Anthraquinone as Fluorescent Chemosensor for Metal Ions

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ABSTRACT

This review article provides information on fluorescent chemosensors for metal ions based on anthraquinone moiety.

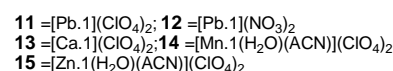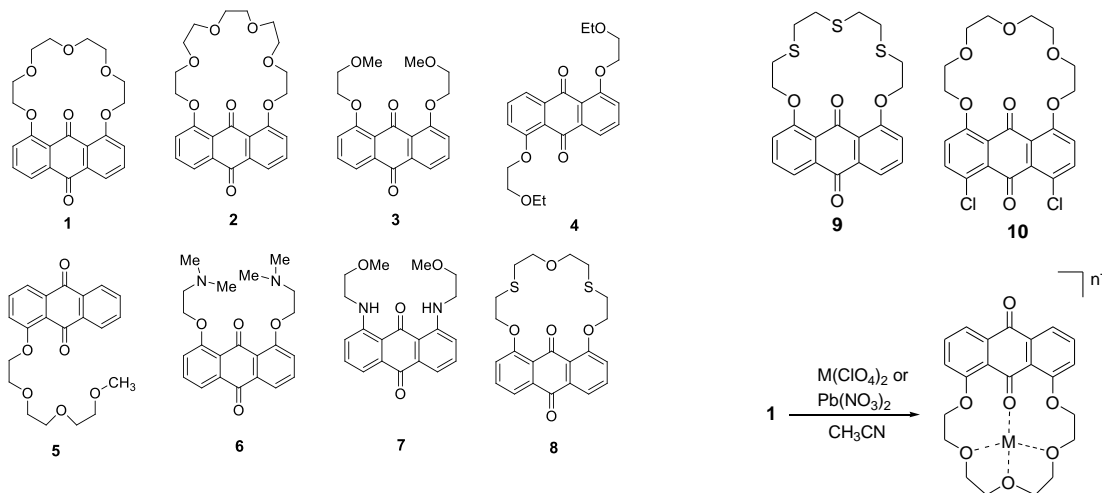**Keywords :** Chemosensor, Anthraquinone, Fluorescent, Metal Ions

I. INTRODUCTION

Quinones[1] are unsaturated α, β-ketones commonly found in all respiring animals and plants, where they develop important functions as components in cellular respiration and photosynthesis. A large variety of quinones including many with fused heterocyclic rings, have been used as synthetic intermediates and in medicinal and industrial chemistry. These also form an important class of metabolites which can be either effective antibacterial, anticancer or even paradoxically citotoxic agents. Quinones are usually divided into benzoquinones, naphthoquinones, anthraquinones, anthracyclinones, condensed quinones etc. Anthraquinones comprise the largest group of natural quinones (about 200 substances). They are found both in higher plants and in fungi (especially aspergillus and penicillium) and lichens. The majority of them exist as coloured phenolic compounds, useful as dyes and pigments. A large number of anthraquinone based chemosensors have been reported till date for metal ions as well as anions. Majority of these chemosensors are colorimetric in nature and have been reviewed earlier.

In the present review article, anthraquinone based fluorescent chemosensors for metal ions have been presented.

II. Anthraquinone Based Fluorescent Chemosensors

A. G. Sykes et al[2] have reported a luminescent molecular sensor based on 1,8-oxybis(ethyleneoxyethyleneoxy) anthracene-9,10-dione (**1**) - an analogue of 18-crown-6 where one ether oxygen has been replaced by a carbonyl group of anthracene-9,10-dione. The addition of oxo acids viz. HNO_3, H_2SO_4, $HClO_4$ and CF_3COOH to **1** caused its luminescence enhancement at 580 nm. The maximum 40 times enhancement was observed on addition of $HClO_4$. The UV-Vis. titration of **1**[3] with dilute perchloric acid in CH_3CN showed that the band at 375 nm is shifted to 400 nm with isosbestic point at 384 nm. The X-ray crystallography of $[1.H_3O]$ ClO_4 complex formed by addition of perchloric acid to a solution of **1** in CH_3CN revealed the encapsulation of hydronium ion[2] in the cavity of crown ether **1**. The addition of halogen acids did not cause any fluorescence enhancement. In macrocycle **1**, on protonation, the lowest energy n-π^* transition of anthracene-9,10-dione is raised in energy and is replaced by strongly emissive π-π^* state.

1   2   3   4

5   6   7   8

9   10

11 =[Pb.1](ClO$_4$)$_2$; 12 =[Pb.1](NO$_3$)$_2$
13 =[Ca.1](ClO$_4$)$_2$; 14 =[Mn.1(H$_2$O)(ACN)](ClO$_4$)$_2$
15 =[Zn.1(H$_2$O)(ACN)](ClO$_4$)$_2$

The macrocycle **2,** having one more ethyleneoxy spacer in comparison to macrocycle **1** has greater affinity for hydronium ion than **1** which has been attributed to less ring strain within the macrocycle due to its larger ring size[4]. Acyclic molecule **3** has only small affinity towards hydronium ion and **4** remains totally nonluminescent after addition of perchloric acid whereas **5** containing single long chain polyether has smaller binding constant than cyclic structures but more than **3**. Acyclic receptor **6** with nitrogen atoms in place of terminal ether groups of receptor **3,** showed only small fluorescence enhancement in on addition of acid. However, on addition of acid no emission enhancement was observed in case of aminoanthracene-9,10-dione moiety based chemosensor **7**.

The replacement of distal oxygen atoms of macrocycle **1** with sulphur atoms in macrocycles **8** and **9** resulted in poor fluorescence enhancement on addition of HClO$_4$ acid. This lower fluorescence enhancement is due to the formation of weaker hydrogen bonds between hydronium ions and distal sulphur atoms of polythioether rings in macrocycles **8** and **9**. X-ray crystal structure of **10** is quite similar to that of **1** with hydrogen bond distances in the structure of [**10**.H$_3$O]ClO$_4$ complex are on average 0.04A° shorter than in [**1**.H$_3$O]ClO$_4$ complex[5].

Sykes et al have reported first photophysical mechanism of inversion of excited states for detection of heavy metals in solution[6]. On addition of Pb(ClO$_4$)$_2$ to **1** in CH$_3$CN, there is red shift in absorbance with concomitant increase in fluorescence at 515 nm (λ_{ex} 398 nm) and is associated with stoichiometry of 1:1 complex both in absorbance and fluorescence. Similarly the addition of calcium perchlorate produces a large emission enhancement and similar red shift in absorbance. But Cu^{2+}, Ni^{2+} and Mn^{2+} did not cause emission enhancements and is attributed to presence of low lying d-d transitions that quench emission internally. Lead and calcium salts showed greatest luminescence enhancements because they have high charge, large affinities and only weakly associate with solvent and perchlorate counter ions in solution. X-ray crystallographic results confirmed 1:1 metal ligand stoichiometries in all cases **11-15**.

Fluorescent PET based chemosensors **16**[7] centered on azacrown linked 2-phenylimidazo[5,4-a]anthraquinone chromophore show fluorescence enhancement at 515 nm on addition of metal ions. The order of fluorescence intensity is Ca^{2+}> Ba^{2+}> Mg^{2+}>> Na$^+$ > Li$^+$ > K$^+$ for **16a** and Ba^{2+}> Ca^{2+} >> Mg^{2+}>> K$^+$ > Na$^+$ > Li$^+$ for **16b**. This fluorescence sensing was not disturbed by thiocyanate counter anions. A large difference in fluorescence enhancement by alkali and

alkaline earth metal ions suggests a strong electrostatic interaction between bivalent metal ions and lone pair of nitrogen atom of aza crown which suppresses more efficiently the photo induced electron transfer processes.

16a n = 1
16b n = 2

17
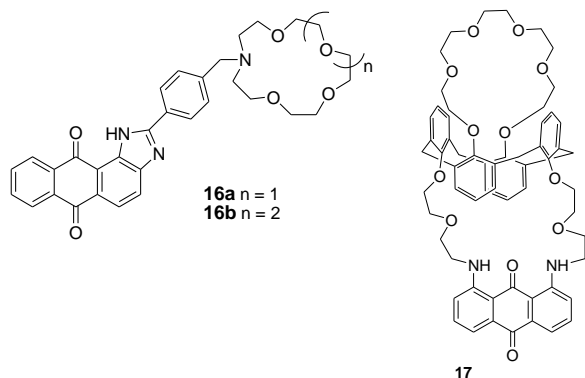
An excited state intramolecular proton transfer-based fluorescent chemosensor[8], 1,8-anthraquinonylcalix[4] monocrown-6 (**17**), showed selective fluorescent change with In^{3+} among various metal ions. On interaction with In^{3+}, a fluorescence decrease at 625 nm, with simultaneous increase at 535 nm was observed.

18
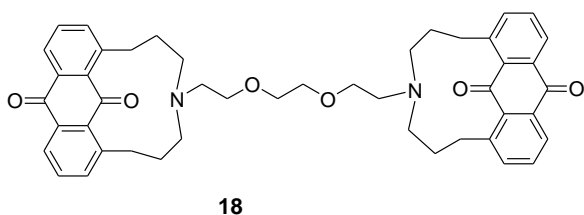
Chemosensor **18**[9] displayed selective fluorescence detection of Mg(II) in the nanomolar range (some interference by Ca(II) ion). Moreover, this chemosensor has also been used in the bioimaging of Mg(II) in embryonic mouse fibroblast NIH3T3 cells.

III. REFERENCES

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