Photoluminescence and upconversion properties of lanthanide-based atomic and molecular layer deposited thin films

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Abstract

Photoluminescence of trivalent lanthanide (Ln) ions is highly relevant to applications such as solar cells, light emitting devices and biological imaging. Organic molecules may potentially be utilized to enhance and tune the luminescence of Ln$^{3+}$ ions when properly combined into Ln-organic hybrids. Such on-demand tailored materials could pave the way to various next-generation applications, especially if the materials could be produced in high-quality thin-film form. However, the conventional thin-film techniques of Ln-organic materials lack the ability to combine the well-controlled deposition and the tunability of the luminescence properties to the needs of various applications.

To address these challenges, efforts to apply the strongly emerging atomic/molecular layer deposition (ALD/MLD) method for lanthanide-organic thin films started recently. While ALD/MLD offers well controlled process development and growth of thin films, the tunability of the luminescence properties of such films has been critically difficult to achieve. In this thesis, the tunability issue was one of the central research questions, and it was addressed by developing a number of ALD/MLD processes with novel organic components.

Within the scope of the thesis, the following organic precursors were investigated for the first time in the context of ALD/MLD: pyridine-3-carboxylic acid (PDA), cytosine (Cyt), 1,3,5-triazine-2,4,6-triol (TZO), and 2-hydroxyquinoline-4-carboxylic acid (HQA). Among these, PDA and Cyt were found particularly interesting as they allowed the remarkable tuning of the absorption and excitation properties of the lanthanide-organic thin films by shifting the excitation wavelength from the typical 250 nm up to 365 nm. More careful selection during this work led to the development of Eu-HQA thin films, which can be excited through an exceptionally wide excitation wavelength range from ultraviolet light of 185 nm up to visible light of 400 nm. Luminescent thin films that can be excited with visible light are of particular interest to biological imaging applications.

Therefore, the new Eu-HQA thin films were tested for the Förster resonance energy transfer mechanism, which is used in various bioimaging and detection techniques.

As another way to tune the luminescence properties challenged in the thesis, different Ln$^{3+}$ were combined into a single thin-film. Here, the combination of Eu$^{3+}$, Tb$^{3+}$, and Er$^{3+}$ yielded interesting thin films with photoluminescence emissions that could be controlled between green, red and white light. On the other hand, using Er$^{3+}$ and Ho$^{3+}$ provided a promising means to achieve upconversion emission, through which near-infrared light can be converted to visible light. These latter results could provide a route to enhance the performance of solar cells that suffer from weak absorption of infrared light.

Keywords Atomic layer deposition; ALD; Molecular layer deposition; MLD; Lanthanide; PhotoLuminescence; Lanthanide; Upconversion

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Espoo, 27.10.2023
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List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals.


IV Amr Ghazy, Mika Lastusaari, Maarit Karppinen. Excitation-wavelength engineering through organic-linker choice in luminescent ALD/MLD lanthanide-organic thin films. Chemistry of Materials, 2023, 35, 15, 5988-5995. DOI: 10.1021/acs.chemmater.3c00955

Author’s Contribution

Publication I: Luminescent (Er, Ho)2O3 thin films by ALD to enhance the performance of silicon solar cells

AG, MS, and MK defined the research plan. AG performed the thin film depositions and characterization by XRR, GIXRD and FTIR techniques. ML performed the laser upconversion measurements. HS offered the solar cells. AA, AT, and MG performed the IV characteristics experiments. The paper was written by contributions from MS, AG, HS, and MK.

Publication II: Effect of carbon backbone on luminescence properties of Eu-organic hybrid thin films prepared by ALD/MLD

MS and MK defined the research plan. MS and AG did the thin film depositions and characterization by XRR, GIXRD and FTIR techniques. MT and ML performed the photoluminescence measurements. The paper was written by contributions from all authors.

Publication III: White light emitting multi-lanthanide terephthalate thin films by atomic/molecular layer deposition

AG and MK defined the research plan. AG performed the thin film depositions and characterization by XRR, FTIR and GIXRD. ML performed the luminescence measurements. AG wrote the paper under the supervision of MK.

Publication IV: Excitation-wavelength engineering through organic-linker choice in luminescent ALD/MLD lanthanide-organic thin films

AG and MK defined the research plan. AG performed the thin film depositions and characterization by XRR, FTIR, and Uv-vis absorption techniques. ML performed the excitation and emission luminescence measurements. AG wrote the paper under the supervision of MK.

Publication V: Atomic/molecular layer deposition of europium-organic thin films on nanoplasmonic structures towards FRET-based applications

AG, NS and MK defined the research plan. AG performed the thin film deposition and characterization XRR, FTIR, and UV-Vis absorption techniques. JY performed the luminescence microscopy, FRET analysis, NS and JY prepared nanoplasmonic structures. AG wrote the paper under the supervision of MK.
List of Abbreviations and symbols

ADA  Anthracene-9,10-dicarboxylic acid
ALD  Atomic layer deposition
c-Si  Crystalline silicon
Cyt  Cytosine
ESA  Excited state absorption
ETU  Energy transfer upconversion
FRET  Förster resonance energy transfer
FTIR  Fourier transform infrared spectroscopy
GPC  Growth-per-cycle
HQA  2-hydroxyquinoline-4-carboxylic acid
LED  Light emitting diodes
Ln   Lanthanide trivalent ions
MLD  Molecular layer deposition
MOSLED  Metal-oxide semi-conductor light emitting devices
NDA  Naphthalene dicarboxylic acid
NIR  Near infrared
PDA  Pyridine-3-carboxylic acid
PZA  Pyrazine-2,3-carboxylic acid
QY   Quantum yield
thd  2,2,4,4-tetramethyl heptanedione
TPA  Terephthalic acid
TZO  1,3,5-triazine-2,4,6-triol
UC   Upconversion
UCNP Upconversion nanoparticles
Ura  Uracil
UV   ultraviolet light
Vis  Visible light
$\lambda_{\text{em}}$ Emission wavelength
$\lambda_{\text{ex}}$ Excitation wavelength
1. Introduction

Lanthanides – especially as their trivalent ions – possess characteristic luminescence properties relevant to various application fields, ranging from bio-imaging and surgical equipment in the medical field, to solar cells, sensors, and screens. A growing trend is that these applications require the luminescent lanthanide (Ln) based materials to be in high-quality thin-film form. Conventionally, Ln-containing thin films have been fabricated from colloidal nanoparticles by applying coating techniques such as spin-coating, dip-coating, or electrodeposition. However, these methods are not optimal for nanoscale device fabrication as they do not provide precise enough control of the film thickness; moreover, they may leave traces of organic solvent in the films.

The state-of-the-art gas-phase atomic layer deposition (ALD) thin-film technique offers a solution to the previously mentioned obstacles in producing high-quality Ln-containing thin films, as it offers precise film thickness control and solvent free production. Owing to these benefits, ALD is now the approach used in many technologies in industry, most importantly in semiconductor industry. Atomic layer deposition, and more recently also its counterpart for organic layers, i.e., molecular layer deposition (MLD), have become an increasingly attractive approach for different Ln-based thin films in research. Figure 1 illustrates the number of scientific articles that have been published over the years on the ALD and ALD/MLD growth of rare earth element (Sc, Y, Ln) related thin films. In particular, the Ln-organic hybrid thin films are currently considered the way forward, and using the combined ALD/MLD approach to fabricate high-quality Ln-organic thin films could be the course that leads us to new functionalities for applications on multiple frontiers.

![Figure 1](image.png)  
**Figure 1** Annually published scientific papers related to ALD and ALD/MLD of rare earth element based thin films, since the first publication in 1992
Most of the lanthanide-based thin films deposited by ALD lack the photoluminescence emission, presumably due to so-called concentration quenching effect, i.e., non-radiative cross-relaxation of the excited electrons occurring when the emitting species are in a too close spatial proximity. However, the use of Ln$^{3+}$ ions as dopants in small concentrations in ALD has shown promising results in electroluminescence and upconversion luminescence.$^{10,11}$

Photoluminescent lanthanide-based thin films without dilution were demonstrated in 2015 using ALD/MLD; here the organic linkers were believed to provide the required spacing between the luminescent Ln$^{3+}$ ions such that the concentration quenching effect could be circumvented.$^{12}$ Additionally, ALD/MLD allowed the deposition of thin films at lower temperatures compared to conventional ALD of lanthanide oxides, which are usually deposited at 300 °C.$^{13}$ This lower deposition temperature offered by ALD/MLD for Ln-organic thin films allowed the deposition of such films on heat sensitive substrates such as flexible polymer sheets. The organic layers in the thin films also enhance the mechanical properties of the films being thus more compatible with flexible substrates.

Research on photoluminescent lanthanide-organic thin films grown by ALD/MLD is still in its infancy regarding in finding the true potential of these hybrid Ln-organic thin films towards various applications. One of the research questions that this thesis aimed to address was the possibility to control the excitation wavelength range in these materials. Different target applications may require different excitation wavelength ranges, and in the few ALD/MLD processes developed prior to this work the excitation wavelength was limited to the short UV range of 250-300 nm. Bio-imaging and biodetection applications, for example require longer excitation wavelengths preferably in the visible light or NIR region to avoid autofluorescence and the loss of the biological tissues upon UV exposure.$^{14}$ By the proper choice of the organic component the light absorption of the ALD/MLD thin films light, thanks to the so called antenna effect.$^{15}$ Another challenge this thesis aimed to address was the low quantum yield values reached in earlier studies for the lanthanide-organic thin films, as the enhanced emission intensity obtained with the lower excitation power could be the gateway to apply the ALD/MLD-grown lanthanide-organic thin films in next generation applications such solar cells, bio-detection, bio-imaging and light emitting devices.

The detailed research questions addressed in the thesis could be formulated as follows:

- Development of novel ALD/MLD processes for Ln-organic thin films based on novel organic precursors with a variety of bonding sites (e.g., O, N) and reactive groups, such as amine groups, hydroxyl groups and heterocyclic aromatic rings. This was a crucial task needed to develop organic components with varied light-absorption properties.
- Control of the excitation wavelength of the ALD/MLD Ln-organic thin films by utilizing on-demand designed organic components; possibility to
manipulate the excitation wavelength within a wide range would widen the scope of potential applications of these films.

- Improved quantum yields for ALD/MLD-grown Ln-organic thin films; this is critical for the successful integration of the films in next-generation applications as this will save the operation power consumption.

- Careful search for optimal Ln element compositions for luminescent thin films; the proper Ln species composition is highly application dependent, each application requiring different luminescence processes and emission wavelengths.

- Testing the newly developed thin films in different potential application set-ups to demonstrate their application relevance; this was considered important to identify their possible weak points and the critical properties requiring further improvements.
2. Lanthanide luminescence

This chapter provides the basics of the different luminescence phenomena seen for trivalent lanthanides.

2.1 Lanthanide transitions

Trivalent lanthanide ions have the electron configuration of \([\text{Xe} 54] 4f^n\), where \(n\) ranges from zero for lanthanum and gradually increase through the series until it reaches fourteen for lutetium. Their luminescence arises from these partially filled \(4f\) orbitals. Since the \(f-f\) transitions are parity forbidden – there is no change in dipole moment - the excited states have long lifetimes, and subsequently slow decay rate.\(^{16}\) Moreover, the \(4f\) electrons are shielded from the coordination environment by the spatially extended 6s and 5d orbitals, which provides the \(\text{Ln}^{3+}\) ions with their characteristic narrow band emissions and allows the \(\text{Ln} 4f-4f\) emissions wavelength to be independent of the host matrix. The \(4f-4f\) emissions independence of the host matrix allows colour pure and well expected line sharp emissions, which distinguishes lanthanides from other phosphors such as organic molecules.\(^{17}\) These energy levels were first explained by Dieke and Crosswhite in the early 1960s and since then have expanded for all lanthanides, leading to the so-called Dieke diagram, shown in figure 2.\(^{18-20}\)

![Figure 2 Energy levels and possible transitions of Ln\(^{3+}\).\(^{20}\) (reprinted with permission. Copyright, 2018, Royal Society of Chemistry)](image)

Some of the \(\text{Ln}^{3+}\) ions show intense visible light emissions. For example, \(\text{Eu}^{3+}\) possesses intense red emission, the main emission peak is usually centred around 615 nm wavelength that corresponds to \((^6\text{D}_0 \rightarrow ^7\text{F}_2)\) transition, another peak is located around 700 nm arising from \((^6\text{D}_0 \rightarrow ^7\text{F}_4)\) transition. \(\text{Tb}^{3+}\) offers a
bright green emission with the main peak centred around 545 nm ($^6D_4 \rightarrow ^7F_5$), while it also shows weaker peaks at 490 nm ($^6D_4 \rightarrow ^7F_6$). Sm$^{3+}$ shows characteristic yellow colour emission, with the main emission centred around 600 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$), and Dy$^{3+}$ show light blue emission with peaks centred at 475 nm ($^4F_{9/2} \rightarrow ^6H_{15/2}$) and 575 nm ($^4F_{9/2} \rightarrow ^6H_{13/2}$). These visible light emitting ions compiled immense importance towards applications such as coloured light emitting diodes and screens. Other Ln$^{3+}$ ions emit at the NIR region such as Yb$^{3+}$ with main emission at 980 nm ($^2F_{5/2} \rightarrow ^2F_{7/2}$), Nd$^{3+}$ that emits at 880 nm ($^4I_{9/2} \rightarrow ^4I_{9/2}$) or Er$^{3+}$ with the main emission at 1500 nm ($^4I_{13/2} \rightarrow ^4I_{11/2}$). NIR emitting Ln have high significance in lasers, telecommunications, and waveguides. On the other hand, Gd$^{3+}$ is most familiar for the UV emission at 311 nm ($^6P_{7/2} \rightarrow ^8S_{7/2}$) These transitions can be seen in figure 2. Other lanthanide emissions such as ones originating from 5d-4f transitions are affected by host matrix. Thus, one Ln$^{3+}$ ion can offer different emission colours based on the environment. 

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2.2 Lanthanide photoluminescence

In photoluminescence, trivalent lanthanide ions absorb the excitation light of high energy, this energy is used to excite an electron from the ground state to an excited state, subsequently this electron undergoes relaxation to a lower energy level losing some of the energy before returning to a lower energy level emitting the energy as a photon, as illustrated in figure 3. The lanthanide photoluminescence occurs based on Stokes mechanism, which means that the emitted energy is lower than the absorbed energy. This can include excitation with UV or visible light and emission can happen in UV, visible light, or infrared region.\(^{24}\)

![Figure 3](image)

**Figure 3** Simplified schematic diagram that illustrates photoluminescence mechanism in a typical trivalent lanthanide ion, where A is absorption, E is emission, and the dashed line represents non-radiative relaxation.

It is noteworthy that when the light is emitted, the electron may not relax to the ground state but to a higher energy level, then it undergoes further relaxation to the ground state. For example, in the case of \(\text{Eu}^{3+}\) the most common transition shows a relaxation to \(^7\!F_2\) instead of \(^7\!F_0\) and in the case of \(\text{Sm}^{3+}\) the most common transition the electron relaxes to \(^6\!H_{7/2}\) instead of \(^6\!H_{5/2}\). In such cases, relaxations to the ground state can also occur immediately, which can result in multiple emissions seen by the same material. Table 1 shows the most common transitions of each trivalent lanthanide ion and its respective emission wavelength.

<table>
<thead>
<tr>
<th>Ln</th>
<th>(f) electrons</th>
<th>radius (Å)</th>
<th>Transition</th>
<th>Emission (\lambda) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>(4f^1)</td>
<td>1.034</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pr</td>
<td>(4f^2)</td>
<td>1.013</td>
<td>(^3!P_0 \rightarrow ^3!H_4)</td>
<td>490</td>
</tr>
<tr>
<td>Nd</td>
<td>(4f^3)</td>
<td>0.995</td>
<td>(^4!F_{5/2} \rightarrow ^4!I_{9/2})</td>
<td>880</td>
</tr>
<tr>
<td>Sm</td>
<td>(4f^5)</td>
<td>0.964</td>
<td>(^4!G_{5/2} \rightarrow ^6!H_{7/2})</td>
<td>600</td>
</tr>
<tr>
<td>Eu</td>
<td>(4f^6)</td>
<td>0.950</td>
<td>(^5!D_0 \rightarrow ^7!F_2)</td>
<td>615</td>
</tr>
<tr>
<td>Gd</td>
<td>(4f^7)</td>
<td>0.938</td>
<td>(^6!P_{7/2} \rightarrow ^8!S_{7/2})</td>
<td>315</td>
</tr>
<tr>
<td>Tb</td>
<td>(4f^8)</td>
<td>0.923</td>
<td>(^5!D_1 \rightarrow ^7!F_5)</td>
<td>545</td>
</tr>
<tr>
<td>Dy</td>
<td>(4f^9)</td>
<td>0.908</td>
<td>(^4!F_{9/2} \rightarrow ^6!H_{5/2})</td>
<td>475</td>
</tr>
<tr>
<td>Ho</td>
<td>(4f^{10})</td>
<td>0.894</td>
<td>(^5!F_{3} \rightarrow ^5!I_8)</td>
<td>550</td>
</tr>
<tr>
<td>Er</td>
<td>(4f^{11})</td>
<td>0.881</td>
<td>(^4!I_{13/2} \rightarrow ^4!I_{15/2})</td>
<td>1500</td>
</tr>
<tr>
<td>Tm</td>
<td>(4f^{12})</td>
<td>1.04</td>
<td>(^1!D_2 \rightarrow ^3!F_4)</td>
<td>450</td>
</tr>
<tr>
<td>Yb</td>
<td>(4f^{13})</td>
<td>1.01</td>
<td>(^2!F_{5/2} \rightarrow ^2!F_{7/2})</td>
<td>980</td>
</tr>
</tbody>
</table>
2.3 Upconversion

Upconversion (UC) is an anti-Stokes luminescence process exhibited by certain materials that are capable of absorbing low-energy photons typically in the near-infrared range and then converting the energy into higher energy photons, typically in the visible range. In an anti-Stokes process, the emitted energy is higher than the absorbed energy. This happens while the law of conservation of energy is non-affected, the UC material sequentially absorb two or more photons, and emit one single photon that is higher than each of the absorbed ones.\(^{25}\)

The lanthanide upconversion process is complex since the relationship between the excitation power and the emission intensity is not linear.\(^{26}\) Upconversion process is also affected by various factors. The properties of a host lattice such as, crystal structure and specific energy transfer routes affect UC properties.\(^{27}\) The crystal structure of the host lattice should provide an asymmetrical crystal field to allow the f-f transitions of the Ln. The host lattice should possess low phonon energies to minimize the non-radiative emissions, and be thermally and chemically stable, and most importantly to be transparent to the IR photons to allow Ln absorption.\(^{28}\) The host lattice should contain ions of relatively close size to the desired Ln\(^{3+}\) ions to facilitate easy doping of Ln. These ions can be yttrium, barium, or strontium.\(^{29}\) Of the most prominent host lattices are metal oxides, which are thermally and chemically stable, but the drawback is their high phonon energy. However, metal fluorides have been recognized as the most promising host material candidates owing to their lower phonon energy; however, they are often hygroscopic, which may be a limitation.\(^{30}\) Among the fluoride hosts lies the flagship NaYF\(_4\). The lattice comes in two versions, a cubic version, and a hexagonal version. The hexagonal NaYF\(_4\), mostly referred to as \(\beta\)-NaYF\(_4\), is considered by most researchers to be the best possible host lattice for upconversion till now.\(^{31}\)

Upconversion of Ln\(^{3+}\) ions occurs through various mechanisms, visualization of such mechanisms is seen in figure 4, UC mechanism can include one ion upconversion and two ions upconversion. Excited state absorption (ESA) is a mechanism of upconversion for one ion, in which a Ln\(^{3+}\) ion sequentially absorb two photons such that the first excitation happens to a metastable intermediate level which then allows the absorption of another photon to an excited state to emit a single high energy photon. While this mechanism happens within one Ln dopant, it requires low concentration of the active ion, and its relative efficiency is not remarkably high.\(^{32}\)
Other mechanisms of Ln UC include more than one ion, usually one ion is called the sensitizer, and the other is called activator, of these mechanisms there is energy transfer upconversion (ETU), where one ion, the sensitizer, absorbs a photon to and transits to a metastable state, the photon is then transferred to another ion, the activator, hence comes the name of the mechanism. However, within ETU, there are different ways the energy transfer happens within ETU. One of them is energy transfer followed by ESA, in this process the sensitizer ion absorbs one photon to an intermediate state, which is transferred to the activator ion, which absorbs another photon to promote a final excited state, then emissive relaxation takes place. Another ETU mechanism is the successive energy transfer, where absorption of the two photons occurs sequentially in the sensitizer ion, and the transfer of energy to the activator occurs on two steps successively.33 Hence, named successive energy transfer, while other ETU mechanisms include cooperative sensitization, where two sensitizer ions transfer one photon each, to an activator ion, then emission occurs.27 One other possible mechanism is cooperative luminescence, in which two ions each absorb one photon, the two photons are combined in a higher level then emitted as one higher frequency photon.34

Figure 4 Different mechanisms of lanthanide-based photon upconversion. The red, purple, and dotted green arrows illustrate direct excitation, radiative emission, and energy transfer processes, respectively.27(reprinted with permission. Copyright, 2020, Royal Society of Chemistry)
Lanthanide upconverting materials usually include more than one Ln\(^{3+}\) ion, one acting as a sensitizer, while the other is the emitting activator. The sensitizer ions are typically Nd\(^{3+}\) or Yb\(^{3+}\), which serve as an IR photon absorber, followed by a non-radiative energy transfer to the activator ions, typically Er\(^{3+}\), Ho\(^{3+}\), or Tm\(^{3+}\), to produce UC luminescence emission. Nd and Yb are often selected as sensitizers due to their larger absorption cross-sections compared to other Ln\(^{3+}\) ions. Furthermore, Yb possesses only one excited 4f level, \(^{2}F_{5/2}\). The absorption band of Yb is located around 980 nm (\(^{2}F_{7/2} \rightarrow ^{2}F_{5/2}\)) transition, see figure 5 for sensitization example, Yb\(^{3+}\) has an absorption cross-section \(\sim 10^{-20}\) cm\(^2\). This Yb\(^{3+}\) transition is well resonant with the f–f transitions of the most common activator ions (Er\(^{3+}\), Tm\(^{3+}\), and Ho\(^{3+}\)), which allows the energy transfer to occur.\(^{36}\) While Nd\(^{3+}\) possess more than one absorption band and it also has a higher absorption cross-section compared to Yb\(^{3+}\), the latter is more favoured as the energy transfer in Yb\(^{3+}\) case is usually more efficient.\(^{37}\)

![Diagram](image)

**Figure 5** Mechanism of energy transfer in upconversion when using Yb\(^{3+}\) as sensitizer and Er\(^{3+}\) or Ho\(^{3+}\) as activator, with solid black line represent absorption, straight dashed lines represent energy transfer, curved dotted lines resemble non-radiative relaxations and coloured solid lines represent emissions in their respective colours.

Careful optimization of the composition is essential when using Ln-sensitized UC. Sensitizer ion should be of a sufficient concentration to absorb more energy; however, too high sensitizer concentration may lead to non-radiative relaxations. Moreover, the activator ion concentration in the material is also vital. A too small concentration of the activator may lead to a very weak UC, while a too high concentration of activator may result in concentration quenching. Indeed, ALD thin films of Ln\(_2\)O\(_3\) are usually not photoluminescent. A typical strategy is to dilute the active Ln\(^{3+}\) species by another Ln\(^{3+}\) species, such that the active species concentration is typically below 10\%.\(^{36,38}\) For example, such low levels of active species led to photon upconverting (Yb,Er)\(_2\)O\(_3\) thin films by ALD.\(^{39}\) In this work,\(^{1}\) upconverting thin films by ALD were realised through the combination of (Er\(_{0.95}\)Ho\(_{0.05}\))\(_2\)O\(_3\).
2.4 Organic ligands as sensitizers

Lanthanide based luminescence suffers from two main drawbacks, one is the so-called concentration quenching; when lanthanide ions are packed together in close proximity, the excited state electron undergoes non-radiative transitions between ions, giving away the absorbed energy.\(^4\) The second problem is the notoriously low absorption cross section of Ln\(^{3+}\) ions, which renders the direct excitation ineffective.\(^10\)

Adding Ln\(^{3+}\) as dopants in low concentrations, typically (1-20\%) is one way to decrease concentration quenching.\(^4\) However, this leaves the weak absorption cross-section issue unsolved. On the other hand, incorporating lanthanide ions in lanthanide-organic hybrid materials offers an answer to both of the previously mentioned problems. On one side, organic molecules within lanthanide-organic hybrids function as building blocks that offer a distance that separates the lanthanide ions, thus offering a separation between Ln\(^{3+}\) ions that decreases to concentration quenching. Moreover, \(\pi\)-conjugated organic materials are well known for their UV absorption through singlet and triplet states. Hence, designing the organic molecules with changing the nature and number of the rings as well as adding different substituents can achieve variation in the range of energy absorption, it can also change the excited state to allow energy transfer to lanthanide ions based on their excited energy levels.\(^4\)

The energy absorbed by such organic ligands can be transferred to the lanthanide ions as long as the excited state of the organic molecule is higher in energy than the excited state of the lanthanide ion, which is known as the antenna effect, first reported in 1942 by Wiessman.\(^15\) Figure 6 shows a simplified schematic diagram to the so-called antenna effect.

A common example of energy transitions from an organic ligand to lanthanide ion is the triplet to Eu\(^{3+}\), where the triplet state that lie on almost the same level with \(\overset{5}{D}\), energy level of Eu\(^{3+}\), where energy transfer takes place, afterwards relaxation occurs to \(\overset{5}{D_o}\) level, which is responsible for the most common Eu\(^{3+}\) emission \((\overset{5}{D_o} \rightarrow \overset{7}{F_2})\) with an emission wavelength around 615 nm.\(^4\) It is also possible to see Eu\(^{3+}\) emissions \(\overset{5}{D}\) energy level to lower levels.\(^43,44\) Much of the current research focuses on the nature of organic molecules to obtain enhanced

![Figure 6](image)
absorption and more efficient energy transfer and more importantly decrease the non-radiative relaxations that occur to improve the emission efficiency.45

The selection of organic ligand is of utmost importance in the designing of Ln-organic luminescent materials. The organic component must have functional groups that can react and bond with Ln, in addition to high absorption of the desired excitation range. Moreover, the excited state of the organic molecule should be of higher energy than that of the corresponding Ln to facilitate energy transfer, the higher absorption and energy transfer efficiency, the higher the emission intensity. Thus, Ln material can be excited with least possible power, while maintaining high luminosity and quantum yield (QY).42

This leads to a dire selection process of the organic ligand that depends on the application, where the material would be used. A myriad of organic ligands have been experimented as potential antennae for Ln$^{3+}$ ions, such as beta diketonate, bipyridine, and other materials that exhibit a wide range of complexity.45 For example, β-diketonate complexes with Eu$^{3+}$ possess good luminescent properties, while many of them are not efficient sensitizers for Tb$^{3+}$, as their triplet state is of a lower energy than $^4$D$_4$ excited state of Tb$^{3+}$.46

The choice of the organic component directly affects the quantum yield (QY) of the material. Quantum yield is defined as the ratio of the number of emitted photons to the number of absorbed photons per unit time.47 In case of Ln-organic hybrid materials, QY is determined by the quantum yield of the direct excitation of the Ln, in addition to the efficiency of the energy transfer from the organic ligand to the metal ion, usually Eu$^{3+}$, Tb$^{3+}$, and Gd$^{3+}$ show the best QY, however, as Gd$^{3+}$ emits only in the UV ($\lambda = 315$ nm) this emission often interferes with the UV absorption of the organic component.10 Another important aspect of organic ligand selection is minimizing the loss of energy due to non-radiative relaxations, one of the main reasons for such loss is the interaction with OH vibrations in water molecules.48 This poses an inherent problem with Ln preference of high coordination number, which would render them coordinating with more water molecules.49 This has led the researchers to prefer polydentate and multifunctional ligands, with different donors including nitrogen and oxygen atoms, several classes of organic materials have been experimented so far but the search for better ligands continues and new classes of Ln-organic hybrid materials.50

There are a few requirements that an organic ligand must fulfil to be considered for its use in an upconverting material. The organic molecules should have high absorption of the targeted excitation NIR range. The emission wavelength of the organic must overlap with the absorption spectrum of the Ln sensitizer ions to allow an energy transfer process to take place. The organic ligands must be transparent to the upconverted photons emitted from the upconverting material. The molecules must possess suitable functional groups, such as carboxylic or sulphate groups, for the coordination of the ligands to the sensitizer metal ions.27 The organic ligands used in photon-upconverting Ln-organic materials are mostly NIR light absorbing dyes with absorption and emission peaks positioned around 780-820 nm and 750-1100 nm.36
In addition to acting as antennas, incorporation of organic molecules in the UC materials can offer additional benefits. For instance, in the current state-of-the-art inorganic upconverting nanoparticles, can be designed in a core-shell form, where a greater fraction of the emitters (activator ions) is embedded inside the nanocrystal core, while leaving only a limited fraction of the emitters in the outer surface of the particle. This results in a limited UC emission for certain applications, such as bioanalytical diagnostics. Ideally, the biomolecules should be positioned in a proximity of the activator ions, which is not the case when nanoparticles are used for UC.
2.5 Förster resonance energy transfer

Förster resonance energy transfer (FRET), also referred to as fluorescence resonance energy transfer, is a non-radiative phenomenon that attracted interest towards several application areas such as bio sensing, light harvesting, and imaging.\(^{52}\) In FRET, energy is transferred from a donor fluorophore molecule to an acceptor fluorophore molecule, when there is an overlap between the emission of the donor fluorophore and the absorption of the acceptor fluorophore. Then, the acceptor releases this transmitted energy by emitting light at a characteristic wavelength. During FRET, the donor and acceptor ground states are coupled by dipole-dipole interactions, see the schematic diagram in figure 7.\(^{53}\) The process, first explained by Theodor Förster in 1948,\(^{54}\) has been employed in biological detection of several viruses in the recent years, including hantavirus, Zika virus, and SARS-CoV-2 (covid-19).\(^{55–57}\) FRET occurs when donor and acceptor are in close proximity up to 10 nm, and the phenomenon is inversely dependent on the distance between donor and acceptor.\(^{58}\)

Trivalent lanthanide ions, mainly Eu\(^{3+}\) and Tb\(^{3+}\) based chelates, have been essential to FRET based applications as donor chromophores. Lanthanides are considered ideal donors for FRET thanks their long luminescence lifetime of the 4f-4f transitions, which may reach up to milliseconds, this allows time distinction between the donor and acceptor FRET signals.\(^{59}\) Typically, colloidal Ln chelates are used as donors, which may hinder the process as the donor molecules are suspended in a mobile phase, which may lead to varying the distance between the donor and acceptor and thus decreasing the efficiency. Therefore, using an immobile fixed Ln donors can overcome this issue, and stabilize the FRET phenomenon by keeping the distance at the optimum range. Thus, it may enhance the success rate of the FRET-based immunoassays. Lanthanide-containing thin film coating can be a straightforward idea to solve this issue.\(^{60}\)

![Figure 7](image-url) A simplified schematic diagram shows the FRET energy transfer mechanism between a donor and an acceptor fluorophore through dipole-dipole energy coupling. Solid lines represent D: donor ground level, D*: Donor excited level, A: absorption and E: emission, and black dashed lines represent non-radiative relaxations and red dotted line resembles the FRET energy transfer.
2.6 Applications of lanthanide luminescence

Lanthanide luminescence show potential towards various applications, where different mechanisms of luminescence, such as upconversion and downconversion can be used for its own target application range. This chapter discusses the application range of different lanthanide luminescence phenomena.

2.6.1 Upconversion

Upconversion is an interesting type of luminescence, especially because of the conversion of NIR into visible light. Thus, the main applications are concentrated in the Biomedical field. Upconverting nanoparticles (UCNP) have achieved a breakthrough in the biomedical field over the recent years. Compared to conventional quantum dots and organic fluorophores in biomedicine, luminescent materials, UCNP can be excited by lower energy, UCNP attain the long luminescence lifetimes and the narrow emission peaks from their Ln component, they show low toxicity allowing in vivo applications. Furthermore, UCNP show enhanced photochemical stability and resistance to photobleaching which offers better contrast features in several applications such as those shown in figure 8.

![Figure 8: Examples of applications based on lanthanide upconversion luminescence.](image)

**Biological Imaging and biosensing:** The conventional optical imaging using fluorescence and down shifting faces multiple hurdles in case of biological imaging. Such problems range from damage of biological samples when excitation happens by UV or visible light, autofluorescence from a biological background making large noises and poor penetration depth. Upconversion offers solutions to such issues, as the source of excitation is NIR irradiation lower in energy than UV, which makes it milder for the samples and avoid phototoxicity of the samples. Additionally, very weak autofluorescence occurs, which leads to high signal to noise ratio that translates into a higher sensitivity. Moreover,
UC offers high depth penetration, which makes it favoured for in vivo and deep tissue imaging, achieving even few centimetres of depth.\textsuperscript{14}

UCNP have been used in various imaging techniques mainly multimodal techniques, in which UC based imaging technique is combined with one or more different imaging techniques. Such techniques could be magnetic resonance imaging “MRI”, positron emission tomography (PET) or computed tomography scan “CT scan”. As each of these imaging modes has its own advantages and drawbacks, the current trend to combine more than one of them to synergize the advantage of the imaging.\textsuperscript{64}

UCNP have been researched vigorously in cancer related diagnosis methods and treatments. For example, UCNP showed promising results towards in vitro imaging of tumour cells,\textsuperscript{65} or as nanoprobes for lymphatic metastasis,\textsuperscript{66} or to simultaneously detect and quantify several tumour biomarkers.\textsuperscript{67} Efforts for biosensing of tumour markers have been intensified in the last two decades, for examples, thymidine kinase 1 mRNA is a significant biomarker for monitoring tumour growth, which renders its biosensing an essential diagnostic tool, which can be probed in living cells using UCNP.\textsuperscript{68} Glutathione, the main reducing agent in living cell, is another cancer biomarker that needs to be monitored in vivo. However, optical methods using quantum dots or organic fluorophores suffer from a very weak signal to noise ratio due to the background autofluorescence, while using UCNP based probes offers a breakthrough to the signal to background ratio issue.\textsuperscript{69}

UCNPs can also be used as FRET donors to develop luminescence sensors to probe metal ion concentration within human cells.\textsuperscript{70} UCNP based biosensing of metals covers a wide range of essential intracellular metal ions including Cu\textsuperscript{2+}, Ca\textsuperscript{2+}, Zn\textsuperscript{2+}, and Fe\textsuperscript{3+}.\textsuperscript{64} It also extends to sensing harmful or poisonous metals such as Hg\textsuperscript{2+}.\textsuperscript{71} Bio molecules, such as proteins and nucleic acids, are essential for body functions that makes them a target for intracellular or in vitro sensing and detection for clinical diagnostics. Extensive research on UCNP-based monitoring biomolecules has been conducted recently, which included Adenosine triphosphate, a molecule essential to energy production in the mitochondria of living organisms.\textsuperscript{72}

Upconversion based biosensing goes beyond diagnostics and can also be used to detect toxic substances, for example detection of acrylamide, a substance that is potentially carcinogenic to humans.\textsuperscript{73} Furthermore, detection of toxic gases such as hydrogen sulphide (H\textsubscript{2}S), nitric oxide (NO) using UCNP sensing.\textsuperscript{64}

\textbf{Photodynamic therapy:} This established cancer treatment uses toxic reactive oxygen species to destroy tumours and cancer cells. Generation of reactive oxygen species arises from photosensitization that follows a wavelength specific irradiation. The UV-Vis radiation is limited by its inefficiency to penetrate deep tissue, a limitation that can be solved by using NIR irradiation instead, which poses UCNP as prime candidates in photodynamic therapy.\textsuperscript{74} UCNP allow passive targeting of tumour cells as the nano-sized particles can pass through the blood vessels surrounding tumours. Moreover, the small size allows high drug-loading capacity to enhance the whole process.\textsuperscript{75} While UCNP size on its own
allows passive targeting of cancer cells, there are two main techniques through which, UCNP can actively target the tumour, which minimizes the side-effects. Active targeting can be achieved through tuning the UCNP to the changes that occur in the environment of cancer cells but not the healthy ones, or through adding ligands that can bind only to receptors expressed on the cancer cell surface and not the healthy ones.

### 2.6.2 Lanthanide-organic photoluminescence

Lanthanide-organic hybrid materials are already widespread in our daily life, in a wide range of applications such as the examples given in figure 9.

**Figure 9** Examples of applications based on lanthanide-organic materials photoluminescence.

**Light emitting diodes:** The sharp emission lines exhibited by Ln$^{3+}$ ions lead to colour pure emissions, which has led to the widespread use of Ln-organic materials in coloured light emitting diodes (LED)s. The colour purity is difficult to achieve through using organic dyes or other luminescent materials. Moreover, the sensitization mechanism reduces the thermal energy losses and improves the luminous efficiency compared to broadband emitters.

White LEDs are demanded for a wide variety of applications such as backlight sources. Ln generated white light has been under extensive research over the last two decades. Red emission of Eu$^{3+}$ and green from Tb$^{3+}$ can be combined with a blue emitter such as Dy$^{3+}$ or Tm$^{3+}$. As Tb$^{3+}$ shows a blue emission band at around 490 nm, in some cases Eu$^{3+}$ and Tb$^{3+}$ are enough to achieve white light emission. In other cases, blue emitters can be combined with yellow emitters like Sm$^{3+}$ to get white light emission.

**Sensors:** Mechanism of luminescence in Ln-organic materials poses them as one of the optimal candidates for a wide array of sensing applications. The most direct sensing application would be UV sensing, as the absorption is done by the
organic ligand, designing the organic ligand to absorb at a certain narrow band or a broadband UV range would lead to the ability of sensing UV.

Cation and anion sensing is another significant application for Ln-organic luminescence. In cation sensing the mechanism can be a turn on one, in which case the presence of analyte increases the luminescence intensity, or a turn off, in which the presence of the analyte diminishes the intensity. Lanthanide-organic sensors can have a very low detection limit for some of these analytes. For example, the limit is 6 nM for Zn$^{2+}$, 3.7 nm for Cu$^{2+}$, 24 nM for F$^-$, and 3.5 nM for HS$^-$.

Temperature sensing is considered one of the main targets for Ln-organic luminescence sensors, as the temperature affects the electrostatic interactions that lead to energy transfer between the organic component and the Ln$^{3+}$ ion, subsequently affecting the emission intensity and lifetime. Moreover, traditional direct contact temperature sensors are limited in cases of microelectronics, which renders non-invasive thermometry, such as optical thermometry, with highly accuracy and sensitivity a necessity. Traditional thermometers are hindered by the inability to use conventional batteries, when attempting to measure very high temperatures accurately. In such cases, optical thermometry using Ln based probes, which emission intensity changes by temperature manifest as an obvious method of choice.

Security: Counterfeiting is growing rapidly, and Ln luminescence found its way as one of the most important anticounterfeiting tools, which is essential for authorities everywhere. Luminescent materials that emit a specific wavelength when activated by a certain tool offer a valuable anticounterfeiting instrument. Developing Ln based materials, with a line sharp emission upon a specific UV excitation is considered a direct method for that. Ln-organic hybrids have also been examined for latent fingerprint detection using powder dusting technique.

Photocatalysis: Traditional photocatalysts such as TiO$_2$, ZnO, and ZrO$_2$ suffer from weak light absorption capacity, easy electron-hole recombination, which leads to difficulty of activation. This pushes the researchers to search for new photocatalysts. Lanthanide-based metal organic frameworks constitute promising photocatalysis candidates. The ability to design the organic structure of the MOF, and the easily activated Ln luminescence component generated an attractive photocatalysis candidates.

In the research for future clean energy, Ln-MOFs photocatalysts have shown promise to the production of hydrogen, which stands as a route for future clean energy. Additionally, the photocatalytic reduction of CO$_2$, a promising approach for solar energy conversion was also achieved by Ln-MOFs. Such an approach combines combating global warming by capturing CO$_2$ from the environment, and simultaneously using it to convert solar energy to chemical energy.
3. Atomic/molecular layer deposition of Ln-based thin films

In this chapter, atomic layer deposition technique and its organic analogue molecular layer deposition technique are discussed briefly, with the main focus on thin films based on lanthanide oxides and lanthanide-organic thin films. Additionally, this chapter discusses key parameters of the growth of lanthanide based thin films by ALD and ALD/MLD, including processes developed in this work.

3.1 ALD and ALD/MLD in brief

Atomic layer deposition is the state-of-the-art thin film technology; it is currently employed in various key technologies in modern industry, such as semiconductors. However, in research, it is now used to explore thin films for various technologies, such as batteries, thermoelectric devices, magnetic, and luminescent thin films. ALD is used to deposit metal oxides, nitrides, fluorides, and sulfides, and pure metals. ALD offers competitive advantages against most other thin film deposition techniques, such as the ability to deposit thin films at relatively lower temperatures, which allows the use of several heat sensitive substrates. ALD offers the capability of fabricating conformal thin films on complex topography and the precision of thickness control of the resulting thin films. In ALD, thin films grow in a cyclic behaviour, as seen in figure 10, where two precursors are pulsed in sequentially, to chemically react with the surface of the substrate, while purging steps are added in between each precursor pulse to ensure the removal of excess precursor and any by-products of the reaction. In an ideal ALD process, the growth occurs through self-limiting surface reactions. One ALD cycle ideally produces one monolayer of the target material, when the precursors are pulsed long enough to achieve surface saturation. Nevertheless, practically this is difficult to achieve owing to the steric hindrance of the precursors used that may block the reaction between the metal and the substrate active sites. Therefore, the growth per cycle (GPC) tends to be usually lower than the ideal case. The self-limiting nature of the growth usually lead to the conformality and uniformity of the grown films, however, this requires a well optimized process and accurately controlled environment. In many ALD processes there is usually a temperature range where the growth is constant. Hence, the target thickness of the thin film can be easily controlled by varying the number of ALD
cycles. Therefore, ALD is ideal for the fabrication of micro-electromechanical systems, semi-conductors, transistors, and sensors.\textsuperscript{102}

The concept of ALD has been applied to depositing thin films of organic materials and thus named molecular layer deposition.\textsuperscript{103} The combination of the two techniques opens the gate to what is known now as atomic/molecular layer deposition. ALD/MLD offers the capability to deposit a wide variety of metal-organic hybrid thin films such as metal organic frameworks (MOFs), or coordination polymers.\textsuperscript{92}

In ALD/MLD metal-organic hybrid thin films grow by alternating a metal precursor and an organic precursor with purging steps in between. While many processes in ALD possess a temperature range where the GPC is independent on temperature, GPC generally decreases with increasing the deposition temperature in ALD/MLD. This was evident in this work in \textbf{Publications II and V}. This behavior also exists in pure MLD processes, and other Ln based ALD/MLD processes.\textsuperscript{104,105} Regardless, most ALD/MLD processes show a reproducible growth rate at a given temperature. Nevertheless, the conditions of the ALD reactor and the environment should be taken into consideration, as these processes when transferred to a different reactor or a clean room environment they may need to be reoptimized for pulse and purge length of precursors.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{An illustrative diagram of one cycle of atomic layer deposition of an oxide using O\textsubscript{3} as a co-reactant and one cycle of atomic/molecular layer deposition of a metal-organic hybrid.}
\end{figure}
3.2 Lanthanides as dopants in ALD

In ALD, the first use of lanthanide ions was as dopants, Ln-doped ALD films, were utilized in 1992 for Tb$^{3+}$-doped (2%) ZnS films, and little later for CaS films doped with different concentrations of Ce$^{3+}$, Tb$^{3+}$ and Eu$^{3+}$,106,107 Thanks to the interesting electroluminescent properties of lanthanide and their potential use in electronic displays. More recently, the emission wavelength of Eu$^{3+}$ in CaS was shown to be tunable by means of introducing oxide ion defects, and thereby increasing the oxidation state of europium. This was achieved by replacing the Eu(thd)$_3$ + H$_2$S cycle for CaS: Eu films with the Eu(thd)$_3$ + O$_3$ cycle for CaS: Eu-O films. It was found that the emission wavelength of CaS: Eu (647 nm) was blue-shifted by ca. 20 nm for CaS: Eu-O (625.8 nm). Such a defect control as achieved here might be difficult to achieve by other synthesis techniques.108

![Supercycle Diagram](image)

**Figure 11** An illustrative diagram of doping in ALD of a metal oxide, showing the concept of ALD supercycle, where the user can control the amount of doping by varying the number of cycles.

Doping thin films in ALD is a straightforward concept, yet hard to fully control, using more than one metal precursor in ALD is commonly referred to as ALD supercycle shown in figure 11. In an ALD supercycle, the user chooses the order and number of cycles of two or more metal precursors, aiming at a target composition of the resulting thin film. Ideally, this could give rise to a well-controlled composition doping, but practically this is hard to achieve as there are many variables that affect the growth of the doped film, including CVD component growth, the nature of the deposited materials, the metals and dopant used, precursor reactivity and stearic hinderance. However, it is relatively possible to achieve doping of the desired concentration. It is common to have full cycles as dopants i.e. (Metal $\rightarrow$ co-reactant $\rightarrow$ dopant $\rightarrow$ co-reactant), but also it is possible to have half cycles for doping i.e. (Metal $\rightarrow$ dopant $\rightarrow$ co-reactant). In such cases, the order of precursor supply must be noted as exchange reactions may happen.
Another doping strategy is the synthesis of a mixed precursor that contains different metals, or the mechanical mixing of precursors. However, the latter is more difficult to achieve composition control since the different precursors may possess different vapor pressure leading to the final film composition be different than the initial mixing composition.\textsuperscript{39} This technique was followed in the deposition of Er\textsubscript{0.95}, Ho\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} thin films to achieve upconverting thin films.\textsuperscript{1}

Luminescent Ln dopants are also useful for metal-oxide semiconductor light-emitting devices (MOSLEDs), with application potential in optoelectronic devices, waveguides, and lasers; such Ln-doped MOSLEDs have attracted great attention for their outstandingly intense electroluminescence emission.\textsuperscript{113} The first ALD studies regarding the optoelectronic and waveguide applications are from 2004, and the research is still actively going on.\textsuperscript{114} For example, a NIR (\(\lambda = 977\) nm) emitting MOSLED was fabricated by depositing nanolaminates of Yb\textsuperscript{3+}-doped Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{115} However, Er\textsuperscript{3+} emission at ca. 1530 nm has been of a particular interest for MOSLEDs, as it concurs with the minimum loss window of optical telecommunications. Therefore, Er\textsuperscript{3+} has been intensively investigated in ALD.\textsuperscript{116}
3.3 ALD of Ln-based thin films

Atomic layer deposition of Ln based thin films has been in focus for more than twenty years. Binary oxides (Ln$_2$O$_3$) was targeted as high-k gate dielectric materials to replace SiO$_2$ in microelectronics. Comprehensive studies on ALD grown Ln$_2$O$_3$ thin films were published in 2005 and 2013. These oxides processes were developed using the Ln(thd)$_3$ precursor (thd = 2,2,6,6-3,5-heptanedione), structure is drawn in figure 12, and ozone as oxidizing agent. The main feature of the ALD processes of Ln$_2$O$_3$ is the low GPC rate, that ranges between 0.22 Å/cycle for the heavy lanthanides to 0.43 Å/cycle for the light ones, growth of (Er, Ho)$_2$O$_3$ in this work seemed to be consistent with these results at ~0.25 Å/cycle.

It is interesting to notice the critical role, which deposition temperature plays in the ALD processes of the Ln oxides. As the films grow amorphously until a threshold temperature, then films deposited at higher temperatures grow in-situ crystalline. For early lanthanides and La$_2$O$_3$ deposition of films below 300 °C showed amorphous films, while at 300 °C polycrystalline cubic thin films grow with (2, 2, 2) peak is the strongest, this changes by increasing the deposition temperature to 325 °C where the (4, 0, 0) peak appears the most favoured. For heavier Ln oxides such as Er$_2$O$_3$, the threshold temperature is down at 250 °C, where depositions below this temperature yield amorphous films. The same orientation-favouring temperature dependence exists, as films deposited between 275-350 °C prefer the (4,0,0) cubic orientation, and within the 375-400 °C temperature range (2,2,2) orientation is preferred.

The deposition temperature affects the optical properties of the Ln$_2$O$_3$ thin films as well. Ln$_2$O$_3$ films deposited at low temperatures show no or weak absorption peaks, while cubic crystalline films show distinct absorption peaks. Oddly enough, Nd$_2$O$_3$ films grown at higher temperatures showing hexagonal phase has an additional absorption peak. A similar behaviour is shown in the refractive indices of the films. All Ln$_2$O$_3$ films deposited at lower deposition temperatures seemed to show lower refractive indices than the ones grown at higher temperature.
While most Ln-based ALD process are oxides or oxide derivatives, other ALD processes were developed including sulphides, fluorides, and nitrides.\textsuperscript{108,122,123} During these processes, several lanthanide precursors were experimented, while the Ln(thd)\textsubscript{3} remained the most prominent Ln precursors for ALD. Ln(thd)\textsubscript{3} precursors belong to the β-diketonate group, which have been used as a precursor for multiple CVD and ALD processes. In this work, all the Ln precursors used were (thd)-based, i.e., Er(thd)\textsubscript{3}, Ho(thd)\textsubscript{3}, Tb(thd)\textsubscript{3} and Eu(thd)\textsubscript{3}, have been synthesized in-house from Hthd and the respective Ln nitrate. One of the main advantages of Ln(thd)\textsubscript{3} is the low sublimation temperature which ranges between 120-155 °C. This offers versatility required in many ALD processes to scan a wide deposition temperature range.

Ln(thd)\textsubscript{3} precursors are highly stable, they are not reactive with oxygen or water and can be stored in dry conditions for long time. While this is considered an advantage, it highlights the main disadvantage of using them for Ln\textsubscript{2}O\textsubscript{3} processes, as they lack the reactivity with either water or oxygen to form Ln\textsubscript{2}O\textsubscript{3}. Therefore, all the Ln\textsubscript{2}O\textsubscript{3} have been deposited from Ln(thd)\textsubscript{3} required ozone as the oxygen source. Ozone is a highly reactive oxygen source, and a toxic gas that requires precautions handling in the lab, which is why some researchers prefer using oxygen or water instead.

More reactive Ln precursor is required to avoid ozone, such as cyclopentadienyl complexes, including cyclopentadienyl or its substituted versions such as methyl, isopropyl or tertiary butyl cyclopentadienyl complexes.\textsuperscript{124} Other precursor groups include guanidinate based precursors, such as tris (N, N'-diisopropyl-2-dimethylamido-guanidinato)-Ln have also been experimented and found to be reactive to water. Nonetheless, such compounds are highly reactive that they need strict storing conditions, in a glovebox for example. Some of them react violently with water, flammable and unstable in moisture or ambient conditions. Additionally, they are expensive to purchase and methods of synthesis of such complexes are usually more difficult, which makes the scale up of such processes challenging.\textsuperscript{125}

Recently, ALD of lanthanide fluorides is becoming a hot topic, owing to their interesting optical properties.\textsuperscript{126} Several LnF\textsubscript{3} processes have been developed using Ln(thd)\textsubscript{3} as a main lanthanide precursor. However, many fluoride sources have been experimented. Through the history of ALD, HF was the main fluoride precursor.\textsuperscript{127} However, safer and easier to handle precursors are preferred to avoid the using of HF. In the lanthanide new fluoride processes, three fluoride precursors were utilized, TiF\textsubscript{4} has been experimented with Tb\textsuperscript{3+}, NH\textsubscript{4}F with Gd\textsuperscript{3+}, and NbF\textsubscript{5} with Ho\textsuperscript{3+}.\textsuperscript{122,126,128}

In this work, Publication 1, 5% Ho-doped Er\textsubscript{2}O\textsubscript{3} thin films were deposited using a mixed precursor Er, Ho(thd)\textsubscript{3}. The growth rate in this work was 0.24 Å/cycle, which lies within the comparable range with the same process by other works shown in table 2.
Table 2 Growth per cycle (GPC) of lanthanide oxide thin films by ALD based on the processes from the respective lanthanide-thd precursor and ozone as a co-reactant.

<table>
<thead>
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<th>Material</th>
<th>Temperature (°C)</th>
<th>GPC (Å/cycle)</th>
<th>Reference</th>
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</thead>
<tbody>
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<td>129</td>
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<tr>
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</table>
3.4 ALD/MLD of lanthanide-organic thin films

The interest in Ln-organic hybrid thin films is growing, specifically because of the ability of organic molecules to act as an antenna and sensitize Ln³⁺ ions, which provides luminescent thin films. ALD/MLD of Ln-organic thin films is a relatively new field, which has only started in 2015 by fabricating luminescent Eu³⁺-organic thin films with different organic molecules. It was clear from the beginning, that the organic component remarkably affects the absorption and excitation properties of the resulting film. This thrust the following research to change the organic precursors used with lanthanides, in attempts to control the luminescent properties of the films.

3.4.1 Growth rate

While most of the Ln-organic thin film processes have been developed using Ln(thd)₃ precursors, attempts to deploy other more reactive precursors showed significantly higher GPC reaching 5.4 Å/c in case of Ce-TPA and 6.4 Å/c for Er-TPA from Ce (DPDMG)₃ and Er (DPDMG)₃. However, the following discussion focuses only on process developed using Ln(thd)₃ precursors.

Multiple factors affect the GPC of ALD/MLD processes. Deposition temperature has a strong impact on the GPC of lanthanide-organic thin film processes. Typically, GPC decreases upon increasing the deposition temperature, while keeping all other parameters constant. This is evident in the results in the work presented in this thesis. Figure 13 showcases the effect of increasing the deposition temperature on Nd-terephthalate process, where at 200 °C the process shows a 3.1 Å/cycle, which goes down to 1.8 Å/cycle at 240 °C and even lower of 1.2 Å/cycle at 280 °C. Similar effect was noticed for all the processes developed in this thesis.

![Figure 13 Decreasing trend of the GPC of Nd-TPA thin films grown by ALD/MLD with increasing deposition temperature](image)

Varying the organic component affects the GPC of lanthanide-organic ALD/MLD processes heavily. Generally, organic precursors with highly reactive substituents lead to a higher GPC. Having two carboxylic acid groups offers high reactivity, Eu-PZA process shows a GPC of 3.5 Å/cycle at 180 °C, in this process 2,3-pyrazine dicarboxylic acid is used, while Eu-PDA process which uses a pyridine-3-carboxylic acid at the same temperature shows a GPC of 1.7 Å/cycle. Such results highlight the difference in GPC from an organic component with one carboxylic acid group compared to two carboxylic acid groups. Table 3
shows the GPC of all the lanthanide-based ALD/MLD processes experimented in this work.

### Table 3
Growth rate expressed as growth per cycle (GPC) of the lanthanide-organic thin films processes, at specific deposition temperatures \((T_{\text{dep}})\) performed in this thesis.

<table>
<thead>
<tr>
<th>Thin film</th>
<th>abb.</th>
<th>(T_{\text{dep}}) (°C)</th>
<th>GPC (Å/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd-Terephthalate</td>
<td>Nd-TPA</td>
<td>200</td>
<td>3.20</td>
</tr>
<tr>
<td>Eu-Terephthalate</td>
<td>Eu-TPA</td>
<td>190, 220</td>
<td>3.00, 2.40</td>
</tr>
<tr>
<td>Eu-1, 4-Naphthalenicdicarboxylate</td>
<td>Eu-NDA</td>
<td>220</td>
<td>3.00</td>
</tr>
<tr>
<td>Eu-9, 10-Anthracenedicarboxylate</td>
<td>Eu-ADA</td>
<td>250</td>
<td>3.00</td>
</tr>
<tr>
<td>La-Terephthalate</td>
<td>La-TPA</td>
<td>190</td>
<td>3.25</td>
</tr>
<tr>
<td>Eu-pyridine-3-carboxylate</td>
<td>Eu-PDA</td>
<td>180</td>
<td>1.70</td>
</tr>
<tr>
<td>Eu-2,3-pyrazinedicarboxylate</td>
<td>Eu-PZA</td>
<td>180</td>
<td>3.50</td>
</tr>
<tr>
<td>Eu-Uracil</td>
<td>Eu-Ura</td>
<td>250</td>
<td>2.10</td>
</tr>
<tr>
<td>Eu-Cytosine</td>
<td>Eu-Cyt</td>
<td>250</td>
<td>1.50</td>
</tr>
<tr>
<td>Eu-2, 4, 6- hydroxy- 1, 3, 5- triazine</td>
<td>Eu-TZO</td>
<td>250</td>
<td>2.10</td>
</tr>
<tr>
<td>Eu-2-hydroxyquinoline-4-carboxylate</td>
<td>Eu-HQA</td>
<td>210</td>
<td>7.28</td>
</tr>
</tbody>
</table>

### 3.4.2 Coordination

Each organic precursor will bind to the lanthanide metal in a specific way, understanding the bonding and coordination between the lanthanide ion and the organic molecule can offer a lot of insight when discussing the properties of these films. Fourier transform infrared spectroscopy (FTIR) is the method of choice when studying the composition of the lanthanide-organic thin films by ALD/MLD, in this work. As each bond holds a set of characteristic vibrations, a comparison between the free organic precursor and the Ln-organic thin film offers an indispensable tool for researchers when studying such thin films in general. The energy of those vibrations is also crucial, in the scope of this thesis, FTIR at the range of 400-4000 cm\(^{-1}\) shows mostly all the important vibration modes of the used organic molecules. Some Ln-organic thin films in this thesis are based on carboxylic acid or dicarboxylic acid organic precursors, which makes the vibrations of the carboxylic acid group of the most critical to be studied.

Upon reaction of Ln precursor with a carboxylic acid, there are several modes in which the Ln can coordinate, mainly unidentate, bidentate, bridging or ionic coordination.\(^{135}\) In all coordination modes, Ln substitutes hydrogen of the acid group. Therefore, the O-H stretching peaks usually shows between 2500 cm\(^{-1}\) and 3000 cm\(^{-1}\) disappear. The C=O asymmetric stretching vibration of the carboxylate group usually centred around 1700 cm\(^{-1}\) in a free carboxylic acid group gets shifted to a lower wavenumber. This confirms that the reaction between the organic molecule and the Ln precursor occurred. The coordination yields new peaks, the metal-carboxylate coordination mode with the metal is determined through the separation between the asymmetric and symmetric stretching peaks \((\Delta \nu_{\text{as}}-\nu_{\text{s}})\). The separation between 50 and 150 cm\(^{-1}\) \((150 > \Delta > 50)\) denotes a bidentate complex, while when the separation is between 150 and 200 cm\(^{-1}\)
(200 > Δ > 150) suggests the coordination is in bridging mode, separation of exactly 200 cm⁻¹ (Δ = 200) denotes an ionic bonding and separations larger than 200 cm⁻¹ denote unidentate coordination (Δ > 200). Table 4 shows the bonding modes of all the Ln-organic thin films, where the organic precursors was carboxylic acid based in this work Publications II-V, while figure 14 shows each bonding mode with an example from this work.

Table 4 Type of coordination between lanthanide ions and carboxylic acid groups based organic precursors, with the difference between asymmetric and symmetric stretching modes in the respective FTIR spectra.

<table>
<thead>
<tr>
<th>Organic precursor</th>
<th>Ln used</th>
<th>(Δνas-νs)</th>
<th>Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terephthalic acid</td>
<td>La, Eu</td>
<td>151 cm⁻¹</td>
<td>Bridging</td>
</tr>
<tr>
<td>2,6-Naphthalenedicarboxylate</td>
<td>Eu</td>
<td>119 cm⁻¹</td>
<td>Bidentate</td>
</tr>
<tr>
<td>9,10-Anthracenedicarboxylate</td>
<td>Eu</td>
<td>113 cm⁻¹</td>
<td>Bidentate</td>
</tr>
<tr>
<td>Pyridine-3-carboxylic acid</td>
<td>Eu</td>
<td>126 cm⁻¹</td>
<td>Bidentate</td>
</tr>
<tr>
<td>2,3-pyrazinedicarboxylate</td>
<td>(Y,Yb,Er), Eu</td>
<td>241 cm⁻¹</td>
<td>Unidentate</td>
</tr>
<tr>
<td>2-hydroxyquinoline-4-carboxylate</td>
<td>Eu</td>
<td>200 cm⁻¹</td>
<td>Ionic</td>
</tr>
</tbody>
</table>

In this thesis, all four possible metal-carboxylate coordination schemes were observed. Eu-PDA shows bidentate coordination, Eu-PZA shows unidentate coordination, Eu-TPA and Nd-TPA both show bridging mode and Eu-HQA exhibits ionic bonding. From these results, it is tentatively suggested that the organic precursor may be the main controller of the bonding mode. Even with different Ln precursors, e.g., Ce-TPA from Ce-guanidinate based precursor resulted in bridging mode connected films. On another hand, this was also confirmed with pyridine-3,5-dicarboxylic acid, when combined with Eu(thd)₉, or Er-guanidinate based precursor, both yielded Ln-3,5-pyridine thin films with bridging mode. On another note, the ionic bond nature in Eu-HQA may explain the larger than usual GPC observed in this process.

![Figure 14](image.png)

Figure 14 Different coordination modes between Eu ions and carboxylic acid groups in different organic precursors presented in this work.
Different organic precursors with functional groups or hetero rings can be more complex to analyse, the comparison between Eu-uracil and Eu-cytosine highlights the importance of studying the coordination by FTIR, as seen in figure 15, where both organic precursors comprise the same pyrimidine ring but differ in the substituents. The shifting of C=O stretching peaks of uracil from 1700 cm\(^{-1}\) to a lower wavenumber confirms that Eu binds to uracil through two C=O at C2 and C4 of the ring. Similarly, in the case of Eu-cytosine, the stretching peak of C=O at C2 shows the similar shifting behaviour, confirming it bonds with the Eu\(^{3+}\), while the presence of the stretching peaks of NH\(_2\) group at C4 confirms that the amine group remains free and uncoordinated to the metal.

Additionally, the N1H and N3H of the uracil ring are coordinated to the Eu\(^{3+}\), which the missing N1H and N3H stretching peaks at \(\sim 3000\) cm\(^{-1}\) confirm. In the case of Eu-cytosine, N1H stretching peaks and are missing. However, N3 in cytosine is completely occupied in the aromaticity of the ring with no additional hydrogen atom. Therefore, it is evident that cytosine coordinates with Eu\(^{3+}\) only through N1 of the ring and not both N1 and N3 as in uracil.

Through this FTIR study, it is confirmed that uracil is coordinated to Eu\(^{3+}\) through N1 and N3 of the ring, and two C=O substituents at C2 and C4, while cytosine coordinates to Eu\(^{3+}\) through N1 of the ring and one C=O substituent at C2, leading us to believe that uracil shows higher reactivity towards the metal precursor. This explains the relatively higher GPC (2.1 Å/cycle) of the Eu-uracil process compared to the relatively lower GPC (1.5 Å/cycle) of the Eu-cytosine process, which concludes that FTIR can be a key characterization method that unlocks many doors in understanding the Ln-organic thin films developed by ALD/MLD.

![Figure 15](image_url) Comparison between the FTIR spectra of 50 nm films of Eu-Cyt and Eu-Ura, done in this work Publication IV. (Adapted from American Chemical Society under CC BY 4.0)
4. Luminescence in ALD/MLD Ln thin films

One important achievement of Ln-organic thin films by ALD/MLD is the success in decreasing concentration quenching. Thanks to the organic molecules, Ln-organic thin films may show photoluminescence compared to their respective oxides that are usually non-photoluminescent. The antenna effect allows the organic layers to act as sensitizers for Ln3+ ions, to strengthen the emission. Additionally, Ln-organic thin films by ALD/MLD show high chemical stability. While physical stability is one of their drawbacks, because of the moisture adsorption that could change the thin film properties, and the inability to withstand high temperatures for prolonged time as the organic layers may decompose. Applying a moisture barrier layer can be quite effective in eliminating moisture absorption in these thin films.105

4.1 Effect of the organic component

Selection of the organic component is a crucial step in fabricating photoluminescent lanthanide-organic thin films with ALD/MLD. Ln-organic processes require lower deposition temperatures compared to the Ln2O3 processes by Ln(thd)3, which usually require a temperature ~ 300 °C. The organic precursor sublimation temperature and decomposition temperature control the lowest and the highest possible deposition temperature, respectively. It is important during the selection of the organic component that it would be reactive towards the available lanthanide precursors, particularly the less reactive Ln(thd)3. Therefore, highly reactive organic precursors are usually preferred such as, dicarboxylic acids, however other precursors with functional groups can also be reactive with such precursors and can potentially be more efficient. Figure 16 shows the organic precursors that have been experimented in this work.114

Most importantly, the organic component controls the absorption of light since the Ln3+ ions are notoriously known for low absorption cross-section. The absorbed light undergoes transferred to the Ln3+ ions, which emit their characteristic emissions. Therefore, the organic component of the film immensely affects its optical properties. UV-Vis absorption characteristics of the film and subsequently the selected excitation wavelength are crucial elements when transferring such photoluminescent thin films into applications.
The excitation wavelength can be manipulated through the careful selection of the organic precursor. From the excitation point of view, Eu-TPA films possess absorption that peaks around $\lambda = 250$ nm, while changing the benzene dicarboxylic acid precursor to a pyridine dicarboxylic acid resulted in shifting the peak of the absorption to a $\lambda$ of 270 nm.\textsuperscript{12} The sensitization of aromatic compounds has also resulted in luminescent films based on rare earth metals that are not typically luminescent such as La and Y, it is worthy to note that changing the organic component from terephthalic acid to naphthalene dicarboxylic acid has changed the colour of emission of yttrium-organic films.\textsuperscript{132,136}

Table 5 Absorption and excitation wavelength range of different Ln-organic thin films presented in this work.

<table>
<thead>
<tr>
<th>Organic precursor</th>
<th>$T_{dep}$ ($^\circ$ C)</th>
<th>Absorption (nm)</th>
<th>Excitation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terephthalic acid (TPA)</td>
<td>190–250</td>
<td>250–300</td>
<td>250–300</td>
</tr>
<tr>
<td>1,4-Naphthalenedicarboxylate (NDA)</td>
<td>220–250</td>
<td>200–250</td>
<td>250–260</td>
</tr>
<tr>
<td>9,10-Anthracenedicarboxylate (ADA)</td>
<td>150–220</td>
<td>200–265</td>
<td>----</td>
</tr>
<tr>
<td>Pyridine-3-carboxylic acid (PDA)</td>
<td>150–220</td>
<td>215–320</td>
<td>200–320</td>
</tr>
<tr>
<td>2,3-pyrazinedicarboxylate (PZA)</td>
<td>160–240</td>
<td>230–320</td>
<td>220–320</td>
</tr>
<tr>
<td>Uracil (Ura)</td>
<td>210–250</td>
<td>250–300</td>
<td>250–300</td>
</tr>
<tr>
<td>Cytosine (Cyt)</td>
<td>210–250</td>
<td>200–360</td>
<td>200–360</td>
</tr>
<tr>
<td>Cyanuric acid (TZO)</td>
<td>200–250</td>
<td>200–350</td>
<td>200–250</td>
</tr>
<tr>
<td>2-hydroxyquinoline-4-carboxylate (HQA)</td>
<td>210–250</td>
<td>200–430</td>
<td>200–400</td>
</tr>
</tbody>
</table>
The luminescence of Ln-organic thin films by ALD/MLD is arguably the most important character of such films, which makes studying the optical properties of these films essential. Light absorption and excitation of these films is mainly controlled by the organic precursor of the film thanks to the antenna effect, while the emission wavelength remains fairly similar thanks to the characteristic Ln 4f-4f emissions. Table 5 summarizes the UV-Vis absorption and excitation wavelength range of the different organic precursors presented in this work, while figure 17 shows a relevant comparison between the excitation range of some precursors used in this work. It is evident that 2-hydroxyquinoline-4-carboxylic acid gives the best possible result, regarding excitation wavelength range. Eu-HQA films show emission that is strikingly strong over a broad excitation wavelength range that includes UV range from 185 nm, as well as a portion of visible light with up to 400 nm.

![Figure 17](image17.png)  
*Figure 17 Excitation spectra of different Eu-organic thin films all of ca. 50 nm thickness seen in this work. Showing the excellence of Eu-HQA thin films when compared to other precursors, particularly the wide excitation wavelength range extending until visible light region. N.B, intensity is in log scale. (Adapted from American Chemical Society under CC BY 4.0.)*

Emission spectra of the Eu-based ALD/MLD thin films follow the expected 4f-4f transitions discussed earlier in section 2.1. Figure 18 shows that films deposited from different organic combined with Eu³⁺ show qualitatively the same emission, while the intensity may vary upon the efficiency of absorption and energy transfer provided by the organic molecule.

![Figure 18](image18.png)  
*Figure 18 Emission spectra of different Eu-organic thin films all of ca. 50 nm thickness seen in this work. (reproduced from American Chemical Society under CC BY 4.0)*
4.2 Effect of dilution

The typical way to overcome luminescence concentration quenching is the use of lanthanides as dopants in host lattices. The deposition of lanthanide-organic hybrid thin films was already established as a route to overcome concentration quenching, however, during this work, it was also found that dilution of the emissive ion by a non-emissive rare earth possibly decreases concentration quenching further, as it strengthens the emission of the luminescence. Therefore, the combination of both organic building blocks and diluting the concentration of the Ln emissive centres offers better results for photoluminescent thin films. Such combination maintains the merits of the organic component towards the excitation wavelength, while enhancing the emission by reducing concentration quenching further.

The dilution affects the excitation and emission intensity of the films significantly compared to non-diluted films in most cases. However, this should be carefully studied further from two angles. First, what metal would be used for diluting the Ln content, non-emissive rare earth metals are considered prime candidates, such as Y, Sc, La and Lu. As these ions are non-emissive, simultaneously they possess similar chemical properties when reacting with the organic precursors, while other lanthanide metals with no emission at the target range might not be as useful, as these metals might absorb the energy transferred from the organic component. The second angle to be noted is the organic molecule involved, as one of the most important cases found here is that the dilution had almost no effect on the excitation and emission at longer wavelength, which definitely needs to be researched further.

It is worth noting that each of these metals may show different effect upon using as a diluting agent. For example, as seen in figure 19 when Y is used to dilute Eu-TPA, the best result is seen at 88% Y and 12% Eu. On the other hand, when using La to dilute Eu-HQA, the best result is seen at 50% dilution. One hypothesis is that this difference could arise from the difference of the size and the radius of each ion, as La$^{3+}$ is larger and have a longer radius than Y$^{3+}$, then the optimal distance between emissive ions could be reached with less dilution. However more systemic research is further required to better understand such effect. It is important to note that having a second metal ion may lead to increases difficulties in process optimization.
4.3 Mixing Lanthanides

ALD and ALD/MLD facilitate doping in thin films, they particularly allow control and flexibility of the selected precursors. Thanks to the similar chemistry of the lanthanides, synthesizing a mixed lanthanide precursor is straightforward and follows the same logic as synthesizing single Ln$^{3+}$ ion precursor, this can be one way of doping or mixing of different Ln$^{3+}$ ions in one film. The concentration of different Ln$^{3+}$ ions in a mixed precursor, can be determined by techniques such as X-ray fluorescence or X-ray photon spectroscopy, through this method a promising result of upconverting lanthanide-organic thin films was already achieved.\textsuperscript{137}

The concept of supercycle -discussed before in section 3.2- that was applied to use Ln as dopants, can be similarly applied to obtain mixed lanthanides thin films. Such concept may allow the mixing of any number and proportions of lanthanides, where the only limitation would be the number of precursors the ALD equipment can hold simultaneously. Since white light emitting materials are in increased demand for a wide range of application, lanthanide white light emitting thin films by ALD/MLD are important to explore with their high colour rendering index.\textsuperscript{77} In this thesis,\textsuperscript{131} the mixing of Eu$^{3+}$ and Tb$^{3+}$ in one film was led to films emitting either red or green emission. Only upon the addition of Er$^{3+}$ the emission colour was shifted into warm white. It is also noticeable that the emission intensity was drastically reduced. Such reduction could be resulting from absorption of energy by Er$^{3+}$. This could be confirmed by further experiments, if such energy is emitted by Er$^{3+}$ at around 1500 nm in the NIR range, which is the typical emission range of Er$^{3+}$. On the other hand, adding La$^{3+}$ to the mixture of Er$^{3+}$, Eu$^{3+}$ and Tb$^{3+}$ maintained the warm white light emission, while strikingly increasing the emission intensity. This could be attributed to the dilution effect explained in section 4.2. The experimental results of the latter films are comparable to commercial white light emitting devices, see figures 20 and 21.

![Figure 20](image.png)

**Figure 20** White light emitting thin film consists of Eu, Tb, Er and La as the lanthanides and terephthalic acid as the organic part done in this work.\textsuperscript{131} (Reprinted from Royal Society of Chemistry under CC BY 3.0. License)

Mixing of several lanthanide ions in ALD/MLD opens the door to a different strategy when designing those thin films. Commonly in a doped or mixed ALD process, the mixing strategy aims to ensure homogeneity, such that the film consists of one layer of mixed or doped metals. However, a new strategy could be designing Ln$^{3+}$-organic films in a multi-layer or nanolaminate structure, where each layer could be either undoped or doped by other lanthanide species. Such multi-layering already exists for ALD, for example nanolaminate thin films of
ZrO$_2$

and Er$_2$O$_3$. On the other hand, in ALD/MLD an emerging growing strategy is the nanolaminates of an inorganic materials, such that metal oxides layers could be separated with one or a few organic layers. In Publication III, multi-layering of lanthanide-organic hybrid thin films by ALD/MLD was studied for the first time.

Interestingly, the multi-layered film showed better and enhanced emission properties compared to a homogenously-deposited one-layer thin film, even when the final number of ALD/MLD cycles was the same, and the final number of pulses of each Ln species was also the same, which resulted in a white light emitting thin film with comparable colour emission and characteristics as commercial white light sources.

![Figure 21 Comparing between ALD/MLD thin film sample (purple circle) and commercial LED lamp (LED), incandescent bulb (Inc.), and a fluorescent tube (Fluor.) in the CIE 1931 diagram. (reprinted from Royal Society of Chemistry under CC BY 3.0.]

4.4 Substrate selection

One of the important advantages of hybrid Ln-organic thin films is the added flexibility that comes from the organic part of the film, in contrast to the purely inorganic films. However, to fully maximize the potential of such films the substrate selection is a delicate matter. ALD/MLD combines the ability to have flexible lanthanide-organic thin films, with the low processing temperature that reached, in this work, as low as 160 °C. At such relatively low temperature heat sensitive substrate materials can be used, more interestingly polymer sheets, such as polyimide “Kapton”, see figure 22. One of the main important advantages of Kapton sheets is that it can withstand the deposition temperatures without losing its mechanical properties. Therefore, flexible luminescent thin films have been achieved in this work, the films have shown continuous luminescence, even after bending in different directions, or in a cylindrical shape, as seen in Figure 22.

Si substrates are the most used in this work and commonly in Ln$^{3+}$-organic thin film research, as thin films on Si are easier to characterize. Particularly, X-ray and FTIR measurements are easily performed on Si substrates, while it
proves more difficult on other kind of substrates, such as polyimide sheets. While the advantage of Si is the simple characterization, and the advantage of polyimide sheets is the mechanical flexibility, they absorb a large fraction of the excitation, or the emitted light. This absorption results in a lowered excitation and emission intensity, and more importantly lower quantum yield. Quantum yield is the ratio calculated mainly from the absolute emitted light from the film to the absolute absorbed light by the film, using substrates with high absorption in either the excitation or the emission range would lead to a low quantum yield. The typical quantum yield of Ln-organic thin films deposited over Si or Kapton is less than or equal 2%. The low quantum yield issue can be addressed by careful substrate selection. Materials with low UV and visible light absorption, such as quartz glass would be advantageous when depositing layers of Ln-organic materials. E.g., when depositing 50 nm Eu-PDA layer over quartz glass, the resulting quantum yield rose from ~2% on a silicon substrate to a total of 14.6%, achieving an over 7 folds improvement.

Figure 22 (Top) Eu-PDA thin film deposited on Kapton sheet at 180 °C in room light and under λ<sub>ex</sub> = 302 nm, showing flexible properties without discontinuation in the luminescence. (Middle) Eu-HQA thin film deposited on Kapton sheet, held into a cylindrical shape showing the red emission from Eu<sup>3+</sup> while maintaining the flexibility. λ<sub>ex</sub> = 302 nm. (Bottom) Eu PDA on quartz glass substrates deposited at 180 °C offering relatively high quantum yield of ~14.6%.
5. Upconverting ALD thin films

The global demand of environmentally friendly energy increases rapidly, renewable and sustainable energy sources such as solar energy is one of the main sources for a greener future regarding energy production. Research for new photovoltaic technologies and materials to improve solar energy harvesting tackles one of the main obstacles to enhance solar cell performance generally. While the solar energy could potentially be sufficient to power the world, one of the major issues is the band gap of the materials used in solar cells that leaves a major part of this solar energy unused. Mainly the current solar cell technologies absorb visible radiations and NIR in some cases. However, they are transparent to UV photons with higher energy than the band gap, and photons with energy lower than the bandgap usually in the NIR region of the solar spectrum.\textsuperscript{139}

Amorphous silicon (a-Si) has a wide bandgap of \(~1.8\) eV, which is why solar cells based on a-Si absorb photons up to only \(700\) nm. However, crystalline silicon (c-Si) possesses a narrower bandgap of \(~1.1\) eV which allows cells to absorb up to \(1100\) nm.\textsuperscript{140} More emerging solar cell technologies such as, dye sensitized solar cells has usually a bandgap of \(~1.8\) eV limiting its absorption at \(750\) nm and materials used in perovskite solar cells usually enjoys a bandgap of \(1.55\) eV that allows perovskite solar cells to absorb up to \(800\) nm.\textsuperscript{141} It is clear that current solar cell technologies are severely limited in absorption of NIR, which created an interest of applying materials that are capable of absorbing NIR photons. Upconverting materials can absorb NIR photons and convert it to visible light photons that is absorbed by the solar cell. Hence, they allow better energy harvesting and improving the solar cell efficiency.\textsuperscript{142}

Therefore, UC materials gained considerable research attention in solar cell applications over the last decade, particularly Ln based UC materials. Thanks to their line sharp emission and ability absorb light in different NIR ranges. For example, Yb\textsuperscript{3+} is well known for absorbing NIR around \(980\) nm, while Nd\textsuperscript{3+} possess several NIR absorption peaks around \(820\) nm, \(900\) nm, \(1000\) nm, \(1600\) nm, and \(2400\) nm. While Yb\textsuperscript{3+} and Nd\textsuperscript{3+} are the most commonly used NIR absorbers, other Ln\textsuperscript{3+} ions also show NIR absorption, such as Er\textsuperscript{3+} at \(1500\) nm mainly, with lower absorption peaks at around \(980\) nm and \(2000\) nm, Tm\textsuperscript{3+} also shows NIR absorption around \(1200\) nm and \(1600\) nm and Ho\textsuperscript{3+} has absorption peaks around \(1150\) nm, \(1200\) nm, \(1850\) nm, and \(1950\) nm. Such absorption bands can be useful for different solar cell technologies, see figure 23. Even Ln that are commonly used for downconversion show absorption bands in the NIR, such as
Sm$^{3+}$ around 1100 nm, 1250 nm, 1400 nm, and 1550 nm. Some of these absorption bands are of a higher intensity than Sm$^{3+}$ visible light absorption bands.\textsuperscript{143}

The synthesis of new UC materials and fine-tuning of the currently known ones depends on developing new host materials or tailoring of the sensitization using organic molecules when possible. Additionally, fine tuning the lanthanide doping composition, considering the sensitization and emission efficiency. As Ln based UC materials is considered most promising for the PV technology. It’s crucial to consider the careful choice and selection of Ln$^{3+}$ ions depending on the type of solar cell to be used.

The relatively narrow bandgap of c-Si allows this type of solar cells to absorb light up to ~1100 nm, which renders Yb$^{3+}$ less significant as it shows one absorption band around 980 nm. Therefore, in such cases the use of Nd$^{3+}$, Ho$^{3+}$, in addition with Er$^{3+}$ can offer a better enhancement, tuning the composition of such materials can be a challenge, particularly if the more than two Ln species will be used as dopants in one single material. Yb$^{3+}$ based materials can be then directed towards more emerging dye synthesized solar cells and perovskite solar cells.

Another aspect includes the integration of UC materials in the novel solar cell technologies, all thin film solar cells are in the centre of such research, which places thin film deposition technologies like ALD and ALD/MLD at the centre of attention. ALD and the organic analogue MLD have been used extensively to research Ln based thin films, however there is little research on the UC properties of thin films grown by this technique. Utilizing the advantages of ALD technique such as, high conformality and depositing on high aspect ratio samples may offer a new perspective on how to improve UC of Ln films.\textsuperscript{137,144}
Upconverting thin films could be Ln-organic thin films, such as the (Y, Yb, Er)-pyrazine, or incorporating an NIR organic absorbing molecules with (Yb, Er)-IR-806.\textsuperscript{137,144} It can also be Ln oxide films such as (Yb,Er)\textsubscript{2}O\textsubscript{3},\textsuperscript{39} or (Er,Ho)\textsubscript{2}O\textsubscript{3} presented in this thesis,\textsuperscript{1} see figure 24, which shows upconversion emission spectrum and possible mechanisms of a 60 nm sample of (Er\textsubscript{0.95}Ho\textsubscript{0.05})\textsubscript{2}O\textsubscript{3}. Since the final aim was to test these films for c-Si solar cell assistance, Yb\textsuperscript{3+} was replaced with Ho\textsuperscript{3+} to offer more significant enhancement.

![Figure 24](image)

After proving that the films exhibit upconversion emission, an enhancement of up to 3% in the short circuit current density of a bifacial c-Si solar cells was seen in \textit{Publication I}, when the films were used as a back reflecting layer, see figure 25. Thus, photons emitted from the thin films can be then absorbed by the rear side of the solar cell.

Three thin films of (Er\textsubscript{0.95}Ho\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} with different thicknesses 30 nm, 45 nm and 60 nm were experimented by being placed at the back side of the same solar cell, while the front face of the solar cells was illuminated by an equivalent of 16 Suns. The c-Si solar cell was held with a fixture to allow placing the thin films below the backside. The fixture shadows part of the backside of cell, which led to the backside being partially illuminated. The c-Si solar cell was maintained in the same position all the time to allow tracking of only the effect of changing the thin films. The films were alternated in their position behind the backside, allowing the area shadowed by the fixture to be the same during all measurements.

![Figure 25](image)
The 30 nm thin film showed almost no enhancement in terms of short circuit current density, while the 45 nm and 60 nm thin films showed a better enhancement in short circuit current density, with 60 nm proving to be the best of the three experimented films with almost 3% enhancement. While it can be tentatively suggested that having thicker films offer better enhancement for the solar cell, more systematic investigation should be further carried out in this regard.
The emission of Ln-organic thin films, such as Eu-HQA films can be utilized as a gateway for FRET emission when combined with commercial FRET kit Alexa Fluor 647. This molecule can absorb the light emitted by Eu\(^{3+}\) at 615 nm and emit itself light at 660 nm. The FRET phenomenon on the bulk material scale has been well established with some lanthanides, e.g. Eu\(^{3+}\), as donor materials.\(^{52}\) FRET phenomenon has been implemented as a diagnostic tool in various ways, including viral infection detection, immune assays, tumour markers detection, DNA detection, drugs of abuse detection.\(^{55-57,145-148}\)

As FRET phenomenon deal with biological samples, this leads to few limitations. One of these limitations is the autofluorescence of the biological samples, which may lead to a high background noise and subsequently reduced sensitivity of the measurements. This issue can be solved by employing the time-resolved measuring mode. In time-resolved Förster resonance energy transfer (TR-FRET), The signal is collected in a retarded mode, which allows enough time, usually in ns range, for the autofluorescence to decay before the actual signal collection in µs-ms range. In such cases, the long luminescence lifetime of the lanthanide ions offers a suitable option for luminescence.\(^{149}\)

Another limitation of the FRET-based diagnostics is the use of UV light for excitation, which may damage biological samples quickly. Hence, the use of visible light or NIR for excitation is usually preferred. In bulk Ln\(^{3+}\) materials, visible light excitation of downconverting lanthanide ions, such as Eu\(^{3+}\), is achieved by having large organic sensitizing molecules. However, such molecules usually have difficult synthesis routes, which are difficult to scale up.\(^{150,151}\) Additionally, the traditional synthesis routes lack the ability of having conformal nano-scale precise thin films that is essential to having an immobile Ln\(^{3+}\) donor.

In **Publication V**, a practical and simple ALD/MLD approach to fabricate Eu-HQA thin films was shown, such films can be excited at visible light range “400 nm”. The films have also been experimented successfully as FRET donor species, as seen in figure 26, by using a commercial FRET kit that contains Alexa Fluor ™ 647, as an acceptor fluorophore. In the experiment, illustrated in figure 27, ALD/MLD thin films were deposited on a nanoplasmonic substrate that enhances the Eu\(^{3+}\) emission ~20 folds compared to silicon substrates, and the films were excited at 400 nm, and the emission from Eu\(^{3+}\) can be seen at 615 nm, see the left side of figure 26, the emission is then switched to 660 nm i.e.,
darker red colour, as seen in the right side of figure 26, after the addition of a droplet of Alexa Fluor™ 647. The results show a remarkable achievement of the first FRET enabled emission by using the emerging ALD/MLD technology for the fabrication of an immobile donor fluorescent thin films.

![Eu-HQA and AF 647](image)

**Figure 26** (Left) 615 nm emission from Eu-HQA thin films. (right) 660 nm of Alexa Fluor 647 FRET kit when a drop of the molecule was added on top of the Eu-HQA. (reprinted from Royal Society of Chemistry under CC BY 3.0.)

The emission intensity at 615 nm from Eu$^{3+}$ decreased upon adding the Alexa Fluor 647 droplet on the Eu-HQA film. This decrease could be through the transfer of energy from Eu-HQA to Alexa Fluor 647. However, the emission intensity at 660 nm only slightly increased. Therefore, a better enhancement in energy transfer and further optimization is still required. Therefore, further research towards enhancing the FRET emission is required to bring such initial results towards bioassay or biodetection technologies.

![Eu-HQA and AF 647](image)

**Figure 27** Using Eu-HQA thin films deposited on plasmonic substrates as FRET donors, excited by visible light. (reprinted from Royal Society of Chemistry under CC BY 3.0.)
7. Conclusions

The unique advantages offered by ALD could be in principle an important asset to pave the way for the successful incorporation of different luminescent thin films in novel applications. In this work, doping erbium oxide with small amounts (~5%) of Ho$^{3+}$ allowed the films to show upconversion luminescence. These upconverting thin films were shown to improve the performance of the market dominant c-Si solar cell by 3% under a solar concentration of 16 suns, when added as a back reflecting layer in Publication I. Further improvement could be expected by incorporating the upconverting layer in the passivation layer of the c-Si solar cell. Additionally, compositional tuning of the erbium/holmium ratio is still required. On the other hand, for other emerging solar cell technologies such as perovskite solar cells, lanthanide ions with larger absorption cross-section such as Yb$^{3+}$ should be added to the matrix.

Organic molecules in lanthanide-based thin films fabricated by ALD/MLD offer several additional advantages. Firstly, organic molecules act as building blocks to offer proper separation distance between Ln$^{3+}$ ions to thereby decrease the so-called concentration quenching effect. Secondly, thanks to the antenna effect, the organic molecules can enhance the luminescence intensity of such thin films. Finally, one of the main conclusions from this thesis is that by the proper tailoring of the organic component the excitation wavelength range of the ALD/MLD-grown lanthanide-organic thin films can be significantly altered. Prior to this work, TPA was routinely used as the organic MLD precursor for the luminescent Ln-organic film fabrication. However, e.g. Eu-TPA films were found to show a narrow excitation energy range on short wavelengths from 185 nm to 280 nm (Publication II). It was highly difficult to obtain efficient luminescent films working with longer excitation wavelengths. In this work, numerous novel organic precursors were tested, and the most interesting of these processes are reported in Publications II, IV, and V. These precursors now offer a variety of Ln-organic ALD/MLD processes that can cover a wide range of excitation wavelengths relevant to several application areas. For example, Eu-PDA films possess a stronger excitation and emission intensity than Eu-TPA and an extended excitation range up to 320 nm. Additionally, Eu-Cyt films extend the excitation range up to 365 nm. Most interestingly, Eu-HQA thin films can be efficiently excited with wavelengths up to 400 nm in the visible range. This presents the first ALD/MLD deposited lanthanide-organic thin films that can be excited using visible light. This eliminates the need for UV excitation sources that are detrimental to biological samples in potential bioimaging and biodetection applications. Searching for higher excitation and emission intensities
should not end here, as examining more carefully the selected organic precur-
sors could lead to even better results, particularly if the ALD/MLD processes
would be expanded to more than just Eu$^{3+}$ based films.

Thin films fabricated by ALD/MLD that can be excited by visible light also of-
fer a potential immobile donor phase for FRET emissive materials, as was
shown in Publication V. As FRET intensity is inversely related to the distance
between the donor and acceptor chromophore, having an immobile donor phase
can help in maintaining a shorter distance between the donor and acceptor
phase. This can be optimized further in the future for FRET-based diagnostic
assays. In this work, using ALD/MLD-fabricated Eu-HQA thin films of 25 nm
thickness as a FRET donor chromophore, the 660 nm emission from the FRET
emitter chromophore Alexa Fluor 647 was demonstrated for the first time. In
this thesis, emission intensity of photoluminescent thin films fabricated by
ALD/MLD was significantly enhanced by dilution of the active Ln$^{3+}$ ion with
non-emissive rare earth ions, such as Y$^{3+}$ and La$^{3+}$. Other non-emissive rare
earth metals such as Sc$^{3+}$ and Lu$^{3+}$ could also be experimented in the future. On
the other hand, doping of Ln$^{3+}$ by other emissive Ln$^{3+}$ ions was demonstrated in
this work to show the ability of ALD/MLD to tune the photoluminescence emis-
sion colour. The emission colour of the films ranged between red, green, and
warm white. Changing the Ln$^{3+}$ ions involved and their respective composition
by controlling the number of cycles for each Ln precursor was the way to tune
the emitted light colour. Further compositional tuning and even varying the Ln
species used could be the way to take this research to the next step. The present
thesis also highlights the previously undiscovered potential of ALD/MLD re-
garding the multi-layering of the Ln-organic emissive layers (Publication III).
Such multi-layering can be examined more extensively in future research, for
example to enhance emission strength, quantum yield or to gain multi-func-
tional thin films. Finally, this work has underlined the importance of the sub-
strate choice, as improved quantum yields were realized with substrates show-
ing less own absorption in the excitation and emission ranges used, compared
to ones that absorb in either region.

To conclude, the ALD/MLD approach towards different luminescence lantha-
nide-organic thin films is still very new, but currently emerging. In this thesis,
concrete steps were taken to advance this approach and addressing the many
initial research questions, including the excitation wavelength range extension,
manipulation of the emission range, enhancement of the emission intensity and
taking the initial steps in applying such films to potential applications with rea-
sonable results. However, further research is still required, as there is definitely
plenty of room to improve the current results.
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