Towards the sensing applications of luminescent lanthanide Periodic Mesoporous Organosilicas

Dissertation submitted in fulfillment of the requirement for the degree of Doctor of Science: Chemistry

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The work described in this thesis was carried out in the Luminescent Lanthanide Lab (L³), NanoSensing Group and Center for Ordered Materials, Organometallics and Catalysis (COMOC), Department of Chemistry, Faculty of Sciences, Ghent University. This work was supporting by the China Scholarship Council (CSC), No. 201804910742.



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Acknowledgements

During the almost four years of PhD study, I had an unforgettable and special experience. It is a very precious gift in my whole life and made me what I am now. The memories of these four years will be deeply remembered in my mind. The path to the PhD was full of difficulties, which made me much stronger and excellent after solving these difficulties every time. I cannot complete my PhD on time without the people who helped me a lot during my PhD studies. Here I would like to express my gratitude and thanks to my promoter, copromoters, kind colleagues, friends and family.

First, I would like to express my sincere gratitude to my country, China, for the financial support for my PhD studies. If I did not obtain the grant from China Scholarship Council (CSC), I would not have the opportunity to be a PhD student in Ghent University and carry out my research work in Prof. Rik Van Deun's group.

I would like to show my great thanks to Prof. Rik Van Deun for giving me an opportunity of pursuing my PhD in the luminescent lanthanide lab (L^3) . You are always ready to support and help me in my research. You are a very kind professor with rigorous scientific attitude. I still remember that the first time I came to S3, you warmly introduced me to the people here. Your support and suggestions on research give me more freedom in designing my own research work.

I would like to express my heartfelt appreciation to my copromoter Prof. Anna M. Kaczmarek, for opening a door for me to the field of periodic mesoporous organosilicas which was unknown before I came here. There were quite a lot of difficulties for me at the beginning of my PhD, and you helped me work out the project and showed me how to make PMO precursors and gave me more detailed research guidance. You always help me in time when I encounter any problems and give me more confidence to solve them. Your hardworking and rigorous research attitude is an example I have always been learning from. Also, many thanks for your patience to read the first version of the draft, especially for the first manuscript.

I would also like to thank Prof. Pascal Van Der Voort, especially in giving me very

useful advice on every presentation at research meetings. Besides, you have always given good suggestions on the writing of manuscript.

I would like to thank my kind colleague Chaoqing for picking me up at the Gent-Sint-Pieters station when I first arrived in Belgium. Thank you for telling me how to live a better life here, and for taking me to IKEA to buy daily necessities. You have also helped me a lot in setting the parameters of our PL equipment during the past three years.

I would also like to thank my very friendly colleagues Min and Jing. Thanks for your help and encouragement when I felt depressed in my PhD studies. Thank you, my kind colleague Dimitrije, for teaching me how to do NMR measurement. Even after you graduated, you still enthusiastically sent me very detailed emails explaining how to measure the instrument response function (IRF) using our PL setup. Thank you very much. I also would like to thank Hui for giving me more help in organic synthesis. I have benefited a lot from you. You are not only good at organic synthesis but also cooking delicious Chinese food.

I would like to thank to our warm-hearted secretaries, Pierre and Kathleen. Thanks for help me with the administrative documents from the government department. I would also like to thank technical staff, Bart, Pat, Tom, Funda and Katrien. Thanks, Bart for helping repair the broken devices in the L³ lab. Thank you, Pat, for helping me deal with the problems with my laptop. Funda, thanks a lot for your kind help with the nitrogen sorption measurement and XRD training. Thank you Katrien for TEM measurement for me. Thank you, Tom, for giving support on the Raman measurement. I cannot work smoothly in the department without all your help.

I would also like to thank to my colleague Maya, Manjari, Kai, Jieqi and all the XStruct members, Laurens, Marina, Marek, Min, Subhrajyoti. Thank you all for sharing the office and lab with me and all the good moments you brought. I also want to thank Sonali, Simona, Mirijam, for sharing the lab and sometimes very nice help and comfortable communications. Thanks for all COMOC members. Himanshu, thanks for giving me suggestions on organic synthesis and other issues. Mahdieh, Roy, Parviz,

Karen, Andreas, Geert, Wafaa, etc. You are very nice persons. It is very lucky for me to meet a group of very interesting Chinese girls and boys. Hui, Yujin, Chunhui, Jiamin, Xinyuan, Yaxu, thank all of you for making me feel at home. I also want to thank my boyfriend, Lei. Thank you for all the days and time I have spent with you, for taking me to travel around Europe, for much help both on my life and research work.

Lastly, I would like to thank my parents and young sister for giving me all your support. Thank you for all the support you have given me in the past years, for listening to my complaints, talking with me more about how to keep in a good health. You are my greatest support in spirit!

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Oct 2021

List of abbreviations

Ln	lanthanide
Ln^{3+}	lanthanide ions
РМО	periodic mesoporous organosilica
PMOs	periodic mesoporous organosilicas
ePMO	ethenylene-bridged PMO
НРМО	hollow periodic mesoporous organosilica
SiO ₂	silica
MOFs	metal organic frameworks
NIR	near-infrared
PA	picolinic acid
UV	ultraviolet
Hacac	acetylacetone
Htfac	1,1,1-trifluoroacetylacetone
Hhfa	hexafluoroacetone
Htta	2-thenoyltrifluoroacetone
Hdbm	dibenzoylmethane
hfa	1,1,1,5,5,5-hexafluoro-2,4-pentanedionate
$S_{0,1}$	singlet
T_1	triplet
ISC	intersystem crossing
ETs	energy transfer from singlet
ET _T	energy transfer from triplet
FRET	Förster resonance energy transfer
MR	multiphonon relaxation
DS	downshifting
QC	quantum cutting
UC	upconversion
PL	photoluminescence
CTAB	cetyltrimethylammonium bromide
SDS	sodium dodecyl sulfate

NPs	nanoparticles		
UCNP	upconversion nanoparticle		
EISA	evaporation induced self assembly		
Ph	phenylene		
PXRD	powder X-ray diffraction		
TEM	transmission electron microscopy		
TEOS	tetraethyl orthosilicate		
TMOS	tetramethyl orthosilicate		
PEO	polyethylene oxide		
PPO	polypropylene		
POM	polyoxometalates		
BTEE	1,2-bis(triethoxysilyl)ethane		
BTSE	1,2-bis(triethoxysilyl)ethene		
TMAPS	N-(trimethoxysilyl)propyl-N,N,N-trimethylammonium chloride		
DPA-Si	N,N-bis(trimethoxysilylpropyl)-2,6-pyridine dicarboxoamide		
PDT	photodynamic therapy		
2D	two-dimensional		
3D	three-dimensional		
DMF	dimethylformamide		
DETA	diethylenetriamine		
DMSO	dimethyl sulfoxide		
DRIFTs	diffuse reflectance infrared Fourier transform spectroscopy		
МСТ	Mercury Cadmium Telluride		
ICP-MS	inductively coupled plasma mass spectrometry		
EDX	energy dispersive X-ray		
HRTEM	high-resolution transmission electron microscopy		
dppz	dipyridyl-pyridazine		
TGA	thermogravimetry		
SEM	scanning electron microscopy		
STEM	scanning transmission electron microscopy		
LOD	limit of detection		
LUMO	lowest unoccupied molecular orbital		
НОМО	highest occupied molecular orbital		

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Outline

This thesis consists of five chapters which divide the thesis into three parts. The first part consists of an introduction which provides a background on lanthanides, luminescence and introduces an overview concerning the synthesis, applications, and other relevant information of lanthanide periodic mesoporous organosilica (PMO) materials, presented in Chapter 1. The second part consists of three chapters and contains the experimental work and their results, as presented in Chapters 2 to 4. In the final part, Chapter 5 provides a summary including the overall conclusions of this work and an outlook given based on the research and work done during this PhD thesis.

In **Chapter 1** a general background is provided, which consists of an overview of lanthanides, lanthanide luminescence and PMOs, presented in the first two sections of this chapter. Also, several approaches for the functionalization of PMOs are summarized. The third section provides the preparation of lanthanide PMOs, followed by a short discussion of two kinds of lanthanide PMOs with different luminescence mechanism: downshifting and upconversion luminescence. It also discusses the applications of lanthanide PMOs, and emphasis is mostly placed upon sensors, which was the main application explored in this thesis. At the end of this chapter, the fundamentals of chemical sensors and the aim of this PhD thesis are presented.

Chapter 2 is the first out of three chapters in which the experimental work and results of this thesis are presented. This chapter presents details concerning the synthesis of three nano-sized PMO materials with different approaches, DPA-PMO, Am-PMO and ePMO. Besides, further functionalization for these PMOs by introducing near-infrared (NIR) emitting lanthanide ions (Nd³⁺ and Yb³⁺) and their corresponding β -diketonate complexes are presented and then the luminescence properties are explored.

Chapter 3 explores the possibility of choosing a less commonly used carboxylic acid, picolinic acid (PA), instead of β -diketonates for introducing the antenna effect in the lanthanide ePMOs shown in **Chapter 2**, however, here the visible-emitting lanthanide ion - Eu³⁺ was used. The main part in this chapter deals with the luminescence

properties of ePMO@Eu_PA and the detailed studies on its sensing properties as an ion sensor as well as a pH sensor.

Chapter 4 describes a novel type of Hg^{2+} sensor and water sensor in alcohols based on unique hybrid materials combining a nano-sized ethylene-bridged PMO material with upconversion NaYF₄: Ln^{3+} nanoparticles grown inside the pores of the PMO.

Chapter 5 summarizes the main findings of this PhD thesis and gives an outlook and suggestions for further research based on the materials and applications that we have studied.

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1.1 Lanthanide luminescence

1.1.1 Lanthanide elements

The lanthanide (Ln) series comprises of a group of elements with atomic numbers from 57 to 71, from lanthanum to lutetium. These 15 metallic chemical elements are lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). The Ln series has a unique position in the periodic table of elements occupying the first period of the f-elements block with general electronic configuration [Xe]4fⁿ5d⁰⁻¹6s², where the 4f orbitals are gradually filled as the atomic number increases (see Table 1.1).

Compared to any other series in the periodic table, such as the alkali metals, the lanthanides exhibit some unique features. Lanthanides are relatively soft metals, and their hardness increases somewhat with high atomic numbers. The densities of elementary Ln vary significantly, from minimum 5.244 g/cm^3 for Eu to maximal 9.841 g/cm³ for Lu. With increasing atomic number, from La to Lu the atomic and ionic radius decrease, which is known as the "lanthanide contraction". The lanthanide contraction is the result of a poor shielding effect of the 4f electrons. The 4f orbitals in the Ln³⁺ ion do not substantially participate in bonding due to the fact that they are shielded by filled 5s and 5p orbitals. Consequently, their spectroscopic and magnetic properties are virtually unaffected by the ligand. Another important feature of the lanthanides is that they are highly electropositive, and their most stable oxidation state is +3, although there are elements which can be reduced to the +2 oxidation state (Sm, Eu and Yb) or be oxidized to the +4 oxidation state (Ce, Tb and Pr) under given conditions. Lanthanides can act as strong Lewis acids which prefer anionic ligands with highly electronegative donor atoms (such as O or F).

	Atom	Ln ³⁺	Ln^{4+}	Ln^{2+}
La	$[Xe] 5d^{1}6s^{2}$	[Xe]		
Ce	$[Xe] 4f^15d^16s^2$	[Xe] 4f ¹	[Xe]	
Pr	$[Xe] 4f^36s^2$	[Xe] 4f ²	[Xe] 4f ¹	
Nd	$[Xe] 4f^46s^2$	[Xe] 4f ³	[Xe] 4f ²	[Xe] 4f ⁴
Pm	$[Xe] 4f^{5}6s^{2}$	[Xe] 4f ⁴		
Sm	$[Xe] 4f^{6}6s^{2}$	[Xe] 4f ⁵		[Xe] 4f ⁶
Eu	$[Xe] 4f^{7}6s^{2}$	[Xe] 4f ⁶		[Xe] 4f ⁷
Gd	$[Xe] 4f^{7}5d^{1}6s^{2}$	[Xe] 4f ⁷		
Tb	$[Xe] 4f^96s^2$	[Xe] 4f ⁸	[Xe] 4f ⁷	
Dy	$[Xe] 4f^{10}6s^2$	[Xe] 4f ⁹	[Xe] 4f ⁸	[Xe] 4f ¹⁰
Но	$[Xe] 4f^{11}6s^2$	$[Xe] 4f^{10}$		
Er	$[Xe] 4f^{12}6s^2$	[Xe] 4f ¹¹		
Tm	$[Xe] 4f^{13}6s^2$	[Xe] 4f ¹²		[Xe] 4f ¹³
Yb	$[Xe] 4f^{14}6s^2$	[Xe] 4f ¹³		$[Xe] 4f^{14}$
Lu	$[Xe] 4f^{14}5d^{1}6s^{2}$	$[Xe] 4f^{14}$		

Table 1.1 Electron configurations of the lanthanides and their common ions.¹

1.1.2 Lanthanide photoluminescence



Figure 1.1 Energy level diagrams of trivalent Ln^{3+} ions. Corresponding typical upconversion emissive excited levels are highlighted with red bold lines.²

The photoluminescence of trivalent lanthanide ions (Ln^{3+}) originates from the electrons in the 4f orbitals which are shielded by the filled 5s and 5p "outer" orbitals,

resulting that the Ln³⁺ are weakly affected by the chemical surroundings, for example the external electromagnetic fields. Benefiting from the abundant energy levels of 4f configurations, trivalent lanthanide ions are endowed with unique and fascinating optical properties. As shown in Figure 1.1, these 4f-4f transitions of Ln³⁺ are easily predictable and very narrow covering a range from the ultraviolet (UV) to near-infrared (NIR). Although most lanthanide ions are luminescent (with the exception of La³⁺ and Lu^{3+}), some are more emissive than others, and thus not equally useful or commonly applied. The emissive properties of a lanthanide ion are governed by the facility with which its excited state(s) can be populated and the non-radiative de-activation paths minimized. The quantum yield of the luminescent lanthanide ion Q_{Ln}^{Ln} substantially depends on the energy gap (ΔE) between the emitting level of the lanthanide ion and the highest (accepting) sublevel of the ground state manifold. The smaller the energy gap is, the easier de-excitation will happen via non-radiative processes, for instance through vibrations of bound ligands, especially high energy vibrations such as O-H. Considering the energy gap requirement, it is obvious that Eu^{3+} , Gd^{3+} , and Tb^{3+} are the 'best' ions. The most commonly used lanthanide ions Eu³⁺ and Tb³⁺ have the strongest luminescence and particularly long lifetimes in the visible wavelengths.³ The usefulness of Gd³⁺ as luminescence probe for bioanalyses is limited as it emits in the UV region. On the other hand, Gd³⁺ can act as an efficient sensitizer for downconversion luminescence, and a good additional dopant in fluoride nanoparticles. Dy^{3+} and Sm^{3+} also have found many applications, but their use has been limited because of their inferior luminescence quantum yields and shorter lifetimes.⁴ The visible emitting lanthanides, such as Tm³⁺, Dy³⁺ and Sm³⁺ can find their applications in laser output, white LEDs and sensors. The NIR emitting lanthanides (Nd³⁺, Er³⁺, and Yb³⁺) are quiet widely used for biological applications, including bioimaging, therapy, and biosensing.⁵ Tm^{3+} , Dy^{3+} , Er^{3+} , and Ho^{3+} ions are dominant in the photon upconversion phenomenon.

Due to the parity-forbidden nature by Laporte's rule, these f-f transitions of Ln^{3+} have low absorption coefficients (typically less than 10 L mol⁻¹cm⁻¹) and relatively long luminescence lifetimes (up to several milliseconds). Consequently, the emission

intensity is typically also low when direct excitation happens into the 4f excited states. It could only be enhanced by using high power light excitation sources such as lasers, until a new way was proposed to overcome this drawback in 1942 by Weissman.⁶ This is known as the "antenna effect" for sensitizing Ln³⁺ emission.

In general, the Ln^{3+} can be coordinated with an organic ligand or matrix which functions as an "antenna" and possesses good "light harvesting" properties. This can allow indirect excitation of the lanthanide ions by exciting the ligand's ground level electrons to higher levels, followed by energy transfer to the lanthanide ions. For the visible emitting Ln^{3+} , the choice of antenna ligand is restricted to UV absorbing chromophores, while for the NIR emitting Ln^{3+} this requires antenna ligands which have singlet and triplet energies closely matching the Ln^{3+} accepting levels. The most popular organic ligands as antenna ligands that are in use for coordination to Ln^{3+} include β -diketones, dipicolinic acid and its derivates, macrocyclic ligands, etc. The well-known β -diketones consist of ligands such as: acetylacetone (Hacac), 1,1,1trifluoroacetylacetone (Htfac), hexafluoroacetone (Hhfa), 2-thenoyltrifluoroacetone (Htta), dibenzoylmethane (Hdbm), etc.

In a typical sensitization process (Figure 1.2), the organic ligand is effectively excited from the ground state (S₀) to a singlet excited state (S₁) by absorbing photon energies. Subsequently, the ligand relaxes to the triplet excited state (T₁) through intersystem crossing (ISC), followed by excitation energy transfer to the lanthanide ion. In some cases, a direct energy transfer from singlet excited state of the ligand to the lanthanide ions has also been observed. The singlet excited state is short lived, and this process is therefore much less probable than ISC, radiative or non-radiative decay. The triplet energy transfer is dominant during the sensitization process since the energy transfer via the singlet state is not fast enough to compete with ISC or fluorescence. The quantum yield of the overall process, which is related to the ratio of radiative and nonradiative relaxation (deactivation) processes of the excited energy levels, depends on the efficiency of these individual steps: the intersystem crossing efficiency (η_{ISC}), the energy transfer efficiency (η_{ET}), and the lanthanide luminescence quantum yield (ϕ_{Ln}). The quantum yield is also related to the extent of the energy gap between the lowest excited energy level of the ion (called the emissive or radiative energy level) and the highest sublevel of its ground state multiplet.⁷

The reasons why ligand-to-metal energy transfer from the triplet states is favored is because of the pronounced spin-orbit coupling induced by the heavy and paramagnetic lanthanide ions. This heavy atom effect promotes the ISC mechanism on the ligand. The ligand's triplet excited state is then populated and undergoes intermolecular energy transfer to a Ln^{3+} excited state rather than relaxation through phosphorescence or nonradiative thermal decay.

Ligand-to-metal energy transfer depends on the distance as well as on the energy overlap between the sensitizer and the lanthanide ion. For efficient energy transfer to a Ln^{3+} ion from the triplet state of the ligand, the energy of the triplet state must be closely matched to or slightly above, the Ln^{3+} accepting levels, but not so close that the energy back transfer competes effectively with Ln^{3+} emission. Typically, an energy gap (between the ligand's triplet state and the excited states of lanthanide ion) of at least 1500 cm⁻¹ should be recommended to prevent this detrimental phenomenon, but ideally an energy difference of around 2500-3500 cm⁻¹ is aimed for to avoid this energy back transfer.



Figure 1.2 Simplified Jablonski diagram illustrating the pathway for sensitization of the luminescence in lanthanide ions. S_0 : singlet ground state; S_1 : singlet excited state; T_1 : triplet excited state; ISC: intersystem crossing; ET_S: energy transfer from singlet; ET_T: energy transfer from triplet.

The ligand-to-metal energy transfer can be described by two main types of lanthanide sensitization mechanisms (Figure 1.3): Förster resonance energy transfer (FRET), and Dexter energy transfer (electron exchange mechanism). Förster resonance energy transfer is a through-space mechanism based on a Coulombic dipole-dipole interaction between the ligand (donor) and the Ln^{3+} (acceptor) and works in a relatively long donor-acceptor distance (r, 1-10 nm) with a $1/r^6$ dependence.⁸ Whereas Dexter energy transfer is based on electron exchange and thus only works in the close proximity (<1 nm), as its distance dependence is e^{-r} .⁹ In addition, both FRET and Dexter energy transfer mechanisms require an effective spectral overlap of the emission spectrum of the ligand with the absorption spectrum of the Ln^{3+} .



Figure 1.3 Schematic illustrations of (a) Förster resonance energy transfer and (b) Dexter energy transfer process. D and A denote the donor and acceptor. * represents an excited state.¹⁰

There exist several non-radiative deactivation processes which exist and can influence and limit the emission quantum yield and lifetime of the lanthanide complexes regardless of how efficient the sensitization process through the antenna ligand is. The non-radiative deactivation process is usually predominated by the multiphonon relaxation (MR) from the excited state of lanthanides to the overtones of molecular vibrations in the vicinity of metal center, either in the ligands bound or in the surrounding medium.¹¹ The best candidates for MR are high-energy and highly

anharmonic oscillators, such as local-mode X-H (X = O, N, C) or C=O stretching vibrations.¹² The vibrational transition probability is inversely proportional to the vibrational quantum number v (Franck–Condon theory), therefore quenching via vibrational excitation drastically decreases for superior harmonics of deactivating oscillators. The NIR-emitting lanthanide ions (generally being Nd³⁺, Yb³⁺ and Er³⁺) have energy gaps corresponding to their radiative (f-f) transitions that match well with the energy of the vibrational overtones of O-H and C-H groups (with vibrational quanta v = 2 and v = 3). These then act as efficient quenchers via vibrational excitation.¹³ Taking Yb³⁺ as an example, the excited and ground state of Yb³⁺ can be bridged by the third C-H overtone and second O-H overtone in the molecules or solvents, while it requires higher overtones of C-D, O-D and C-F vibration (Figure 1.4).¹⁴ The higher overtone that the relaxation requires, the less the quenching effect is. Undoubtedly, water molecules are the most powerful quenchers for NIR luminescence, especially in the case of Er³⁺ emission at 1500 nm, since the first overtone of the H-O-H vibration falls around 1420 nm.



Figure 1.4 Schematic representation of the Yb³⁺ electronic levels and vibrational overtones of C-H, O-H, C-D, O-D and C-F bonds.

Three typical energy transfer modes of Ln³⁺ are shown in Figure 1.5, namely downshifting (DS), quantum cutting (QC) and upconversion (UC) emissions.¹⁵ DS is the normal photoluminescence (PL) process (Stokes process), in which one absorbed high-energy photon is converted to one low-energy photon and so its quantum

efficiency does not exceed 100%.¹⁶ QC (also known as downconversion, DC) is a process that can transform the energy of one absorbed photon into two (or more) lowerenergy photons, with a quantum efficiency of more than 100% (up to 200%). It can be realized in single lanthanide ions, particularly in Pr³⁺ and Gd³⁺, as well as between different sets of Ln^{3+} through an energy transfer process. The most effective energy transfer was observed for Gd^{3+} (of the host matrix) to different Ln^{3+} , such as Eu^{3+} , Tb^{3+} , Er³⁺, etc.¹⁷ UC is the process that two (or more) photons (mostly infrared photons) are converted into one photon (in visible/UV), with a quantum efficiency much less than 50%.¹⁸ Low photon frequency hosts are necessary for avoiding the non-radiative losses in this process. Er^{3+} , Ho^{3+} and Tm^{3+} are generally chosen as activators to give rise to efficient visible emissions under low pump power densities, due to their ladder-like energy levels.¹⁹ Additionally, the Yb³⁺ ion is usually co-doped as excellent sensitizer because of its relatively large absorption cross-section at a range of 900-1100 nm, corresponding to the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition.²⁰ Doping concentrations of 18-25% for Yb^{3+} sensitizers and 0.3%-2% for Tm^{3+} and Er^{3+} activators have been commonly used to generate brighter emissions.²¹ Figure 1.6 shows typical downshifting luminescence of Eu^{3+} emission; quantum cutting luminescence of $Pr^{3+}-Yb^{3+}$ emission (a single UVvis photon absorbed by Pr^{3+} is thereby converted into two ~1000 nm photons of Yb^{3+}); and upconversion luminescence of Yb³⁺-Er³⁺ emission excited by a 980 nm NIR laser.



Figure 1.5 Schematic illustrating three energy transfer modes of Ln^{3+} . From left to right, these are downshifting (DS), quantum cutting (QC), and upconversion (UC). Upward and downward full arrows stand for photon excitation and emission processes, respectively. The dashed line represents a non-radiative relaxation process.²



Figure 1.6 Typical schematic energy level diagram of Ln^{3+} assemblies (Eu^{3+} , $Pr^{3+}-Yb^{3+}$ and $Yb^{3+}-Er^{3+}$) of the downshifting, quantum cutting and upconversion luminescence mechanism.²²⁻²⁴

1.2 Periodic Mesoporous Organosilicas (PMOs)

The development of nanoporous materials is currently an area of extensive research with countless researchers involved worldwide. Two types of hybrid materials, combining organic and inorganic properties in one material, were proposed during the last decades and are considered as important subjects in this field. The first class is Metal Organic Frameworks (MOFs), which consists of metal ions (clusters) connected with organic linkers. The most well-known representative of this class is MOF-5, first reported by Yaghi.²⁵ This report attracted more attention and opened a new chapter for the development of MOFs. Subsequently, a series of famous MOFs were synthesized and employed in a very broad area of applications such as catalysis, drug delivery, small molecules sensing, and gas adsorption and separation.^{26, 27}

Kresge *et al.* first synthesized surfactant-templated mesoporous silicas in 1992 and since then much attention has been paid to develop their synthesis and applications.²⁸ In 1998, large-pore mesoporous silica was reported by Zhao *et al.* at the University of California, Santa Barbara and thus the material was named Santa Barbara Amorphous type 15 material (SBA-15).²⁹ The organic functional groups can be introduced on silica materials by two major synthesis routes namely grafting or co-condensation.³⁰ Later, a third method to prepare ordered mesoporous hybrid materials with organic functionalities was proposed in 1999 by three independent research groups, namely Stein *et al.*,³¹ Inagaki *et al.*,³² and Ozin *et al.*³³ and the resulting materials are called

Periodic Mesoporous Organosilicas (PMOs).

As the second class of hybrid nanomaterials, PMOs have some unique features: highloading of organic content, chemically reactive sites, and homogeneous distribution of functional groups.³⁴ PMOs represent an exciting new class of organic-inorganic hybrid nanomaterials with high surface area and large uniform mesopores and have made advances in the development of many fields such as catalysis, adsorption, separation, optic, electronic, sensor, and biological applications.^{35, 36}

According to the most restricted definition, PMOs are materials which are 100% made from a certain PMO precursor. Moreover, a mixed PMO-type material exists, where a simple, non-bulky PMO precursor is used as a diluting agent for a bulky precursor. This enables obtaining ordered materials despite the use of bulky precursors (only at a low percentage).³⁷ Such materials are considered in the text of this thesis also as PMO materials and do not follow the very strict definition of PMOs.

1.2.1 Fundamentals of PMO synthesis

PMOs are prepared by the sol-gel process involving the hydrolysis of a bis-silane and subsequent polycondensation in the presence of a surfactant template. Figure 1.7 shows a schematic overview of a general synthesis procedure with the triblock copolymer $PEO_{20}PPO_{70}PEO_{20}$ (Pluronic P123) as a template and a bis-silane. The bissilane is represented by (OR')₃ Si-R-Si (OR')₃, where OR' is a hydrolysable alkoxy group (e.g., OC_2H_5) and R is a non-hydrolysable organic functional linker (e.g., ethylene and phenylene). The template will aggregate to form micelles around which the bis-silane will polycondense in the aqueous environment, either in acidic (H⁺) or basic (OH⁻) conditions. In this process, ionic surfactants or amphiphilic block polymers are mainly used as the templates. After a certain aging period, the surfactant is removed by solvent extraction or calcination under inert atmosphere, and a highly porous PMO material remains. The pore diameters can be tuned within the range of 1.5-30 nm by the appropriate selection of surfactants.³⁸



Figure 1.7 Schematic representation of the synthesis of a PMO.³⁹

In addition, a range of conditions, such as the reaction temperature and time, pH, cosolvent, auxiliary substances and the optimized reactant ratio, need to be considered for the synthesis of PMOs.⁴⁰ The reaction temperature can influence the pore size of the PMO. The pH of the reaction mixture will determine the specific interaction between the surfactant and the organosilane precursor. The addition of inorganic salts have shown to potentially lead to highly ordered materials in a wide range of acidic concentrations, such as NaCl, KCl, Na₂SO₄ and K₂SO₄.⁴¹ It especially improves the interaction between the surfactant and the hydrolyzed organosilane precursor that are formed during the hydrolysis and condensation.

The differences of the structure and synthetic pathways between PMOs and other organosilica materials are shown in Figure 1.8.⁴² In general, the undoubted advantage of porous materials is their particularly high surface area that allows for a high degree of functionalization. Obviously, PMOs are the most promising materials with high surface area, structure ordering and plenty of organic moieties for post-modification (such as lanthanides grafting). The pores of the PMO can allow ions or small molecules

to pass through, expanding its range of applications, such as sensing and drug delivery applications.



Figure 1.8 Structures and synthetic pathways of various organosilica nanocomposites: mesoporous organosilica NPs (A and B), non-porous organosilica NPs (C and D), periodic mesoporous organosilica NPs (E and F), and non-porous silsesquioxane NPs (G and H). CTAB: cetyltrimethylammonium bromide; NPs: nanoparticles. *Not sensu stricto but generally with a disorganized low micro or mesoporosity.⁴²

A variety of organosilanes and surfactants exists and can be used in different conditions (acidic, basic or neutral) to create different PMO materials with proposed functionalities, pore structures and morphologies. The functional organic groups of a PMO are homogeneously distributed, not only on the surface of the material, but also inside the pore walls. These organic bridges can be very simple (such as a methylene, ethylene and phenylene function) or very complex bridges involving hetero-atoms or chiral, metal complexes. Thus, a large amount of PMO materials can be obtained with specific properties originating from the used organic bridge, which enlarges the applicability of PMOs to very different fields. For example, PMO materials with chiral bridges have already been developed for high-technology applications, such as chiral chromatography, chiral separation and asymmetric catalysis.⁴³

By changing the molar ratios in the initial synthesis mixture, as well as the particular surfactants and additives used and synthesis temperature, the pore structures of the asmade PMO particles with two-dimensional hexagonal (*P6mm*), three-dimensional hexagonal (*P63/mmc*), and cubic (*Pm3n, Ia3d, Fm3m*) symmetries have been obtained.^{44, 45} PMOs with worm-like structures have also been produced from a 100% bridged organosilane precursor having relatively large organic groups.⁴⁶

In general, the particulate and macroscopic morphologies of PMO materials can be powders or films, intended for specific applications, ranging from use as adsorbents and catalysts to optical materials. Typically, powder samples are obtained by precipitation from an aqueous solution. Thin films can be prepared by sol-gel polycondensation on solid substrates in the presence of a large excess of volatile organic solvents, via the *Evaporation Induced Self Assembly* (EISA) process.⁴⁷ Additionally, the PMO powder samples have been reported with a wide variety of morphologies (Figure 1.9), such as spheres,⁴³ dodecahedra,⁴⁸ cubes,⁴⁹ rope, gyroid,⁵⁰ crystal-like,⁵¹ rods,⁵² hollow nanoparticles and nanorattles.⁵³ The sizes of the PMO nanoparticles can also be influenced through the control of hydrolysis and polycondensation steps by varying the synthesis conditions.

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Figure 1.9 PMO materials with a range of morphologies (spheres, dodecahedra, cubes, rope, gyroid, crystal-like, rods, hollow nanoparticles and nanorattles, from top to bottom, left to right.)

A remarkable feature of PMOs synthesized from a single precursor is the introduction of the molecular-scale periodicity in the framework. Mesoporous organosilicas functionalized with organic groups usually consist of amorphous frameworks. In contrast, the frameworks of PMOs with specific bridged groups can form "crystal-like" layered structures with molecular-scale periodicity as shown in Figure 1.10. PMOs have a crystal-like framework with repeating units of alternating organic silica layers (5.6– 11.9 Å depending on the organic bridges). The first report of PMOs with crystal-like frameworks was made for a 1,4-phenylene (Ph)-bridged PMO in 2002 by Inagaki *et al.*⁵⁴ Molecular-scale periodicity was confirmed by both powder X-ray diffraction (XRD) and transmission electron microscopy (TEM), showing the existence of a periodicity of 7.6 Å on the molecular scale. Aromatic-bridged PMOs with crystal-like frameworks can allow tuning of the interactions between the aromatic organic groups and introducing special optical and electrical properties within the pore walls, which may enable new material design peculiar to PMOs.



Figure 1.10 Schematic illustration of amorphous and crystal-like frameworks of PMO and TEM image of Nph-bridged PMO with a crystal-like framework.³⁸

1.2.2 PMO precursors and surfactants

In PMOs, the presence of dense, homogenously distributed organic bridges (R) within the framework is of great importance. In early research, these moieties were limited to relatively simple aliphatic (such as methylene, ethylene)^{55, 56} and rigid (phenylene, thiophenylene) bridging groups.⁵⁷⁻⁵⁹ Organic bridges in the PMO framework were then extended to large heterocyclic ^{60, 61} as well as bifunctional organic groups combining the characteristics of "rigid" phenylene and "short flexible" methylene bridges.⁶² The organosilane precursors have now even been expanded to include several hydrocarbon-bridged trialkoxysilane.⁶³ Therefore, the development of PMOs is followed up by the expanding of bridged organosilane precursors.

An overview of the structures of the organosilane precursors, which have been successfully used to create PMOs, is presented in Scheme 1.1. It is worth noting that some organosilane precursors with long and flexible functionalities containing hetero atoms such as nitrogen or sulfur are difficult to assemble in rigid PMOs.⁴⁴ In these cases, a small bis-silane (such as 1,2-bis(triethoxysilyl)ethane), tetraethyl orthosilicate (TEOS)

or tetramethyl orthosilicate (TMOS) are added to increase the rigidity of the walls.

In general, the mesostructured of PMOs will collapse when the molar ratios of monosilanes in the reaction mixture exceed 40 mol%.⁶⁴ The highest loading of monosilylated moieties in the final products are of about 30 mol%. These observations could be ascribed to the fact that increasing the amounts of monosilanes leads to an increase of homo-condensation reactions instead of cross-linking reactions with the bridged organosilane precursors. Furthermore, the terminal organic groups protruding into the pore channels cause negative effects on the mesostructural order and porosity properties. We do not consider hybrid materials synthesized only by monosilanes because the utilization of bis- or multi-silanes is a prerequisite for PMOs.

Furthermore, a variety of surfactants can act as a template in the synthesis of mesoporous materials. Table 1.2 provides an overview of the most used surfactants together with their chemical structure. They can roughly be divided into two types, ionic and nonionic surfactants. The ionic surfactants form micelles in water through a hydrophilic head group consisting of a cationic or anionic moiety, e.g., cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) respectively, combined with a lipophilic tail, typically a long aliphatic group. A nonionic surfactant is generally comprised of a block co-polymer in which one part is more hydrophilic than the other e.g., Pluronic-type surfactants with hydrophilic polyethylene oxide (PEO) moieties spaced by a hydrophobic polypropylene block (PPO).

A: Monosilanes as precursor







Scheme 1.1 Limited overview of organosilane precursors used in the synthesis of PMOs.^{44, 64}

Table 1.2 Limited overview of the most common surfactants used for the synthesis of PMOs.⁴⁴





1.2.3 Functionalization of PMOs

In the pioneering study of PMOs, one organosilane was employed to obtain the materials in which only one kind of organic bridge exists within the framework. In later studies, two or more organosilane precursors were used to obtain PMOs with multifunctionalities. Generally, there are three different approaches for introducing additional functionalities to PMOs: (1) the subsequent modification of the pore surface of a PMO material ("grafting"), (2) the simultaneous condensation of different organosilane precursors ("co-condensation"), (3) the direct chemical modification of organic bridges within the framework.
1.2.3.1 Post synthetic functionalization of PMOs ("grafting")

Grafting refers to the subsequent modification of the pore surface of PMOs with organic groups, such as monosilanes of the type R'-Si(OR)₃. This modification is usually made by grafting an organosilane to free silanol groups of the PMO material (Figure 1.11). In principle, functionalization with a variety of organic groups can be realized in this way by the variation of the organic moiety R'. The mesostructure of the start PMO is usually retained, whereas a reduction in the porosity of the final PMO material can be observed (although depending upon the size of the organic residue and the degree of occupation). Another disadvantage is the fact, that this technique tends to give a nonhomogeneous distribution of organic groups and even pore blockage. If the monosilanes react preferentially at the pore openings during the initial stages of the synthesis process, the diffusion of further molecules into the center of the pores can be hampered, resulting in a nonhomogeneous distribution of the organic moiety R' and a lower degree of occupation. In some extreme cases, for example, where R' is a very bulky organic residue, this can lead to a complete closure of the pores (pore blockage).



Figure 1.11 Grafting for organic modification of PMOs with monosilanes of the type R'-Si(Oet)₃.⁶⁵

1.2.3.2 Co-Condensation (direct synthesis)

An alternative method for introduction of additional functionalities into PMOs is the co-condensation method (also called one-pot synthesis). This technique is used to produce multifunctional PMO materials by simultaneous introduction of multifunctional organosilanes with different functional moieties at various ratios. Usually two pathways are considered (Figure 1.12): (1) bridged organosilane and monosilane, (2) more than two different bridged organosilanes. Since the organic functionalities are structural components of the PMO framework, this approach gives a more homogenous distribution of the organic groups, without pore blockage. Also,

these organic functionalities can impart unique physical characteristics on the framework. However, the co-condensation method also has some disadvantages: the mesoscopic order of the PMOs decreases with the increasing of the concentration of the monosilane precursor. There is a limited amount of introducing bulky large organosilane, otherwise, the structural order will be diminished. Furthermore, the accessibility of the functional groups is undetermined and a network former (such as tetraethoxysilane or bis(triethoxysilyl)ethane) is needed to maintain structural integrity. As indicated in Figure 1.12, the organic functional groups can be incorporated into the pore channels of PMOs as well as their wall framework.



Figure 1.12 Co-condensation for the introduction of organic groups into a PMO.⁶⁵

1.2.3.3 Chemical modification of organic bridges

In addition to post synthetic surface modification using silanol groups, the postmodification of the organic bridges within the framework is a versatile approach to further functionalize PMOs. The PMOs with aromatic or unsaturated organic bridges, such as phenylene and ethenylene, can react with a variety of reagents to produce novel functionalized PMOs.

The most common unsaturated organic bridge in PMO materials is -C=C-. A wide variety of organic reactions can be performed to convert the double bond on the surface to a more appropriate functionality. These reactions include bromination,⁶⁶ epoxidation,⁶⁷ ozonolysis of the double bond,⁶⁸ Diels-Alder reaction,⁶⁹ Friedel-Crafts reaction,⁷⁰ and thiol-ene click reaction.⁷¹ A schematic overview of the functionalization possibilities is depicted in Figure 1.13. The bromination of the C=C is very

straightforward and performed with gaseous bromine or bromine dissolved in a chlorinated solvent (e.g., dichloromethane). This reaction must be carried out with extreme care because of the harmfulness of the irritating bromine and the volatile solvents. Generally, bromination with gaseous bromine results in a higher yield than dissolved bromine in dichloromethane. Subsequently the bromine groups in PMOs can be substituted by various useful organic groups via a nucleophilic substitution reaction. In the case of ethenylene-bridged PMOs, the Diels-Alder reaction between the ethenylene bridge and benzocyclobutene gives a new functionality incorporated in the PMO material. The resulting PMO material can be subsequently sulfonated with concentrated sulfuric acid to give sulfonic acid groups on the pore surface (Figure 1.13 (d)).⁷² A very interesting post synthetic modification on ethenylene-bridged PMO is thiol-ene click reaction using cysteamine or cysteine to introduce a thioether linkage (Figure 1.13 (f)).⁷¹

PMOs with aromatic bridges have also been functionalized. For example, a phenylene-bridged PMO was sulfonated to obtain an acidic PMO with benzenesulfonic acid groups.⁷³ Moreover, amine groups can also be introduced to phenylene-bridged PMOs through a nitration of the benzene moiety followed by a reduction of the nitro groups.⁷⁴



Figure 1.13 Reaction pathways to post-functionalize the unsaturated bridges.

1.2.4 Reaching the nanoscale

Although a wide variety of bulk PMO materials has been reported, reaching the nanoscale for such materials is much less investigated due to the ongoing challenge to control the morphology, porosity, and organization of silsesquioxane materials. In most cases, bridged organosilane had to be diluted with a silica precursor to maintain satisfying porosities and reach the controlled nano sizes.⁷⁵⁻⁷⁷ The drawback of this strategy is a sharp decrease of the organic content in the nano PMOs which directly impairs the properties of materials.

Despites these challenges, PMO nanoparticles (NPs) are rapidly emerging as the next

generation of mesoporous functional organosilica nanomaterials. Pioneering works in drug delivery, catalysis, sensing and separation have demonstrated the superior properties of PMO NPs when compared to organosilica analogues.^{49, 76, 78-81} One of the key requirement of PMO NPs as sensors is the control of their particle size, which affects their colloidal stability and dispersity. The control of particle size is mainly governed by the employed synthesis method and specific experimental parameters. Generally, there are two synthetic pathways for the synthesis of nano PMOs, soft templating method and hard templating method.

The morphologies of PMO nanoparticles include spherical nanoparticles, nanorods, nanofibers, nanotubes, metal or metal oxide core PMO shell nanoparticles, etc. In this section, spherical PMO nanoparticles are discussed more in detail.

1.2.4.1 Soft templating method

The first nano PMO materials were reported with a hollow spherical morphology in 2006.⁸² Ethylene-bridged hollow PMO nanoparticles (HPMO NPs) were prepared from 1,2-bis(trimethoxysilyl)ethane by using co-structure directing agents, FC-4 and CTAB, with a sodium hydroxide catalyzed sol-gel reaction. The size of this PMO nanomaterials ranges from 100 to 400 nm in diameter. Moreover, by varying the ratio of FC-4/CTAB the shell thickness of the hollow PMO could be tuned. Later, in 2012, monodisperse methylene-, ethenylene-, and phenylene-bridged PMO nanoparticles with highly ordered pore structures were reported using CTAB as a template and ammonia as a catalyst, with nanoparticle diameters of 100 to 200 nm (Figure 1.14).⁸³

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Figure 1.14 TEM images of ethylene- (a, b), *methylene-* (c, d), *ethenylene-* (e, f), and phenylenebridged PMO NPs (g, h) at low and high magnification.⁸³

1.2.4.2 Hard templating method

As an alternative to the soft templates, the use of hard templates such as silica or metal oxide has emerged. The synthesis of these nanoparticles with controlled sizes and nanostructures (hollow and rattle-like) is well mastered. Furthermore, the differential reactivity towards acids or bases allows etching the core template without degrading the PMO shell.

A silica sphere template is commonly employed due to its easy preparation by the Stöber method or using reverse microemulsions, with a narrow size distribution.⁸⁴ Typically, dense silica spheres are first prepared, and the PMO shells are grown on them. Finally, the silica core is partially or fully etched by the aqueous Na₂CO₃ or NaOH solution to obtain PMO nanorattles or hollow PMO NPs, respectively (Figure 1.15). This method was first proposed in 2010 for the formation of core-shell nano PMOs with silica cores of 400 nm in diameter, surrounded by thick phenylene-bridged PMO shells (75 nm).⁸⁵ Interestingly, a shrinkage or partial dissolution of the silica core was observed when increasing the temperature of the shell synthesis from 25 to 100 °C, which led to nanorattles or yolk-shell NPs.



Figure 1.15 (a) Schematic representation of the silica spheres hard templating strategy for the design of HPMO NPs. TEM images of SiO₂@HPMO NPs before etching (b), SiO₂@HPMO nanorattles after partial etching (c), and HPMO NPs after complete etching (d).³⁶

To compare the two approaches, the soft templating method is simpler and faster since it does not require the preparation and removal of a hard template. HPMO NPs can be designed employing both soft and hard templating methods. However, hard templating method often provides more monodisperse and controlled NPs. Hard templating method enables the preparation of silica@HPMO nanorattles, as well as the presence of metal and metal oxide NPs within HPMO NPs, which is of particular interest for catalysis.³⁶

1.3 Luminescent lanthanide PMOs

1.3.1 Synthesis of lanthanide PMOs

In general, there are two synthesis procedures for introducing lanthanides into PMOs. The one-pot synthesis employing a lanthanide complex and organosilane in the presence of a surfactant made all lanthanide complexes integrate into the organosilica framework or onto the surface of the pore walls.⁸⁶ On the other hand, post-synthesis impregnation can be used to coordinate lanthanides to the functional organic moiety of the hybrid mesoporous materials affording stable lanthanide-modified luminescent

materials that retain the ordered mesostructure and shape of the pristine PMO material. The lanthanide ions or organic complexes can be covalently grafted into the framework of PMOs in a post-functionalization synthesis procedure, shown in Figure 1.16.⁸⁷ Besides, the lanthanide inorganic complexes (e.g., polyoxometalates) can be incorporated within the porous channels of PMOs, as shown in Figure 1.17.⁸⁸ The amine-functionalized BPMOs are able to promote a stronger electrostatic binding of the anionic lanthanide -containing polyoxometalates (LnPOM) to the support resulting in a more efficient anchoring and minimizing leaching issues. In addition, a completely different approach, "ship-in-a-bottle" approach, was proposed to construct hollow PMOs with lanthanide nanoparticles built inside the PMOs (Figure 1.18).⁸⁹



Figure 1.16 Schematic overview of the synthetic pathway to the Dpdp-ePMO and predicted structure of the resulting organic-inorganic luminescent hybrid mesoporous materials grafted with europium ions or complexes.⁸⁷



Figure 1.17 Schematic overview of the synthetic pathway to the ethylene-bridged TMAPSfunctionalized BPMOs and to the corresponding $[Eu(W_5O_{18})_2]^{9-}$ polyoxometalate (POM) incorporated EuPOM@BPMO composite.(BTEE: 1,2-bis(triethoxysilyl)ethane; TMAPS: N-(trimethoxysilyl)propyl-N,N,N-trimethylammonium chloride)⁸⁸



Figure 1.18 (a) Schematic illustration of the "ship-in-a-bottle" approach for the synthesis of UC nanorattles. TEM images of (b) HPMO and (c) HPMO-UCNP⁸⁹

1.3.2 Downshifting luminescent lanthanide PMOs

Downshifting luminescence means the transformation from higher energy light to lower energy light.⁹⁰ Here, we mainly focus on the lanthanide PMOs that produce visible or near infrared (NIR) emission via one photon processes. As promising downshifting luminescent materials, lanthanide PMOs not only show the extraordinary luminescence properties of the lanthanide ions but also exhibit the unique properties of

PMOs, such as large surface area, high porosity, easy modification to the organic moiety, which gives lanthanide PMOs great advantages in sensing, lighting, telecommunications, displays and bioimaging. By changing the organic ligands and replacing the lanthanide ions, various lanthanide PMOs can be obtained to detect different analytes (such as heavy metal ions, anions, organic solvents).

The commonly reported lanthanide ions in PMOs are Eu³⁺, Tb³⁺ for visible emission, and Nd³⁺, Yb³⁺, Er³⁺ for NIR emission. The visible emitting lanthanide PMOs can produce visible light, such as red, green and yellow, which can be observed by the naked eyes. The luminescence color of lanthanide PMOs depends not only on the lanthanide ion, but also on the PMO matrix. For NIR emitting lanthanide PMOs, NIR light is generally invisible to human's eyes. Anwander *et al.* reported a nano-sized PMO obtained via co-condensation of N,N-bis(trimethoxysilylpropyl)-2,6-pyridine dicarboxoamide (DPA-Si) with TEOS (DPA-PMO).⁸⁶ This PMO showed spherical particles with a size of around 70 nm in diameter. Furthermore, in this work three different lanthanide PMOs were obtained by grafting with Eu³⁺, Tb³⁺, Eu³⁺-Tb³⁺. These lanthanide PMO materials exhibited the characteristic red (Eu-PMO), green (Tb-PMO) and yellow (Eu,Tb-PMO) emission in water suspensions under UV irradiation (Figure 1.19).



Figure 1.19 Emission spectra of (a) Eu-grafted DPA-PMO, (b) Tb-grafted DPA-PMO and (c) Eu/Tb-grafted DPA-PMO. Images of the three samples under sunlight (d) and under a UV lamp (e).⁸⁶

In 2012, a near infrared emitting lanthanide PMO material was reported, $Ln(dbm)_3bpd$ -PMO.⁹¹ After grafting of Nd(dbm)₃, Yb(dbm)₃ and Er(dbm)₃ complexes onto the PMO, upon excitation with visible light, the hybrid materials showed the characteristic emission peaks for these lanthanides (shown in Figure 1.20). In addition, the luminescence decay times were calculated to be 0.095 µs for the Nd(dbm)₃bpd-PMO, 5.97 µs for the Yb(dbm)₃bpd-PMO and 2.37 µs for the Er(dbm)₃bpd-PMO. These good NIR-luminescence properties of the Ln(dbm)₃bpd-PMO with the visible-light excitation showed a new possibility to use these materials in the NIR optical field.



Figure 1.20 (a) Schematic illustration of the $Ln(dbm)_3bpd$ -PMO; normalized excitation and emission spectra of (b) Yb^{3+} , (c) Nd^{3+} and (d) Er^{3+} complexes grafted bpd-PMOs.⁹¹

1.3.3 Upconversion luminescent lanthanide PMOs

The upconversion phenomenon was first studied by Bloembergen using an infrared quantum counter device capable of detecting and counting infrared photons in 1959.⁹² Photon UC processes were extensively studied throughout the 1960s, and were proposed to occur via energy transfers between excited-state ions by Auzel in 1966.⁹³ In 2004, Auzel reviewed the history and fundamentals of UC materials in a detailed report.¹⁸ The process of upconversion luminescence involves excitation of a material with lower energy photons which stimulates the emission of higher energy photons. Each higher energy emission photon requires two or more lower energy excitation photons. The upconversion luminescence mechanism is different from other processes which also use two or more lower energy photons to produce high energy emissions, such as multiphoton fluorescence and second (third, fourth etc.) harmonic generation.^{94, 95} Intermediate electronic states are involved in the process of upconversion

luminescence, while in multiphoton fluorescence and second (third, fourth etc.) harmonic generation, such intermediate electronic states do not take part.

Over the past decades, many efforts have been devoted to broadening the family of upconversion materials. The interest in this field intensified further when high brightness upconversion was reported in nanomaterials.^{96, 97} Lanthanide-doped materials are most frequently investigated for upconversion, and the lanthanide ions used are Er³⁺, Tm³⁺, Ho³⁺, Pr³⁺, and Nd³⁺, although transition metal and actinide ions are also capable of upconversion.¹⁸ Lanthanide-doped upconversion nanoparticles (UCNPs) have been proposed as a new generation of fluorescent probes with great potential in biomedical imaging, accompanied by the emergence of various structures of UCNP-based nanoparticles, such as core-shell structured UCNPs@SiO₂, UCNPs@polymer, UCNPs@noble metal (Au or Ag), and hybrid structured UCNPs-based nanocomposites.⁹⁸

Interests in coating UCNPs with a PMO shell have grown in the field of nanomedicine since PMOs exhibit good biocompatibility and their surfaces are easily functionalized by various groups (e.g., -COOH, -NH₂, etc.), which make them feasible to combine with different kinds of biological molecules, functional nanoparticles, and responsive molecules for imaging, drug delivery and so on. Depending on the amount of UCNP cores covered by one PMO shell, the UCNP@PMO structure usually includes two categories as shown in Figure 1.21 (a) and (b). In addition, the PMO can act as a core and the UCNP acts as a shell (Figure 1.21 (c)). In 2020, Kaczmarek *et al.* reported on three unique hybrid organic-inorganic materials prepared by combining PMOs and β -NaGdF₄ co-doped with Er³⁺/Yb³⁺.⁹⁹ The structure of these hybrid materials was proven by TEM imaging. These hybrid materials showed excellent thermometry performance even in aqueous environment and are no toxicity to human cells, which makes them very promising candidates for real biomedical thermometry applications.



Figure 1.21 Schematic illustration for the preparation of three hybrid upconversion inorganic-PMO hybrid materials.⁹⁹

1.4 Applications of PMO nanoparticles

Thanks to the rich chemistry available in the pores of PMO materials, various applications have been extensively explored in the past few years, such as for catalysis, adsorbents, sensors, biomedical supports, and optical applications, to name a few. Here, a brief introduction to these applications is discussed in this section, and mainly focus on the optical applications, specifically as sensors.

1.4.1 PMOs as catalysts

PMOs are increasingly studied to use as a catalyst or catalytic support.¹⁰⁰ However, nanosized catalysts are more efficient than bulk catalysts for three main reasons: (1) the smaller the catalyst material is, the higher the outer surface area to volume ratio, thus producing higher catalytic efficacies, (2) the smaller a porous material is, the smaller the diffusion pathways for reactants and products, (3) PMO NPs can possess a hollow structure to become nanoreactors.³⁶

Catalysis can only be performed when a catalytic site or function is present. A PMObased catalyst is developed by introducing organic functionalities in a PMO, using cocondensation, or grafting methods. PMO materials containing acid groups have been

used widely as acid catalysts because the acidic functional sites act as reaction sites for a range of reactions. Among these, sulfonic acid is one of the versatile functional groups for acid catalyst applications. Besides, various types of catalysts can be supported on PMOs, such as metal nanoparticles, metal complexes, or organocatalysts, for acid/base catalysis, oxidation and reduction, or carbon-carbon bond forming reactions. As an example, a MacMillan catalyst could be anchored on phenylene-bridged HPMO NPs (100-200 nm) by a co-condensation process and a "click chemistry" post-modification (Figure 1.22).¹⁰¹ Excellent catalytic activities were reported for the Diels-Alder reaction of cinnamaldehyde with cyclopentadiene in water, with a good reusability (up to 7 runs), but slightly lower enantioselectivities than the homogeneous catalyst.



Figure 1.22 Schematic representation of the hard template preparation of phenylene-bridged hollow *PMO* (*H-PhPMO*, path *A*), and further functionalization with MacMillan catalyst (*H-PhPMO-Mac*, path *B*) through a co-condensation process and click chemistry post-modification.¹⁰¹

1.4.2 PMOs as adsorbents

Since the discovery of PMOs, the possibility of using them as adsorbents for metals, organic compounds and gasses has also been explored and the main challenge is to develop PMO materials that can outperform the classical functionalized silica materials as well as commercial adsorbents such as activated carbon.⁴⁴ The adsorption capacity and selectivity are important parameters to assess the performance of an adsorbent.

Additionally, the reuse of adsorbent and recovery of adsorbate are also key parameters.

For metal ion adsorption, Burleigh *et al.* reported a remarkable approach known as molecular imprinting.¹⁰² The metal salts of nickel, copper or zinc was used during the synthesis of PMO together with BTEE, N-[3-(trimethoxysilyl)propyl]ethylenediamine and cetyltrimethylammonium chloride. The metal ion forms a complex with the amines during the synthesis and after preparation of the materials, the Ni(II), Cu(II) or Zn(II) is removed with HNO₃. This results in a material possessing cavities shaped as the metal with identical chemical environment. When using this material in an adsorption process, the metal ions of the same type which were used during synthesis, will selectively bind to the cavity, especially with solutions containing high concentrations. Furthermore, the materials prepared *via* the imprinting technique exhibited a higher metal binding capacity than the non-imprinted material.

For gas adsorption applications, it is important to consider the pore structure of PMOs (2D *versus* 3D), and the interactions with the functionalities present on the organic bridges. The 3D-structured materials outperform the 2D-structured and that the attachment of sulfonic acid groups even improves the adsorption. PMOs containing π -electrons adsorb more hydrogen than the ethane PMO.

PMOs containing aromatic bridges have been used and investigated as adsorbents for organic compounds in liquid phase.^{103, 104} The presence of benzene moieties is particularly beneficial when the adsorption of aromatic pollutants is concerned due to the π - π interactions between the adsorbate and the adsorbent.

1.4.3 PMOs as biomedical supports

Compared with mesoporous silica, the PMOs present low hemolytic behavior, improved biocompatibility, and higher loading capacities, which are particularly important for their biomedical applications. ^{105, 106} Most importantly, the size of PMOs is crucial since the size of PMOs governs their biological interactions and lifespan with parameters such as the cellular uptake, blood circulation, tumor accumulation, etc. Besides, the introduction of particular organic groups into the PMO matrix greatly

modifies the biodegradability. Currently, PMO NPs have been used as supports for the immobilization of drug, protein delivery and enzymes, and for photodynamic therapy. 78, 107, 108

Photodynamic therapy (PDT) is the main light-actuated cancer therapy used in clinics. It is an approved treatment based on the production of electrons via photosensitive molecules called photosensitizers.¹⁰⁹ Photosensitizers have been formulated in upconversion nanoparticles (UCNPs) and are activated under NIR excitation to generate cytotoxic singlet oxygen ($^{1}O_{2}$) and thus enable the treatment of large or internal tumors.¹¹⁰ Chen *et al.* prepared novel rattle-structured upconversion luminescent materials by growing a benzene-bridged organosilica shell around β -NaLuF4:Gd,Yb,Er core (Figure 1.23).¹¹¹ The particle had a void between the β -NaLuF4 particle (20 nm) and PMO shell (thickness around 10 nm), obtained through SiO₂ shell etching. The void was used to load with photosensitizer and tested for NIR-triggered upconversion induced PDT. The biological safety of the material was demonstrated *in vitro*.



Figure 1.23 Illustration of multifunctional nanocomposites based on rattle-structured organosilicashelled UCNPs.¹¹¹

1.4.4 PMOs as sensors

In the past years, sensors have been developed for detection applications in a wide range of scientific, medical, and security realms. One classification system for understanding sensors is to divide them into two categories: those that are sensitive and those that are selective.¹¹² Selective sensors, in this classification, refer to those that detect only one analyte, whereas sensitive sensors refer to those that use multidimensional analyses for the detection of multiple analytes. Another classification is to divide them into various sensor categories according to their basic sensing functions: gas sensors, chemical sensors, temperature sensors, etc. Currently, chemical sensors and temperature sensors are the most interesting sensors based on luminescent lanthanide materials.

Well-performing luminescent chemical sensors are of good selectivity in distinguishing one analyte from another, often structurally related or commonly coexisting compounds, excellent sensitivity for low concentrations of the target analyte, and work well in a real-world environment. Another important characteristic in sensors is the limit of detection and quantification. Determining a detection limit, the smallest amount of analyte that will give an unmistakable signal, and a quantification limit, the smallest amount of analyte that can be accurately quantified, of a given system is invaluable for the analysis of any sensor that could potentially have any commercial or industrial application.¹¹³ The most common approach is to obtain a calibration line of the system in question and to use the equation of that line to calculate the concentration of analyte at the point where the signal is three times the standard deviation of the blank, for the quantification limit.

PMO NPs offer the possibility of designing advanced luminescent hybrid materials comprising of organic components, yet with higher stability and very good processability.³⁷ Thanks to their promising possibilities, pristine PMO NPs and PMO NPs grafted with lanthanides are now attracting more interest. However, not too many works have been reported up to date, yet the number of works is increasing steadily. The long luminescence lifetime and large Stokes shifts of lanthanide f-f transitions,

together with tunable luminescence by varied energy transfer efficiency, absorption intensity and different extent of quenching, make them quite unique and beneficial for use as sensors. In this section, lanthanide PMO nanomaterials as sensors were discussed more in detail.

Generally, the luminescent responses of lanthanide PMOs as sensors include turn-on, turn-off, or ratiometric color change. The analytes detection based on lanthanide PMOs can proceed via the following mechanisms. (A) Energy transfer between the ligand and analyte; (B) weak interactions between analytes and lanthanide PMOs (e.g., hydrogen bonds, π - π stacking); (C) on the basis of the hard–soft acid–base theory, such as pyridine nitrogen atoms can act as binding sites in the lanthanide PMOs. The soft-acid metal cations (such as Zn²⁺, Cd²⁺, Cu²⁺, etc.) are able to form much stronger coordination bonding with the N donor organic ligands than those with the carboxylate ligands. Up to date, a very few studies have been done utilizing lanthanide PMO NPs for sensing ions, organic solvents, temperature, pH, etc.

1.4.4.1 Metal ion sensors

Among the various analytical techniques, luminescent detection of metal ions has received significant research attention because of its fast detection speed, high sensitivity, good selectivity, relatively low cost, and simple operation. The response in the luminescence intensity can vary depending on different ions, and ion sensors can be achieved due to high selectivity. The functional organic groups incorporated into PMOs play an important role in the selective detection of metal ions. The organic groups consist of electron-rich donor atoms such as N, O, P, S, etc. Several mechanisms have been explored for luminescent PMOs to sense metal ions on the basis of metal-ligand coordination interactions (weak binding of metal ions to heteroatoms (N or O) within the ligands) and intramolecular energy transfer from the ligand to the metal ion.

Yu *et al.* reported a bulk PMO functionalized with 4'-(4-carboxy-methyleneoxy phenyl)-2,2':6',2"-terpyridine (L-COOH) by co-condensation of the modified L-COOH (L-COOH-NH₂) with 1,2-bis(triethoxysilyl)ethane in the presence of P123.¹¹⁴ A novel

luminescent hybrid material was developed via linking $Eu(NTA)_3(H_2O)_2$ to L-COOHfunctionalized PMO material. The presence of the phenyl oxygen atom and amide nitrogen atom enables the interaction with Cu^{2+} , demonstrating its potential use as a selective Cu^{2+} sensor.

Kaczmarek *et al.* reported nano-sized (50-70 nm) PMOs (synthesized from 5% N,Nbis(trimethoxysilylpropyl)-2,6-pyridine dicarboxoamide precursor and 95% TEOS; called DPA-PMO) grafted with Eu^{3+} , Tb^{3+} or a 50:50 mixture of Eu^{3+} and Tb^{3+} .⁷⁶ Two different co-ligands were additionally used-1,10-phenantroline and 5,5'-dimethyl-2,2'dipyridyl. The materials without a co-ligand showed no specific selectivity for any of the metal ions. However, the materials with a co-ligand showed strong "turn on" fluorescence for Pb²⁺ and Cr³⁺ ions. Some selectivity was also observed for the highly toxic Hg²⁺ ions. The hybrid materials containing the two different co-ligands showed very similar sensing performance. The enhancement of the luminescence in the presence of Pb²⁺, Cr³⁺ and Hg²⁺ ions can most likely be linked to a strong antenna effect from the second co-ligand after their formation of complexes with the metal ions.

An amine contained nano-sized (20 nm) PMO was reported from a long linear amine precursor (3-trimethoxysilylpropyl)diethylenetriamine (10%) and 1,2bis(triethoxysilyl)ethane.¹¹⁵ A lanthanide PMO nanomaterial was obtained by grating the PMO with o-vanillin and further post-grafting with Eu(tfac)₃ complex. This material also showed significant "turn on" fluorescence in the presence of Hg²⁺ ions.

1.4.4.2 Organic solvent sensors

The common lanthanide ions used for solvent sensing are Eu^{3+} and Tb^{3+} . Kaczmarek *et al.* employed the same nano-sized DPA-PMO with Eu^{3+} - Tb^{3+} co-grafted and 1,10phenanthroline and 5,5'-dimethyl-2,2'-dipyridyl as co-ligands. All the investigated materials, both with and without co-ligand, showed significant solvatochromism, which was caused by the change in the Tb-to-Eu ratio of the emission peaks. The hybrid materials could effectively distinguish protic and aprotic solvents, due to the variation of the Tb-to-Eu energy transfer (Figure 1.24).⁷⁶



Figure 1.24 (a) Schematic representation of the PMO constructed from the N,Nbis(trimethoxysilylpropyl)-2,6-pyridine dicarboxamide linker and tetraethyl orthosilicate (at a 5 : 95 ratio). (b) Photo taken under a UV lamp (302 nm excitation) of PMO@Eu,Tb_bpy dispersed in different solvents: (from left to right) water, methanol, ethanol, n-butanol, iso-propanol, DMF, chloroform, and acetone. (c) Excitation spectra and (d) emission spectra of PMO@Eu,Tb_bpy in the solid-state and dispersed in different solvents.⁷⁶

1.4.4.3 Temperature sensors

Non-invasive sensors can measure the temperature remotely, which gives them tremendous growth potential in the medicinal field. The temperature will affect the luminescence of the lanthanide PMO materials. The changes can be detected and include several different types, such as the integrated emission intensity of a single transition or a pair of transitions, lifetime, spectral shift, polarization, or bandwidth of a certain transition.¹¹⁶ Here, much attention are paid to ratiometric temperature sensors. The ratiometric temperature sensing method is based on the measurement of the relative change in the intensity ratio of two independent energy-close transitions. Both emission bands can be generated from a single emitting center or two distinct emitting centers.¹¹⁷ For lanthanide PMOs, the Ln³⁺ can be excited through the antenna effect, direct excitation and upconversion, which give to this type of thermometers versatility in excitation and emission.^{99, 118, 119} Also the lanthanide PMO materials can be used in different temperature ranges such as cryogenic (up to 100 K), medium (100-300 K),

physiological (298-323 K) and high temperature range (≥450 K).

Kaczmarek *et al.* synthesized a nano-sized (50-70 nm) DPA-PMO starting from 5% N,N-bis(trimethoxysilylpropyl)-2,6-pyridine dicarboxamide precursor and 95% TEOS, and grafted different ratios of Tb^{3+}/Eu^{3+} and Tb^{3+}/Sm^{3+} chloride salts onto the material.¹¹⁹ To enhance the luminescence, 1,10-phenanthroline was added as a co-ligand in the grafting process. The Tb^{3+}/Eu^{3+} grafted PMO nanoparticles showed temperature dependent behaviour in the region 260–460 K. $Eu_{0.25}Tb_{0.75}DPA$ -PMO has a maximum relative sensitivity of 1.22 % K⁻¹ (440 K), $Eu_{0.50}Tb_{0.50}DPA$ -PMO a maximum of 1.56 % K⁻¹ (360 K) and $Eu_{0.75}Tb_{0.25}DPA$ -PMO a maximum of 1.45 % K⁻¹ (340 K). The sensor $Sm_{0.95}Tb_{0.05}DPA$ -PMO is operational in the region 280-460 K with a maximum relative sensitivity of 2.38 % K⁻¹ (340 K).

Shortly after, Kaczmarek et al. developed Dy-Dy and Tb-Sm based bipyridine PMOs, a pure 2,2'-bipyridine PMO (BPy-PMO) and a bipyridine-ethane co-condensed PMO (BPy-Et-PMO).¹²⁰ Grafting of Dy(acac)₃ complexes onto BPy-PMO and BPy-Et-PMO, resulted in a sensor operational in the temperature region 200-400 K with a maximum relative sensitivity of 2.85 % K^{-1} (200 K) and 1.46 % K^{-1} (300 K), respectively. Furthermore, the BPy-PMO showed temperature dependency in the region 253-333 K, BPy-PMO@Sm_{0.9}Tb_{0.1}(acac)₃ with a maximum relative sensitivity as high as 4.93 % K⁻¹ (253 K) and BPy-PMO@Sm_{0.8}Tb_{0.2}(acac)₃ a maximum of 4.82 % K⁻¹ (253 K). The sensors based on BPy-Et-PMO are operational in the region 253-373 K, BPy-Et-PMO@Sm_{0.9}Tb_{0.1}(acac)₃ shows a maximum sensitivity of 3.83 % K⁻¹ (323 K), BPy-Et-PMO@Sm_{0.8}Tb_{0.2}(acac)₃ a maximum of 3.72 % K⁻¹ (323 K). The sensors consisting of pure bipyridine linkers are better thermometers, furthermore, a higher amount of Sm³⁺ over Tb^{3+} is beneficial. The (grafted) PMO materials were tested for their toxicity towards normal human dermal fibroblasts, showing almost complete absence of toxicity. Furthermore, the materials were tested in water, forming stable colloidal suspensions, and showing very good thermometric properties. The investigated materials could therefore be promising candidates for biomedical temperature sensing.

1.4.4.4 pH sensors

Optical pH sensors have certain advantages over electrodes including their low cost, rapid response, they can be easily miniaturized, provide contactless sensing, and they can operate even in a strong electromagnetic field. They rely on the use of materials that respond to pH with a change in their luminescence properties. To date, there are only a few examples of lanthanide PMO-based pH sensors.^{121, 122} Several common sensing mechanisms include the protonation-deprotonation of groups or the change in the coordination geometries around the lanthanide ions. Lanthanide PMOs with special groups, such as carboxyl groups, show pH-dependent luminescence emission due to the protonation-deprotonation of uncoordinated carboxyl groups.¹²¹

1.5 Underlying principles of chemical sensors

For a chemical sensor to detect an analyte of interest, the presence of the analyte must induce a measurable change in a read-out signal that can be detected by the sensing device. This requires association between the analyte and the sensor, which can occur either via covalent or noncovalent interactions. Common noncovalent interaction between the analyte and the sensor include hydrophobic association, electrostatic interactions, intermolecular hydrogen bonding, cation- π and anion- π interactions, and other aromatic interactions, including π - π stacking and edge-face interactions.¹¹²

The using of lanthanide materials as sensors depends on the variation in their luminescence intensity before and after their interaction with analytes ("turn on" for enhancement or "turn off" for quenching). However, "turn off" is the most extensive, which is based on luminescence quenching resulting from the interaction between the analyte and the fluorophore, causing energy transfer from the fluorophore to the analyte. On the contrary, the luminescence sensing method of "turn on" detection is based on a new emission peak evolving from a previously dark background or an increase in luminescence intensity to show the apparent color change.¹²³

There are several different mechanisms to explain the "turn on" and "turn off" sensing behaviors: Förster resonance energy transfer (FRET), Dexter energy transfer and photoinduced electron transfer (PET). These two mechanisms, Förster resonance

energy transfer (FRET) and Dexter energy transfer, have been discussed in subsection 1.1.2. PET can be explained by predicting the electron distribution and energy of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). In PET, an electron moves from the ground state HOMO of the donor to the excited state HOMO of the acceptor, when the former is higher in energy than the latter (Figure 1.25 a) or an electron is relocated directly from the LUMO of the excited state donor to the LUMO of the ground state acceptor, in the case where the LUMO of the donor to the donor is higher in energy than that of the acceptor (Figure 1.25 b). As is known, dynamic quenching occurs owing to the collision between the excited-stated fluorophore and the quencher, whereas static quenching occurs because of the formation of non-emissive intermediates.



Figure 1.25 (*a*) photoinduced electron transfer (PET) between HOMOs and (*b*) photoinduced electron transfer (PET) between LUMOs.

1.6 Aims of this thesis

The aim of this thesis was to develop novel luminescent lanthanide-containing nanosized periodic mesoporous organosilicas and to investigate their luminescence properties. The thesis combines lanthanides with periodic mesoporous organosilicas in order to utilize the most important advantages of both systems: the large Stokes shift of Ln³⁺ ions and several unique features of PMOs, such as high-loading of organic content, insignificant pore blockage, chemically reactive sites and homogeneously distributed functional groups. In this thesis, these as-prepared PMOs involve very simple organic bridges to complex organic bridges. The lanthanides can be incorporated within the pores of the PMOs by coordination with ligands or by physical doping.

The ideas behind this research are to explore the factors that affect the particle size and luminescence properties to obtain excellent visible or NIR emitting nano-sized PMO hybrid materials. The water content, pH value, the molar ratio of additives and aging period all have influences on the morphology and particle size of PMOs. The introduction of extra ligands can act as a good antenna ligand for effectively improving the luminescence performance. The experimental details and luminescence properties will be discussed throughout the thesis.

This thesis also aimed to explore the potential applications of as-prepared lanthanide PMOs. We can take advantage of the response of the luminescence intensity to different environments, thus the response to metal ions can be used for ion detection; the response to different pH values can be used for pH detection; the response to organic solvents can be used for solvent detection. The nano-sized lanthanide PMOs in this thesis are made of different functional ligands, suggesting various potential applications.

Normally, lanthanide ions/complexes are employed to incorporate in PMOs for further studies. The lanthanide ions are connected to the PMO through coordination bonds. Considering the porous structures of PMOs, the lanthanide-based inorganic materials can build into the pores to get PMO composites, in which no interactions between the lanthanide ions and the PMOs exist. In this thesis, I have investigated advanced luminescence applications, metal ions and trace water detection based on upconversion luminescent PMO@NaYF4: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺, Tm³⁺, Ho³⁺) nanocomposites.

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Chapter 2. Rational design of lanthanide grafted nano Periodic Mesoporous Organosilicas (Ln-nano-PMOs) for near-infrared emission



The results of this chapter were published in: W. Liu, A. M. Kaczmarek, K. Folens, G. Du Laing, P. Van Der Voort and R. Van Deun, Rational design of lanthanide nano periodic mesoporous organosilicas (Ln-nano-PMOs) for near-infrared emission. *Dalton Trans.*, 2021, 50, 2774-2781.

Abstract

We present three Periodic Mesoporous Organosilica (PMO) materials: a PMO material functionalized with pyridine dicarboxamide (DPA-PMO) and two amine functionalized PMO materials (Am-PMO and Am-ePMO). The pyridine dicarboxamide ligands in the DPA-PMO material provide the tethering sites for Ln³⁺- coordination. A Schiff base reaction was carried out on the amine functionalized PMOs to introduce similar lanthanide coordination sites. The Nd and Yb modified nano-PMOs are evaluated as near-infrared (NIR) emitting luminescence materials. The DPA-PMO and Am-ePMO materials can act as good platforms for NIR luminescence. A significant enhancement in the decay time can be observed upon grafting an Yb(hfa)₃ complex to the PMO materials instead of YbCl₃. All of the DPA-PMO@Ln(hfa)₃ and Am-ePMO@Ln(hfa)₃ materials show characteristic NIR emission performance both in the solid state and in aqueous suspension.

2.1 Introduction

Near-infrared (NIR) emitting lanthanide ions, for example neodymium (Nd³⁺), samarium (Sm³⁺), praseodymium (Pr³⁺), erbium (Er³⁺), and ytterbium (Yb³⁺), exhibit characteristic narrow emission bands and large Stokes shifts, making them attractive for potential use in a wide range of applications, such as medical diagnostics and optical amplifiers.¹⁻⁴ A downside of NIR-luminescent lanthanide ions is their low absorption coefficients caused by the parity-forbidden nature of the 4f-4f transitions. This results in weak light absorption and therefore low emission intensities. To overcome this, lanthanide ions can be chelated with sensitizing ligands (β-diketonates, aromatic carboxylic acids, macrocyclic ligands or neutral ligands^{5, 6}). These antenna ligands enable the harvesting of light with high efficiency and transfer this energy to the lanthanides, resulting in better excitation of the Ln³⁺ ions.² To improve the thermal stability and mechanical properties of lanthanide complexes for practical applications, it is therefore advantageous to incorporate these lanthanide complexes within stable host matrices, such as silica-based materials, polymers, or liquid crystals.^{7, 8} A class of mesoporous organosilica materials, called Periodic Mesoporous Organosilicas (PMOs), have a higher hydrothermal and mechanical stability than silica, and incorporate organic functional groups in the framework. PMOs have had already a wide range of applications.9-12

PMO materials are obtained by a sol-gel process involving hydrolysis and the subsequent polycondensation of polysilsesquioxane, a bis-silylated organosilica precursor ((R'O)₃–Si–R–Si–(OR')₃, in which R represents an organic bridging group and R' is usually a methyl or ethyl group).¹³ Many PMOs have already been studied with different organic bridging groups (R), such as phenylene, ethylene, ethenylene and ethylbenzene, and also more attention has been given to flexible and complex organic bridging groups.^{14, 15} The bridging group can be modified to fine-tune the material for effective coordination with free lanthanide ions and efficient energy transfer to obtain bright and intense near-infrared luminescence.

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Developing strongly emitting NIR PMOs remains challenging, and only few papers have appeared on the topic.^{8, 16, 17} Sun *et al.* reported that the Ln(dbm)bpd-PMO (bpd = 4,4'-bis [Si(OEt)₃(CH₂)₄]-2,2'-bipyridine, Ln = Er, Nd, Yb) showed characteristic NIRluminescence of the corresponding Ln³⁺ ions upon visible light excitation.⁸ Also Yb³⁺ grafted ethenylene-bridged PMO material was investigated for the use as ratiometric thermometers in the 110-310 K temperature range.¹⁶ Recently, unique materials prepared by combining Er^{3+} - Yb³⁺ doped β -NaGdF₄ and PMOs were proposed, which showed visible and NIR luminescence properties. The materials were non-toxic for normal human dermal fibroblastic cells and showed excellent thermometry performance.¹⁷ Most reported NIR PMOs are powders. The synthesis of nano-sized NIR PMOs is not easy and has hardly been described in literature. These nano-sized PMOs could find potential applications in nanothermometers, drug and protein delivery, photodynamic therapy, etc.

Several strategies have been reported to introduce coordination sites for lanthanide ions in PMOs.^{9, 16, 18-24} The commonly used method is the synthesis of functional organosilica precursors already containing the required functional groups, which can provide oxygen/nitrogen sites to coordinate the Ln³⁺ centers. Subsequently, cocondensation of the precursor (as a functional monomer) and simple organosilane (like tetraethoxysilane or 1,2-bis(triethoxysilyl) ethane as a structural monomer) is executed to obtain PMO materials. In this work, an N,N-bis(trimethoxysilylpropyl)-2,6-pyridine dicarboxamide precursor (DPA-Si) was used as a functional monomer to prepare the DPA-PMO material.

Another strategy to introduce coordination sites is based on the post-modification of the organic bridging groups embedded into the PMO framework. By the reaction between the amine groups and an aldehyde/ketone, the formed Schiff base ligands can provide nitrogen sites to chelate the Ln³⁺ ions. Amine PMOs, with dangling amine groups in the pores of the PMO, are a class of interesting PMOs, since the amine group can be further functionalized for many applications.^{9, 25} In this work we prepared two different amine PMOs for NIR emission. The first material, Am-PMO, was prepared in

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a one-step procedure and was loaded with 10% of the amine precursor N-[3-(trimethoxysilyl)propyl]ethylenediamine. The amount of amine precursor participating in the formation of the Am-PMO should be limited, because otherwise the bulky precursors will hamper the formation of an ordered material. The second amine PMO is based on the trans-ethenylene-bridged PMO (ePMO), which was further brominated on the C=C double bonds and substituted with an amine, yielding the Am-ePMO material. Then both Am-PMO and Am-ePMO materials were further functionalized with o-vanillin to form Schiff base ligands on the surface and in the pores of the PMO materials. Table 2.1 overviews the precursors used as well as the framework structures of the PMOs in this work.

Herein, we studied three different nano-sized PMOs prepared with different approaches to introduce coordination sites for NIR emitting lanthanide ions. Additionally, post synthesis impregnation was used to coordinate lanthanide chloride salts and β -diketonate complexes (Ln(hfa)₃, hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) to the functional organic moiety of the PMOs for researching NIR luminescence properties.



 Table 2.1 Overview of three PMO materials in this work.





2.2 Experimental section

2.2.1 Sample preparation

All reagents and solvents were used as received without further purification. The $Ln(hfa)_3 \cdot 2H_2O$ (Ln = Nd³⁺ and Yb³⁺, Hhfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) complexes were synthesized using a literature method with additional modification.²⁶ Ln³⁺ ions are hard Lewis acids and they therefore prefer to coordinate to hard Lewis bases containing oxygen and nitrogen atoms in the PMO framework.

Synthesis of Ln(hfa)₃ complexes

The synthesis of $Ln(hfa)_3 \cdot 2H_2O$ (Ln = Nd and Yb) complexes were carried out as follows. As an example, 4 mmol of NdCl₃ $\cdot 6H_2O$ was dissolved in distilled water (solution 1). A solution of Hhfa (12 mmol) was dissolved in 33 mL of diethyl ether and then the Hhfa molecules in the resulting solution were deprotonated by adding 0.83 mL ammonia solution (solution 2). Solution 1 was extracted twice, each time with half volume of solution 2, then the diethyl ether phase was separated. The organic phase was washed with 3.3 mL H₂O and dried with Na₂SO₄, then the diethyl ether was removed
by using the vacuum evaporator. The crude products (mixture of oil and crystals) were then extracted several times with boiling hexane solvent. The resulting crystals were obtained by filtration, followed drying for a few hours in air. The compositions of synthesized complexes were characterized by elemental analysis.

Nd(hfa)₃•2H₂O (NdC₁₅H₁₀F₁₈O₈) calculated: 22.49% C; 0.87% H; found: 22.84% C; 0.68% H. Yb(hfa)₃•2H₂O (YbC₁₅H₁₀F₁₈O₈) calculated: 21.60% C; 1.20% H; found: 21.97% C; 1.47% H.

Synthesis of DPA-PMO

The PMO precursor was synthesized according to a previously reported procedure.²⁷ Firstly, pyridine 2,6-dicarbonyl chloride was dissolved in dry diethyl ether in a roundbottom flask. Subsequently, a mixture of (3-aminopropyl) trimethoxysilane and pyridine in dry diethyl ether was added dropwise under argon atmosphere. The mixed solution was stirred at ambient temperature for 4 h. Then the above solution was filtered. Eventually, the PMO precursor -N,N-bis(trimethoxysilylpropyl)-2,6-pyridine dicarboxamide- was obtained as a yellow oil after removing the diether ether and pyridine by rotary evaporation. The obtained DPA-PMO precursor was characterized by ¹H NMR (Figure S2.1).

The PMO was synthesized by hydrolysis and condensation in aqueous alkaline solution in the presence of surfactant cetrimonium bromide. 1.646 mmol of cetrimonium bromide was dissolved into a solution of 300 mL distilled water and 4.2 mmol NaOH. After having stirred for 30 minutes at 80 °C until the surfactant was fully dissolved, 13.43 mmol of pre-synthesized precursor and tetraethoxysilane (TEOS, 0.2552 mol) in ethanol (1 mL) was added dropwise under vigorous stirring. A white suspension was immediately formed, which was continuously stirred at 80 °C for 2 h. A white powder was obtained by centrifugation and then washed with water (twice) and ethanol (once). Finally, the surfactant was removed by solvent extraction three times to ensure full removal of the surfactant template. The detailed procedure of the solvent extraction was as follows: the as-synthesized material (ca. 1 g) was stirred into a

solution which contains 200 mL of ethanol and 0.4 mL of concentrated hydrochloric acid at 65 °C for 6 h.

Synthesis of Am-PMO

The PMO precursors: N-[3-(trimethoxysilyl)propyl]ethylenediamine and 1,2bis(triethoxysilyl)ethane are commercially available. As the amine precursor is very bulky, the used amount is much lower than 1,2-bis(triethoxysilyl)ethane to obtain the highly ordered structure of the PMO.

The Am-PMO was synthesized by the co-condensation of 10% N-[3-(trimethoxysilyl)propyl]ethylenediamine and 90% 1.2-bis(triethoxysilyl)ethane. 0.5 g of cetrimonium bromide was dissolved in 300 mL of distilled water. Additionally, 3.235 mL of 25% ammonium solution was added to the above solution in an ice water bath, then it was naturally heated to room temperature after stirring 30 minutes. Then mixed solution obtained. Next, N-[3-А was the precursors (trimethoxysilyl)propyl]ethylenediamine (10%) and 1,2-bis(triethoxysilyl)ethane (90%) were dissolved in 10 mL of ethanol to get solution B. Afterwards, the solution B was added dropwise to the solution A, and was left to stir for 3 h at 80 °C. The precipitate was collected by centrifugation and washed with water and acetone. Later it was dried in a vacuum oven at 120 °C overnight. The surfactant was extracted by refluxing the white powder (ca. 1g) in a mixture of HCl (2 mL) and ethanol (66 mL) for 6 h at 50 °C. The powder was filtered and washed with water and ethanol. The procedure of surfactant removal was repeated 3 times to ensure complete surfactant removal.

Synthesis of Am-ePMO

The precursor of the ePMO was synthesized by following a published procedure.²⁸ In a typical synthesis of pure E-diastereoisomer of 1,2-bis(triethoxysilyl)ethene (BTSE), (PCy₃)₂Cl₂Ru=CHPh (Grubb's catalyst 1st generation, 0.065 mmol) and vinyltriethoxysilane (42.95 mL) were added to a round bottom flask under argon. The mixture was left to stir for 2 h and subsequently refluxed for an additional 3 h. The unreacted vinyltriethoxysilane was destilled off, after which the BTSE was distilled

under vacuum to get a clear colorless liquid.

In order to obtain ethenylene-bridged PMO (ePMO), a solution containing P123 surfactant (1.00 g), HCl (2.12 mL), BuOH (1.17 mL), and 48.70 mL of H₂O was stirred at room temperature for 2 h. Then pure BTSE (1.86 mL) was added dropwise to the above clear solution. The mixture was stirred at 35 °C for 2 h and subsequently aged at 90 °C for 6 h under static conditions. After cooling down, a white powder was collected by filtration and washed with H₂O. The surfactant was removed by the method of Soxhlet extraction in acetone for 5 h at 100 °C.

The ePMO was then functionalized by a bromination reaction, achieved by adding Br₂ in the gaseous phase to the ePMO. Afterwards, the solid was heated at 120 °C to remove any physiosorbed bromine molecules, after which ePMO@Br was obtained. The amount of bromine was determined gravimetrically. Subsequently, the Br was substituted with diethylenetriamine (DETA; 99%) to gain Am-ePMO. In a typical synthesis, 0.1 g of ePMO@Br was mixed with DETA (5 mol equivalents with regard to the amount of bromine) in 50 mL of dimethylformamide (DMF; >99.5%) under an inert atmosphere. After stirring at 100 °C for 5 h, the powder was collected by filtration and washed thoroughly with DMF, distilled water and acetone. Finally, it was dried under vacuum at 90 °C. The material is named as Am-ePMO. The above reactions are depicted in Scheme 2.1.



Scheme 2.1 Schematic overview of the modification performed on the ePMO material: (a) bromination of the double bond; (b) substitution with DETA where R represents (CH_2)_2NH(CH_2)_2

Synthesis of DPA-PMO material grafted with lanthanide salts/complexes

DPA-PMO@LnCl₃: In a typical procedure, 12.5 mg of the as-prepared PMO and 0.026 mmol of lanthanide chloride salt (NdCl₃·6H₂O or YbCl₃·6H₂O) were placed in a flask. Then, 10 mL of ethanol was added. The mixture was placed in an ultrasound bath for 15 minutes and was then heated at 80 °C for 24 h. Finally, the mixture was

cooled down to room temperature, centrifuged and washed several times with ethanol, and dried in an oven at 80 °C.

DPA-PMO@Ln(hfa)₃: A similar procedure was used as for the synthesis of DPA-PMO@LnCl₃ except that Ln(hfa)₃ complexes were used. The molar ratio of Ln(hfa)₃ complexes to PMO was maintained the same as the molar ratio of LnCl₃ · 6H₂O to PMO.

Synthesis of Am-PMO material grafted with lanthanide salts/complexes

A Schiff base ligand was first formed on the PMO material to obtain Am-PMO@ovan. In a typical procedure, 0.05 g of Am-PMO and 0.1 g of o-vanillin were dissolved in 25 mL of methanol in a round bottom flask, which was then heated at 60 °C for 6 h. The solid was filtered and washed with methanol and dried in an oven at 60 °C for 24 h. A noticeable color change of the solid from white (Am-PMO) to pale yellow (Am-PMO@o-van) was observed, indicating the successful Schiff base reaction of the aldehyde with the amine ligands of the PMO material.

Am-PMO@LnCl₃: 0.01 g of the Am-PMO@o-van and 0.26 mmol of LnCl₃ \cdot 6H₂O were placed in a Pyrex test tube and 5 mL of methanol was added. The tube was closed tightly and heated at 80 °C for 24 h using a heating block. The solid product was collected by centrifugation and washed with methanol. Finally, it was dried in an oven at 60 °C.

Am-PMO@Ln(hfa)₃: a similar procedure was used as for the synthesis of Am-PMO@LnCl₃ except that Ln(hfa)₃ complexes were used. The molar ratio of Ln(hfa)₃ complexes to PMO was the same as the molar ratio of LnCl₃ · 6H₂O to PMO.

Synthesis of Am-ePMO material grafted with lanthanide salts/complexes

Am-ePMO@o-van: 0.05 g of Am-ePMO and 2 g of o-vanillin were dissolved in 50 mL of methanol in a round bottom flask, which was then heated at 60 °C for 6 h. The solid was filtered and washed with methanol and dried in an oven at 60 °C for 24 h. A noticeable color change of the solid from white to bright yellow indicated the successful Schiff base reaction.

Am-ePMO@LnCl₃: 0.01 g of the Am-ePMO@o-van and 0.26 mmol of LnCl₃ · 6H₂O

were placed in a Pyrex test tube and 5 mL of methanol was added. The tube was closed tightly and heated at 80 °C for 24 h using a heating block. The solid product was collected by centrifugation and washed with methanol. Finally, it was dried in an oven at 60 °C.

Am-ePMO@Ln(hfa)₃: a similar procedure was used as for the synthesis of AmePMO@LnCl₃ except that Ln(hfa)₃ complexes were used. The molar ratio of Ln³⁺ to PMO was unchanged in the two different PMOs.

2.2.2 Characterization

Powder X-ray diffraction (PXRD) patterns were obtained by a Thermo Scientific ARL X'TRA diffractometer equipped with a Cu K α ($\lambda = 1.5405$ Å) source, at a scanning rate of 0.2° min⁻¹ in Bragg-Brantano configuration in the range of 0.50-10.00° 20. ¹H NMR spectra were measured at 25 °C in CDCl3 solution on a Bruker Advance 300 MHz NMR spectrometer. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs) was performed on a hybrid IR-Raman spectrophotometer, a Thermo Scientific Nicolet 6700 equipped with a nitrogen-cooled Mercury Cadmium Telluride (MCT) detector, using a Graseby Specac diffuse reflectance cell. The data were recorded in the region of 650-4000 cm⁻¹ using a DRIFT chamber with KBr/sample mixtures. The lanthanide content was determined upon digestion of 20 mg material with 8 mL Aqua Regia and heating for 2 h at boiling point. The digest was cooled down to room temperature, diluted with Milli-Q water and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) on a NexION 350D instrument (Perkin Elmer, US) using 3.6 mL min⁻¹ He as collision gas to annihilate the interference of polyatomic species. Quantification was done using external standards and 10 µg L⁻¹ Rh internal standard. Transmission Electron Microscopy (TEM) images were obtained using a Cscorrected JEOL JEM2200FS transmission electron microscope with a working voltage of 200 kV. HAADF-STEM and energy dispersive X-ray (EDX) mapping analysis was performed to illustrate the existence of lanthanide ions inside and on the surface of the PMO materials. Nitrogen adsorption-desorption isotherms were carried out on a Chapter 2 Rational design of lanthanide grafted nano Periodic Mesoporous Organosilicas (Ln-nano-PMOs) for near-infrared emission

Micromeritics TriStar 3000 analyzer at 77 K. All samples were degassed for 24 h at 120 °C prior to measurement. The Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to calculate the surface areas and pore size distributions of the samples, respectively. Elemental analysis (CHNS) was performed on a Thermo Flash 2000 elemental analyzer by using V_2O_5 as catalyst. The excitation and emission spectra were recorded using an Edinburgh Instruments FLSP920 UV-vis-NIR spectrometer setup with a 450 W xenon lamp as the steady state excitation source and a Hamamatsu R5509-72 NIR photomultiplier tube (PMT, Hamamatsu, Shizuoka, Japan) operating at -80 °C. Luminescence decay times were recorded using a 60W pulsed xenon lamp for Yb³⁺-doped PMO materials. For Nd³⁺-doped PMO materials, the luminescence decay times were measured using the third harmonic (355 nm) of a 20Hz Nd:YAG OPO laser as excitation source. Solid samples were placed between quartz plates (Starna cuvettes for powdered samples, type 20/C/Q/0.2) when measuring the luminescence properties. Colloidal suspensions of the PMO were measured in quartz cuvettes with a path length of 10 mm (at a concentration of 5 mg of the sample dispersed in 1 mL distilled water). The low temperature phosphorescence spectra of Gd³⁺ grafted PMO materials were also measured to determine the lowest triplet levels of the PMO materials using the Edinburgh Instruments FLSP920 UV-vis-NIR spectrometer setup with a 450 W xenon lamp as the excitation source.

2.3 Results and discussion

2.3.1 DRIFTs analysis

The efficient incorporation of pyridine dicarboxamide moieties into the DPA-PMO framework was confirmed by DRIFTs, which is depicted in Figure 2.1(a). Both the siloxane framework and the organic functional moieties can be confirmed in the DRIFTs spectra of DPA-PMO and DPA-PMO@Nd³⁺. A strong broad band around 980–1230 cm⁻¹ is attributed to the asymmetric stretching vibrations of the Si-O-Si framework and the stretching vibrations of Si-C bonds originating from the hydrolysis and co-condensation of the DPA-PMO precursor and TEOS. The band at 798 cm⁻¹ is

assigned to the symmetric stretching vibrations of the O-Si-O units. A wide band around 3400 cm⁻¹ is attributed to the O-H stretching vibrations of silanol groups and/or residual water molecules. A band at 945 cm⁻¹ is assigned to the asymmetric stretching vibration of the Si-OH group. These bands confirm the formation of the siloxane framework. The characteristic bands at 1538 cm⁻¹ and 1660 cm⁻¹ corresponding to the absorption of δ (NH)-v(CN) moieties (from the pyridine ring) and C=O, respectively, prove the successful incorporation of the pyridine dicarboxamide functionalities in the structure.²⁹ The N contents in DPA-PMO is 3.03 wt%.

Figure 2.1(b) shows the DRIFTs spectra of Am-PMO and Am-PMO@o-van materials. For the Am-PMO material, two bands at 1629 cm⁻¹ and 3300 cm⁻¹ are attributed to the N-H bonds. A strong broad band around 960–1230 cm⁻¹ is ascribed to the asymmetric stretching vibrations of the Si-O-Si framework. The bands centered at 773 cm⁻¹ and 907 cm⁻¹ correspond to the symmetric stretching vibrations of O-Si-O units and asymmetric stretching vibrations of Si-OH, respectively. These bands indicate the successful formation of the siloxane framework. A new band at 1539 cm⁻¹ appearing in the Am-PMO@o-van material is attributed to the C=N bonds.

Figure 2.1(c) shows the DRIFTs spectra of the ePMO materials before and after functionalization. All samples show characteristic silanol peaks around 3720 cm⁻¹. The peaks at 2950 cm⁻¹ represent the C–H stretching from the ethylene bridge and the diethylenetriamine group. The large bands in the range of 1188–800 cm⁻¹ are attributed to the siloxanes, indicating the formation of a silica framework. A vibration at 1660 cm⁻¹ arises indicating the presence of primary amines in Am-ePMO material.³⁰ A new band at 1540 cm⁻¹ appearing in the Am-ePMO@o-van is attributed to the C=N bonds, which further indicates the formation of Schiff base bonds in the material. No changes can be found in the DRIFTs spectra of Ln³⁺ grafted materials, such as Am-ePMO@NdCl₃ and Am-ePMO@Nd(hfa)₃ materials.

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Figure 2.1 DRIFTs spectra of (a) DPA-PMO; (b) Am-PMO; (c) ePMO materials before and after functionalization.

2.3.2 XRD analysis

Figure 2.2 shows the XRD spectra of DPA-PMO, Am-PMO and ePMO materials before and after functionalization. A strong signal corresponding to the (100) reflection at low 2 θ is clearly visible for the three pristine PMO materials, indicating the presence of mesoporous structures. For ePMO (Figure 2.2 (c)), two weak reflections (110) and (200) can be observed (around $2\theta = 1.5^{\circ}$), attributed to a hexagonally ordered mesoporous structure. The reflection (100) of ePMO@Br material slightly shifts towards higher degrees, suggesting a smaller d₍₁₀₀₎ value (Table S2.1). The mesoporous structure is still maintained after the nucleophilic substitution and the Schiff base formation reaction. The intensity of reflection (100) becomes very weak for AmePMO@NdCl₃ or even disappears for Am-ePMO@Nd(hfa)₃. This indicates that the mesoporous structures almost collapse. For DPA-PMO (Figure 2.2 (a)), the PMOs mesostructure remains intact after grafting the lanthanide chloride salt or β -diketonate $(Ln(hfa)_3, Ln = Nd)$ complex to the PMO. For Am-PMO (Figure 2.2 (b)), the PMO material also retains its mesostructure after functionalization with o-vanillin.



Figure 2.2 Powder XRD diffractograms of PMO materials before and after functionalization. (a) DPA-PMO; (b) Am-PMO; (c) ePMO materials (a. ePMO; b. ePMO@Br; c. Am-ePMO; d. Am-ePMO@o-van; e. Am-ePMO@NdCl₃; f. Am-ePMO@Nd(hfa)₃)

2.3.3 Nitrogen adsorption analysis

Nitrogen adsorption-desorption measurements were carried out to characterize the mesoporosity of the PMO materials. Figure 2.3 shows the N₂ adsorption-desorption isotherms of DPA-PMO, Am-PMO and ePMO materials before and after functionalization. All the pristine PMO materials and modified variants exhibit the typical type IV isotherms for mesoporous materials according to the IUPAC classification and the sharp capillary condensation step that indicates the presence of uniform mesopores.³¹ The absence of the hysteresis loop (in DPA-PMO, Am-PMO and their modified variants) is typically for materials with small mesopores, as the cavitation point (point below which no hysteresis is possible) is at P/P° = 0.42 for

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nitrogen at 77 K. For ePMO and its modified variants, the isotherms display H1-type hysteresis loops at relative pressures in the range 0.45-0.8, suggesting larger mesopores than other PMO materials. The physical properties of all materials are presented in Table S2.1. A pronounced decrease of the BET surface area and pore volume can be observed after functionalization of the pristine PMOs (DPA-PMO, Am-PMO and ePMO), indicating the presence of functionalities inside the pores.



Figure 2.3 N_2 adsorption-desorption isotherms of PMO materials before and after functionalization. (a) DPA-PMO; (b) Am-PMO; (c) ePMO materials (a. ePMO; b. ePMO@Br; c. Am-ePMO; d. Am-ePMO@o-van; e. Am-ePMO@NdCl₃; f. Am-ePMO@Nd(hfa)₃)

2.3.4 TEM and ICP-MS analysis

Figure 2.4 (a) and (b) show the TEM images of DPA-PMO, uniform spheres with an average particle size of 50-70 nm. To optimize the synthesis procedure for nano-sized Am-PMO, we modified the pH value by increasing the amount of water and analyzed the morphologies of the obtained Am-PMO materials by TEM (Figure S2.3). The Am-PMO prepared with 300 mL water has the most uniform spherical nanoparticles with an average diameter around 200 to 250 nm (Figure 2.4 (c)). Figure 2.4 (d) reveals clearly the presence of parallel aligned mesochannels. Therefore, this Am-PMO was

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selected for investigation in this work. A functionalization degree of 1.20 wt% N via elemental analysis per gram Am-PMO material is obtained, indicating a rather limited amount of dangling amines in the pore walls. The amount of Schiff base bonds in the Am-PMO@o-van material is therefore also very low, which is further illustrated by the pale yellow color of the Am-PMO@o-van material. It is therefore expected that only a small number of lanthanide ions can coordinate with the Am-PMO@o-van material.



Figure 2.4 TEM images of (a)(b) DPA-PMO (scale bars are 50 nm); (c)(d) Am-PMO (300 mL water; scale bars are 200 nm and 50 nm from left to right); (e)(f) ePMO materials ($V_{HCl}:V_{BuOH} = 1.81$, aged at 90 °C for 6 h; scale bars are 100 nm).

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The ePMO material was prepared by the co-condensation of 1.2bis(triethoxysilyl)ethene (BTSE) for further functionalization. Generally, the molar ratio of HCl:BuOH, the amount of water and aging period all have influences on the morphology of the ePMO material. To obtain nano-sized ePMO particles, we optimized the synthesis procedure by changing the amount of BuOH and by avoiding the aging treatment. The morphologies of ePMO materials prepared with different conditions are presented in Figure S2.5. The ePMO material synthesized under the condition $(V_{HCI}: V_{BuOH} = 1.81, aged at 90 \degree C for 6 h)$ has the best morphology. It shows uniform nanoparticles around 500 nm in size (Figure 2.4 (e)) and straight mesoporous channels (Figure 2.4 (f)). TEM measurements were also employed to investigate the functionalized ePMO materials (Figure S2.6), which show good agreement with the XRD results. The amount of bromine in ePMO@Br was determined and amounts to 3.1 mmol g⁻¹. It was further used as a substrate for a nucleophilic substitution reaction to obtain Am-ePMO (the nitrogen content is 3.06 wt%), and subsequently reacted with o-vanillin to obtain more Ln³⁺ coordination sites.

The presence of Nd³⁺ in the DPA-PMO@NdCl₃, Am-PMO@NdCl₃ and AmePMO@NdCl₃ material was confirmed by dark-field TEM. The corresponding elemental maps obtained by EDX analysis are shown in Figure S2.2 for DPA-PMO@NdCl₃, Figure S2.4 for Am-PMO@NdCl₃ and Figure S2.7 for AmePMO@NdCl₃, respectively.

Additionally, the actual Ln^{3+} contents in the DPA-PMO@ Ln^{3+} , Am-PMO@ Ln^{3+} and Am-ePMO@ Ln^{3+} materials were determined using ICP-MS analysis. The results are shown in Table S2.2. The content of Ln^{3+} in Am-PMO@ Ln^{3+} is lower than that in DPA-PMO@ Ln^{3+} and Am-ePMO@ Ln^{3+} .

2.3.5 Luminescence properties of Ln^{3+} functionalized PMOs ($Ln = Nd^{3+}$ and Yb^{3+})

In this section, two types of PMO@Ln³⁺ materials are investigated more closely: PMO@LnCl₃ and PMO@Ln(hfa)₃ (Ln³⁺ = Nd³⁺ or Yb³⁺). The lanthanide ions can coordinate with the nitrogen/oxygen sites provided by the pyridine dicarboxamide ligands (of DPA-PMO) or the Schiff base ligands (of Am-PMO@o-van and Am-ePMO@o-van). All Ln³⁺ grafted materials were washed with excessive amounts of ethanol or methanol after synthesis. It is therefore not expected that any free lanthanide ions/complexes are trapped in the pores of the PMOs. The luminescence properties of all Ln³⁺ grafted PMO materials were investigated at room temperature. Unfortunately, no luminescence could be detected from Am-PMO@Ln³⁺, which might be due to a very low grafting amount of lanthanide ions. Therefore, we mainly studied the photoluminescence properties of DPA-PMO@Ln³⁺ and Am-ePMO@Ln³⁺.

Figure 2.5 displays the combined excitation-emission spectra of DPA-PMO@NdCl₃, DPA-PMO@Nd(hfa)₃, Am-ePMO@NdCl₃ and Am-ePMO@Nd(hfa)₃. In the excitation spectra of all four materials, a broad band ranging from 250 nm to 450 nm can be observed. The maximum of the broad band is at 285 nm for DPA-PMO@NdCl₃, attributed to the $\pi^* \leftarrow \pi$ transition of the chromophores in DPA-PMO. The maximum of the broad band is located at 323 nm for DPA-PMO@Nd(hfa)₃, which is assigned to the $\pi^* \leftarrow \pi$ transition of the hfa ligands. The maximum of the broad band for AmePMO@NdCl₃ is at 372 nm and at 323 nm for Am-ePMO@Nd(hfa)₃. Additionally, two peaks can be seen in the excitation spectrum of Am-ePMO@Nd(hfa)₃. The peak at 323 nm corresponds to the $\pi^* \leftarrow \pi$ transition of the hfa ligands and the other one at 372 nm is assigned to the $\pi^* \leftarrow \pi$ transition of the chromophores in Am-ePMO. The intensity of the peak at 372 nm is much lower than the peak at 323 nm, indicating that the efficiency of energy transfer from the hfa ligands to Nd^{3+} is greater than that from the Schiff base ligands. In the case of all four Nd³⁺ grafted PMO materials, the emission spectra consist of three bands centered at 895, 1065 and 1335 nm, which are attributed to three characteristic f-f transitions of Nd³⁺: ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$, ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ and ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$, respectively. The intensity of the transition at 1065 nm is the strongest among all three transitions. The luminescence decay times of all Nd³⁺ grafted PMO materials have been determined by fitting a biexponential function to the curves (Figures S2.8-S2.11). The decay times are summarized in Table S2.3. There are two different coordination environments of Nd³⁺ grafted to the PMO materials. As one decay time is shorter, some Nd³⁺ ions might be located in an unfavorable environment (e.g., in the presence of several water molecules in its first coordination sphere).



Figure 2.5 Combined excitation-emission luminescence spectra of (a) DPA-PMO@NdCl₃; (b) AmePMO@NdCl₃; (c) DPA-PMO@Nd(hfa)₃ and (d) Am-ePMO@Nd(hfa)₃. All of the emission spectra were recorded upon excitation into the maximum of the broad bands (a. 285 nm, b. 372 nm, c. 323 nm, d. 323 nm) and the excitation spectra were observed at 1065 nm (the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ transition peak).

In Nd³⁺ grafted PMO materials, sensitising the formation of the Nd³⁺ excited state is through the triplet mediated pathway. The electrons of the ligands are excited from the singlet ground state (S₀) to the singlet excited state (S₁) by absorbing UV or visible light, followed by intersystem crossing to form the chromophore-centred triplet excited state (T), or direct energy transfer to the lanthanide centre (at the same time, ligand fluorescence and nonradiative de-activation can compete with this mechanism). Where the intersystem crossing dominates, the excitation energy of the triplet state is transferred to the 4f states of lanthanide ions, which ultimately results in the corresponding lanthanide ion emission. The lowest triplet state level energies of the PMO materials, DPA-PMO and Am-ePMO, are calculated to be 24390 and 23364 cm⁻ ¹, determined by Figure S2.18-S2.21, respectively. The triplet energy of the hfa ligand is 22300 cm⁻¹ and therefore lower than that of the PMO materials. It can thus provide a better energy match with the accepting levels of neodymium.³²



Figure 2.6 Combined excitation-emission luminescence spectra of (a) DPA-PMO@YbCl₃; (b) AmePMO@YbCl₃; (c) DPA-PMO@Yb(hfa)₃ and (d) Am-ePMO@Yb(hfa)₃. All of the emission spectra were recorded upon excitation into the maximum of the broad bands (a. 306 nm, b. 372 nm, c. 323 nm, d. 372 nm) and the excitation spectra were observed at 980 nm.

Figure 2.6 presents the combined excitation-emission spectra of DPA-PMO@YbCl₃, DPA-PMO@Yb(hfa)₃, Am-ePMO@YbCl₃ and Am-ePMO@Yb(hfa)₃. In the excitation spectra of all four materials, a strong and broad band ranging from 250 to 450 nm can be observed. The maximum of this broad band varies a bit and seems to be related to the matrix material and hfa ligand. As for the DPA-PMO material, the maximum is at 306 nm for DPA-PMO@YbCl₃ and 323 nm for DPA-PMO@Yb(hfa)₃, respectively. Yet for Am-ePMO@Yb³⁺ materials, the maximum of the broad band is at 372 nm. There are two peaks in the excitation spectrum of Am-ePMO@Yb(hfa)₃. The peak at 323 nm corresponds to the $\pi^* \leftarrow \pi$ transition of the hfa ligands and the other one at 372 nm is assigned to the $\pi^* \leftarrow \pi$ transition of the chromophores in Am-ePMO. The intensity of the peak at 372 nm is higher than the peak at 323 nm, indicating the efficiency of energy transfer from the Schiff base ligands to Yb^{3+} is greater than that from the hfa ligands, causing an alternative excitation possibility for Yb^{3+} .³³ Upon excitation of the Yb^{3+} hybrid material at the maximum of the broad band, the emission spectra of all four materials display a strong broad peak with a maximum around 980 nm, which is assigned to the transition from the excited state (${}^{2}F_{5/2}$) to the ground state (${}^{2}F_{7/2}$) of Yb^{3+} . The decay times of Yb^{3+} grafted PMO materials have been determined by plotting a biexponential function (Figure S2.12-S2.15). The resulting decay times can be observed in Table S2.3. It is quite clear that the decay times of $Yb(hfa)_{3}$ grafted mesoporous materials are slightly higher than those of $YbCl_{3}$ grafted mesoporous materials.

All the Nd³⁺ or Yb³⁺ grafted DPA-PMO and Am-ePMO show characteristic NIR emission, but no signal can be detected for Er^{3+} grafted PMOs. There is a report that Er^{3+} grafted dppz-ePMO showed weak NIR emitting, where the dppz-ePMO and our reported Am-ePMO have the same pristine ePMO but with different modifications.¹⁶ Besides, the decay times of our reported PMO@Ln³⁺ are longer comparing to other materials *e.g.* Sun *et al.* reported that the decay times of Ln(dbm)₃bpd-PMO are 0.095 µs for Nd(dbm)₃bpd-PMO and 5.97 µs for Yb(dbm)₃bpd-PMO), respectively.⁸

Additionally, we also investigated the luminescence properties of Ln(hfa)₃ grafted PMOs when suspended in water (Figure S2.16). All materials show characteristic NIR emission performance corresponding to Ln³⁺ ions even when dispersed in water, which could make these nano-sized PMO materials very promising for biological applications. We also selected two materials (DPA-PMO@Yb(hfa)₃ and Am-ePMO@Yb(hfa)₃) for further study their emission properties when the PMOs were suspended in water for a long period of time. There was no significant change in emission intensity and decay time even after 7 days for both materials (Figure S2.17), indicating that the materials are very stably in water, proving that the Ln-PMO materials do not fall apart in this environment.

2.4 Conclusions

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In this work, we have reported three nano-sized PMO materials (DPA-PMO, Am-PMO and Am-ePMO) corresponding to different approaches to introduce coordination sites for lanthanide ions. The PMOs were grafted with Nd³⁺ and Yb³⁺ chloride salts or β -diketonate complexes to obtain NIR emitting materials. Both DPA-PMO and AmePMO are good 'platform' materials for the further functionalization towards the binding of NIR emitting lanthanide ions. The emission spectra of both DPA-PMO@Ln³⁺ and Am-ePMO@Ln³⁺ materials show the characteristic NIR luminescence of the corresponding lanthanide ions. The Yb(hfa)₃ grafted PMO materials show an overall increase in the decay times compared to the YbCl₃ grafted PMO materials. Moreover, both Ln(hfa)₃ grafted DPA-PMO and Am-ePMO materials show good NIR luminescence properties when dispersed in water, which suggests potential application in optical amplification, laser systems or biomedicine.

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Supporting Information for Chapter 2



Figure S2.1 ¹*H NMR spectrum of the DPA-Si precursor.*



Figure S2.2 TEM-EDX mapping of DPA-PMO@NdCl₃ for the following elements: Si, O, Nd (from top to bottom).



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Figure S2.3 TEM images of *Am-PMO* prepared with different amounts of water employed in the synthesis. (a)(b): 200 mL water; (c)(d): 250 mL water; (e)(f): 300 mL water.

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*Figure S2.4 TEM-EDX mapping of Am-PMO@NdCl*₃ *for the following elements: Si, O, Nd (from top to bottom).*

(a) (b) <u>100 nm</u> mn 001 (d) (c) 100 nm 100 nm (e) (f) 100 nm 100 nm (g) (h) 100 nm 100 nm

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Figure S2.5 TEM images of ePMO prepared in different conditions $(a)(b)V_{HCl}: V_{BuOH} = 1.81$, aged at 90 °C for 6 h; $(c)(d) V_{HCl}: V_{BuOH} = 1.57$, aged at 90 °C for 6 h; $(e)(f) V_{HCl}: V_{BuOH} = 0.16$, aged at 90 °C for 6 h; $(g)(h) V_{HCl}: V_{BuOH} = 1.81$, no aging period. The amount of P123, H₂O and HCl is fixed at 1g, 48.7 mL and 2.12 mL, respectively.

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Figure S2.6 TEM images of (a) ePMO@Br; (b) Am-ePMO; (c)Am-ePMO@o-van; (d) Am-ePMO@NdCl₃.



*Figure S2.7 TEM-EDX mapping of Am-ePMO@NdCl*³ *for the following elements: Si, O, Nd (from top to bottom).*

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Figure S2.8 Decay profile of DPA-PMO@NdCl3.



Figure S2.9 Decay profile of DPA-PMO@Nd(hfa)₃.



Figure S2.10 Decay profile of Am-ePMO@NdCl3.

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Figure S2.11 Decay profile of Am-ePMO@Nd(hfa)3.



Figure S2.12 Decay profile of DPA-PMO@YbCl₃. (Orange dots indicates IRF.)



Figure S2.13 Decay profile of DPA-PMO@Yb(hfa)3. (Orange dots indicates IRF.)

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Figure S2.14 Decay profile of Am-ePMO@YbCl₃. (Orange dots indicates IRF.)



Figure S2.15 Decay profile of Am-ePMO@Yb(hfa)3. (Orange dots indicates IRF.)



Figure S2.16 Emission spectra of (a) DPA-PMO@Nd(hfa)₃; (b) DPA-PMO@Yb(hfa)₃; (c) AmePMO@Nd(hfa)₃ and (d) Am-ePMO@Yb(hfa)₃ recorded in water suspension. The spectra were recorded upon excitation at 323 nm (a, b, c) and 372 nm (d).

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Figure S2.17 Emission intensity versus time (1.5 hours, 3 hours, 4.5 hours, 6 hours and 7 days): (a) DPA-PMO@Yb(hfa)₃, (b) Am-ePMO@Yb(hfa)₃; Decay time profiles versus time: (c) DPA-PMO@Yb(hfa)₃, (d) Am-ePMO@Yb(hfa)₃.

To confirm that the lowest triplet levels of PMO materials are well above the accepting levels of lanthanide ions Nd³⁺ and Yb³⁺. The emission spectra of DPA-PMO and Am-ePMO grafted with GdCl₃ at 77 K in ethanol/methanol mixture (4:1) were measured to determine the triplet levels of the PMO materials. ¹ One band can be distinguished when measured at 77 K in Figure S2.18, as well as in Figure S2.20. Subsequently, the maximum decay time was recorded and observed microsecond range lifetimes, confirming the band belongs to the triplet level of the PMO materials (Figure S2.19 and S2.21). The triplet level of the PMO material corresponds to the high-energy edge of the band, the lowest triplet levels are therefore located around 410 nm (DPA-PMO) and 428 nm (Am-ePMO), respectively.

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Figure S2.18 Emission spectra of DPA-PMO grafted with $GdCl_3$ (DPA-PMO@GdCl_3), measured in ethanol:methanol (4:1) solution at RT (black line) and at 77 K (red line).



Figure S2.19 Luminescence decay time of DPA-PMO@GdCl₃ recorded at 410 nm. (Orange dots indicates IRF.)



Figure S2.20 Emission spectra of Am-ePMO grafted with GdCl₃ (Am-ePMO@GdCl₃), measured in ethanol:methanol (4:1) solution at RT (black line) and at 77 K (red line).

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Figure S2.21 Luminescence decay time of Am-ePMO@GdCl₃ recorded at 428 nm. (Orange dots indicates IRF.)

Table S2.1 Physicochemical properties of the PMOs studied in this research. (a determined via the BET equation. b calculated by using BJH model on the desorption branch. c Lattice parameter calculated by $a_0 = 2d_{100}/\sqrt{3}$. d Calculated as the difference between a_0 and D_p .)

Sample	$\frac{S_{BET}}{(m^2g^{-1})}$	V_{p}^{b} (cm ³ g ⁻¹)	D _p ^b (nm)	a ₀ ^c (nm)	d ₁₀₀ (nm)	Wall thickness ^d (nm)
DPA-PMO	977	0.77	3.00	4.80	4.16	1.80
DPA-PMO@NdCl3	835	0.66	2.93	4.76	4.12	1.83
DPA-PMO@Nd(hfa)3	542	0.39	2.77	4.63	4.01	1.86
Am-PMO	856	0.66	3.07	6.14	5.32	3.07
Am-PMO@o-van	528	0.34	2.83	6.14	5.32	3.31
ePMO	911	1.07	5.92	11.32	9.81	5.40
ePMO@Br	704	0.79	4.78	10.19	8.83	5.41
Am-ePMO	648	0.76	5.08	10.19	8.83	5.11
Am-ePMO@o-van	553	0.66	4.97	10.19	8.83	5.22
Am-ePMO@NdCl ₃	458	0.60	5.06	-	-	-
Am-ePMO@Nd(hfa) ₃	433	0.54	5.10	-	-	-

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Table S2.2 Actual Ln^{3+} contents for the Am-PMO@ Ln^{3+} and Am-ePMO@ Ln^{3+} materials determined by ICP-MS analysis.

Sample	Nd ³⁺ (mmol/g)	Yb^{3+} (mmol/g)
DPA-PMO@NdCl ₃	0.1058	-
DPA-PMO@Nd(hfa)3	0.1477	-
DPA-PMO@YbCl3	-	0.1835
DPA-PMO@Yb(hfa)3	-	0.2867
Am-PMO@NdCl3	0.0189	-
Am-PMO@Nd(hfa)3	0.0092	-
Am-PMO@YbCl3	-	0.0274
Am-PMO@Yb(hfa) ₃	-	0.008
Am-ePMO@NdCl ₃	0.1177	-
Am-ePMO@Nd(hfa)3	0.0843	-
Am-ePMO@YbCl ₃	-	0.1377
Am-ePMO@Yb(hfa)3	-	0.1162

Table S2.3 Fitting results of the decay curves of the studied hybrid mesoporous materials.

Samples	Ln	$ au_{l}$ (µs)	$ au_2 (\mu s)$	$ au_{ave}$ (µs)
DPA-PMO@LnCl3	Nd	1.80	0.38	0.62
	Yb	2.67	15.32	8.02
DPA-PMO@Ln(hfa)3	Nd	5.30	1.11	3.66
	Yb	3.23	16.39	10.51
Am-ePMO@LnCl ₃	Nd	3.89	0.80	1.83
	Yb	15.68	3.02	10.11
Am-ePMO@Ln(hfa)3	Nd	2.93	0.61	1.25
	Yb	15.35	3.53	12.35

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The results of this chapter were published in: W. Liu, A. M. Kaczmarek, H. Rijckaert, P. Van Der Voort and R. Van Deun, Chemical sensors based on a Eu (III)-centered periodic mesoporous organosilica hybrid material using picolinic acid as an efficient secondary ligand. *Dalton Trans.*, 2021, **50**, 11061-11070.

Abstract

Through a series of post synthetic modification methods applied to the 100% trans ethenylene-bridged Periodic Mesoporous Organosilica (ePMO), the lanthanidefunctionalized hybrid nanomaterial ePMO@Eu_PA (PA= picolinic acid) has been prepared. The pristine and lanthanide-grafted ePMO materials were characterized by powder X-ray diffraction, DRIFTs, TGA, N₂ sorption, SEM and TEM. The selected PA ligand could effectively sensitize the Eu³⁺ ion, leading to the characteristic luminescence of Eu³⁺ in ePMO@Eu_PA. The luminescence properties of the ePMO@Eu_PA were studied in detail in the solid state and after dispersing in water. The material was investigated for the use as ion sensor and showed a selective monitoring of Fe³⁺, Co²⁺ and Cu²⁺ ions with luminescence quenching. In addition, the material showed a linear relationship between the luminescence intensity and the pH value in the pH range from 7.7 to 10.2. These findings demonstrate that ePMO@Eu_PA possesses potential practical applications in ion sensing as well as in pH sensing.

3.1 Introduction

In recent years, a lot of attention has been given to the research topic of lanthanide materials as luminescent sensor materials, especially lanthanide Metal-Organic Frameworks (MOFs).¹⁻³ In the meantime, Periodic Mesoporous Organosilicas (PMOs), another class of periodic porous materials, are developing into novel sensing support matrices. PMOs are fascinating hybrid materials because of their ordered structure, tunable pore size, tailorable surface properties, and high hydrothermal and mechanical stability. Also, sensitive receptors can be immobilized on the exterior surface or entrapped inside the channels of the PMO framework. For example, Meng et al. investigated a PMO with tetraylnitrilomethylidyne-hexaphenyl (TH) units embedded within the framework. The PMO displayed highly fluorescent and selective sensing towards Cu²⁺ ions.⁴ In another work, a bis(rhodamine Schiff-base derivative) bridged PMO was reported and showed ultra-high selective Cu²⁺ detection compared to other tested metal ions.⁵ Another PMO, which covalently integrated ethidium bromide to its framework, showed high selective sensing towards Hg^{2+} and Fe^{3+} ions and could be used to monitor these two metal ions in water and biological cells even in trace amounts.⁶ As reported many times in literature, ethenylene-bridged PMOs are very interesting hybrid materials, as they offer plenty of opportunities for further surface modification based on olefin chemistry. ⁷⁻¹⁰ To date, ethenylene-bridged PMOs have been synthesized using pure E-diastereoisomer, pure Z-diastereoisomer or a diastereoisomeric mixture of 1,2-bis(triethoxysilyl)ethene. Also, the synthesis of pure diastereoisomeric precursors is more complicated. It was reported that the diastereoisomerically pure E-configured ethenylene-bridged PMOs have higher structural ordering, narrower pore size distributions, and a higher hydrothermal stability than others.¹¹ This very promising PMO is likely to be used in the field of chemical sensing, although it has not been reported so far.

To date, only a few studies have been published regarding lanthanide grafted PMOs for sensing applications. Visible-emitting lanthanide PMOs are being studied and

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developed for sensing applications due to the ease of detection (or by the naked eye) and high sensitivity of luminescence.¹²⁻¹⁴ The lanthanide ions most commonly used in sensing applications are Eu^{3+} or Tb^{3+} because of their strong red or green luminescence, respectively. The direct excitation of electrons in tripositive lanthanide ions is cumbersome due to the parity-forbidden nature of the 4f-4f transitions. One way to overcome this downside, and greatly enhance the luminescence intensity, is to introduce a suitably chosen sensitizing chromophore as a ligand, to excite the lanthanide by the so-called antenna effect.¹⁵ In this effect, light is absorbed by the chromophore, and its energy is transferred to the lanthanide, resulting in sensitized emission.¹⁶ Many ligands have been investigated, mainly focusing on β -diketones, heterobiaryl ligands, cryptands, calixarenes, carboxylic acids, macrocyclic ligands, terphenyl ligands, etc. Picolinic acid is a kind of aromatic carboxylic acid and is regarded as a natural chelator.¹⁷ Picolinic acid facilitates the absorption of minerals such as zinc, copper, iron, magnesium, and probably molybdenum.¹⁸ The presence of the nitrogen atom of the pyridine ring and an oxygen atom of the carboxylate group in picolinic acid enable the formation of a fivemembered chelating ring with the metal ion.¹⁹ Many picolinic acid complexes of metal ions have already been reported, such as some transition metal cations (Cu^{2+} , Fe^{3+} , Zn^{2+} , and Ni²⁺) and lanthanide ions (Sm³⁺, Eu³⁺, Pr³⁺, Nd³⁺, and Ce³⁺).^{20, 21} The picolinic acid complex of Eu³⁺ shows interesting luminescence behaviour both in solid-state and in aqueous solution due to the highly efficient energy transfer from the aromatic groups to Eu^{3+} .²¹ Yong et al. reported that the picolinic acid: Eu^{3+} complex dispersed in SiO₂ xerogels constitutes a thermally stable material, producing a high luminescence intensity, through an in-situ synthesis method.²² As far as we know, only few studies have been reported regarding the introduction of lanthanide picolinate complexes into porous materials. Researchers have studied that the picolinate Tb or Eu complex encapsulated in a silica shell can be used in bioapplications, such as fluorescence biolabeling. ^{23, 24} It is also worth noting that no studies on attaching picolinic acid with Eu³⁺ to PMOs through the post-synthesis impregnation technique have been reported so far.

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Based on the above considerations, herein we first prepared the pure Ediastereoisomer of 1,2-bis(triethoxysilyl)ethene as the organosilica precursor by following a published procedure.^{25, 26} The 100% trans ethenylene-bridged PMO was prepared using the triblock copolymer P123 as a surfactant under acidic conditions. Afterwards, several modifications were made to obtain Am-ePMO@o-van (Am: aminated, o-van: o-vanillin). The Schiff base ligand from Am-ePMO@o-van provides the coordination sites for lanthanide ions. Eventually, the Eu³⁺ ion and picolinic acid were successfully grafted to the variant PMO to obtain the final product ePMO@Eu PA. The hybrid material exhibits characteristic emission of Eu³⁺ because of the efficient 'antenna effect' provided by the picolinic acid ligand. The picolinic acid's strong coordination capability makes this PMO suitable to be used for chemical sensing, such as ion sensing and pH sensing. In this work, this lanthanide grafted PMO material was investigated for its response to different metal ions (Fe³⁺, Hg²⁺, Pb²⁺, Co²⁺, Cr³⁺, Cd²⁺, Ca^{2+} , Zn^{2+} , Cu^{2+}) at a 1000 ppm concentration. On the other hand, the material showed pH-dependent luminescence in alkaline aqueous solution, illustrating its potential application as a pH sensor.

3.2 Experimental section

3.2.1 Sample preparation

Materials The homemade pure E-diastereoisomer of 1,2-bis(triethoxysilyl)ethene (BTSE) was synthesized according to a previously reported procedure.²⁵ All reagents and solvents were used as received without further purification. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123, Aldrich), BuOH (Acros Organics, 99%), diethylenetriamine (DETA, Aldrich, 99%), dimethylformamide (DMF, Aldrich, >99.5%), o-vanillin (Aldrich, 99%), picolinic acid (Acros Organics, 99%) and europium(III) chloride hexahydrate (EuCl₃•6H₂O, Aldrich, 99.9%).

Synthesis of 100% trans ethenylene-bridged PMO (ePMO)

The 100% trans ethenylene-bridged PMO (ePMO) was synthesized by following a

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published method.²⁶ In a typical procedure, a solution containing P123 surfactant (1.00 g), HCl (2.12 mL), BuOH (1.17 mL), and 48.70 mL of H₂O was stirred at room temperature for 2 h. Then pure E-diastereoisomer of 1,2-bis(triethoxysilyl)ethene (BTSE, 1.86 mL) was added dropwise to the above clear solution. The mixture was stirred at 35 °C for 2 h and subsequently aged at 90 °C for 6 h under static conditions. A white powder was harvested by centrifugation and washed with distilled water. At last, Soxhlet extraction was performed on ePMO to remove the surfactant (by using acetone as solvent and operating at 100 °C for 5 h).

Synthesis of brominated-ePMO (ePMO@Br) and aminated-ePMO (Am-ePMO)

The ePMO was functionalized by a bromination reaction to obtain ePMO@Br, achieved in a gaseous phase of Br_2 for 3 h. Then the solid was heated at 120 °C under vacuum to remove any physiosorbed bromine molecules. Subsequently, the ePMO@Br was further modified by a nucleophilic substitution reaction to obtain Am-ePMO. In a typical synthesis, 0.1 g of ePMO@Br was mixed with diethylenetriamine (DETA, 99%; 5 mol equivalents with regard to the amount of bromine) in 50 mL of dimethylformamide (DMF; >99.5%) under an argon atmosphere. After stirring at 100 °C for 5 h, the powder was collected by centrifugation and washed thoroughly with DMF, distilled water and acetone. Finally, it was dried under vacuum at 90 °C.

Synthesis of Am-ePMO@o-van

A Schiff base reaction was carried out by mixing 0.02 g of Am-ePMO and 0.4 g of o-vanillin in 25 mL of methanol and heating at 60 °C for 6 h. Afterwards, the product was collected by centrifugation and washed with methanol and dried in an oven to obtain a yellow solid, named Am-ePMO@o-van.

Synthesis of ePMO@Eu_PA

12.5 mg of Am-ePMO@o-van and 9.6 mg of picolinic acid were dissolved in 6.25 mL THF with stirring. EuCl₃•6H₂O (9.52 mg) was then added into the above mixture. After having reacted for 24 h at 80 °C, the reaction mixture was centrifuged to give the
product (named ePMO@Eu_PA), which was washed three times with THF and dried at 60°C in an oven. The material prepared in THF has superior luminescence properties than the one prepared in methanol, such as a longer luminescence decay time, as shown in Figure S3.1. The post-functionalization procedures for ePMO and the predicted structures of the resulting variant ePMO materials are outlined in Scheme 3.1.



Scheme 3.1 Post-functionalization procedures for ePMO and predicted structures of the resulting variant ePMO materials.

3.2.2 Characterization

Powder X-ray diffraction (PXRD) patterns were recorded using a Thermo Scientific ARL X'TRA diffractometer equipped with a Cu K α (λ = 1.5405 Å) source, at a scanning rate of 0.2° min⁻¹ in Bragg-Brentano configuration in the range of 0.50-10.00° 20. Also, high angle PXRD (2-50° 20) was employed to analyse the final samples for checking the presence of the picolinate europium complex. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs) was performed on a hybrid IR-Raman spectrophotometer, a Thermo Scientific Nicolet 6700 equipped with a nitrogen-cooled Mercury Cadmium Telluride (MCT-A) detector, using a Graseby Specac diffuse reflectance cell. The data were recorded in the region of 650-4000 cm⁻¹ using a DRIFT chamber with KBr/sample mixtures. Thermo-gravimetric analysis (TGA) was carried

out on an SDT Q600 analyser in the temperature range of 25-900 °C under air flow at a heating rate of 10°C min⁻¹. Nitrogen adsorption-desorption isotherms were measured by using a Micromeritics TriStar 3000 analyser at -196 °C. The samples were vacuum dried for 24 h at 120 °C prior to measurement. The Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to calculate the surface areas and pore size distributions of the samples, respectively. Elemental analysis was performed on a Thermo Scientific Flash 2000 CHNS/O analyser by using V2O5 as catalyst. Scanning electron microscopy (SEM) images were collected by using a FEI Quanta 200 FSEM and an FEI Nova 600 Nanolab Dual-Beam focused ion beam in secondary electron mode. Transmission Electron Microscopy (TEM) images were obtained using a Cs-corrected JEOL JEM2200FS transmission electron microscope with a working voltage of 200 kV. Scanning TEM (STEM) images were taken with high-angle annular dark field (HAADF) detector. The presence and distribution of lanthanide ions was determined via energy dispersive X-ray (EDX) spectroscopy in HAADF-STEM mode. The luminescence excitation and emission spectra were recorded using an Edinburgh Instruments FLSP920 UV-vis-NIR spectrometer setup with a 450 W xenon lamp as the steady state excitation source. The emission signals were detected using a Hamamatsu R928P photomultiplier tube. All emission spectra in the manuscript have been corrected for detector response. Luminescence decay times were recorded using a 60W pulsed xenon lamp, operating at a frequency of 100 Hz. Small amounts of solid samples were placed between quartz plates (Starna cuvettes for powdered samples, type 20/C/Q/0.2) when measuring the luminescence properties. Colloidal suspensions of the PMO were measured in quartz cuvettes with a path length of 10 mm. For the ion sensing experiments, the suspensions for luminescence measurement were obtained by treating the samples (1 mg) in the metal nitrate solutions (200 µL) with ultrasound irradiation for 5 minutes. For the pH-dependent luminescence sensing experiments, 1 mg of the samples was immersed in 1 mL of distilled water at different pH values ranging from 2.32 to 11.47 (adjusted with HCl or NaOH) for approximately 5 minutes under ultrasonication treatment. Details for limit of detection

calculation (section S3.1) and stability study (section S3.2) are included in Supporting Information.

3.3 Results and discussion

3.3.1 Material characterizations

In this work, we first prepared ePMO and then modified it to obtain ePMO@Eu_PA. The obtained ePMO is nanostructured, which has already been investigated in our previous study.²⁵ Additionally, in the process of obtaining the ePMO@Eu_PA material, the physical properties of the intermediate products (such as ePMO@Br, Am-ePMO and Am-ePMO@o-van) have also been reported in our previous work.²⁵ The C, H, N contents of the ePMO and its variants are shown in Table S3.1, which reveals the change in composition after modification of the ePMO material. The pristine ePMO and ePMO@Eu_PA were analysed by various characterization techniques.



Figure 3.1 Structural characterization of ePMO, Am-ePMO and ePMO@Eu_PA materials: (a) powder X-ray diffraction (XRD) patterns; (b) diffuse reflectance infrared Fourier transform (DRIFT) spectra; (c) nitrogen adsorption-desorption isotherms; (d) thermogravimetric analysis (TGA) curves of ePMO and ePMO@Eu PA.

To characterize the ordering structure of the materials, powder X-ray diffraction

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(PXRD) analysis was performed, as shown in Figure 3.1(a). A strong signal corresponding to the (100) reflection at low 2 θ (around 0.88°) is clearly visible for ePMO. This is typical for a material with a mesoporous structure. The intensity of reflection (100) becomes weak for both Am-ePMO and ePMO@Eu_PA materials, suggesting that the mesoporous structure is maintained after several modifications. The (100) reflections of the above two materials slightly shift towards higher degrees (2 θ is around 1°), indicating small d₍₁₀₀₎ values.



Figure 3.2 SEM (a) and TEM (b, c) images of ePMO; SEM (d) and TEM (e, f) images of ePMO@Eu PA.

SEM images of ePMO and ePMO@Eu_PA show mostly aggregated particles (Figure 3.2 (a), (d)). Both materials are of non-uniform particle sizes. TEM measurements were also employed to investigate the structure of ePMO and ePMO@Eu_PA. As shown in Figure 3.2 (b) and (e), the particle size is around 500 nm for ePMO and 400 nm for ePMO@Eu_PA. The channel structures in Figure 3.2 (c) and (f) show good agreement with the XRD results. In addition, the presence of the Eu³⁺ ions in the ePMO@Eu_PA material was confirmed by the EDX system coupled to the dark-field TEM. The corresponding elemental maps are shown in Figure S3.2.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs) measurements were carried out to further confirm the successful functionalization of the ePMO material. Figure 3.1(b) shows the DRIFTs spectra of the ePMO, Am-ePMO and ePMO@Eu_PA materials. A broad band around 1200-975 cm⁻¹ is attributed to the asymmetric stretching vibrations of the Si-O-Si framework. A vibration at 1660 cm⁻¹ arises, indicating the presence of primary amines in the Am-ePMO material. Two bands at 1400 cm⁻¹ and 1585 cm⁻¹ can be observed in the spectrum of ePMO@Eu_PA, which can be attributed to the symmetrical stretching vibration and the asymmetrical stretching vibration of the COO⁻ group, respectively.²⁷

The mesoporosity of the materials was evaluated by nitrogen adsorption-desorption measurements. As can be seen in Figure 3.1(c), all the PMO materials show the typical type IV isotherms according to the IUPAC classification with H1-type hysteresis loops at relative pressure in the range 0.45-0.8.²⁸ The BET surface area was calculated to be 656 m²g⁻¹, with an average pore size diameter of 5.3 nm for the ePMO material. It is expected that a pronounced decrease in the BET surface area can be observed after functionalization of the ePMO material. After the nucleophilic substitution reaction, the BET surface area for the Am-ePMO material was calculated to be 475 m²g⁻¹, with an average pore size diameter of 4.9 nm. As for the ePMO@Eu_PA material, the BET surface area was calculated to be 236 m²g⁻¹, with an average pore size diameter of 4.2 nm. From the desorption branch, BJH analysis of the above three materials reveals a narrow pore size distribution (shown in Figure S3.3).

The thermal stability of the pristine and final PMO materials was determined by thermogravimetric analysis (TGA). The TGA profiles of the two materials in Figure 3.1(d) show that both PMO materials are thermally stable up to approximately 300 °C, and gradually decompose at higher temperature. In the beginning of the heating process (below 150 °C), a weight loss of about 12 % for ePMO and 2% for ePMO@Eu_PA happened corresponding to the loss of physically adsorbed water and residual organic solvent, without any decomposition of chemical bonds. The ePMO@Eu_PA is of better thermal stability than ePMO, probably due to the smaller pore size to physically adsorb water or solvent molecules and the existence of lanthanide ions inside the channel. The Eu³⁺ ions grafted inside the channels of the ePMO@Eu_PA are able to stabilize the structure, prevent agglomeration and maintain the mesopores.²⁹

3.3.2 Luminescence properties of ePMO@Eu PA

The photoluminescence excitation and emission spectra of the Am-ePMO@o-van material were recorded at room temperature and have been presented in Figure S3.4. The excitation spectrum was recorded by monitoring the maximum of the emission band. The excitation spectrum consists of a broad band in the range from 260 to 500 nm, with a maximum at 372 nm. A broad band between 400 to 650 nm is observed in the emission spectrum, with a maximum at 500 nm.

The photoluminescence properties of ePMO@Eu_PA were also studied both in the solid state and in an aqueous colloidal suspension at room temperature. The combined excitation-emission spectra are shown in Figure 3.3. The ePMO@Eu_PA sample in the solid state shows strong red emission when placed under a UV lamp (302 nm excitation; see Figure 3.3(a), inset). The peak assignment of the labelled peaks has been done in the Table S3.2 for the sample in the solid state as well as for the suspension. In both ePMO@Eu_PA in the solid state as well as in aqueous suspension, the emission spectra consist of five distinct peaks. These five peaks are attributed to the characteristic 4f-4f transitions from the ⁵D₀ excited state to the lower-lying ⁷F_J (J = 1, 2, 3, 4 and 5) levels of the Eu³⁺ ion.¹² The intensity of the hypersensitive ⁵D₀ \rightarrow ⁷F₂ transition at 615 nm is

the strongest among the five transitions, indicating that the Eu³⁺ ion is sitting in a site with low symmetry. It is worth noting that the emission band of the picolinic acid ligand is not observed, indicating highly efficient energy transfer from the ligand to the Eu³⁺ ion. In the excitation spectra, a strong broad band in the range of 250-300 nm can be observed, which can be ascribed to the energy transfer from the ligand to the metal. The locations of the maximum of the ligand band for both solid state and suspension are the same, indicating that water molecules have almost no influence on the maximum excitation wavelength. The luminescence decay profiles of the ePMO@Eu_PA samples in the solid state and suspension are given in Figure S3.5. The decay profiles could all be well fitted by a double-exponential function, indicating that more than one coordination environment of the Eu³⁺ ion is present in the hybrid material. We also observe a decrease in the decay time when the ePMO@Eu_PA sample is in the suspension ($\tau = 0.20$ ms) compared to that in the solid state ($\tau = 0.63$ ms), most likely due to the quenching effect caused by water molecules.



Figure 3.3 (a) RT solid-state combined excitation-emission spectrum of ePMO@Eu_PA; (b) RT combined excitation-emission spectrum of ePMO@Eu_PA in aqueous suspension (at a concentration of 1 mg of the sample dispersed in 1 mL of water).

3.3.3 Sensing of different ions in aqueous solution

To explore selective metal ion sensing by the ePMO@Eu_PA material, we prepared nine different standard nitrate solutions containing 1000 ppm nitric acid metal salts (Fe³⁺, Hg²⁺, Pb²⁺, Co²⁺, Cr³⁺, Cd²⁺, Ca²⁺, Zn²⁺, Cu²⁺). The colloidal suspensions were obtained by treating the samples (1 mg) in the nitrate solutions (200 μ L) with ultrasound irradiation for 5 minutes. The emission spectra of the ePMO@Eu_PA suspension in the

presence of different metal ions are shown in Figure 3.4 (a). In the presence of Ca^{2+} the material shows enhanced emission intensity compared to the blank sample. Other metal ions have varying degrees of quenching effect on the emission intensity of the ePMO@Eu PA suspension compared to the blank suspension. The emission intensities of the samples in different metal ion solutions have been compared to the blank in Figure 3.4 (b) (luminescence intensities recorded for the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition peak of the ePMO@Eu PA). Interestingly, three metal ions (Fe³⁺, Co²⁺ and Cu²⁺) cause much stronger quenching in the emission intensity than other metal ions $(Hg^{2+}, Pb^{2+}, Cr^{3+}, Pb^{2+})$ Cd^{2+} , Zn^{2+}). In the presence of certain metal ions (such as Fe^{3+} , Co^{2+} and Cu^{2+}), a broad ligand band in the range from 450 to 570 nm can be observed in the emission spectra. This may indicate that the presence of metal ions in the suspension has an influence on the energy transfer mechanism from the ligand to Eu³⁺. These ion sensing results suggest that the ePMO@Eu PA material possesses great potential as a luminescent hybrid material for ion sensing purposes. It shows selective 'turn on' fluorescence for Ca^{2+} and 'turn off' fluorescence for Fe^{3+} , Co^{2+} and Cu^{2+} . Possible reasons for the luminescence 'turn on' and 'turn off' are complex. The 'turn on' fluorescence for Ca²⁺ could possibly be attributed to the interactions between ligands and Ca²⁺ ions, to restrict the O-H bond stretching and thus reduce its quenching effect. It is known that some dblock element ions, such as Co²⁺ and Cu²⁺, have unsaturated d electronic configurations, which enable them to accept energy from lanthanide ions through d-d electron transitions, resulting in the quenching of lanthanide luminescence through $f \rightarrow d$ energy transfer.³⁰

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Figure 3.4 (a) Emission spectra of the colloidal suspensions of ePMO@Eu_PA in the presence of different metal ions when excited at 277 nm; (b) emission intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition peak of the ePMO@Eu_PA material in the presence of different metal ions compared to the blank sample; (c) photograph taken under a UV lamp (302 nm illumination) of ePMO@Eu_PA dispersed in different metal ion nitrate solutions.

The emission intensity of the ePMO@Eu PA suspension was studied at different concentrations of an enhancing ion - Ca^{2+} and of quenching ions - Fe^{3+} , Co^{2+} and Cu^{2+} . To quantitatively investigate the luminescence response of ePMO@Eu PA towards different metal ions, the luminescence enhancement or quenching effect can be rationalized by the Stern–Volmer (S-V) equation: $I_0/I = K_{SVC} + 1$, where I_0 and I represent the luminescence intensities of the ePMO@Eu PA suspension before and after addition of metal ion, respectively; K_{SV} is the Stern–Volmer constant and the value of K_{SV} reflects the luminescence enhancement or quenching efficiencies; c is the molar concentration of the metal ion.^{12, 31} Based on the equation, the K_{SV} values are retrieved from a linear regression fitting and these have been illustrated in Figures 3.5 (b), (d), (f) and (h). The responses of ePMO@Eu PA to the addition of different concentrations of metal ions (Ca^{2+} , Fe^{3+} , Co^{2+} and Cu^{2+}) have been plotted along with the S–V curve (shown in Figures 3.5 (a)-(h)). Regarding the enhancing metal ion Ca^{2+} , the plots for Ca^{2+} can be fitted with a straight line, with a linear correlation coefficient $R^2 = 0.990$. The K_{SV} value is calculated to be 262.8 M⁻¹. As for the quenching metal ions Fe³⁺, Co²⁺ and Cu²⁺, the plots could be also well fitted with a straight line, with very good fits

around 0.99. From the slope we calculated the K_{SV} values, which were determined to be 300 M⁻¹ for Fe³⁺, 3500 M⁻¹ for Co²⁺ and 2100 M⁻¹ for Cu²⁺, respectively. Based on the above results we also determined the limit of detection (LOD), supposing that LOD = $3\sigma/K_{SV}$, where σ is the standard deviation.³² The LOD was calculated to be 0.26 mM for Ca²⁺, 64.5 μ M for Fe³⁺, 26.9 μ M for Co²⁺ and 35.2 μ M for Cu²⁺, respectively. A comparison with other reported porous materials that have been used as metal ion sensors is shown in Table 3.1. It can be concluded that the ePMO@Eu_PA exhibits multi-responsive luminescence sensing towards metal ions and more effective selective detection for Co²⁺. The LOD of Fe³⁺ is comparable to the previous reported Fe³⁺ ion sensor systems. To date, due to the lack of research work on porous luminescent chemosensors for Co²⁺, our research work may provide a reference for others.



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Figure 3.5 Comparison of the luminescence intensity of ePMO@Eu_PA in aqueous suspension treated with various concentrations of metal ions and S–V curves for these ions: (a) and (b): Ca^{2+} , (c) and (d): Fe^{3+} , (e) and (f): Co^{2+} and (g) and (h): Cu^{2+} .

Table 3.1 Comparison between the proposed ePMO@Eu_PA and other reported porous materials for sensing of metal ions.

Porous material	Analyte	Detection solution	LOD (µM)	Ref.
TH-PMO	Cu ²⁺	acetonitrile/water	0.04	4
BRhPMO	Cu ²⁺	ethanol /water	10	5
534-MOF-Tb	Fe ³⁺	water	130	33
FM-SBA-15 FD-SBA-15 FT-SBA-15	Fe ³⁺	water	20.7 43.5 45.6	34
PMBA-SBA	Fe ³⁺	ethanol /water	1.98	35
LMOFs	Fe ³⁺	water	1.77	36
Co-MOF	Fe ³⁺	ethanol	264	37
Tb-MOF	Co^{2^+}	DMF		38
TMU-5S	Ca^{2+}	water	0.017	39
ePMO@Eu_PA	Ca ²⁺ Fe ³⁺ Cu ²⁺ Co ²⁺	water water water water	260 64.5 35.2 26.9	this work

Possible quenching mechanisms for the luminescence response to Fe³⁺, Co²⁺ and Cu²⁺ are further discussed. The I_0/I versus *c* plots are all linear for the whole range of quencher concentrations. The luminescence quenching can be attributed either to being purely dynamic, or purely static. On the contrary, if both static and dynamic quenching were occurring in the sample, an upward curvation of the I_0/I versus *c* plot would be

expected.⁴⁰ This is obviously not the case in our systems, in which a good linear fit can be found. Luminescence lifetime measurements were carried out to further evaluate the nature of the quenching process. As depicted in Figures S3.6-S3.8, the decay profiles of ePMO@Eu_PA in aqueous suspension are almost unchanged with increasing concentration of metal ions. The above behaviour indicates that the quenching is static in all cases. The quenching mechanism by Fe³⁺, Co²⁺ and Cu²⁺ ions may be related to the interactions between the quencher and the non-coordinated picolinate oxygen atom or the amine nitrogen atom.^{13, 17} We have also performed anti-interference tests for ePMO@Eu_PA (shown in Figure S3.9). The presence of a quenching ion (e.g., Zn²⁺, Cu²⁺) caused a decrease in the emission intensity compared to the Ca²⁺ ion intensity. This suggests that the luminescence quenching and enhancing processes are competing in the system. In the coexistence of two metal ions, Ca²⁺ and Co²⁺, the luminescence intensity shows a significant decrease compared to the Ca²⁺ intensity, indicating that the luminescence quenching process is dominant in this system. Therefore, even in a mixed solution, the presence of Co²⁺ can be detected.

3.3.4 pH sensing in aqueous solutions

Due to the existence of the protonated carboxylate in the framework of ePMO@Eu_PA, it can react with an -OH group to be deprotonated, which may cause the change of the local coordination environment, therefore affecting the luminescence properties. As shown in Figure 3.6(a), the luminescence spectra of ePMO@Eu_PA in solutions with different pH values (from 2.32 to 11.47) were measured. When the materials are dispersed in acidic (pH = 2.32) or basic (pH = 11.47) solutions, the characteristic peaks of Eu³⁺ are hardly observed. With the increase of the pH value from 2.32 to 7.73, the luminescence intensity increases. The intensity reaches a maximum when pH = 7.73, which may be attributed to the introduction of Na⁺ ions into the channels of the porous structure, highly influencing the luminescence of Eu³⁺. The Na⁺ ions come from the basic solution adjusted with NaOH. However, when the pH value increases further from 7.73 to 10.23, the intensity of the luminescence gradually

decreases. Interestingly, the luminescence intensity is in linear relation with the pH value in the range from 7.73 to 10.23 (the inset of Figure 3.6(b)). The reason for this may be that the -OH groups react with the proton (of picolinic acid) at lower basicity. That would destroy the electron transfer and the conjugate system, influencing the characteristic transitions of the Eu³⁺ ion and resulting in the quenching of the luminescence. The quenching mechanism is similar to that proposed in previous studies by other researchers.^{41, 42} As compared to the reported pH sensors in Table 3.2, we can find that the linear range of ePMO@Eu PA for detecting pH is limited and only covers alkaline environments. As is known, it is of great importance for health to keep blood and other body fluids slightly alkaline (pH = 7.35-7.45). ePMO@Eu_PA has a linear relationship between the luminescence intensity and pH value from 7.73 to 10.23, and shows the strongest luminescence intensity when pH = 7.73, which may suggest that ePMO@Eu PA material can act as a pH-dependent luminescent sensor in widespread fields spanning from environmental analysis and bioanalytical chemistry to medical diagnostics.⁴³ The recyclability of ePMO@Eu PA as sensing materials were also studied. As shown in Figure S3.10, the red emission signals of the samples almost have no significant change after 5 cycles for pH sensing experiments. The red becomes lighter after 1 cycle, but no change in the following cycles for Co^{2+} sensing experiments. These results mean the Eu³⁺ ions did not come off the PMO. Further PXRD patterns and DRIFT spectra confirmed the retention of the framework of PMO after different treatments (Figure S3.11), which indicated good chemical stability of ePMO@Eu PA.

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Figure 3.6 (a) pH dependent luminescence of ePMO@Eu_PA in solutions with pH value ranging from 2.32 to 11.47. (b) normalized intensity I vs. pH plot. Inset: the linear relationship between I and pH value in the range from 7.73 to 10.23. (c) photograph taken under a UV lamp (302 nm illumination) of ePMO@Eu PA dispersed in solutions with different pH value.

Table 3.2 Comparison between the proposed ePMO@Eu_PA and other reported porous materials in pH detection performances.

Ln porous material	Method	Linear ranges	Ref.
Eu MOF	fluorometric	7.5-10	41
Eu0.05Tb0.95(OBA)(H2O)Cl	fluorometric	3-11	42
Eu ³⁺ @UiO-67-bpydc	fluorometric	1.06-10.99	44
$Eu_{x}Tb_{1-x}Hdpda$	colorimetric, fluorometric	3.9-7.5	45
Eu/Tb-MOFs (PMA)	fluorometric	2-5.5	46
Eu-MOF	fluorometric	3-4	47
ePMO@Eu_PA	fluorometric	7.7-10.2	this work

3.4 Conclusions

In summary, a new Eu³⁺ grafted periodic mesoporous organosilica was developed with the addition of picolinic acid as an efficient co-ligand for creating an antenna effect. Luminescence studies have revealed that the ePMO@Eu_PA shows the characteristic emissions of Eu³⁺ both in the solid state and after dispersing in water. The mesoporous framework and the existence of carboxylate groups in ePMO@Eu_PA make it possess multiple potential applications, for example as an ion sensor or a pH sensor. On the one

hand, we studied ePMO@Eu_PA for ion sensing. The standard solutions we used were 1000 ppm nitric acid metal salts (Fe³⁺, Hg²⁺, Pb²⁺, Co²⁺, Cr³⁺, Cd²⁺, Ca²⁺, Zn²⁺, Cu²⁺). It was observed that the ePMO@Eu_PA could monitor Fe³⁺, Co²⁺ and Cu²⁺ ions with luminescence quenching. It is also to be noted that the ePMO@Eu_PA exhibits greatly sensitive and selective detection of Co²⁺ ions in aqueous suspension among other test ions. More detailed analysis showed that most likely a static quenching mechanism is responsible for the decrease of the luminescence intensity of the ePMO@Eu_PA material in the presence of certain metal ions. On the other hand, the material shows a linear relation between the luminescence intensity and the pH value in the pH range from 7.7 to 10.2. These results indicate that such multi-functional PMO materials have great potential as luminescent sensors for sensing ions in aqueous solution as well as for pH-dependent luminescent sensing in alkaline environments, e.g., in the treatment of environmental sewage and medical diagnostics.

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Supporting Information for Chapter 3



Figure S3.1 Decay profiles of ePMO@Eu_PA prepared in THF or methanol.



Figure S3.2 TEM-EDX mapping of ePMO@*Eu_PA for the following elements: Si, O, Eu (from top to bottom, left to right).*

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Figure S3.3 BJH pore size distribution of PMO materials: ePMO, Am-ePMO and ePMO@Eu_PA (from top to bottom).



Figure S3.4 RT combined excitation-emission spectrum of Am-ePMO@o-van (the dashed line represents the excitation spectrum. The continuous line represents the emission spectrum).



Figure S3.5 Left: decay profile of ePMO@Eu_PA in solid-state form; right: decay profile of ePMO@Eu_PA in aqueous suspension.

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Figure S3.6 Luminescence decay times of an aqueous suspension of $ePMO@Eu_PA$ observed at different concentrations of Fe^{3+} .



Figure S3.7 Luminescence decay times of an aqueous suspension of $ePMO@Eu_PA$ observed at different concentrations of Co^{2+} .



Figure S3.8 Luminescence decay times of an aqueous suspension of ePMO@Eu_PA observed at different concentrations of Cu^{2+} .

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Figure S3.9 (a) Emission spectra and (b) emission intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition peak of $ePMO@Eu_PA$ in the presence of Ca^{2+} and competing ions. (The mixed solution contains: 1 mg $ePMO@Eu_PA / 1$ mL water; 20 μ L Ca^{2+} (1000 ppm) and 20 μ L competing ions (1000 ppm)).

S1. Limit of Detection (LOD) for Ca²⁺, Fe³⁺, Co²⁺ and Cu²⁺

The blank suspensions were prepared by immersing 1 mg of ePMO@Eu_PA in 1 mL water (LOD calculation for Fe³⁺, Co²⁺ and Cu²⁺). The blank suspension for Ca²⁺ was prepared by immersing 1 mg of ePMO@Eu_PA in 200 μ L water. The suspensions with different metal ion concentrations were prepared by adding different volume of metal ion nitrate solutions (1000 ppm) to the blank suspensions for the determination of limit of detection.

Limit of detection (LOD) was calculated using the plots of concentration versus and fluorescence intensity in Figure 3.5. Limit of detection was calculated using the below equation.

$LOD = 3\sigma/k$

Where σ stands for the standard deviation of 3 blank fluorescence intensities, k stands for the slope of the graph (S-V curve). Here, k can be calculated by using Stern–Volmer (S-V) equation: I₀/I = $K_{SV}c+1$. The fitted curves and calculated LOD results are displayed in Figure 3.5 and Table 3.1 in the main text.

S2. Recyclability and stability of ePMO@Eu_PA

Given the importance of recyclability in practical applications, a fast and simple method of recycling as metal ion sensor (Co^{2+} was selected as an example) as well as pH sensor was measured.

For the metal ion sensing experiment, ePMO@Eu_PA was soaked in the Co²⁺

solution for a few minutes for the first quenching experiment. Afterward, the powder of ePMO@Eu_PA was centrifuged and washed several times with distilled water and dried at 80°C. The recovered solid was collected and then used in the successive quenching experiments (four times). For the pH sensing experiment, the recyclability was examined by cyclic detection of pH at pH 7.73 and 10.23. After each treatment, the sample was centrifuged and washed with distilled water, and finally dried in an oven at 80°C.

After each experiment, the recovered sample (in solid-state) was placed under a UV lamp (302 nm illumination) to observe the color change. Eventually, the final recovered samples were characterized by PXRD and DRIFTs to evaluate the stability of ePMO@Eu_PA.



Figure S3.10 Photographs taken under a UV lamp (302 nm illumination) of ePMO@Eu_PA in solid state (top: Co²⁺ sensing; bottom: pH sensing, pH values are 7.73, 10.23, 7.73, 10.23 and 7.73 from left to right, corresponding to cycle 1-5, respectively.)



Figure S3.11 PXRD patterns and DRIFT spectra of ePMO@Eu_PA after different treatments.

Chapter 3 Chemical sensors based on a Eu (III)-centered Periodic Mesoporous Organosilica hybrid material using picolinic acid as an efficient secondary ligand

Sample	C (wt%)	H (wt%)	N (wt%)
ePMO	17.67	2.95	0.14
Am-ePMO	13.43	2.79	3.06
Am-ePMO@o-van	11.51	1.93	5.39
ePMO@Eu_PA	19.42	2.10	5.94

Table S3.1 CHN analysis results of ePMO and its variant materials.

Table S3.2 Assignment of peaks labeled in Figure 3.2 (in the main text).

Label	Wavelength (nm)	Transitions
	Excitation	
a	277	$\pi^* \leftarrow \pi$
b	316	${}^{5}\text{H}_{3} \leftarrow {}^{7}\text{F}_{0}$
с	359	${}^{5}\text{D}_{4} \leftarrow {}^{7}\text{F}_{0}$
d	375	${}^{5}L_{7} \leftarrow {}^{7}F_{0}$
e	392	${}^{5}L_{6} \leftarrow {}^{7}F_{0}$
	Emission	
f	578	${}^{5}D_{0} \rightarrow {}^{7}F_{0}$
g	591	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$
h	615	${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$
i	649	${}^{5}D_{0} \rightarrow {}^{7}F_{3}$
j	699	${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{4}$

Chapter 4. Periodic Mesoporous Organosilica @ NaYF₄: Ln³⁺ nanocomposites as upconversion luminescent sensors for Hg²⁺ ion detection and for water detection in alcohols



The results of this chapter are the subject of a submitted manuscript.

Abstract

Lanthanide-doped upconversion nanoparticles have received growing attention in the development of highly sensitive and selective sensors. Here, three unique organicinorganic hybrid nanocomposite materials prepared by combining NaYF4: Yb³⁺, Ln³⁺ $(Ln^{3+} = Er^{3+}, Tm^{3+}, Ho^{3+})$ and periodic mesoporous organosilica (PMO) are proposed for both metal ion sensing and solvent sensing. The luminescence properties of the developed hybrid materials, PMO@NaYF4: Yb³⁺, Ln³⁺, were studied in detail in the solid state and after dispersing in water. It is found that PMO@NaYF4:Yb³⁺, Er³⁺ showed selective "turn on" luminescence for Hg^{2+} with the detection limit of 24.4 μ M in an aqueous solution. Additionally, the above three materials showed different luminescence emission responses towards water and organic solvents. It is worth noting that all three PMO@NaYF4: Yb³⁺, Ln³⁺ materials showed "turn on" luminescence towards alcohols. PMO@NaYF4: Yb³⁺, Er³⁺ and PMO@NaYF4: Yb³⁺, Ho³⁺ were selected and further developed into sensitive sensors for the detection of water in alcohols by taking advantage of their quenching behavior in water. The detection limit for sensing of water was determined to be 0.21 %, 0.18 % and 0.29 %, corresponding to isopropanol (PMO@NaYF4: Yb³⁺, Er³⁺), n-butanol (PMO@NaYF4: Yb³⁺, Er³⁺) and ethanol (PMO@NaYF4: Yb³⁺, Ho³⁺), respectively. The above results illustrate the potential of these hybrid materials for applications in environmental fields as well as in chemical industries.

4.1 Introduction

Luminescent materials have been widely studied in sensing applications, such as for probing metal ions, as well as detecting specific organic molecules, gas molecules, biomolecules, anions and so on.¹ Lanthanide-doped upconversion nanoparticles have been identified as promising candidates for sensing, bioimaging, and other optical fields in recent years.^{2, 3} By using near-infrared (NIR) light as the excitation source, typical lanthanide-doped upconversion nanoparticles (UCNPs) show anti-Stokes emission (in the visible or ultraviolet region with higher energy) using a stepwise multiphoton process.^{4, 5} The unique upconversion luminescence properties of UCNPs include high photoluminescence intensity, narrow emission bands, superior chemical stability, and excellent photostability.⁶ Furthermore, UCNPs show many advantages including the ability of high penetration depth in biological or environmental samples without causing any significant photodamage to living cells, low autofluorescence, enlarged signal-to-noise ratio and high detection sensitivity. As one of the most excellent upconversion luminescent materials, Ln³⁺-doped NaYF₄ was widely investigated due to its low phonon energy, avoiding excessive losses from non-radiative relaxation.⁷ As far as we know, most research has been focused on its temperature sensing properties, whereas in this work we introduce their chemical sensing properties.

As functionalized nanoparticles, UCNPs have been extensively employed as basic units to construct novel hybrid materials by combining them with mesoporous silica material. The silica coated lanthanide-doped UCNPs have been widely investigated for a large number of applications such as in the development of a new generation of imaging agents for bioimaging ⁸⁻¹¹, photodynamic therapy ¹², and drug delivery ¹³. Ordered mesoporous silica, SBA-15, has also been combined with UCNPs to develop some new composites.^{14, 15} Additionally, periodic mesoporous organosilica materials (PMOs) are especially interesting, as they show higher loading capacities of hydrophilic and hydrophobic molecules than silica as well as excellent biocompatibility. ¹⁶ They also possess good thermal and mechanical stability, resulting in highly stable functionalized composites in combination with UCNPs.¹⁷ PMOs are synthesized from organic-bridged silane precursors R-[Si(X)₃]_n ($n \ge 2$, R = organic group, X = OMe, OEt, O*i*-Pr, allyl) by a surfactant-directed self-assembly approach.¹⁸ In our work, ethylene-bridged PMO was synthesized and then combined with UCNP for obtaining nanocomposites.

Only a few studies have been reported regarding the combination of upconversion inorganic materials with PMOs to obtain PMO@UCNP hybrid materials.^{19, 20} The mesopore walls of PMOs can play a role in the dispersing of lanthanide ions, providing a more homogeneous distribution of lanthanide ions. The presence of additional voids would allow theranostic applications, for example loading drugs within mesoporous structures for additional drug delivery. Recently, three novel hybrid materials prepared by combining β -NaGdF₄: Er³⁺, Yb³⁺ with PMOs were proposed, which showed strong green upconversion emission in the solid state as well as in suspension.¹⁹ In these compounds, the inorganic materials are located inside the hollow PMOs or form a shell around the PMOs. These materials were proven to be non-toxic to human fibroblastic cells and promising candidates for physiological thermometry applications. Up to date, to the best of our knowledge, research towards chemical sensing properties of PMO@UCNP composites involving metal ion and solvent sensing is quite scarce, especially studies reporting composites doped with different lanthanide ions (Yb³⁺/Er³⁺, Yb³⁺/Tm³⁺ or Yb³⁺/Ho³⁺).

In this work, taking advantage of the combined properties of PMOs and UCNPs, we designed three new hybrid materials developed by using a simple method to immobilize NaYF₄: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺, Tm³⁺, Ho³⁺) into the mesopores of nanosized ethylene-bridged PMOs, named PMO@NaYF₄, Yb³⁺, Ln³⁺. The hybrid materials were investigated for their response to different metal ions (Fe³⁺, Hg²⁺, Pb²⁺, Co²⁺, Cr²⁺, Cd²⁺, Ca²⁺, Zn²⁺, Cu²⁺) at a 1000 ppm concentration.

As far as we know, tremendous effort has been devoted to the water detection and quantitative analysis in organic solvents, with the potential applications in food, textile, ceramics, electronic, pharmaceutical, petroleum, and environmental monitoring Chapter 4 Periodic Mesoporous Organosilica @ NaYF₄: Ln³⁺ nanocomposites as upconversion luminescent sensors for Hg²⁺ ion detection and for water in alcohols detection

industries.²¹ In chemical industry, water is often identified as a common impurity and contaminant when producing dry solvents and moisture-sensitive chemicals, which usually results in the decrease of yields and activities in chemical reactions or other industrial production process. The presence of water in petrol engines may cause the engine's performance decrease, resulting in engine damage.²² Undoubtedly, luminescence-based determination of the water content is a much simpler approach than the traditional Karl Fischer titration which requires well-trained operators, special expensive instruments, etc.²¹ Additionally, luminescence sensing analysis for water detection in organic solvents has been proven to be an efficient method for remote and in situ monitoring with ease of fabrication, operational simplicity, intrinsic sensitivity and short response time.²³⁻²⁶ Therefore, with the purpose of investigating these materials as water sensors in organic solvents, we studied the luminescence properties of all hybrid materials when dispersing in various solvents (water, methanol, ethanol, isopropanol, n-butanol, acetone, DMSO, DMF and chloroform). Interestingly, an enhanced luminescent behavior was found when dispersing in alcohols for all three hybrid materials. Therefore, this kind of hybrid materials is capable of water detection in alcohols and in fact, the present PMO@UCNP is the first PMOs example showing such sensing capability.

4.2 Experimental section

4.2.1 Sample preparation

Materials All starting materials were obtained from commercial suppliers and used directly without further purification: cetyltrimethylammonium bromide (CTAB, Acros Organics, 99+%), ammonia (25% aqueous solution) and bis(triethoxysilyl)ethane (ABCR, 97%). Ln (CF₃COO)₃ (Ln = Y, Yb, Er, Tm, Ho) precursors were prepared according to a previously reported protocol.²⁷ For detailed luminescent studies for water detection in organic solvents, the solvents used are: isopropanol (anhydrous; 99.5%; <0.003% water), ethanol (absolute anhydrous; 99.9%; <0.1% water), n-butanol (anhydrous; 99.9%; <0.01% water).

Synthesis of nanosized ethane PMOs

For the synthesis of ethane PMO, we propose a modified procedure according to a published procedure.²⁸ 0.21g of CTAB and 1.5 mL of ammonia were dissolved in 93.5 mL distilled water. The solution was stirred for 30 min to form a clear solution at room temperature. Next, this solution was heated to 50 °C in an oil bath, and bis(triethoxysilyl)ethane (0.72 g) in 4.2 mL ethanol was added dropwise under stirring. The mixture was cooled down to room temperature after 6 h, and then aged overnight without stirring. The product was collected by centrifugation and washed two times with water and once with ethanol. The surfactant template was removed by solvent extraction in acidic ethanol for three times. For 0.5 g of product, 100 mL of ethanol and 0.2 mL of 37% HCl were used (65 °C for 6 h).

Synthesis of PMO@NaYF4: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺, Tm³⁺, Ho³⁺)

In a typical procedure for the synthesis of PMO@NaYF₄: Yb³⁺, Er³⁺, 0.044 g of the as-prepared nanosized ethane PMO was placed in a flask.¹⁹ 3 mmol of CF₃COONa, 1.17 mmol of Y(CF₃COO)₃, 0.3 mmol of Yb(CF₃COO)₃, and 0.03 mmol of Er(CF₃COO)₃ and 5 mL of distilled water were added to the flask, which was then sealed and heated to 40 °C under continuous stirring for 24 h in order to allow the diffusion of the ions inside the mesopores of the ethane PMO. Afterwards, the suspension was centrifuged the next day at 2000 RPM and left to dry at 80 °C in air. Finally, the sample was heat treated under air atmosphere at 300 °C for 3 h. PMO@NaYF₄: Yb³⁺, Tm³⁺, PMO@NaYF₄: Yb³⁺, Ho³⁺ products were prepared in a similar procedure by adding the corresponding Tm(CF₃COO)₃ or Ho(CF₃COO)₃ into the precursor mixture.

Sensing experiments

The sensing ability of the PMO@NaYF₄: Yb³⁺, Ln^{3+} ($Ln^{3+}=Er^{3+}$, Tm^{3+} , Ho^{3+}) hybrid materials was investigated by dispersing 1 mg of the solid sample in 1 mL of metal nitrate solution (1000 ppm) or organic solvent, forming a suspension at a concentration

of 1 mg/1 mL.

4.2.2 Characterization

Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 Advance diffractometer equipped with a Cu K α ($\lambda = 1.5405$ Å) source in a 2 θ range from 10° to 80° with a step size of 0.02°. The reference data were taken from the JCPDS database (Joint Committee on Powder Diffraction Standards). Nitrogen adsorptiondesorption isotherms were measured by using a Micromeritics TriStar 3000 analyzer at -196 °C. The samples were vacuum dried for 24 h at 120 °C before the measurements. The specific surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) method. Transmission Electron Microscopy (TEM) images were obtained using a Cs-corrected JEOL JEM2200FS transmission electron microscope with a working voltage of 200 kV. Scanning TEM (STEM) images were taken with a high-angle annular dark field (HAADF) detector. The composition of the sample was determined via energy dispersive X-ray (EDX) spectroscopy in HAADF-STEM mode. UV-vis absorption spectra were recorded with a Perkin Elmer Lambda 950 spectrometer. The photoluminescence spectra were recorded on an Edinburgh Instruments FLSP920 UVvis-NIR spectrofluorometer with a continuous wave (CW) 975 nm laser with a maximum output power of 400 mW as the steady state excitation source. The emission signals were detected using a Hamamatsu R928P photomultiplier tube.

4.3 Results and Discussion

4.3.1 Characterization of ethane PMO and PMO@NaYF4: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺,





Figure 4.1 (a) Schematic illustration for the preparation of three PMO@NaYF₄: Yb³⁺, Ln³⁺ (Ln³⁺ = Er^{3+} , Tm^{3+} , Ho^{3+}) hybrid materials. TEM images of (b)(c) ethane PMO nanoparticles and (d) PMO@NaYF₄: Yb³⁺, Er^{3+} nanocomposite (scale bar 200 nm or 50 nm or 20 nm). (e) HAADF-TEM image and EDX mapping of PMO@NaYF₄: Yb³⁺, Er^{3+} nanocomposite. The following elements were mapped: Si, O, Na, Y, F, Yb, Er (scale bar 50 nm).

An overview of the developed PMO@NaYF₄: Yb³⁺, Ln³⁺ hybrid materials is given in Figure 4.1 (a). The detailed synthesis routes of the materials are presented in the Experimental Section. The powder XRD pattern of ethane PMO before loading inorganic particles is depicted in Figure S4.1. TEM images of ethane PMO are depicted Chapter 4 Periodic Mesoporous Organosilica @ NaYF₄: Ln³⁺ nanocomposites as upconversion luminescent sensors for Hg²⁺ ion detection and for water in alcohols detection

in Figure 4.1 (b) and (c), showing globular shape with the size distribution in the average particle diameter of 150 nm. Figure 4.1 (d) shows a TEM image of PMO@NaYF4: Yb³⁺, Er³⁺. Figure 4.1 (e) visualizes the PMO nanoparticles after loading with NaYF₄. The presence of NaYF₄: Yb³⁺, Er³⁺ was confirmed by EDX mapping. EDX mapping showed that Na, Y, F, and the lanthanide elements are only distributed in certain areas of the ethane PMO nanoparticles. This observation suggests that most likely small NaYF₄ nanoparticles crystallize inside the pores of the ethane PMO. It is not completely clear how the NaYF₄ builds into the PMO support, therefore N₂ sorption measurements were performed to evaluate the porosity of the obtained hybrid materials (shown in Figure 4.2 (a)). It is expected that a decrease in the BET surface area of PMO@NaYF4: Yb³⁺, Ln³⁺ hybrid materials compared to the pure ethane PMO should be observed. We can observe a clear drop of the surface area from 991 m^2g^{-1} (for pure ethane PMO) to 544 m^2g^{-1} (for PMO@NaYF₄: Yb³⁺, Er³⁺), 710 m^2g^{-1} (for PMO@NaYF₄: Yb³⁺, Tm³⁺) and 619 m²g⁻¹ (for PMO@NaYF₄: Yb³⁺, Ho³⁺), which suggests an incomplete blockage of the pores. All N2 sorption isotherms are type IV with no hysteresis loops, confirming that there was no significant damage to the PMO structure as observed by TEM images. N₂ sorption and EDX mapping suggest that the NaYF₄ is located in some areas of the ethane PMO incompletely clogging up the pores. The powder XRD patterns of PMO@NaYF₄: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺, Tm³⁺, Ho³⁺) hybrid materials are shown in Figure 4.2 (b). The powder XRD patterns of three hybrid materials show broad Bragg peaks, which confirms the ultrasmall size of NaYF4 nanocrystals. It is consistent with EDX mapping and N₂ sorption results which show that NaYF₄ builds into the pores. All samples show a mix of crystal phases of NaYF₄ (hexagonal, JCPDS No. 28-1192, and cubic phases, JCPDS No. 77-2042), with some NaF impurities. The reasons for the existence of two crystal phases are probably due to the time of heat treatment and mesoporous structure of ethane PMO. The walls of the mesopores may limit the growth of the NaYF₄ nanoparticles. Considering the physical dimensions of the NaYF₄ nanoparticles, high surface tension leads to a superior thermodynamic stability of the cubic phase NaYF₄ over that of the hexagonal phase,

even though normally cubic phase stops forming at high temperature.²⁹



Figure 4.2 (a) N_2 adsorption-desorption isotherms of ethane PMO nanoparticles and PMO@NaYF₄: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺, Tm³⁺, Ho³⁺). (b) Combined powder XRD patterns of PMO@NaYF₄: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺, Tm³⁺, Ho³⁺).

4.3.2 Upconversion-luminescence properties of PMO@NaYF4: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺, Tm³⁺, Ho³⁺)

The upconversion luminescence spectra for PMO@NaYF₄: Yb^{3+} , Ln^{3+} ($Ln^{3+} = Er^{3+}$, Tm³⁺, Ho³⁺) have been recorded and are presented in Figure 4.3. The general appearance of the emission spectrum of the PMO@NaYF4: Yb³⁺, Er³⁺ colloidal suspension did not change compared to the solid-state emission spectrum. Green upconversion emissions with the peaks at 521 nm and 540 nm could be assigned to the ${}^{2}\text{H}_{11/2} \rightarrow {}^{4}\text{I}_{15/2}$ and ${}^{4}\text{S}_{3/2} \rightarrow {}^{4}\text{I}_{15/2}$ transitions of Er^{3+} , respectively (Figure 4.3 (a) and (b)). A red emission peak centered at 654 nm is also observed, for the transition from the ${}^{4}F_{9/2}$ excited state to the ${}^{4}I_{15/2}$ ground state. The luminescence properties of PMO@NaYF4: Yb³⁺, Tm³⁺ and PMO@NaYF4: Yb³⁺, Ho³⁺ under excitation of a 975 nm laser at room temperature were also studied. Interestingly there are no significant changes in the emission spectra for both samples in the solid state as compared to the colloidal suspension. As expected, typical emission bands of Tm³⁺, located at 474 nm, 646 nm and 798 nm, which are attributed to the ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$, ${}^{1}G_{4} \rightarrow {}^{3}F_{4}$, and ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transitions, respectively, can be observed in Figure 4.3 (c) and (d). In addition, the upconversion emission intensity at 798 nm is the largest. For PMO@NaYF₄: Yb³⁺, Ho³⁺, three transitions ${}^{5}S_{2}$, ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$, ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ and ${}^{5}S_{2}$, ${}^{5}F_{4} \rightarrow {}^{5}I_{7}$ can be observed at around 540 nm, 643 nm and 751 nm, respectively (in Figure 4.3 (e) and (f)).





Figure 4.3 Upconversion emission spectra of (a) (b) $PMO@NaYF_4$: Yb^{3+} , Er^{3+} , (c) (d) $PMO@NaYF_4$: Yb^{3+} , Tm^{3+} and (e) (f) $PMO@NaYF_4$: Yb^{3+} , Ho^{3+} in the solid state and water suspension (1 mg/mL) under 975 nm laser excitation.

4.3.3 Metal ion selectivity of PMO@NaYF4: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺, Tm³⁺, Ho³⁺)

Up to date, most reported materials used for ion sensing are based on downshifting behavior of mesoporous organosilicas or inorganic materials. Here we explore the possibility to use upconversion luminescence materials-PMO@NaYF₄ nanocomposites for metal ion sensing applications. To explore the metal ion selectivity behavior of PMO@NaYF₄: Yb³⁺, Ln³⁺ (Ln³⁺= Er³⁺, Tm³⁺, Ho³⁺), as-synthesized samples were added into different standard solutions containing 1000 ppm of metal nitrate salts ((Fe³⁺, Hg²⁺, Pb²⁺, Co²⁺, Cr³⁺, Cd²⁺, Ca²⁺, Zn²⁺, Cu²⁺). The target suspensions were obtained by treating the samples (1 mg) in the nitrate solutions (1 mL) with ultrasound irradiation

for 10 minutes (the suspension was freshly prepared, followed by immediate measurements).



Figure 4.4 (a) Luminescence spectra of the colloidal suspensions of PMO@NaYF₄: Yb³⁺, Er³⁺ in the presence of different metal ions, (b) luminescence intensity of the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition (at 540 nm) of PMO@NaYF₄: Yb³⁺, Er³⁺ in the presence of different metal ions compared to the blank sample, (c) luminescence spectra of the colloidal suspensions of PMO@NaYF₄: Yb³⁺, Tm³⁺ in the presence of different metal ions, (d) luminescence intensity of the ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transition (at 798 nm) of PMO@NaYF₄: Yb³⁺, Tm³⁺ in the presence of different metal ions, (d) luminescence of different metal ions compared to the blank sample, (e) luminescence spectra of the colloidal suspensions of PMO@NaYF₄: Yb³⁺, Ho³⁺ in the presence of different metal ions, and (f) luminescence intensity of the ${}^{5}S_{2}$, ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$ transition (at 540 nm) of PMO@NaYF₄: Yb³⁺, Ho³⁺ in the presence of different metal ions, and (f) luminescence intensity of the ${}^{5}S_{2}$, ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$ transition (at 540 nm) of PMO@NaYF₄: Yb³⁺, Ho³⁺ in the presence of different metal ions compared to the blank sample, of different metal ions, and (f) luminescence intensity of the ${}^{5}S_{2}$, ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$ transition (at 540 nm) of PMO@NaYF₄: Yb³⁺, Ho³⁺ in the presence of different metal ions compared to the blank sample.

The luminescence spectra of PMO@NaYF₄: Yb³⁺, Er³⁺ suspensions in the presence of different metal ions have been presented in Figure 4.4 (a). From the column chart presenting the luminescence intensity of the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition (at 540 nm) when in the presence of different metal ions (Figure 4.4 (b)), it can be seen that the luminescence emission intensity was enhanced by the addition of Hg²⁺ in comparison to the blank

sample. Other metal ions have varying slight degrees of quenching effect on the emission intensity of the PMO@NaYF4: Yb³⁺, Er³⁺ suspension compared to the blank suspension. The sensing abilities of PMO@NaYF4: Yb³⁺, Tm³⁺ and PMO@NaYF4: Yb³⁺, Ho³⁺ were also investigated in detail, displayed in Figure 4.4 (c)-(f). As can be seen in Figure 4.4 (d), the PMO@NaYF₄: Yb³⁺, Tm³⁺ suspensions show enhanced luminescence intensity by the addition of Zn^{2+} , Fe^{3+} and Ca^{2+} , but decreased luminescence intensity when adding other metal ions. Zn²⁺ shows stronger enhancement, whereas Pb²⁺ shows stronger quenching in the emission intensity. For PMO@NaYF4: Yb³⁺, Ho³⁺ suspensions (Figure 4.4 (f)), the luminescence intensity shows a slight enhancement in the presence of Pb^{2+} , Zn^{2+} , Cr^{3+} , and Ca^{2+} . The other test metal ions have a quenching effect on the luminescence intensity, especially Fe³⁺ causes stronger quenching behavior. It is noteworthy that the above materials showed different metal ion sensing behavior, most likely due to the different dopant ions Er³⁺, Tm³⁺, and Ho³⁺. In several different studies lanthanide compounds (like inorganic phosphors or MOFs) were also reported to show diverse quenching behaviors. The possible reasons for luminescence enhancement or quenching are complex in PMO@NaYF4: Yb³⁺, Ln³⁺ suspensions when adding different metal ions. It is apparent that the chemical or physical surroundings are altered by the presence of the certain metal ions in PMO@NaYF4: Yb³⁺, Ln³⁺ systems.³⁰ Considering the above results, PMO@NaYF4: Yb³⁺, Er³⁺ shows better ion sensitivity (especially for Hg²⁺) than other two hybrid materials.

Generally, quenching can occur during the excited state lifetime (such as collisional quenching, energy transfer or charge transfer reaction) or they can occur in the ground state due to the formation of complexes.³¹ There are two common quenching process, dynamic quenching and static quenching. Dynamic quenching originates from the collision between the excited fluorophore and quencher that can facilitate non-radiative transitions to the ground state. Static quenching occurs when a nonfluorescent ground-state complex is formed through the interaction between fluorophore and quencher. To gain knowledge about the mechanism of ion sensing behavior in our systems, further
studies were carried out on the sensing properties for PMO@NaYF₄: Yb^{3+} , Er^{3+} towards Hg^{2+} and Ca^{2+} .



Figure 4.5 Luminescence spectra of a colloidal suspension of PMO@NaYF₄: Yb^{3+} , Er^{3+} in the presence of different concentrations of (a) Hg^{2+} and (c) Ca^{2+} . Stern-Volmer plots of PMO@NaYF₄: Yb^{3+} , Er^{3+} for various concentrations of (b) Hg^{2+} and (d) Ca^{2+} . Inset is the linearity of the Stern-Volmer plots for (b) Hg^{2+} and (d) Ca^{2+} and (c) Ca^{2+} . Inset is the linearity of the Stern-Volmer plots for (b) Hg^{2+} and (c) Ca^{2+} .

Figure 4.5 presents the change in the emission intensity of the PMO@NaYF₄: Yb³⁺, Er^{3+} suspensions at different concentrations of the enhancing ion Hg²⁺ and a quenching ion Ca²⁺. The luminescence enhancement or quenching efficiency (K_{SV}) was analyzed using the Stern–Volmer (S–V) equation, I₀/I = K_{SV} c +1 (I and I₀ are the luminescence intensity of a colloidal suspension of PMO@NaYF₄: Yb³⁺, Er^{3+} in the presence and absence of the metal ion, and c is the concentration of the metal ion). The Stern-Volmer (S-V) plot for PMO@NaYF₄: Yb³⁺, Er^{3+} colloidal suspensions treated with different Hg²⁺ concentrations (Figure 4.5 (b)) shows a linear behavior at low Hg²⁺ concentrations and a nonlinear upward curvature at high concentrations. This enhancing phenomenon indicates that the luminescence enhancing effect can be attributed to a combination of dynamic and static enhancement. It may be related to the stabilization effect of the composites originating from the Hg²⁺ addition, as mentioned in the previous studies.³²

The S-V plot can be fitted with a straight line at low Hg²⁺ concentrations ($0\sim214.6 \,\mu\text{M}$), $I/I_0 = 0.0165c + 0.8679$, $R^2 = 0.99$. Moreover, we observe an increase of the slope with a temperature increase from 25 °C to 45 °C suggesting the existence of some dynamic enhancement (Figure S4.2). The limit of detection (LOD) is determined by assuming that LOD = $3\sigma/K_{SV}$, where σ is the standard deviation.³³ The LOD for Hg²⁺ was calculated to be 24.4 µM and a comparison with other reported upconversion luminescence materials that have been used as Hg^{2+} sensors is shown in Table S4.1. From the table we see that our proposed material PMO@NaYF4: Yb³⁺, Er³⁺ for Hg²⁺ sensing has not the lowest detection limit, but shows a wider linear range than other materials, which suggests a good performance in the quantification of Hg^{2+} . Additionally, we have also analyzed the emission intensity of PMO@NaYF₄: Yb³⁺, Er^{3+} suspension in the presence of different concentrations of Ca²⁺, as an example for showing the quenching luminescence behavior (Figure 4.5 (c) and (d)). The S-V plot shows an upward curvature, suggesting the quenching process follows a dynamic and static mechanism. The S-V plot could also be fitted linearly with $R^2 = 0.98$ and quenching constant K_{SV} = 900 M⁻¹ at low Ca²⁺ concentrations. The LOD was calculated to be 26.8 µM.

The anti-interference tests were also performed, and the results are shown in Figure S4.3. In the coexistence of a quenching ion (e.g., Ca^{2+} , Fe^{3+} , Co^{2+} ...) and Hg^{2+} , the luminescence intensity shows an enhancement compared to the intensity of the quenching ion, indicating that the luminescence enhancing process is dominant in this system. Therefore, even in a mixed solution where other ions are present, the presence of Hg^{2+} can be detected based on the stronger emission intensity of the solutions.

4.3.4 Organic solvent selectivity and water detection in organic solvents

To examine the potential of PMO@NaYF4: Yb^{3+} , $Ln^{3+}(Ln^{3+} = Er^{3+}, Tm^{3+}, Ho^{3+})$ for the sensing of small molecules, their luminescence properties in various solvents were investigated. The solvents used were water, methanol, ethanol, isopropanol, n-butanol, acetone, DMSO, DMF, and chloroform.



Figure 4.6 (a) Luminescence spectra of PMO@NaYF₄: Yb³⁺, Er³⁺ dispersed in different solvents, (b) luminescence intensity of the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition (at 540 nm) of PMO@NaYF₄: Yb³⁺, Er³⁺ dispersed in different solvents, (c) luminescence spectra of PMO@NaYF₄: Yb³⁺, Tm³⁺ dispersed in different solvents, (d) luminescence intensity of the ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transition (at 798 nm) of PMO@NaYF₄: Yb³⁺, Tm³⁺ dispersed in different solvents, (e) luminescence spectra of PMO@NaYF₄: Yb³⁺, Tm³⁺ dispersed in different solvents, (e) luminescence spectra of PMO@NaYF₄: Yb³⁺, Tm³⁺ dispersed in different solvents, (e) luminescence spectra of PMO@NaYF₄: Yb³⁺, Ho³⁺ dispersed in different solvents, and (f) luminescence intensity of the ${}^{5}S_{2}$, ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$ transition (at 540 nm) of PMO@NaYF₄: Yb³⁺, Ho³⁺ dispersed in different solvents.

As shown in Figure 4.6, the general appearance of the luminescence spectra for PMO@NaYF₄: Yb³⁺, Ln³⁺ in different solvents is the same as that of the metal nitrate solutions (in Figure 4.4). The luminescence intensity of the strongest emission peak for these three materials dispersed in different solvents are displayed in Figure 4.6 (b), (d), (f), corresponding to PMO@NaYF₄: Yb³⁺, Er³⁺, PMO@NaYF₄: Yb³⁺, Tm³⁺ and PMO@NaYF₄: Yb³⁺, Ho³⁺, respectively. The first observation which can be made is that the intensity varies for all samples when dispersed in different solvents, showing a

different degree of enhancement (or quenching as in the case of PMO@NaYF4: Yb³⁺, Tm³⁺ dispersed in acetone or chloroform) compared to the water suspension. It is noted that the luminescence intensity for PMO@NaYF4: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺, Tm³⁺, Ho³⁺) dispersed in n-butanol is the strongest compared to other solvents. Interestingly, as the number of carbon atoms in the alcohols increases (from methanol, ethanol, isopropanol to n-butanol), the luminescence intensity for PMO@NaYF4: Yb³⁺, Ln³⁺ (Ln³⁺ = Er³⁺, Tm³⁺, Ho³⁺) suspensions is gradually enhanced, which could be ascribed to the decrease of solvent polarity.

The above observations, especially the weak luminescence intensity of the PMO@NaYF4: Yb³⁺, Er³⁺ and PMO@NaYF4: Yb³⁺, Ho³⁺ materials in water suspensions, prompted us to test the performance of these two materials as water detector in organic solvents. As examples, the addition of water into a suspension of PMO@NaYF4: Yb³⁺, Er³⁺ in anhydrous isopropanol or n-butanol as well as a suspension of PMO@NaYF4: Yb³⁺, Ho³⁺ in anhydrous ethanol were investigated. As shown in Figure 4.7 (a), (c) and (e), the luminescence emission is gradually quenched with the increase of water in organic solutions. The changes in luminescence intensity upon addition of water shown in Figure 4.7 (b), (d) and (f) exhibit two-separated linearity, indicating a nonlinear quenching effect. Figure 4.7 (b) shows the luminescence intensity decreased with the addition of water in isopropanol solution of PMO@NaYF₄: Yb³⁺, Er^{3+} . It can be found that when the water content exceeds 0.75%, the decrease of luminescence intensity gradually slows. The same trend can also be found in n-butanol solution of PMO@NaYF4: Yb³⁺, Er³⁺ and ethanol solution of PMO@NaYF4: Yb³⁺, Ho³⁺. The resulting calibration curves for water show good linearity for the low concentration range below 0.75% with correlation coefficient of 0.97, 0.98 and 0.94, corresponding to Figure 4.7 (b), (d), and (f), respectively. The detection limit for water was calculated to be 0.21 % in isopropanol solution, 0.18 % in n-butanol solution and 0.29 % in ethanol solution. The limit of detection is comparable to the previous results reported (Table S4.2). Therefore, these materials could have the possibility for the determination of the water content of organic solvents in chemical

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industries producing anhydrous solvents and for industries manufacturing oils and petroleum products, in which water is a common contaminant and impurity. In addition, the phase structures of PMO@NaYF₄: Yb³⁺, Tm³⁺ materials after sensing experiments are shown in Figure S4.4. The composites still maintain its original crystal phase, indicating the well phase stability for the composites.



Figure 4.7 (a) Changes in the luminescence spectra of PMO@NaYF₄: Yb³⁺, Er³⁺ in anhydrous isopropanol upon addition of water, and (b) corresponding normalized emission intensity of the ${}^{4}S_{3/2}$ $\rightarrow {}^{4}I_{15/2}$ transition (at 540 nm) dependence on water concentration. (c) changes in the luminescence spectra of PMO@NaYF₄: Yb³⁺, Er³⁺ in anhydrous n-butanol upon addition of water, and (d) corresponding normalized emission intensity of the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition (at 540 nm) dependence on water concentration. (e) changes in the luminescence spectra of PMO@NaYF₄: Yb³⁺, Ho³⁺ in anhydrous ethanol upon addition of water, and (f) corresponding normalized emission intensity of the ${}^{5}S_{2}$, ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$ transition (at 540 nm) dependence on water concentration.

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The mechanism of luminescence "turn off" behavior for the detection of water in organic solvents (alcohols) is complex. The organic solvent molecules may interact with both NaYF4: Yb³⁺, Ln³⁺ particles and water molecules, which affect the upconversion emission. The third vibrational overtone of OH-stretching of water can bridge the gap of ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition (~10 200 cm⁻¹) of Yb³⁺ causing relaxation to ground state.³⁴ Water molecules in dispersion can also accept the energy from excited lanthanide ions.³⁵ In addition, the direct water absorption of part of the excitation energy is another effect for water induced upconversion luminescence quenching. Based on the above information, we proposed the probable energy upconversion pathway, as illustrated in Figure 4.8. Figure S4.5 shows the absorption of isopropanol solvent containing varied water content. At very low concentration, water absorption at around 975 nm is almost negligible. An obvious water absorption can be observed when the water content reaches 1%. Similar absorption behavior was also observed while measuring ethanol solvent with varied water content (Figure S4.7). Interestingly, the water absorption at 975 nm can be seen even if only a small amount of water (0.2%) is present in n-butanol (Figure S4.6). We therefore deduce that the significant influence of water absorption on upconversion emission quenching usually refers to the high water concentration (typically >1 %).



Figure 4.8 Schematic illustration of water molecule induced upconversion emission quenching of $PMO@NaYF_4:Yb^{3+}$, Er^{3+} nanoparticles. Energy level diagrams on the right panel illustrate the proposed upconversion mechanisms of $PMO@NaYF_4:Yb^{3+}$, Ln^{3+} ($Ln^{3+} = Er^{3+}$, Tm^{3+} , Ho^{3+}). (The dashed-dotted, dashed, dotted, blue wavy, and colored solid arrows represent photon excitation, energy transfer, multiphonon relaxation, water induced energy depletion, and emission process, respectively.

4.4 Conclusion

 $PMO@NaYF_4:Yb^{3+}$, Ln^{3+} ($Ln^{3+} = Er^{3+}$, Tm^{3+} , Ho^{3+}) composites have been successfully synthesized via an easy method and were further studied for the potential use as chemical sensors. The synthesized particles are nano-sized and exhibit a mix of crystal phases of NaYF4 (hexagonal and cubic phases). The small NaYF4 nanoparticles crystallize inside the pores of the PMO, which was confirmed by N₂ sorption and EDX mapping analysis. The luminescence spectra of both the solid state and colloidal suspensions of PMO@NaYF₄:Yb³⁺, Ln³⁺ have been investigated at room temperature. To the best of our knowledge this is the first study where PMO@UCNP composites are investigated for their use as ion sensors and water sensors in organic solvents. Therefore, this work may open a new window for designing PMO-based upconversion luminescent sensors. On the one hand, all three samples, PMO@NaYF4:Yb³⁺, Er³⁺, PMO@NaYF4:Yb³⁺, Tm³⁺ and PMO@NaYF4:Yb³⁺, Ho³⁺, were used to prepare colloidal suspensions containing various metal ions (Fe³⁺, Hg²⁺, Pb²⁺, Co²⁺, Cr²⁺, Cd²⁺, Ca^{2+} , Zn^{2+} , Cu^{2+}) for evaluating the metal ion sensing properties. It is found that PMO@NaYF4:Yb³⁺, Er³⁺ showed better selectivity and sensitivity for Hg²⁺ at concentrations ranging from 0 to 214 µM, with a detection limit of 24.4 µM. On the other hand, the organic solvent sensing ability was studied for all hybrid materials. All three materials showed gradually enhanced luminescence properties when dispersed in alcohols (from methanol to n-butanol), which makes them promising materials for the detection of water in organic solvents. The as-prepared PMO@NaYF4:Yb³⁺, Er³⁺ was adopted as a luminescent probe for the detection of water in isopropanol and n-butanol. Additionally, the detection of water in ethanol was employed by using PMO@NaYF₄:Yb³⁺, Ho³⁺. The detection limit for water was calculated to be 0.21 %, 0.18 % and 0.29 %, corresponding to isopropanol, n-butanol and ethanol, respectively. The possible mechanisms for water detection in alcohols are attributed to the energy transfer between Yb^{3+} and water molecules, water absorption of the excitation energy, and partially due to the increase of the solvent polarity caused by the increase of the water concentration.

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Supporting Information for Chapter 4



Figure S4.1 Powder XRD pattern of ethane PMO used for the preparation of PMO@NaYF₄: Yb^{3+} , Ln^{3+} (Ln = Er; Tm, Ho) nanocomposites.



Figure S4.2 The Stern-Volmer plots of PMO@NaYF₄: Yb^{3+} , Er^{3+} in the presence of Hg^{2+} ions at different temperatures (25 °C and 45 °C). An increase of the slope with temperature increase suggests presence of dynamic quenching mechanism.



Figure S4.3 Luminescence emission intensity of PMO@NaYF₄: Yb^{3+} , Er^{3+} in the presence of a single competing ion (red bars) and in the mixture of Hg^{2+} and competing ions (black bars).



Figure S4.4 Combined powder XRD patterns of PMO@NaYF₄: Yb^{3+} , Tm^{3+} before and after sensing experiments.



Figure S4.5 Absorption spectra of isopropanol containing varied water content.



Figure S4.6 Absorption spectra of n-butanol containing varied water content.

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Figure S4.7 Absorption spectra of ethanol containing varied water content.

Table S4.1	Comparison	of various	upconverison	luminescence	sensors for	Hg ²⁺ detection
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Sanaana	Structure	Linear range	Limit of	Def	
Sensors	property	(µM)	detection (µM)	Kel.	
A-DMSA-UCNPs	Core-Shell	24-120	2.47	1	
A-PAA-UCNPs	Core-Shell	13.4-40	8.15	1	
Ru-UCNP@HmSiO2-PEI	Core-Shell	0-46	0.16	2	
UCNPs-aptamers-GNPs	Mixture	0.2-20	0.06	3	
UCNP/ QDs	Composites	0.01-2.8	0.015	4	
$DMO@NeVE ·· Vh^{3+} Er^{3+}$	Composites;	0 214 6	24.4	This	
	porous	0-214.0	24.4	work	

Table S4.2 Comparison of various materials for determination of water content in organic solvents.

Sensors	Measured media	Linear range (v/v)	Limit of detection (v/v)	Ref.
Lignin-derived red- emitting CDs	Ethanol	10-60%	0.36	5
MOF:Tb	Ethanol	0-11.76%	1.12%	6
FS@ZIF-9/Co-formate	Ethanol isopropanol	0-10%	0.43% 0.63%	7
Eu ³⁺ @UiO-66-NH ₂ -IM	Ethanol	0-2%	0.088%	8
PMO@NaYF4: Yb ³⁺ , Er ³⁺	Isopropanol n-butanol	0-0.75%	0.21% 0.18%	This work
PMO@NaYF ₄ : Yb ³⁺ , Ho ³⁺	Ethanol	0-0.75%	0.29%	This work

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Chapter 5. Summary and outlook

5.1 Summary

The goal that was put forward for this PhD thesis comprised the preparation of novel nano-sized lanthanide PMO materials and the exploration of their potential applications as sensors. I started with three different functional nano-sized lanthanide PMOs with different synthesis approaches for near-infrared emission. Then I selected one of the above PMO materials, ePMO, for further functionalization with Eu³⁺ ions accompanied with picolinic acid acting as antenna ligand, obtaining the final PMO material for metal ions and pH sensor applications. At last, I proposed novel PMO composites combined with upconversion NaYF₄:Ln³⁺ nanoparticles for detecting Hg²⁺ ions and water in alcohols. Two different PMO systems were adopted in this thesis, one is a PMO grafted with lanthanides, and the other is a PMO in which lanthanide upconversion luminescent PMO materials were studied in this work for sensing applications.

In Chapter 2 the work on near-infrared emitting lanthanide PMO materials was presented, describing the characterization of these materials, and their luminescence properties. Three nano-sized PMO materials were proposed: a PMO material functionalized with pyridine dicarboxamide (DPA-PMO) and two amine functionalized PMO materials (Am-PMO and Am-ePMO). These PMOs were grafted with Nd³⁺ and Yb³⁺ chloride salts or β -diketonate complexes to obtain NIR emitting materials. In this study 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (Hhfa) was selected as the ligand to prepare lanthanide β-diketonate complexes. The pyridine dicarboxamide ligands in the DPA-PMO material provided the tethering sites for Ln³⁺-coordination. A Schiff base reaction was carried out on the amine functionalized PMOs to introduce similar lanthanide coordination sites. All pristine PMOs and lanthanide PMOs were characterized through PXRD, N2 sorption, DRIFTs, ICP-MS and TEM. The DPA-PMO and Am-ePMO materials acted as good platforms for NIR luminescence. A significant enhancement in the decay time was observed upon grafting an Yb(hfa)₃ complex to the PMO materials instead of YbCl₃. All of the DPA-PMO@Ln(hfa)₃ and AmePMO@Ln(hfa)3 materials showed characteristic NIR emission performance both in the solid state and in aqueous suspension. The stability of DPA-PMO@Yb(hfa)₃ and Am-ePMO@Yb(hfa)₃ in water suspensions were also studied. It was found that no significant changes in emission intensity were observed, nor in the decay time, even after 7 days. The promising results obtained for all of the DPA-PMO@Ln(hfa)₃ and Am-ePMO@Ln(hfa)₃ materials with regard to their luminescence properties, more specifically their good NIR luminescence properties when dispersed in water, makes them very promising materials for biological applications.

In Chapter 3 a study was presented on chemical sensing (ion sensing and pH sensing) by a lanthanide ePMO material. A new Eu³⁺ grafted PMO material was developed with the addition of picolinic acid (PA) as an efficient co-ligand for creating an antenna effect. Luminescence studies revealed that the ePMO@Eu PA showed the characteristic emissions of Eu³⁺ both in the solid state and after dispersing in water. The luminescence intensity of the ePMO@Eu PA suspensions in the presence of Fe^{3+} , Co^{2+} and Cu^{2+} ions decreased a lot, while for the material in Ca²⁺ solution, the emission intensity increased. The material exhibited sensitive and selective detection of Co^{2+} ions in aqueous suspension among other tested ions, with LOD of 26.9 µM. More detailed analysis showed that most likely a static quenching mechanism is responsible for the decrease of the luminescence intensity of the ePMO@Eu PA in the presence of quenching metal ions. Here in this study the selectivity of Co^{2+} is reported, which is rarely found in other research work on porous luminescent chemosensors and which forms an added value to this study. Furthermore, the material showed a linear relationship between the luminescence intensity and the pH value in the pH range from 7.7 to 10.2. At last, the excellent chemical stability of ePMO@Eu PA was proven by PXRD and DRIFTs analysis after 5 cycles of sensing experiments. These findings demonstrate that ePMO@Eu PA possesses great potential as a luminescent sensor for ion sensing in aqueous solution as well as for pH-dependent sensing in alkaline environments.

In **Chapter 4** a study was reported on three unique organic-inorganic hybrid nanocomposite materials prepared by combining an ethane PMO with NaYF₄: Yb³⁺, Ln^{3+} ($Ln^{3+} = Er^{3+}$, Tm^{3+} , Ho³⁺) for the potential use as metal ion sensors and solvent

sensors. Unlike the PMO material in Chapter 3, where lanthanide complexes were covalently grafted into the framework of PMOs in a post-functionalization synthesis procedure, here in Chapter 4, the upconversion nanoparticles were immobilized inside the PMO channels by a very simple method. The NaYF₄ nanoparticles crystallized inside the pores of the PMO, which was confirmed by N2 sorption and EDX mapping analysis. The luminescence properties of PMO@NaYF4: Yb³⁺, Ln³⁺ were studied in detail in the solid state and after dispersing in water. It was found that PMO@NaYF4:Yb³⁺, Er³⁺ showed selective "turn on" luminescence for Hg²⁺ with a detection limit of 24.4 µM in an aqueous solution. Additionally, all three materials showed gradually enhanced luminescence properties when dispersed in alcohols (from methanol to n-butanol), which makes them promising materials for the detection of water in organic solvents. For example, the detection of water in ethanol was employed by using PMO@NaYF4: Yb³⁺, Ho³⁺, with a detection limit of 0.29 %. In addition, an excellent phase stability for the composites was proven by analysing PXRD patterns of PMO@NaYF4: Yb³⁺, Tm³⁺ after the sensing experiments. The above results illustrate the potential of these hybrid materials for applications in environmental fields as well as in chemical industries (producing anhydrous solvents), and in fact the present PMO@UCNP in this study is the first PMO example showing such sensing capability.

5.2 Outlook

In this final section, I would like to state my personal outlook regarding luminescent lanthanide PMO materials.

The research performed in this thesis shows that great potential lies within the hybrid mesoporous materials. However, many challenges remain for further improvement of their overall properties and potential future application of these hybrids can be found in other fields, like catalysis, adsorption, low-*k* materials and biomedicine. Even though various nano-sized PMO materials were proposed in this thesis, the size-controllable and uniformly distributed nanoparticles are still difficult to synthesize. In **Chapter 2** I only tried to change some experimental conditions such as the aging period, for obtaining nano-sized PMO materials. A series of changes on pH, additives, temperature,

reaction time and reactant ratio can be carried out for comprehensive understanding of the effects of these factors on the morphologies of PMO materials. Additionally, it is possible to prepare hollow PMO materials by using hard templates such as silica for all of the above reported hybrid materials, since the synthesis of these nanoparticles with controlled sizes is well mastered. Nano-sized PMOs are more efficient than bulk PMOs, especially in sensing and biomedical applications. Considering the excellent luminescence properties of these lanthanide PMO materials, it will be interesting to explore the possibility for nanomedical application in the future.

In **Chapter 3 and 4**, I studied the sensing properties of these lanthanide PMOs in known systems. However, for practical applications the reaction systems would be complex, so it will be more useful to explore the luminescence sensing performance when these samples are dispersed in real environments, such as wastewater or drinking water. Furthermore, the luminescence enhancement/quenching mechanism can be clearer in the presence of some metal ions. If more advanced characterization methods (XPS, ICP-MS) could be introduced, more information will be known, for instance, whether there are new chemical bonds formed and the percentages of the metal ions remaining in the samples, which will help to investigate the mechanism for the selective sensing of metal ions.

Additionally, there is still a need to work further to improve the luminescence efficiency, for instance, by introducing other antenna ligands to PMOs. The ligand can be built into the PMO framework or grafted with lanthanides as a secondary ligand. The ligand should contain a number of properly organized binding sites providing a complete saturation of the Ln^{3+} first coordination sphere, in order to minimize the nonradiative deactivation by vibronic quenchers. Additionally, the energy gap between the triplet state of the ligand and the resonance level of the Ln^{3+} cation should be proper, to ensure the efficient energy transfer and to avoid possible back energy transfer deactivation processes. In conclusion, the further development of novel well-designed functional PMOs with more complex frameworks, as well as the expansion of lanthanide PMOs applications holds great potential but requires much more work to

fully explore this topic.

Nederlandse Samenvatting

De doelstelling vooropgesteld voor deze PhD thesis bevat de bereiding van nieuwe lanthanide PMO materialen op nanoschaal en daarbij het onderzoek naar hun mogelijke toepassingen als sensors. Ik ben begonnen met drie verschillende functionele, lanthanide PMOs met nano-afmetingen, gesynthetiseerd volgens verschillende methodes, voor nabij-infrarood emissie. Daarna heb ik 1 van deze PMOs geselecteerd, namelijk ePMO, voor verdere functionalisering met Eu³⁺ ionen gecombineerd met picolinezuur (dat dient als antenne ligand) waaruit het finale PMO materiaal werd behaald voor metaalion en pH sensor toepassingen. Tot slot, heb ik PMO-composiet materialen, gecombineerd met upconversion NaYF4:Ln³⁺ nano-deeltjes, voorgesteld voor de detectie van Hg²⁺ ionen en water in alcoholen. Zowel downshifting als upconversion luminescente PMO materialen zijn onderzocht in dit project voor sensing toepassingen.

In Hoofdstuk 2 is het werk omtrent nabij-infrarood emitterende, lanthanide PMO materialen weergegeven, waarin hun karakterisering en luminescentie eigenschappen beschreven worden. Drie PMO materialen van nano-afmetingen werden voorgesteld: een PMO materiaal gefunctionaliseerd met pyridine dicarboxamide (DPA-PMO) en twee amine gefunctionaliseerde PMO materialen (Am-PMO en Am-ePMO). Aan deze PMOs werden Nd^{3+} en Yb^{3+} chloride zouten of β -diketon complexen toegevoegd om NIR emitterende materialen te bekomen. In deze studie werd 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (Hhfa) gekozen als ligand voor de bereiding van lanthanide βdiketon complexen. De pyridine dicarboxamide liganden in het DPA-PMO materiaal zorgden voor de nodige bindingssites voor Ln³⁺-coördinatie. Een Schiff-base reactie werd uitgevoerd op de amine gefunctionaliseerde PMOs om gelijkaardige lanthanide coördinatiesites te introduceren. De oorspronkelijke PMOs en de lanthanide PMOs werden gekarakteriseerd door PXRD, N2 sorptie, DRIFTS, ICP-MS en TEM. Zowel de DPA-PMO als Am-ePMO materialen functioneerden als goede platforms voor NIR luminescentie. Het toevoegen van een Yb(hfa)₃ complex, in plaats van YbCl₃, op de PMO materialen leidde tot een significante verbetering van de vervaltijd. Al de DPA-

PMO@Ln(hfa)₃ en Am-ePMO@Ln(hfa)₃ materialen bevatten karakteristieke NIR emissies in vaste toestand en in waterige suspensie.

In **Hoofdstuk 3** is de studie beschreven over chemische sensing door middel van een lanthanide ePMO materiaal. Een nieuw Eu³⁺-PMO materiaal werd ontwikkeld, gecombineerd met picolinezuur (PA) als een efficiënt co-ligand, voor het creëren van een antenne-effect. Aan de hand van luminescentie studies werd aangetoond dat ePMO@Eu_PA de karakteristieke emissies van Eu³⁺ bevatte zowel in de vaste toestand als na dispersie in water. De luminescentie intensiteit van ePMO@Eu_PA suspensies daalde aanzienlijk in de aanwezigheid van Fe³⁺, Co²⁺ en Cu²⁺ ionen, terwijl de intensiteit steeg voor het materiaal in een Ca²⁺-oplossing. Sensitieve en selectieve detectie van Co²⁺ ionen in een waterige suspensie werd waargenomen voor dit materiaal, met een LOD van 26.9 μ M. Bovendien vertoonde het materiaal een lineair verband tussen de luminescentie intensiteit en de pH-waarde in het pH-interval van 7.7 tot 10.2. Deze resultaten tonen aan dat ePMO@Eu_PA een groot potentieel bezit als luminescente sensor voor ion sensing in waterige oplossing alsook voor pH-afhankelijke sensing in alkalische omgevingen.

In Hoofdstuk 4 zijn 3 unieke, organische-anorganische hybride nano-composiet materialen beschreven, die gesynthetiseerd werden door het combineren van NaYF₄:Yb³⁺, Ln³⁺ (Ln³⁺ = Er^{3+} , Tm³⁺, Ho³⁺) met een ethaan PMO, voor het mogelijk gebruik als metaalion sensors en solvent sensors. De NaYF4 nano-deeltjes kristalliseerden binnenin de poriën van de PMO, wat aangetoond werd door N₂ sorptie mapping analyse. De luminescentie eigenschappen en EDX van het PMO@NaYF₄:Yb³⁺, Ln³⁺ materiaal werden tot in detail onderzocht in de vaste toestand en na dispersie in water. Er werd vastgesteld dat er selectieve "turn on" luminescentie was voor Hg^{2+} ionen met een detectielimiet van 24.4 μM in een waterige oplossing. Daarnaast werd er voor alle drie de materialen waargenomen dat de luminescentie eigenschappen geleidelijk toenamen wanneer ze gedispergeerd werden in alcoholen (van methanol tot n-butanol). Dit maakt ze veelbelovende materialen voor de detectie van water in organische solventen, bijvoorbeeld de detectie van water in ethanol was

mogelijk door het gebruik van PMO@NaYF4:Yb³⁺, Ho³⁺ met een detectielimiet van 0.29%. Bovenstaande resultaten illustreren het potentieel van deze hybride materialen voor toepassingen in de milieusector alsook in de chemische industrie.

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