Dual channels Fluorescent Sensor based on [5]helicene derivative for the selective detections of Cu(II) or Zn(II)

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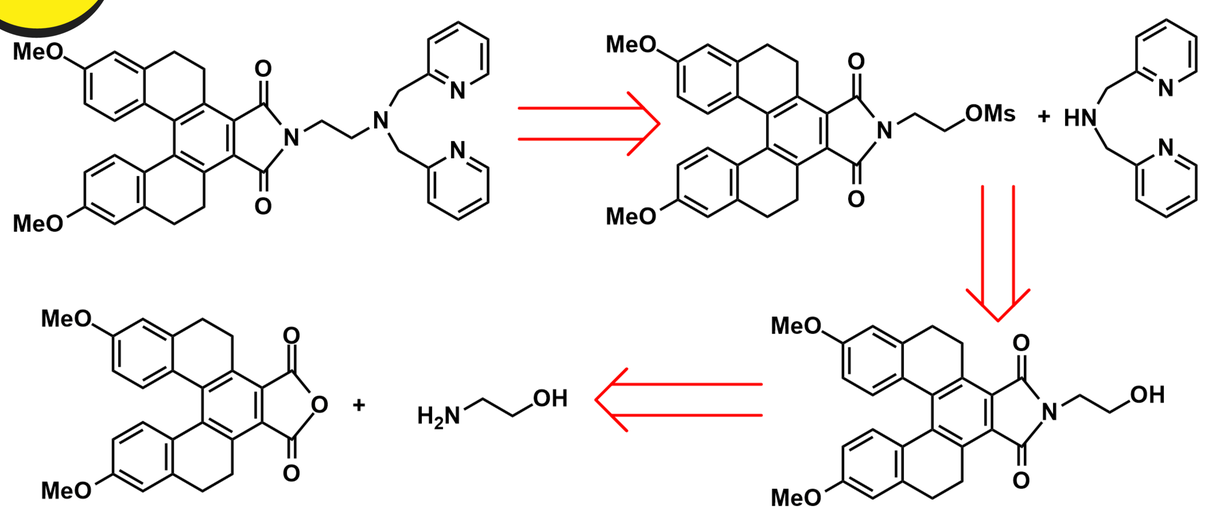
1. Abstract

A new Cu(II) and Zn(II) fluorescent sensor based on [5]helicene derivative and di-2-picolylamine, M201-DPA, has been successfully synthesized. The compound selectively bound to Cu(II) or Zn(II) depending on the solvent system used for testing. Sensor M201-DPA demonstrated the selective ON-OFF fluorescent response toward Cu(II) in aqueous ACN indicated by the fluorescent quenching at 537 nm. On the other hand, M201-DPA showed the selective OFF-ON response toward Zn(II) in aqueous MeOH specified by the blue shift and the enhancement fluorescent at 447 nm. The detection limits of the sensor were examined to be approximately 33 and 34 ppb for Cu(II) and Zn(II), respectively, which are lower than drinking water permission concentrations by the United States Environmental Protection Agency (US EPA).

2. Introduction

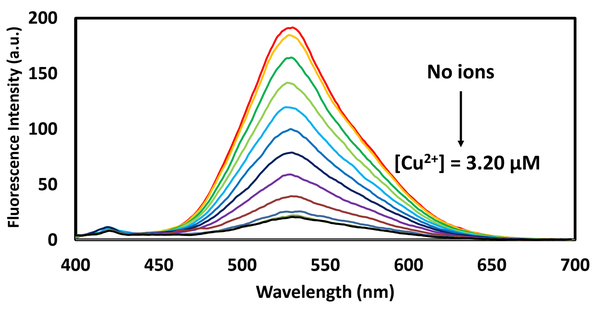
The design and synthesis of chemosensor for selectively binding toward heavy metal ions were essential and become more popular in many researches. Many types of heavy metal ions could be found naturally in the environment. The excess amount of them caused hazardous to life in ecosystem including human and resulted in many diseases. In order to detect the trace amounts of metal ions, fluorescence sensors binding to expected metal ions became interesting research topics. In this study, the sensor containing [5]helicene derivative and novel di-2-picolylamine which was responsible for recognizing Zn(II) and Cu(II) was proposed for coordinating with Zn(II) and Cu(II). The fluorescence signal from sensor will be changed upon metal ions bound.

3. Retrosynthetic



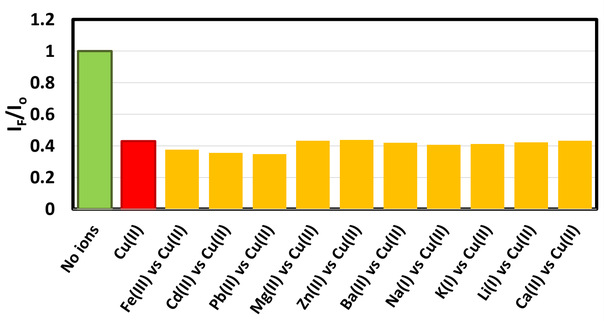
4. Results of Sensor M201-DPA in ACN:H_2O

Sensitivity Studies



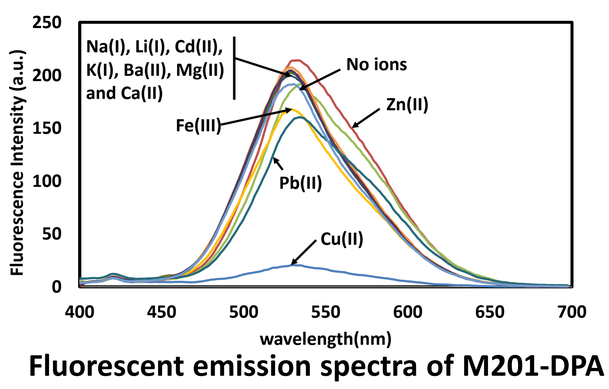
Fluorescent titration of M201-DPA in aqueous ACN with addition of Cu(II).

Competitive Studies

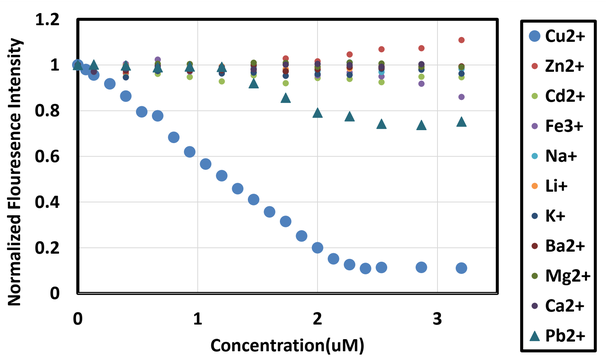


Competitive studies of M201-DPA in aqueous ACN with other metal ions.

Selectivity Studies



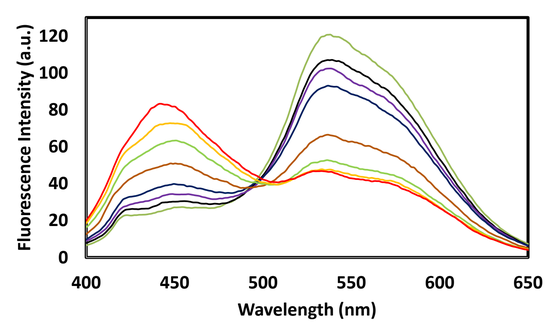
Fluorescent emission spectra of M201-DPA in aqueous ACN at the presence of various metal ions.



Normalized fluorescence intensity of M201-DPA in aqueous ACN for each metal ions.

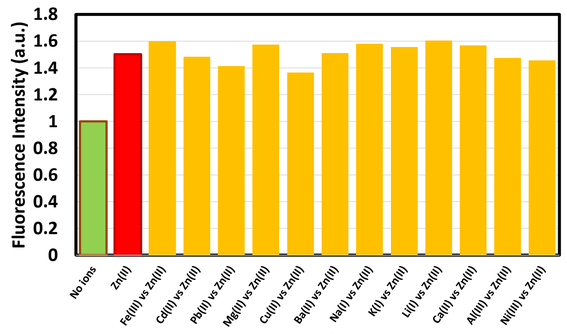
5. Results of Sensor M201-DPA in MeOH:H_2O

Sensitivity Studies



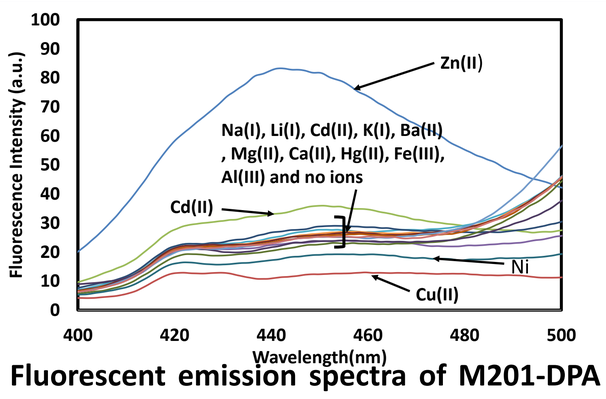
Fluorescent titration of M201-DPA in aqueous MeOH with addition of Zn(II)

Competitive Studies

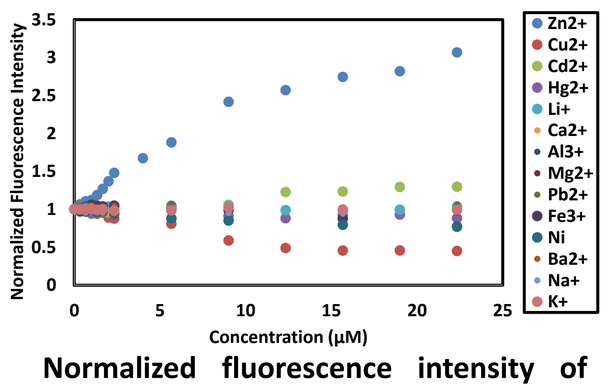


Competitive studies of M201-DPA in aqueous MeOH with known metal ions

Selectivity Studies



Fluorescent emission spectra of M201-DPA in aqueous MeOH at the presence of various metal ions.



Normalized fluorescence intensity of M201-DPA in aqueous MeOH for each metal ions.

6. Conclusion

M201-DPA, based on [5] helicene derivative, has been successfully synthesized for binding Cu(II) and Zn(II) using di-2-picolylamine (DPA) as an ionophore. **M201-DPA** selectively bound to both Cu(II) and Zn(II) depending on the solvent systems used for testing and provided low detection limits. **M201-DPA** can be used for examining drinking water permission concentrations in the future.

7. References

1. J. Org. Chem., 2007, 72, 3554-3557.
2. Organometallics., 2009, 28, 3621–3624

8. Acknowledgement

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- National Metal and Materials Technology Center (MTEC)

9. On going Outputs

The results form this study are in the process of preparation for the patent and the manuscript.