



## Review

# Development of responsive visibly and NIR luminescent and supramolecular coordination self-assemblies using lanthanide ion directed synthesis



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## ARTICLE INFO

## Article history:

Received 9 January 2014

Received in revised form 19 March 2014

Accepted 20 March 2014

Available online 4 April 2014

This review is dedicated to Professor David Parker FRS for his inspiration, guidance, support and friendship for the last 18 years.

## Keywords:

Supramolecular chemistry

## ABSTRACT

This review details the progress made in our laboratory in Dublin within the area of supramolecular lanthanide chemistry; where the main objective has been to develop functional lanthanide luminescent systems that emit within the visible or the near-infrared regions of the electromagnetic spectrum. The application of the lanthanide-centred assembly is two-fold, firstly to use it for sensing application of biologically and environmentally relevant anions, and secondly to use the emission to report on the formation of lanthanide directed self-assembly processes. This review begins with the progress made from the use of lanthanide cyclen (1,4,7,10-tetraazacyclododecane) complexes: to develop: displacement assays for sensing or probing applications; for their incorporations onto gold nanoparticles where the lanthanide emission can be ‘switched on-off’ by external stimuli; and their application in the formation of mixed f–d metal ion based self-assemblies and sensors and imaging agents for DNA. The second part of this review focuses on the development of self-assemblies formed using 2,6-diamidopyridyl based ligands. A variety of ligands are presented that have been employed in the formation of chiral self-assembly bundles,

**Abbreviations:** BTA, benzene-1,3,5-tricarboxamide; Cyclen, 1,4,7,10-tetraazacyclo-dodecane; bipy, 2,2'-bipyridine; CD, circular dichroism; CPL, circularly polarised luminescence; DNA, deoxyribose nucleic acid; dpa, dipicolinic acid; EDCI, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide; EDX, energy-dispersive X-ray spectroscopy; ESMS, electro-spray mass spectrometry; HEMA, (2-hydroxyethyl)methacrylate; HRMS, high resolution mass spectrometry; IR, infrared; MLCT, metal-to-ligand charge transfer; MRI, magnetic resonance imaging; NMR, nuclear magnetic resonance; phen, 1-10-phenanthroline; MMA, methylmethacrylate; RCM, ring closing metathesis; SAMs, self-assembled monolayers; SEM, scanning electron microscopy; TEM, transmission electron microscopy; *terpy*, 2,2':6',2''-terpyridine.

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dimetallic triple stranded helicates and Langmuir–Blodgett films that give rise to circularly polarised luminescence. The formation of such organised self-assembly monolayers of water–air interface brings us to the last topic of this review, along with the formation of novel soft-material such as gels, where the lanthanide emission is employed to report on the formation of three dimensional supramolecular structures, and their application as ‘nano-gardens’ in growing ionic structures with novel morphologies.

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## 1. Introduction

In this short review some of the highlights of the work carried out in our laboratory in Trinity College Dublin in the last decade, within the area of lanthanide luminescent based supramolecular self-assembly chemistry, are described. The story is in three main sections, being told, in part, chronologically beginning with our effort in developing cyclen (1,4,7,10-tetraazacyclo-dodecane)-based self-assembly structures, which sprung from an interest in the development of responsive luminescent sensors for cations and anions. This is then followed by the immobilisation of such complexes onto solid surfaces and incorporation into soft matter before we pay our attention to the development of self-assemblies such as bundles, helicates and interlocked supermolecules. These were formed by using lanthanide directed synthesis, unlike those discussed within the context of the cyclen chemistry, the ions are employed to bring together acyclic ligands, both chiral and achiral, in a templating manner. Finally, the development of novel materials, such as soft gels, based on the use of lanthanide directed synthesis will be discussed, highlighting results from this fast growing area within the field of lanthanide chemistry.

Over the last two decades there has been a surge in the development and application of lanthanide based coordination compounds within the field of supramolecular chemistry [1–9]. This increased interest is mainly due to their unique physical properties, particularly photo and magnetic properties, which have been capitalised on in both sensing and imaging applications [10,11]. This review focuses on the use of lanthanide luminescence to detect and report the presence of an ion or a molecule and the formation of self-assembly structures in real time. The unique photophysical properties of the lanthanides (such as Eu(III), Tb(III) and Sm(III), which emit dominantly in the visible region of the electromagnetic spectrum, and the near infrared emitting ions such as Nd(III) and Yb(III)) are very exciting and now well documented [12–15]. As the emphasis of this review is to give a more concentrated account of our own work rather than the field itself, nor the fundamental principles of the luminescence, we will only deal with these in passing throughout our discussion. Therefore interested readers are directed to the aforementioned established literature for a more detailed discussion on the subject; as well as to past reviews of the applications of lanthanide luminescence in sensing and self-assembly chemistry [16–20].

## 2. Cyclen based self-assemblies

### 2.1. Simple cyclen systems as luminescent sensors and probes

Having been inspired by the supervision of Professor David Parker at Durham University, England [21–24], our interest in lanthanide cyclen chemistry dates back to 1996 [25,26]. Since moving to Trinity College Dublin the research group has maintained a strong interest in exploring this area. Therein we have developed series of sensors and probes for cations, anions and molecules, particularly biological substrates, exploiting the cyclen motif. Some established, and more recent examples, from our laboratory within these areas include the development of compounds 1–5, Fig. 1. Compound 1 is an early example, a simple quinaldine based

sensor, which functions as a sensor for protons, in the case of the use of Eu(III) [27], yet also may transform into a O<sub>2</sub> sensor, where the Tb(III) complex is employed [28]. For these complexes, the changes in the intensities (as well as quantum yield and excited state lifetimes) of the various Eu(III) and Tb(III) transitions were monitored as a function of pH and O<sub>2</sub> concentrations. While these systems can be viewed as ‘pure’ sensors for pH and pO<sub>2</sub>, the luminescence output (emission) can also be expressed in terms of ‘on’ or ‘off’ signalling (as only intensity changes were observed with no shift in wavelength). As such, outputs can be treated as binary numbers (*i.e.* 0 or 1) and the luminescent outcome expressed as the product of molecular logic gate mimics. Hence, while the Eu(III) complex possesses a simple OR gate function, the output from the Tb(III) complex, could be viewed as an INHIBIT logic gate operation [29]. We later showed that the combination of two such Eu/Tb-sensors within the same matrix gave rise to more complexed logic gate mimic operations, which could be expressed as parallel processing operations [30]. Compound 2 is a recent development from the laboratory designed as a luminescent probe for observing enzymatic activity in real-time. The conjugated maleimide unit of the cyclen macrocycle in 2 functions as an Michael acceptor for thiols and, biologically speaking, the product of the enzymatic reduction of the oxidised form of glutathione by glutathione reductase. In this case the Tb(III) emission is switched ‘on’ upon formation of the irreversibly formed C–S bond signalling the sequestration of the enzymatic product [31].

In contrast to that above, the Eu(III) complex 3 was developed as an imaging agent for bone structure analysis [32]. The luminescence was shown to be pH independent within the physiological pH range, with the agent able to bind easily to exposed Ca(II) sites and micro-image cracks in bovine bones. The agent was highly sensitive, and was shown to only bind to micro-cracks and not to the bulk surface of the bone with the same affinity over a period of time. The ability of this agent was explored using confocal fluorescence imaging in competitive media. Further to complex 3, analogues of this compound have been advanced in our laboratory in the last few years for potential clinical applications in imaging, including *in vivo* magnetic resonance imaging (MRI).

### 2.2. Self-assembled f-d metal ion structures

While the previous examples are based on simple lanthanide complexes, compounds 4 [33] and 5 [34] are examples of a new type of design strategy within our group for sensing *d*-metal ions. These are based on the principles of displacement assays, inspiration originating from our interest in anion sensing [35] and the chemistry of Parker et al. [36]. These systems are, in their own right, examples of self-assembly complexes as they are formed as ternary complexes between a cyclen lanthanide complex and a coordinating ligand (directly coordinated to the lanthanide ion) that can be used itself to bind *d*-metal ions. The primary function of the ligand is to populate the excited state of the lanthanide (hence, functioning as a sensitising antenna). Then in the presence of competitive *d*-metal ions (that have higher affinity for the ligand than the lanthanide cyclen complex) ‘extraction’, or displacement, of the antenna from the ternary complex occurs. Upon doing so, the lanthanide emission is quenched, as the antenna is no longer available to populate

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