Single-step approach to sensitized luminescence through bulk-embedded organics in crystalline fluorides

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Luminescent materials enable warm white LEDs, molecular tagging, enhanced optoelectronics and can improve energy harvesting. With the recent development of multi-step processes like down- and upconversion and the difficulty in sensitizing these, it is clear that optimizing all properties simultaneously is not possible within a single material class. In this work, we have utilized the layer-by-layer approach of atomic layer deposition to combine broad absorption from an aromatic molecule with the high emission yields of crystalline multi-layer lanthanide fluorides in a single-step nanocomposite process. This approach results in complete energy transfer from the organic molecule while providing inorganic fluoride-like lanthanide luminescence. Sm$^{3+}$ is easily quenched by organic sensitizers, but in our case we obtain strong fluoride-like Sm$^{3+}$ emission sensitized by strong UV absorption of terephthalic acid. This design allows combinations of otherwise incompatible species, both with respect to normally incompatible synthesis requirements and in controlling energy transfer and quenching routes.
uminescent materials based on lanthanides are a well-developed field with respect to materials, physical mechanisms and use in applications like lighting, laser, optoelectronics and solar cells. An increasing amount of research is focused on advanced optical systems, requiring interactions between two or more different types of ions. Examples are downconversion and upconversion. There are two major bottlenecks slowing down this development. (1) The dopants must be controlled on a (sub-)nanometre scale to prevent unwanted cross-relaxations and other quenching processes while at the same time optimizing the desired energy transfers, and (2) combining the weak narrow line-absorbing lanthanides with a strong broad band-absorbing and tunable sensitizer.

Twenty years ago, the term downconversion was coined and an efficiency of 190% was demonstrated to be possible. Four years later, an efficiency of 194% was shown in BaF2:Gd3+–Eu2+–13. Recently, record high upconversion efficiencies were realized in multi-shell nanoparticles of NaGdF4:Nd3+,Yb3+,Tm3+. Common for both cases is the use of crystalline fluoride host matrices and multiple lanthanides. For materials using more than two different optically active ions, it is beneficial to separate these in a multi-shell/layered structure so that only two ions can interact at a time, preventing cross-relaxation and quenching. The material systems demonstrated so far that both allow multi-shell designs and can incorporate trivalent lanthanides, is limited, and the majority of literature revolve around NaYF4-type fluorides. Another common factor for downconversion and upconversion is that these processes are difficult to combine with a strongly absorbing sensitizer. One reason is that there are limited options of possible ions that easily fit into the cation sites in these crystalline fluorides. Recently, Fischer et al. showed that, even though Ce3+ cannot normally be used as a ultraviolet (UV) sensitizer for Eu3+ due to a quenching Ce3+–Eu3+ charge transfer state, they were successful in avoiding this quenching mechanism by separating Ce3+ and Eu3+ in separate layers and using Tb3+ ions to allow energy migration from Ce3+ to Tb3+ to Eu3+ while spatially separating Ce3+ and Eu3+ in core–shell TbF3 nanoparticles. It is still a challenge to find suitable sensitizer of the number of possible sensitizer ions that easily fit into TbF3 and similar matrices is limited. Aromatic molecules belong to a material class that show excellent sensitizing abilities, very strong absorption and full tunability of the absorption range. One solution is to anchor such organic sensitizer molecules on fluoride nanoparticles, but also this is challenging without causing concentration quenching in the organics. An easy, controllable way of combining strongly absorbing species with multilayered crystalline fluorides is still lacking.

Using atomic layer deposition (ALD), we have previously shown that multilayered structures of luminescent oxides with layer thicknesses <0.4 nm can be synthesized in addition to multilayer structures with multi-lanthanide incorporation. Deposition of nearly all lanthanide oxides can similarly be realized by ALD and organic molecules can relatively easily be incorporated into solid films. ALD is also called molecular layer deposition when including organic molecules. Lanthanide fluorides have been successfully deposited by ALD at low (175 °C) temperatures, minimizing the risk of thermal decomposition when incorporating organic components. ALD is in fact well suited for all the different components in organic sensitized multi-component luminescent systems.

Here we combine the known ALD chemistries of metal fluorides from metal-thd (thd = 2,2,6,6-tetramethyl heptane-dione) and NH4F with strongly UV-absorbing aromatic acid-based hybrid materials to combine the conversion and luminescence properties of multilayer crystalline lanthanide fluorides with the strong absorption strength and sensitization of organics.

We successfully combine two different material classes and obtain a molecule-doped crystalline multilayer film structure while also preventing quenching of the phonon-sensitive Sm3+ by the high-energy phonons on the acid. The nanocomposite structure is illustrated in Fig. 1, along with an energy-level diagram to show the energy flow, a photo of a sample and an energy-level diagram showing the emission lines from the lanthanides included in this work. The essence is that by combining organics and inorganic fluorides in a nanocomposite, we have achieved a combination of very strong absorption and highly efficient luminescence that would not be possible in either the organic or fluoride alone. In addition, embedding organic sensitizers into the bulk of inorganic materials also overcomes the often encountered photobleaching, as the molecules are now protected from (photo)chemical degradation by air or moisture.

This layer-by-layer nanocomposite design is generalizable for combinations of other optical material classes as well. ALD is capable of depositing nearly the entire periodic table including most inorganic material classes like oxides, sulfides, nitrides, fluorides and phosphates in addition to organic–inorganic hybrid and purely organic materials. In the recent years, several different combinations of material classes have been synthesized as nanocomposites by ALD. This includes multiple different oxides, oxide–nitride, oxide–sulfide, oxide–metal, oxide–hybrid and controlled crystalline oxide–amorphous oxide nanocomposites. Several of these are used to control optical properties or in optics. ALD is a powerful synthesis tool allowing very complex designs that also includes two or more material classes. With this in mind, it is our opinion that there is large unexplored terrain within advanced optical materials that can and should be investigated with ALD.

**Results**

**ALD growth.** Fluoride depositions with ALD is by far not as well explored as oxide depositions, and indeed lanthanide fluorides have not been deposited before using the Ln(thd)3 and NH4F precursor pairs. Exploring this ALD chemistry in detail is outside the purpose of this work. Nonetheless, for controlled growth of our multilayer design, we explored the saturation conditions for the LnF3 cycles, Fig. 2a. Despite clear indications of ALD growth in the initial 1 and 2 s for the cation and anion, respectively, the growth did not saturate completely for longer pulse times up to 12 s. We also found that the growth rate had a large dependence on how much NH4F was loaded in the precursor boat, with growth rate per cycle (GPC) varying between 11 and 21 pm/cycle. In addition, there was almost a gradient of 5–20% between samples spaced 8 cm apart along the gas flow direction. Nevertheless, increasing any pulsing or purging parameters longer than 1.5/1/3/1 s had negligible effect on both growth rate and gradients. Based on this, we decided to use 1.5/1/5/1 as pulsing and purging parameters for all cycles. Note that all quartz crystal microbalance (QCM) results use 1.5/1/3/1 as standard parameters.

For the aromatic–lanthanide hybrid Ln2bdc3 cycles (bdc = benzene dicarboxylate), it was found that the parameter 1.5/1/2/1 resulted in very even films throughout the reaction chamber and was found to be suitable for proper surface saturation with a GPC of 175.7 pm/cycle with a thickness difference of 0.6% between samples 8 cm apart. We also experience that these hybrid depositions give identical results between different ALD reactors of the same type. Thus we did not investigate the growth chemistry of the hybrid cycles further. Nevertheless, it was decided to use longer H2bdc pulses (5 s, as for NH4F) to ensure saturation also when combining Ln2bdc3 cycles with LnF3 cycles.

To investigate whether and how combining hybrid Ln2bdc3 and fluoride LnF3 cycles affect each other’s growth, a multilayer
deposition consisting of one Ln$_2$bdc$_3$ and nine LnF$_3$ cycles was investigated with QCM, Fig. 2b. This represents a 4Sm sample according to the naming convention used here. In addition, pure TbF$_3$ and pure Tb$_2$bdc$_3$ cycles are shown for comparison. Each of the three data sets is averaged over 16 cycles for 4Sm (named Nanocomposite in Fig. 2b) and Tb$_2$bdc$_3$, and 80 cycles for TbF$_3$. For the pure Tb$_2$bdc$_3$ and TbF$_3$ cycles, three identical cycles are plotted after each other to illustrate the continuous growth. For the nanocomposite, only five of the nine TbF$_3$ cycles are shown in addition to the Tb$_2$bdc$_3$ cycle.

The LnF$_3$ cycles do not show any significant changes after the Ln$_2$bdc$_3$ cycle, indicating that the hybrid cycle does not change the total mass deposited during each LnF$_3$ cycle. On the other hand, it can be seen that the H$_2$bdc pulse causes a mass gain for the following Tb(thd)$_3$ pulse. During the H$_2$bdc pulse, there is an initial mass decrease. This is rapidly followed by a similar sized
mass increase for pure Tb$_2$bd$_3$, and a delayed mass increase for
the nanocomposite.

There are several possible surface reactions during these
nanocomposite depositions. The following reactions show the
possible reactions between [-Tb(thd)$_x$] (x = 1 or 2) species on the
surface and H$_2$bd$_c$ and HF (from NH$_4$F) anion pulses. Ideal
reactions would be a simple ligand exchange mechanism,
releasing Hthd as a leaving molecule. It is also possible that
H$_2$bd$_c$ can etch TbF$_3$ surfaces as H$_2$bd$_c$ is a stronger acid than
HF. The opposite etching of Tb-bd$_c$ by HF is less likely. Lastly, it
is possible for the bd$_c$ molecule to bond to two different Tb$_3^+$
ions, creating a "bridge" between them. All of these reactions during
the anion pulse will cause a mass decrease, apart from the
etching reaction. The mass difference $\Delta m$ is calculated with
respect to one mole Tb$_3^+$ surface species. For comparison, the
masses of Tb$_3^{3+}$, thd$^-$, F$^-$ and bd$_c$ are 159, 183, 19 and 164 g/
mol, respectively.

Ideal reactions

\[
\begin{align*}
\text{(-Tb(thd)$_x$)} + \text{HF(g)} & \rightarrow \text{(-Tb(thd)$_{x-1}$F + Hthd(g)} \\
\Delta m_1 & = -164 \text{ g/mol} \\
\text{(-Tb(thd)$_x$)} + \text{H$_2$bd$_c$(g)} & \rightarrow \text{(-Tb(thd)$_{x-1}$(Hbd$_c$) + Hthd(g)} \\
\Delta m_2 & = -18 \text{ g/mol}
\end{align*}
\]

Etching reactions

\[
\begin{align*}
\text{-TbF$_x$ + H$_2$bd$_c$(g)} & \rightarrow \text{-TbF$_{x-1}$(Hbd$_c$) + HF(g)} \\
\Delta m_1 & = +146 \text{ g/mol}
\end{align*}
\]

Bridging reactions

\[
\begin{align*}
2\text{-Tb(thd)$_2$ + H$_2$bd$_c$(g)} & \rightarrow \text{2(-Tb(thd)$_{1.5}$ + 2Hthd(g)} \\
\Delta m_4 & = -101 \text{ g/mol} \\
2\text{-Tb(thd)$(bdc)_{0.5}$ + H$_2$bd$_c$(g)} & \rightarrow 2\text{-Tb(thd)(Hbd$_c$)} \\
\Delta m_5 & = +83 \text{ g/mol} \\
2\text{-Tb(thd)$(bdc)_{0.5}$ + 3H$_2$bd$_c$(g)} & \rightarrow 2\text{-Tb(Hbd$_c$)$_2$ + 2Hthd(g)} \\
\Delta m_6 & = +65 \text{ g/mol}
\end{align*}
\]

Among these reactions, only Eq. 4 can provide an overall mass
gain during the anion pulse. In the case of a bridging bd$_c$ molecule,
the overall mass gain is negative even though Eqs. 5 and 6 show
positive mass gains. This is because the bridging reactions
(Eq. 4) are followed by the bridge-opening reaction (Eq. 5) and ideal
reactions (Eq. 2) removing the last thd$^-$ groups. Bridge-opening
and ideal thd reactions are shown in Eq. 6, showing the mass gain
in this step is smaller than the mass reduction during the initial
bridging reaction (Eq. 4). This bridging mechanism will then cause
a temporary mass decrease followed by a mass increase while still
maintaining a small overall mass decrease from start to finish. Only
the etching reaction (Eq. 3) will cause a net mass gain.

Figure 2c shows the X-ray diffraction (XRD) patterns of the
deposited xSm layers in addition to a deposition of 2000 cycles TbF$_3$.
It is seen that the films are amorphous for $x \leq 50$ and crystallize as
orthorhombic TbF$_3$ (PDF# 32-1290) for larger x values.

**Optical properties.** Figure 3a shows the photoluminescence (PL)
and photoluminescence excitation (PLE) spectra of four selected
samples. These are Tb$_2$bd$_3$ showing Tb$^{3+}$ emission, Eu$_2$bd$_3$
showing red $^{3}D_{0} \rightarrow ^{7}F_{2}$-dominated emission, 200Eu showing
orange $^{3}D_{0} \rightarrow ^{7}F_{1}$-dominated emission and 100Sm showing
Sm$^{3+}$ emission. Sm$_2$bd$_3$ gives no detectable emission in the
200–1100 nm range upon 280 nm excitation. The 200Eu sample
show two additional peaks (marked *$+$) that are at too high
energies to originate from $^{5}D_{0}$. Based on their peak positions
matching those of Tb$^{3+}$, these are likely Tb$^{3+}$ emissions. The PL
is obtained using a 280-nm diode while PLE spectra are recorded
monitoring the highest emission peak for all samples. All the
samples clearly show the two excitation bands of the aromatic
molecule.

Figure 3b shows normalized PL spectra of the xSm samples. In
addition, Tb$_2$bd$_3$ is included to show the Tb$^{3+}$ emission peaks as
some Tb$^{3+}$ emission is seen in all xSm samples. Note that the
total emission intensity of samples with $x \leq 10$ is very low (see
Fig. 3c). The 100Sm and 25Sm spectra show clear differences in
the number and sharpness of the peaks, while 50Sm shows a
superposition of these two spectra (most clearly seen by the
additional hump around 600 nm).

Figure 3c shows the PL intensity of one Sm$^{3+}$ and one Tb$^{3+}$
peak integrated over the 595–615 and 540–550 nm range,
respectively, as well as the PL lifetime of Sm$^{3+}$ emission at 594 nm,
as a function of TbF$_3$ cycles separating the Tb$_2$bd$_3$ and SmF$_3$
cycles. As there is quite a bit of overlap between the Sm$^{3+}$ and the
weaker Tb$^{3+}$ emission peaks, these ranges were chosen. An
estimate of the TbF$_3$ layer thickness (in nm) separating Sm$^{3+}$
and the organic molecules is given in numbers over the data points.
This estimate is calculated by taking the total film thickness (of
the stack of 10 supercycles) from ellipsometry, subtracting 10 nm
for the 10 Tb$_2$bd$_3$ layers, which are about 1 nm thick according
to Fig. 4a, and dividing by 2 as there are 20 bridging layers (one
on each side of Sm$^{3+}$, Fig. 1b). Both the PL intensity and the PL
lifetime of Sm$^{3+}$ increase as the number of TbF$_3$ cycles increases,
showing that the emission intensity is dominated by the
quenching rate of Sm$^{3+}$. At a TbF$_3$ layer thickness of 100 cycles,
the intensity reaches a maximum while the lifetime still increases for
200Sm. This could indicate that not all excited states manage to
migrate all the way to Sm$^{3+}$ at 200 TbF$_3$ cycle layer separating
the aromatic molecule and Sm$^{3+}$ ion. The integrated Tb$^{3+}$ peak
intensity is small until 50Sm, indicating that at this thickness the
migration starts to become incomplete and some excited Tb$^{3+}$
ion will start to emit light. The apparent plateau for 50Sm, 100Sm
and 200Sm is surprising. One possible explanation is that the
Tb$^{3+}$ emission, which is a balance between the rates for radiative
emission on one side and migration and transfer to Sm$^{3+}$ on the
other side, is more affected by the local symmetry than the Sm$^{3+}$
emission, which is not depopulated by migration or transfer to
another ion. The 50Sm and 100Sm samples marks the difference
between amorphous and (partly) crystalline TbF$_3$, meaning that
the ratio between high emission and transfer rates of 50Sm could
be similar to the ratio between lower emission and transfer rates
for 100Sm. 200Sm has a higher Tb$^{3+}$ emission than 100Sm, also
supporting that increasingly incomplete transfer to Sm$^{3+}$ is the
reason for decreasing intensity and increasing lifetime of the
Sm$^{3+}$ emission between 100Sm and 200Sm. However, the Tb$^{3+}$
emission of 3Sm is substantially higher than what should be
expected from this explanation. Thus the apparent plateau might
be caused by random variations of the samples.

Figure 3d shows the UV-visible absorbance of 100Sm sample
deposited on silica substrate. The molar absorption coefficient, or
epsilon value, of terephthalic acid dissolved in ethanol is shown for
comparison. The 100Sm film show two absorption peaks at
approximately 250 and 300 nm that correspond well with the
absorption spectrum of terephthalic acid. The absorption peaks
also correspond well with the excitation profiles in Fig. 3a.

The nanocomposite samples all contain exactly 10 Ln$_2$bd$_3$
cycles. It is remarkable to obtain an emission spectrum from a
fluoride lattice with over 15% absorbance in a thin film only
55.9 nm thick.
**Fig. 3 Photoluminescence characterization.** a PL and PLE spectra of the four selected samples: Tb2bdc3, Eu2bdc3, 200Eu, and 100Sm. PL was recorded using a 280-nm diode while PLE was recording while monitoring the highest peak in each spectrum. Photographs show these samples under 254 nm UV light. The two 200Eu peaks marked asterisk (*) is likely Tb3+ emission. b Luminescence spectra of xSm samples and Tb2bdc3, normalized to the most intense peak. Note the difference in 560 and 600 nm peaks between 255Sm and 100Sm. c PL intensity integrated over the 595–615 nm range (Sm3+, black, left axis), 540–550 nm (Tb3+, green, left axis) and lifetime of the 594 nm Sm3+ emission (red, right axis). Noted that the Tb3+ integrated intensity has been multiplied by 3 for clarity. The estimated thickness (in nm) of TbF3 separating Sm3+ are separated molecules as inclusions between the organic layers. This could indicate that the organic molecules do not form a dense layer, as in the illustration in Fig. 1a, but rather layers are about 7 nm thick, separated by darker organic layers. d UV-Vis absorbance data from 100Sm on silica substrate; literature data of the molar absorption coefficient of terephthalic acid for comparison. e Decay of the 4G7/2 → 6H5/2 and 5D0 → 7F2 transitions of xSm and 200Eu. An initial rise in the emission is seen for 200Sm and 200Eu only. f Decay lifetime modelling of these transitions using a single exponential function.

Figure 3e, f shows the PL decay of the most intense emission of 50Sm, 100Sm, 200Sm (4G9/2 → 6H9/2) and 200Eu (5D0 → 7F1). All decay curves can be fitted with a single exponential decay function. For both 200Sm and 200Eu, a small initial rise can be seen, indicating that there is some delay before the excited state energy generated in the aromatic acids reaches the Sm3+ and Eu3+ ions. For 200Eu, the rise is slower than for 200Sm. The slower rise in 200Eu indicates that the transfer from Tb3+ to Eu3+ is slower than Tb3+ to Sm3+, which could lead to a higher degree of incomplete transfer in the 200Eu case and more Tb3+ emission is expected. This combined with the matching peak positions makes it plausible that the two higher energy emission peaks for 200Eu in Fig. 3a are Tb3+ emissions.

**Multilayer and nanocomposite structure.** Figure 4a show a scanning transmission electron microscopy–high-angle annular dark field (STEM-HAADF) image of the 200Sm sample. The sample structure is also illustrated above. The bright fluorite layers are about 7 nm thick, separated by darker organic layers. The red line highlights crystalline planes that pass through several organic layers. This indicate that the organic molecules do not form a dense layer, as in the illustration in Fig. 1a, but rather are separated molecules as inclusions between the fluoride layers that have the possibility to continue the growth around them.

To investigate the chemical composition of these layers, coreloss and energy-dispersive X-ray spectroscopy (EDS) was used to map the carbon, terbium and fluorine contents, Fig. 4b, c. It is clear that the dark thin layers are rich in carbon and deficient in terbium and fluorine. In Fig. 4d, it is also seen that the oxygen level follows the same trend as carbon, showing peaks at the thin, dark layers. Although deficient in fluorine, it is also evident that the fluorine content only decrease by about 50% in these layers, further supporting that these dark layers contain both the aromatic acid and TbF3, which allows crystalline TbF3 to grow uninterrupted alongside the deposited bdc molecules.

To investigate the nanocomposite structure further, X-ray reflectivity (XRR) was performed on all samples. XRR data for 200Sm is shown in Fig. 4e, where three features can be seen. The top model (red) show a simple sample model consisting of one uniform 88.1 nm film on top of a 13.2 nm SiO2 layer. This model reproduces the rapid oscillations at small angles and long oscillations at large angles but not the two non-sinusoidal peaks in the middle. The second model is similar to the first, but the uniform film is replaced by 10 supercycles of 7.7 and 1.0 nm of high and low electron density materials. This model also reproduces the first of the two middle peaks to some extent, indicating that these two peaks stems from the multilayer structure. We were not able to produce a model that properly reproduced all the features at the same time. One explanation of this is that the sample is likely somewhat inhomogeneous with respect to crystallinity, which can be clearly seen in Fig. 4a. This will also affect the film thicknesses in each superlayer and in particular the crystallinity will affect the roughness between each layer which XRR is very sensitive towards.

**Discussion**

**Film growth.** Combining LnF3 and Ln2bdc3 cycles on the (sub) nanometre scale was successful for all LnF3/Ln2bdc3 cycle ratios. The crystallinity changes around a ratio of 20:1, i.e. the 100Sm sample where each Ln2bdc3 cycles is separated by 100 TbF3 cycles. The difference between 50Sm and 100Sm is clear both from XRD in Fig. 2c and the PL spectra in...
Fig. 3b. XRD shows that all samples with $x < 100$ is amorphous while $x \geq 100$ shows reflections from orthorhombic TbF$_3$ similar to the reflections seen for deposition of pure TbF$_3$. The PL emission spectra show a clear difference in peak shapes, indicating a symmetry change around the Sm$^{3+}$ ion for compositions between 50Sm and 100Sm. This agrees well with the onset of crystallinity. Deposition of pure TbF$_3$ at 250 °C results in polycrystalline films, and, not surprisingly, adding the very different Ln$_2$bd$_3$ cycle in between LnF$_3$ cycles interrupts such crystal formation. A sufficiently thick layer is constructed for $x > 100$ to regain crystal growth, while also maintaining this across the bd$_2$-dopant layer.

The STEM image of 200Sm in Fig. 4a also shows clear crystallinity and the LnF$_3$ crystallites are larger than the LnF$_3$ layer thickness and spans several organic layers. The only way such large crystallites can form is if the aromatic acid molecules only occupy a fraction of the possible surface sites. In this case, following LnF$_3$ cycles can continue the crystalline growth uninterrupted between the organic molecules. This is partly shown in Fig. 4b where the level of carbon is out of phase with the level of fluorine. However, the fluorine level only decreases to about 50%. As each bd$_2$ contains 8 carbon atoms and the level of carbon is only about 20%, there should be space between each molecule. Similar results with crystallites growing past organic layers have been obtained in ZnO-zincone multilayers deposited by ALD, using 1,4-dihydroxybenzene as the organic molecule$^{37}$. Also in this case it did seem like there was sufficient room between the organic molecules to continue the growth of inorganic crystals.

The QCM in Fig. 2b show an unusual response with an initial mass decrease before an overall increase during the H$_2$bd$_3$ pulses for both pure Tb$_3$bd$_3$ and nanocomposite depositions. A detailed analysis of the growth mechanics is outside this work, but we can offer a possible explanation. When H$_2$bd$_3$ is pulsed it reacts with |-Tb-thd$_x$ surface species, producing Hthd as a leaving molecule and at least one Tb-bd$_3$ bond. This is a net mass decrease of only 10%. However, each H$_2$bd$_3$ molecule can react with two |-Tb-thd$_x$ sites, producing 2 Hthd molecules and a net mass decrease of 55%. As the H$_2$bd$_3$ is about 7 Å long, this probably involves two different |-Tb-thd$_x$ sites. Such bridging |-Tb-bd$_3$-Tb- species can further react with an additional H$_2$bd$_3$ and produce two |-Tb-bd$_3$-H species. This will in turn restore the net mass decrease to 10% as compared to the initial thd terminated surface. Such an approach can explain the initial mass decrease followed by a delayed mass increase back to about the same initial level but also implies that the kinetics of these reactions are significantly different. Our group have previously shown that the growth of metal–bd$_3$ hybrids can be affected by co-pulsing with other
structures is not trivial, in particular with respect to detecting a resulting multilayer structure of 200Sm. Probing such small organic sensitizer and the phonon-sensitive Sm \(^{3+}\) ion to Sm\(^{3+}\) results in between vibrations than for Eu\(^{3+}\). Both show similar emission energy vibrations on this organic molecule. The higher energy of these two lanthanides are not strongly quenched by the high-energy organic (C-H) vibrations, thus the main difference between these two materials is the symmetry around Eu\(^{3+}\). Directly linking bdc\(^{2-}\) and Eu\(^{3+}\) produces an amorphous-like emission spectrum while separating them and using TbF\(_3\) as an energy migration layer produces a YF\(_3\)-like Eu\(^{3+}\) emission spectrum\(^{41}\). Although the emission spectrum of all lanthanides is affected by symmetry, this effect is particularly important for Eu\(^{3+}\) as emission from the non-degenerate \(S_{D0}\) level can be used to determine the local site symmetry around the Eu\(^{3+}\) ion. Readers interested in the symmetry dependence of Eu\(^{3+}\) emission and in particular how this ion is used a probe for local site symmetry are referred to the review article from Binnemans on this topic\(^{42}\). Since the energy level positions of Ln\(^{3+}\) ions are nearly insensitive to the surrounding matrix, Tb\(^{3+}\) can act as a bridge in most types of matrices. Thus, in this example with Eu\(^{3+}\), the Eu\(^{3+}\) emission spectrum of any matrix can be chosen more or less completely independently of the sensitizer by simply choosing a different Tb\(^{3+}\) containing matrix with a different site symmetry than TbF\(_3\). The Eu\(^{3+}\) ion will then have the emission properties of the Tb matrix, independent of the sensitizer species which in turn also can be something else than an organic molecule as long as it can donate energy to Tb\(^{3+}\). The only requirement is that the ALD chemistry of this Tb matrix is compatible with the ALD chemistry of the aromatic molecules (or other sensitizer). Interestingly, the 200Eu sample is fundamentally quite similar to the core–shell TbF\(_3\)-Ce\(^{3+}\)-Eu\(^{3+}\) nanoparticle structure by Fischer and Jüstel\(^{15}\) where TbF\(_3\) was used as an energy bridge between Ce\(^{3+}\) and Eu\(^{3+}\). The main difference being that, instead of Ce\(^{3+}\), we have achieved similar sensitization from a completely different material class while maintaining the solid, inorganic multilayered TbF\(_3\)-Ln\(^{3+}\) structure.

The situation for Sm\(^{3+}\) ions is in some aspects similar to Eu\(^{3+}\), but the main difference is that the Sm\(^{3+}\) emission is effectively quenched by high-energy phonons due to its lower energy gap. Generally, it is sufficient to consider the maximum phonon energies in the crystalline or amorphous glass matrix, but in this nanocomposite case we have to take the high-energy vibrations of the organic molecule into account and the distance, \(R\), between the luminescent lanthanide and these vibrations. The multi-phonon quenching rate decreases with the \(1/R^6\) \(^{43}\). For Sm\(^{3+}\), where the energy gap is small enough to be strongly quenched by these molecules if present in the immediate coordination, the critical factor is whether or not there are any organic molecules within interaction distance of the Sm\(^{3+}\) ion. If so, the situation is similar to a lanthanide close to the surface of a nanoparticle being able to interact with the solvent or capping agent. If the molecule is outside interaction distance, Sm\(^{3+}\) will behave as if doped into a normal, unsensitized crystalline fluoride matrix. Figure 3c shows the PL intensity of Sm\(^{3+}\) and Tb\(^{3+}\) emissions from the samples, integrated over the 595–615 and 540–550 nm ranges, respectively, in addition to the lifetime of the 594 nm Sm\(^{3+}\) emission. There is a clear correlation between the number of bridging TbF\(_3\) cycles on one side and the PL intensity and lifetime on the other. Both increase as the distance between the Sm\(^{3+}\) ions and high-energy organic vibrations is increased by a thicker TbF\(_3\) layer. The lifetime is approaching a plateau for 200Sm while the PL intensity reaches a maximum at 100Sm. This difference is likely due to a trade-off between migration through a thicker TbF\(_3\) layer making it less likely to reach the Sm\(^{3+}\) ion and reduced quenching of the Sm\(^{3+}\) emission. This is supported by the decay data in Fig. 3d where it is seen that the Sm\(^{3+}\) emission of 200Sm has an initial rise during the first 100 µs while 100Sm does not have this rise. The rise indicates that the population of Sm\(^{3+}\) ions is slightly delayed. A possible explanation for this is the required energy migration through the TbF\(_3\) layer. The decay of Eu\(^{3+}\) in 200Eu is also shown in Fig. 3d and show the same rise quenched by the high-energy organic (C-H) vibrations, thus
as 200Sm, again indicating a delay caused by the required energy migration. This rise spans about 300 μs, compared to 100 μs for 200Sm. Baur et al. found a similar rise time for Tb4Mo5O12 doped with ≤1% Eu3+ when exciting Tb3+ 44. The rise time decreased with increasing Eu3+ concentration and disappeared completely >20%, supporting the explanation that the rise comes from slow migration through the Tb3+ network in Tb4Mo5O12.

The difference in rise time between 200Sm and 200Eu can be explained by the differences in energy levels for Sm3+ and Eu3+ (Fig. 1d). In order to have an energy transfer from Tb3+ to Sm3+ or Eu3+, there must be an overlap between the emission of Tb3+ and the absorption of the receiving ion for a Förster resonance energy transfer and matching energy level energies for a Dexter energy transfer. The energy levels of Sm3+ are much denser in this range than for Eu3+. Thus a possible explanation for the longer rise time of 200Eu compared to 200Sm is that the Tb3+ → Eu3+ energy transfer is slightly slower than the Tb3+ → Sm3+ energy transfer. There is also the onset of crystallinity for 100Sm compared to 500Sm as seen in Figs. 2c and 3b that causes a change in emission spectra. But from Fig. 3c, there is no particular abrupt change in either the integrated emission intensity or the lifetime between 500Sm and 100Sm, which rather changes gradually with the number of bridging TbF3 cycles. Thus the overall emission intensity of Sm3+ is dominated by the distance between Sm3+ and the organic molecules.

It is difficult to precisely measure the Sm3+-molecule distance as we were not able to identify the Sm3+ layer in either XRR or STEM due to its characteristics being very similar to Tb3+ and the overall doping concentration being very low. However, we can estimate it by assuming that Sm3+ is situated in the middle of the TbF3 layer, that the organic molecules occupy about 1 nm and using the total film thickness from ellipsometry. These estimates are given above the data points in Fig. 3c. Based on this estimate, the fact that the lifetime is still increasing for 200Sm and that the energy migration efficiency through TbF3 seemingly starting to decline at 100Sm, we can conclude that there is a fine thickness range for the bridging layer where it is wide enough to prevent quenching while also being thin enough to enable efficient migration. With ALD, this fine thickness control and optimization of luminescence efficiency are possible.

The third remarkable feature of these films is the realization of emission spectra identical to those of bulk crystalline inorganic materials while also having such a strong absorption than only a few tenth or hundreds of nanometre is possible to design novel luminescent materials that have the emission and conversion properties of a crystalline inorganic material while also having the benefit of a broader and tunable absorption.

Conclusion
In this work, we have developed a multilayered nanocomposite design for organically sensitized inorganic luminescent materials. This approach has been successful in producing aromatically sensitized Sm3+ emission where this emission is normally fully quenched by high-energy organic vibrations. By precisely controlling the separation between Sm3+ and the aromatic sensitizer with a TbF3 energy migration layer, we were able to both prevent direct Sm3+ → molecule interactions while maintaining efficient energy migration from sensitizer to Sm3+. The films shows the emission and conversion properties of the inorganic component while also having the absorption strength of the organic component, resulting in >15% UV absorption in a 55.9-nm film. This design can be generalized to other luminescent species as well. We obtain orange 5D0→F1 YF3-type emission from our nanocomposite while direct sensitization gives red 5D0→F2 emission where both materials show the same excitation profile originating from the aromatic sensitizer. This shows that, with our nanocomposite design, we can control the conversion and emission properties of the inorganic layer independently of the sensitizer. The only requirements for this design to be efficient is to have a migration ion like Tb3+ or Eu3+ that can accept energy from the chosen sensitizer and donate it to any type of luminescent acceptor ion and that the ALD chemistries of the sensitizer and inorganic layer is compatible. The ALD literature show that there is a wide variety of examples combining very different materials type due to ALD’s unique chemical flexibility coming from the low temperature and layer-by-layer deposition. With the chemical flexibility of ALD, this multilayer nanocomposite design can bridge the gap to strongly sensitized multi-component luminescent systems like upconversion and downconversion.

Methods
Sample structure and design. The general sample structure is illustrated in Fig. 1a. It consists of repeating supercycles, where each supercycle consist of a single organometallic acid pulse, followed by a varying number of TbF3 cycles where the cycle in the centre is replaced by an SnF2 enriched TbF3 layer. This produces a TbF3 layer with a single, atomically thin dopant layer of Sm3+ or Eu3+ in the middle. Figure 1b illustrates the energy levels through the multilayered structure, showing broadband UV absorption in the aromatic terephthalic acid molecules (Ar), transfer to TbF3 and migration through the TbF3 layer before final transfer onto Sm3+ and subsequent emission. The major variable in this design is the number of TbF3 cycles that separates the aromatic acid and the second lanthanide (Sm or Eu). Sm3+ is strongly quenched by high-energy vibrations on organic species, so the emission intensity of Sm3+ also works as an efficient probe for the Tb3+/ Sm3+-acid distance to detect if the distance is sufficient to prevent direct Sm3+ → acid interactions. We have chosen to use the less explored NH4F fluorine source rather than the already established Ln(thd)3-TiF4 route because TiF4 is known to leave small impurities22,45. Due to the energy migration in the TbF3 layer, even small amounts of TiF4 can completely quench the excited state due to the long energy Tb3+ → Tb3+ charge transfer state 46.

The films were deposited in an F-120 research-type ALD reactor (ASM Microchemistry Ltd) at 250 °C. Ln-β-diketonate Ln(thd)3 (Strem Chemicals, ≥99.9%, Ln = Sm, Eu, Tb) were used as lanthanide precursors, while terephthalic acid (H2bdc) and NH4F were used as anion precursors for metal organic hybrid cycles and LnF3 cycles. Nitrogen was used as carrier and purge gas, supplied from gas bottles (AGA, 99.999%). p-type Si(100) substrates were used for all depositions. In addition, 0.5 × 4 cm2 Si(100) strips were placed some 8 cm apart in the gas inlet and exhaust sides of the deposition chamber to monitor thickness gradients. The native oxide on the silicon substrates was not removed. All substrates were dry wiped and dust was removed using pressurized air prior to the ozone treatment. The sublimation temperature used for Ln(thd)3, was 150, 145 and 140 °C for Sm, Eu and Tb, respectively, 210 °C for H2bdc and 85 °C for NH4F. Pulse parameters for LnF3 and Ln2bdc3 cycles were 1.5/1/5/1 s for Ln(thd)3/purge/anion/purge, where anion is either NH4Fo rH 2bdc.

Two sets of samples were deposited. Those named Ln-bdc are 100–500 cycles of Ln2bdc3, These were deposited to investigate the bdc → Ln3+ energy transfer, Ln3+ → Tb3+ energy migration.
luminescence and quenching of this emission. The second set of samples all consist of 10 supercycles of 1 Tb–bdc3 cycles, x TbF3 cycles, 1 LnF3 cycle (La = Sm or Eu) and x TmF3 cycles. These samples will have a similar total amount of organic molecules and emitting EuII/SmII ions, and thus similar absorption and number of emissive sites, simplifying the comparison of their luminescence. The major difference between these samples is the x number of cycles separating the bdc molecule and the non-Tb LuI3 ion. The samples are named xL_n, i.e. 50Sm means a sample of 10 supercycles of (1 Tb–bdc3, 50 TbF3, 1 SmF3, 50 TmF3). In situ QCM analyses were conducted using a 6-MHz AT cut quartz crystal. The crystal was mounted in a home-made holder and was used to monitor the mass increase during the deposition in order to determine saturation conditions with respect to pulse and purge parameters. The standard parameters for both TbF3 and Tb–bdc3 cycles were 1.5/1/5/1 for all QCM experiments. Only one parameter was changed at a time. The signal was recorded using a Colnatec Eon-LT and processed by averaging over 16 consecutive ALD cycles. The temperature was stabilized for 90 min before any experiments were conducted to ensure a reliable response from the QCM crystals.

**Structural and optical characterization.** The crystallinity of the samples was determined with a Bruker D8 Discover X-ray diffractometer (XRD), using CuKa1 radiation and a Ge(111) monochromator. XRR was measured on a PanAnalytical X’Pert Reflectivity software. Film thickness and refractive index were determined with a J.A. Woollam alpha-SE spectroscopic ellipsometer in the 380–900 nm range. The ellipsometry data were modelled using a Cauchy model.

PL and PLE measurements were done using two different set-ups. A 280 nm diode and a USB2000+ spectrometer from OceanOptics were used for recording the PL spectra in Fig. 3a, while an Edinburgh Instruments FL5920 fluorescence spectrometer with a 450 W Xe lamp as excitation source and a Hamamatsu R928 PMT for detection was used for the PLE spectra in Fig. 3a and the PL spectra in Fig. 3b. c. PL decay measurements were performed with the third harmonic of a Nd:YAG laser as excitation source of the OpotekHE 355 II with an ~10 ns pulse width and a repetition rate of 20 Hz. The decay was recorded with MultiChannelScaling function incorporated in the Edinburgh Instruments Spectrofluorimeter. Absorbance data were obtained by combining transmittance and reflectance measurements in a Shimadzu UV3600 spectrophotometer using an integrating sphere. STEM investigations of the samples were conducted after standard sample preparation techniques, by cutting, manual grinding and polishing. Final thinning was done with a Gatan PIPS II ion mill using argon ions, with gradually decreasing voltages and angles and increasing polishing time. Plasma cleaning with a Fischione Model 1020 for 5 min was applied prior to the TEM experiments. STEM was performed with a monochromated FEI Titan G2 60–300 kV TEM, equipped with a Gatan CEOS probe-corrector. The microscope was operated at 300 kV with a convergence angle of 20 mrad, where HAADF imaging was done with collection angles 40 mrad, where HAADF imaging was done with collection angles 40 mrad, where HAADF imaging was done with collection angles 40 mrad, where HAADF imaging was done with collection angles 40 mrad, where HAADF imaging was done with collection angles 40 mrad, where HAADF imaging was done with collection angles 40 mrad, where HAADF imaging was done with collection angles 40 mrad, where...
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Author contributions

All authors have contributed to the interpretation of data. P.-A.H. designed the nano-composite structure, organized the work and wrote the paper. T.Z. deposited all samples except Eu-containing samples that J.N.K. deposited, both under supervision by O.N. QCM, XRD and XRR measurements were performed by T.Z. and J.N.K. PL, PLE and decay measurements were conducted by T.Y. under supervision by A.M, while UV-Vis and some PL was conducted by P.-A.H. STEM experiments and interpretation was conducted by T.A. with input from Ø.P.

Competing interests

The authors declare no competing interests.

Additional information

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