



Review

Colorimetric metal ion sensors – A comprehensive review of the years 2011–2016

Baljeet Kaur^a, Navneet Kaur^{a,*}, Subodh Kumar^b^a Panjab University, Chandigarh, Punjab, India^b Guru Nanak Dev University, Punjab, India

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ABSTRACT

A chemosensor is a synthetic chemical system which is capable of binding with an analyte in a selective and reversible manner followed by change in one or more properties of the system in the form of color or fluorescence or redox potentials. The choice of a chromophore has tremendous effect on these properties. The well established and indispensable role of metal ions in connection to their medicinal, biological and environmental concern makes their sensing one of the major research domains out of other domains including detection of anions, bio molecules, pesticides, explosives, etc. Therefore, the number of research articles is growing at a high rate dedicated to pave path for more reliable and sophisticated chemosensors. In this context, continuous compilation of research work is highly desirable (or acceptable) in order to generate a library of chromophores helping the budding researchers to access the present trends in limited (short) time. In this review, we have focused on colorimetric sensors for metal ions, viz. alkali and alkaline earth, Al^{3+} , Cr^{3+} , Mn^{2+} , $\text{Fe}^{3+}/\text{Fe}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} , $\text{Zn}^{2+}/\text{Cd}^{2+}$, Hg^{2+} , Ag^+ , $\text{Sn}^{4+}/\text{Sn}^{2+}$, Pd^{2+} , Pb^{2+} , Zr^{4+} , Mo^{6+} , due to their numerous advantages such as, easy detection without requiring sophisticated instruments, high selectivity and sensitivity in terms of different color change for different species, over other chemosensors. This work is a comprehensive survey of colorimetric sensors for metal ions developed in the years from 2011 to 2016 (>450 references).

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Abbreviations: ICT, intramolecular charge transfer; MLCT, metal-to-ligand charge transfer; LMCT, ligand-to-metal charge transfer; BODIPY, 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene; ATP, adenosine tri phosphate; SEM, scanning electron microscopy; DPA, di-(2-picolyamine).

* Corresponding author.

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1. Introduction

Supramolecular chemistry has its roots in the biological functions occurring on their own in the body since time immortal involving functions of enzymes to provide suitable cavity to substrates, H-bonding interactions in DNA base pairs which is responsible for its functional helical structure and many more. The concept of supramolecular chemistry as a research field came into light in 1960s when Charles J. Pederson accidentally isolated 16-crown-4 ether which could encapsulate alkali metal ions [1]. Later on, this concept was taken forward by the Cram and Lehn for synthesizing spherands, cavitands, lariat ethers and macrocyclic ligands with the help of concepts of preorganization and complementarity of host binding sites to the binding guest [2]. The present state-of-art of supramolecular chemistry has reached its sophisticated and mature form owing to the pioneering efforts of Jean-Pierre Sauvage, J. Fraser Stoddart and Bernard L. Feringa in the nano-architectures including nano machinery and mechanically interlocked rotaxanes and catenanes which completely rely on mechanical interactions [3].

Amongst numerous applications of supramolecular chemistry, molecular recognition is one of the most studied area which is related to detection of ionic or neutral species through selective interactions between the host molecule and the guest species utilizing the non-covalent interactions with energy ranging from less than 5 kJ/mol up to 300 kJ/mol [4,5] to form a host-guest complex. Formally, a chemosensor is a chemical species of abiotic origin that reversibly transforms binding event of an analyte into an analytically useful and measurable signal. The binding event results in the electronic changes in the host molecule which is responsible for the induction of signal in the chromophoric unit. There are usually three parts that constitute a chemosensor, a receptor (which is responsible for the selective analyte binding), a photoactive unit (whose properties should change upon the aforementioned binding) and, in some cases, a spacer, which is able to modify the geometry of the system and tune the electronic interaction between the receptor and photoactive unit (Fig. 1).

Chemosensors can be classified into three categories according to the nature of the signal emitted by the signalling subunit; (i) colorimetric sensors related to change in electronic properties in the

form of intra/intermolecular Charge Transfer (ICT) [6–8] (including LMCT and MLCT transitions), (ii) Fluorogenic sensors related to Photo-induced Electron Transfer (PET) [7,9], Excited State Intramolecular Proton Transfer (ESIPT) [10], Fluorescence Resonance Energy Transfer (FRET) [11,12], Through Bond Energy Transfer (TBT) [13], excimer-excimer formation [14], etc. and (iii) electrochemical sensors related to measurement of changes in redox potential.

Colorimetric chemosensing technique is a promising technique allowing qualitative and quantitative detection of medically and environmentally important ionic or neutral species without any sophisticated instrumentation. Its utilization as a test kit for on-site detection, short-time detection, simplicity, reversibility along with high selectivity and sensitivity, which does not need any pre-treatment of sample and manual expertise, makes it a desirable technique among the researchers.

Recognition of cationic species, specially, has witnessed an upsurge in the recent years as an important domain of supramolecular chemistry due to their relevance in medicinal, environmental and biological fields [15–17]. The colorimetric determination of cations have been achieved utilizing various photoactive moieties such as pyrene, BODIPY, anthracene, rhodamine, fluorescein, nitrophenyls, julolidine, 1,8-naphthalimide, Near Infra Red (NIR) absorbing dyes (squarines, hemocyanines), coumarin, nitrobenzoxazole (NBD), etc. (several of which act as chelators as well) conjugated to an appropriate binding unit mainly through Schiff base, diazo and amide linkages.

To achieve colorimetric detection of metal ions, mainly two types of chemosensors have been used: (i) chemosensor with a D- π -A system and (ii) Rhodamine containing chemosensors. A D- π -A system can be achieved by introduction of electron donating (ED) groups and electron acceptor (EW) groups in the chemosensor molecule at appropriate positions. The deciding factor for whether a particular metal ion will bind ED or EW group depends upon the HSAB concept of the hardness and softness of the binding sites and analyte. Generally, the binding of metal ion with ED group decreases its donating ability which virtually converts the D- π -A system to A- π -A system reducing the conjugation and results in blue shift in the absorption spectrum and increases the chances

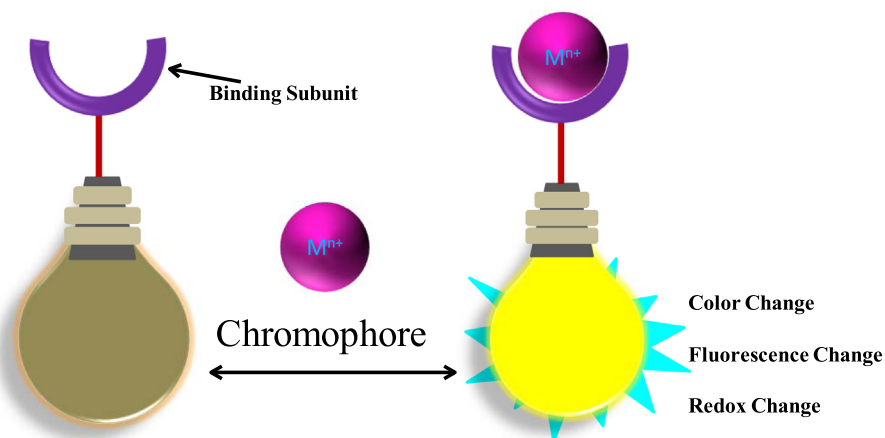


Fig. 1. Diagrammatic representation of binding of chemosensor with cation.

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