



## Review

## Lanthanide–organic frameworks for gas storage and as magneto-luminescent materials

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## ABSTRACT

Smart and careful design strategies need to be adopted for the synthesis of lanthanide–organic framework materials to strike a balance between the high coordination requirement of lanthanide metal ions and the formation of stable and permanently porous structures. Literature reports have documented successful synthesis of such porous lanthanide frameworks with potential application for gas storage. Lanthanide–organic frameworks have also shown promise in a number of magneto-luminescent applications. The diverse emission profiles of the lanthanide ions have resulted in tuning the emission colour to generate white-light as well as sense a host of cations, anions and small molecules alike. The permanent porosity has also been used to apply these frameworks as gas storage and separation materials. The exciting magnetic property of the lanthanide–organic frameworks arises from the high orbital contribution and single-ion anisotropy of the lanthanide ions. This eventually ushers the slow relaxation of magnetization with high energy barrier making such systems potential candidates for future magnetic sensory and memory devices. This review will discuss the porous properties of lanthanide–organic frameworks and the progress in utilizing them in gas storage and sensing properties. Colour tunability, white-light emission and magnetic properties in lanthanide–organic frameworks have also been discussed. In conclusion, an overall summary of the properties of these materials and future outlook will be proposed.

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## 1. Introduction

The fascinating growth of lanthanide coordination chemistry and supramolecular chemistry during the last two decades have stemmed from the practical successes in catalysis [1,2], biomedical analysis [3], diagnostic and possibly therapeutic medicine

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PCPs	porous coordination polymers
MOFs	metal organic frameworks
LOFs	lanthanide organic frameworks
UMS	unsaturated metal sites
BDC	1,4-benzene dicarboxylate
BPDC	4,4'-dicarboxylate-2,2'-dipyridine
CCS	carbon capture and sequestration
DMF	N,N-dimethyl formamide
MIL	Material of Institut Lavoisier
PDC	pyridine-3,5-dicarboxylate
BTC	1,3,5-benzenetricarboxylate
DFT	density functional theory
H <sub>2</sub> FTZB	2-fluoro-4-(1H-tetrazol-5-yl)benzoic acid
MBB	molecular building block
PDA	1,4-phenylenediacetate
SBU	secondary building unit
imidc	4,5-imidazolecarboxylic acid
dhbdc	2,5-dihydroxyterephthalate
H <sub>3</sub> L	4,4',4''-(benzenetricarbonyltris-(azanediyl))tribenzoic acid
Mu <sup>2-</sup>	mucate
BTB	4,4',4''-benzene-1,3,5-triyl-tri-benzoate
ICP	infinite coordination polymer
3-TPyMNTB	tris((pyridin-3-ylmethyl)benzimidazol-2-ylmethyl)amine
L	1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetrapropionic acid
G	guest solvent
pzdc	2,5-pyrazinedicarboxylate
H <sub>2</sub> ox	oxalic acid
TATB	triazine-1,3,5-tribenzoate
DMA	N,N-dimethylacetamide
SMM	single molecule magnet
SCM	single chain magnet
pza	2,3-pyrazinedicarboxylate
H <sub>3</sub> pimda	2-propyl-1H-imidazole-4,5-dicarboxylic acid
suc	succinate dianion
PTM	perchlorinated triphenylmethyl (trityl)
TDA	thiophene-2,5-dicarboxylic acid
tdc	deprotonated thiophene 2,5-dicarboxylic acid
hpd	4-hydroxypyridine-2,6-dicarboxylic acid

[4]. The intrinsic Lewis acidity, magnetic and luminescent properties of these lanthanides (Ln) ions are often not matched by the transition metal ions; thus synthesis of lanthanide based novel functional materials is useful for different applications. The optical properties in lanthanide complexes are particularly interesting, which arise mainly from the 4f–4f electronic transitions [5] and are well studied. But these have weak emission intensities and low quantum yields as they are Laporte forbidden transitions. However, in coordination compounds based on suitable  $\pi$ -conjugated ligands, an energy transfer process occurs from the ligand excited state to the metal excited state and subsequent enhanced emission intensities from the metal centre is realized. This phenomenon is known as ‘antenna effect’ [6–10]. These types of complexes therefore can overcome the “optical handicap” and show enhanced optical properties. In general, lanthanide ions (Eu<sup>III</sup>, Pr<sup>III</sup>, Sm<sup>III</sup>), (Tb<sup>III</sup>, Er<sup>III</sup>) and (Tm<sup>III</sup>, Ce<sup>III</sup>) exhibit red, green and blue emission, respectively and by adjusting the relative amounts of these metal ions in a material, multiple colours including white light emitting materials can be accomplished [11–14]. The other significant property of lanthanide-based compounds is magnetism, which has attracted enormous research interest despite its

complexity. The magnetic signatures are often difficult to interpret because of the high orbital contribution of the Ln ions and the associated anisotropy. The single-ion anisotropy of Ln ions ushers exciting features like slow relaxation of magnetization which makes the lanthanide-based compounds promising candidates for molecule based magnetic materials. The Ln ions exist almost exclusively in their trivalent state in a coordination complex. The nature of the coordination sphere with variable coordination numbers ( $6 \leq CN \leq 13$ ) is controlled by a subtle interplay between electrostatic interactions and inter-ligand steric constraints. Such versatile coordination geometry of the lanthanide complexes has led to limited success in the design of extended predetermined structures of different dimensionalities. However, by adopting an appropriate synthetic methodology, it is feasible to fabricate stable lanthanide based frameworks with novel functions. These compounds can then be cultivated for a host of magneto-luminescent applications.

Furthermore in recent years, porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) using transition metal ions have developed into a significant area of research because of its potential applications in gas storage (like H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>) [15–18], catalysis [19–21], separations [22,23], luminescence [24] and drug delivery [25,26]. For a lanthanide–organic framework (LOF), the gratification of higher coordination number in lanthanides are frequently fulfilled by the coordinating solvent molecules and thus the desolvated framework with unsaturated Lewis acidic Ln<sup>III</sup> sites can be exploited for specific catalytic activities and interesting adsorption properties like selective adsorption of gases [56]. But the design and synthesis of porous LOFs were less explored compared to the transition metal based frameworks. This is probably due to the difficulty in controlling and predicting the overall structure as the large coordination sphere of lanthanide needs to be filled by multiple linkers that would result in a highly stable condensed structure rather than a porous structure. However, by employing judicious ligand design strategies, it is possible to furnish novel porous LOFs, which can be attractive candidates to study gas storage, sensing of small molecules and guest dependent magnetic and luminescent properties (Scheme 1).

This review will be highlighting mainly the reported extended structures, i.e. coordination polymers of lanthanide based metal ions with different organic linkers. Focus will be on their synthetic approaches, porous, luminescent and magnetic properties. We would then conclude by giving a broad summary and a future perspective of this fascinating material which can be further exploited in different fields of materials science and technology.

## 2. Synthesis and design strategy for the construction of higher dimensional lanthanide–organic frameworks (LOFs)

Synthetic recipes for lanthanide based frameworks have been less discussed compared to the *d*-block elements despite the fact that LOFs are much more interesting in regard to their versatile coordination geometries and the tunable emission, magnetic and porous properties. The scantiness in literature probably stems from the fact that the coordination spheres as well as the structure of lanthanides based frameworks are quite difficult to control and straightforward recipes to synthesize such systems are yet to be developed. It should be noted that although such systems are quite complicated to predict beforehand, the higher coordination number can result in unanticipated and remarkable unprecedented structural topology. In addition to such structural novelty, these compounds can also render high thermal stability which is not easily achievable in other cases (transition metal based framework). The high coordination number of the metal ions is advantageous in another way too. Solvent molecules often coordinate to the metal to fulfil the coordination sphere and in such instances, removal of

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