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Cristina Balogh, Isis N'Dala-Louika, Iurii Suleimanov, Anaïs Pons, Matthias Jouffrieau, et al.. Luminescence of Lanthanide Complexes in Mesoporous Silica Matrices: A Textbook Example of Tris-Dipicolinate Europium Complex Adsorbed in SBA-15. *Advanced Optical Materials*, 2024, 10.1002/adom.202400091 . hal-04628180

HAL Id: hal-04628180

<https://hal.science/hal-04628180v1>

Submitted on 28 Jun 2024

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Luminescence of lanthanide complexes in mesoporous silica matrices: a textbook example of tris-dipicolinate europium complex adsorbed in SBA-15

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Keywords: europium, luminescence, luminance, adsorption, silica, SBA-15

Abstract

Incorporation of luminescent lanthanide complexes in inorganic matrices opens appealing possibilities in the rational upstream conception of new luminescent materials with easier recyclability. In this regard, the influence of SBA-15 mesoporous silica, as a host matrix, on the photophysical properties of Europium-trisdipicolinate cesium salt was investigated. The lanthanide complex can be completely and reversibly adsorbed on the silica, using incipient wetness impregnation (IWI) in water, without the need of anchoring groups or covalent bonding on the silica surface. This specific procedure allows the homogeneous dispersion of the lanthanide complex into the host silica matrix. Appropriately assessing the photophysical properties of the targeted luminescent material proved remarkably challenging, demanding utmost caution, particularly due to the strong scattering of the mesoporous matrices.

Additionally, while our observations confirm an important increase of luminescence lifetimes of lanthanide complexes upon integration into these mediums, we attribute this variation to the differing refractive indexes and not to specific surface interactions or confinement effect. Indeed, it appeared that previous literature precedents depicted erroneous exhalations of the complexes intrinsic quantum yield due to the repeated use of erroneous refractive index values. In the meantime, the luminance of these materials under UV irradiation improves drastically in comparison to what is obtained with the physical dispersion of micro-crystals of the lanthanide complex onto silica. We demonstrate that this improvement is due to a reduced inner filter effect in the adsorbed samples. In this regards, IWI of lanthanide complexes in mesoporous matrices method could be of interest in the development of recyclable emitting layers, less demanding in terms of emitter quantity.

1. Introduction

Since the seminal observation of the europium oxide luminescence by Urbain in 1906,^[1] the lanthanide-based phosphors have become ubiquitous for lighting and displays.^[2] Nowadays, despite their high efficiency, these materials are called to be replaced due to the rising use of lower consuming LED based lighting devices. In particular, they suffer from a growing criticism concerning their need of laboriously extracted rare earths and their difficult recycling.^[3] In this regard, existing procedures to retrieve lanthanides from used phosphors are similar to the treatment of ores, using harsh acidic conditions, due to the inherent inertness of these materials.^[4] Thus, a rational upstream conception of new lanthanide based luminescent materials should also anticipate their future end-of-life recycling, allowing an easier and environmentally friendlier process to recover rare earths from the luminescent matrices.

During the last century, molecular chromophores incorporating lanthanides with high brightness have emerged and found applications, in particular for bio-imaging purposes.^[5] This development was possible through the use of tailor-made ligands that protect the rare earth from the surrounding luminescence quenchers (in particular water molecules) and allow the indirect sensitization of the lanthanide excited level by an energy transfer from the ligand – the so-called “antenna effect”.^[6] Despite the advantages offered by the molecular approach in term of modulation of the spectroscopic properties and high absorption cross-section, the lighting applications based on lanthanides have remained in the field of inorganic materials, advantageous in terms of production and processability, thanks to large-scale synthesis and excellent stability.

For the last ten years, a few fundamental work was initiated in order to incorporate luminescent lanthanide complexes in different matrices such as polymers, zeolites, nanoparticles or mesoporous materials,^[7] mostly via covalent grafting.^[8] Thanks to possible stability improvements of the molecular complex, such solids already offer interesting prospects in the field of biological imaging, sensing and lighting applications.^[9] The photophysical characterization of these materials has shown evidences of improvement in the luminescence of the complexes within the host matrix compared to solution or pure solid crystals. If confirmed, these materials would possibly compete with current phosphors in terms of efficiency, gaining better light absorption and inertness, allowing their recyclability under milder conditions. However, the origin of this phenomenon remains unclear till now, even if a possible stabilization of the molecular structure or effects due to confinement were mentioned.^[10]

To get insight into these phenomena, we decided to insert a tris-dipicolinate europium(III) complex (**Figure 1**), namely $\text{Cs}_3[\text{Eu}(\text{DPA})_3] \cdot 8\text{H}_2\text{O}$ and noted as [Eu], into a SBA-15 type mesoporous silica. Tris-dipicolinate europium(III) was chosen as a molecular emitter because of its well-established photophysical properties in both solution and solid state.^[11] Furthermore, its straightforward synthesis on a large scale made it a realistic alternative to classical phosphors. On the other hand, we choose the SBA-15 hierarchically ordered silica as the host matrix to benefit from its large porous volume, and its 2D hexagonal arrangement of large calibrated pore-channels, allowing easy impregnation of a large quantity molecules in its internal porosity.^[12] We thus describe here the development of a hybrid material containing a homogeneously dispersed tris-dipicolinate europium(III) complex into its silica pore-channels and investigated in details the luminescence properties of the resulting solid.

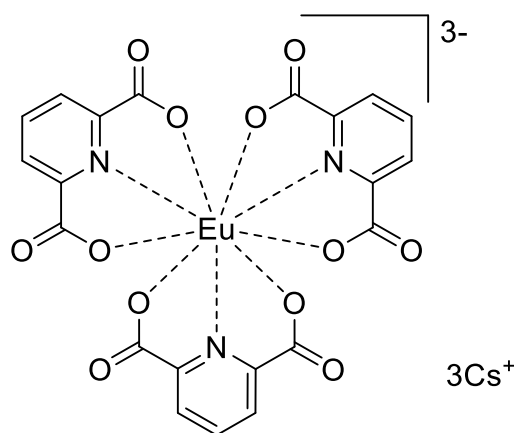


Figure 1. Structure of complex [Eu].

2. Results and discussion

2.1. Synthesis and characterization of tris-dipicolinate europium doped SBA-15

2.1.1. SBA-15 synthesis and characterization

Unlike previously reported examples of lanthanide complexes incorporation into mesoporous silicas,^[13] and in order to study the sole influence of the host silica matrix on the photophysical properties of the guest, we used pure SBA-15 silica instead of functionalized mesoporous silicas that contain surface organic groups presumably interacting with the lanthanide complex. SBA-15 silica was prepared using a previously reported procedure (see ESI) and was characterized by both N₂ adsorption-desorption at 77 K and Transmission Electron Microscopy (TEM).^[14] As expected, the material was found to be highly mesoporous with a large specific surface area of ca 1035 m².g⁻¹, a total pore volume of 1.2 cm³.g⁻¹ and a narrow pore size distribution with a mean pore size diameter of 9 nm measured from the adsorption branch of the N₂ adsorption/desorption isotherm (**Figure S1**). The 2D hexagonal arrangement of the porous network was also confirmed by TEM (**Figure S2**).

2.1.2. Preparation of the tris-dipicolinate europium complex and further adsorption on SBA-15 silica

The tris-dipicolinate europium(III) complex Cs₃[Eu(DPA)₃].8H₂O was prepared as a crystalline powder using europium(III) chloride, dipicolinic acid and cesium carbonate as a base.^[15] In order, to insure a homogeneous dispersion of the lanthanide complex within the SBA-15 inner porosity, Incipient Wetness Impregnation (IWI) method was chosen.^[16] IWI consisted into dissolving an chosen quantity of complex (to reach the targeted complex loading in the final material) in a volume of water that corresponds to the porous volume of the silica. This solution was then added drop-by-drop onto the silica while mixing in a mortar to ensure a homogeneous wetting of the powder. The solvent was further slowly evaporated under argon flow. This procedure (IWI/drying) can be repeated several times to reach the desired [Eu] loading if needed. In the present case, we used a concentrated solution of [Eu] (70 mg.mL⁻¹) and a single IWI procedure enabled us to reach a theoretical loading of 7 %_{wt}. The target material was finally dried at 175°C under high vacuum (10⁻⁵ mbar) for 12 hours to ensure the removal of water (see ESI for details). For the sake of clarity, this material will be referred to as [Eu]@SBA-15^{dry}, “dry” standing for the intensive drying procedure and subsequent storage of this material under argon atmosphere. As expected, this first material turned out to be highly hygroscopic and a second material stored under ambient atmosphere, [Eu]@SBA-15^{air}, was also considered-. It is

worth mentioning that a comparative impregnation experiment was performed with a larger amount of water (100 times higher than the porous volume of silica, called Wet Impregnation (WI)). This latter WI procedure led to the crystallization of the complex outside the silica pores upon evaporation of the solvent as observed in the TEM micrographs (**Figure S4**) and further confirmed by the strong modification of resulting solid texture (**Figure S3** and **Table S1**).

The two doped solids prepared by IWI were further analyzed by IR (DRIFTS) spectroscopy. The spectrum of [Eu]@SBA-15^{dry} exhibited signals corresponding to the stretching bond vibration of surface silanols around 3750 cm⁻¹ along with an additional contribution attributed to C=O vibration of the dipicolinate ligand at 1623 cm⁻¹, confirming the presence of the complex in the material. Upon exposure to air, an increase of the broad signal corresponding to O-H bond vibration is observed, underlining the hygroscopic character of the hybrid material (**Figure S5**).

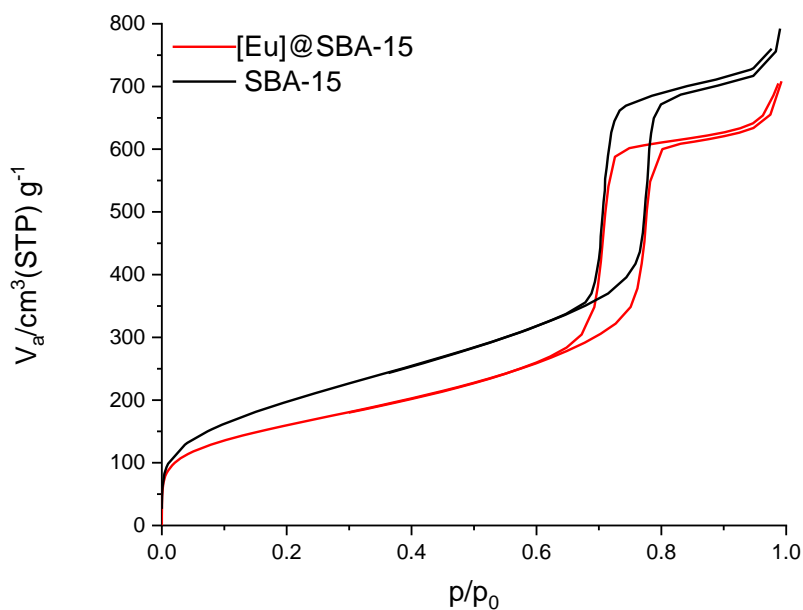


Figure 2. Comparison of N₂ adsorption/desorption isotherms of SBA-15 (black) and [Eu]@SBA-15^{air} (red).

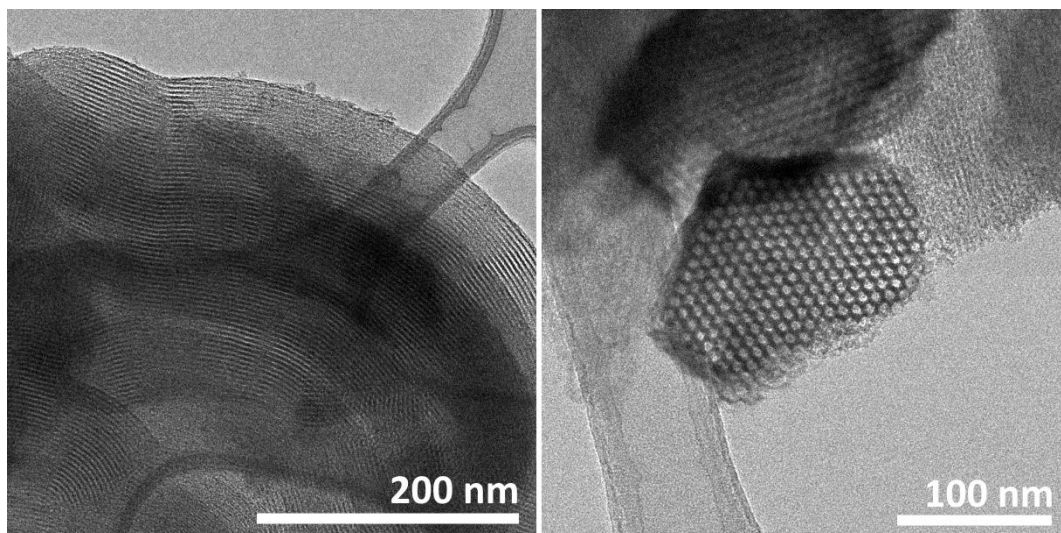


Figure 3. TEM micrographs of [Eu]@SBA-15^{air}.

The N₂ adsorption-desorption isotherm of [Eu]@SBA-15^{air} was found identical to that of the host silica material showing both the preservation of the silica texture and the absence of localized accumulations of complex (aggregates or crystals) in the inner porosity (**Figure 2**).^[17] The slight porous volume decrease, to 1.08 cm³.g⁻¹, is in accordance with the volume occupied by the inserted complex.

High-resolution TEM microscopy and Powder X-ray diffraction (PXRD) further confirmed the absence of precipitation or crystallization of the complex either outside or inside of the pores (**Figure 3, Figure S6**). Furthermore, EDX analysis performed on different areas of the sample highlighted the homogeneity of the [Eu] complex adsorption throughout the host material with a constant Eu/Si atomic ratio $(4.6(2) \cdot 10^{-3})$ that corresponds to the expected one $(4.5 \cdot 10^{-3})$ for a complete homogeneous adsorption of the complex in the silica (**Figure S7-8**). The loading of complex (0.80%_{wt} Eu; 2.17%_{wt} Cs, 39.1%_{wt} Si) was also determined by elemental analysis and was found equal to 6.2 wt% (vs 7%wt for the theoretical loading) and confirmed the loading found by EDX. It is worth noticing that EDX measurement also indicated a homogeneous distribution of cesium counter-cation throughout the entire solid with the same Cs/Eu ratio than that of the starting complex. This thus suggests that no protonation of dipicolinate ligands occurred upon adsorption and that the complex is intact in the host solid.

2.2. Luminescence properties

2.2.1. Excitation and emission properties

The europium emission is a good local probe of the symmetry of the coordination sphere of the lanthanide.^[4] Indeed, relative intensities and crystal field splitting of each $^5D_0 \rightarrow ^7F_J$ ($J = 0-6$)

transitions is directly linked to the local symmetry of the coordination sphere and thus, in a certain extent, the emission spectrum is the characteristic fingerprint of one specific complex. In the case of the coordination of europium by dipicolinate ligands, the effect of the successive coordination of 1, 2 and 3 ligands on the luminescence spectrum has already been reported.^[18] Thus, in order to further assess the stability of [Eu] upon adsorption into SBA-15, we examined its emission spectrum in both the pure complex (microcrystalline form) and each adsorbed material (**Figure 4**). The excitation spectrum, recorded by monitoring the 615 nm emission corresponding to the ${}^5D_0 \rightarrow {}^7F_2$ of the Eu^{3+} , is dominated by an intense band at 280 nm corresponding to the absorption of the dipicolinate moiety (**Figure S11**). Although, low intensities transitions related to the direct f–f excitation of the Eu^{3+} (${}^5L_6 \leftarrow {}^7F_0$ at 395 nm) were also observed, it is clear that the most efficient excitation pathway involved the organic moiety confirming that the Eu^{3+} is still coordinated to the ligand. Upon excitation at 280 nm, the material emitted the characteristic bands of the Eu^{3+} ion with, in particular, bands at 579, 593, 615, 649 and 695 nm corresponding to the respective ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$ and 4) transitions. There is no residual emission originating from the ligand, evidencing a full sensitization of the lanthanide and the absence of free dipicolinate ligand in the silica. The emission spectra of both $[\text{Eu}]@SBA-15^{\text{dry}}$ and $[\text{Eu}]@SBA-15^{\text{air}}$ were found rather similar to the pure complex before adsorption (**Figure 4 left**) with an intense band corresponding to the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition and almost no contribution from both ${}^5D_0 \rightarrow {}^7F_0$ and ${}^5D_0 \rightarrow {}^7F_3$, as expected for a Eu^{3+} in a crystal field with a D_3 symmetry.^[11a] These observations further support that the complex is adsorbed into silica without alteration of its molecular structure upon adsorption and drying. Considering the texture of SBA-15, mainly constituted of mesopores (with a minor amount of micropores), it is reasonable to assume that the adsorbed complexes do not sit in a rigorous homogeneous environment. This assumption is consistent with the fact that the luminescence decay of the [Eu] emission is not perfectly intercepted by either a mono-exponential or bi-exponential fitting model. The luminescence decay was thus fitted using stretched exponential model that introduces a more relevant nonlinear exponent to consider such local inhomogeneity:^[19]

$$I_t = C + I_0 e^{-(t/\tau)^\beta}$$

For the hybrid materials $[\text{Eu}]@SBA-15^{\text{air/dry}}$, several batches of solids were examined and the following lifetimes are mean values. For $[\text{Eu}]@SBA-15^{\text{air}}$, the [Eu] luminescence decays according to a 1.92 ± 0.05 ms lifetime with a β parameter close to unity (0.96), (**Figure S12**), indicating a very small distribution of local environments in agreement with the similar emission profile. These values are significantly higher than those of pure $\text{Cs}_3[\text{Eu}(\text{DPA})_3] \cdot 8\text{H}_2\text{O}$

crystals (lifetime of 1.65 ± 0.05 ms).^[11a] Upon drying ($\text{Eu}@SBA-15^{\text{dry}}$), the lifetime values further increase, reaching 2.75 ± 0.10 ms ($\beta > 0.95$)^[20] (**Figure 4 right**) thanks to the loss of second sphere water quenchers.^[21] In both cases, the measured luminescence lifetime of the lanthanide complex is enhanced drastically upon adsorption on silica in agreement to previous reports using functionalized silicas as hosts.^[13b, 22] The absence of anchoring moieties at the surface of the host matrix in the present study allows us to seriously question the previous attributions of such lifetime enhancements to a “stabilization” of the complex that would be promoted upon docking at the silica surface though the use of specific organic tethers.^[7c]

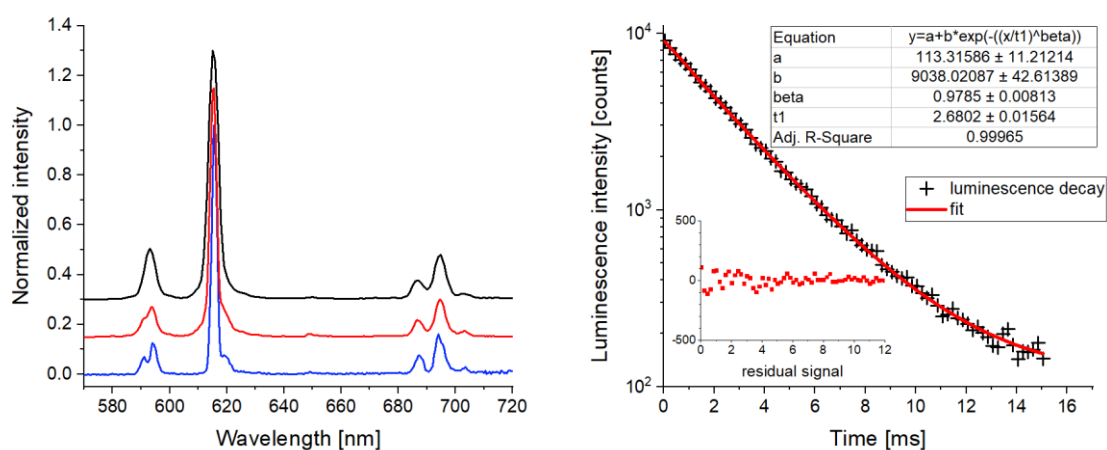


Figure 4. On the left, overlay of the emission spectra of $\text{Cs}_3[\text{Eu}(\text{DPA})_3] \cdot 8\text{H}_2\text{O}$ crystalline powder (black), $[\text{Eu}]@SBA-15^{\text{air}}$ (red) and $[\text{Eu}]@SBA-15^{\text{dry}}$ (blue). On the right, representative luminescence decay of $[\text{Eu}]@SBA-15^{\text{dry}}$.

2.2.2. Quantum yield measurements

As already presented, the adsorption of the $[\text{Eu}]$ in SBA-15 has a clear influence on its luminescence properties. However, the sole lifetime measurement of the lanthanide complex cannot assess for an improvement of the emission intensity. Unfortunately, our attempts to perform absolute quantum yield measurements with these materials were unsuccessful. Indeed, a poor reproducibility of the values obtained with integrating spheres was noticed despite several attempts using four different set-ups.

Integration spheres are well-suited to determine the absolute quantum yield of pure solids strongly absorbing the excitation light and we perfectly reproduced Bünzli’s quantum yield determination on pure $[\text{Eu}]$ micro-crystalline powder. However, a progressive dispersion of a pure crystalline $[\text{Eu}]$ in SBA-15 by grinding showed that the results were irrelevant below a 20% w/w mixture of the complex and silica (**Table S3** and **Figure S13**). To our understanding, this problem originates from the wrong estimation of light absorption by the hybrid material,

obtained by a comparison of the scattering intensity with respect to a blank sample. This observation is in accordance with previous reports and can be anticipated for any high scattering material (such as silica) with a low absorption coefficient.^[23] This inherent measurement error raises concerns about the growing use of integrating spheres for quantum yield measurements on highly scattering samples such as nanomaterials and this should be more deeply addressed, in particular when excitation is localized in the UV range. In any cases, this explains why it is impossible to obtain robust results for our doped materials (see ESI for details).

In order to get more insight into the photophysical properties of the adsorbed europium complex, we decided to perform an indirect measurement of its intrinsic quantum yield thanks to the estimation of its radiative lifetime.^[24] For an emitting center such as a lanthanide ion, the intrinsic quantum yield can be expressed as:

$$\phi_{Ln}^{Ln} = \frac{\tau_{obs}}{\tau_{rad}}$$

where τ_{rad} represents the radiative lifetime of the lanthanide, also called the natural lifetime, that would be observed in absence of non-radiative processes. Contrary to a popular belief, τ_{rad} is not the luminescence lifetime observed at 77 K or lower temperature,^[25] neither in D₂O,^[26] where there is no evidence that all non-radiative processes are totally suppressed. In general, the radiative lifetime can be retrieved thanks to the Judd-Ofelt theory that can be reduced to the following expression in the case of Eu³⁺:^[18a, 26]

$$\frac{1}{\tau_{rad}} = A_{MD,0} n^3 \left(\frac{I_{tot}}{I_{MD}} \right)$$

where $A_{MD,0}$ is the spontaneous emission probability for the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition in vacuum ($A_{MD,0}=14.65 \text{ s}^{-1}$), I_{tot}/I_{MD} the ratio of the total integrated area of the emission spectrum over the area of the band corresponding to the $^5D_0 \rightarrow ^7F_1$ transition and n the refractive index of the medium. The latter was generally assumed to have of value ranging from 1.50 to 1.55 for all the measurements that have been performed on pure crystals of Eu³⁺ complexes while its experimental determination has rarely been performed. In the present case, the refractive index of Cs₃[Eu(DPA)₃].8H₂O crystals was previously measured at 1.517.^[11a] The corresponding error on the estimation of τ_{rad} is relatively small for pure solids but a particular attention has to be taken when dealing with diluted samples. Indeed, the refractive index of the matrix medium is poorly affected by the presence of the lanthanide complex at low loading. Thus, solution measurements usually considered the refractive index of the solvent. To our understanding, the same should be done in the case of lanthanide complexes adsorbed onto solids, considering the refractive index of the solid matrix. However, through our

bibliographical scrutiny, we observed that, except rare examples,^[28] most of the reports presenting such calculations used inappropriate values of n around 1.5 leading to huge underestimation of the τ_{rad} and subsequent overestimation of the $\phi_{\text{Ln}}^{\text{Ln}}$. Direct measurement of the SBA-15 refraction index is impossible due to the important scattering of the material. However, a good approximation of this value is to consider that SBA-15 is composed of two components: silica and air/vacuum, in a ratio corresponding to its porosity. Indeed, at the wavelength scale, the inhomogeneity of the medium can be discarded considering the small pore size.^[29] According to this assumption, we estimated that the SBA-15 used here has an effective refractive index close to 1.12 (see detailed calculation in ESI). The calculations of τ_{rad} and $\phi_{\text{Ln}}^{\text{Ln}}$ were thus performed for the pure $\text{Cs}_3[\text{Eu}(\text{DPA})_3] \cdot 8\text{H}_2\text{O}$ powder and for the doped solids and are reported in **Table 1**.

Table 1. Determination of the radiative lifetime and intrinsic quantum yield of [Eu] in crystals ($\text{Cs}_3[\text{Eu}(\text{DPA})_3] \cdot 8\text{H}_2\text{O}$) and after adsorption in SBA-15.

	n	$I_{\text{tot}}/I_{\text{MD}}$	τ_{obs} [ms]	τ_{rad} [ms]	$\phi_{\text{Ln}}^{\text{Ln}}$
$\text{Cs}_3[\text{Eu}(\text{DPA})_3] \cdot 8\text{H}_2\text{O}$ ^{a)}	1.517 ^{b)}	7.39	1.65 ±0.05	2.64	0.62 ±0.1
[Eu]@SBA-15 ^{air}	1.12	8.02	1.92 ±0.05	6.05	0.32 ±0.1
[Eu]@SBA-15 ^{dry}	1.12	7.98	2.75 ±0.10	6.09	0.45 ±0.1

^{a)} Crystalline sample; ^{b)} from literature^[11a]

As already mentioned, the adsorption has a mild impact on the emission profile of the complex and consequently, the ratio $I_{\text{tot}}/I_{\text{MD}}$ is not particularly affected. Consequently, the variation of the refractive index is mostly responsible for the drastic increase of the radiative lifetime calculated within the mesoporous matrix. Similar comments have already been made upon comparison of the photophysical data of $\text{Cs}_3[\text{Eu}(\text{DPA})_3]$ in water solution and in the solid state (crystals).^[11a] Thus, the intrinsic quantum yield of [Eu]@SBA-15^{air/dry} is not enhanced in comparison to that the pure crystalline complex. At the contrary, we observed a moderate decrease of the value. It is worth mentioning that the refractive index of the silica is still an estimation and could be slightly underestimated (as for $\phi_{\text{Ln}}^{\text{Ln}}$ by extension). As we did not expect any significant changes in the efficiency (η) of the energy transfer from the organic antenna to

the lanthanide, we assumed that the overall quantum yield of the complex ($\Phi = \Phi_{Ln}^{Ln} \times \eta$) should be affected in the same magnitude.

In conclusion, the quantum yield of the europium(III) complex is in the same range for both materials and seemingly lower once adsorbed on the silica. In addition, the role of water molecules adsorbed on silica, acting as second sphere Eu(III) luminescence quenchers, is clearly highlighted and explained the significant difference observed between [Eu]@SBA-15^{dry} and [Eu]@SBA-15^{air}.

2.2.3. Impact of [Eu] dispersion on the luminance of the resulting doped solids

Despite remarkable quantum yields at the molecular level, the practical use of pure lanthanide complexes (crystals) as luminescent materials is cost-prohibitive because most of the solid is not involved in the actual emission of light. Indeed, within the absorption range of the ligand (UV), the inner filter effect hinders light transmission and prevents the excitation of complexes located in the core of the crystals. We previously took advantage of this effect to prepare composite core-shell crystals that could be selectively excited in either their core or their surface using an appropriate wavelength.^[30] Thus, a perfect dispersion of emitting centers, avoiding the presence of micro- or nano-crystals in the emitting materials, could theoretically improve the overall excitation of the sample and by consequence its luminance.

In order to confirm a possible benefit arising from the dispersion of the complex in SBA-15 through the IWI process, we decided to compare the emitting performances of two families of solids containing an identical quantity of lanthanide complex: [Eu]@SBA-15^{air} featuring a very homogeneous dispersion of emitting centers without any crystallites (**Figure S6**), resulting from the adsorption of the complex by IWI and an intimate physical mixing of Cs₃[Eu(DPA)₃].8H₂O crystals with SBA-15 by grinding. This latter new material containing 7%wt of Eu is called [Eu]ΩSBA-15^{air}. The presence of small crystals of starting Cs₃[Eu(DPA)₃].8H₂O in [Eu]ΩSBA-15^{air} is unambiguously evidenced by PXRD (**Figure S6**). TEM - EDX mapping (O, Si, Eu, Cs) also confirm the presence of [Eu] crystals outside the SBA-15 pores (**Figure S9**). Conventional optical microscopy was also performed on [Eu]ΩSBA-15^{air} and [Eu]@SBA-15^{air} (**Figure S10**). Under UV irradiation ($\lambda_{ex} = 254$ nm), micrometric size red luminescent particles can be unambiguously identified on [Eu]ΩSBA-15^{air} micrograph. In marked contrast, under an identical illumination, the luminescence from [Eu]@SBA-15^{air} is perfectly homogeneous confirming previous PXRD and TEM measurements, and appears as more intense than for [Eu]ΩSBA-15^{air} (**Figure S10**).

Facing the impossibility of a reliable absolute quantum yield measurement (*vide supra*), we turned to a comparison of the luminance obtained from the different samples under identical UV light exposure. To do so, a home-made UV illuminating system working at 280 nm was built to measure the luminance of the sample by a dedicated luminance camera. The complete system is described in supporting information (**Figures S14-S16**). Quartz petri dishes containing about 50 mg of each solid samples were introduced in an opaque box. 8 LEDs distributed in a ring in the upper part of the set-up ensured a homogeneous irradiance of the powders and the emission was collected and quantified by the camera (Westboro Photonics P501F, sensitivity 3 mCd.m⁻²).

Three [Eu]ΩSBA-15^{air} samples were prepared by the progressive grinding of Cs₃[Eu(DPA)₃].8H₂O crystals with dried SBA-15 for 30 s, 1 min and 5 min and compared to the [Eu]@SBA-15^{air} doped solid from IWI. The latter was also grinded for 5 min to avoid any artefacts that could originate from a difference of the powder granulometry. For the same reason, all samples were then dried (2h under a 10⁻⁵ mbar vacuum) and stored one day under ambient atmosphere. The luminance measurements were then performed and the results are shown in **Figure 5** and **Table 2**.

	Sample	Average luminance (Cd.m ⁻²)	Luminance image
<i>adsorption</i>	[Eu]@SBA-15 ^{dry} <i>in inert cell</i>	3.75	
	[Eu]@SBA-15 ^{air}	2.88	
<i>physical mixing</i>	[Eu]ΩSBA-15 ^{air} <i>grinding 5 min</i>	0.89	
	[Eu]ΩSBA-15 ^{air} <i>grinding 1 min</i>	0.65	
	[Eu]ΩSBA-15 <i>grinding 0.5 min</i>	0.12	

Figure 5. Luminance images of the different materials obtained with the UV-lighting system working at 280 nm according to the false-colour scale of the camera (on the right).

Table 2. Luminance measurements and corresponding lifetimes of progressively grinded [Eu]@SBA-15^{air}, [Eu]@SBA-15^{air} and [Eu]@SBA-15^{dry} samples.

Dilution process	τ_{obs} [ms] (β)	Luminance [cd.m ⁻²]
30 s grinding	1.68 ±0.05 (0.99)	0.12
1 min grinding	1.66 ±0.05 (0.97)	0.65
5 min grinding	1.64 ±0.05 (0.96)	0.89
[Eu]@SBA-15 ^{air}	1.92 ±0.05 (0.96)	2.88
[Eu]@SBA-15 ^{dry}	2.75 ± 0.1 (0.95)	3.75

The results indicate a clear impact of the mixing process on the lighting performances of the grinded [Eu]@SBA-15^{air} materials. The grinding progressively improved the final luminance. This phenomenon can be attributed to the progressive fragmentation of Cs₃[Eu(DPA)₃].8H₂O crystals into smaller pieces, increasing the “active” area exposed to UV. It is worth noticing that the constant luminescence lifetime observed on this series confirmed that these higher luminances were only due to an improvement of the sample absorption and not to an increase of its quantum yield. In the meantime, the doped material prepared through the IWI process ([Eu]@SBA-15^{air}) demonstrated a supplementary three-fold improvement of the luminance in comparison to the other samples. In fact, the IWI adsorption on silica prevented any crystallization of the complex inside or outside the silica matrix. Thus, this material can be considered as a perfect dispersion of the complex in a scattering matrix that optimizes the absorption of light by the chromophore. This result clearly demonstrates that the simple adsorption of a [Eu] complex into a mesostructured silica by IWI is of great potential for the optimization of the overall lighting properties of the resulting luminescent material; a result that could readily be extended to any luminescent molecule and other solid matrices.

Finally, luminance measurements of the solids in a home-made sealed quartz cell reveals a spectacular enhancement up to 3.75 Cd.m⁻². A partial opening of the cell, allowing a progressive

rehydration of silica was monitored through luminance measurement (**Figure S17**). An exponential decrease of the luminance was observed, leading to a 22% loss after 15 min (2.91 Cd.m^{-2}) and a complete hydration of the material after 2 hours (2.85 Cd.m^{-2}). This experiment underlined the highly hygroscopic nature of $[\text{Eu}]\text{@SBA-15}^{\text{dry}}$ material and the crucial detrimental role of second sphere water molecules on the photophysical performances.

2.2.4. Desorption of the europium complex.

The presumed advantage that adsorbed materials could have in terms of recyclability was finally tested. The complex recovery was investigated by a simple filtration test in which 50 mg of a 20% w/w loaded $[\text{Eu}]\text{@SBA-15}^{\text{air}}$ was placed in a glass funnel filter with a sintered glass disk and washed with 200 mL of distilled water. The unchanged emission spectrum observed in the filtrate indicated that the starting europium(III) complex was recovered without alteration. By comparison to a known standard solution of $[\text{Eu}]$, the absorption spectrum indicated a 37 mg.L^{-1} concentration of the complex in the filtrate, meaning that 74% of the lanthanide complex was successfully removed from the doped solid and recovered in solution (**Figure S18**). In order to improve the recovery of the complex by disrupting potential interactions between the lanthanide complex and the silica matrix, the same washing/filtration procedure was used with slightly acidic water ($\text{pH} = 4$). Such conditions resulted in the desorption of almost 93% of the starting complex (**Figure S18**). This easy and straightforward recovery of intact lanthanide complex in mild conditions presents a huge recycling advantage compared to classical phosphors which recycling is very complicated.

3. Conclusion

In conclusion, we demonstrate here that a tris-dipicolinate europium complex could be quantitatively inserted into a mesostructured silica matrix (namely SBA-15) using a simple adsorption method (Incipient Wetness Impregnation). Accurately evaluating the photophysical properties of the specific luminescent material proved unexpectedly challenging and demanded meticulous care. From our observations, we determined that the adsorption of the complex does not affect either its molecular structure or its photophysical properties. We assume that the observed luminescence enhancements in some previous studies may have resulted from potential instrumental artefacts and a lack of consideration for the impact of lowering the

refractive index of the medium on the emitter luminescence lifetimes, particularly apparent through to the repeated use of wrong values for n in calculating intrinsic quantum yields.

The luminescent properties of our doped materials were found to compete with those of lanthanide complexes introduced into functionalized matrices through covalent or supramolecular interactions with surface ligands. The simple adsorption of lanthanide complexes in mesoporous silicas with Incipient Wetness Impregnation is a very promising approach for the preparation of luminescent materials that are brighter than traditional inorganic phosphors, due to an ideal dispersion of the emitting centres onto the matrix surface. Moreover, these materials offer very promising recycling possibilities since the absorbed complexes can be easily extracted from the host matrix by simple aqueous washings. These results thus open new possibilities towards the development of highly luminescent materials that rely less on rare earths and more easily recyclable.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Authors acknowledge "Auvergne-Rhône-alpes région" for the grant to Cristina Balogh and the "Agence Nationale de la Recherche" (project ECOPHOS ANR-17-CE09-0014) for grants to Isis N'Dala Louika and Iurii Suleimanov. Cristina Balogh & Isis N'Dala Louika contributed equally to this work.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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A tris-dipicolinate europium complex is quantitatively inserted into a mesostructured silica matrix using a simple physisorption method, yielding a highly emitting and recyclable material. The luminance of the solid is remarkable due to an ideal dispersion of the emitting centres into the silica matrix surface and the absorbed complexes can be easily extracted from the host matrix by simple washings.

ToC figure

