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4,7-Diazacrown Ether Ruthenium *tris*-Phenanthroline: an All-Rounder Among Metal Ion Chemosensors

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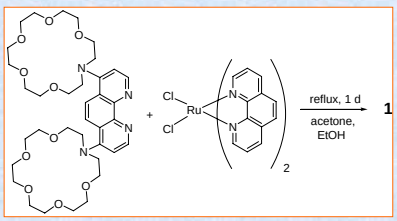
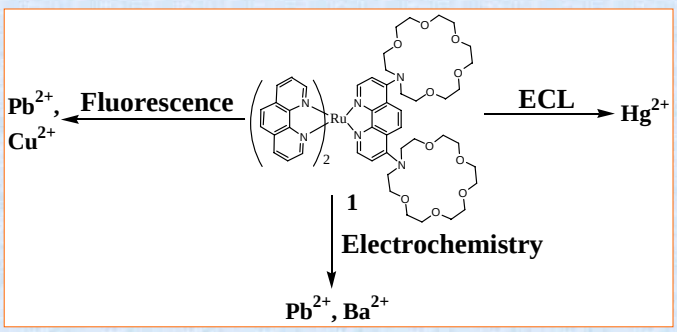
Introduction

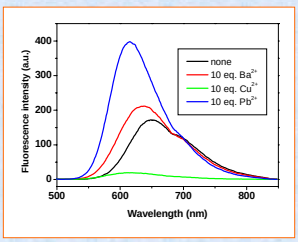
Metal ion sensors play an important role in detection and quantification of metal ions in many fields of application.[1] Herein, we present a versatile chemosensor based on the azacrown ether-containing *tris*-phenanthroline ruthenium complex 1.[2] It showed diverse response to various metal ions (Na^+, K^+, Ca^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+} and Pb^{2+} etc.) by a number of spectroscopic methods.

Synthesis and general description

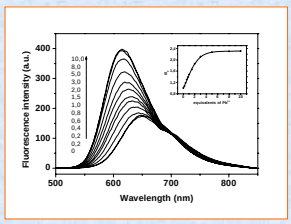




I Complex 1 used as a fluorescence chemosensor for Pb^{2+} and Cu^{2+}

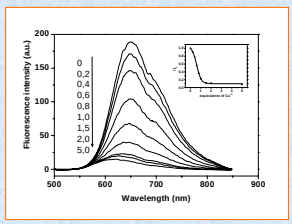


Fluorescence spectra of 1 (10 μM) in ACN with 10 eq. of different metal ions addition. All of the other metal ions, such as Na^+, K^+, Ca^{2+}, Cr^{3+},Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} only have very lightly effect. (excitation at 429 nm)

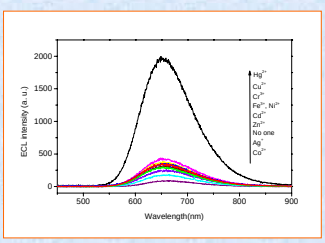


Titration curve of 1 (10 μM) in ACN with various amounts of Pb^{2+} addition. (excitation at 429 nm)
Stern-Volmer plots of complex (I) with various amount of Pb^{2+} addition. (insert)

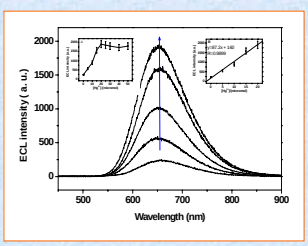
Titration curve of 1 (10 μM) in ACN with various amounts of Cu^{2+} addition. (excitation at 429 nm)
Stern-Volmer plots of 1 with various amount of Cu^{2+} addition. (insert)



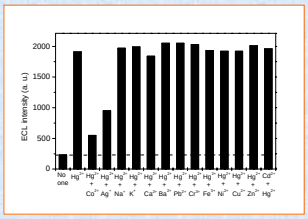
II Complex 1 used as an electrochemiluminescence (ECL) chemosensor for Hg^{2+}



ECL spectrum of 1 (10 μM) in tetra-butylammonium phosphate buffer (0.1 M) solution (pH 7.0) in the presence of different metal ions (50 μM), showing nearly no response to some other metal ions, such as Na^+, K^+, Ca^{2+}, Ba^{2+}, Pb^{2+}.

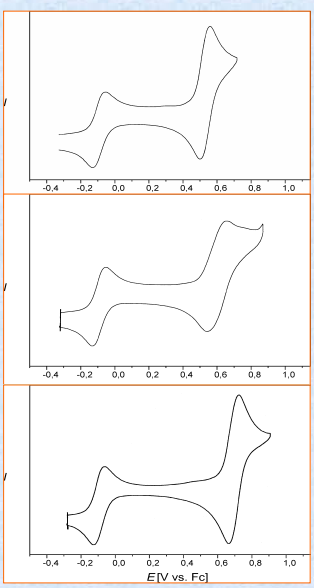


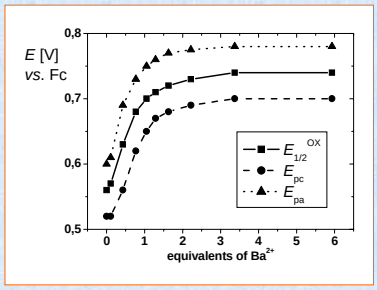
ECL intensity of 1 (10 μM) vs $[Hg^{2+}]$ in tetrabutylammonium phosphate buffer (0.1 M) solution (pH 7.0). $[Hg^{2+}]$ are 0, 5, 15, 20 μM (from bottom to top).
Titration curve of $[Hg^{2+}]$ from 0 to 50 μM (insert A)
Titration and fitting curve of $[Hg^{2+}]$ from 0 to 20 μM. (insert B)



ECL intensity change profile of 1 (10 μM) in a mixture metal ions (Hg^{2+} and other metal ions are 20 μM, respectively) in tetrabutyl-ammonium phosphate buffer (0.1 M) solution (pH 7.0).

III Complex 1 used as an electrochemical chemosensor for Pb^{2+}or Ba^{2+}





Electrochemistry responses of 1 with various amounts of Ba^{2+} addition.

Redox potential of 1 without (left top) and with 0.5 eq. (left middle), 10 eq. (left bottom) of Ba^{2+} addition. The left reversible wave is 1,1´-di-methylferrocene internal standard.

Pb^{2+} shows very similar electrochemical responses as Ba^{2+}.

Conclusions

A versatile all-rounder metal ion chemosensor was developed, showing diverse metal ion selectivity depending on the detection method.

Acknowledgments

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References:

[1] **a) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* 1997, *97*, 1515-1566; b) M. H. Keefe, K. D. Benkstein, J. T. Huup, *Coord. Chem. Rev.* 2000, *205*, 201-228.**

[2] **a) M. Schmittel, H. Ammon, *J. Chem. Soc., Chem. Commun.* 1995, 687-688; b) M. Schmittel, H. Ammon, C. Wöhrle, *Chem. Ber.* 1995, *128*, 845- 850.**