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Luminescent sensor molecules based on coordinated metals: a review of recent developments

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Abstract

Recent developments (1994 to early 1999) in coordination chemistry as they relate to luminescence-based chemical sensing are reviewed. Included are developments involving assemblies for luminescence-based sensing of metal cations, organic and inorganic anions, small neutral molecules in solution, and various volatile organic chemicals. Emphasized in the review are: (a) the chemical features that permit the sensors to function selectively, and (b) the mechanistic schemes that permit analyte recognition and binding events to be converted to luminescence responses. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction and scope

The discovery by the broader inorganic chemistry community of the existing realm of synthetic host: guest chemistry, together with the discovery by the broader synthetic organic chemistry community of the existing world of coordination chemistry, has helped to drive the development of the increasingly popular field of metal-based supramolecular chemistry. With the emergence of the chemistry has come an interest in real and potential applications. As indicated in part by the theme of this special issue of *Coordination Chemistry Reviews*, chemical sensing is a particularly compelling area of application. Furthermore, the manipulation of (supra)molecular excited-state luminescence is a particularly compelling approach to signal transduction in many chemical sensing schemes. A generic representation of a selective-recognition/chemical-sensing/emission-based-binding scheme is shown below. In the sections that follow, we have reviewed recent developments in coordination chemistry as they relate to luminescence-based chemical sensing. We have restricted the survey to papers appearing since 1994. We have excluded from the review the many interesting luminescent molecules designed primarily for DNA intercalation, membrane binding, or micelle encapsulation, as well as the many interesting luminescent sensors that rely upon diffusional quenching mechanisms. We have also excluded sensor assemblies that report primarily on pH, and sensors that contain transition metals but do not make use of metal orbitals in generating luminescence.



Nevertheless, apart from these exclusions, we have attempted to make the survey both comprehensive and complete.

2. Luminescent sensors with pendant binding groups

The focus of this section is luminescent molecular sensors with pendant groups designed to bind specific analytes. This overview is organized by the groups of analytes detected: cations, anions and neutral molecules. Although a large number of sensors has been developed, a common set of design themes can be identified. In each case one or more inorganic signaling centers have been linked to acyclic, macrocyclic, calixarene, terpyridine or related ligand frameworks capable of analyte binding. Sensors for cations have tended to utilize crown or calixarene based receptors, while sensors for anions or salts have typically incorporated crown, calixarene, pyridine or metallocene based receptors with amide (CONH) moieties. The amides generally serve as hydrogen-bond donors. In addition, sensors for anions typically carry a net positive charge, thereby adding a coulombic component to the binding.

2.1. Cation sensing

Cation sensing has become very important for both biological and environmental applications within the last 35 years [1]. In response, a large class of cation sensors based on coordination chemistry has been developed [2–9]. Several are selective for either alkali and alkaline earth metals (for example — lithium, sodium, potassium, zinc, calcium and magnesium) in which detection is necessary to monitor and regulate a number of cellular functions. Heavy metal cations such as lead and mercury have also been studied, due to their deleterious effects on biological systems [10–12]. In addition, there are several other environmental concerns regarding cations. For example, more than two-thirds of the Superfund and DOD sites, and about half of the RCRA and DOE sites contained within the United States require remediation for various types of metal cation contamination [13].

2.1.1. Alkali and alkaline earth metal ions

Spectrochemical detection of group IA and IIA metal cations has been demonstrated by Beer et al. with functionalized coordination compounds such as 1-5 [2]. In these compounds, recognition and binding is achieved with pendant crown moieties (well known cation receptors), while signal transduction is accomplished via changes in ³MLCT emission from the Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) fragment. For the aza crown compounds (1b-4b), Na⁺ binding is signaled by both an increase in luminescence intensity and a red shift in emission energy.



The intensity increase is a consequence of inhibition of reductive quenching of the Ru(bpy)* excited state: Cation binding by the crown creates an electrostatic penalty for oxidation of the available tertiary amine, thereby rendering it much less effective as a reductant [14]. The shifts in emission energy following binding are readily interpreted in terms of electrostatic stabilization of the coordinated bipyridine radical anion generated by the MLCT excitation: Bpy anion stabilization lowers the energy of the photoexcited state with respect to the ground state, thereby decreasing the emissive energy gap. Given the cationic nature of assemblies 1-5, their ability to bind positively charged analytes present at only millimolar concentration levels in CH₃CN as solvent is remarkable. For comparison, 15-crown-5 by itself is capable of binding Na⁺ present at concentrations on the order of 10^{-5} M in the same solvent [15,16]. Also noteworthy for the luminescent assemblies is their selectivity: Compounds 1b-4b, for example, display strong responses to Na⁺, weak responses to Mg²⁺, and no response to N(CH₂CH₂CH₂CH₃/4⁺.

This chemistry was further elaborated by Beer and co-workers with an ethynyl functionalized $\text{Ru}(\text{bpy})_3^{2+}$ center (5) where the reversible redox responses of the coordinated bipyridines were exploited to initiate electropolymerization and thinfilm formation [2,17]. The configuration of these assemblies as insoluble films offers real advantages in a chemical sensing context by: (a) eliminating contamination of the analyte solution by the sensor assembly, and (b) enormously simplifying the problem of sensor regeneration and re-use. Films of 5 readily bind Na^+ and report on the binding via shifts in emission energy — in retrospect, a somewhat surprising finding given the potential for the polycationic film framework to exclude positively charged analytes via Donnan membrane effects [18].

Harriman et al. evaluated two photoactive supramolecular assemblies composed of a luminescent $Ru(bpv)^{2+}_{2+}$ fragment connected via a methylene spacer to a benzoquinone functionalized calix[4]arene (6.7) [3]. These proved to be unusually efficient sensors for several alkali and alkali earth metal ions. In the absence of cationic metal guests, luminescence from both 6 and 7 is guenched due to light-induced electron transfer (ET) from the triplet state of the excited metal complex to a nearby quinone. Cation complexation results in exceptionally large increases in luminescence intensity. Preliminary studies indicate that the encapsulated cations force the lumophore away from the quinones and thereby destabilizes putative cofacial configurations of the reactive components [3]. The change in conformation prevents intramolecular electron transfer from the bpy anion to the quinone and restores the luminescence of the $Ru(bpv)^{2+}_{2+}$ fragment. Note that the lowest ³MLCT states, based on ligand substituent electronic considerations, are likely to be those that place the electron on one of the two available underivatized bpy ligands. The decrease in the intramolecular ET rate, and the corresponding increase in luminescence intensity is observed to scale with the charge of the metal ion: Monocations gave ca. 30-fold decreases in ET rate, while dications yielded 300-fold decreases and exposure to tripositive lanthanide ions resulted in a 1700fold reduction. Qualitatively, this trend is attributed to the separation distance



between the lumophore and quinone being varied due to variations in coulombic effects.

Harvey and coworkers have reported on preferential sensing of Li⁺ over Na⁺ by two metallocalix[4]arene complexes of iridium (I) (8 and 9) [4]. When 8 and 9 are confined to solvent glasses at 77 K, luminescence is observed at 619 and 597 nm ($\tau = 13.5$ and 13.7 ± 0.1 ns) from a ³MLCT excited state. Weak luminescence, centered at 592 nm, is also observed for 9 at 298 K in EtOH. Binding of Li^+ or Na⁺ inside the ionophoric calix[4]arene cavities, or to the ester groups near the metal center of 8 or 9 decreased the emission lifetimes, with Li^+ having the greater effect (and exhibiting the larger affinity for the molecular hosts). It should be noted that the overall changes in lifetime are small (ca. 8%), and that high concentrations of guest are required, indicating that the interactions between the luminescent hosts and cationic guests are weak.



2.1.2. Transition metal ions and other main group metal ions

Tzeng et al. designed a tetranuclear Au(I)-phenylacetylide complex (10) containing a tetraazamacrocycle which serves as both a structural 'organizer' for the four available chromophores and as a potential binding site for soft metal ions [5]. Stacking of the Au(C=CPh) units of $\{[Au(C=CPh)]_{4}L\}$ (in solution) yields intramolecular Au^I-Au^I interactions together with weak emission (565 nm) from binuclear metal fragments. Addition of Cu⁺ leads to binding as evidenced by a shift in emission wavelength to 530 nm, a large increase in luminescent intensity. and a 10-fold increase in luminescence lifetime. Addition of Ag⁺, on the other hand, yields only a 2 nm shift in emission wavelength and only a factor of three increase in excited-state lifetime. Interactions between $\{[Au(C=CPh)]_{a}L\}$ and Ag^{+} or Cu⁺ are believed to entail 1:1 complex formation — consistent with the availability of just one receptor site per gold cation assembly. A second emission from 10, associated exclusively with the phenylacetylide groups, is observed at 425 nm. This band is unresponsive to Cu^+ and Ag^+ binding, but is strongly enhanced in the presence of alkali metal ions, increasing in the order $Li^+ < Na^+ < K^+$. The emission enhancement here is ascribed to inhibition of non-radiative decay pathways of the intraligand excited state of the coordinated phenyacetylides when alkali metal cations are trapped inside the tetraazamacrocycle. Emission spectra of 10 in CH₂Cl₂ in the presence of K⁺, Na⁺, Li⁺, Cu⁺, and Ag⁺ are shown in Fig. 1.



Fig. 1. The emission spectra of **10** (10^{-4} M) in CH₂Cl in the presence of 10^{-3} M of: (a) KClO₄, (b) NaBF₄, (c) LiClO₄, (d) CuClO₄, and (e) AgClO₄. Adapted from Tzeng et al. [5].



Barigelletti, Sauvage, and Collin designed a sensor or 'optical switch' for Zn^{2+} based on the Ru(II)-terpyridine (tpy) containing chromophore, **11** [19]. In



 CH_3CN/H_2O as solvent, uncomplexed 11 weakly emits at 660 nm from a ³MLCT state. Upon addition of Zn^{2+} , a rod-like complex, 11: Zn^{2+} :11, is formed. The

light emission properties of $11:Zn^{2+}:11$ differ significantly from uncomplexed 11: The emission maximum is shifted from 660 to 700 nm, the emission intensity is enhanced 8-fold, and the luminescent lifetime increases from 1.6 to 84 ns. The luminescence properties were attributed to the ability of the chromophore to delocalize charge over both tpy-tpy ligands in the molecular excited state, once Zn^{2+} is bound. In effect, Zn^{2+} binding expands the π -system in the ³MLCT state to six pyridyl rings (i.e. the full tpy-tpy ligand). π -system expansion has been shown elsewhere to diminish energy gaps (accounting for the red shift) and decrease excited-state/ground-state normal coordinate displacements (leading to diminished Franck–Condon factors for excited-state decay, diminished rates for nonradiative decay, and increases in emissive excited-state lifetime) [20]. A similar system containing a phenyl spacer between the tpy fragments showed no change in luminescence with the addition of Zn^{2+} — consistent with a decoupling of the Ru-based chromophore from the appended tpy:Zn site [6,21].

A variety of receptor/chromophore assemblies utilize emissive states obtained via excitation of tricarbonyl Re(I) polypyridine complexes. For example, **12** and **13** have been evaluated by Sullivan and Shen for the detection of Pb^{2+} and Hg^{2+} in a methanolic environment [7,8]. Treatment of **12** with Pb^{2+} yields a limiting red shift of 20 nm in the room temperature emission spectrum and a 3-fold increase in emission intensity [7]. Assembly **13** responds similarly when exposed to either Pb^{2+} or Hg^{2+} [8]. Selectivity for Pb^{2+} over Hg^{2+} and Ba^{2+} was demonstrated for **12** and **13**, respectively. Curiously, the luminescence enhancement effect arises from



a binding-induced inversion of the lowest and second lowest lying electronic excited states. In the absence of heavy metal ions, **12** and **13** both luminescence from ligand-localized states. Cation binding leads to MLCT emission, presumably by imparting electrostatic stability to the charge-transfer excited state.

The last transition metal ion sensor discussed contains four $Ru(bpy)_3^{2+}$ groups pendant to a tetraazacyclotetradecane (cyclam) (14) and was designed by Josceanu and co-workers [9]. At pH 7, 14 exhibits fluorescence characteristic of the $Ru(bpy)_3^{2+}$ chromophore centered at 600 nm. The fluorescence is greatly reduced upon protonation or inclusion of either Ni²⁺ or Cu²⁺ into the cyclam unit. This presumably reflects a very rapid quenching of the ³MLCT excited state by either electron or energy transfer mechanisms.



2.1.3. Actinides and lanthanides

The iridium metallocalix[4]arene complexes (8, 9), developed by Harvey et al. and discussed above (alkali metal ion sensing), also bind UO_2^{2+} [4]. Binding is signaled by decreases in excited state lifetime. It is worth noting that the sensitivity of each of the hosts to UO_2^{2+} exceeds by roughly 4-fold the sensitivity to Li⁺ (the most easily sensed alkali metal ion).

Poly-ruthenium assemblies developed by Harriman and coworkers (6, 7) have been shown to bind Ln^{3+} ions (Gd³⁺ and La^{3+}) [3]. Lanthanide ion binding induces a roughly 1000-fold enhancement in host luminescence, where the mechanism of enhancement is evidently the same as that discussed above in Section 2.1.1.

2.2. Anion sensing

Sensing of anionic guests of biological and environmental importance has only recently become an area of focus [22–36]. Anions play fundamental roles in many biological and chemical processes [37]. The chloride ion, in particular, is crucial in several phases of human biology and in disease regulation [38]. A pertinent example is the hereditary disease cystic fibrosis that is known to result from a misregulation of chloride ion channels [39]. In addition, the role of selected anions as environmental pollutants has been recognized [40]. For example, nitrate and phosphate contamination of ground water, due to agricultural runoff, has become increasingly problematic.

2.2.1. Chloride and hydrogen phosphate

Beer and co-workers have developed two classes of sensors for Cl^- and $H_2PO_4^-$. The first relies upon one or more light-collecting $Ru(bpy)_3^{2+}$ fragments incorporated via amide moieties into cyclic, macrocyclic, or calix[4]arene structural frameworks (anion binding units; see structures 15-30) [29,31,33]. In all cases, emission originates from a ³MLCT state, where L is presumably the amide-functionalized ligand.



In 29, however, dual emission (Os and Ru ³MLCT states) is observed. Upon addition of either Cl⁻ and $H_2PO_4^-$, assemblies 15–19 uniformly display blue shifts in emission spectra and large increases in emission quantum yield [29]. Similar responses were shown for 22–29 for Cl⁻ ions [31,23]. In addition, 22–26 were evaluated in the presence of K⁺ to probe whether cation binding to the crown moiety would enhance the binding ability of the complexes for Cl⁻ due to an increased electrostatic interaction. NMR studies indicated that only 24 had a stronger binding constant for Cl⁻ in presence of K⁺. Presumably, the enhancement effects are manifestations of so-called 'energy gap law' behavior, whereby an









n= 2

increase in emissive excited-state/ground-state separation leads to a decrease in Franck–Condon factors and a decrease in the rate of nonradiative decay. If the decay process is dominated by nonradiative pathways, then a corresponding increase in excited-state lifetime and emission quantum yield will be observed. Note that anion binding provides an obvious electrostatic basis for destabilizing the coordinated bpy (amide) anion in the charge-transfer excited state and shifting the emission to higher energy, as observed experimentally. Nevertheless, an alternative explanation for binding-induced emission intensity enhancement is that binding imparts rigidity to the assembly and thereby inhibits the nonradiative decay process.

Selective sensing of $H_2PO_4^-$ over Cl^- was demonstrated with ion induced luminescence intensity enhancements for **20** and **21**, where the preference for the complex anion presumably is due to amide-proton/phosphate-oxygen hydrogen bonding [29].

A structurally similar complex (30), displays tunable anion selectivity (Cl⁻ vs. $H_2PO_4^-$) [34]. In the absence of K⁺, the assembly binds $H_2PO_4^-$ preferentially in











30





The second group of receptors, shown above, contains $Ru(bpy)_3^{2+}$ -metallocene or metallocenium units (**31–33**) [28,30]. Weak luminescence is observed from these complexes, relative to the $Ru(bpy)_3^{2+}$ prototype, due to either electron or energy transfer quenching of the emissive ³MLCT state by the tethered metallocene/metallocenium units [41]. Assemblies **31** and **32** show significant emission wavelength blue shifts and emission intensity enhancements following Cl⁻ addition, but no changes in emission characteristics upon addition of $H_2PO_4^-$ [28]. Interestingly,

assembly 33 behaves in precisely the opposite fashion: $H_2PO_4^-$ addition induces a 20-fold increase in emission intensity, while additions of Cl⁻ or HSO₄⁻ ions had no effect on the emission [30]. Anion binding causes the emission wavelengths for 31-33 to shift to ca. 690 nm, rather far removed from the usual emission wavelength of 640 nm. The large shifts have been ascribed to exciplex formation. The mechanism for luminescent enhancement is apparently the same as that encountered with assemblies 15-19: Receptor:anion complex formation increases the rigidity of the receptor, thereby disfavoring nonradiative decay processes.

Yet another example of chloride anion sensing is demonstrated by the tetrakis $Ru(bpy)_3^{2+}$ organic-cavitand assembly, **34**: Consistent with the availability of hydrogen-bond donors within the receptor site, however, the assembly showed a stronger response to carboxylate containing anions such as acetate and benzoate, than Cl^{-} [33].

2.2.2. Phosphodiesters

Another $\text{Ru}(\text{bpy})_3^{2^+}$ based assembly with amide functionalities (35), designed by Watanabe and co-workers, binds anionic phosphodiesters [36]. For example addition of ten equivalents of anionic tetraethylamminonium diphenyl phosphate to a 0.02 mM acetone solution of 35 yields a factor of 1.3 increase in the luminescence intensity. The authors suggested that the increase is a consequence of binding-induced rigidification and inhibition of activity in vibrational modes responsible for nonradiative decay. Again, an alternative interpretation is that anion binding electrostatically destabilizes the coordinated bpy anion created in the emissive ³MLCT state. Destabilization, in turn, should increase the excited-state/ground-state energy gap, thereby decreasing the nonradiative decay rate and increasing the emission quantum yield.



2.2.3. Neutral molecule sensing

One example of neutral molecule sensing has been reported. Watanabe et al. found that assembly **35** could bind dibenzyl hydrogen phosphate (DBHP) in acetone as solvent, and that the binding was detectable as a modest reduction in the luminescence intensity [36]. The reduction was attributed to proton transfer from

the bound DBHP molecule to 35 and a subsequent enhancement in the rate of nonradiative decay.

3. Indirect excitation of luminescent, chemoresponsive metal centers

The use of encapsulated lanthanides as sensitized photoactive centers capable of analyte binding has emerged as a compelling strategy for luminescent supramolecular sensor development [42-56]. These hybrid systems utilize the large absorption cross sections of selected organic molecules and the long life time and sharp emission characteristics of lanthanide ions to generate very efficient molecular devices.

In the absence of sensitizers, lanthanide ions display very weak luminescence due to the low extinction coefficient ($< 1 \text{ M}^{-1} \text{ cm}^{-1}$) for direct excitation into the ${}^{5}\text{D}_{j}$ emitting state. However, when the lanthanide ion excitation is sensitized through ligand-centered or charge transfer absorption, intense emission can occur. Sensitization and emission provide a basis for chemical sensing. Detection is achieved by an absorption/energy-transfer/emission (AETE) sequence involving direct absorption of UV light by an organic ligand which is normally the analyte, energy transfer from the absorber to the metal center and finally monitoring the long-lived luminescence from the lanthanide, as shown in Scheme 1.

Generally, in order to achieve analyte sensing, the supramolecular assembly must: (i) shield the lanthanide ion from hydroxylic solvent molecules that would otherwise quench the lanthanide luminescence; (ii) place the chromophoric site sufficiently close to the emissive site to permit efficient energy transfer; and (iii) contain docking sites for specific guests. The efficiency of signal transduction is dependent on the efficiency of the component steps: light absorption, energy transfer and light emission. Because lanthanides are large ions (typical coordination number of nine), they can accommodate both the shielding agent (encapsulation agent) and the analyte in their inner coordination sphere, thus facilitating efficient energy transfer.

3.1. Acids

The Nocera group reported that lanthanide-cryptate assemblies such as **36** luminesce upon complexation with UV-light-absorbing, organic acid molecules [43,44].



Scheme 1.



In **36**, two nitrogens and five oxygens from the cryptand occupy seven of the nine available coordination sites, leaving two sites available within the inner coordination sphere for analyte ligation. Exposure of the assembly to picolinic or benzoic acid results in binding to Eu^{3+} , energy transfer, and sensitized lanthanide emission (see Fig. 2).

3.2. Aromatic hydrocarbons

Nocera and coworkers devised a similar methodology to sense aromatic hydrocarbons [44,47]. However, because the hydrocarbons do not coordinate to lanthanide ions a new family of systems was designed such that each member contained two binding sites: A diaza crown ether ligand for the lanthanide and a functionalized cyclodextrin (CD) for the hydrocarbon substrate.

The aza crown is oriented, or swung, away from the CD cup in assembly 37 and fixed directly below the cup in 38 [44]. Benzene addition to a solution of 37 resultsin a factor of two enhancement of Eu^{3+} luminescence intensity. In contrast, 38 displays no luminescence in the presence of aromatic hydrocarbons. At least in part, the failure of 38 to function as a sensor is due to the inhibition of CD-based binding of the hydrocarbons because of the proximity of the CD receptor to the highly charged lanthanide center.



Fig. 2. Relative emission intensities from aqueous solutions of the $Eu^{3+:36}$ complex upon addition of light harvesting guest molecules, picolinic acid and benzoic acid. Adapted from Pikramenon et al. [44].



To neutralize the charge of the lanthanide ion, and hence increase the strength of binding of the aromatic hydrocarbons within the CD cup, the third complex within this series, **39**, was designed with a tri-anionic diethylenetriaminepentaacetate based binding site [47]. Titration of solutions of **39** with aromatic substrates greatly enhanced the lanthanide luminescence through the AETE process. Specific substrate induced enhancements are dependent on the absorption coefficient of the substrate and on the strength of the host–guest binding.



3.3. Halide ions

Parker and co-workers have shown that halide ions can be sensed by *quenching* an intramolecular AETE process associated with Eu^{3+} complexes of 40 and 41 [48]. Octadentate monoamindetriphosphinate (40) or chiral tetraamide (41) complexes based on 1,4,7,10-tetraazacyclododecane were tethered to an *N*-alkylated



phenanthridine chromophore. Upon excitation with light at wavelengths ≥ 340 nm, intramolecular energy transfer occurred from the triplet excited state of the phenanthridine ligand to yield the emissive ${}^{5}D_{j}$ state of the lanthanide ion. Addition of halide ions (chloride, bromide, iodide) to aqueous solutions of $Eu^{3+}:40$ and $Eu^{3+}:41$ resulted in reduction of luminescence from both the directly excited chromophore and the metal center.

Stern–Volmer relations for the fluorescence of the metal center indicated that the rate of quenching of the chromophore excited state was competitive with the rate of inter-system crossing. (Inter-system crossing is necessary to reach the triplet state of the chromophore which, in turn, transfers energy to create the emissive lanthanide ${}^{5}D_{j}$ state). The selectivity of these sensors for halide ions over other bioactive oxyanions (citrate, lactate, hydrogen carbonate and hydrogen phosphate) was demonstrated both in the presence and absence of chloride in solution.

3.4. Alkali metal ions

The detection of alkali metal ions has also been demonstrated by de Silva et al. with lanthanide ion aza crown molecular complexes $42a,b:Eu^{3+}$ [57]. The diphenyl terpyridine unit is an excellent near-UV chromophore and serves as a sensitizer for Eu^{3+} . Following sensitization, weak Eu^{3+} emission is observed at ca. 600 nm at 298 K. The emission is enhanced by more than an order of magnitude when either Na⁺ and K⁺ cations are bound by the aza crown units.



The luminescence enhancement effect has been ascribed to suppression of electron transfer from the nitrogen of the aza crown to the excited Eu^{3+} ion, in much the same fashion as described for compounds 1–5. Note that the inhibited reductive quenching explanation for luminescence intensity enhancement would likely require cation binding at both receptor sites. Conceivably, somewhat lower detection limits could be obtained if structures like 42a or b were prepared with only one pendant aza crown moiety. An analogous experiment with 42a:Tb³⁺ and 42b:Tb³⁺ complexes showed no change in the luminescence profile in the presence of Na⁺ and K⁺. The failure was ascribed to the existence of an additional deactivation channel for the Tb³⁺ ⁵D₄ excited state.

The use of lanthanides for detection of analytes in liquid chromatography was first described in 1985 by DiBella and coworkers [49]. Since then, the technique has been extended to numerous other species including single stranded nucleic acids [50], hormones [51,52], amino compounds [53] and labeled thiols [54,55]. Detection is achieved by the AETE scheme with the organic analyte coordinating to the lanthanide and acting as the light absorber. Encapsulating agents such as ethylene-diaminetetraacetic acid (EDTA) can be added to aid in solubilizing the Ln(III) ion in basic solution or in the presence of phosphate buffers [56]. The lanthanide is typically added to the post-column mobile phase so as to allow optimization of the conditions necessary for luminescent detection without disrupting the separation on the column.

A recent innovation, and a representative example of the detection technique in general, has been described by Wenzel and coworkers [58]. Instead of adding the lanthanide to the post-column mobile phase, which has the drawback of lowering the detection limit due to dilution of the mobile phase, the researchers immobilized the terbium(III) on silica through the use of either EDTA or diethylenetriaminepen-taacetic acid. The modified silica was then packed into a flow cell which was attached to the end of the column, and luminescence was monitored by a standard spectrofluorimeter with a modified cuvette holder. Separation was conducted under normal conditions, with the addition of potassium acetate to assist in dissociation of the analytes from the Tb(III) (to prevent tailing) and triethylenetetraamine was added to prevent discoloration of the silica by transition metals present as impurities in the mobile phase. Clean separation and detection of indole-3-acetic acid, 5-methoxyindole-2-carboxylic acid and indole-2-carboxylic acid was achieved (Fig.



Fig. 3. Separation of indole-3-acetic acid (1), 5-methoxyindole-2-carboxylic acid (2), and indole-2-carboxylic acid (3) with a detection phase of DTPA-Tb(III) modified silica gel and an excitation wavelength of 300 nm (a) or 285 nm (b). Adapted from Wenzel et al. [58].

3). As expected, the detection limit was improved by ca. 1 order of magnitude over schemes which rely upon a post-column addition of lanthanide ions.

4. Luminescent sensor assemblies lacking pendant binding groups

This section describes a variety of sensors and probes which do not feature a specific binding group or cavity (Sections 1 and 4), and which do not involve indirect photo excitation (Section 2). Included are sensor assemblies in which the analyte interacts directly with the metal center, and several examples of sensors whose solid state emission is affected by interaction of the solid with vapors of volatile organic chemicals.

The sensors in this section are used for a variety of analytes: the organofluorophosphorous nerve agents Sarin and Soman which were reportedly used during the Iraq/Iran war and more recently in a terrorist attack on a Tokyo subway, volatile organic compounds (VOCs) which can influence workplace air quality [59], and the ions K^+ and Cl^- which are of obvious biological significance [38,39].

4.1. Direct coordination of the analyte to the metal center

Jenkins and coworkers have developed a lanthanide-based solid state luminescent sensor which selectively detects the hydrolysis product of the nerve agent Soman in water through direct interaction of the analyte with the europium(III) metal center [60]. Europium(III) was chosen because its narrow excitation and emission bands allow selective analyses.



The Eu³⁺ was complexed by three units of methyl-3,5-divinyl-benzoate, DVMB, two nitrate counter ions and one unit of the hydrolysis product of Soman, pinacolyl methylphosphonate, PMP, to give a coordination number of nine and an overall neutral complex. The complexes were then polymerized in a styrene matrix. The PMP was replaced in the coordination sphere of the Eu³⁺ with NO₃₋ by washing the polymer with methanol/water and then with dilute nitric acid. Upon exposure to an aqueous solution of PMP (lower concentration limit of 750 ppq), an emission peak at 610 nm grew in, which corresponded to the emission from the parent Eu(DVMB)₃PMP(NO₃)₂ complex, demonstrating the reversibility of this detection system. The selectivity of the Eu³⁺ emission for PMP was determined by examining several chemically analogous pesticides (concentrations of up to 1000 ppm) which often give false positives when evaluated by other methods. As shown in Fig. 4, only PMP triggers the emission at 610 nm, demonstrating that this Eu³⁺ system is quite selective for PMP when compared with structurally similar analytes.



Fig. 4. Response of a Eu^{3+} based sensor to PMP (a) and selected interferences: dichlorvos (b), dimethoate (c), malathion (d), phosdrin (e), dibutylchloendate (f), methyl parathion (g). Adapted from Jenkins et al. [60].

Chan and coworkers have reported preliminary work on a another complex which produces a change in luminescence upon coordination of the analyte to the emissive metal center. A robust and selective phosphine sensor, $Au(dpdo)^+$ (dpdo = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane) **43**, is described, where the Au(I) atom is bound by the two phosphorous atoms in a nearly linear fashion (P-Au-P bond angle of 172°) [61]. They found that, like the Au(PPh₃)² parent



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compound, **43** interacts with phosphines in acetonitrile according to the equilibrium shown below at 298 K to turn on luminescence [61]. The enhanced luminescence is likely due to the high quantum yield of the three coordinate trisphosphine Au(I) species that is in equilibrium with **43** and gives an emission band at 510 nm for PPh₃ with concentrations $\geq 10^{-5}$ M and at 610 nm for bis-(diphenylphosphino)methane with concentrations of ca. 10^{-4} . The large difference in the emission maxima for the two analytes is likely due to an Au–Au interaction which becomes possible when the diphosphine simultaneously coordinates two molecules of **43**. Notably, other nucleophiles such as Et₂S, SCN⁻



and CN^- do not induce significant changes in luminescence, even at concentrations as high as 10^{-2} M. The ineffectiveness of the potentially interfering nucleophiles in inducing luminescence possibly reflects low formation constants. In any case, **43** is able to function as a selective sensor in solution for phosphines or for analytes containing one or more-non ligated phosphine moieties.

4.2. Luminescent solid state sensors for volatile organic chemicals

While only preliminary work has been done with respect to using the complex as a sensor, the trimetallic cycle (44) examined in the Balch group is particularly noteworthy because it displays a unique luminescence phenomenon which has been termed solvoluminescence [62,63]. The complex is based on a nuclear gold(I) ring with bridging organic ligands, and was first prepared in 1974 [64,65]. While the



44

complex is only weakly luminescent in solution, when polycrystalline samples are irradiated with a UV lamp (366 nm) and subsequently placed in contact with a liquid which can act to solvate some or all of the sample, the substance gives off intense yellow light ($\lambda_{em} = 552$ nm for CHCl₃) for tens of seconds. Interestingly, the emission occurs at a lower energy than the emission seen for 44 in solution ($\lambda_{em} = 422$ nm). Balch and co-workers have proposed that the solvoluminescence is associated with molecular stacking interactions unique to the solid state which allow energy storage. This is supported by the emission spectrum of 44 in the solid state which shows two emission bands centered at 422 and at 552 nm when there is no contact with a liquid. Work is reportedly underway in the Balch group to exploit the energy-storage/dissolution/emission phenomenon in sensing schemes.

Mansour and coworkers reported that in the solid state, linear chains of the dimeric gold complex, $[Au(S_2CN(C_5H_{11})_2)]_2$, **45**, display vapochromatic behavior, i.e. in the solid state, the complex shows spectroscopic changes upon exposure to the vapors of organic solvents [66]. Dry films of **45** are colorless and non-emissive, but upon exposure to selected volatile organic compounds, they become orange

 $(\lambda_{abs} \text{ ca. } 460 \text{ nm})$ and become luminescent $(\lambda_{ems} \text{ ca. } 625 \text{ nm})$. The effect is reversible: with drying the films become colorless and non-emissive. Single crystal X-ray diffraction studies of a solvate of **45** show that the solvated crystal contains dimeric subunits featuring dithiocarbamate bridges between Au atoms, and a 2.77 Å Au-Au bond. Additionally, between selected dimer units, there exists a weak Au-Au interaction $(d_{Au-Au} = 3.02 \text{ Å})$ causing the dimers to form linear chains as defined by the Au atoms. In the non-solvated, non-emissive structure however, the dimers exist as discrete units with no intermolecular Au-Au interaction. It was concluded that intermolecular interaction is facilitated by solvent in the solid state matrix, and is necessary for emission to occur. However, there appears to be little variation of the emission or absorption of **45** with changes in the identity of the organic vapor.



The Mann group has examined the solid state vapochromism of coordination compounds based on the double platinum salt, $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt) [67,68]. They find that films of $[Pt(CNC_6H_4C_nH_{2n+1})_4][M(CN)_4]$ (n = 1, 6, 10, 10)12, 14; M = Pd(II), Pt(II)), 46, show significant changes in both the absorption and emission maxima upon exposure to various organic vapors. They also find that n = 10 gives the best results in terms of VOC detection, and that salts with $Pt(CN)^{4-}_{4}$ are more stable than their Pd(II) counterparts. The diplatinum salts also show greater vapochromic shifts and an overall lower energy absorbance. The complex forms linear chains in the solid state with alternating cationic and anionic platinum complexes, and significant metal-metal interactions along the chains. Because of the large difference in size between the cation and anion, there exist large pockets in the solid state which can accommodate and exchange solvent molecules without disrupting the overall structure. For the homometallic diplatinum salt, the absorption maximum for a dry film is at 746 nm, and is assigned to a spin-allowed component of the $d\sigma^* \rightarrow p\sigma$ transition. Excitation of this band leads to emission which has a maximum at 944 nm. Upon exposure of the films to various volatile organic species (MeOH, EtOH, 2-PrOH, Et₂O CH₃CN, hexanes, acetone, benzene, CH₂Cl₂ or CHCl₃), a reversible change in the emission maximum is observed with $\Delta \lambda_{em}$ ranging from 2 (MeOH) to 74 nm (CHCl₃). The changes are due to perturbations of the solid state Pt–Pt interactions by the sorbed VOC, though the overall structure is largely unperturbed. Hydrogen bonding interactions between the ligated cyanides of the anionic component of the salt and hydroxylic VOCs provides some of the driving force for binding of the latter. Lypophilic interactions involving the aryl group on the Pt(II) cation, on the other hand, contribute to the binding and vapochromic shifts associated with nonpolar VOCs such as benzene.

5. Multimetallic luminescent sensors with the metal integrated into the cavity framework

Over the past few years, there has been considerable interest in the development of small molecule sensors based on transition metals, where the metal is part of the cavity framework (for very recent reviews of assembly chemistry see Stang and Olenyuk [69], Jones [70], Fujita [71], and Slone et al. [72]). A few of these systems have incorporated luminescent metal centers into the architecture, and we will discuss those here. Most use rigid ligands to create a semi-rigid cavity which can, depending on the structure and charge of the cavity framework, accommodate a range of guest species. Also presented is an example of using transition metals to bring together an encapsulating macrocycle. Guests examined to date include inorganic anions, carboxylates, aromatic hydrocarbons, and methyl viologen.



Slone and coworkers reported a molecular square which used alternating Re(CO)₃Cl and Pd(dppp)²⁺ (dppp = 1,3-bis(diphenylphosphino)propane) corners and bridging 4,4'-bipyridine links (47) [23]. In solution (acetone), emission from the triplet MLCT (Re $\rightarrow \pi^*$ bpy) state is detected at 610 nm. Because of the cationic nature of the inorganic cyclophane, it was expected to act as a host for anions, possibly with changes in the luminescence. Addition of ClO₄⁻ to solutions of 47 indeed does cause an increase in the emission intensity, and in the emission lifetime



Fig. 5. Growth in luminescence intensity of **48** with addition of tetraethylammonium perchlorate (\diamondsuit) , sodium triflate (\Box) , and tetraethylammonium tetrafluoroborate (\bigtriangleup) . Solid lines correspond to the binding curve fit for each anion. Adapted from Slone et al. [72].

(17–21 ns). The enhancement effect derives from a binding-induced inhibition of redox quenching by the Pd(II) sites. Addition of BF_4^- , which binds more strongly than ClO_4^- ($K = 6000 \text{ M}^{-1}$ compared to 900 M⁻¹) induces a larger enhancement of the luminescence. Addition of trifluoromethanesulfonate which has a binding constant of intermediate size (3000 M⁻¹) enhances the luminescence to a degree between that observed for BF_4^- and ClO_4^- (Fig. 5, adapted from Slone et al.; [72].

While the cyclic trimetallic copper complex, **48**, has been known for some time [73], its luminescence properties have only recently been investigated. Provencher and Harvey found that the complex luminesces strongly in solution at and in the solid state [74]. The luminescence ($\lambda_{em} = 540$ nm, $\tau_{em} = 89 \pm 9$ µs at 298 K in ethanol) has been described as phosphorescence from an excited state delocalized throughout the tricopper frame. Interaction of **48** with carboxylates (either acetate or 4-aminobenzoate) quenches the luminescence, apparently because of host:guest exciplex.



Uang and coworkers reported the synthesis of luminescent metallomacrocycles based on gold(I) and silver(I) complexes of 2,7-bis(diphenylphosphino)-1,8-naph-thyridine, **49** ($\mathbf{a} = Au$, $\mathbf{b} = Ag$) [75]. In CH₂Cl₂ as solvent, the gold assembly emits

from an MLCT excited state ($\lambda_{em} = 625$ nm), while the silver assembly emits from an intraligand excited state ($\lambda_{em} = 550$ nm). Only preliminary work has been done on using this system as a sensor for guest molecules, but the studies have shown that aromatic hydrocarbons quench the luminescence of **49b**.



Lai and coworkers have reported a hexametallic host, **50**, which uses platinum(II) and chelating dicarbene and bridging cyanide ligands [76]. The cavity of the complex adopts a hexagonal form with Pt(II) at each vertex. In CH₂Cl₂ as solvent, the compound luminesces at 514 nm when subjected to MLCT (Pt $\rightarrow \pi^*$ (carbene)) excitation in the near-UV region. It was found that the emission from **50** was quenched by addition of *N*,*N'*-dimethyl-4,4'-bipyridinium hexafluorophosphate. However, quantitative studies were not reported, and a determination of whether binding was taking place or whether the quenching was limited by diffusion apparently was not made.

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