



## Review

## Strategies in detection of metal ions using dyes



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## ABSTRACT

Recent time has witnessed unprecedented activity in the colorimetric sensing because of its low cost, practicability, selectivity as well as sensitivity. In addition to the ease in visual “naked eye” qualitative assessment of the colorimetric sensing events, the quantification can be done by resorting to spectrophotometric analysis. Additionally, a number of smart materials based on nanoparticles, carbon nanotubes, mesoporous materials, synthetic pores, conjugated polymers, etc. have been developed and used for colorimetric detection. Herein, we focus on the recent developments (last five years) in colorimetric sensing using dyes.

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**Abbreviations:** A, acceptor; AcOH, acetic acid; ADD, acridine-1,8-dione; AuNP, gold nanoparticle; AuNR, gold nanorod; BODIPY, boron-dipyrrromethene; CB, cucurbituril; CCL, core cross-linked; CD, cyclodextrin; CHEF, chelation enhanced fluorescence; CHEQ, chelation enhanced quenching; Cou, coumarin; D, donor; DFT, density functional theory; DHAQ, dihydroxyanthraquinone; DMF, N,N-dimethylformamide; DMSO, dimethylsulfoxide; DNA, deoxyribonucleic acid; DPA, di-picolyl amine; ds, double stranded (DNA); EDTA, ethylenediaminetetraacetic acid; equiv, equivalent; ESIP, excited-state intramolecular proton transfer; FAM, fluorescein amidite; FRET, fluorescence resonance energy transfer; GO, graphene oxide; H-bond, hydrogen bond; HEPES, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid; HOMO, highest occupied molecular orbital; ICT, intramolecular charge-transfer; ILCT, intraligand charge-transfer; LOD, limit of detection; LUMO, lowest unoccupied molecular orbital; MB, molecular beacon; NDI, naphthalene diimide; NIR, near-infrared; *p*-, para; PBS, phosphate buffered saline; PET, photo-induced electron transfer; QD, quantum dot; RLS, resonance light scattering; SQ, squaraine; ss, single stranded (DNA); T, thymine; TBET, through-bond energy transfer; TD-DFT, time-dependent DFT; *ter*-, tertiary; THF, tetrahydrofuran; TICT, twisted ICT; tren, tris(2-aminoethyl)amine; v/v, volume by volume; w.r.t., with respect to.

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## 1. Introduction

The detection and control of chemical constituents comprised of cations, anions and neutral molecules has become an indispensable task in many applications related to the management of minimum standards of edible products, environment, agriculture sciences, medicine and health sciences. The stringent requirements imposed by regulating enacting agencies and the need for sensitive, selective and easy detection methods have led to the development of a vast range of chemosensors capable of detecting and controlling different analytes. These essentially comprise of receptors whose physico-chemical characteristics are modified in the presence of appropriate target analyte and the transducer (signalling unit) signals the detection process through electrochemical, mass, optical and a variety of other changes.

One of the efficient ways to detect analytes is through the use of chemosensors, which show a distinct “naked-eye” colour transition upon a recognition event. The change in the characteristic absorption and/or emission band(s) of the sensor is used to quantify the detection process, in terms of binding constant, stoichiometry of the resultant complex, selectivity and sensitivity, *etc.* Among various designs, the most widely used one consists of a signalling unit covalently linked through a spacer to the receptor. Most of the sensors of this design consist of an electron rich donor (D), linked through a conjugated spacer to an acceptor (A). The modulation of the intramolecular charge-transfer (ICT), upon binding of an analyte serves as a strong basis of detection and is usually attended by a colour transition. The sensitivity, selectivity as well as magnitude of spectroscopic properties and/or colour change depend upon the nature and strength of the binding interactions between D and A.

Among a large variety of molecules utilized as chemosensors, dyes constitute one of the most significant library of molecules owing to the diversity in their structural type as well as the physico-chemical characteristics in the context of the ICT. Besides their application in several fields of chemistry, material science, colouration, near-infrared (NIR) applications, reprographics, medical diagnostics, non-linear optics, *etc.* [1], the extensive use of dyes in the field of chemosensing could be attributed to the ease in their availability in sufficient quantities among different chemical classes of chromophores.

**Table 1**  
Emission, absorption and/or colour properties and limit of detection of analyte recognition by acridine, anthraquinone and di-/triarylmethane dyes.

Probe	Analyte	Colour change	$\Delta E$ (eV) <sup>a,b</sup>	Emission properties ( $\lambda$ /nm)	LOD <sup>f</sup> (nM)	Ref.
<b>1b</b>	—(NR <sub>4</sub> ) <sup>+</sup>	Orange → green	–	–	10,000	[4]
<b>1b</b>	Hg <sub>2</sub> <sup>2+</sup>	Pink-red → blue	1.98 <sup>c</sup>	80% (538) <sup>e</sup>	30	[5]
<b>6a</b>	Hg <sub>2</sub> <sup>2+</sup>	–	–	93% (450) <sup>e</sup>	–	[7]
<b>6b</b>	Cd <sup>2+</sup>	–	–	93% (450) <sup>e</sup>	–	[7]
<b>7c</b>	Ca <sup>2+</sup>	–	0.02	64% (436) <sup>e</sup>	–	[8]
<b>8a</b>	Ca <sup>2+</sup>	–	0.39	54% (440) <sup>e</sup>	–	[9a]
<b>9a and 9b</b>	Ca <sup>2+</sup> and Mg <sup>2+</sup>	–	0.26	80% (775) <sup>d</sup> 56% (430) <sup>e</sup>	–	[9b]
<b>10a</b>	Cu <sup>2+</sup>	Red → blue	0.46	–	5000	[10a]
<b>10b</b>	Cu <sup>2+</sup>	Red → blue	0.43	–	1000	[10a]
<b>10b</b>	Co <sup>2+</sup>	Red → lilac	0.50	–	1000	[10a]
<b>10b</b>	Ni <sup>2+</sup>	Red → lilac	0.50	–	–	[10a]
<b>10c</b>	Cu <sup>2+</sup>	Red → blue	0.40	–	–	[10a]
<b>10c</b>	Co <sup>2+</sup>	Red → blue	0.44	–	1000	[10a]
<b>10c</b>	Ni <sup>2+</sup>	Red → purple	0.53	–	–	[10a]
<b>10d</b>	Cu <sup>2+</sup>	Yellow → russet	0.54	–	1000	[10a]
<b>10d</b>	Co <sup>2+</sup>	Yellow → russet	0.56	–	1000	[10a]
<b>10d</b>	Ni <sup>2+</sup>	Yellow → russet	0.56	–	1000	[10a]
<b>10d</b>	Zn <sup>2+</sup>	Yellow → colourless	–0.28	–	–	[10a]
<b>11</b>	Cu <sup>2+</sup>	Yellow → pink	0.46	75% (525) <sup>d</sup>	1000	[10c]
<b>12a</b>	Hg <sub>2</sub> <sup>2+</sup>	Blue → pink	–0.23	–	3500	[11]
<b>13a</b>	Al <sup>3+</sup>	Violet → pink	–0.10	–	–	[12]
<b>13a</b>	Cu <sup>2+</sup>	Violet → blue	0.32	–	–	[12]
<b>13b</b>	Pb <sup>2+</sup>	Violet → pink	–0.12	–	–	[12]
<b>13b</b>	Cu <sup>2+</sup>	Violet → blue	0.33	–	–	[12]
<b>13c</b>	Pb <sup>2+</sup>	Violet → pink	–0.20	–	210	[12]
<b>13c</b>	Cu <sup>2+</sup>	Violet → blue	0.45	–	–	[12]
<b>14</b>	Ba <sup>2+</sup>	Colourless → yellow	–	87% (500) <sup>e</sup>	–	[13]
<b>15</b>	In <sup>3+</sup>	–	–	$\Delta E = -0.34$ eV <sup>b</sup>	–	[14]
<b>16</b>	Cu <sup>2+</sup>	Red → purple-red	0.21	87% (552) <sup>d</sup>	270	[15]
<b>18</b>	Cu <sup>2+</sup>	Yellow → purple	0.26, 0.42	84% (550) <sup>d</sup>	3.0	[16]
<b>18:Cu<sup>2+</sup></b>	Cr <sup>3+</sup>	Purple → yellow	–0.60, –0.76	64% (550) <sup>e</sup>	3.75	[16]
<b>19</b>	Hg <sub>2</sub> <sup>2+</sup>	–	–	96% (611) <sup>e</sup>	1.7	[18]

<sup>a</sup> Shifts of the major absorption band upon complexation.

<sup>b</sup> Negative  $\Delta E$  values refer to the shifts towards high energy.

<sup>c</sup> New band.

<sup>d</sup> Quenching of emission bands at the specified wavelength.

<sup>e</sup> Enhancement of emission bands at the specified wavelength.

<sup>f</sup> Limit of detection.

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