

16	9	33	92
<b>S</b>	<b>F</b>	<b>As</b>	<b>U</b>
32.06	18.99	74.91	238.03

# Urea-bis(Coumarin-enamine) Chemosensor for Relay Recognition of Anion and Cation

Marlene Zepeta-Rodriguez and Rashid Mia\*

Department of Chemistry and Biochemistry, Stephen F. Austin State University, Nacogdoches, Texas 75962

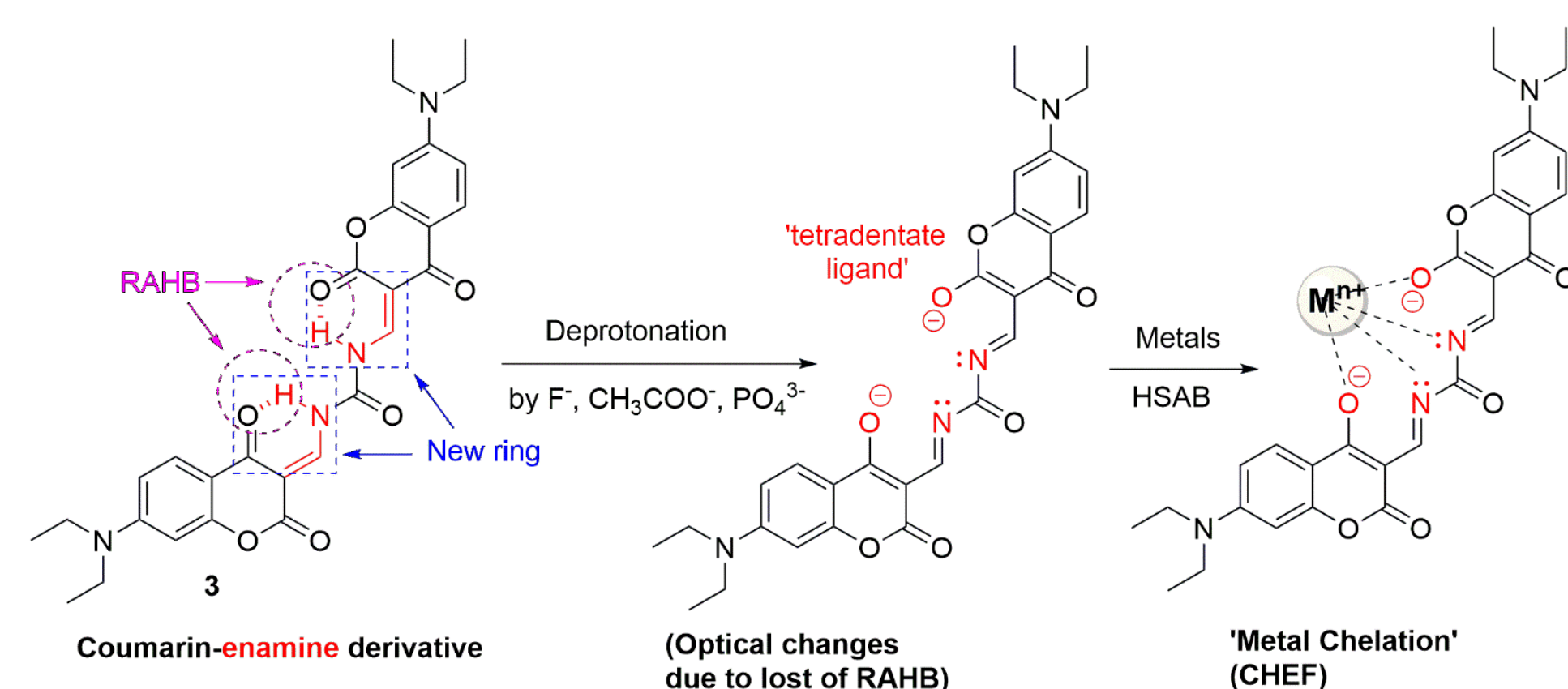


## Abstract

A urea-bis(7-DEA-coumarin-enamine) molecular probe has been synthesized that shows relay recognition of anion and cation via optical spectroscopy. Incorporating enamine-moiety to hydroxycoumarin allows to form two new six-membered ring system through Resonance-assisted-hydrogen-bonding (RAHB) that extends conjugation hence fluorescence intensity. Photophysical properties have been studied in different solvent systems. In DMSO, solution produced a pale greenish color with two broad absorptions band at 388nm and 475nm and emission at 550nm. Upon the addition of the various anions, only  $\text{CH}_3\text{COO}^-$ ,  $\text{F}^-$ ,  $\text{CN}^-$ ,  $\text{PO}_4^{3-}$  anions perturbed the new ring system (RAHB) and generate optical response both in UV-vis and fluorescence. Cyanide ions produced distinct absorption and emission band than due to Michael-addition to enamine moiety whereas  $\text{CH}_3\text{COO}^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$  abstract proton from RAHB and form a tetradentate ligand cage. Upon the addition of various metals, only  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions shows optical response, absorption spectra shift bathochromically from 361nm to 370nm and emission spectra at 451nm quenched which means fluorescence turned 'OFF' via chelation quenched fluorescence (CHQF) mechanism. Furthermore, based on Hard-soft acid base (HSAB) theory  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions are hard acids and the tetradentate ligand is a combination of hard bases, thus due to hard-hard interaction they form strong coordination bond. Size of the  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions also compatible as  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions shows weak interactions (copper ions size is in between nickel and zinc)

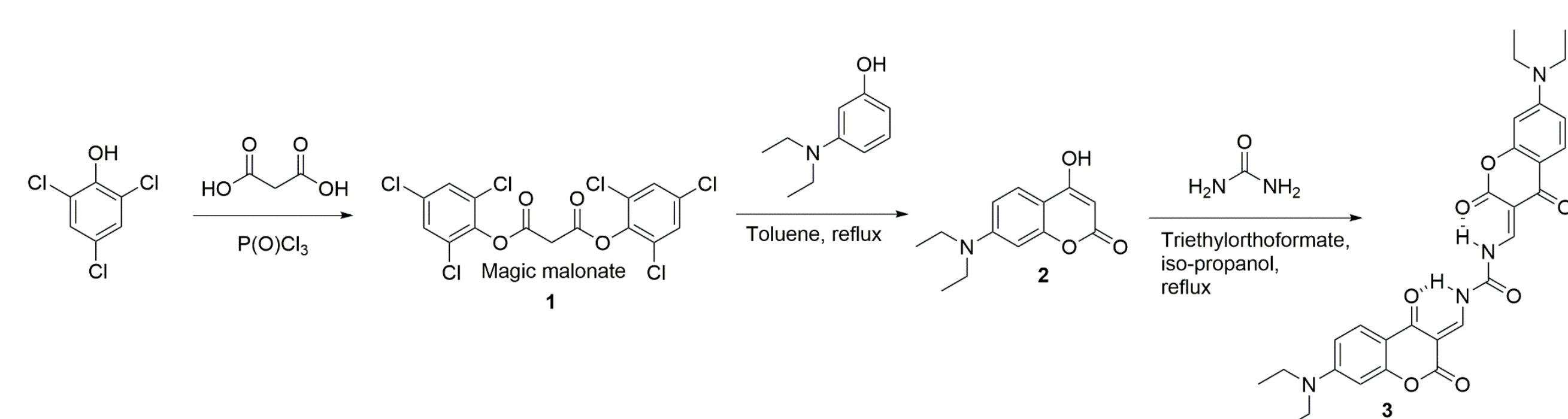
## Hypothesis

Incorporating enamine moiety allows molecular probe to form two new ring through RAHB which enhance conjugation via *double ESIPT* mechanism. This weak Conjugation (RAHB) can be perturbed by certain anions which lead to form tetradentate ligand. Subsequently hard and borderline acids such as 3d transition metals can form coordinated complex with the ligand as ligand is a combination of Hard-Soft bases. Thus, molecular probes will act as relay recognition of anions and cations.



Scheme 1. Proposed sensing mechanism of molecular sensor 3.

## Synthesis



Scheme 2. Synthetic route of molecular sensor 3.

## Results: Solvent Study & Anion Screening

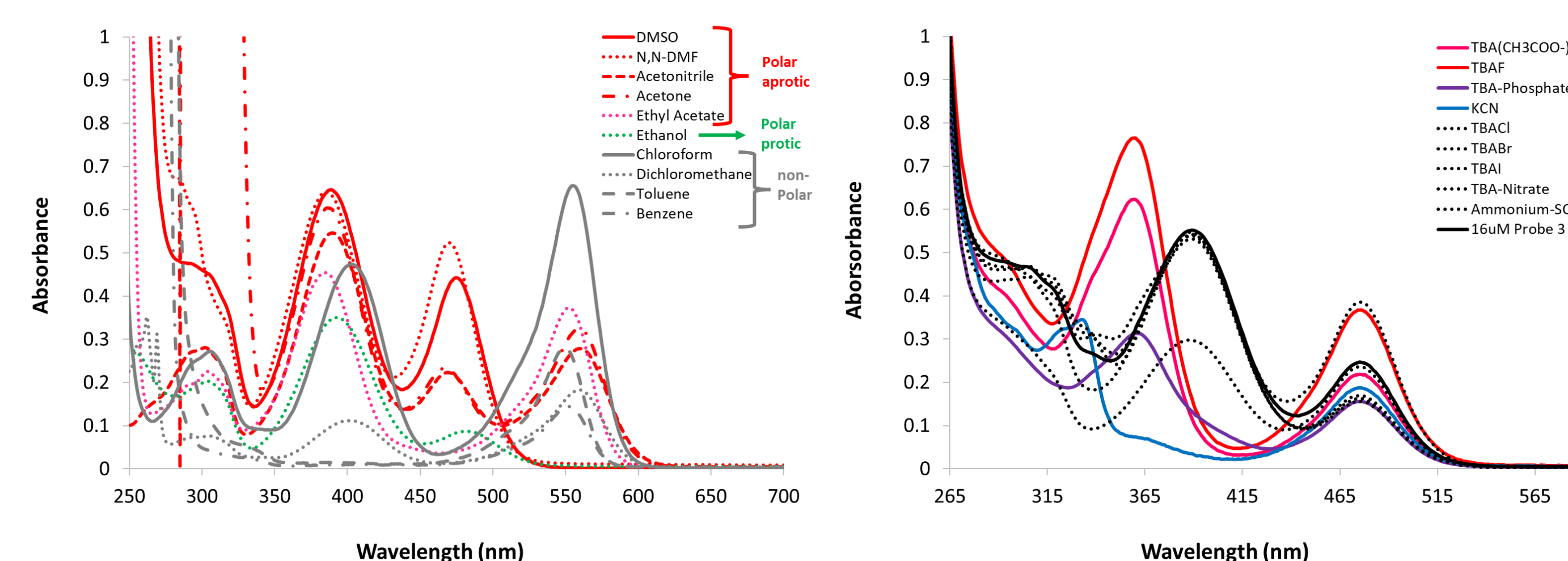


Figure 1. Solvent Study of Molecular Probe 3.

Figure 2. Anion Screening of Probe 3 for RAHB perturbation.

## Results: Optical Study – UV Vis

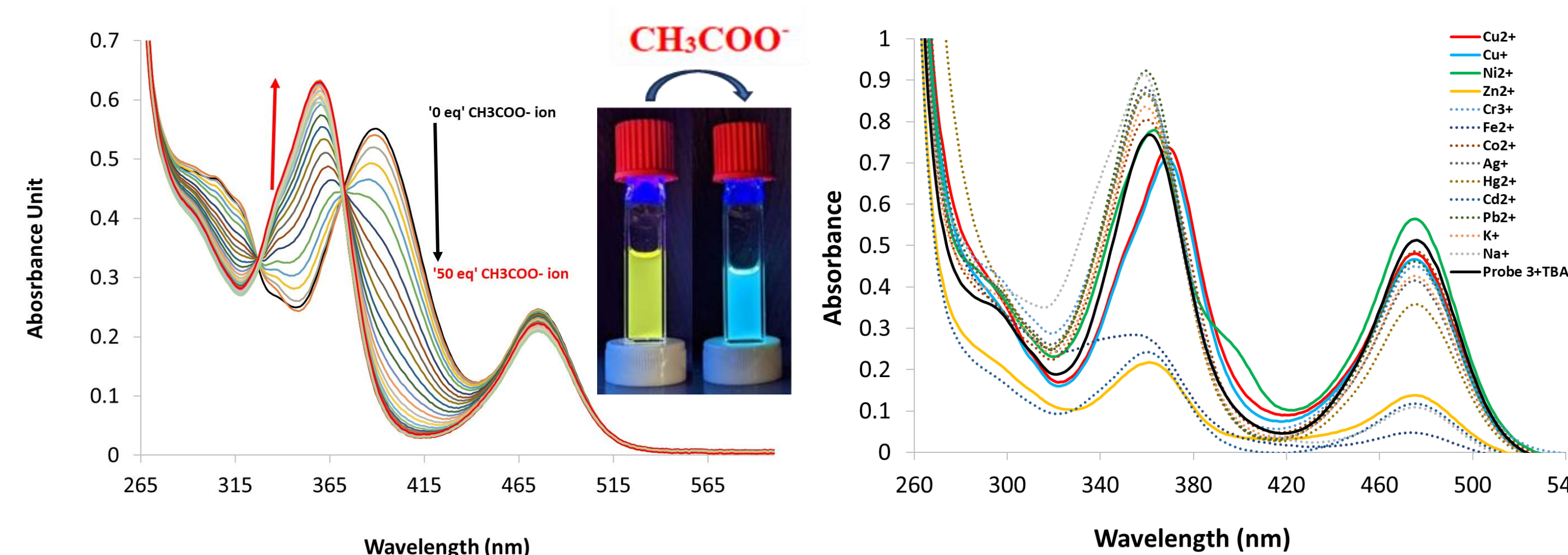
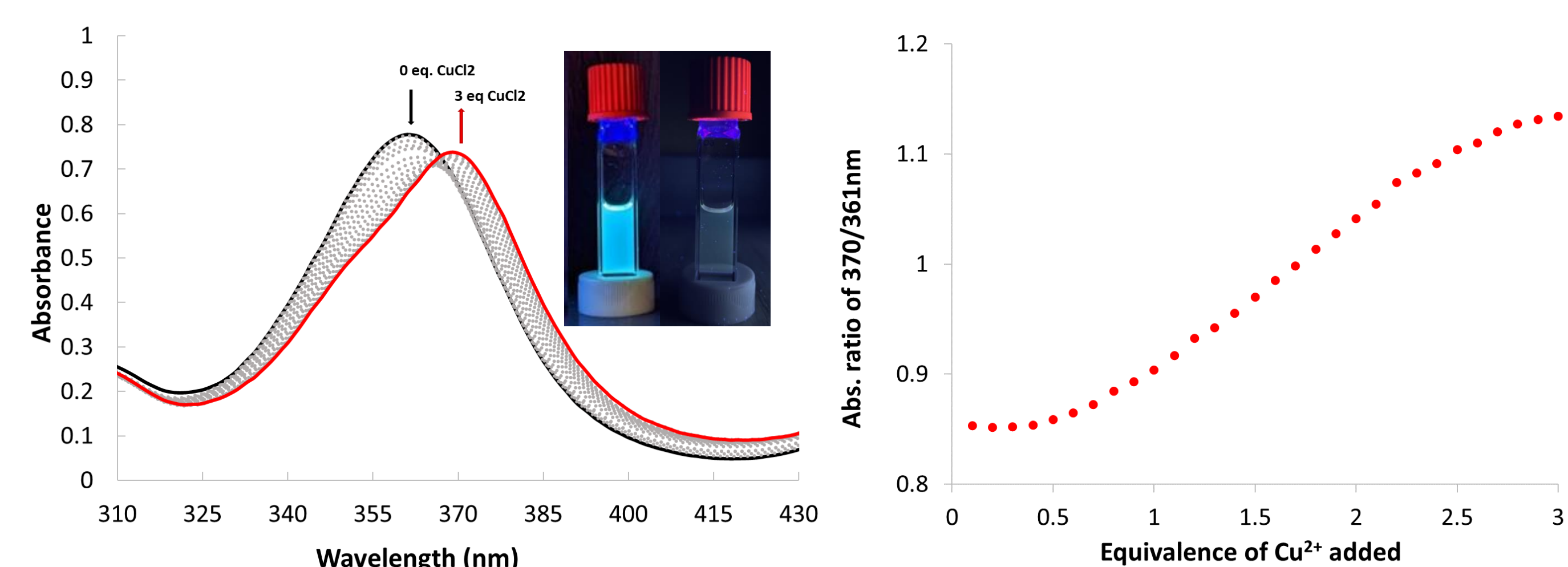
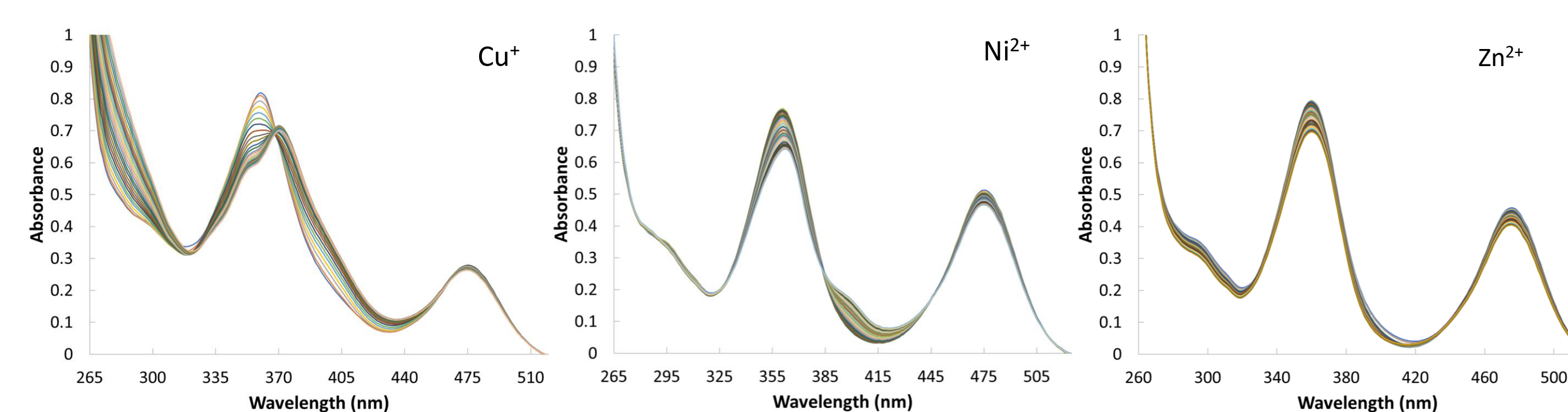
Figure 3. UV-vis study of 16uM Probe 3 upon the addition of TBA( $\text{CH}_3\text{COO}^-$ ) in DMSO.

Figure 4. Metal screening of Probe 3 for relay recognition.

Figure 5. UV-vis study of 16uM Probe 3+50eq. TBA( $\text{CH}_3\text{COO}^-$ )+Metals in DMSO.Figure 6. Fluorescence study of 16uM Probe 3 + 50eq TBA-( $\text{CH}_3\text{COO}^-$ )+Metals in DMSO. Ex359nm and slit 1.5nm

## Conclusions

- ❖ Coumarin-enamine derivative synthesized, and Solvent studies carried out.
- ❖ Molecular probe 3 can detect  $\text{CH}_3\text{COO}^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{CN}^-$  over a range of anions both in UV-vis and Fluorescence study.
- ❖ Molecular probe 3 can detect  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions over a range of metals both in UV-vis and Fluorescence study via fluorescence quenching.
- ❖ Thus, molecular sensor utilize relay recognition mechanism.

## Future Work

- ❖ ESI-MS analysis of probe 3 and anions and metal ions interaction
- ❖ NMR study of probe 3 and anions, and metal ions.
- ❖ Computation studies of anions and metals with probe 3.
- ❖ Growing crystal of probe 3.

## Contact

Rashid Mia, PhD  
Assistant Professor  
Department of Chemistry and Biochemistry, Stephen F. Austin State University  
Bush Mathematical Sciences Building, Nacogdoches, Texas 75962  
Rashid.mia@sfasu.edu

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