



## Review

# Prevailing paradigms in novel lanthanide optical probes from molecular complexes to hybrid materials



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## ABSTRACT

Since lanthanide luminescent materials generally possess striking and special spectroscopic or photo-physical features such as sharp emission bands and long lifetimes, they have emerged as new platforms in sensory and diagnostic fields. This review aims to summarize the recent development relevant to the assembly of ligand design and fluorogenic species for a wide range of analytes. Moreover, the flexible and rigid optical frameworks include not only the molecular-based functional complexes, numerous lanthanide hybrid nanocomposite materials that lie between the interface of organic and inorganic hosts also provide possibilities to fabricate tailor-made optical probes due to their unique chemical and physical properties. The remarkable examples of newly-designed lanthanide hybrid sensing materials (siloxane or titania based hybrids, carbon-related nanomaterials, polymeric composites and noble metal based probes) are discussed in this review.

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## 1. Introduction

Chemical sensors for the detection of different analytes are being extensively investigated in the fields of biological, clinical, environmental and supramolecular sciences [1–3]. The key point for the design of new chemical sensor is based on various molecular interactions such as covalent linkages, hydrogen bonds, charge transfer, proton migration, van der Waals' force and  $\pi$ - $\pi$  stacking etc. The assembled chemical sensors refer to the molecular based devices which can respond dynamically to changes in analytes concentration during the course of measurement. A number of new sensing principles and techniques including electrochemical, electrical, surface acoustic waves, magnetic, thermometric or biochemical have been developed in the signal transduction process over the recent years [4–6]. Interesting as well is using fluorescence to report a recognition event because it hardly consumes analytes and no reference sample is necessary. Fluorescent signals are easy to capture with high resolution and possible to perform remote observation. Upon the excitation of the optical sensors, emitted signals can be trapped by spectroscopy or microscopy through their luminescence, lifetime or photothermal effects. The well-established probes may be derived from low molecular-weight organic fluorophores, polymers, quantum dots, proteins or transition metal complexes [7]. But most of the above mentioned species have broad emissions or short-lived excited states which will be difficult to recognize from background signals or scattering. In this regard, the special optical properties of lanthanide elements have received considerable interests from last decades [8,9]. These *f-f* transition ions are essentially used for the assembly of smart sensors due to their large Stoke shifts, narrow emission bands and long lifetimes. It has to be mentioned that lanthanide inorganic nanocrystals especially the upconversion nanoparticles have been investigated as new stimuli responsive materials. The upconversion luminescence is regarded as the nonlinear optical process that involves lower excitation photons and leads to higher energy emission. The corresponding nanoparticles demonstrate enough photostability, low toxicity, tunable emission and high penetration depth. Consequently, these lanthanide inorganic materials have aroused considerable interests in the fields of optical sensing, theranostics and pH measurement [10–15].

Except the above-mentioned inorganic nanocrystals, in this review, we mainly summarize the latest fruitful results concerning lanthanide coordination complexes especially organic-inorganic hybrid edifices as functional sensors. Furthermore, we concentrate on their structural aspects and discuss their rational assembly processes that are able to express the signal changes under diverse conditions. It will be hard to offer a complete list of all the related works in this field. However, very typical examples from complexes to hybrid networks based on lanthanide luminescence are described here and this review covers the well-focused articles during the past few years.

## 2. Newly prepared lanthanide molecular-based sensors

### 2.1. Functional lanthanide chemosensors based on cyclen and its derivatives

Extensive research efforts for assembling rare earth molecular level sensors have been devoted to robust multifunctional 1,4,7,10-tetraazacyclododecane (cyclen) and its derivatives. It generally involves finely-controlled synthesis procedures where various functional groups or moieties can be precisely adjusted. This affords the superiority of convenience in water solubility and biomedical diagnosis. Therefore, we will begin with the well developed tetraaza type ligand in the following section and some

newly-reported cases will be outlined. The simple heptadentate cyclen Eu(III) complex was reported and a water soluble antenna 4,7-diphenyl-1,10-phenanthroline-disulfonate was incorporated. This complex (**Compound 1**) can be used for detection of Fe(II) ions with a detection limit of 10 pM [16]. The detailed results indicated the incorporation of Fe(II) induced decomposition of the original complex structure. By observing the photophysical studies, the displacement of the antenna (ligand) from the previous ternary complex occurred and Fe(II) participated into the coordination with 4,7-diphenyl-1,10-phenanthroline-disulfonate. Therefore the red emission was switched off. The same group designed an octadentate macrocyclic terbium (III) cyclen conjugate possessing a maleimide functionality (**Compound 2**) and it had weak green emissions (Fig. 1). However, significant enhancement for the luminescence was observed upon the addition of glutathione (GSH) in physiological pH range. With the aim of demonstrating its selectivity, more than 20 kinds of naturally occurring amino acids (40  $\mu$ M) were added in H<sub>2</sub>O (20 mM HEPES, 135 mM KCl, pH = 7.4) as the first step. Subsequently GSH (40  $\mu$ M) was added in the respective solutions. Except that two thiol based amino acids (cysteine and homocysteine) would cause emission changes, no significant changes were observed in the terbium luminescence by using other amino acids [17]. Parker developed a series of pyrazoyl-aza-xanthone chromophore attached cyclen molecules and corresponding terbium complexes (terbium quantum yield could reach 61%, 295 K, H<sub>2</sub>O) exhibited excellent cellular permeability. Investigation of the loaded cells through fluorescence revealed the complex uptake may follow endocytosis within endosomes of cytoplasm [18]. This team also prepared five kinds of europium complexes with heptadentate type ligands (**Compound 3**) and they possessed a brightness of more than 10 mM<sup>-1</sup> cm<sup>-1</sup> in water. Their overall quantum yields were in the range of 15–23%. As for the reported europium complexes with heptadentate ligand in aqueous media, the above results were quite high. These complexes can pass through the cell membrane and enter mammalian cells efficiently. Results showed a mitochondrial localization at the early stage, then the emissive species moved to other organelle such as lysosome. Responses to bicarbonate permitted the rapid determination of the anion in human serum. In vitro distribution features for the complex has been discussed and oxy-anions induced lanthanide-based luminescence changes were studied [19]. Recently, terbium (III) cyclen macrocyclic complex (**Compound 4**) has been attached to a peptide. When it would bind to its target boxB RNA hairpin, the conformation of this peptide has changed. More interestingly, the luminescence emission increased dramatically. It can be used as a highly sensitive and selective probe for this RNA hairpin [20]. The collected circular dichroism spectra indicated that the improvement of emission intensity in the presence of target species was caused by the folding of the disordered peptide chain into an alpha helical structure upon specific binding interactions. Four new macrocyclic-phthalimide ligands (**Compounds 5–8**) were synthesized via the coupling of *N*-(3-bromopropyl)phthalimide either to cyclen itself or its carboxylate-functionalized analogues (Fig. 1). The highest quantum yield of the terbium complex could reach 46% in HEPES buffer. Luminescence intensities were in 'switched off' mode at lower pH conditions, and were activated on progression to basic conditions as the phthalimido functions were hydrolyzed to their corresponding phthalamates [21]. In order to develop new derivative in this field, a benzimidazole heterocycle was attached to 1,4,7-tris(carboxymethyl)-1,4,7,10-tetraazacyclododecane. It showed sensitization effects to europium(III), terbium(III) and ytterbium(III). Moreover, it had a pH dependent coordination change due to protonation of the chelator [22]. In view of its molecular structure, the organic ligand bears six protonation constants that were associated with the macrocyclic nitrogen atoms, acetate

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