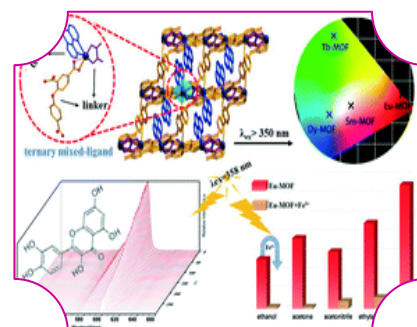




APPLICATIONS OF LANTHANIDE MOFS AND CPS

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ABSTRACT

The Metal–Organic Frameworks (MOFs), due to their exceptional structural tunability and properties, have a significant advantage over other candidates for chemosensory materials.

MOFs include the possibility to manipulate and extends its basic characteristics, like versatile building blocks (left or ligands) with a special chemical reactivity, thus Post-Synthetic Modification (PSM). The connectors in the majority of MOFs have aromatic subunits which can easily display light after ultraviolet, or visible (normally blue) excitation.

KEYWORDS: Lanthanide Chemistry, Lanthanide, Metal–Organic Framework, MOFS and CPS.

INTRODUCTION

Photoactive lanthanide ions (Ln^{3+}) can be inserted into MOF hosts to generate new light-emitting signals at positions different from the MOF hosts, but this depends on intramolecular energy (antenna effect) transmission from the MOF (linkers) to the Ln^{3+} ions. MOF hybrids may build many luminescent centres by controlling the Ln^{3+} material. The design of the specific lighting centres, which can provide a new opportunity for researching luminescence with applications for chemical sense sensing, can lead to various reactions to sensing species (i.e., ratiometric sensing).

A Brief History:

In the eighteenth century, two "rare earth" compounds started to be found in a riveted background of Lanthanides (Ln) sequence (elements 57-71 on the periodic table). Professor Johan Gadolin researched a black mineral in a quarry situated in Ytterby, Sweden in 1787. In 1794, yttria, an impure form of yttrium oxide, was detached and later found to contain terbium, erbium, ytterbium, holmium, thulium, gadolinium, dysprosium, and lutetium oxides. A few decades before Yttria, the second rare-earth compound has been identified. In 1751, in Sweden's Bastnäs mine, Swedish chemist Axel Frederik Cronstedt found a hard stone. After years of study, ceria, cerium oxide, in 1803, was eventually isolated from stone by a small group of scientists.

Lanthanide Chemistry:

a) Physical Properties of Lanthanides:

One of the two f-block series comprises of lanthanides. The 4f-orbit is gradually filled over the time. They prefer to form trivalent cations, as lanthanides are typically most stable in the formal oxidation state (Ln^{3+}). As a result, it is widely accepted that the electronic configuration is $[\text{Xe}]4f^n$ ($n = 0-14$). In the +2 or +4 states of oxidation, some lanthanides are stable, as they may acquire empty, half-filled or fully filled 4f

shells. Stable divalent ions can be formed by samarium, neodymium, promethium, europium, thulium and ytterbium. Praseodymium, cerium, dysprosium, and terbium are able to form stable tetravalent ions.

b) Lanthanide Coordination Chemistry:

A small radial expansion of the orbits for 4f valence allows ligands in a number of directions to reach the metal centre. This is because 4f orbitals, which stretch over and above 4f orbitals, are heavily protected from the ligand atmosphere by filled 5s or 5p orbitals. The 17 beyond 4f orbitals have limited interactions with ligand-based orbitals as a result of this blindness effect and result in bonds that are mainly ionic. This also leads to the creation of steric complexes that involve distorted coordinate geometries (the ligands surround the metal centre in such a way that the repulsion of the intraligands is so minimised). Trivalent lanthanide ions can form complexes ranging between 6 and 12 coordinate numbers (CN), with 8 to 9 being the most prevalent.

Applications of Lanthanide MOFs and CPS:

In scientific science research and industrial environments, metal-organic structure and coordination polymers offer various potential applications. The micro porosity of MOFs is one of the most sought after features. Although it is unknown that many of these materials have wide area areas and high porosity, which can be measured via the carefully chosen metal and organic connector. There is no method for calculating MOF's structural topology in the predictive way. This enables special host-guest chemistry that can be used for potential uses including gas storage/sorption, chemical sensing and drug distribution. Their peculiar chemical, magnetic and optical characteristics can be combined with porosity in LOFs to create new materials.

The characteristic of lanthanide materials are their separate magnetic properties. Since the 4f electrons are positioned far in the 5s and 5p orbits, surrounding ligands usually will not impact the 4f orbital. The ligand effects of the field are therefore negligible, and the magnetism observed is mainly environmental independent. Lanthanides typically provide high spin numbers of the soil, high spin-orbit coupling and solid magnetic moments in the 4f orbits. Paramagnetic Ln³⁺ ions in NMR spectroscopy are used as shift reagents. They can also be used as a single molecule magnet and as MRI conflicting agents because of their magnetic properties LOFs.

Furthermore, Lanthanide MOFs and CPs have impressive optical characteristics. Luminescence in lanthanides results from Laporte's prohibited 4f-4f transitions, triggered by a donor ligand's enthusiasm, in which an energy transfer occurs between the respective ligand or 'antenna' and the metal iodine. This "antenna effect" can produce higher quantum outputs and/or longer lifespan. Similar to porosity, by choosing the metal centres and organic connectors, the visual properties of luminescent LOFs can be changed (enhanced or decreased). The impressive luminescence properties of certain materials containing lanthanides have been fully used in molecular sensing, bioimaging, fluorescent pH sensing and display techniques.

Catalysis:

The broad surface areas and extremely versatile coordination of the lanthanide metal ions will coordinately generate unsaturated metal sites that can be used as heterogeneous catalysts in the production of LOFs.

- **Catalytic Porous Lanthanide-based Materials:**

A multi-faceted platform for the production of heterogeneous catalysts, including supramolecular, porous materials like CPs and MOFs, especially for reactions in the liquid stage. As mentioned above, metal-organic frames have many unique characteristics which make them ideal candidates for catalytic responses. They differentiate themselves from conventional catalytic materials by the relatively large tunable microporosity of MOFs. These normal, cage-like cavities provide an atmosphere that is regulated and post-

modifiable for host-guest interactions and typical catalytically active areas. The pore size/shape can be tailored, and the surface feature can be modified by choosing the appropriate metal ion and connector. The high stability of the frameworks over a number of different solvents that can contribute to a recyclability of the catalyst and a post-reaction separation are another important feature of MOFs for potential catalytic operation.

Experimental Methods:

Many methods for the synthesis of microwave aided, sonochemical, ion-thermal, sol-gel and microfluidic syntheses are available. But Solvothermal/hydrothermal synthesis is by far one of the most common and probably most common MOF synthesis methods.

Hydrothermal synthesis is a process in which substances are crystallised under autogenous pressure in a screened container from high-temperature aqueous solutions. The vessel consists usually of a steel pressure cylinder, with an insert (iron, gold, silver, quartz, teflon etc.) without carbon-free pressure which can withstand high temperatures and pressure for longer periods. This reaction vessel uses an (autoclave or mineralizing bomb). Two phases are accompanied by hydrothermal crystallisation. Temperature and pressure facilitate the breakdown of precursors in the first stage so that reactivity dependent on solutions can be found. The second phase is the phase of crystallisation, nucleation and particle formation. The synthesis of Solvothermal is similar except for the use in place of water of an organic solvent.

The benefit of a hydrothermal synthesis is that reactions in solution take place in contrast to traditional solid state reactions, so lower temperatures are appropriate. This can result in the 27 products being cinematically managed and metastable phases are generated. The hydrothermal approach appears to facilitate the production of single crystals as opposed to other synthetic MOF methods.

CONCLUSION:

The hydrothermal synthesis of 1,2, 4, 5 benzene tetracarboxylic acid lanthanide salts gives rise to 4 distinct metal-organic isostructural frameworks: Compound 1 (La, Ce, Pr, Nd, Sm), Compound 2 (Eu, Gd, Tb), Compound 3 (Dy, Ho, Er, Tm) and Compound 4 (Yb, Lu). This occurrence is relatively rare, as lanthanide MOFs can produce the same structure in similar reaction conditions throughout the sequence. In others, one structure is formed in the first half of the lanthanide spectrum and another half in the second. The role of lanthanide contraction is seen in comparisons of the four structures.

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