Hybrid luminescence materials assembled by $[\text{Ln}(\text{DPA})_3]^3^-$ and mesoporous host through ion-pairing interactions with high quantum efficiencies and long lifetimes

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A kind of mesoporous hybrid luminescence material was assembled through the ion exchange method between $[\text{Ln}(\text{DPA})_3]^3^-$ and ionic liquid functionalized SBA-15. $[\text{Ln}(\text{DPA})_3]^3^-$ was successfully anchored onto positive-charge modified SBA-15 by the strong electrostatic interaction. In $[\text{Ln}(\text{DPA})_3]^3^-$, Ln³⁺ ions are in 9-fold coordination through six oxygen atoms of carboxyl groups and three nitrogen atoms of pyridine units, leaving no coordination site for water molecules. Therefore the hybrids possess prominent luminescent properties, SBA-15-IMI-Tb(DPA)₃ and SBA-15-IMI-Eu(DPA)₃ exhibit high quantum yield values of 63% and 79%, and long lifetimes values of 2.38 ms and 2.34 ms, respectively. Especially, SBA-15-IMI-Eu(DPA)₃ presents a high color purity, and the red/orange intensity ratio is as high as 7.6. The excellent luminescence properties and ordered mesoporous structures give rise to many potential applications in optical and electronic areas.

Lanthanide complexes with excellent luminescence properties have attracted considerable attention due to their outstanding emission properties such as long luminescence lifetime, photostability, narrow and easily identifiable emission lines. These distinctive properties make them be suitable for application in lighting devices and biomedical analysis²⁴. In such complexes, appropriate organic ligands such as β-diketones³–⁵, phenanthroline⁶ and heterocyclic carboxylic acid group⁷–⁹ usually act as antenna or sensitizers which could absorb the light energy and transfer the energy from the lowest triplet state energy level (T₁) of these organic groups to the resonance level of the lanthanides. Furthermore, the organic ligands also shield the lanthanides from coordinated solvent molecules (such as water), and these solvent molecules can diminish the luminescence of the complexes because the high energy vibration of O-H will induce the non-radiative transition of lanthanides.

However, the pure lanthanide complexes are not suited for use in optical devices mainly due to their poor thermal stabilities and low mechanical strength. As a result, increasing attention has been focused on the design and synthesis of organic-inorganic hybrid materials by grafting of lanthanide complexes on polymer matrices¹⁰–¹², silica-based materials¹³–¹⁸, and liquid crystals¹⁹,²⁰, et al. For example, Reddy and coworkers reported a luminescence carbon material by bonding the visible sensitized Eu⁺⁺ β-diketonate complex to carboxyl functionalized multi-walled carbon nanotube²¹. Wang and coworkers prepared a hybrid luminescence material by linking Eu⁺⁺ or Tb⁺⁺ complexes with a new polycarboxylate amide ligand to mesoporous silica nanospheres (MSNs) for the recognition of fluoride ions²². Lin and coworkers designed a paramagnetic hybrid material by grafting Gd⁺⁺ complex to the thiol-functionalized MSNs through a disulfide tether, which could act as a magnetic resonance imaging contrast agent²³. Generally, the novel hybrids will exhibit superior physicochemical and optical properties, including high thermal stabilities and mechanical strength, long luminescence lifetimes, as well as promising application. Among all of the lanthanide hybrids, mesoporous silicas with unique properties (large surface area, uniform and adjustable pore sizes, as well as easy surface modification) are frequently used as the scaffolding materials due to their potential applications in sensing, drug delivery, biomedical imaging, etc. Up
to now, lanthanide complexes have been incorporated into mesoporous silica matrices, such as MCM-41, SBA-15 by a covalent bond grafting technique or a non-covalent, assembling method\textsuperscript{24,25}.

Ionic liquids functionalized mesoporous materials have drawn considerable attentions over the past decades, owing to theirs application in electrochemistry, catalysis and separation and adsorption\textsuperscript{26,27}. Recently, Mesoporous silicas modified with alkylimidazolium chloride (IMI\textsuperscript{Cl}) and the hybrid mesoporous luminescence material (SBA-15-IMI-Ln(DPA))\textsubscript{3} is shown in Figure 1. Fourier transform infrared (FT-IR) spectrum is commonly used for structural characterization of hybrid materials because it can provide surface information of samples for identification of chemical functional groups. The FT-IR spectra of SBA-15 and functionalized SBA-15 are shown in Figure 2. As shown in Figure 2B and E, the characteristic absorbance for skeleton vibration of imidazolium ring functional groups. The FT-IR spectra of SBA-15 and functionalized SBA-15 display the bands cor responding to the vibration of saturated C-H and unsaturated C-H appear at 2935 cm\textsuperscript{-1} and 3100, 3157 cm\textsuperscript{-1}, respectively, implying that IMI\textsuperscript{Cl} has been successfully grafted onto the framework of SBA-15\textsuperscript{26}. Furthermore, the formation of the Si-O-Si framework is evidenced by the bands located at 1080 cm\textsuperscript{-1} (\nu\textsubscript{as}, Si-O), 795 cm\textsuperscript{-1} (\nu\textsubscript{s}, Si-O) and 463 cm\textsuperscript{-1}(\delta, Si-O-Si)\textsuperscript{26,36}, respectively (Figure 2A). The coordination sphere of the lanthanide ion through the incorporation of europium \beta-diketone complexes into functionalized mesoporous materials, which exhibit a bright red photoluminescence upon illumination with ultraviolet light. However, \beta-diketones are not the efficient ligands for sensitizing the luminescence of terbium ion, because the lowest triplet state of \beta-diketones can not match the emission energy level of terbium ion very well\textsuperscript{30}.

Pyridine-2, 6-dicarboxylic acid (DPA) is an efficient tridentate N, O-chelating ligand for sensitization of terbium or europium ions luminescence. Three DPA ligands are able to coordinate with the lanthanide ion through six oxygens of carboxyl groups and three nitrogen atoms of pyridine units, resulting in the formation of [Ln(DPA)]\textsuperscript{3}\textsuperscript{−} (Ln: Tb, Eu)\textsuperscript{11,32}. The coordination sphere of the lanthanide ion is saturated by the ligands, leaving no coordination site for water molecules. Therefore, [Ln(DPA)]\textsuperscript{3}\textsuperscript{−} exhibit excellent luminescence properties in aqueous solution\textsuperscript{32}. Moreover, [Ln(DPA)]\textsuperscript{3}\textsuperscript{−} with three negative charges could be incorporated into the positive-charge modified mesoporous materials using an ion exchange method. In addition, the luminescence properties of the complexes formed by lanthanides and DPA derivatives can be adjustable by changing the substituents on the DPA or lanthanides. In this work, we propose a suitable and convenient method to assemble a novel mesoporous luminescence material (SBA-15-IMI-Ln(DPA))\textsubscript{3}, Ln = Tb or Eu. [Ln(DPA)]\textsuperscript{3}\textsuperscript{−} was incorporated into the alkylimidazolium quaternary ammonium salt functionalized mesoporous materials by ion-pairing interactions. The coordination feature of Ln\textsuperscript{3+} and well energy match between the energy levels of DPA and Ln\textsuperscript{3+} make the hybrids possess excellent luminescent properties such as high luminescent quantum yields, long lifetimes, high color purity and multi-color luminescence (red and green) under the excitation of a single wavelength ultraviolet light.

**Results**

The synthetic scheme of 1-methyl-3-(3-trioxyxysilylpropyl) imidazolium chloride (IMI\textsuperscript{Cl}) and the hybrid mesoporous luminescence material (SBA-15-IMI-Ln(DPA))\textsubscript{3} is shown in Figure 1. Fourier transform infrared (FT-IR) spectrum is commonly used for structural characterization of hybrid materials because it can provide surface information of samples for identification of chemical functional groups. The FT-IR spectra of SBA-15 and functionalized SBA-15 are shown in Figure 2. As shown in Figure 2B and E, the characteristic absorbance for skeleton vibration of imidazolium ring is found at about 1574 and 1456 cm\textsuperscript{-1}\textsuperscript{30}, meanwhile the bands corresponding to the vibration of saturated C-H and unsaturated C-H appear at 2935 cm\textsuperscript{-1} and 3100, 3157 cm\textsuperscript{-1}, respectively, implying that IMI\textsuperscript{Cl} has been successfully grafted onto the framework of SBA-15\textsuperscript{26}. Furthermore, the formation of the Si-O-Si framework is evidenced by the bands located at 1080 cm\textsuperscript{-1} (\nu\textsubscript{as}, Si-O), 795 cm\textsuperscript{-1} (\nu\textsubscript{s}, Si-O) and 463 cm\textsuperscript{-1}(\delta, Si-O-Si)\textsuperscript{26,36}, respectively (Figure 2A). The spectra of those lanthanide complex functionalized SBA-15 display two new peaks at 1437 and 1392 cm\textsuperscript{-1}, which can be assigned to the asymmetric and symmetric stretch of the carboxylate group, respectively (Figure 2C and D)\textsuperscript{36}. This means that the lanthanide DPA complexes have been anchored onto the ionic liquid modified SBA-15 frameworks by anion exchange. Figure 3 shows the X-ray powder diffraction (XRD) patterns of pure SBA-15 and modified SBA-15. All the samples clearly display a high-intensity (100) reflection and two weak reflections that can be indexed as the (110) and (200) diffractions respectively, which are characteristic of well-ordered mesoporous material with 2D-hexagonal structure. The hexagonal structures were still clearly observed.

![Figure 1](image-url)
in the functionalized SBA-15, indicating that the ordered hexagonal mesoporous is maintained during the functionalization of SBA-15 with lanthanide complexes.

The N$_2$ adsorption-desorption isotherms of the SBA-15, SBA-15-IMI-Tb(DPA)$_3$ and SBA-15-IMI-Eu(DPA)$_3$ are displayed in Figure 4. All of the samples exhibit the type IV adsorption isotherms with H1-type hysteresis loops at high relative pressure, which is a typical characteristics of ordered mesoporous materials. A sharp adsorption step occurs approximately at P/P$_0$ = 0.6–0.8, which reveals that those samples possess a well-defined array of regular mesoporous. The results indicated that the mesoporous structure of SBA-15 has been successfully retained under the functionalization environment. The structure data of these mesoporous materials are summarized in Table S1. As expected, the surface area, pore volume and average pore diameter of the modified SBA-15 decrease considerably compared to pure SBA-15, which is consistent with the presence of anchored lanthanide complexes inside the channels of SBA-15.

The morphology and the porous structure features of the mesoporous materials can be observed in Figure S1 and Figure 5. The scanning electron microscopy (SEM) images of SBA-15 and modified SBA-15 display the short rod-shaped external morphology.
whereas the transmission electron microscopy (TEM) images exhibit a well-ordered 2D hexagonal (P6mm) mesostructure, which is the characteristic structure feature of the SBA-15. This result clearly indicates that the mesoporous structure of SBA-15 is not disrupted after modifying with lanthanide complexes. The energy dispersive X-ray spectroscopy (EDS) analysis indicated that Tb or Eu-element has been detected in SBA-15-IMI-Tb(DPA)₃ or SBA-15-IMI-Eu(DPA)₃ (Figure S2).

Thermogravimetric analysis is one common used thermal analysis technique, which is particularly useful for observing the thermal decomposition of organic-inorganic hybrid materials. The thermogravimetric (TG) curves and the corresponding derivative thermogravimetric (DTG) curves of SBA-15-IMI-Tb(DPA)₃ and SBA-15-IMI-Eu(DPA)₃ are shown in Figure 6. The weight loss observed for all the functionalized samples is at two temperatures range. The first important weight loss below 200°C is related to physically adsorbed and coordinated water molecules. The relatively large weight loss occurs between 300 and 550°C, which is assigned to the decomposition of organic species. Beyond this temperature, the weight loss is less obvious. The total weight losses for SBA-15-IMI-Tb(DPA)₃ and SBA-15-IMI-Eu(DPA)₃ are about 35.2% and 30.5%, respectively, which indicates that the organic groups have been anchored onto the surface of SBA-15

The excitation and emission spectra of SBA-15-IMI-Tb(DPA)₃ and SBA-15-IMI-Eu(DPA)₃ are shown in Figure 7. The excitation spectra were recorded by monitoring the 5D₄ → 7F₅ transition at 543 nm for Tb³⁺ and the 5D₀ → 7F₂ transition at 615 nm for Eu³⁺. Both of the spectra display a broad excitation band between 240 nm to 350 nm (λ_max = 280 nm), which can be ascribed to the absorption of the complexes. Meanwhile, the maximum absorption of the lanthanide complexes could also be observed at 280 nm in the UV-Vis diffuse reflection spectra (Figure S3). Upon excitation with 280 nm ultraviolet light, the obtained SBA-15-IMI-Tb(DPA)₃ material gives characteristic emission of Tb³⁺, and the emission peaks at 492, 543, 583 and 622 nm can be assigned to the 5D₄ → 7F_j (j = 6, 5, 4, 3) transitions, respectively, with the 5D₄ → 7F₂ transition as the most prominent one. Under the excitation of ultraviolet light with the same wavelength, SBA-15-IMI-Eu(DPA)₃ reveal the characteristic Eu³⁺ emission peaks centered at 594, 615, 649 and 695 nm, corresponding to the 5D₀ → 7F_j (j = 1, 2, 3, 4) transitions respectively. Among these transitions, the 5D₀ → 7F₂ transition (the strongest one) is a typical electric dipole transition which is fairly sensitive to the local symmetry of Eu³⁺ ions, whereas the 5D₀ → 7F₁ corresponds to a magnetic dipole transition that is independent of the host material. According to the transition probabilities, the 5D₀ → 7F₂ electron dipole transition becomes the strongest emission when Eu³⁺ is in a non-inversion symmetry site, while in a center with inversion, the 5D₀ → 7F₁ magnetic dipole transition is dominant. Therefore, the relative intensity ratio (R₁) of 5D₀ → 7F₂ (red light) to 5D₀ → 7F₁ (orange red light) depends strongly on the local symmetry around the Eu³⁺ ion. The value of R₁ for SBA-15-IMI-Eu(DPA)₃ is 7.6, suggesting that the local surrounding of Eu³⁺ is highly asymmetric without an inversion center. In addition, the full width at half maximum of the strongest band is less than 4 nm, which shows that the SBA-15-IMI-Eu(DPA)₃ exhibits a high color purity. As observed by the luminescence photos (Figure 7 b and d, insets), the hybrid materials SBA-15-IMI-
Tb(DPA)_3 and SBA-15-IMI-Eu(DPA)_3 exhibit bright green and red color luminescence respectively upon irradiation with a single wavelength (280 nm) ultraviolet light.

The chromaticity diagram (CIE) shown in Figure S4 indicates that the emission of both hybrids lie in green and red region with the chromaticity coordinates (x = 0.35, y = 0.59) for SBA-15-IMI-Tb(DPA)_3 and (x = 0.66, y = 0.33) for SBA-15-IMI-Eu(DPA)_3, respectively. Moreover, the chromaticity coordinate of the SBA-15-IMI-Eu(DPA)_3 is close to the edge of the CIE diagram, which also shows this sample with high color purity.

The luminescence decay curves of SBA-15-IMI-Tb(DPA)_3 and SBA-15-IMI-Eu(DPA)_3 are shown in Figure 8. Both of the curves can be well fitted by a single exponential function described as equation (1)

\[ I(t) = I_0 \exp(-t/\tau) \]  

Where \( \tau \) stands for the luminescence lifetime and \( I_0 \) is the corresponding fitting parameter. The values of \( \tau \) are determined to be 2.38 ms for SBA-15-IMI-Tb(DPA)_3 and 2.34 ms for SBA-15-IMI-Eu(DPA)_3, respectively. The results indicate that the average chemical environments of Tb\(^{3+}\) or Eu\(^{3+}\) are uniform. The luminescence lifetime of lanthanides is greatly affected by the vibration of the nearby hydroxyl groups and ligands. The vibrations of hydroxyl groups and ligands will absorb the excitation energy of Tb\(^{3+}\) or Eu\(^{3+}\), leading to decrease the lifetime of the lanthanides. As for our hybrid luminescence materials, the strong electrostatic interaction between the matrix and the lanthanide complexes limits the vibration of the ligands around lanthanides. Furthermore, \([\text{Ln(DPA)}_3]^{3-}\) have no coordinated water molecules, leading to long luminescence lifetimes of lanthanides. The quantum efficiencies (\( \eta \)) of the SBA-15-IMI-Tb(DPA)_3 and SBA-15-IMI-Eu(DPA)_3 are about 63% and 79%, respectively. The photoluminescence data including excitation wave-
length, emission wavelength, quantum efficiency and lifetime of our samples and other analogous materials are listed in Table 1, it appears that the lifetime in SBA-15-IMI-Ln(DPA)₃ (Ln = Tb, Eu) is longer than that in other hybrid materials containing a similar lanthanide complexes. The high quantum efficiencies and long luminescence lifetimes suggest that this method is a preferable way for constructing hybrid mesoporous materials with bright green or red emission.

The reason that the excellent luminescent properties of SBA-15-IMI-Ln(DPA)₃ is mainly attributed to two aspects. On the one hand, as can be seen in Figure S5, three DPA ligands are able to coordinate with the Ln³⁺ through six oxygen atoms of carboxyl groups and three nitrogen atoms of pyridine units, and the coordination sphere of Ln³⁺ is saturated by the ligands, leaving no coordination site for water and other solvent molecules. On the other hand, the energy levels between DPA ligand and Ln³⁺ are well matched and there exist efficient energy transfer between them. It has been confirmed that the matching degree between the lowest triplet state energy level of ligand and emission energy level of Ln³⁺ is a critical factor which affects the luminescence properties of the lanthanide complexes. Generally, the energy transfer between the organic ligand and Ln³⁺ is well matched and there exist efficient energy transfer between them. For the DPA ligand, the lowest energy of the triplet state of the ligands is higher than the energy of the resonance levels of the lanthanides. For the DPA ligand, the lowest energy of the triplet state of the DPA (26600 cm⁻¹) is higher than the resonant energy level of Tb³⁺ (‘D₀, 21500 cm⁻¹) and Eu³⁺ (‘D₀, 17250 cm⁻¹), indicating that DPA would be an efficient ligand for sensitizing the luminescence of Tb³⁺ and Eu³⁺. The simplified energy levels, electron transition schematic diagram and the luminescent mechanism are illustrated in Figure 9. First, the DPA complex is excited from the singlet ground state (S₀) to excited singlet states by absorbing the light energy, and then relaxed to the lowest excited singlet states (S₁) through non-radiative transitions. Secondly, the energy of excited singlet state (S₁) of the ligand is transferred to its excited triplet state (T₁) through intersystem crossing. Thirdly, the intramolecular energy transfer from the excited triplet state of the ligands to the excited 4f states of the Tb³⁺ ions (‘D₀) or Eu³⁺ ions (‘D₀) through non-radiative transition. Finally, the radiative transition of Ln³⁺ produces the characteristic luminescence of Ln³⁺.

**Conclusions**

In this work, two novel luminescence mesoporous hybrid materials have been prepared by incorporating [Ln(DPA)₃]³⁻ into ionic liquid modified SBA-15 through strong electrostatic interactions. The mesoporous structures of SBA-15 can be retained after functionalization with [Ln(DPA)₃]³⁻ (Ln: Tb, Eu). Under the excitation of ultraviolet light with the same wavelength (280 nm), the hybrid materials show the characteristic emission of Tb³⁺ (green) and Eu³⁺ (red) with long luminescence lifetimes and high quantum efficiencies, which indicates that [Ln(DPA)₃]³⁻ are very suitable as the luminescence center for construction of the hybrid luminescence materials.
Methods

Synthesis of 1-methyl-3-(3-triethoxysilylpropyl) imidazolium chloride (IMI$^+Cl^-$). 1-methyl-3-(3-triethoxysilylpropyl) imidazolium chloride was synthesized from (3-Chloropropyl)triethoxysilane and 1-methylimidazole as previously reported$^{48}$.

Synthesis of mesoporous material SBA-15$^{49}$. Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (Pluronic P123, EO$_{20}$PO$_{70}$EO$_{20}$, $M_w$ = 5800, 4.0 g) was dissolved in hydrochloric acid (120 mL, 2 mol/L) and distilled water (30 mL) under stirring. Then tetraethoxysilane (TEOS, 8.4 g) was added dropwise to the above mixture solution under vigorous stirring at 313 K. After TEOS was completely added, the mixture was left to stirred at 313 K for 24 h and then

Table 1 | Photoluminescence data of the SBA-15-IMI-Ln(DPA)$_3$, (Ln = Tb, Eu) and previously reported hybrid luminescence mesoporous materials. excitation wavelength ($\lambda$ (ex)), emission wavelength ($\lambda$ (em)), lifetime (\(\tau\)), quantum efficiency ($\eta$), Reference (Ref)

| Samples                  | $\lambda$ (ex) | $\lambda$ (em) | $\tau$ (ms) | $\eta$ (%) |
|--------------------------|----------------|----------------|-------------|------------|
| SBA-15-IMI-Tb(DPA)$_3$   | 280 nm         | 492, 543, 583, 622 nm | 2.38        | 63         |
| SBA-15-IMI-Eu(DPA)$_3$   | 280 nm         | 594, 616, 649, 695 nm | 2.34        | 79         |
| Tb-dpa-Si-MSNs$^{9}$      | 281 nm         | 490, 546, 582, 622 nm | 0.86        |            |
| Eu-dpa-Si-MSNs$^{9}$      | 281 nm         | 592, 614, 650, 694 nm | 0.62        |            |
| Eu[PEG-SBA-15]$_{13}$     | 349 nm         | 590, 611, 650, 700 nm | 0.943       | 37.77      |
| Eu[PEG-SBA-15]$_{13}$phen$^{9}$ | 351 nm     | 590, 611, 650, 700 nm | 0.952       | 71.11      |
| 4a$^{3a,10}$              | 350 nm         | 590, 611, 650, 700 nm | 0.596       | 12.81      |
Synthesis of hybrid mesoporous material SBA-15-IMI\(^{5}\). 1-methyl-3-(3-triethoxysilylpropyl) imidazolium chloride (IMI\(^+\)) (3 mL) were added dropwise to a suspension of SBA-15 (2 g) in dry toluene (60 mL). Triethoxysilylpropyl) imidazolium chloride (IMI\(^+\)). containing Light-Emitting Organic-Inorganic Hybrids: A Bet on the Future. Divya, V. & Reddy, M. L. P. Visible-light excited red emitting luminescent bis[3,5-bis(diphenylphosphino)-9,9-dimethylxanthene Oxide]. The resulting mixture was refluxed at 115 °C for 24 h under a nitrogen atmosphere. After cooling, the suspension was centrifuged and the adsorbent ion liquid was removed by Soxhlet extraction with hydrochloric acid and ethanol solution under reflux for 2 d. Fourier transform infrared (FT-IR) spectrum was measured using a Nicolet 5700 spectrometer. Sample FT-IR spectrum was measured in the range of 4000–400 cm\(^{-1}\). The mixture was transferred into a hermetically sealed Erlenmeyer flask, and kept at 353 K for 48 h. Finally the product was recovered by filtration, washed with distilled water and air-dried. The template was removed by Soxhlet extraction with hydrochloric acid and ethanol solution under reflux for 2 d.

Synthesis of hybrid mesoporous luminescent material SBA-15-IMI(Ln(DPA)\(_3\))\(^{3+}\) system. Non-rad = nonradiative transitions, ISC = intersystem crossing, ET = energy transfer, S = Singlet, T = triplet. The template was removed by Soxhlet extraction with hydrochloric acid and ethanol solution under reflux for 2 d.

Excitation Energy (10\(^{-19}\) J

Em

D\(_{1}\)

D\(_{2}\)

D\(_{3}\)

D\(_{4}\)

T\(_{1}\)

S\(_{1}\)

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**Author contributions**

L.Q.F. and W.Z.L. performed the experiments and wrote the paper. Y.D. prepared all the figures. L.W., Z.X.L. and L.C.Y. carried out the materials characterization. All authors discussed the experimental results and reviewed the manuscript.

**Additional information**

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