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Electrogenerated Chemiluminescence of Transition Metal Octaethylporphyrin and Tetraphenylporphyrin/Tri-n-Propylamine System

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ELECTROGENERATED CHEMILUMINESCENCE OF TRANSITION METAL OCTAETHYLPORPHYRIN AND TETRAPHENYLPORPHYRIN/TRI-N-PROPYLAMINE SYSTEMS

A Masters Thesis

Presented to

The Graduate College of

Missouri State University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science, Chemistry

By

Jamie Lee Gray

August 2018

ELECTROGENERATED CHEMILUMINESCENCE OF TRANSITION METAL OCTAETHYLPORPHYRIN AND TETRAPHENYLPORPHYRIN/TRI-N-PROPYLAMINE SYSTEM

Chemistry

Missouri State University, August 2018

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ABSTRACT

The electrogenerated chemiluminescence (ECL) of octaethylporphyrin (OEP), tetraphenylporphyrin (TPP) and a series of metal-ligand porphyrin complexes (Zinc, Copper, Palladium, Platinum, Ruthenium, Vanadium, Cobalt and Nickel) in CH_2Cl_2 is reported. ECL was generated upon sweep to positive potentials using tri-n-propylamine (TPrA) as an oxidative-reductive coreactant. ECL efficiencies were between 0.010 and 0.770 using $Ru(bpy)_3(PF_6)_2$ (bpy = 2,2'-bpyridine) as a relative standard ($\phi_{ecl} = 1$). The ECL intensity peaks at a potential corresponding to oxidation of the complexes and TPrA, suggesting that the same excited states are formed in both photoluminescence and ECL. Although the ECL was weaker than corresponding PL efficiencies, similar trends were observed in both experiments, again suggesting identical excited states are formed.

KEYWORDS: electrogenerated chemiluminescence, ECL, metalloporphyrins, coreactants, porphyrin

This abstract is approved as to form and content

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Mark M. Richter, Ph.D.
Chairperson, Advisory Committee
Missouri State University

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Finally to my husband, to whom I owe everything.

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CHAPTER 1: INTRODUCTION TO ELECTROGENERATED CHEMILUMINESCENCE

Electrogenerated chemiluminescence (ECL) is a method to detect organic, inorganic and biochemical molecules. ECL, first discovered in the mid-1960s, [1,2] involves the formation of excited-state compounds at an electrode surface followed by chemiluminescence reactions. [3,4,5] It provides a sensitive way of examining electron and energy-transfer processes at charged interfaces. [6] Many reviews, some quite comprehensive, are available on ECL and its applications. [3,4,5,6]

ECL has many advantages compared to fluorescence or photoluminescence (PL) methods. Unlike PL methods, ECL does not involve the use of an external light source so has fewer problems with scattered light. Also, fewer complexes undergo ECL leading to fewer luminescent impurities.

The majority of tests use $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bpyridine) derivatives as the ECL luminophore or label with TPrA (tri-n-propylamine) as the coreactant. The advantage to this is upon formation of the luminescent excited state, $^*Ru(bpy)_3^{2+}$, emission of a photon regenerates $Ru(bpy)_3^{2+}$ in its ground state near the electrode surface. This means that a single $Ru(bpy)_3^{2+}$ complex can participate in many different ECL reaction cycles to produce multiple photons, increasing sensitivity and lowering detection limits. $Ru(bpy)_3^{2+}$ was the first metal complex studied via ECL. [7]

There have been many fundamental and applied studies on organic, inorganic and biochemical systems. For example, the first species studied in ECL were polyaromatic hydrocarbons such as 9,10-diphenylanthracene. [8,9,10] They undergo electrochemically

reversible oxidation and reduction reactions, and their excited states are accessible in the solvent window of most organic solvents (e.g., acetonitrile and methylene chloride). The solvent window is the oxidative and reductive potentials where the solvent itself does not undergo oxidation and reduction, typically between +2.5 V and -2.5 V vs SCE. These excited states were formed by annihilation ECL. Annihilation ECL is when the emitter (R) can electrochemically produce both a sufficiently stable radical cation ($R^{\cdot+}$) and anion ($R^{\cdot-}$). Each radical ion is annihilated by the oppositely charged radical ion to generate the excited state (R*).

$$R - e- \rightarrow R^{\cdot+}$$

$$R + e- \rightarrow R^{\cdot-}$$

$$R^{\cdot+} + R^{\cdot-} \rightarrow R + R*$$

$$R* \rightarrow R + h\nu$$
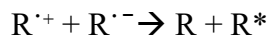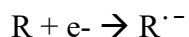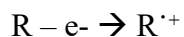
$h\nu$ is a photon of light. Another method of generating ECL is coreactant ECL where emission is generated in one potential sweep (either oxidative or reductive, not both) with the solution containing the luminophore species and the coreactant. For example, the proposed mechanism for $Ru(bpy)_3^{2+}$/TPrA is shown in Figure 1. $Ru(bpy)_3^{2+}$ is oxidized to $Ru(bpy)_3^{3+}$ at the surface of an electrode upon application of an oxidizing (or anodic) potential. Similarly, TPrA is oxidized to $TPrA^{\bullet+}$ upon loss of an alpha proton (a hydrogen nearest to the amine group). Upon proton loss a tripropylamine radical is formed, presumably $TPrA^{\bullet}$, that then reacts with $Ru(bpy)_3^{3+}$ to form the excited state, $^{*}Ru(bpy)_3^{2+}$, followed by emission.
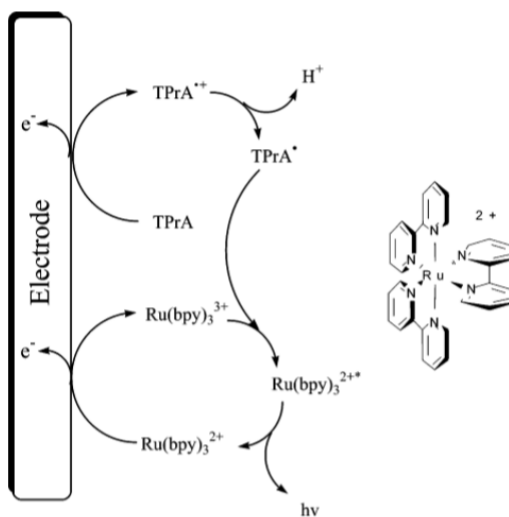
Figure 1. Proposed mechanism for $Ru(bpy)_3^{2+}$/TPrA reaction sequence.

ECL-active species have been used as biological tags for DNA analysis as well as many different forms of immunoassays.[5] ECL has recently been incorporated into enzyme linked immunosorbent assays (ELISA) as electrochemical ELISA for a portable and direct way to perform at the point of care analysis in rural clinics as well as for the purpose for natural disaster aid. ECL has been proven to provide much lower limits of detection as opposed to traditional color spectroscopy for ELISA.

Many transition metal systems have been studied using ECL. Representative systems include main group metals (e.g., Si and Al)[11,12] transition metal complexes incorporating Ru, Os and Pt[13-18] as well as rare earth chelates.[14,15] There has been particular emphasis on characterizing the nature of the excited state, discerning the mechanisms by which these states were formed and determining the efficiency of excited state formation.

Metal centered porphyrin complexes (Figure 2) display many of the chemical and spectroscopic qualities required of ECL-luminophores, such as stable oxidative and reductive electrochemistry and strong photoluminescence. As an added benefit, many are commercially available.

Figure 2. Structures of OEP (left) and TPP (right); M=metal center.

Several porphyrins, including those containing metal ions, have been shown to act as ECL luminophores.[16-24] For example, the EC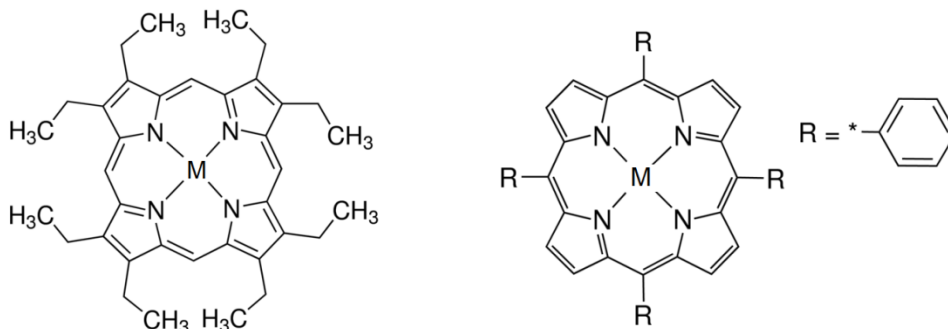L of Pt(TPP) was reported in nonaqueous solution using an annihilation mechanism[16] (the formation of oxidized and reduced forms of the complex at an electrode that can then diffuse together and undergo energy or electron transfer to form the excited state).

$$Pt(TPP)^+ + Pt(TPP)^- \rightarrow Pt(TPP)^* + Pt(TPP)$$
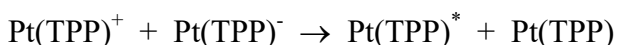
Tetraphenylporphyrin itself has also been shown to generate ECL in the absence of a metal ion.[17] Other studies include platinum octaethyl porphyrin using annihilation[18] and coreactant methods,[19] the ECL of sterically hindered porphyrins in aqueous media,[20] the ECL of ruthenium TPP and OEP using TPrA as coreactant,[21] and the ECL and PL of the porphyrin/ruthenium complex [H$_2$(MPy3,4DMPP)Ru(bpy)$_2$Cl](PF$_6$), where H$_2$MPy3,4DMPP = *meso*-tris-3,4-dimethoxyphenyl-mono-(4-pyridyl)porphyrin and bpy = 2,2'-bpyridine and its porphyrin analog.[22] To our knowledge, however, a systematic study has not been reported. Such studies have been performed for the PL properties of metal porphyrin systems.[23] In this work, transition metal porphyrin systems including

Zinc and Copper tetraphenylporphyrin, as well as Zinc, Copper, Palladium, Platinum, Ruthenium, Vanadium, Cobalt and Nickel octaethylporphyrin were used as a "luminophore" to convert electrical energy into radiative energy using TPrA. This light is then measured using a photomultiplier tube (PMT) so that comparison to photoluminescence (PL) data could be made. This thesis introduces multiple transition metal centered porphyrin compounds into the ECL library of luminophores.

CHAPTER 2: EXPERIMENTAL METHODS

Materials

All porphyrin complexes (Tetraphenyl-21H,23H-porphine copper(II); Octaethyl-21H,23H-porphine copper (II); Tetraphenyl-21H,23H-porphine zinc (II); Octaethyl-21H,23H-porphyrin zinc (II); Octaethyl-21H,23H-porphine ruthenium (II) carbonyl; Octaethyl-21H,23H-porphine cobalt (II); Octaethyl-21H,23H-porphine nickel (II); Octaethyl-21H,23H-porphine palladium (II); Octaethyl-21H,23H-porphine vanadium (IV) oxide; Octaethyl-21H,23H-porphine platinum (II); 5,10,15,20-Tetraphenyl-21H,23H-porphine; 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine) were commercially available (Sigma Aldrich) and used as received. The solvent methylene chloride (CH_2Cl_2) and the supporting electrolyte tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, $C_{16}H_{36}F_6NP$) were also from Sigma Aldrich. $Ru(bpy)_3(PF_6)_2$ was from Strem Chemicals in Newburyport, Massachusetts. Argon gas provided by the Chemistry Department at Missouri State University was used to deoxygenate solutions for electrochemical analyses.

Methods

Electrogenerated Chemiluminescence. ECL experiments used a conventional three-electrode system, a CH Instruments electrochemical analyzer and a Leader 718-5D Photomultiplier Tube (PMT) contained in a "light-tight" box. The working electrode was a platinum mesh electrode, with a platinum wire auxiliary electrode and a Ag/AgCl quasi-reference electrode. A 0.05M $TPrA/CH_2Cl_2/Bu_4NPF_6$ stock solution was prepared by adding approximately 10 g of Bu_4NPF_6 (0.05 M) and 4.76mL of TPrA (0.05M) to

500mL of CH_2Cl_2. This stock solution was used as a blank to test for background ECL, and in all dilutions to make working solutions containing luminophore.

All ECL experiments utilized around 80 mL of solution, placed 15 cm from the PMT. ECL efficiencies (ϕ_{ecl} = photons generated per redox event) were obtained by literature methods,[24,25] using $Ru(bpy)_3^{2+}$ (ϕ_{ecl} = 1) as the standard. ECL efficiencies are based upon the mean of at least three runs with a relative standard deviation of ±5%.

A 0.05M $TPrA/CH_2Cl_2/Bu_4NPF_6$ stock solution was prepared by adding approximately 10 g of Bu_4NPF_6 (0.05 M) and 4.76mL of TPrA (0.05M) to 500mL of CH_2Cl_2. A 10^{-4} M stock solution of porphyrins was initially prepared by placing the porphyrin in a 100mL volumetric flask and diluting to the mark with the stock solution of Bu_4NPF_6/CH_2Cl_2. The contents of the solution were then mixed by inversion as well as ultrasonication. The working solution of 10^{-7} M $Ru(bpy)_3(PF_6)_2$ was prepared by diluting a solution of 10^{-3} M $Ru(bpy)_3(PF_6)_2$. The 10^{-3} M solution of $Ru(bpy)_3(PF_6)_2$ was prepared by placing 0.0078 g of $Ru(bpy)_3(PF_6)_2$ in a 10mL volumetric flask and diluted to the mark with the stock solution of $TPrA/CH_2Cl_2$. Then 0.01 mL was taken from this initial 10^{-3} M solution of $Ru(bpy)_3(PF_6)_2$ and placed in a 100mL volumetric flask and diluted to the mark with the stock solution of $Bu_4NPF_6/TPrA/CH_2Cl_2$.

The working electrode was cleaned before each run by repeated cycling (+2.5 to -2.5 V) in a 6.0 M solution of sulfuric acid followed by rinsing with doubly deionized water. ECL efficiencies (ϕ_{ecl}=photons/redox event) were obtained by literature methods using $Ru(bpy)_3^{2+}$ as a standard (ϕ_{ecl} = 1).[26]

Electrochemistry (cyclic voltammetry and bulk electrolysis). A 0.05M $TPrA/CH_2Cl_2/Bu_4NPF_6$ stock solution was prepared by adding approximately 10 g of

Bu$_4$NPF$_6$ (0.05 M) to 500mL of CH$_2$Cl$_2$. All cyclic voltammograms were obtained using a glassy carbon working electrode that was cleaned using silica, then rinsed with doubly deionized water between each run. For bulk electrolysis the standard setup described above for ECL was used.

A 10^{-4} M stock solution of porphyrins was initially prepared by placing the porphyrin in a 100mL volumetric flask and diluting to the mark with the stock solution of Bu$_4$NPF$_6$/CH$_2$Cl$_2$. The contents of the solution were then mixed by inversion as well as ultrasonication. The working solution of 10^{-7} M Ru(bpy)$_3$(PF$_6$)$_2$ was prepared by diluting a solution of 10^{-3} M Ru(bpy)$_3$(PF$_6$)$_2$. The 10^{-3} M solution of Ru(bpy)$_3$(PF$_6$)$_2$ was prepared by placing 0.0078 g of Ru(bpy)$_3$(PF$_6$)$_2$ in a 10mL volumetric flask and diluted to the mark with the stock solution of TPrA/CH$_2$Cl$_2$. Then 0.01 mL was taken from this initial 10^{-3} M solution of Ru(bpy)$_3$(PF$_6$)$_2$ and placed in a 100mL volumetric flask and diluted to the mark with the stock solution of Bu4NPF6/CH$_2$Cl$_2$.

Spectroscopy (UV/Vis and PL). UV-Vis and Photoluminescence spectra were obtained using a Cary-100 UV-Visible Spectrophotometer (Varian Inc., Palo Alto, CA) and Shimadzu RF-5301 Spectrofluorophotometer (Shimadzu Corporation, Japan), respectively. Excitation for photoluminescence was at the maximum absorbance intensity using slit widths of 3 nm and detection between 500 and 900 nm. Photoluminescence efficiencies (ϕ_{em}; photons emitted per photons absorbed) were obtained relative to Ru(bpy)$_3$$^{2+}$ (ϕ_{em} (CH$_3$CN) = 0.042)[27] and are the average of at least three scans with a standard deviation of $\pm5\%$.

A stock solution was prepared by adding approximately 10g of electrolytes to 500mL of CH$_2$Cl$_2$. Two solutions were prepared, the first stock solution of 10^{-5} M

Ru(bpy)$_3$(PF$_6$)$_2$ was prepared by placing 0.0078g of Ru(bpy)$_3$(PF$_6$)$_2$ in a 100 mL flask and diluting to the mark with the stock solution of CH$_2$Cl$_2$ and mixed initially by inversion and ultrasonification.

Another stock solution of 10^{-7}M was prepared by transferring 1mL of the 10^{-5} M Ru(bpy)$_3$(PF$_6$)$_2$ solution to a 100mL volumetric flask and diluting to the mark with the stock solution of CH$_2$Cl$_2$ and mixing by inversion and ultrasonification. A 10^{-4} M stock solution of porphyrins was prepared by placing the porphyrin in a 100mL volumetric flask and diluting to the mark with the stock solution of CH$_2$Cl$_2$. This solution was then mixed by inversion and ultrasonification.

CHAPTER 3: METAL CENTERED PORPHYRINS

Results and Discussion

Electrochemistry. The oxidative electrochemistry of the porphyrins and metal-porphyrin complexes are presented in Table 1. Representative cyclic voltammograms (CVs) are presented in Figures 3-6, with the rest in the Appendix. Although a detailed study of the electrochemistry of these systems has been reported[18,19,20,21] the experiments were repeated to make comparisons between electrochemical, spectroscopic and ECL data more valid. However, the results are extremely consistent with previous research. For example,[18] Pt(OEP) undergoes a one electron oxidation to form Pt(OEP)$^+$ at +0.97 V vs Ag/AgCl (+0.40 V vs Fc/Fc$^+$) in CH_2Cl_2 (0.05 M TBAPF$_6$). No other oxidative waves were observed under these conditions prior to oxidation of the solvent. The other metal complexes display between 1 and 2 oxidations, some electrochemically reversible (Figures 3-5, Appendix and Table 1). These are most likely ligand based oxidations by comparison to the ligands themselves (Table 1) and since most metal centers do not have oxidation potentials within the solvent window from 0.0 to +2.0 V vs Ag/AgCl.[17] Also, the potentials for oxidation and re-reduction shifted slightly depending on the metal in the porphyrin cavity, showing that there are electronic interactions between the porphyrin and metal ions.

Table 1. Electrochemical oxidation (E_a) and re-reduction (E_c) potentials vs Ag/Ag$^+$ reference electrode. 0.1mM complex, 0.05 M Bu$_4$NPF$_6$ in CH$_2$Cl$_2$.

Compound	E_{a1} (V)	E_{c1} (V)	E_{a2} (V)	E_{c2} (V)
Cu(OEP)	0.892	0.281	1.60	1.01
Cu(TPP)	1.07	0.772	1.48	1.18
Zn(TPP)	0.913	0.648	1.24	0.977
Zn(OEP)	0.398	0.085	0.990	1.212
Ru(OEP)	0.903	0.238	1.55	0.876
V(OEP)	1.07	0.712	1.60	1.25
Co(OEP)	1.097	0.574	1.743	1.587
Pd(OEP)	0.968	0.576	1.74	1.41
Ni(OEP)	0.881	0.565	1.57	1.25
Pt(OEP)	0.968	0.636		
H$_2$OEP	0.417	0.445	1.568	1.590
H$_2$TPP	0.418	0.554	1.406	1.200

Feb. 6, 2017 16:46:31
Tech: CV
File: jkb2p27f

Init E (V) = 0
High E (V) = 2
Low E (V) = 0
Init P/N = P
Scan Rate (V/s) = 0.1
Segment = 2
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 1e-4

Segment 1:
Segment 2:

Figure 3. Cyclic Voltammetry of 0.1 mM TPP and 0.05M Bu_4NPF_6 in CH_2Cl_2.

Nov. 18, 2016   14:40:31
Tech: CV
File: jkb2p7c

Init E (V) = 0
High E (V) = 2
Low E (V) = 0
Init P/N = P
Scan Rate (V/s) = 0.1
Segment = 2
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 1e-5

Segment 1:
Ep = 1.071V
ip = -5.329e-6A
Ah = -6.321e-6C

Ep = 1.481V
ip = -6.981e-6A
Ah = -7.808e-6C

Segment 2:
Ep = 1.183V
ip = 6.379e-6A
Ah = 6.868e-6C

Figure 4. Cyclic Voltammetry of 0.1 mM Cu(TPP), and 0.05M Bu_4NPF_6 in CH_2Cl_2.

Feb. 6, 2017   16:28:46
Tech: CV
File: jkb2p27a

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Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 0.001

Segment 1:
Segment 2:

Figure 5. Cyclic Voltammetry of 0.1 mM OEP, and 0.05M Bu_4NPF_6 in CH_2Cl_2.

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Figure 6. Cyclic Voltammetry of 0.1 mM V(OEP), and 0.05M Bu$_4$NPF$_6$ in CH$_2$Cl$_2$.

Spectroscopy. Ultraviolet-Visible (UV-Vis) absorbance and photoluminescence data are presented in Table 2. Representative spectra are shown in Figures 7-14 with the rest in the appendix. The complexes display absorption features typical of heavy-metal porphyrin complexes with maximum absorbances around 390 and between 500 – 540 nm, assigned to the Soret- and Q-bands, respectively.[28,29] Excitation into these bands produces room temperature photoluminescence in CH$_2$Cl$_2$. The spectra are sensitive to the nature of the metal center suggesting an interaction between the metal center and porphyrin cavity. Also, the emission spectra are essentially the same regardless of the excitation wavelength.[30] The narrow emission peak centered around 650 nm are characteristic of triplet excited states[28,29,] with quantum efficiencies (ϕ_{em}) reported in the table. The efficiencies were measured using Ru(bpy)$_3$$^{2+}$ (ϕ_{em} = 0.042) as standard. Further discussion of the emission efficiencies will be done in the ECL section.
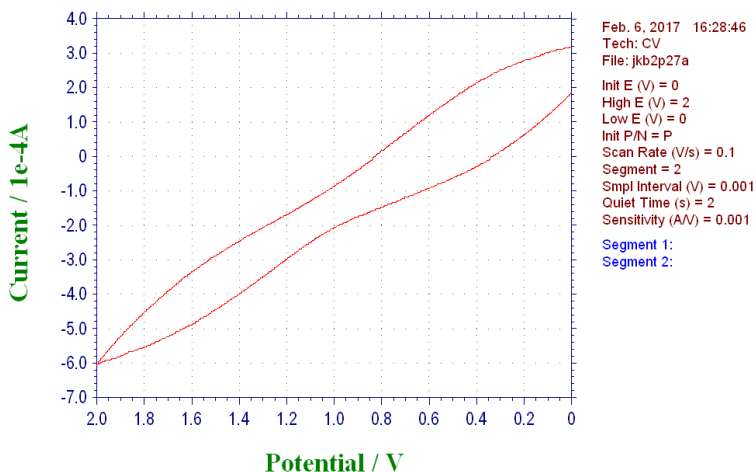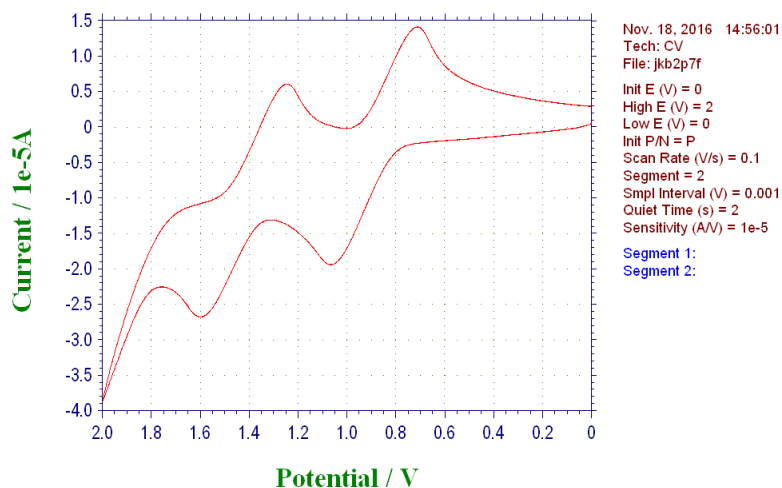
Table 2. PL Efficiencies of porphyrin complexes. 0.01mM compound in CH_2Cl_2. Efficiencies were obtained using $Ru(bpy)_3^{2+}$ ($\phi_{PL} = 0.042$) as a standard.

Compound	Φ_{EM} (au)
$Ru(bpy)_3^{2+}$	1.00
TPP	2.11
Zn(TPP)	3.09
Cu(TPP)	0.477
OEP	15.8
Zn(OEP)	6.38
Cu(OEP)	0
Ni(OEP)	0
V(OEP)	0.0867
Pd(OEP)	0.0632
Ru(OEP)	0.0343
Co(OEP)	0.0102
Pt(OEP)	0.0198
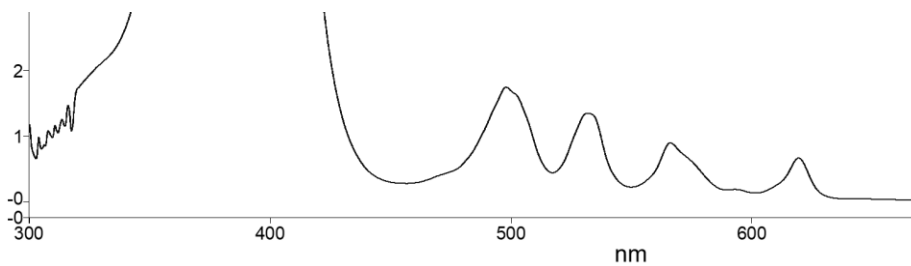
Figure 7. UV-Vis of 0.01mM OEP in CH_2Cl_2.
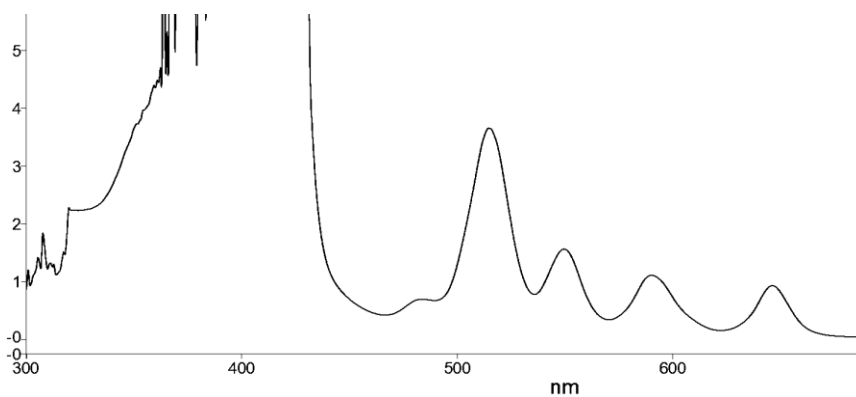
Figure 8. UV-Vis of 0.01mM TPP in CH_2Cl_2.
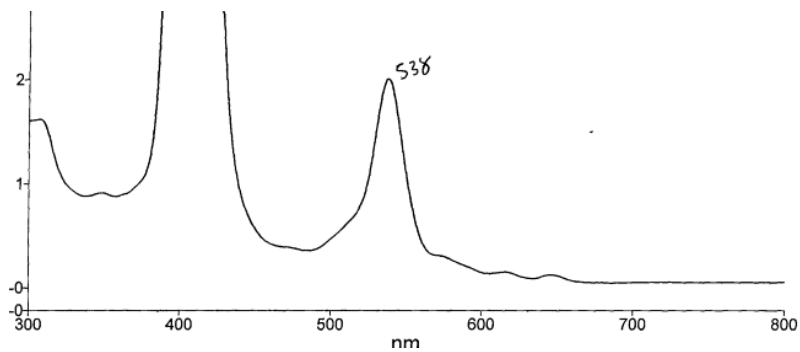
Figure 9. UV-Vis of 0.01mM Cu(TPP) in CH_2Cl_2.
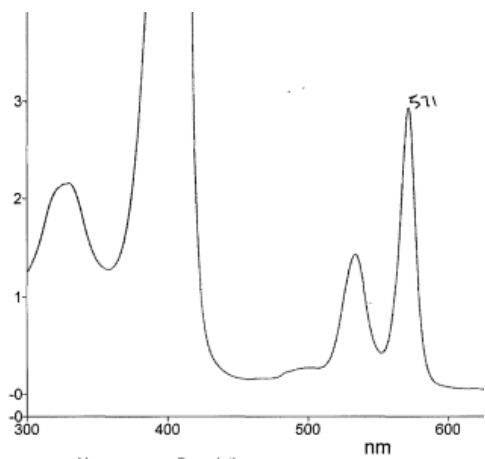
Figure 10. UV-Vis of 0.01mM V(OEP) in CH_2Cl_2.
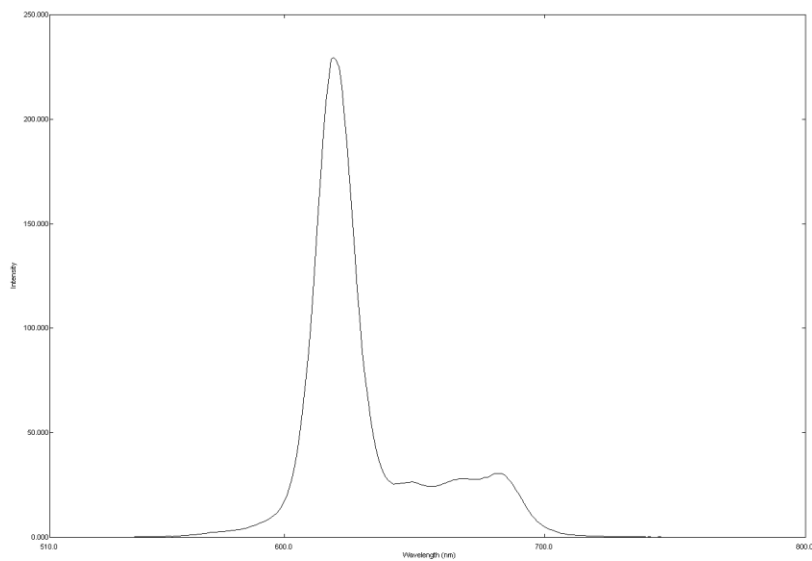
Figure 11. Photoluminescence of 0.01mM OEP in CH_2Cl_2.
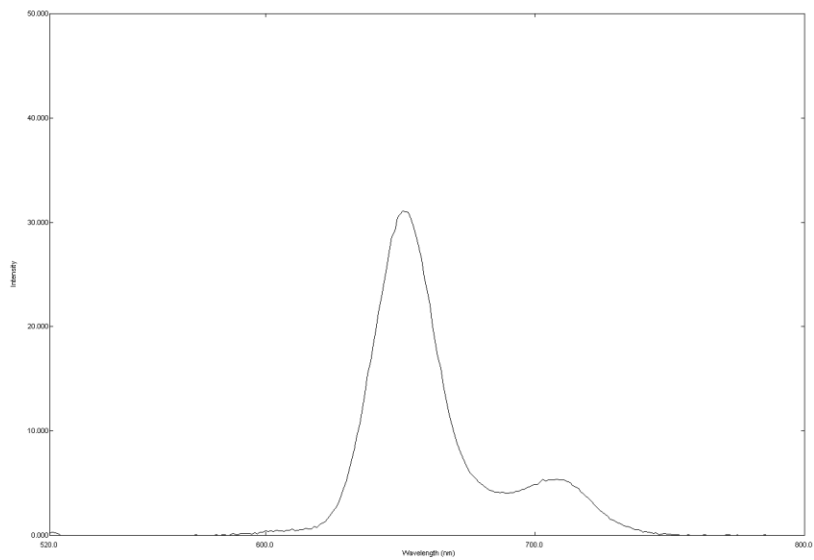
Figure 12. Photoluminescence of 0.01mM TPP in CH_2Cl_2.
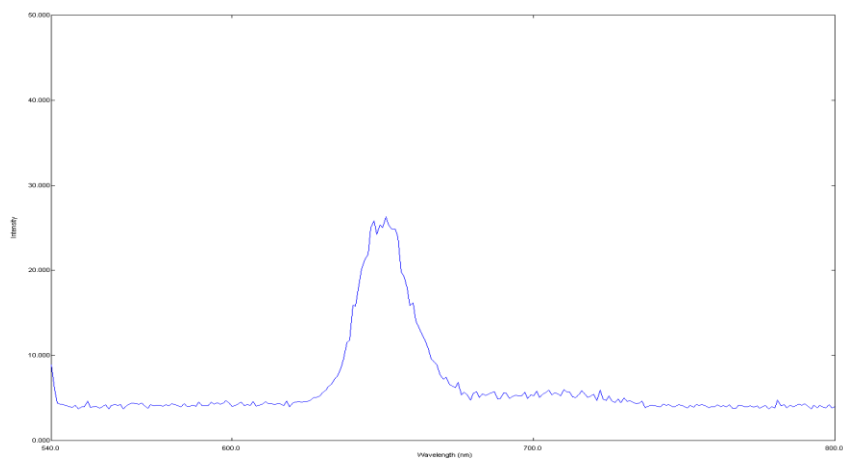
Figure 13. Photoluminescence of 0.01mM Cu(TPP) in CH_2Cl_2.
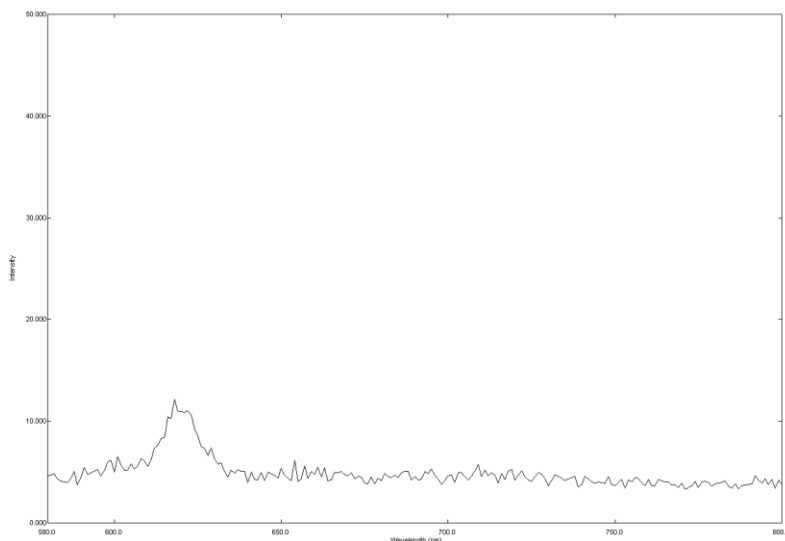
Figure 14. Photoluminescence of 0.01mM V(OEP) in CH_2Cl_2.

Electrogenerated Chemiluminescence: ECL versus potential. ECL was produced by sweeping to positive potentials using a platinum electrode in the presence of TPP, OEP or a metal complex, the electrolyte tetra-*n*-butylammonioum hexafluorophosphate (Bu_4NPF_6), and tri-*n*-propylamine (TPrA) as an "oxidative-reductive" coreactant, in methylene chloride. As seen in Figures 15 - 18 and the Appendix, the onset of ECL is at potentials corresponding to oxidation of TPrA and the porphryin or metal porphyrin complex.

On the basis of photoluminescence emission wavelengths, the energy needed to generate the emission around 600 nm is approximately 1.89 eV. Therefore, for direct generation of the excited state the energy of the electron or energy-transfer events between the electrogenerated coreactant and luminophore molecules must exceed these values. Since studies on a series of polyaromatic hydrocarbons have indicated that TPrA[•] is sufficiently energetic to generate excited states below 2.32 eV,[31] directly population of the excited state(s) in these systems is possible.

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ECL efficiencies (photons emitted per redox event) were between 0.010 and 0.770, respectively, lower than the $Ru(bpy)_3^{2+}$ standard ($\phi_{ecl} = 1$), Table 3. This is not surprising, given the complex nature of their electrochemistry. With the exception of Cu(OEP), Pt(OEP) and Ni(OEP) the ECL efficiencies are higher for the metal complexes than the ligands themselves. Since the metal centers can bond via the lone pairs on ligand nitrogens, bonding may prevent non-radiative decay from solvent-solute interactions. Closed shell, diamagnetic, Zn(II) porphyrins are highly photoluminescent, and have the highest ECL efficiencies. While open-shelled, paramagnetic metal porphyrins (e.g., Cu(II), Ni(II), etc) have lower PL and ECL efficiencies. In PL, this is due to mixing of the spin multiplicity paramagnetic center and the porphyrin ring that lowers the PL intensity.[32] However, open-shelled Cu(II) porphyrins do emit moderately strong phosphorescence in fluid solution at room temperature,[32] as is also reflected in the ECL. This suggests that the same states formed in PL are being formed in ECL. Detailed discussion of the excited states in metal porphyrins, as well as excited state assignments, can be found in the literature[32,33] and are beyond the scope of this work.
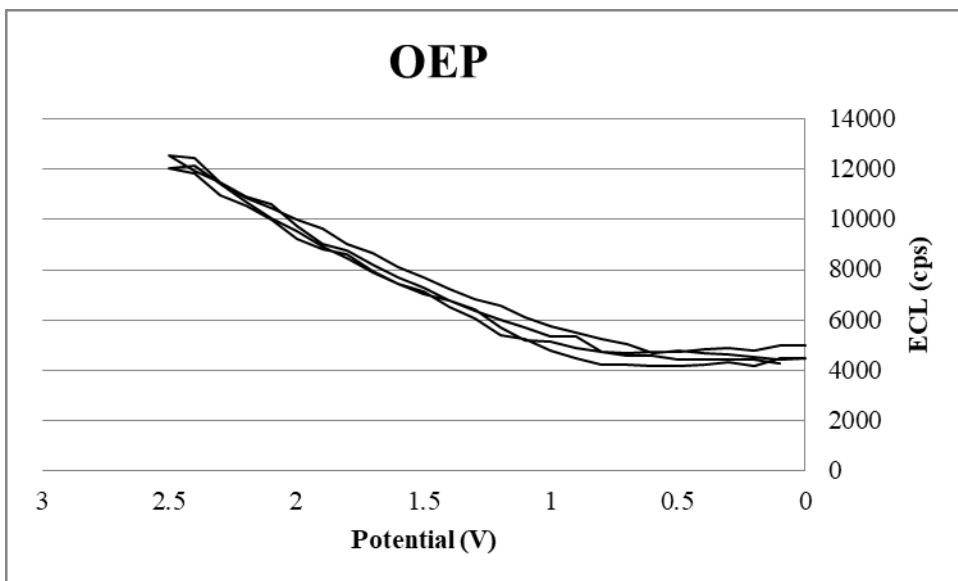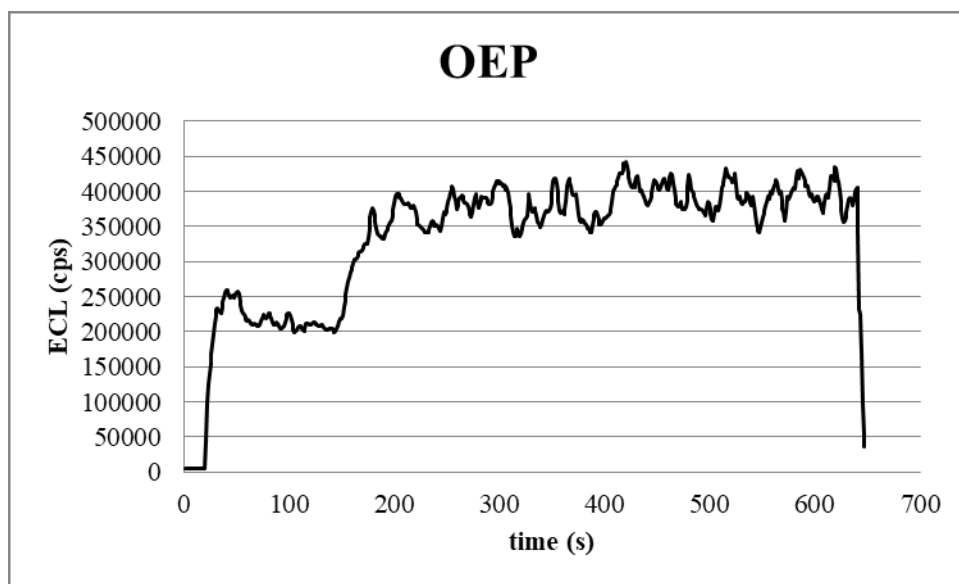
Figure 15. ECL intensity versus potential of 0.01mM OEP in CH_2Cl_2 (0.05M TPrA and 0.05 M Bu_4NPF_6).
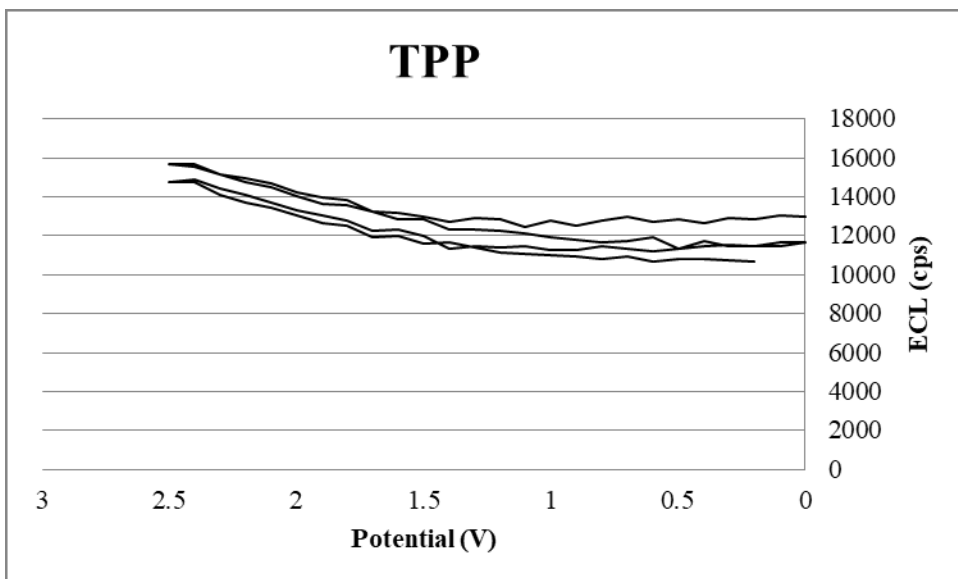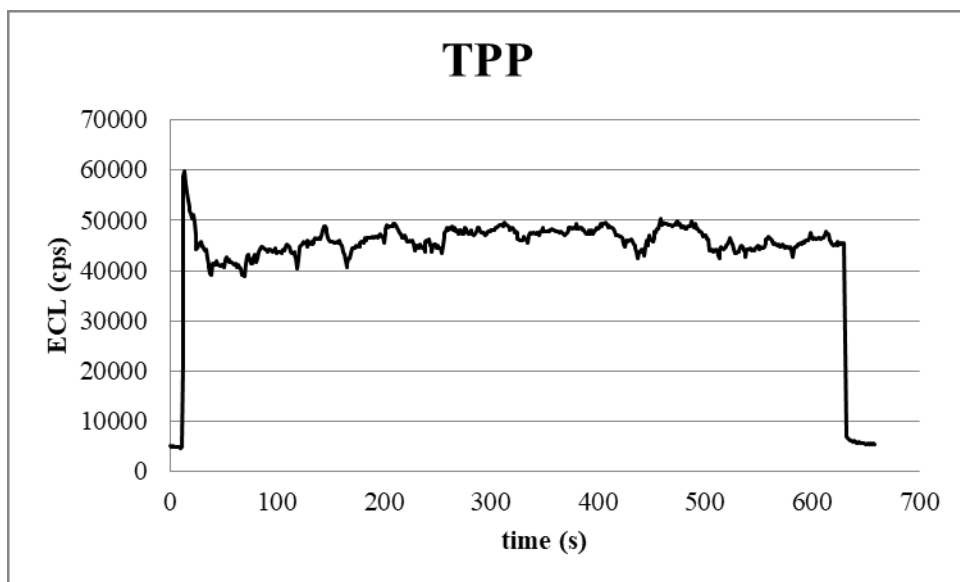

Figure 16. ECL intensity versus potential of 0.01mM TPP in CH_2Cl_2 (0.05M TPrA and 0.05 M Bu_4NPF_6).
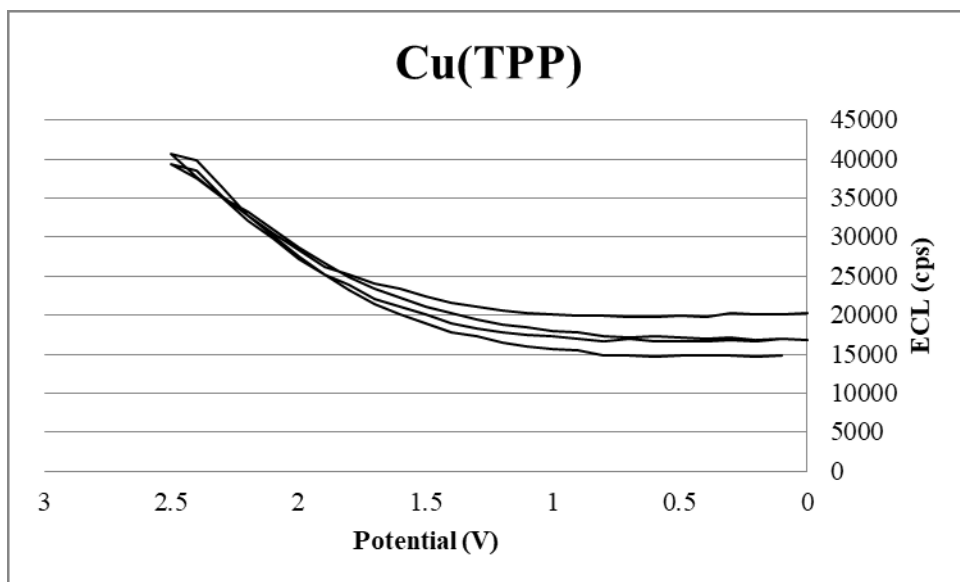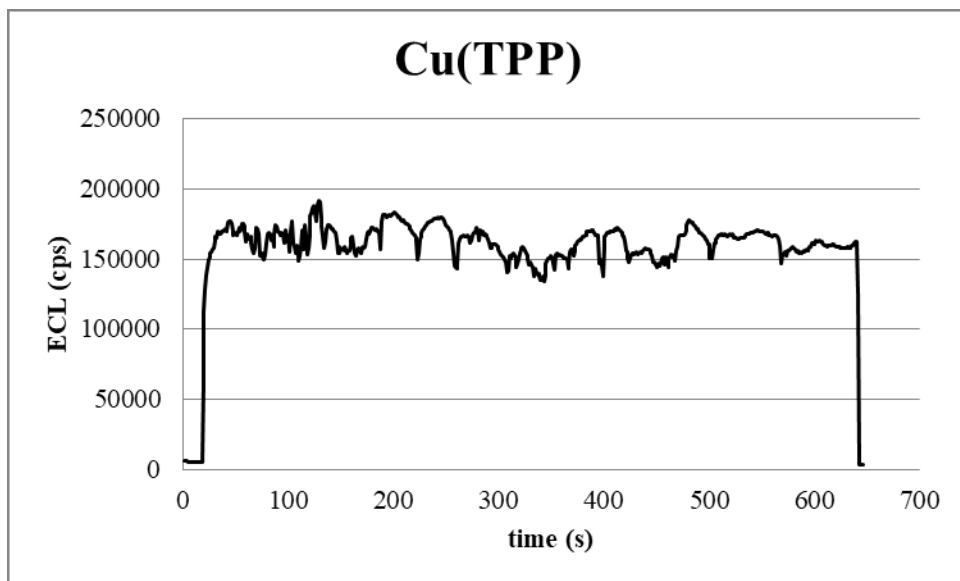
Figure 17. ECL intensity versus potential of 0.01mM Cu(TPP) in CH_2Cl_2 (0.05M TPrA and 0.05 M Bu_4NPF_6).
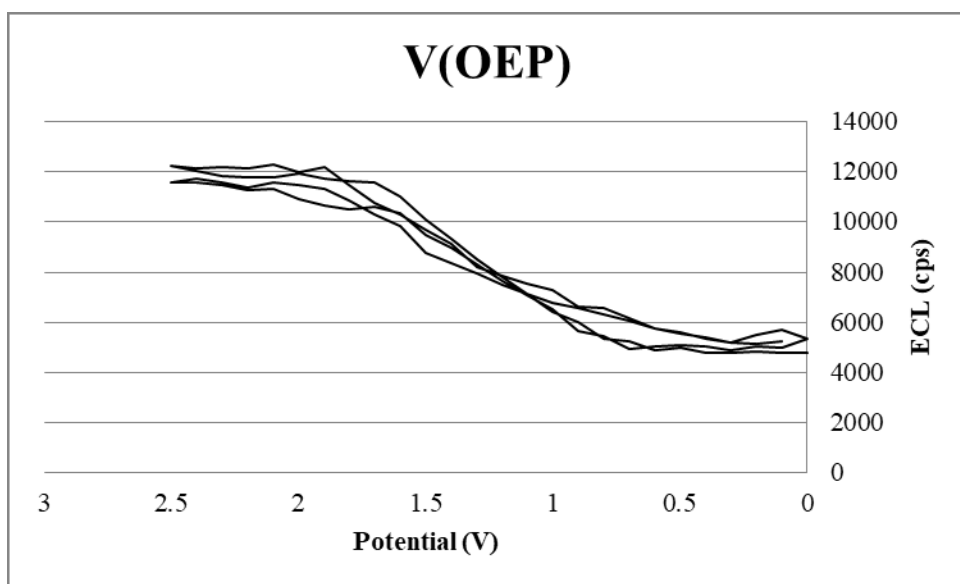
Figure 18. ECL intensity versus potential of 0.01mM V(OEP) in CH_2Cl_2 (0.05M TPrA and 0.05 M Bu_4NPF_6).
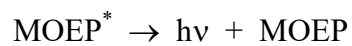
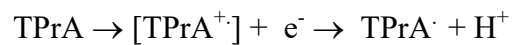Table 3. ECL Efficiencies of porphyrin complexes. 0.01mM compound in CH_2Cl_2; 0.05M TPrA; 0.05 M Bu_4NPF_6. Efficiencies were obtained using $Ru(bpy)_3^{2+}$ ($\phi_{ECL} = 1$) as a standard.

Compound	Φ_{ECL}
$Ru(bpy)_3^{2+}$	1.00
TPP	9.66×10^{-3}
Zn(TPP)	7.70×10^{-1}
Cu(TPP)	2.41×10^{-1}
OEP	3.16×10^{-2}
Zn(OEP)	2.11×10^{-1}
Cu(OEP)	1.40×10^{-1}
Ni(OEP)	4.57×10^{-3}
V(OEP)	1.50×10^{-2}
Pd(OEP)	4.23×10^{-1}
Ru(OEP)	9.65×10^{-2}
Co(OEP)	4.12×10^{-3}
Pt(OEP)	2.97×10^{-2}

Electrogenerated Chemiluminescence: ECL versus time. ECL intensity versus time scans are in Figures 19 - 22 and in the Appendix. The potential of the working electrode was cycled from 0 to +2.0 V and back to 0 over the course of several hundred seconds, and the ECL intensity was measured. For Ru(bpy)$_3^{2+}$/TPrA there was a sharp decrease in light intensity over time due to lower concentrations of coreactant and luminophore near the electrode surface and fouling of the electrode surface. This also indicates that the ECL is diffusion controlled. For the porphyrin complexes the ECL versus time spectra are much different. They do not reach peak intensity for several seconds and most do not achieve diffusion control within the time frame of the experiment. This could be due to many factors, including the production of luminescent species not observed in the PL experiments. For example, from interactions between the oxidized species, TPrA and/or solvent.

Figure 19. ECL intensity versus time of 0.01mM OEP in CH$_2$Cl$_2$ (0.05M TPrA and 0.05 M Bu$_4$NPF$_6$).

Figure 20. ECL intensity versus potential of 0.01mM TPP in CH_2Cl_2 (0.05M TPrA and 0.05 M Bu_4NPF_6).

Figure 21. ECL intensity versus potential of 0.01mM Cu(TPP) in CH_2Cl_2 (0.05M TPrA and 0.05 M Bu_4NPF_6).
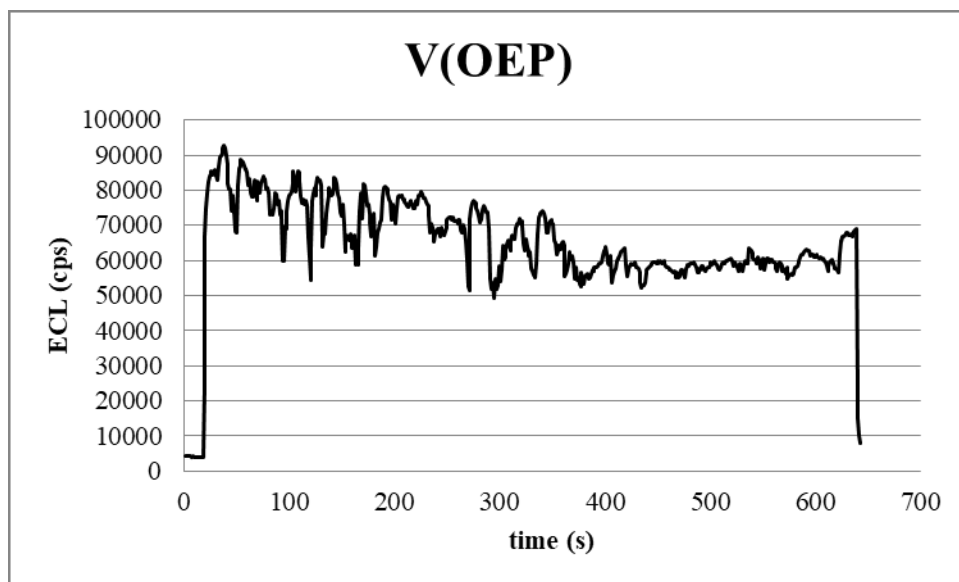
Figure 22. ECL intensity versus potential of 0.01mM V(OEP) in CH_2Cl_2 (0.05M TPrA and 0.05 M Bu_4NPF_6).

Conclusions

ECL Spectra. To determine whether the same excited states are formed in ECL as PL the measurement of ECL spectra are planned. Due to time constraints it was not possible to complete them during the Spring 2018 semester, so they will be run in early Summer 2018. However, in other ECL/Porphryin studies[16, 17,21,22] the same excited states were formed in both experiments, even those that did not obtain diffusion control (i.e., ECL versus time).

Proposed Mechanism. Based on the electrochemical and ECL experiments presented above, and by analogy with the $Ru(bpy)_3^{2+}$/TPrA[26] and other transition metal/TPrA systems,[5] the generation of luminescence from the metal porphyrin systems (and the porphyrins themselves) in the presence of TPrA can be explained by the following reactions:

$$MOEP \rightarrow MOEP^{+\cdot} + e^-$$

25

$$\text{TPrA} \rightarrow [\text{TPrA}^{+\cdot}] + e^- \rightarrow \text{TPrA}^\cdot + H^+$$

$$\text{MOEP}^{+\cdot} + \text{TPrA}^\cdot \rightarrow \text{MOEP}^* + \text{products}$$

$$\text{MOEP}^* \rightarrow h\nu + \text{MOEP}$$
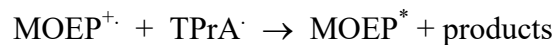
As discussed in the literature, these equations are most likely an oversimplification, as both $\text{TPrA}^\cdot$ and $[\text{TPrA}^{+\cdot}]$ have been shown to transfer electrons in the ECL reaction sequence.[34] It is also possible that the excited state may be formed in the following manner:

$$\text{MOEP} + \text{TPrA}^\cdot \rightarrow \text{MOEP}^{-\cdot}$$

$$\text{MOEP}^{-\cdot} + \text{MOEP}^{+\cdot} \rightarrow \text{MOEP}^* + \text{MOEP}$$
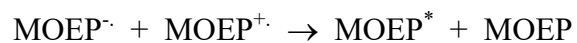
CHAPTER 4: FUTURE WORK

First is the measurement of ECL spectra to determine the probable identity of the excited states, followed by submission of a manuscript to a peer-reviewed journal. Second, it would be interesting to test other metal porphyrin systems to see whether the open-shelled versus closed-shell trends continue as seen in PL and this work. Next, this project be expanded to look at metal-porphyrins important in biological systems, such as hemoglobin and chlorophyll.

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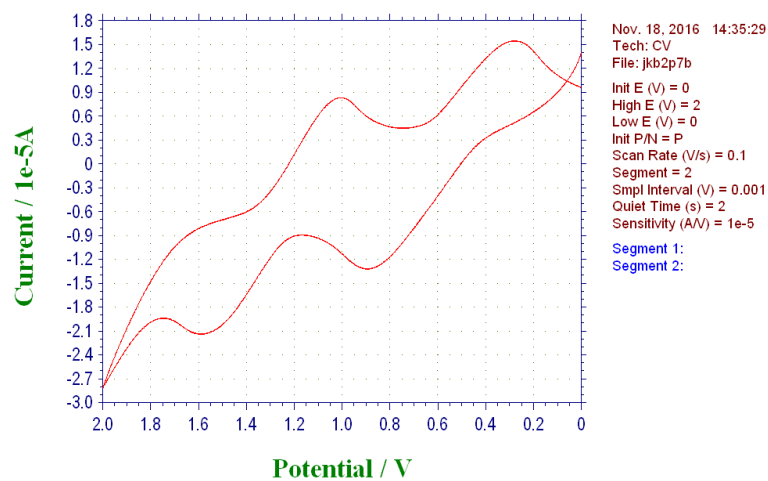[17] N.E. Tokel, C.P. Keszthelyi, A.J. Bard, J. Am. Chem. Soc. 94 (1972) 4872-4877.

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APPENDIX

Electrochemistry
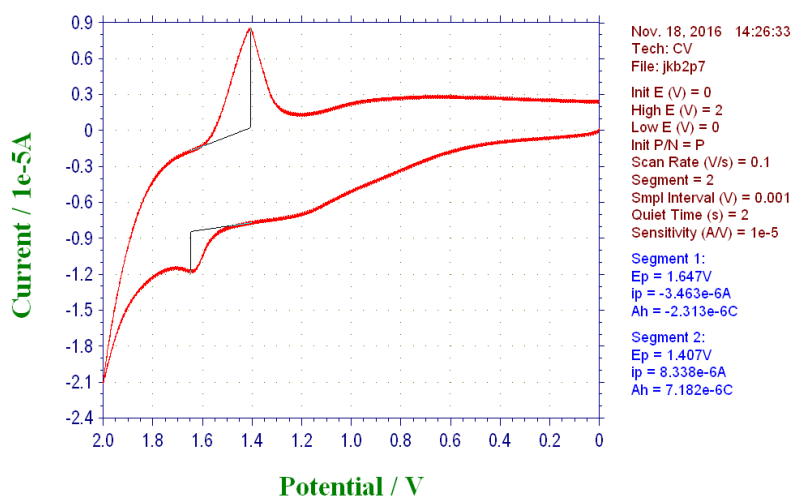
A1. Cyclic Voltammetry of Ru(bpy)$_3{}^{2+}$ in a solution of TPrA/CH$_2$Cl$_2$.

A2. Cyclic Voltammetry of Cu(OEP) in a solution of TPrA/CH$_2$Cl$_2$.

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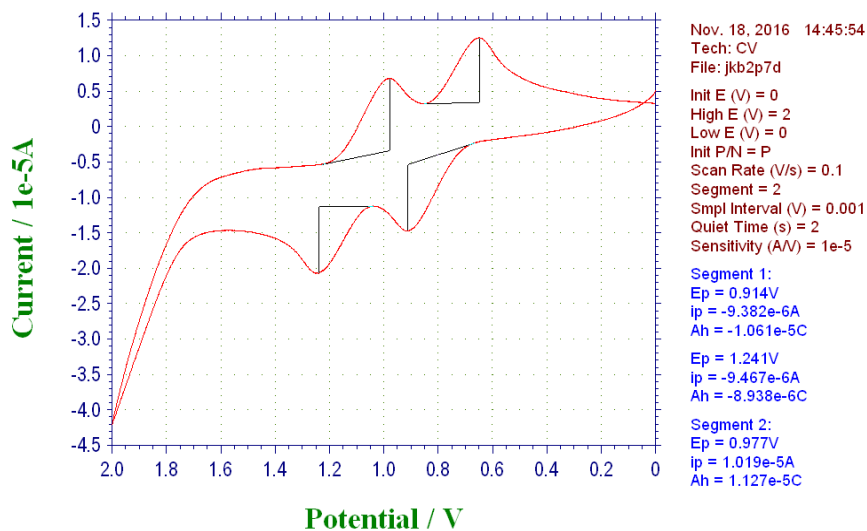
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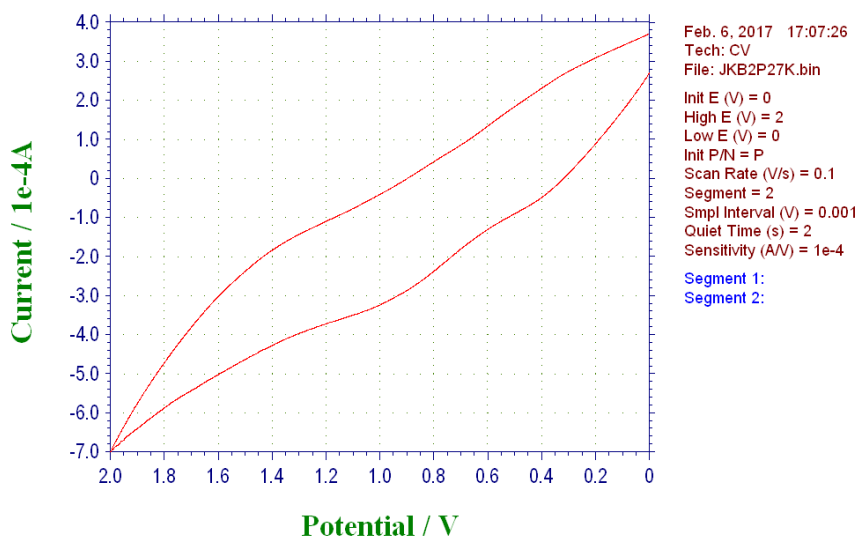
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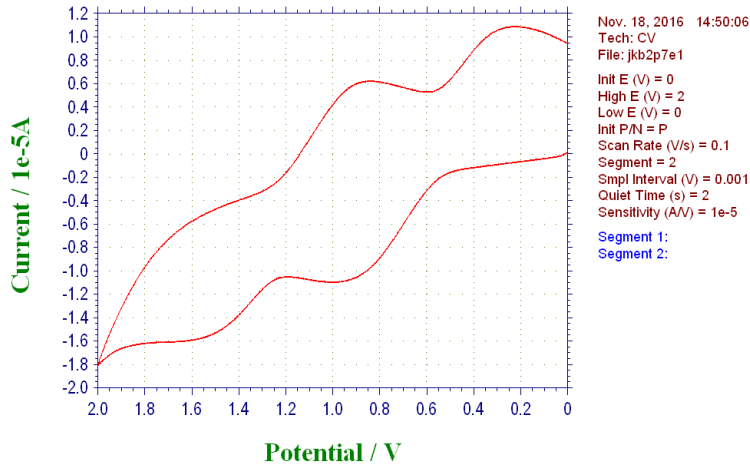
A5. Cyclic Voltammetry of Ru(OEP) in a solution of TPrA/CH₂Cl₂.

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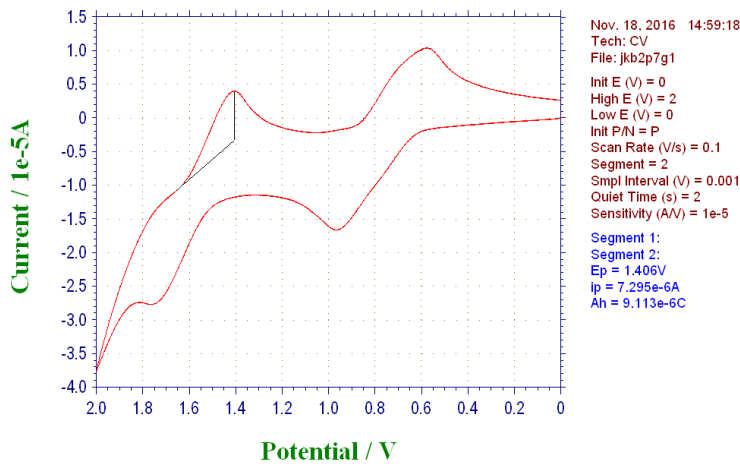
Figure A6. Cyclic Voltammetry of Pd(OEP) in a solution of TPrA/CH₂Cl₂.

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32
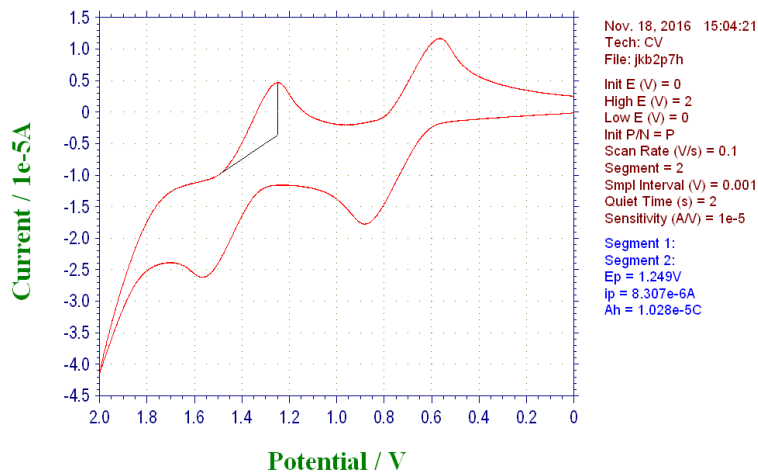
A7. Cyclic Voltammetry of Ni(OEP) in a solution of TPrA/CH₂Cl₂.
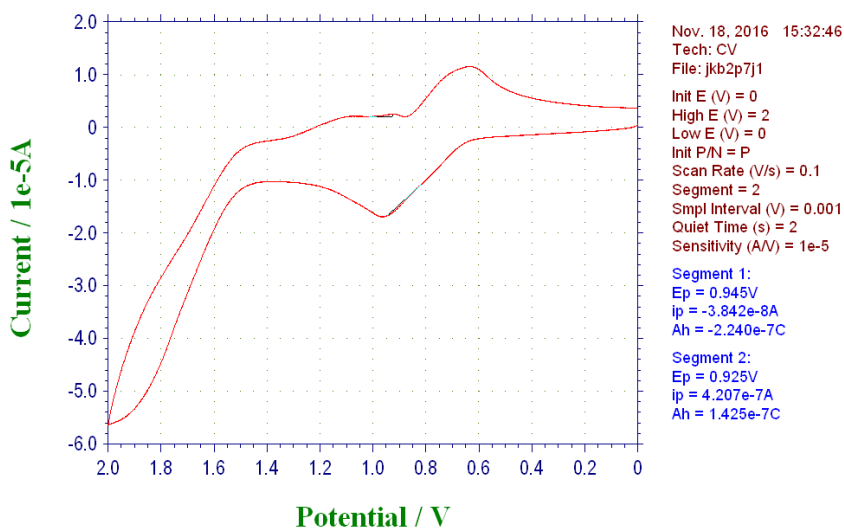
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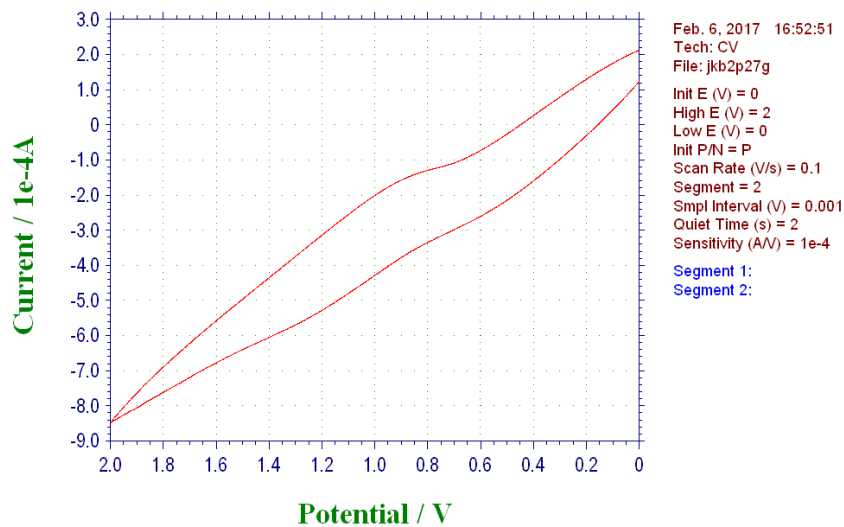
A9. Cyclic Voltammetry of Co(OEP) in a solution of TPrA/CH₂Cl₂.

UV-Vis and PL Spectroscopy
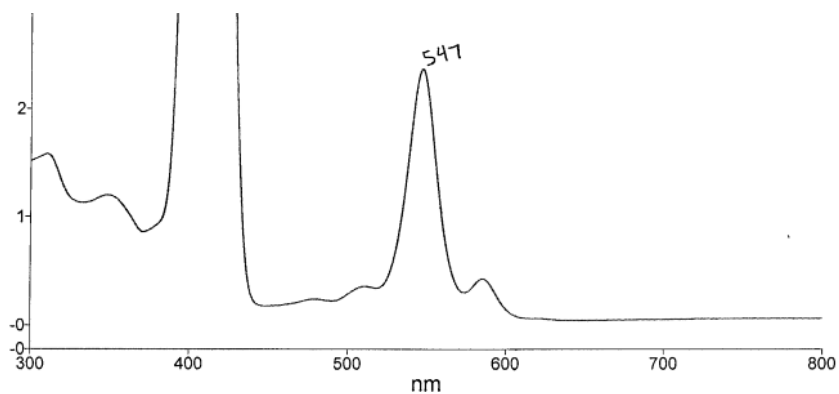
A10. UV-Vis of Zn(TPP) in a solution of CH₂Cl₂.
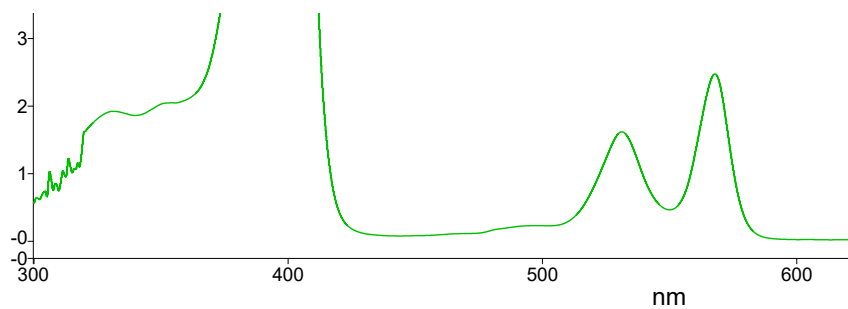
A11. UV-Vis of Zn(OEP) in a solution of CH₂Cl₂.
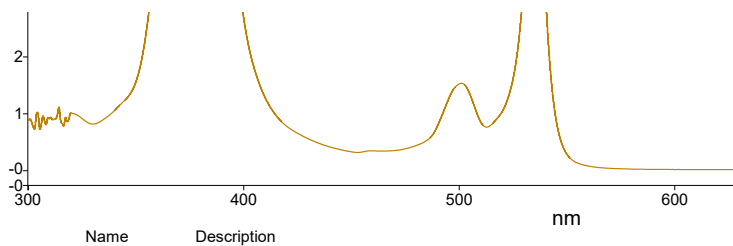
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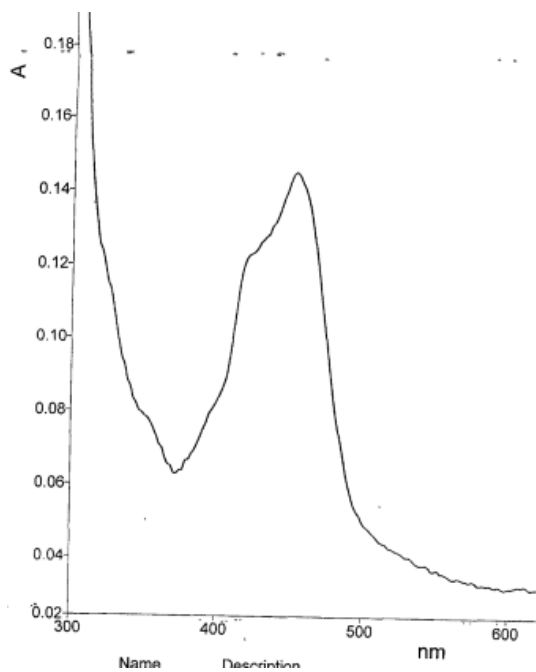
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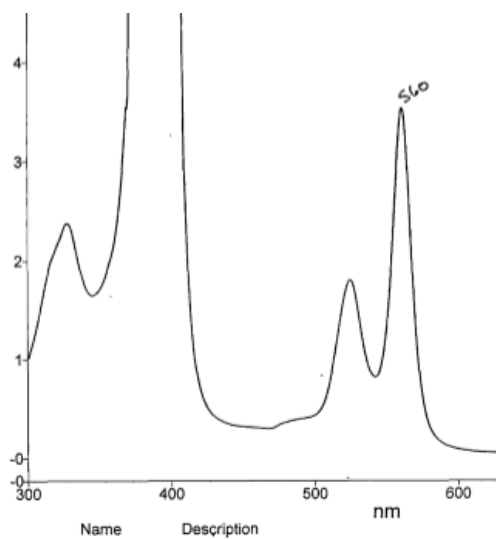
A14. UV-Vis of Cu(OEP) in a solution of CH$_2$Cl$_2$.
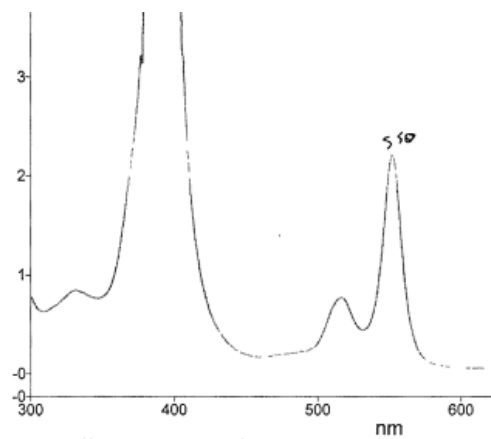
A15. UV-Vis of Ni(OEP) in a solution of CH₂Cl₂.
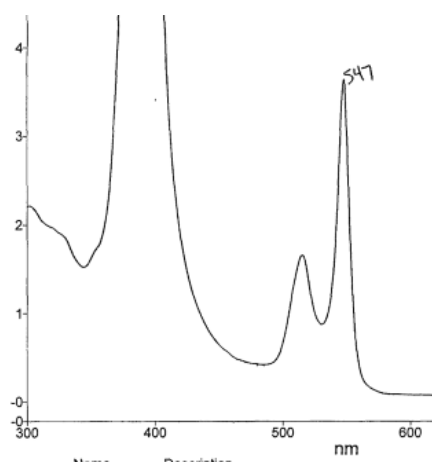
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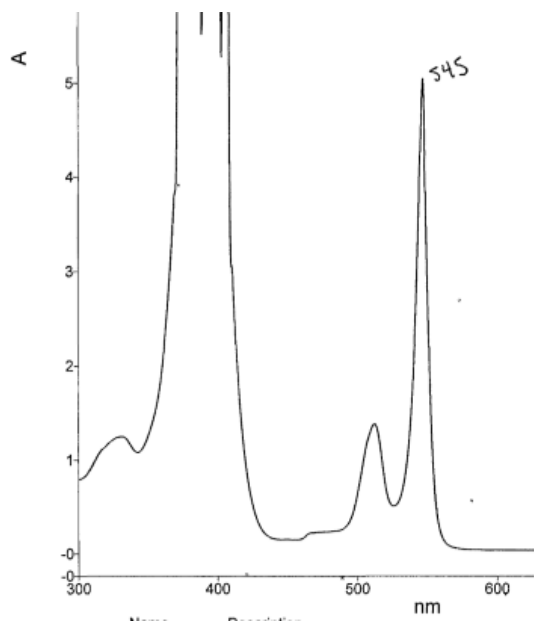
A17. UV-Vis of Pd(OEP) in a solution of CH₂Cl₂.
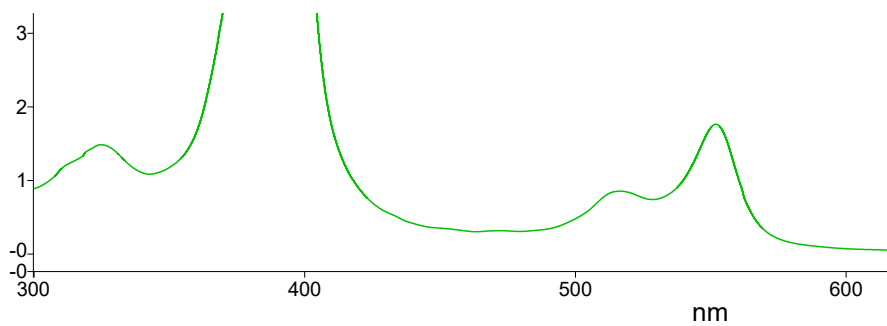
A18. UV-Vis of Co(OEP) in a solution of CH₂Cl₂.
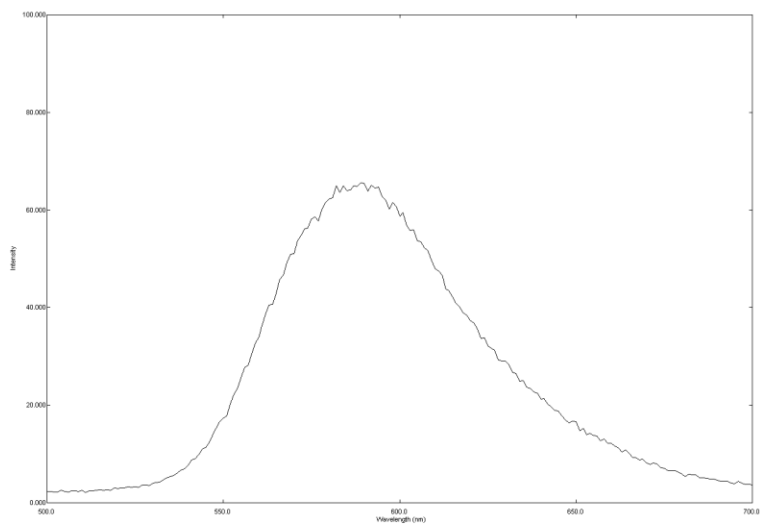
A19. Photoluminescence of $Ru(bpy)_3^{2+}$ in a solution of CH_2Cl_2.
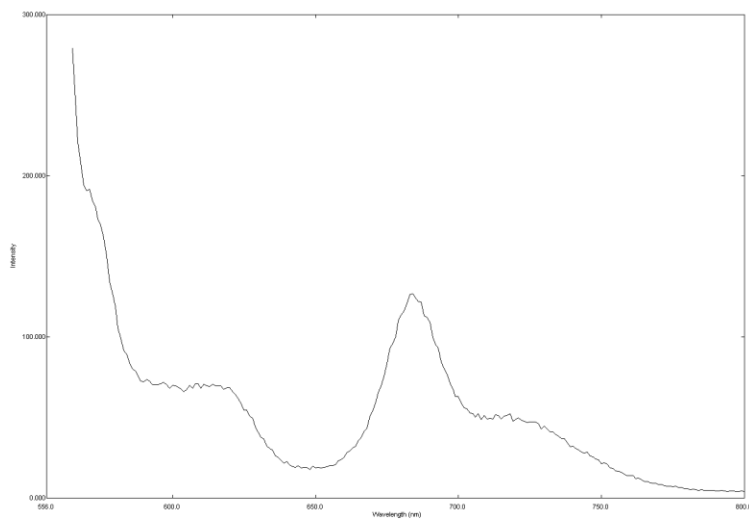
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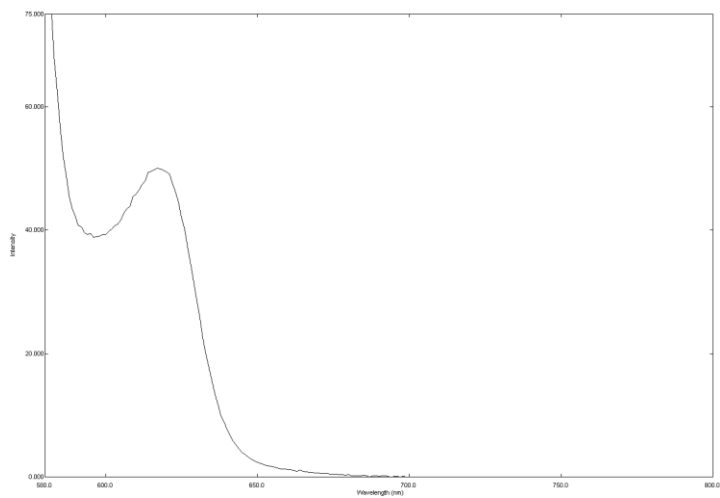
A21. Photoluminescence of Zn(OEP) in a solution of CH₂Cl₂.
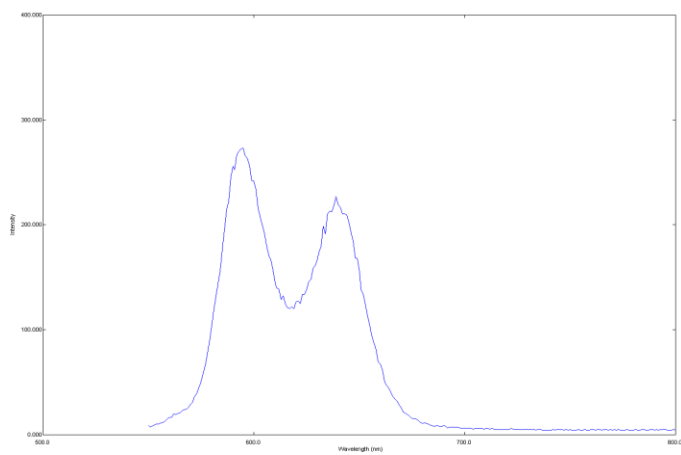
A22. Photoluminescence of Zn(TPP) in a solution of CH₂Cl₂.
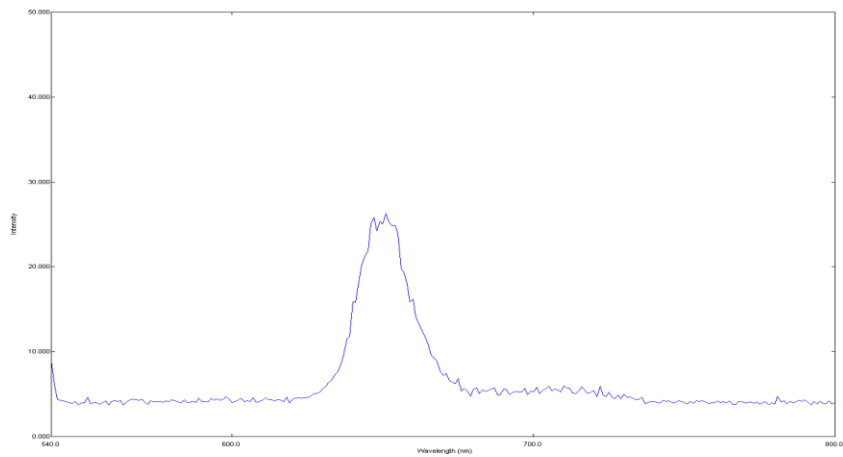
A23. Photoluminescence of Cu(TPP) in a solution of CH₂Cl₂.
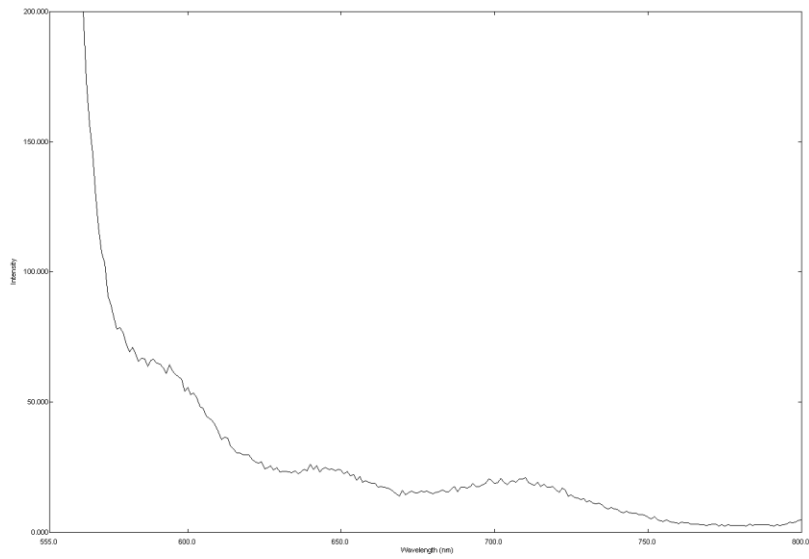
A24. Photoluminescence of Ni(OEP) in a solution of CH₂Cl₂.
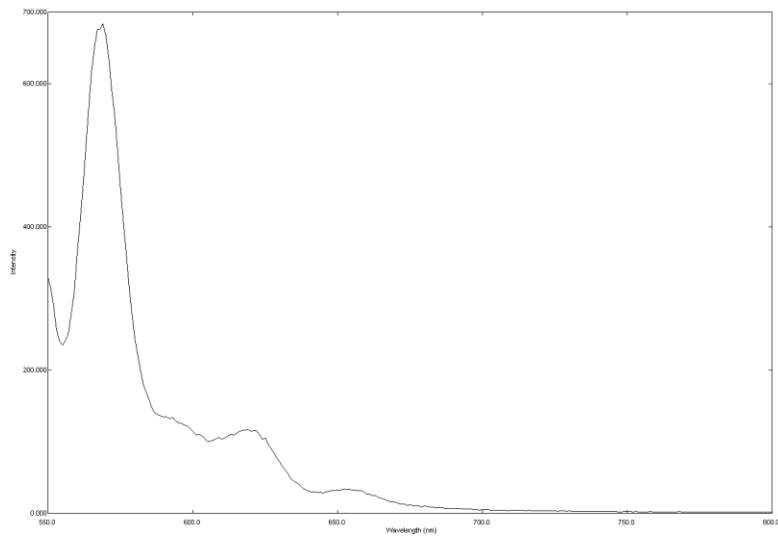
A25. Photoluminescence of Ru(OEP) in a solution of CH₂Cl₂.
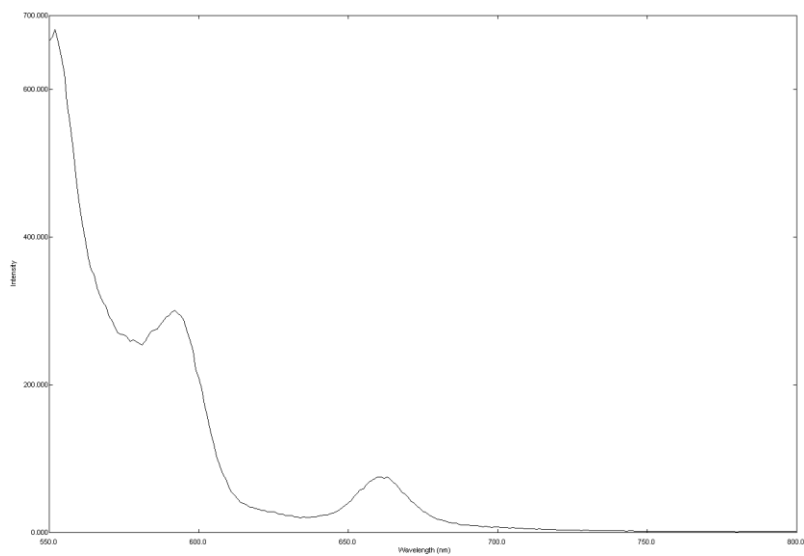
A26. Photoluminescence of Pd(OEP) in a solution of CH₂Cl₂.
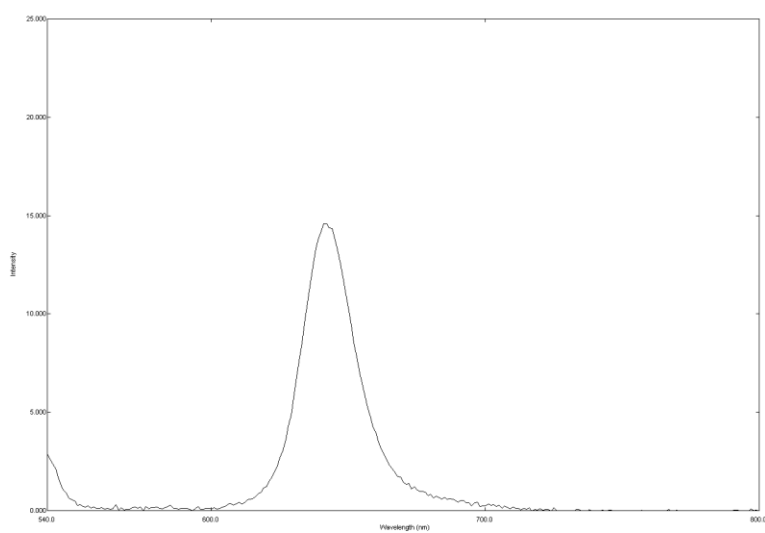
A27. Photoluminescence of Pt(OEP) in a solution of CH₂Cl₂.
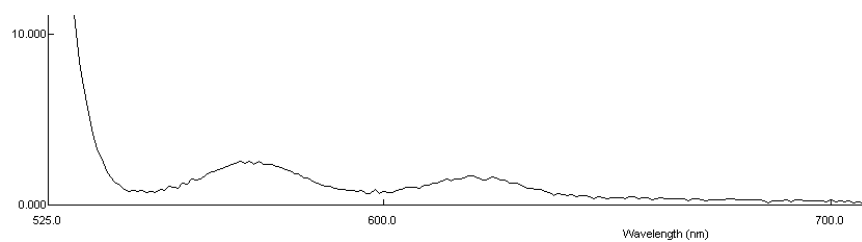
A28. Photoluminescence of Co(OEP) in a solution of CH₂Cl₂.

ECL versus potential
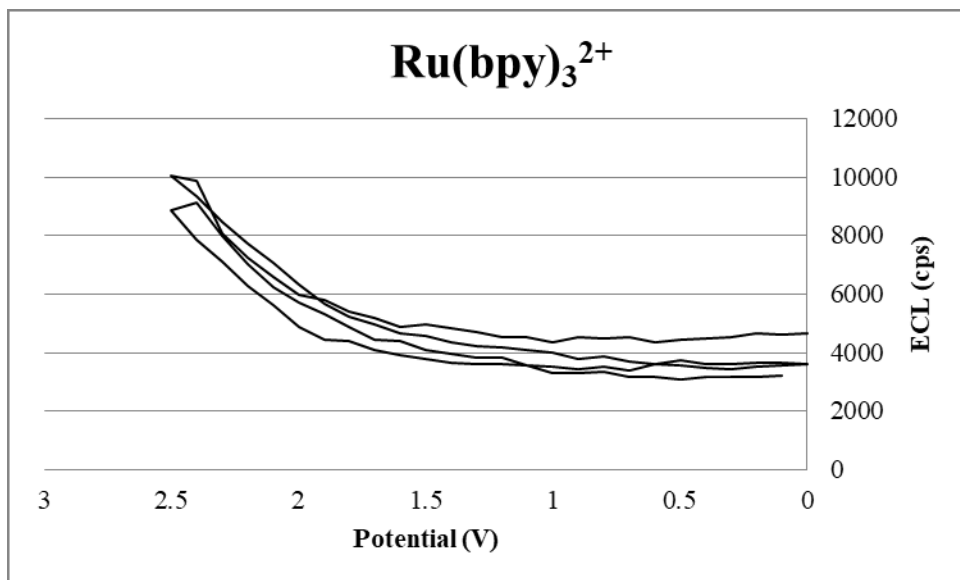
A29. ECL intensity versus potential for Ru(bpy) in a solution of TPrA/CH$_2$Cl$_2$.
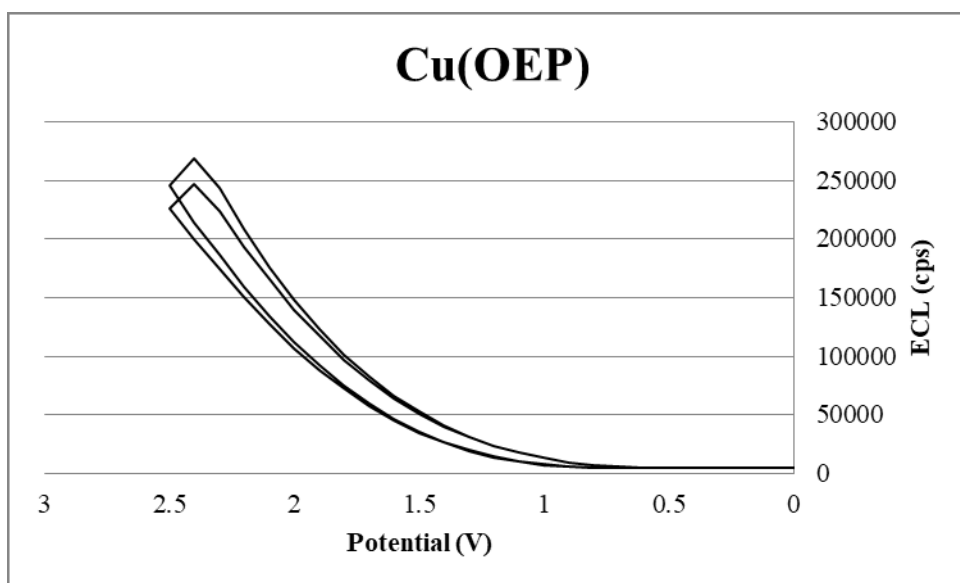
A30. ECL intensity versus potential for Cu(OEP) in a solution of TPrA/CH$_2$Cl$_2$.
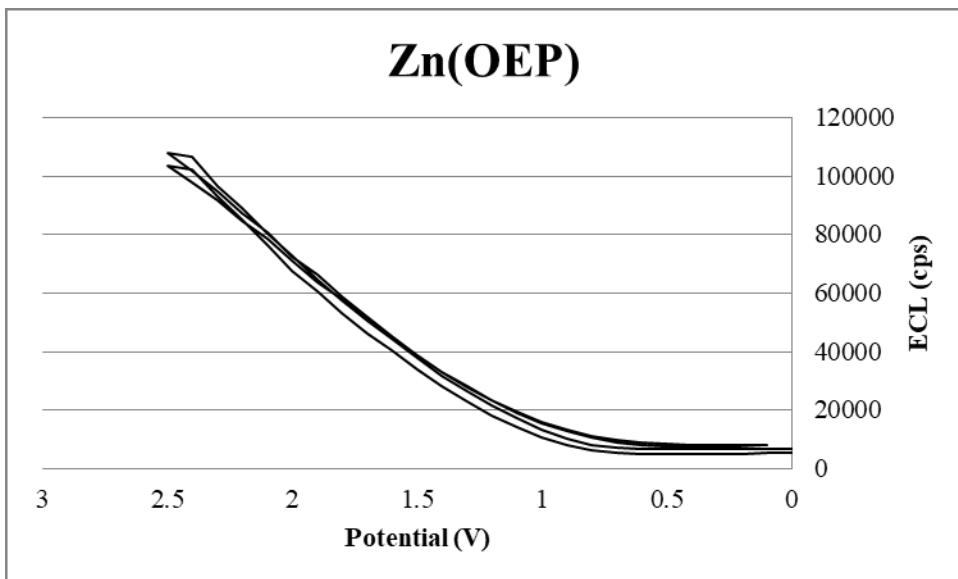
A31. ECL intensity versus potential for Zn(OEP) in a solution of TPrA/CH₂Cl₂.
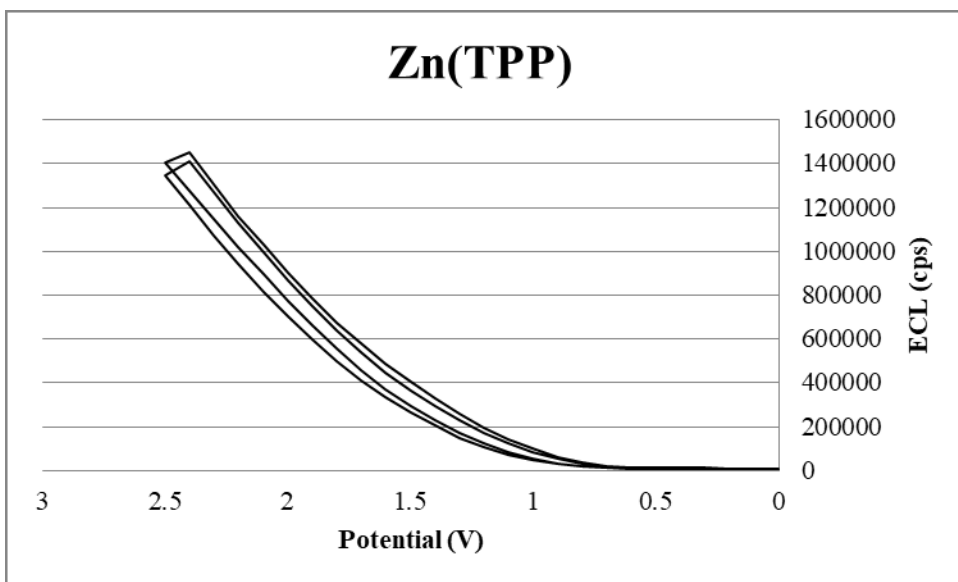
A32. ECL intensity versus potential for Zn(TPP) in a solution of TPrA/CH₂Cl₂.
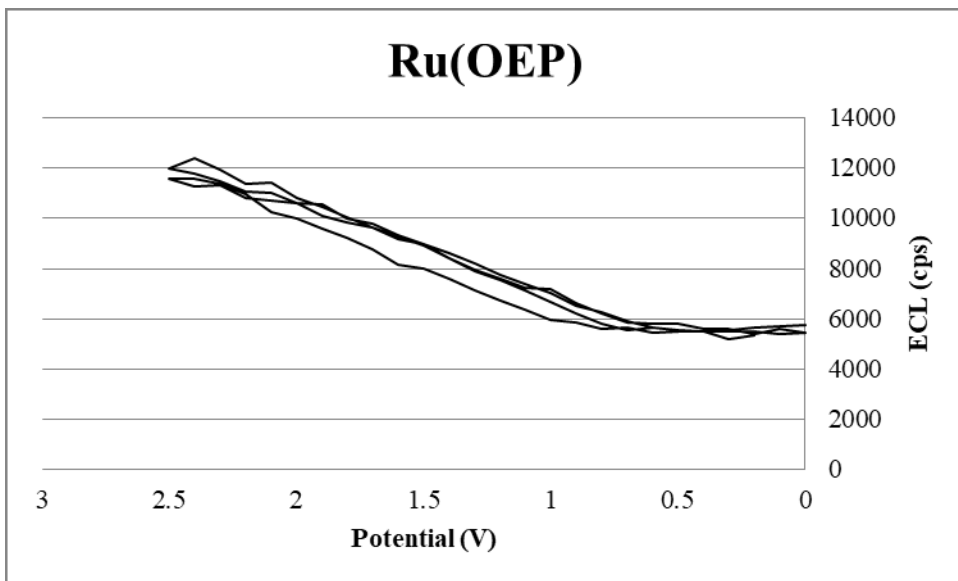
A33. ECL intensity versus potential for Ru(OEP) in a solution of TPrA/CH₂Cl₂.
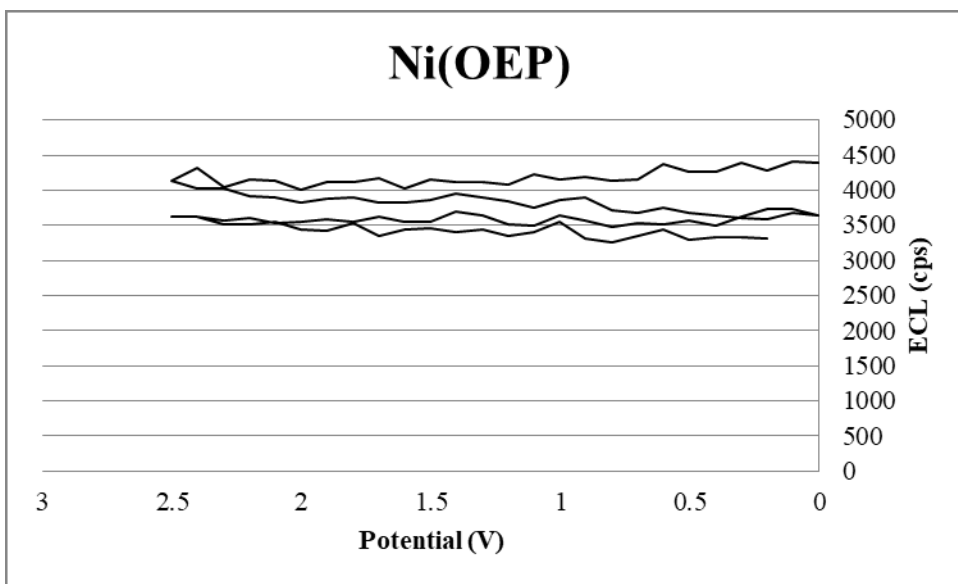
A34. ECL intensity versus potential for No(OEP) in a solution of TPrA/CH₂Cl₂.
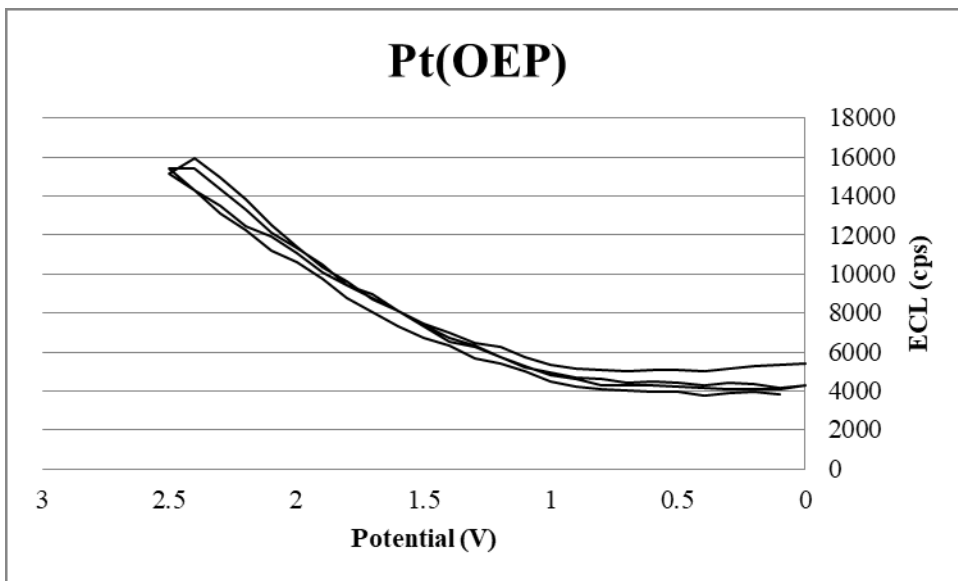
A35. ECL intensity versus potential for Pt(OEP) in a solution of TPrA/CH$_2$Cl$_2$.
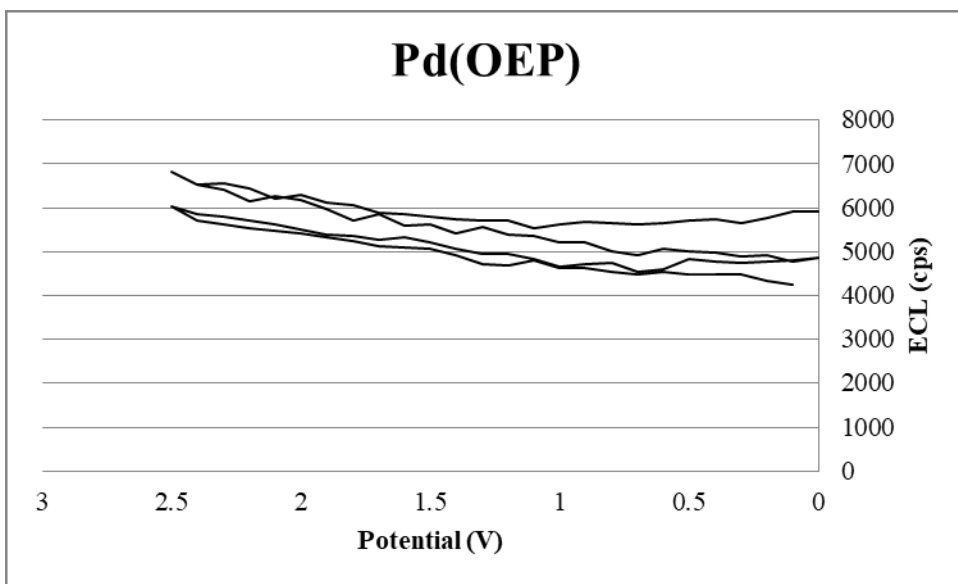
A36. ECL intensity versus potential for Pd(OEP) in a solution of TPrA/CH$_2$Cl$_2$.
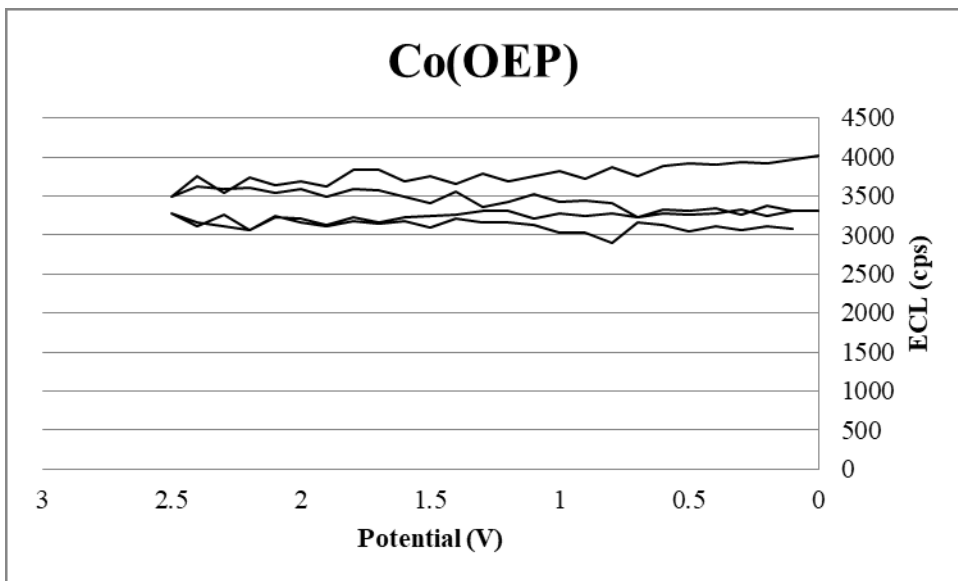
A37. ECL intensity versus potential for Co(OEP) in a solution of TPrA/CH₂Cl₂.

ECL versus time
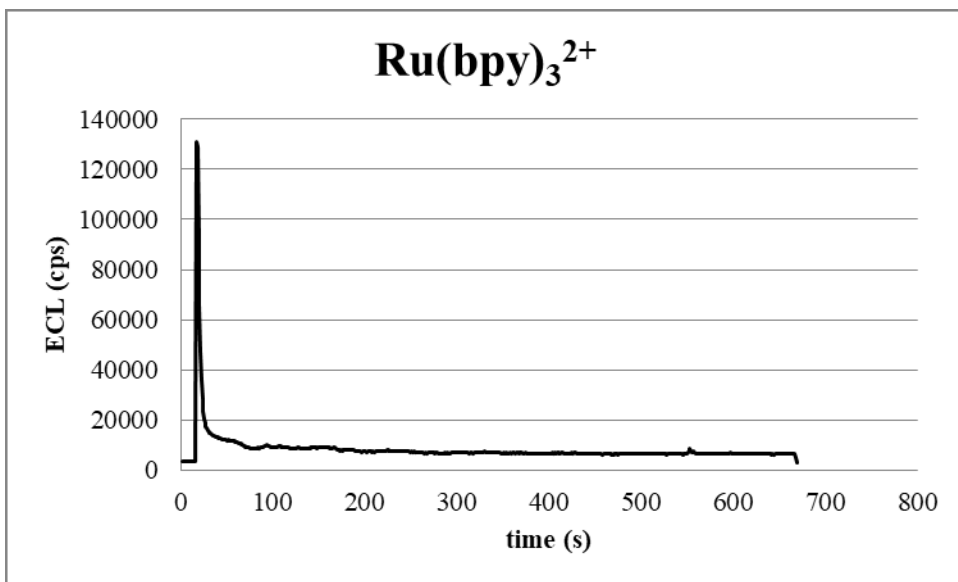
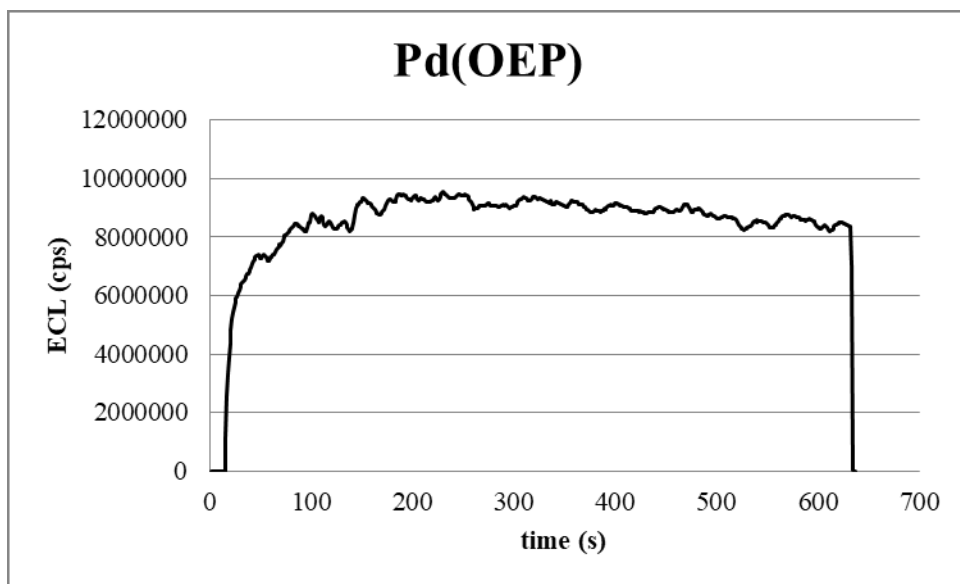A38. ECL vs. time for Ru(bpy)$_3^{2+}$ in a solution of TPrA/CH₂Cl₂.
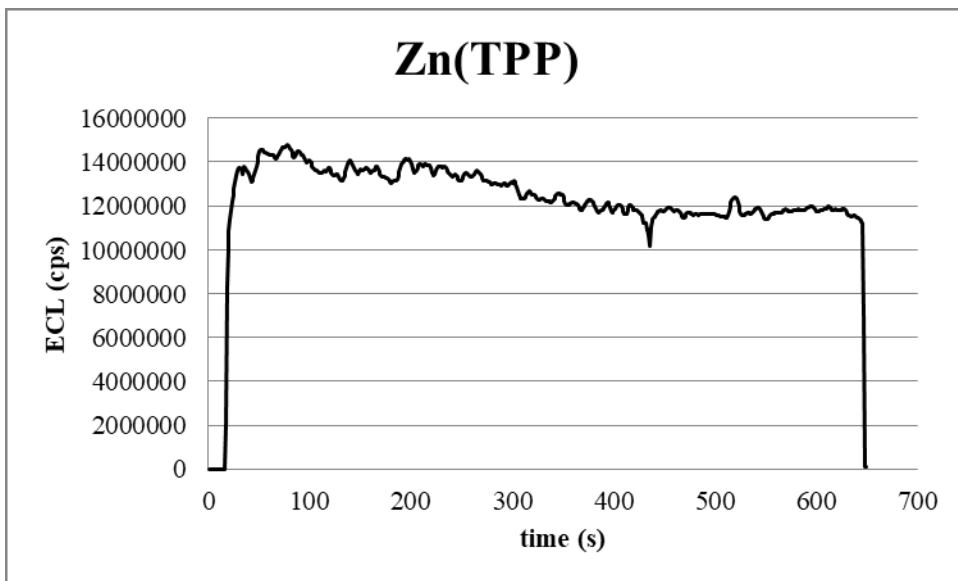
A39. ECL vs time of Zn (TPP) in a solution of TPrA/CH_2Cl_2.
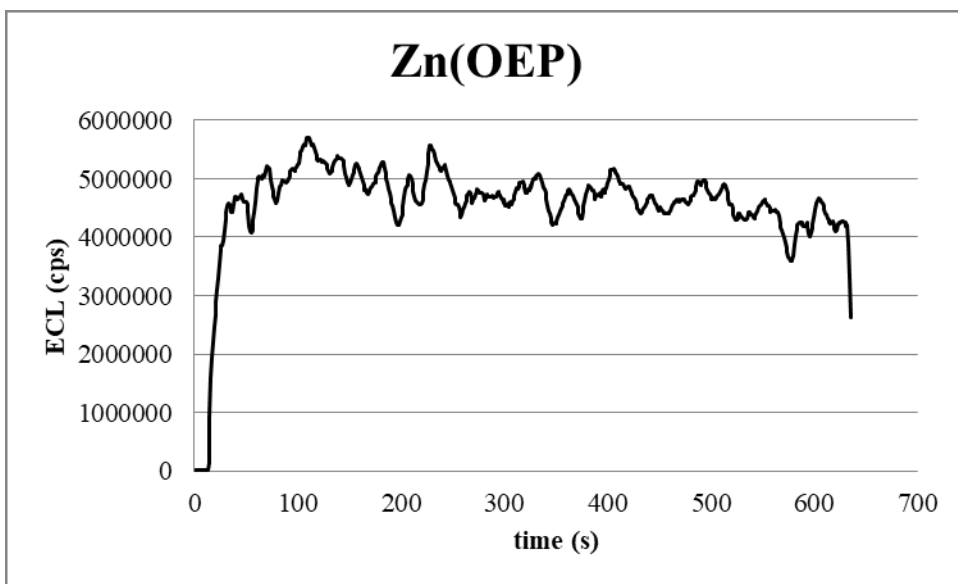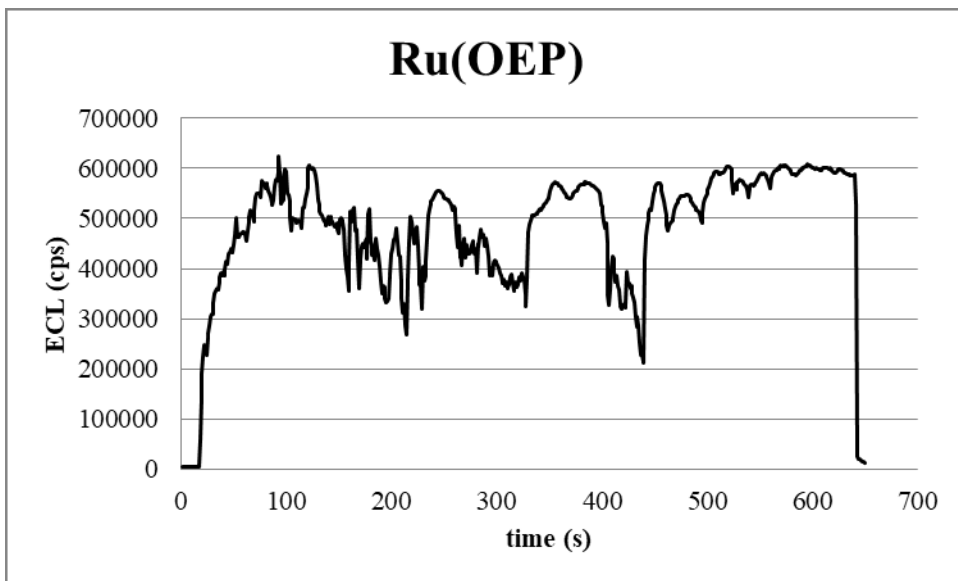

A40. ECL vs time of Zn (OEP) in a solution of TPrA/CH_2Cl_2.
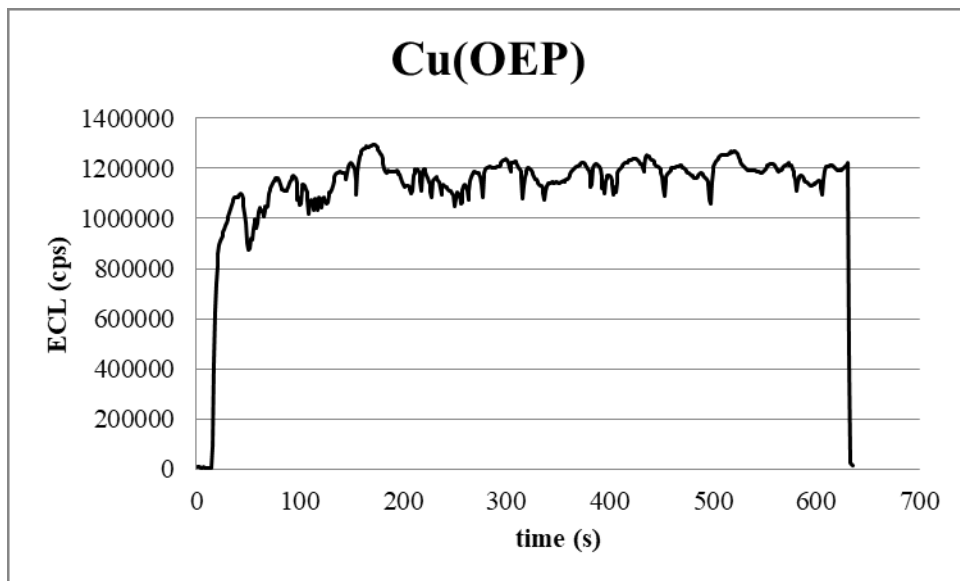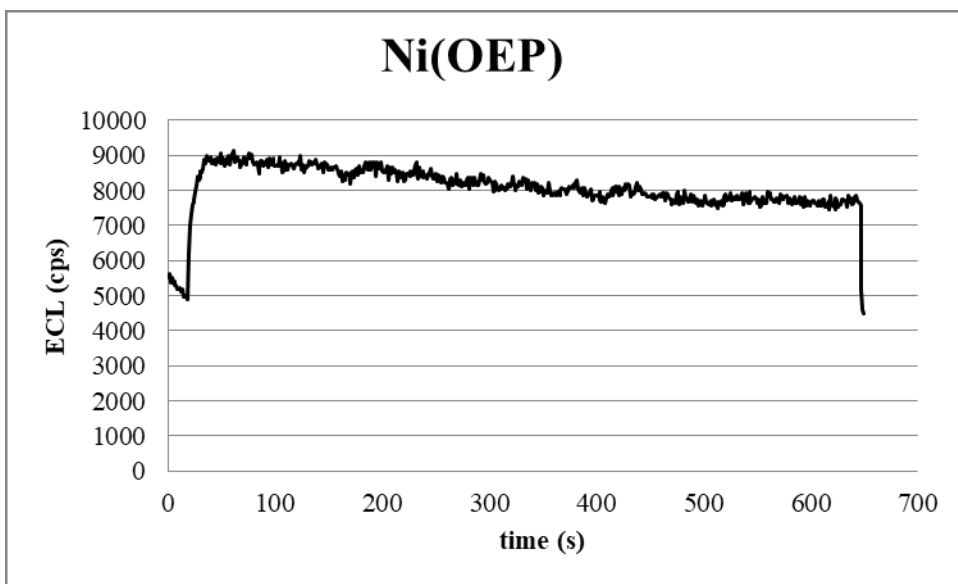
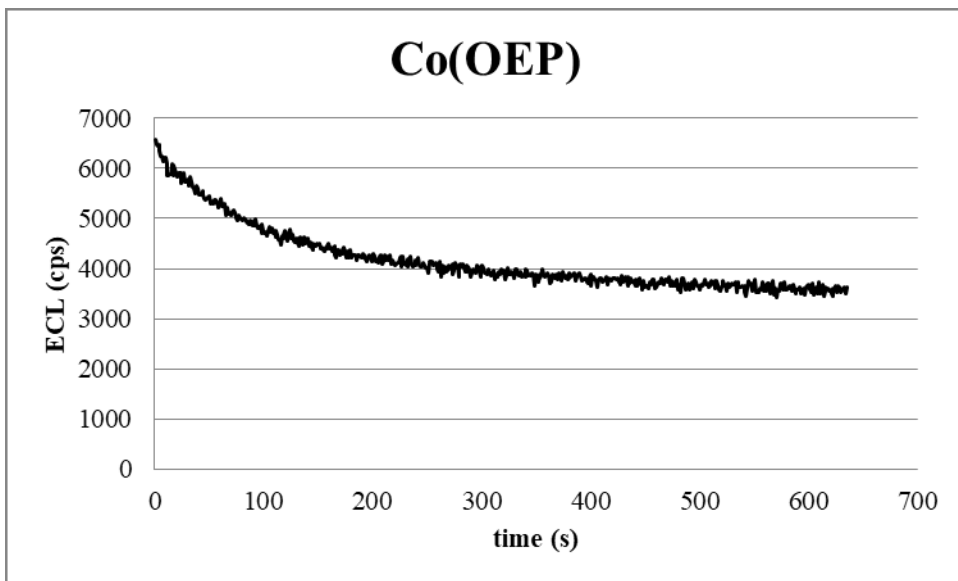A41. ECL vs time of Cu(OEP) in a solution of TPrA/CH$_2$Cl$_2$.

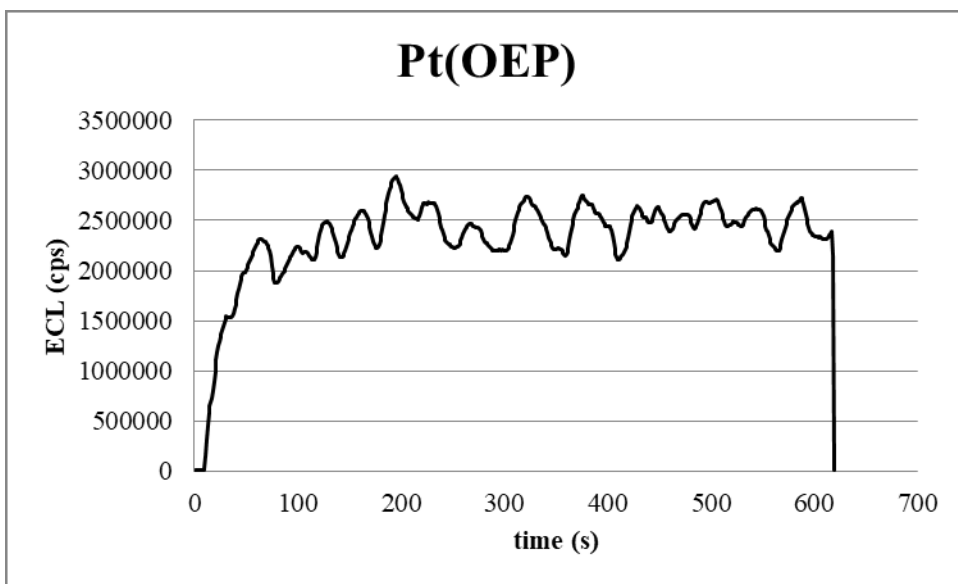A42. ECL vs. time for Pd(OEP) in a solution of TPrA/CH$_2$Cl$_2$.

A43. ECL vs. time for Ru(OEP) in a solution of TPrA/CH_2Cl_2.

A44. ECL vs. time for Ni(OEP) in a solution of TPrA/CH_2Cl_2.

A45. ECL vs. time for Co(OEP) in a solution of TPrA/CH₂Cl₂.

A46. ECL vs. time for Pt(OEP) in a solution of TPrA/CH₂Cl₂.