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## Review

# Luminescent/colorimetric probes and (chemo-) sensors for detecting anions based on transition and lanthanide ion receptor/binding complexes

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## ABSTRACT

Herein, some of the recent developments in the design and study of transition metal (d-metal) and lanthanide (f-metal) based sensors, probes and reagents for detecting anions in organic or competitive media will be reviewed. Some examples of main group and actinide-based sensors are also featured. In all cases, the anion recognition is probed by monitoring changes in the various photophysical properties of these complexes, with particular focus being paid to recent examples from the literature where the anion recognition event is communicated through colorimetric or luminescent (fluorescence or phosphorescence) changes. A select number of examples reported within the last 5 years (since 2011) are featured; the focus of this review is on those developed from organic ligands that can, in a synergetic manner with the metal ions, directly aid or enhance the anion recognition and sensing processes. Examples where such synergy is provided by hydrogen bonding interactions are particularly discussed.

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## 1. Introduction

The development of sensors, probes and reagents that can detect, sense or monitor anions in either organic or aqueous media has become one of the most active areas of research within supramolecular chemistry [1–5]. Due to the cationic, Lewis acidic nature of transition (d-metal) and lanthanide (f-metal) ions, and the fact that many of them exhibit interesting coordination chemistry and photophysical properties, their use in supramolecular anion chemistry has been an obvious choice in the development of novel supramolecular structures, probes and sensors [6–10].

Over the years, many excellent examples of coordination complexes have been developed where the various photophysical properties, such as absorption, emission, lifetimes, and quantum yields are modulated upon interactions with anions [11–15]. While earlier examples often involved a simple electrostatic interaction between such complexes (the hosts) and the anionic guest, the focus in recent times has shifted towards the design of novel functional organic ligands that can coordinate single metal ions (e.g. macrocycles), or form hierarchical and higher-order self-assembly structures [16–18]. This has also resulted in the formation of stable complexes with d- and f-metal ions that possess secondary binding units such as hydrogen bonding sites (amides, ureas, thioureas, etc.). These complexes can increase binding affinity and improve anion selectivity, in a synergetic manner, being inspired by the many beautiful examples of ‘pure organic-based’ systems.

In the period of 2011–2016 a large number of such examples were developed. In this review, we describe a select number of these, focusing on both d- and f-metal ion complexes that can be used in anion sensing/probing processes in either organic or aqueous solution, beginning with examples that communicate the anion recognition using main group and transition metal ions. This is then followed by a discussion of some advances made within the f-metal ions, focusing mostly on examples based on lanthanides, with an example of an actinide-based probe also being included (we want to point out that the formal charge of the individual examples is not stated in the following schemes except when charges are ambiguous). For all of these, the anion recognition process results in a modulation of either their ground-state (UV-vis absorption) or excited-state (fluorescence or phosphorescence emission) properties. This review will focus mostly on examples involving simple anions, including biologically relevant anions; the detection of polymeric anions, such as DNA and RNA will not be covered herein. Furthermore, due to the large volume of examples published within the period covered we have been very selective in choosing the examples discussed above. This does not reflect on any work that we have not discussed in our summary, and we apologise for the omission of such work.

## 2. Luminescent main group sensors and probes

Unlike that of d- and f-metal ion complexes, the use of main group ions in luminescence anion sensing is not common to find. In 2012 Neves, Lodeiro and co-workers [19] synthesised the series of Ga(III) corrole-based complexes **Ga.1–Ga.3**, carry various peripheral moieties, which showed strong sensing abilities for  $F^-$  and  $CN^-$  anions. While the highest association constants were observed for **1** (due to hydrogen bonding interactions), binding of small  $F^-$  and  $CN^-$  anions as well as bulkier  $CH_3COO^-$  and  $H_2PO_4^-$  was observed also in the Ga(III)-containing corroles **Ga.1–Ga.3**. For the Ga(III)-containing systems, the main interactions were proposed to be coordinative to the Ga(III) centres. In the cases of **Ga.2** and **Ga.3** the authors reported high sensitivity for  $F^-$ , as a result of the increased Lewis acidic character of Ga(III) in the electron deficient corroles. Similar association constants were determined for **1** and **Ga.1** for  $F^-$ ,  $CN^-$ ,  $CH_3COO^-$  and  $H_2PO_4^-$  with  $\log K$  ca. 9.5–10.5 in

each case. However, interestingly, for **Ga.2** no fluoride association was observed, this being the result of the axial pyridine ligand reducing the affinity.

In contrast to **1**, which showed a strong enhancement of the emission band at 628 nm and the appearance of a new band at 680 nm, the emission from the Ga(III)-containing corroles **Ga.2** and **Ga.3** was quenched 50% in the band centred at 626 nm and a simultaneous 20% enhancement at 642 nm, as shown in Fig. 1 for **1** and **Ga.2**. Weaker binding affinities (ca. 3 orders of magnitude lower) were observed for **Ga.2** and **Ga.3**, which both possessed a vacant axial site following removal of pyridine, with  $F^-$  and was again consistent with the effect of the electron withdrawing pendant moieties. Significant differences were observed in the stoichiometry of the binding between the systems. While **1** was able to bind two anions with a 1:2 (L:A) ratio, **Ga.1** displayed a binding mode characterised by a 2:1 (L:A) ratio with one  $CN^-$  bridging between two metal ions of two discrete complexes (as demonstrated in Scheme 1, for **Ga.3**). A 1:1 ratio was observed for the **Ga.2**, while the 2:1 binding stoichiometry was reported again in the case of **Ga.3**, although with a lower binding constant compared to **Ga.1** ( $\log K_{1:2} = 6.89$ ). This reduced binding affinity was rationalised by the authors through the repulsion of oxygen atoms from the pendant quinone moieties in the formation of the 2:1 (L:A) adduct (Scheme 1). The binding of  $CH_3COO^-$  and  $H_2PO_4^-$  was also reported by the authors with **1**, **Ga.1** and **Ga.2**, with intermediate binding constants, between those seen for  $F^-$  for  $CN^-$ . No association was measured for these bulkier ions with **Ga.3**, likely as a result of steric exclusion in the stacked corrole adduct.

## 3. Luminescent transition metal anion sensors and probes

### 3.1. General

In the last five years, many elegant examples of d-metal ion based sensors and probes for anions have been developed. Some of these have been reviewed as part of extensive overviews of supramolecular anion chemistry by Gale and co-workers [1–3]. One such example is the Cu(II)-fluorescence probe **Cu.4**, which was reported by Gharami and co-workers and shown to be able to detect  $SO_3^{2-}$  [20]. The phenanthrenequinone thiosemicarbazide (PQTSC) derivative **4** possessed both hydrogen bond donor and potential coordination sites. The authors proposed through IR studies, that there was a coordination of Cu(II) by the imine nitrogen, the thiosemicarbazide sulphur, and possibly even from the carbonyl oxygen. Indeed, similar thiosemicarbazide-based metal complexes in the literature [21–24] have shown analogous complexation patterns. The ligand-centred emission band was reported as being selectively quenched by Cu(II) in solution (Fig. 2) and was demonstrated, by Job plot analysis, to be most likely occurring through a Cu(II) binding in a 1:1 (M:L) fashion; this was found to be the case even in the presence of other competitive d-metal ions. The authors also showed that subsequent addition of  $SO_3^{2-}$  restored the original fluorescence emission. The direct anion binding ability of thiosemicarbazides through hydrogen bonding has been reported [25,26]. However, interestingly, in the case of **Cu.4**, the binding of  $SO_3^{2-}$  occurs at the metal centre, as according to the authors' analysis, and the emission centred at 430 nm was enhanced upon binding of the  $SO_3^{2-}$  to PQTSC–Cu(II). The authors propose that this binding results in the *in situ* reduction of the Cu(II) to Cu(I), causing the formation of a diamagnetic PQTSC–Cu(I) complex, which is not an efficient energy transfer acceptor, and as such the quenching in the PQTSC based emission is diminished. This does not, however, exclude that other anions could interact with this assembly through H-bonding, without effecting the fluoresce emission. Unfortunately, due to the paramagnetic nature of the Cu(II) centre, the authors did not carry out any  $^1H$

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