Near-infrared luminescent xerogel materials covalently bonded with ternary lanthanide [Er(III), Nd(III), Yb(III), Sm(III)] complexes[†]

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A β -diketone ligand 4,4,5,5,5-pentafluoro-1-(2-naphthyl)-1,3-butanedione (Hpfnp), which contains a pentafluoroalkyl chain, was synthesized as the main sensitizer for synthesizing new near-infrared (NIR) luminescent Ln(pfnp)₃phen (phen = 1,10-phenanthroline) (Ln = Er, Nd, Yb, Sm) complexes. At the same time, a series of lanthanide complexes covalently bonded to xerogels by the ligand 5-(*N*,*N*-bis-3-(triethoxysilyl)propyl)ureyl-1,10-phenanthroline (phen-Si) were synthesized *in situ via* a sol-gel process. [The obtained materials are denoted as xerogel-bonded Ln complexes (Ln = Er, Nd, Yb, Sm).] The single crystal structures of the Ln(pfnp)₃phen complexes were determined. The properties of these complexes and the corresponding xerogel materials were investigated by Fourier-transform infrared (FTIR), diffuse reflectance (DR), and field-emission scanning electron microscopy (FE-SEM). After ligand-mediated excitation of these complexes and the corresponding xerogel materials they all show the characteristic NIR luminescence of the corresponding Ln³⁺ ion. This is attributed to efficient energy transfer from the ligands to the Ln³⁺ ion (the so-called "antenna effect").

Introduction

Historically, most of the investigations in the field of luminescent lanthanide ions have been devoted to Eu(III) and Tb(III), which emit in the visible spectral region.¹ Recently, much attention has been paid to near-infrared (NIR) luminescence of trivalent lanthanide ions,² such as Yb(III), Er(III), Nd(III), due to their potential applications as biomolecule labels in luminescent bioassays,³ as functional materials for optical telecommunication networks⁴ and laser systems.5 For instance, the relative transparency of human tissue at around 1000 nm suggests that in vivo luminescent probes operating at this wavelength (Yb-based emission) could have diagnostic value.⁶ NIR luminescence from Er(III) proves very useful when employed in telecommunication network optical signal amplifiers.^{4a,7} Regarding the Nd(III) containing materials, for a long time this metal has been found to have applications within laser systems.^{5a,8} Moreover, the sensitization of other NIR-luminescent trivalent lanthanide ions, such as Sm(III) with abundant emissions from its 4G5/2 excited state to lower manifolds, is of high interest as supplementary emission wavelengths would then also be available.

However, it is difficult to generate luminescence by direct excitation of lanthanide ions due to their poor absorption abilities. A useful way to sensitize the luminescence of lanthanide ions is to employ organic chromophores as antennas for light absorption.9 Weissman reported in 1942 that lanthanide luminescence can be improved by using an intramolecular energy transfer, the so-called "antenna effect".¹⁰ Commonly used ligands are β -diketones (1,3dikeones) and non-charged ligands like 1,10-phenanthroline. β-Diketones containing aromatic groups have strong absorption over a large wavelength range and consequently have been targeted to sensitize lanthanide luminescence.¹¹ Additionally, they have a strong ability to form adducts with lanthanide ions, and the obtained complexes are stable enough for practical use. According to the literature reported previously, the replacement of C-H bonds in a β -diketone ligand with lower-energy C-F oscillators is able to lower the vibration energy of the ligand, which decreases the energy loss caused by ligand vibration and enhances the emission intensity of the lanthanide ion.¹² To accomplish this goal, the ligand Hpfnp [4,4,5,5,5-pentafluoro-1-(2-naphthyl)-1,3butanedione], was synthesized as the main sensitizer for synthesizing the $Ln(pfnp)_3$ phen (Ln = Er, Nd, Yb, Sm) complexes. In addition, phen can serve as the synergistic agent, since an important issue in the design of lanthanide complexes is to prevent water molecules from binding to lanthanide ions. With the help of resonant energy transfer, lanthanide ions in lanthanide complexes may accept energy from the lowest triplet states of ligands. Theoretically, efficient emissions corresponding to internal f-f transitions of lanthanide ions are expected.

The practical applications of these NIR luminescent lanthanide complexes are limited to a large extent by their poor thermal stability and low mechanical strength. One solution is to incorporate lanthanide complexes in a host matrix.¹³ Sol–gel derived hybrid materials have received great interest nowadays,^{14,e,14} as they

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[†] Electronic supplementary information (ESI) available: UV-vis absorption spectra of Hpfnp and phen ligands, excitation and emission spectra of $Er(pfnp)_3phen$, $Nd(pfnp)_3phen$, $Yb(pfnp)_3phen$ and $Sm(pfnp)_3phen$ complexes, the phosphorescence spectra of $Gd(pfnp)_3(H_2O)_2$ complex in DMF at 77 K, XRD patterns of $Er(pfnp)_3phen$, $Yb(pfnp)_3phen$ and $Yb(pfnp)_3phen$ simulated. CCDC reference numbers 699049–699052. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b819644c

combine chemical and thermal stability, the mechanical strength and the process flexibility of silica, together with the functional characteristics of active organic molecules. Physical mixing of the sol-gel materials and lanthanide complexes is easy to do, however, the interactions between lanthanide complexes and silica moieties in such sol-gel hybrid materials are so weak that the phase separation, inhomogeneous dispersion, and optical quenching of the dopants may occur.¹⁵ To overcome these shortcomings, we prepared phen-Si [5-(N,N-bis-3-(triethoxysilyl)propyl)ureyl-1,10-phenanthroline], which plays a double role, *i.e.* as a ligand for lanthanide ions and an organosilane precursor to synthesize the xerogel materials.¹⁶ Moreover, the in situ synthesis technique reported by Qian et al. was selected.17 Thus, the NIR-luminescent lanthanide β-diketone complexes were covalently attached to the xerogel material and the above-mentioned problems of phase separation and inhomogeneous dispersion between organic and inorganic moieties can be avoided effectively.

Herein, we synthesize a β -diketone ligand (Hpfnp), followed by synthesis of Ln(pfnp)₃phen complexes and xerogel-bonded Ln complex (Ln = Er, Nd, Yb, Sm) materials. The crystal structures of the Ln(pfnp)₃phen complexes are reported. The properties of the Ln(pfnp)₃phen complexes and the corresponding xerogel materials were investigated by Fourier-transform infrared (FTIR), diffuse reflectance (DR), field-emission scanning electron microscopy (FE-SEM), and luminescence spectra.

Results and discussion

Crystal structures of the Ln(pfnp)₃phen (Ln = Er, Nd, Yb, Sm) complexes

The single crystal structures of a series of lanthanide complexes containing Hpfnp and phen were studied. The single-crystal X-ray diffraction studies revealed isostructural crystals (triclinic, Z =4) for $Ln(pfnp)_3$ phen (Ln = Er, Nd, Yb, Sm) complexes whose crystals fall into the same $P\overline{1}$ space group (also see Fig. S1, ESI[†]). Thus, only the crystal structure of Nd(pfnp)₃phen will be described in detail as an example. The crystal structure of Nd(pfnp)₃phen with the numbering scheme is displayed in Fig. 1a. Analysis of the crystal structure indicates that the central Nd³⁺ ion is eightcoordinate, with six oxygen atoms from three Hpfnp ligands and two nitrogen atoms from the phen ligand. The coordination geometry of the central Nd³⁺ ion is best described as a square antiprism from the coordination site angles (shown in Fig. 1b). In the β -diketone rings of the Ln(pfnp)₃phen (Ln = Er, Nd, Yb, Sm) complexes, the average distances for the C-C and C-O bonds are shorter than a single bond but longer than a double bond. This can be explained by the fact that there exists a conjugated structure between the naphthyl ring and the coordinated β -diketonate, which leads to the delocalization of electron density of the coordinated β -diketonate chelate ring. Also, the β -diketonate chelate ring itself is a conjugated structure due to the delocalization of electron density. Important experimental parameters for the structure determinations are tabulated in Table 1, and the average Ln-O and Ln-N bond lengths in the crystals are listed in Table 2. It can be seen that the average Ln-O and Ln-N bond lengths decrease from Nd to Yb for the $Ln(pfnp)_3$ phen (Ln = Er, Nd, Yb, Sm) complexes due to the "lanthanide contraction", as expected. As described above, the central Ln³⁺ ion is completely surrounded by



Fig. 1 (a) ORTEP plot for $Nd(pfnp)_3$ phen with ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity. (b) Coordination polyhedron of the central Nd^{3+} ion.

the anionic β -diketone ligand Hpfnp and the synergistic ligand phen. Thus, the ligands (Hpfnp and phen) are able to absorb energy and transfer the absorbed energy to the central Ln³⁺ ion. The characteristic NIR luminescence of the Ln³⁺ ion (Ln = Er, Nd, Yb, Sm) is expected.

Fourier-transform infrared (FTIR) and diffuse reflectance (DR) spectra

The FTIR spectra of the Nd(pfnp)₃phen complex and xerogelbonded Nd complex (the expected structure is outlined in Table 1Crystal data and structure refinements for the $Ln(pfnp)_3phen$ (Ln = Er, Nd, Yb, Sm) complexes

Empirical formula	$C_{57}H_{32}F_{15}N_2O_6Er$	$C_{57}H_{32}F_{15}N_2O_6Nd$	$C_{57}H_{32}F_{15}N_2O_6Yb$	$C_{57}H_{32}F_{15}N_2O_6Sm$	
Formula weight	1293.11	1270.09	1298.89	1276.20	
Temperature/K	293(2)	293(2)	293(2)	293(2)	
Wavelength/A	0.71073	0.71073	0.71073	0.71073	
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	
Space group	P1	P1	<i>P</i> 1	<i>P</i> 1	
Space group number	2	2	2	2	
a/Å	12.222(5)	12.346(5)	12.159(5)	12.633(3)	
b/Å	20.080(5)	20.023(5)	20.061(5)	20.161(4)	
c/Å	21.842(5)	21.938(5)	21.769(5)	21.541(4)	
$\alpha/^{\circ}$	89.163(5)	89.777(5)	88.942(5)	79.599(4)	
$\beta/^{\circ}$	83.064(5)	82.019(5)	83.288(5)	86.203(4)	
$\gamma/^{\circ}$	84.338(5)	83.466(5)	84.378(5)	83.818(4)	
Volume/Å ³	5295(3)	5335(3)	5248(3)	5358.7(19)	
Ζ	4	4	4	4	
$D_{\rm calcd.}/{ m mg}~{ m m}^{-3}$	1.622	1.581	1.644	1.582	
Abs. coeff./mm ⁻¹	1.691	1.078	1.889	1.200	
F(000)	2556	2524	2564	2532	
Crystal size/mm	$0.20 \times 0.16 \times 0.15$	$0.24 \times 0.22 \times 0.18$	$0.24 \times 0.20 \times 0.14$	$0.22 \times 0.18 \times 0.17$	
θ range/°	1.38 to 26.11	1.38 to 26.07	1.39 to 26.10	1.84 to 26.08	
Reflns collected	29900	30313	29729	30412	
Unique reflns (R_{int})	20378(0.0836)	20614(0.0313)	20290(0.0522)	20680(0.0586)	
Refinement method	Full-matrix least-squares on F^2				
Data/restraints/parameters	20378/28/1254	20614/46/1459	20290/45/1339	20680/43/1439	
GOF on F^2	0.958	1.010	0.967	0.969	
$R_1[I > 2\sigma(I)]$	0.1014	0.0598	0.0857	0.0812	
$WR_2 [I > 2\sigma(I)]$	0.1977	0.1263	0.1951	0.1384	
R_1 (all data)	0.2589	0.1063	0.1837	0.2118	
wR_2 (all data)	0.2746	0.1517	0.2497	0.1877	

Table 2Average Ln–O and Ln–N bond lengths for the $Ln(pfnp)_3phen$ (Ln = Er, Nd, Yb, Sm) complexes

	Nd(pfnp)₃phen	Sm(pfnp) ₃ phen	Er(pfnp)₃phen	Yb(pfnp) ₃ - phen
Ln–O/Å	2.397	2.361	2.299	2.277
Ln–N/Å	2.642	2.606	2.520	2.498

Scheme 1) are given as the representative patterns. Fig. 2 presents the FTIR spectra of the Nd(pfnp)₃phen complex, the phen-Si, and the xerogel-bonded Nd complex. The peaks in the range 400–438 cm⁻¹ corresponding to Nd–O vibrations in Fig. 2a can also be seen in Fig. 2c (a very weak peak at 416 cm⁻¹),



Fig. 2 FTIR spectra of the $Nd(pfnp)_3$ phen complex (a), the phen-Si (b) and the xerogel-bonded Nd complex (c).

which suggests the formation of Nd–O bonds in the xerogelbonded Nd complex. The bending vibration frequency of C=N has red-shifted in the xerogel-bonded Nd complex compared with phen, suggesting the formation of a Nd–N bond.^{13/} In Fig. 2c, the formation of the Si–O–Si framework is evidenced by the bands located at 1073 and 450 cm⁻¹.¹⁸ The peak at 1526 cm⁻¹, originating from the CONH group of phen-Si (Fig. 2b), can also be observed in Fig. 2c, which could suggest that the functionalized phen group in the framework remains intact. Thus, we proposed that ternary lanthanide complexes [Ln(pfnp)₃phen, Ln = Er, Nd, Yb, Sm] were formed *via in situ* synthesis methods and covalently bonded to the silica network in the corresponding xerogels.

> The DR spectra of the Ln(pfnp)₃phen complex and the xerogelbonded Ln complex (Ln = Er, Nd, Yb, Sm) are shown in Fig. 3. All broad absorption bands in the UV region of the DR curves were observed and can be assigned to electronic transitions from the ground-state level (S_0) to the excited level (S_1) of the organic ligands. In the visible and NIR region of these curves, each absorption band corresponds to a characteristic transition between two spin-orbit coupling levels of the corresponding lanthanide ions, which can be assigned to the transitions from the ground levels ${}^{4}I_{15/2}$, ${}^{4}I_{9/2}$, ${}^{2}F_{7/2}$, and ${}^{6}H_{5/2}$ to the higher energy levels for erbium,¹⁹ neodymium,^{12b} ytterbium,²⁰ and samarium²¹ based complexes and xerogels, as marked in Fig. 3. It can be seen that the Ln(pfnp)₃phen complexes and the corresponding xerogel materials possess a similar position for the absorption of the ligands, which, together with the appearance of the characteristic absorption of the Ln^{3+} ions (Ln = Er, Nd, Yb, Sm), suggests that the lanthanide complexes were synthesized in situ in the xerogelbonded Ln complexes.





Scheme 1 Synthesis procedure and proposed structure of the xerogel-bonded Ln complex (Ln = Er, Nd, Yb, Sm) materials.

Field-emission scanning electron microscopy (FE-SEM)

As a result of the synthesis process, transparent crack-free monoliths, which have copied the shape of the reaction vessel, were obtained (see Fig. 4, inset). The FE-SEM images of the xerogel-bonded Ln complexes (Ln = Er, Nd, Yb, Sm) are similar to one another, as presented by the representative patterns of the xerogel-bonded Nd complex in Fig. 4. From the FE-SEM images it can be seen that the xerogel material appears homogeneous, and no sign of any phase separation was observed even when the magnification was increased to 80 000. This can be explained by the *in situ* synthesis technique we used and the strong covalent bonds bridging between the organic and inorganic phases.

Photoluminescence studies

The excitation spectra of the lanthanide complexes and the absorption spectra of the ligands Hpfnp and phen are shown in Fig. S2 (see ESI[†]). It is worth noting that the absorption spectrum of Hpfnp and the excitation spectra of the $Ln(pfnp)_3$ phen (Ln = Er, Nd, Yb, Sm) complexes (monitored at the maximum emission of the corresponding Ln³⁺ ion) are a better match than that of phen and the excitation spectra, so Hpfnp is the main antenna ligand transfering energy and sensitizing the Ln³⁺ ions.²²

As shown in Fig. S2^{\dagger} and Fig. 5, a broad band ranging from 250 to 450 nm for the Er(pfnp)₃phen complex and a broad band ranging from 250 to 470 nm for the xerogel-bonded Er complex



Fig. 3 DR spectra of the $Ln(pfnp)_3$ phen complexes and the xerogel-bonded Ln complex [Ln = Er (a), Nd (b), Yb (c), Sm (d)] materials.



Fig. 4 FE-SEM images of the xerogel-bonded Nd complex (a) with a magnification of 20 000 and (b) with a magnification of 80 000. The inset shows the photo of the transparent xerogel-bonded Nd complex.

were observed. The two broad bands can be attributed to the light absorption of the Hpfnp and phen ligands, which is in agreement with the DR spectra (Fig. 3a). Upon excitation of the ligands'



Fig. 5 Excitation (EX, $\lambda_{em} = 1533$ nm) and emission (EM, $\lambda_{ex} = 413$ nm) spectra of the xerogel-bonded Er complex.

absorption band, characteristic Er^{3+} ion emissions were observed for the $Er(pfnp)_3$ phen complex (Fig. S3, ESI[†]) and the xerogelbonded Er complex (Fig. 5), respectively. Both of the emission spectra cover a wide spectral range with the emission maxima centered at 1533 nm. The emission obtained is attributed to the typical ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of the Er^{3+} ion. For many years, Er-doped materials with a high bandwidth and optical gain were of great interest in optical communications technology, because the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition around 1540 nm matches one of the fiber low-loss windows.²³ To enable a wide gain bandwidth for optical amplification, a broad emission band is desirable.²⁴ For the xerogel-bonded Er complex, the full width at half maximum (FWHM) of the 1533 nm emission band is 72 nm. Compared with that of the Er(pfnp)₃phen complex (59 nm) and the other Er-doped materials,²⁵ such a broad spectrum enables a wide gain bandwidth for optical amplification.

Meanwhile, the excitation and emission spectra of the Ln(pfnp)₃phen complexes and the xerogel-bonded Ln complexes (Ln = Nd, Yb, Sm) were obtained as shown in Fig. S2, Fig. S3,† and Fig. 6-8, respectively. After ligand-mediated excitation, all of the emission spectra of the Ln(pfnp)₃phen complexes and the corresponding xerogels show the characteristic NIR luminescence of the corresponding lanthanide ions. For the Nd(pfnp)₃phen complex and the xerogel-bonded Nd complex, the emission at around 1059 nm (${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$) is the strongest, which is potentially applicable for laser systems. Moreover, the emission band at 1332 nm offers the opportunity to develop new materials which are suitable for optical amplifiers operating at 1.3 µm.²⁶ For the emission spectra of the Yb(pfnp)₃phen complex and the xerogelbonded Yb complex, the Yb³⁺ ion emits in the range 910–1145 nm and 900-1150 nm, respectively, with a sharp peak around 978 nm assigned to the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of the Yb³⁺ ion broader vibronic components at longer wavelength.²⁷ Similar splitting has been reported in previous literature.²⁸ This may be the splitting of the energy levels of the Yb³⁺ ion as a consequence of ligand field effects.^{24a} The Yb³⁺ ion plays an important role in laser emission because of its very simple f-f energy level structure. There is no excited-state absorption on reducing the effective laser cross-



Fig. 6 Excitation (EX, $\lambda_{em} = 1059$ nm) and emission (EM, $\lambda_{ex} = 386$ nm) spectra of the xerogel-bonded Nd complex.



Fig. 7 Excitation (EX, $\lambda_{em} = 978$ nm) and emission (EM, $\lambda_{ex} = 376$ nm) spectra of the xerogel-bonded Yb complex.



Fig. 8 Excitation (EX, $\lambda_{em} = 950$ nm) and emission (EM, $\lambda_{ex} = 372$ nm) spectra of the xerogel-bonded Sm complex. Transitions start from the ${}^4G_{5/2}$ level.

section, no up-conversion, no concentration quenching, and no absorption in the visible range. The intense Yb³⁺ ion absorption lines are well suited for laser diode pumping in this range and the smaller Stokes shift between absorption and emission reduces the thermal loading of the material during laser operation.²⁹ These properties of the Yb3+ ion and the obtained emission make xerogelbonded Yb complexes very important for various photonic applications in ionic crystals and glasses.³⁰ Additionally, the relative transparency of human tissue at approximately 1000 nm suggests that in vivo luminescent probes operating at this wavelength of Yb-based emission could have diagnostic value.6 Compared with the NIR luminescence of Er(III), Nd(III), and Yb(III), that of Sm(III) is less well studied, although this situation is being remedied. $^{\mbox{\tiny 28b,c,31}}$ The $^4G_{\mbox{\tiny 5/2}}$ \rightarrow $^6F_{\mbox{\tiny 5/2}}$ transition at 950 nm in the emission spectra of the Sm(pfnp)₃phen complex and the xerogelbonded Sm complex is the most intense.

As described above, the obtained characteristic NIR luminescence of the Ln³⁺ ions is undoubtedly attributable to the contribution of the intramolecular energy transfer from the ligands, since Ln³⁺ ions have no absorption at the corresponding excitation wavelength. This verifies that the lanthanide complexes have been synthesized in situ in the xerogel-bonded Ln complexes, which is in agreement with the preliminary conclusion obtained from the FTIR and DR spectra. The triplet state energy level of Hpfnp is 19685 cm⁻¹, found by examining the phosphorescence spectrum of the $Gd(pfnp)_3(H_2O)_2$ complex in DMF solution at 77 K (see Fig. S4[†]).³² According to Dexter's theory,³³ it can match well with the 4f levels of the Ln3+ ions mentioned above (see Fig. S5[†]), and finally obtain the efficient NIR luminescence of the corresponding Ln3+ ion. However, the emission features of the xerogel-bonded Ln complex (Ln = Er, Nd, Yb, Sm) materials are different from those found for the corresponding $Ln(pfnp)_3$ phen complexes, which may be due to the Ln^{3+} ions being coordinated to the modified phen ligand and the different local environments of the Ln³⁺ ions in the xerogel materials. Furthermore, time-resolved measurements on the Ln(pfnp)₃phen complexes and the xerogel-bonded Ln complex (Ln = Er, Nd, Yb, Sm) materials were carried out at room temperature (RT) by using an excitation wavelength of 355 nm and monitored around the most intense emission line of their corresponding emission

spectra. The luminescence decays of the Ln(pfnp)₃phen complexes are fitted well by a single-exponential function, confirming that the Ln³⁺ ions occupy the same average local environment within each sample.³⁴ The corresponding lifetimes of the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of Er(pfnp)₃phen, the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ transition of Nd(pfnp)₃phen, the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of Yb(pfnp)₃phen, and the ${}^{4}G_{5/2} \rightarrow {}^{6}F_{5/2}$ transition of Sm(pfnp)₃phen are 1.78, 0.99, 11.01, 51.84 µs, respectively. The decay curve for the xerogelbonded Er complex is singly exponential, and the lifetime of the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition is 1.24 µs. The decay curves for the xerogel-bonded Ln complex (Ln = Nd, Yb, Sm) materials are fitted by double-exponential functions. The lifetimes of the ${}^{4}F_{3/2} \rightarrow$ ${}^{4}I_{11/2}$ transition of the xerogel-bonded Nd complex are 0.34 μ s (48.02%) and 85 ns (51.98%). The lifetimes of the $^2F_{5/2} \rightarrow \ ^2F_{7/2}$ transition of the xerogel-bonded Yb complex are 0.85 µs (32.07%) and 4.87 μ s (67.93%). The lifetimes of the ${}^{4}G_{5/2} \rightarrow {}^{6}F_{5/2}$ transition of the xerogel-bonded Sm complex are 4.59 μs (36.96%) and 20 μs (63.04%).

Conclusions

Based on a synthesized β -diketone (Hpfnp), Ln(pfnp)₃phen complexes and the transparent homogeneous NIR-luminescent xerogels covalently bonded with ternary lanthanide (Ln = Er, Nd, Yb, Sm) complexes have successfully been prepared by using an in situ synthesis technique. The structures of the Ln(pfnp)₃phen complexes have been determined by single-crystal X-ray diffraction, and the properties of the Ln(pfnp)₃phen complexes and the corresponding xerogels were also investigated. The complexes have successfully been synthesized in situ in the xerogels. After ligand-mediated excitation, all of the emission spectra of the Ln(pfnp)₃phen complexes and the corresponding xerogels show the characteristic NIR luminescence of the corresponding Ln³⁺ ions through intramolecular energy transfer from the ligands to the Ln³⁺ ions. Of importance here is the observation of efficient NIR luminescence of the Sm³⁺ ion, which has rarely been explored. The excellent NIR properties provide access to NIR-luminescent xerogel materials in optical applications, such as in amplifiers. lasers, and in vivo luminescent probes.

Experimental section

Materials and apparatus

Tetraethoxysilane (TEOS, Aldrich), 3-(triethoxysilyl)propyl isocyanate (TCI), ethyl pentafluoropropionate (98%, Aldrich), 2'acetonaphthone (98%, Acros), fuming nitric acid and anhydrous ethanol were used as received. Sodium metal (\geq 98%, AR) and 1,10-phenanthroline monohydrate (phen·H₂O, 99%, AR) were bought from Beijing Fine Chemical Co. (Beijing, China). The solvent chloroform (CHCl₃) was used after desiccation with anhydrous calcium chloride. Erbium oxide (Er₂O₃, 99.99%), neodymium oxide (Nd₂O₃, 99.99%), ytterbium oxide (Yb₂O₃, 99.99%), samarium oxide (Sm₂O₃, 99.99%), and gadolinium oxide (Gd₂O₃, 99.99%) were purchased from Yue Long Chemical Plant (Shanghai, China). LnCl₃ (Ln = Er, Nd, Yb, Sm, Gd) ethanol solutions were prepared as follows: Ln₂O₃ (Ln = Er, Nd, Yb, Sm, Gd) was dissolved in concentrated hydrochloric acid (HCl), and the HCl was removed by evaporation. The residue was dissolved with anhydrous ethanol. The concentration of the Ln^{3+} (Ln = Er, Nd, Yb, Sm, Gd) ions was determined by titration with a standard ethylenediaminetetraacetic acid (EDTA) aqueous solution.

Fourier-transform infrared (FTIR) spectra were measured within the 4000-400 cm⁻¹ wavenumber range using a Perkin-Elmer model 580B IR spectrophotometer with the KBr pellet technique and operating in the transmittance mode. The diffuse reflectance (DR) measurements were recorded on a SHIMADZU UV-3600 spectrophotometer. NMR spectra were recorded on a Bruker DRX 400 spectrometer. Element analyses were performed using a Vario Element Analyzer. Field-emission scanning electron microscopy (FE-SEM) images were obtained with a XL30 ESEM FEG microscope. The luminescence excitation and emission spectra were recorded on a HORIBA Jobin Yvon FluoroLog-3 spectrofluorometer equipped with a 450 W Xe-lamp as an excitation source and a liquid-nitrogen-cooled R5509-72 PMT as a detector. The time-resolved measurements were performed by using the third harmonic (355 nm) of a Spectra-physics Nd:YAG laser with a 5 ns pulse width and 5 mJ of energy per pulse as a source, and the NIR emission lines were dispersed by the emission monochromator of the HORIBA Jobin Yvon FluoroLog-3 equipped with a liquid-nitrogen-cooled R5509-72 PMT, and the data were analysed with a LeCroy WaveRunner 6100 1GHz Oscilloscope. The luminescence lifetimes were calculated with the Origin 7.0 software package. All the above measurements were performed at RT. The low-temperature phosphorescence spectrum of the Gd(pfnp)₃(H₂O)₂ complex was measured on a Hitachi F-4500 spectrophotometer at liquid nitrogen temperature (77 K).

Syntheses

Synthesis of the ligand Hpfnp. The synthesis procedure of the ligand Hpfnp was similar to that described by our group for the ligand 4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)hexane-1,3dione (Hhfnh).35 A modified method of a typical Claisen condensation procedure was used as follows. Sodium metal thread (2.76 g, 0.12 mol) was added to dry anhydrous ethanol (150 mL). The reaction mixture was stirred for 30 min at RT, after which 2'acetonaphthone (17.02 g, 0.1 mol) and ethyl pentafluorobutyrate (18.0 mL, 0.12 mol) were added. The mixture was then stirred for 48 h at RT. The resulting mixture was acidified to pH = 2-3 using hydrochloric acid (2 M solution), and the solvent was removed under reduced pressure at 70 °C. Dried CH2Cl2 was added to the resulting mixture and stirred for 10 min. The mixture was filtered and washed with dried CH₂Cl₂ several times. The filtrate was collected, and the solvent was removed under reduced pressure to obtain a maroon oil, which was purified by chromatography on a silica gel column with hexane as the eluent to get a maroon liquid (25.91 g, 0.082 mol, yield of 82% based on 2'-acetonaphthone). ¹H NMR (DMSO, 400 MHz): δ, 15.20 (broad, 1H), 8.47 (s, 1H), 8.04 (d, 1H, J = 8.8, 1.6 Hz), 8.01 (d, 1H, J = 8.8 Hz), 8.00 (d, 1H, J =8.0 Hz), 7.91–7.87 (m, 2H), 7.61 (td, 1H, J = 8.0, 1.6 Hz), 7.56 (td, 1H, J = 8.0, 1.6 Hz), 7.26 (s, 1H). ¹⁹F NMR (DMSO, 400 MHz): δ , -46.21 (s, CF₂), -5.57 (s, CF₃). Anal. calcd for C₁₅H₉F₅O₂: C, 56.97%; H, 2.87%. Found: C, 56.87%; H, 2.79%.

Synthesis of the near-infrared luminescent xerogel-bonded ternary Ln complexes [Ln = Er, Nd, Yb, Sm]. The starting reagent 5-amino-1,10-phenanthroline (denoted as phen- NH_2) was

prepared according to the procedure described in the literature.³⁶ phen-Si was synthesized by the reaction of phen-NH₂ and 3-(triethoxysilyl)propyl isocyanate in CHCl₃.³⁷ Then phen-Si was dissolved in ethanol, and TEOS and deionized water (acidified with HCl, pH = 2) were added under stirring. An appropriate amount of Hpfnp and $LnCl_3$ (Ln = Er, Nd, Yb, Sm) ethanol solution were introduced into the starting solution consecutively. The molar composition of the original synthetic mixture was 0.01 phen-Si : 1.0 TEOS : 4.0 H₂O : 0.01 Ln³⁺ : 0.03 Hpfnp. The mixed solution was stirred for 4 h at RT to ensure homogeneous mixing and a single phase was achieved, and then transferred into a plastic container. The precursor solution converted to a wet gel after several days of gelation at 45 °C and then was continuously dried to obtain a transparent monolithic xerogel. The lanthanide complexes were supposed to be synthesized in situ during the corresponding sol to monolithic xerogel conversion accompanied with the evaporation of HCl, respectively. Before the luminescence measurements were made, the xerogel materials were dried under vacuum for 24 h at 80 °C. The obtained xerogel materials were denoted as xerogel-bonded Ln complexes (Ln = Er, Nd, Yb, Sm).

Synthesis of the Ln(pfnp)₃phen (Ln = Er, Nd, Yb, Sm) complexes. An appropriate amount of 1.0 mol L⁻¹ sodium hydroxide solution was added dropwise to the Hpfnp and phen ethanol solution under stirring to adjust the pH value to approximately 8–9. The LnCl₃ ethanol solution was added dropwise into the above mixture under stirring with the molar ratio of Ln³⁺–Hpfnp–phen being 1 : 3 : 1. The mixture was heated under reflux for 6 h and then cooled to RT. After an appropriate amount of water was added, the precipitates were collected by filtration, washed with water and ethanol, and dried overnight at 70 °C under vacuum. The Ln(pfnp)₃phen complexes were recrystallized from ethanol. Block crystals suitable for X-ray single-crystal structural determination were grown from the mother liquor at RT.

Elemental analysis. For Er(pfnp)₃phen (pale pink), anal. calcd: C, 52.94%; H, 2.49%; N, 2.17%. Found: C, 52.88%; H, 2.47%; N, 2.12%. For Nd(pfnp)₃phen (blue), anal. calcd: C, 53.90%; H, 2.54%; N, 2.21%. Found: C, 53.86%; H, 2.51%; N, 2.17%. For Yb(pfnp)₃phen (colorless), anal. calcd: C, 52.71%; H, 2.48%; N, 2.16%. Found: C, 52.68%; H, 2.44%; N, 2.13%. For Sm(pfnp)₃phen (pale yellow), anal. calcd: C, 53.65%; H, 2.53%; N, 2.20%. Found: C, 53.60%; H, 2.51%; N, 2.17%.

Synthesis of Gd(pfnp)₃(H₂O)₂ complex. The synthesis procedure is similar to that of the Ln(pfnp)₃phen (Ln = Er, Nd, Yb, Sm) complexes, except for the absence of phen and the introduction of the GdCl₃ ethanol solution instead of the LnCl₃ ethanol solution. Additionally, the mixture was heated under reflux for 12 h not 6 h. Anal. calcd for C₄₅H₂₈F₁₅O₈Gd: C, 47.46%; H, 2.48%. Found: C, 47.36%; H, 2.55%.

X-Ray diffraction crystallography

X-Ray data for the selected crystal mounted on a glass fiber were collected with a CCD area detector with graphite-monochromated Mo-K α radiation. Reflections were collected with a Bruker SMART APEX detector and processed with SAINT from Bruker. Data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms for the

Ln(pfnp)₃phen (Ln = Er, Nd, Yb, Sm) complexes were refined anisotropically. The hydrogen atoms were included using a riding model. All calculations were performed using the SHELXL-97 crystallographic software package. Crystallographic data and structural refinements for the Ln(pfnp)₃phen (Ln = Er, Nd, Yb, Sm) complexes are summarized in Table 1. CCDC reference numbers 699049 [for Er(pfnp)₃phen], 699050 [Nd(pfnp)₃phen], 699052 [Yb(pfnp)₃phen], and 699051 [Sm(pfnp)₃phen].[†]

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