

Novel perfluorodiphenylphosphinic acid lanthanide (Er or Er–Yb) complex with high NIR photoluminescence quantum yield†

Limei Song,^{a,b} Jin Hu,^{a,b} Jianshe Wang,^{a,b} Xinhou Liu^a and Zhen Zhen^{*a}

Received 10th March 2008, Accepted 6th May 2008

First published as an Advance Article on the web 13th May 2008

DOI: 10.1039/b804117b

A perfluorodiphenylphosphinic acid lanthanide (Er or Er–Yb) complex is synthesized by a one-pot process from perfluorotriphenylphosphine oxide and lanthanide (Er or Er–Yb) chloride; the photoluminescence quantum efficiency reaches 0.98% for the erbium complex and 3.5% for the erbium–ytterbium complex, about 50 times and 175 times, respectively, higher than the usual erbium organic complexes with the hydrogen-containing ligands.

Introduction

Nowadays, great effort is devoted to the realization of the erbium-doped waveguide amplifiers (EDWAs) in photonic integrated circuits. Compared to inorganic hosts, polymers or organic–inorganic hybrid materials can also be used to fabricate EDWA. Erbium organic complexes have attracted much attention for their potential applications in polymeric and organic–inorganic derived systems. Unfortunately, the excited state of Er³⁺ is prone to being efficiently quenched by the vibronic coupling with high energy O–H, N–H, or C–H stretching vibrations in the ligands and coordinated solvent molecules, thus leading to decreased luminescence intensities and shorter emission lifetimes.^{1,2} Some studies have shown that a key strategy to achieve strong luminescence and long luminescence lifetimes for lanthanide ions that emit NIR luminescence is to fluorinate the hydrogen-containing ligands.^{3–6} Consequently, the more efficient ligand design for erbium organic complexes with long lifetimes should be a ligand with no O–H, N–H, or C–H groups and which excludes solvent coordination to Er³⁺ ions.

In recent years, there has been considerable interest in the design of kinetically inert complexes, in which, luminescence properties were optimized. The diphenylphosphinic acid known since 1878,⁷ is available commercially and reacts promptly with lanthanides resulting in kinetically inert, non-hygroscopic, thermodynamically stable complexes. The luminescence of lanthanide complexes with diphenylphosphinic acid in solid state has been extensively investigated.^{8–10} However, to our knowledge, there is no report about lanthanide complexes with perfluorodiphenylphosphinic acid. The organic ligands can act as light-harvesting antennas to sensitize the lanthanide ion *via* an intramolecular energy transfer process, but the maximum absorption bands of organic ligands are usually in the ultraviolet or visible region. For erbium complexes, the sensitization of Er³⁺ luminescence at 1.54 μm by organic

ligands cannot utilize the cheap commercial semiconductor laser diode (980 nm) as the excitation source. Direct excitation on Er³⁺ using 980 nm excitation source is less efficient due to the low absorption coefficient of Er³⁺ ions at 980 nm. One well-known technique to enhance the effective excitation efficiency of Er³⁺ is by co-doping with Yb³⁺ because the absorption cross section of Yb³⁺ at 980 nm is roughly tenfold higher than that of Er³⁺ and the ²F_{5/2} level of Yb³⁺ is resonant with the Er³⁺ ⁴I_{11/2} level.¹¹ In fact, an erbium-doped glass host co-doped with ytterbium has already been implemented in optical fiber amplifiers. However, there is little work on erbium–ytterbium organic complexes, especially fluorinated erbium–ytterbium complexes. In this work, we report on the erbium and erbium–ytterbium complexes with perfluorodiphenylphosphinate ligands.

The complexes were synthesized by a one-pot process, that is, the neutral ligand of perfluorotriphenylphosphine oxide hydrolyzes to perfluorodiphenylphosphinic acid, and subsequently coordinated to lanthanide (Er or Er–Yb) ions to form the final complex in one flask. The prepared erbium–ytterbium complex show very strong NIR luminescence and high photoluminescence (PL) quantum yield (3.5%). In addition, it is interesting that the prepared perfluorinated complexes have a rod-like morphology with a diameter of about 50–200 nm and a length of about several micrometers to tens of micrometer. One-dimensional nanostructures, such as nanorods, nanowires and nanotubes have attracted intensive interest due to their importance in fundamental research areas and potential wide-ranging applications.^{12–14} So far, most studies have focused on these types of nanostructured materials such as metals, metal oxides, metal sulfides, metal nitrides and phosphides, as well as metal oxysalts. However, there have been a few reports on metal complex nanostructured materials^{15,16} and few on lanthanide complex nanostructured materials except europium complex nanowires, which have a longer luminescence lifetime than the europium complex powder.¹⁷

Results and discussion

Synthesis and characterization of [(C₆F₅)₂POO]₃Er and [(C₆F₅)₂POO]₃Er_{0.5}Yb_{0.5}

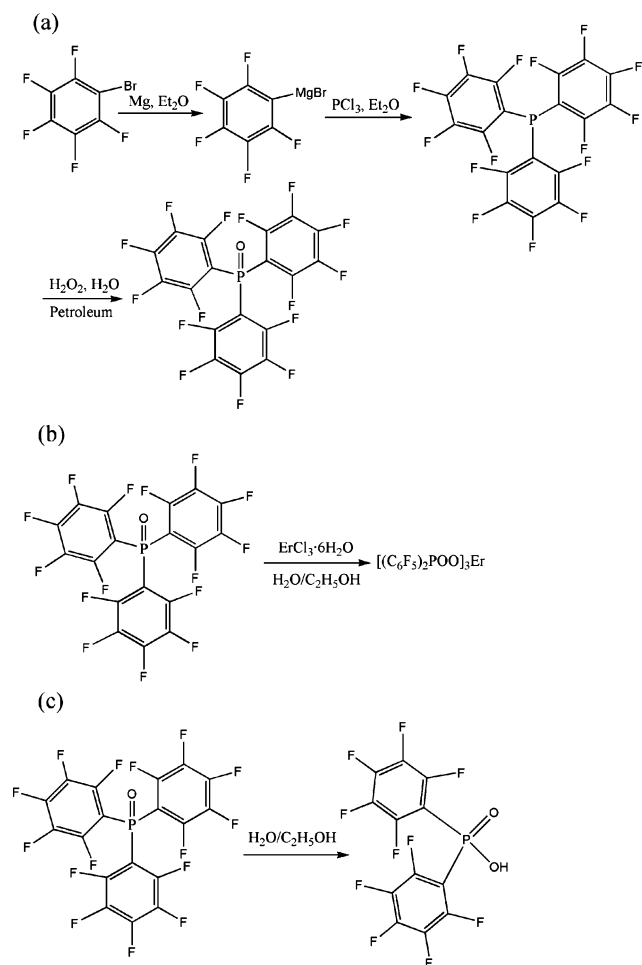
Oliver *et al.* have reported that tri-(pentafluorophenyl)-phosphine oxide was converted to potassium diphenylphosphinic acid by

^aKey Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China. E-mail: zhenz@mail.ipc.ac.cn; Fax: 86 010 62554670

^bThe Graduate University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

† Electronic supplementary information (ESI) available: Additional experimental data. See DOI: 10.1039/b804117b

hydrolysis with aqueous KOH.¹⁸ In our work, the perfluorodiphenylphosphinic acid erbium and erbium–ytterbium complexes, $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$, were prepared from tri-(pentafluorophenyl)-phosphine oxide and lanthanide chloride hydrates in the water–ethanol system under reflux. The initial material of tri-(pentafluorophenyl)-phosphine oxide was synthesized in three steps as shown in Scheme 1(a). The synthesis of $[(C_6F_5)_2POO]_3Er$ complex is shown in Scheme 1(b). The $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complex was synthesized by the same step as that of $[(C_6F_5)_2POO]_3Er$ except that $ErCl_3 \cdot 6H_2O$ and $YbCl_3 \cdot 6H_2O$ with the molar ratio of 1:1 were added to the reaction. The complexes were characterized by elemental analysis (C, H, N) and the results show that the complexes do not contain H and N element. The carbonic content of each complex is identical to its theoretical value. The molar ratio of erbium to phosphorus in the $[(C_6F_5)_2POO]_3Er$ complex is 1/3 analyzed by inductive coupling plasma (ICP). The EDS analysis of the $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complex indicates that the molar ratio of Er to Yb is 1:1 (see ESI, Fig. S1†).



Scheme 1 (a) Synthesis of perfluorotriphenylphosphine oxide; (b) Synthesis of $[(C_6F_5)_2POO]_3Er$; (c) Hydrolysis of perfluorotriphenylphosphine oxide.

To understand the reactive process, we also tried to synthesize perfluorodiphenylphosphinic acid by the hydrolysis of perfluorotriphenylphosphine oxide in the water–ethanol system under

reflux without lanthanide chloride hydrates (see Scheme 1(c)). The ESI mass spectrum (ESI-MS) provides an insight on the nature of the compound formed in the solution. As shown in Fig. S2,† in the negative mode, the molecular peak corresponding to the $[(C_6F_5)_2POO]^-$ anion is observed. Fig. S3† is its infrared spectrum, the bands over the range $450\text{--}1300\text{ cm}^{-1}$ were consistent with that of hydrous perfluorodiphenylphosphinic acid, $(C_6F_5)_2POO \cdot H_3O^+$.¹⁸ The results show that the neutral ligand of perfluorotriphenylphosphine oxide hydrolyzes to perfluorodiphenylphosphinic acid in the water–ethanol system under reflux without any catalyst. Therefore, the one-pot reaction of $[(C_6F_5)_2POO]_3Er$ or $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complex involves initial hydrolysis of perfluorotriphenylphosphine oxide and subsequent coordination to lanthanide ions (Er or Er–Yb) to afford the complex. The TGA diagrams of $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complexes are shown in Fig. 1. Both curves are composed of one obvious weight-loss process, which indicate that there is one type of ligands coordinated to the lanthanide. This provides further the identification of the complexes. The beginning weight loss temperature in the curves is higher than $500\text{ }^\circ\text{C}$, indicating the high thermal stability of the complexes.

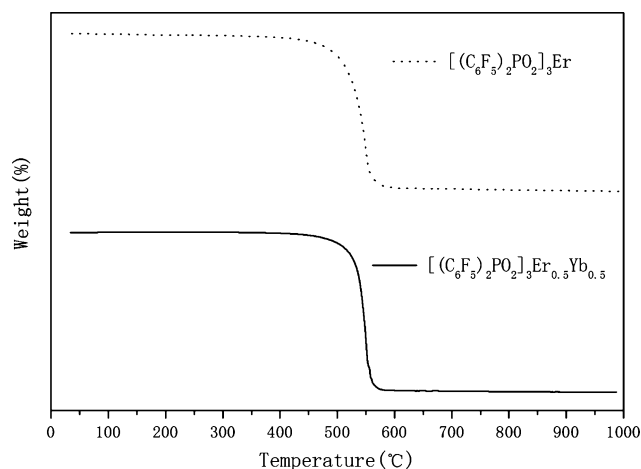


Fig. 1 TG curves for $[(C_6F_5)_2PO_2]_3Er$ (dotted line) and $[(C_6F_5)_2PO_2]_3Er_{0.5}Yb_{0.5}$ (solid line).

The coordination number of Er^{3+} for most of the erbium(III) complexes is eight or nine. In this case, we can see that the Er^{3+} takes a hexa-coordination from the molecular formula. A number of studies showed that metal complexes of R_2POO ($R = \text{alkyl, alkoxy, aryl}$) are more likely to be polymeric, involving bridging $-O-P-O-$ groups. The coordination number of metal ions in complexes of this type is usually six.^{19,20} On the basis of this point, it is reasonable to conclude that the complex $[(C_6F_5)_2POO]_3Er$ or $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ probably has a multi-nuclear structure bridged by phosphinic acid.

Morphology of $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$

Fig. 2 shows the scanning electron microscopy (SEM) images and transmission electron microscope (TEM) images of $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complexes. The SEM images of the synthesized products show a one-dimensional rod-like structure (Fig. 2(a) and (b)). Both the as-prepared

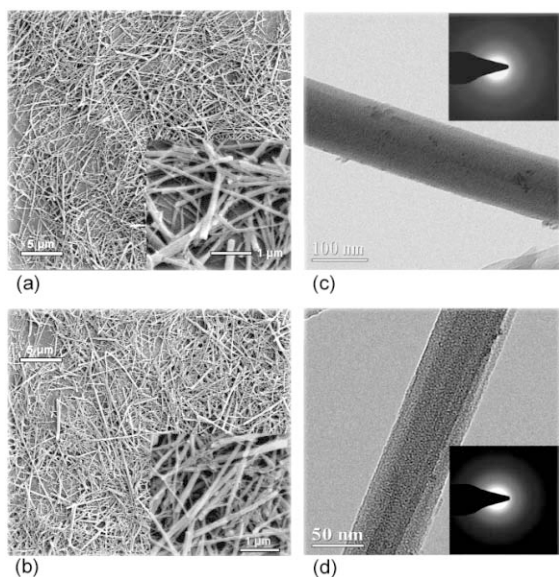


Fig. 2 SEM images of (a) $[(C_6F_5)_2POO]_3Er$ and (b) $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$, and TEM images and SAED patterns (inset) of (c) $[(C_6F_5)_2POO]_3Er$ and (d) $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$.

nanorods of $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complexes have high morphological purity and their morphologies are similar. The diameters of the nanorods for $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complexes normally range from 50–200 nm and the lengths are about several micrometers to tens of micrometer. The morphology of single nanorods and selected area electronic diffraction (SAED) patterns (in the inset) of $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complexes are shown in Fig. 2(c) and (d), respectively. The SAED patterns indicate that the as-prepared nanorods of $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complexes are amorphous.

Near-infrared luminescence of $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$

Fig. 3 shows the excitation spectra of $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complexes. Both the excitation spectra were obtained by monitoring the maximum emission of the Er^{3+} ions at 1535 nm. The excitation spectrum of $[(C_6F_5)_2POO]_3Er$ complex exhibits a weak excitation band around 980 nm, which corresponds to the energy transition $^4I_{15/2} \rightarrow ^4I_{11/2}$ of Er^{3+} . But in the excitation spectrum of complex $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$, the excitation band is so intense and wide in the 860 to 1000 nm spectral range. The wide and intense excitation spectrum of $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complex is mainly attributed to the absorption of Yb^{3+} corresponding to the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition because the absorption cross section of Yb^{3+} at 980 nm is roughly tenfold higher than that of Er^{3+} .¹¹

The NIR photoluminescence spectra of $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complexes excited at 978 nm at room temperature are shown in Fig. 4(a). For each sample, the typical emission around 1535 nm due to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} is observed. The intensity of the emission band of the complex $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ is much stronger than that of the complex $[(C_6F_5)_2POO]_3Er$, which is in agreement with the result of the excitation spectrum. It indicates that Er^{3+} is sensitized effectively

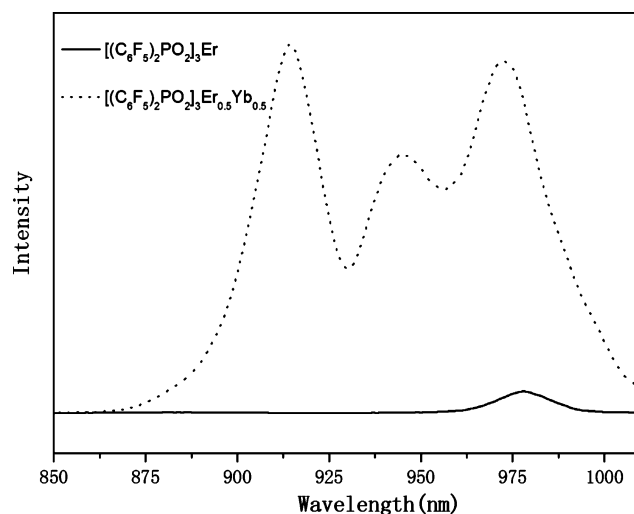


Fig. 3 The excitation spectra of $[(C_6F_5)_2POO]_3Er$ and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ complexes ($\lambda_{em} = 1535$ nm).

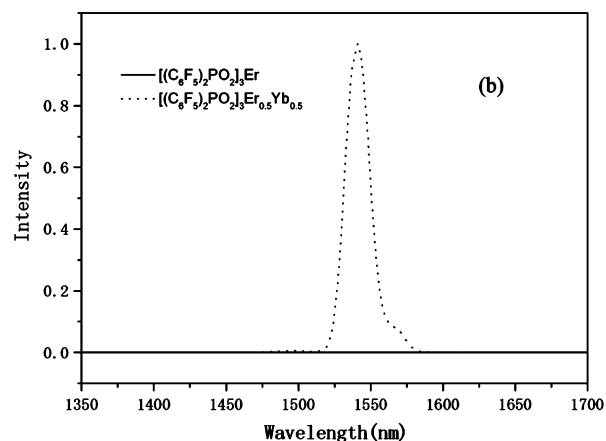
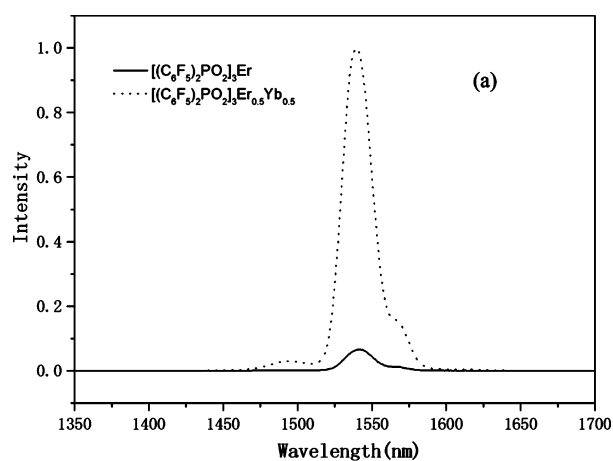


Fig. 4 The emission spectra of $[(C_6F_5)_2POO]_3Er$ (solid line) and $[(C_6F_5)_2POO]_3Er_{0.5}Yb_{0.5}$ (dotted line) excited at 978 nm (a) and 912 nm (b).

by Yb^{3+} . As shown in Fig. 5, the sensitive process of Er^{3+} by Yb^{3+} can be described as follows: the pump energy is absorbed effectively by Yb^{3+} and energy transfer from the energy level $^2F_{5/2}$ of Yb^{3+} to the $^4I_{11/2}$ level of Er^{3+} takes place, this is then followed by a rapid non-radiative relaxation to the $^4I_{13/2}$ level of Er^{3+} , and finally results in the NIR emission of the Er^{3+} ascribed to the

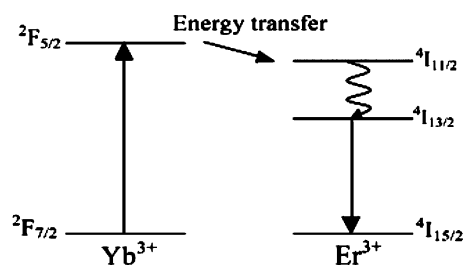


Fig. 5 Schematic drawing for the sensitization process of Er^{3+} by Yb^{3+} .

$^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition. In order to further prove the sensitive effect of Yb^{3+} , both complexes were also excited at 912 nm. As can be seen in Fig. 4(b), no signal peak of Er^{3+} was found in the $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}$ complex because there is no absorption at 912 nm for Er^{3+} . However, a stronger emission of Er^{3+} was observed for the $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}_{0.5}\text{Yb}_{0.5}$ complex, indicating that Er^{3+} is indeed sensitized by Yb^{3+} through effective Yb to Er energy transfer.

The near-infrared luminescence lifetimes of Er^{3+} in $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}$ and $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}_{0.5}\text{Yb}_{0.5}$

The effect of fluorination of the organic ligands is notable for the luminescence lifetime of Er^{3+} . Both $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}$ and $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}_{0.5}\text{Yb}_{0.5}$ complexes display long luminescence lifetimes. The decay is best described by a biexponential process for each complex. Fig. 6 shows the photoluminescence decay curve of the $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}_{0.5}\text{Yb}_{0.5}$ complex. The lifetime of $\text{I}_{13/2} \rightarrow \text{I}_{15/2}$ luminescence in the $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}_{0.5}\text{Yb}_{0.5}$ complex is longer than that in the $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}$ complex. The PL quantum efficiency η was calculated from $\eta = \tau/\tau_{\text{R}}$ to be 0.98% and 3.5% for the $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}$ complex and the $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}_{0.5}\text{Yb}_{0.5}$ complex, respectively, in which $\tau = A_1\tau_1 + A_2\tau_2$ (A_i is pre-exponential factor) and τ_{R} is the value of Er^{3+} in silica (14 ms). It is remarkable that their PL quantum efficiency is about 50 times and 175 times, respectively, higher than that of usual erbium organic complexes with the hydrogen-containing ligands, in which the typical value of the quantum yield is around 0.02%.²¹ This indicates that the replacement of C–H stretching vibrations by C–F bonds significantly reduces the degree of vibrational quenching,

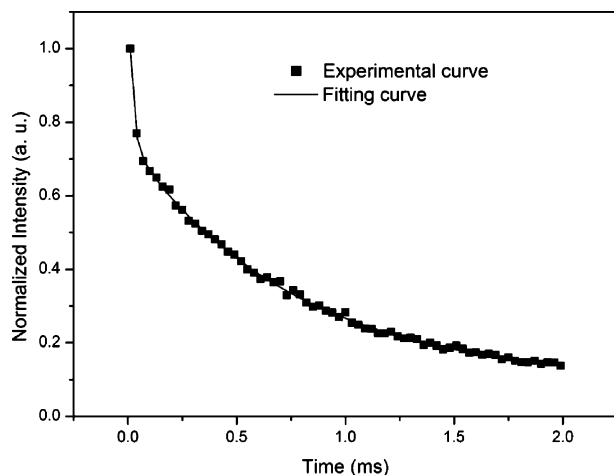


Fig. 6 PL decay curve for $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}_{0.5}\text{Yb}_{0.5}$. The photoluminescence is under excitation at 978 nm. The curve is fitted through a double exponential decay and the correlation coefficient is 0.99883.

Table 1 Measured PL lifetimes and deduced quantum efficiencies of the complexes

	$\tau_1/\mu\text{s}$	$\tau_2/\mu\text{s}$	η (%)
$[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}$	13 (11%)	336 (89%)	0.98
$[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}_{0.5}\text{Yb}_{0.5}$	19 (2%)	748 (98%)	3.5

which is indeed favourable to obtain longer lived Er^{3+} excited states. Table 1 lists the results of measured PL lifetimes and deduced quantum efficiencies of the complexes. The values in parentheses are fractional intensities. The fractional intensities for each lifetime (f_i) were determined from the values of pre-exponential factors (A_i) and the lifetimes (τ_i) as follows: $f_1 = A_1\tau_1/(A_1\tau_1 + A_2\tau_2)$ and $f_2 = A_2\tau_2/(A_1\tau_1 + A_2\tau_2)$.

Conclusions

In summary, we synthesized two perfluorinated erbium and erbium–ytterbium complexes by a one-pot process. The synthetic method is simple without any catalyst and the prepared complexes demonstrate rod-like morphologies. Both the complexes have longer luminescence lifetimes. The NIR PL quantum efficiency of perfluorinated erbium and erbium–ytterbium complexes was found to be as high as 0.98% and 3.5%, respectively.

Experimental

Syntheses

Synthesis of tris-(pentafluorophenyl)-phosphine. This compound is prepared when phosphorus trichloride is added to the Grignard reagent, pentafluorophenylmagnesium bromide, a method similar to that in ref. 22. A solution of bromopentafluorobenzene (25 g, 101.2 mmol) in dry diethyl ether (35 ml) was added dropwise to a suspension of Mg turnings (2.51 g, 103.3 mmol) in dry diethyl ether (15 ml) at a rate to keep the solution under a gentle reflux. After addition was completed, the solution was heated under gentle reflux for 2 h. After cooling to room temperature, phosphorus trichloride (4.63 g, 33.71 mmol) in anhydrous ether (50 ml) was added dropwise to the dark brown solution. The solution was further stirred for 3 h. Then the solution was hydrolyzed with dilute hydrochloric acid. The ether was removed under reduced pressure and the precipitations were filtered, washed with water, dried in vacuum. The crude products were sublimated in 130 °C to give tris-(pentafluorophenyl)-phosphine, white needles, mp 119–120 °C, MS (m/z): 532 [M^+] (Fig. S4†).

Synthesis of tri-(pentafluorophenyl)-phosphine oxide. To a solution of tris-(pentafluorophenyl)-phosphine (2 mmol, 1.064 g) in petroleum ether (60 ml, boiling range 60–90 °C) was added 30 ml of hydrogen peroxide (10%). The mixture was stirred with heating at 60 °C for 4 h. Then the solution was rotary evaporated and the obtained solids were washed with petroleum ether, filtered under reduced pressure and dried in vacuum. Mp 160–162 °C, MS (m/z): 548 [M^+] (Fig. S5†).

Synthesis of $[(\text{C}_6\text{F}_5)_2\text{POO}]_3\text{Er}$ complex. Tri-(pentafluorophenyl)-phosphine oxide (0.3 g, 0.547 mmol) was dissolved in 20 ml of $\text{C}_2\text{H}_5\text{OH}$. To this was added 0.07 g (0.182 mmol) $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ in 10 ml of distilled water. The mixture was refluxed for 6 h. After

cooling, the precipitation was separated by centrifugation, washed with C₂H₅OH several times. Then the products were dried at 50 °C in vacuum. Calcd. for C₃₆F₃₀P₃O₆Er: C, 31.83. Found: C, 31.67.

Synthesis of [(C₆F₅)₂POO]₃Er_{0.5}Yb_{0.5} complex. Tri-(pentafluorophenyl)-phosphine oxide (0.3 g, 0.547 mmol) was dissolved in 20 ml of C₂H₅OH. To this was added a mixture of ErCl₃·6H₂O (0.035 g, 0.091 mmol) and YbCl₃·6H₂O (0.035 g, 0.091 mmol) in 10 ml of distilled water. The mixture was refluxed for 6 h. After cooling, the precipitation was separated by centrifugation, washed with C₂H₅OH several times. Then the products were dried at 50 °C in vacuum. Calcd. for C₃₆F₃₀P₃O₆Er_{0.5}Yb_{0.5}: C, 31.76. Found: C, 31.43.

Synthesis of perfluorodiphenylphosphinic acid. Tri-(pentafluorophenyl)-phosphine oxide (0.3 g) was dissolve in 20 ml of C₂H₅OH. To this was added 10 ml of distilled water. The suspension was refluxed for 6 h. After cooling, the solution was rotary evaporated, and the resulted solids were dried in vacuum. MS (ESI, *m/z*): [M – H][–] calcd for [C₁₂F₁₀PO₂][–], 397.085; found, 397.0. IR (KBr): $\nu = 1644$ (m), 1524 (m), 1480 (vs), 1390 (m), 1299 (m), 1115 (s), 1076 (sh), 1032 (sh), 980 (s), 863 (w), 843 (w), 763.4 (w), 732 (m), 642 (m), 587 (m), 548 (m), 531 (m), 480 (m).

Equipment and measurements

Elemental analysis was carried out with an Elementar Vario EL (Germany) analyzer. The TGA curves were recorded with a 2960 SDT analyzer with a heat rate of 10 °C min^{–1} under air atmosphere. Infrared spectra were carried out with an Excalibur 3100 Fourier-transform infrared spectrometer. The ratio of erbium to phosphorus in the [(C₆F₅)₂POO]₃Er complex was analyzed by inductive coupling plasma (ICP) in a Leeman Profile ICP spectrometer. The stoichiometry of erbium and ytterbium in [(C₆F₅)₂POO]₃Er_{0.5}Yb_{0.5} was confirmed by EDS analysis using a HITACHI S-4300 scanning electron microscope. The ESI-mass and EI-mass spectra were performed with a Lcms 2010 mass spectrometry and a Trio-2000 mass spectrometry, respectively. SEM and TEM analyses were conducted using a HITACHI S-4300 scanning electron microscope and a FEI TECNAI F20 microscopy at 200 kV, respectively. NIR steady-state photoluminescence spectra were recorded on a Fluorolog[®] 3-11 (Jobin Yvon) instrument using a R5509-72 PMT detector (Hamamatsu photonics k.k.) and Xe lamp as the excitation source, and the lifetime measurements at room temperature were performed on the same instrument

equipped with a SPEX 1934D phosphorimeter, monitoring the decay of the luminescence intensity excited at 978 nm. The decay signal raised 10 μs later after the excitation.

Acknowledgements

The authors acknowledge support for this research by the Direction Project of the Chinese Academy of Science (KJCX2. YW. H02).

Notes and references

- 1 G. E. Buono-Core, H. Li and B. Marciniak, *Coord. Chem. Rev.*, 1990, **99**, 55.
- 2 L. Winkless, R. H. C. Tan, Y. Zheng, M. Motevalli, P. B. Wyatt and W. P. Gillin, *Appl. Phys. Lett.*, 2006, **89**, 111115.
- 3 Y. Hasegawa, T. Ohkubo, K. Sogabe, Y. Kawamura, Y. Wada, N. Nakashima and S. Yanagida, *Angew. Chem., Int. Ed.*, 2000, **39**, 357.
- 4 R. Van Deun, P. Nockemann, C. Gorller-Walrand and K. Binnemans, *Chem. Phys. Lett.*, 2004, **397**, 447.
- 5 G. Mancino, A. J. Ferguson, A. Beeby, N. J. Long and T. S. Jones, *J. Am. Chem. Soc.*, 2005, **127**, 524.
- 6 P. B. Glover, A. P. Bassett, P. Nockemann, B. M. Kariuki, R. V. Deun and Z. Pikramenou, *Chem.–Eur. J.*, 2007, **13**, 6308.
- 7 H. Gotter and A. Michaelis, *Ber. Dtsch. Chem. Ges.*, 1878, **11**, 885.
- 8 E. B. Stucchi, S. L. Scarpari, M. A. Couto Dos Santos and S. R. A. Leite, *J. Alloys Compd.*, 1998, **89**, 275–277.
- 9 S. L. Scarpari and E. B. Stucchi, *J. Alloys Compd.*, 2001, **740**, 323–324.
- 10 C. S. Francisco, E. B. Stucchi and E. M. de Abreu, *J. Alloys Compd.*, 2006, **418**, 234.
- 11 M. P. Hehlen, N. J. Cockroft, T. R. Gosnell and A. J. Bruce, *Phys. Rev. B*, 1997, **56**, 9302.
- 12 J. Hu, T. W. Odom and C. M. Lieber, *Acc. Chem. Res.*, 1999, **32**, 435.
- 13 X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, 2000, **404**, 59.
- 14 G. R. Patzke, F. K. Krumeich and R. Nesper, *Angew. Chem., Int. Ed.*, 2002, **41**, 2446.
- 15 L. Guo, C. M. Liu, R. M. Wang, H. B. Xu, Z. Y. Wu and S. H. Yang, *J. Am. Chem. Soc.*, 2004, **126**, 4530.
- 16 G. B. Sun, M. H. Cao, Y. H. Wang, C. W. Hu, L. Ren and K. L. Huang, *Chem. Commun.*, 2005, 1740.
- 17 X. F. Li, W. S. Liu, W. H. Wang and X. Y. Guo, *Chem. Lett.*, 2002, **31**, 1178.
- 18 K. W. Oliver, S. J. Rettig, R. C. Thompson, J. Trotter and S. H. Xia, *J. Fluorine Chem.*, 1997, **83**, 47.
- 19 C. M. Mikulski, N. M. Karayannis, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Inorg. Chem.*, 1970, **9**, 2053.
- 20 G. H. Dahl and B. P. Block, *Inorg. Chem.*, 1967, **6**, 1439.
- 21 G. A. Hebbink, D. N. Reinhoudt and F. C. J. M. Van Veggel, *Eur. J. Org. Chem.*, 2001, 4101.
- 22 L. A. Wall, R. E. Donadio and W. J. Pummer, *J. Am. Chem. Soc.*, 1960, **82**, 4846.