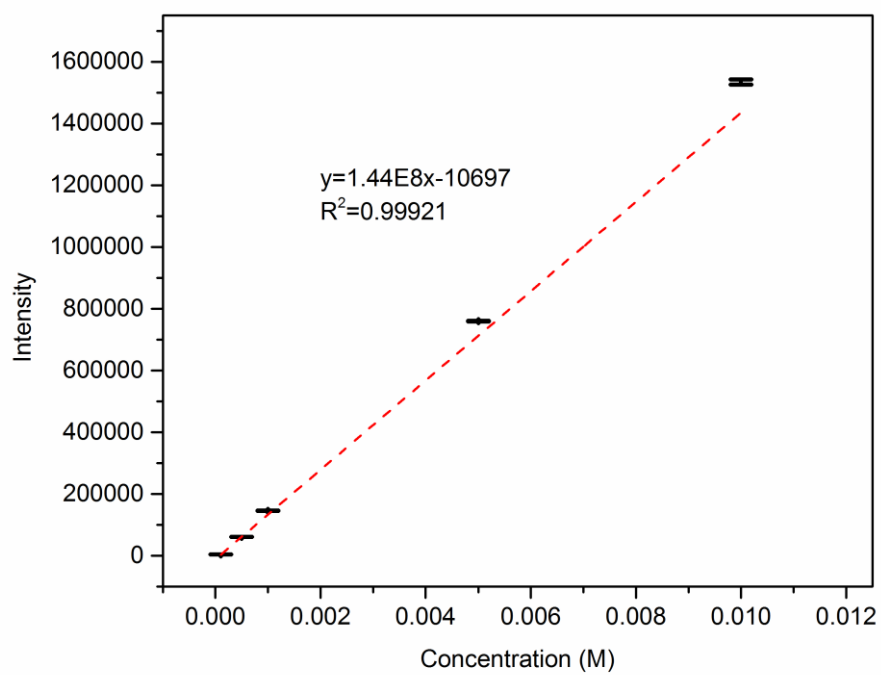


Figure 10. Calibration curve for peak 2

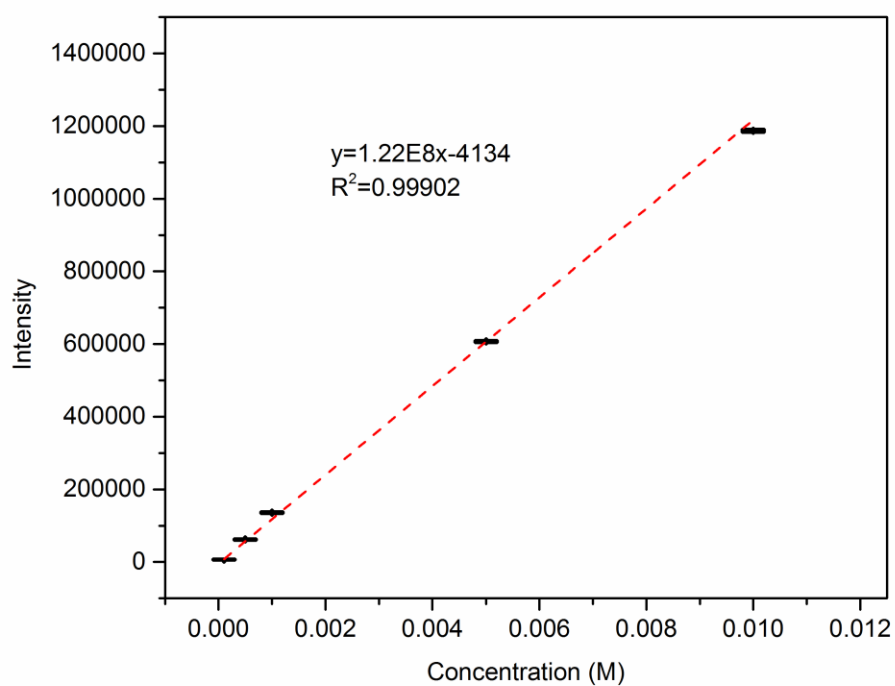


Figure 11. Calibration curve for peak 3

3.3 Standard Calibration Procedure

In order to better quantify the extraction ability of the PMs, the influence of the aqueous solvent needed to be eliminated. By recording the emission profiles at different times, we were able to measure concentration changes of Eu^{3+} with time.

To better understand the quality of the solvent extraction, a partition coefficient D was used:

$$D = \frac{C_O}{C_A}$$

where C_O = concentration in organic phase

C_A = concentration in the aqueous phase.

For example, the partition coefficient of the solvent *o*-dichlorobenzene (DCB) at 10 min was calculated as follows:

$$D = \frac{C_O}{C_A} = \frac{(0.000100 - 0.0000934)}{0.0000934} = 0.0706$$

The partition coefficients D_1 at different times are shown in **Table 5** and **Figure 12**.

After 100 min, the partition coefficient D_1 stays around 0.1, which means some Eu^{3+} is dissolved in the organic solvent. However, the solubility of Eu^{3+} in the organic solvent is such that only 10% of the total cations will be “transferred” to another phase by solution extraction. Upon reaching this solubility limit, the solution has no influence on the concentration change of the cation.

Table 5. Partition coefficient of procedure blank

Sample	Blank 10 (min)	Blank 40 (min)	Blank 100 (min)	Blank 24 (hour)
Area of Peak 1 (Intensity × nm)	2.96×10^5 (±631)	2.85×10^5 (±721)	2.94×10^5 (±758)	2.91×10^5 (±697)
Concentration (M)	9.34×10^{-4}	8.94×10^{-4}	9.07×10^{-4}	9.10×10^{-4}
D₁	7.06×10^{-2}	1.18×10^{-1}	1.02×10^{-1}	9.89×10^{-2}

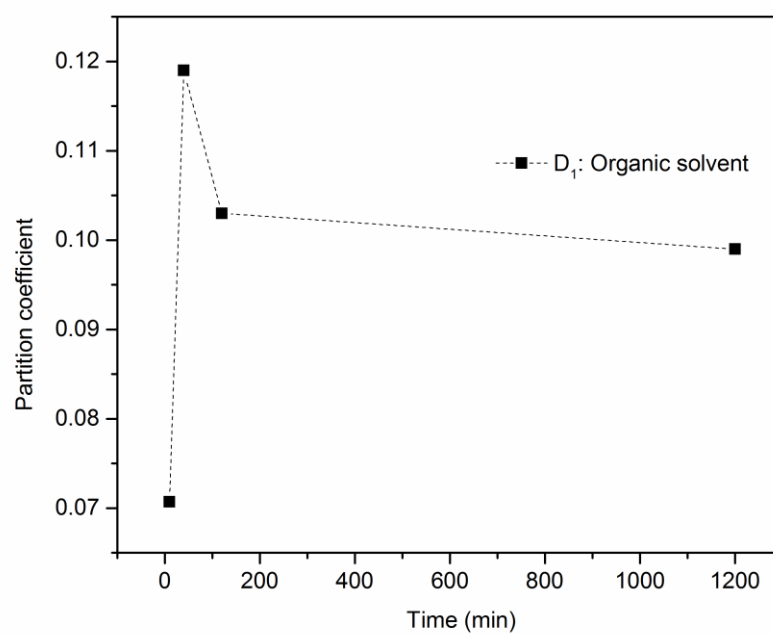


Figure 12. The correlation between the D_1 and time

From **Table 5** and **Figure 12**, we concluded that the organic solvent had a small but consistent influence on Eu^{3+} extraction, which is 10% of the total dissolved in the organic solvent and reached equilibrium after 100 min.

3.4 Eu^{3+} Extraction by Organic Ligand(s)

Using a similar method with that of the procedure blank, we recorded Eu^{3+} emission from the aqueous phase at different times of extraction with PMs. The corresponding concentration(s) from peak 1 was calculated from calibration curve 1. The partition coefficient, D_2 , is Eu^{3+} distribution between the aqueous and organic phases. The organic phase contains the PMs, as shown in **Table 6**. **Figure 13** compares the partition coefficients from the different solutions.

Table 6. Partition coefficient of Eu^{3+} in solution containing photoisomerizable

molecules

Sample	Crown ether 10 (min)	Crown ether 40 (min)	Crown ether 120 (min)	Crown ether 24 (hour)
Area of Peak 1 (Intensity \times nm)	2.76×10^5 (± 821)	2.62×10^5 (± 324)	2.36×10^5 (± 566)	2.30×10^5 (± 612)
Concentration (M)	8.67×10^{-4}	8.18×10^{-4}	7.31×10^{-4}	7.10×10^{-4}
D₂	0.153	0.222	0.368	0.408
D₁	0.0707	0.119	0.103	0.0990
D₂-D₁	0.0823	0.103	0.265	0.309

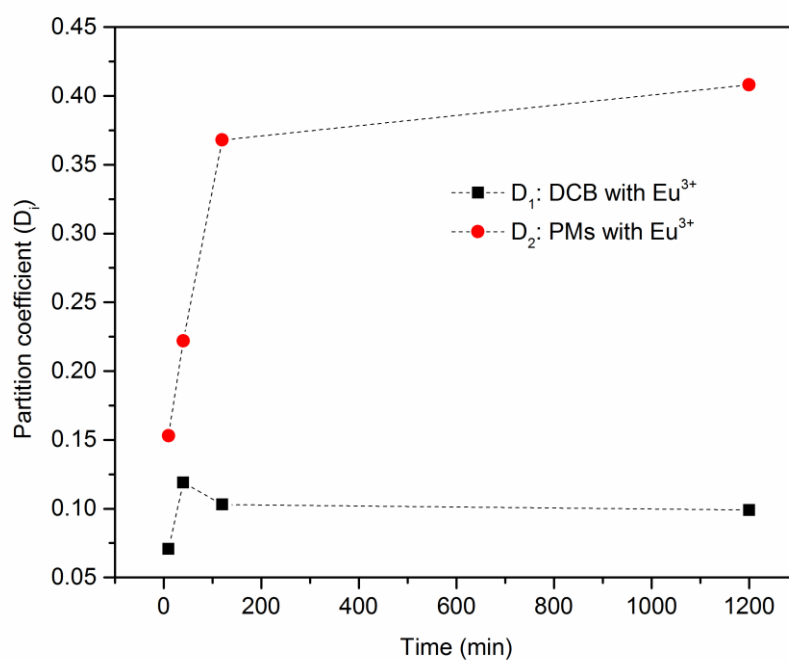


Figure 13. Comparison of partition coefficients for the concentration change of the Eu^{3+} with and without the effect of PMs

From the above information, we found that Eu^{3+} concentration decreases with increasing PM extraction time. This is because cavity size of the crown ether²⁹ properly matched the cation size and the Eu^{3+} was transferred into the organic phase, decreasing Eu^{3+} concentration in the aqueous phase. Eu^{3+} transport equilibrated after 100 min, with a partition coefficient of $D_2 = 0.4$, which corresponds to 30% of the ions being transported into the organic phase.

3.5 Rare Earth Cation Transfer under UV Light

3.5.1 Photoluminescence

We originally planned to use photospectroscopy to measure the concentration of Eu^{3+} in the aqueous solution after UV light exposure. However, we found that the 3 characteristic emission peaks of Eu^{3+} became one broad high intensity peak. This peak concealed the relatively weak characteristic emission peaks of Eu^{3+} . **Figure 14** shows spectra for samples exposed with and without UV light.

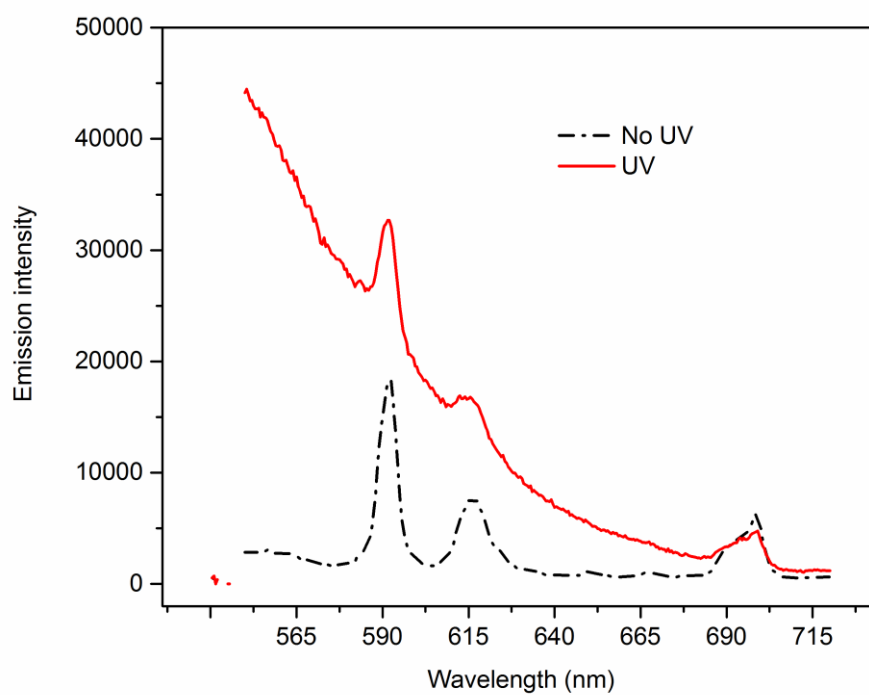


Figure 14. Photospectroscopy of samples with and without UV light

Under 100 watt UV light, the “*trans*-” isomer converted to the “*cis*-” isomer, which is more soluble in the aqueous solution. We assumed the high concentration of “*cis*-” isomers may interfere with the Eu^{3+} emission. In order to test this hypothesis, we measured the spectrum of the blank solution only containing o-dichlorobenzene after the UV light exposure. The emission spectrum showed the same broad, high intensity peak as mentioned before. Benzene-15-crown-5 ether changed its isomeric configuration. Thus, the “*cis*-” isomer of this PMs changed its chemical polarity such that benzene-15-crown-5 became more polar and prefers aqueous environments.

3.5.2 Inductively Coupled Plasma Optical Emission Sepctroscopy (ICP-OES)

From ICP-OES, it is revealed that the concentration of Eu^{3+} in the aqueous phase after exposing to UV light is 149 ppm. This is 42 ppm ($\approx 28\%$) greater than the concentration of Eu^{3+} in the aqueous solution without UV light exposure; this number compared well with the 30% observed from the PL measurement. A summary of data is listed in **Table 7**.

Table 7. Concentration of aqueous solution measurement by ICP

Samples	0.0010 M Eu³⁺	CE (without UV)	CE (with UV)
Concentration (ppm)	156 (±0.85)	107 (±1.15)	149 (±2.08)

The concentration of the ions in the aqueous solution increased again, indicating the Eu^{3+} went back to the aqueous solution during the transformation from “*trans*-” to “*cis*-”. Another finding is that the “*cis*-” isomer does not convert back to “*trans*-” isomer once the PMs in the “*cis*-” structure complexed with Eu^{3+} . The atoms on the crown ether ring formed a “negative oxygen environment” of the heteroatoms and the Eu^{3+} have a dipole interaction with the crown ether through electrostatic attraction. The cations went inside the central cavity and are immobilized. Meanwhile, the exterior of the ring is hydrophobic, which prevent outside water molecules from interacting with sequestered the cations. Specifically, the Eu^{3+} have an empty 6s – shell, and the oxygen ring provides the lone paired electrons to form a coordinate bond. This ion-dipole interaction stabilized the complexing of cations and crown ether, and then the crown ether sequesters the Eu^{3+} cations from the hydrate-complex while remaining meta-stable in the aqueous solution.

3.6 Summary

The major achievements of the thesis work are summarized as: (1) The photoisomerizable molecules of benzene-15-crown-5 ether was synthesized. (2) It has two forms namely the “*trans*-” and “*cis*-” configuration; the “*trans*-” isomer captured the Eu^{3+} and formed a stable complex in the organic phase. (3) The UV light induced the change from “*trans*-” to “*cis*-”. The “*cis*-” configuration changed the chemical polarity so that it developed a strong affinity to the aqueous solution. The Eu^{3+} complex of the “*cis*-” configuration is stable and soluble in the aqueous solution.

Chapter 4: Future Work

This thesis presents a method to transport rare earth ions between two different liquid phases, yet further improvement is necessary. Synthetic yield of the photoisomerizable molecules must be improved as the precursor materials are relatively expensive. A proposed alternative synthesis method is to use the reduction reaction to confer “photoswitch” function to the molecules; however, large quantities of aniline will be generated as a result. Another route in the synthesis of the PMs should be explored. In order to obtain higher cation selectivity, PM structure requires further modification. Different crown ether cavity sizes sequester specific sized cations. Changing the cation valence may affect the capture ability. The behavior of both the organic molecules and the cations with respect to solution pH and capture/extraction, as changing pH may affect stability, photosensitivity, and efficacy. In addition, further research into recycling the PMs after releasing captured cations should be conducted as to validate this method as a potential means of selectively and inexpensively capturing rare earth ions from waste streams. Finally, the presented research demonstrates single cation separation by organic molecules. However, industrial waste streams are mixtures of different kinds of ions, and we need to understand how the photoisomerizable molecules work to target specific cations in the presence of other cations that are in much greater concentrations with respect to the cation of interest.

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