Preparation, Structure and Near-infrared Luminescent Property of Yb(III) Complex with 2,4,6-Pyridinetricarboxylic Acid

Hong-Sheng Wang • Gong-Chun Li • Jun Xia • Bin Zhai • Ming-Li Liu

Received: 29 March 2012 / Accepted: 28 July 2012 / Published online: 25 August 2012 © Springer Science+Business Media, LLC 2012

Abstract A rare earth ytterbium complex with 2,4,6-pyridinetricarboxylic acid (H₃pta) has been synthesized by hydrothermal method, the formula is {[Yb₂(pta)₂(H₂O)₃]·H₂O}_n. The complex crystallized in monoclinic system, P2₁/c space group with lattice parameters a=11.6556(19)Å, b=7.8364(12), c= 22.020(4), $\alpha = \gamma = 90^{\circ}$, $\beta = 92.120(3)$, Z=4, GOF=1.026, R1= 0.0334, wR2=0.0660. The pta anions connect four rare earth Yb(III) ions with two different coordination modes. The complex exhibit intense characteristic near-infrared luminescence of Yb(III) ions at 990 nm with excitation of UV-rays.

Keywords 2,4,6-pyridinetricarboxylic acid · Fluorescence · Near infrared · Ytterbium

Introduction

The Metal organic frameworks (MOFs) synthesized from trivalent lanthanide cations and aromatic carboxylic acids have attracted much attention due to their unique luminescent properties and potential applications in the field of luminescent materials [1–4]. Among them the photoluminescent properties in visible region of Sm(III), Eu(III), Tb(III) and Dy(III) complexes have received a huge amount of attention. Some of them have good luminescent properties and attractive topological structure [5–10]. In recent years, the luminescent materials with the emissions in near-infrared region attracted

H.-S. Wang (⊠) · G.-C. Li
College of Chemistry and Chemical Engineering,
Xuchang University,
Xuchang, Henan 461000, People's Republic of China
e-mail: xcuwaller@163.com

H.-S. Wang · J. Xia · B. Zhai · M.-L. Liu Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China more and more researchers [11–16]. The emission of Nd(III) and Yb(III) complexes is at about 1,064 and 980 nm, respectively. They are promising probe for bioassays [17, 18] because human tissue is relatively transparent to near-infrared light around 1,000 nm. The Er(III) complexes usually have emission at about 1,550 nm. They have possible use in optical amplifiers and datacom applications [19, 20]. The pyridinediand tri-carboxylic acids are important organic linkers for constructing MOFs as the nitrogen atom can also coordinate with center metal ions besides the oxygen atoms of carboxyl groups. Much attention has been paid to this field [21–26]. Two series of lanthanide complexes with 2,4,6-pyridinetricarboxylic acid have been reported a few years before [27, 28] and a 1D chain Yb(III) conplex has been reported [27].

In this paper, we used ytterbium chloride and 2,4,6-pyridinetricarboxylic acid as the reactants and synthesized a new ytterbium complex with 2,4,6-pyridinetricarboxylate anion under hydrothermal condition. The structure is completely different from the reported one even if the metal ion and the ligand are the same. It proves that reaction condition can seriously affect the structure of complexes. The photoluminescent property was studied and the results showed that the complex emit strong characteristic fluorescence of Yb(IIII) ion in near-infrared region.

Experimental Section

Synthesis of the Ligand

2,4,6-pyridinetricarboxylic acid was synthesized by oxidization of 2,4,6-trimethylpyridine with potassium permanganate [29]. Anal. Calcd. for $C_8H_5NO_6$ (%): C, 45.51; H, 2.39; N, 6.63. Found: C, 45.74; H, 2.08; N, 6.49. Ytterbium chloride was obtained by reacting hydrochloric acid with Yb₂O₃ (\geq 99.99 %) purchased from Grirem Advanced Materials Co. Ltd. Beijing.

Table 1 Crystallographic data for the titled complex

Empirical formula	$C_{16}H_{12}N_2O_{16}Yb_2\\$	
Formula weight	834.36	
<i>T</i> (K)	294(2)	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
a/Å	11.6556(19)	
b/Å	7.8364(12)	
c/Å	22.020(4)	
α /deg	90	
β/deg	92.120(3)	
γ∕deg	90	
$V(\text{\AA}^3)$	2009.9(6)	
Ζ	4	
$D (Mg \cdot m^{-3})$	2.757	
$\mu \text{ (mm}^{-1})$	9.344	
F(000)	1,560	
Crystal size (mm)	$0.18 \times 0.14 \times 0.08$	
θ Ranges (°)	1.75 to 26.39	
Max. and min. transmission	1.000000 and 0.545121	
h/k/l	-11/14, -9/9, -26 27</td	
Reflections collected / unique	11028 / 4114 [R(int)=0.0635]	
Data / restraints / parameters	4114 / 12 / 325	
Refinement method	Full-matrix least-squares on F ²	
GOF	1.026	
Final R indices [I>2sigma(I)]	R1=0.0334, wR2=0.0660	
R indices(all data)	R1=0.0525, wR2=0.0718	
Largest diff. peak and hole $(e.A^{-3})$	1.945 and -1.950	

Preparation of $\{ [Yb_2(pta)_2(H_2O)_3] \cdot H_2O \}_n$

A mixture of 2,4,6-pyridinetricarboxylic acid (0.2 mmol), YbCl₃·nH₂O (0.2 mmol) and deionized water (15 mL) was placed in a 25 mL Teflon-lined bomb, which was heated to 180 °C for 72 h. After the mixture was cooled to room temperature at a rate of 3 °C/h, colorless block crystals were obtained in a 34 % yield. Anal. Calcd. for $C_{16}H_{12}N_2O_{16}Yb_2$ (%): C, 23.03 ; H, 1.45; N, 3.36. Found: C, 22.62; H, 1.53; N, 3.35. IR bands (KBr pellets, cm⁻¹): 3373sb, 1,651 s, 1,618 s, 1,560 s, 1,444 s, 1,384 s, 1,348 m, 1,320 m, 1,278 m, 1169w, 1091w, 1029w, 943w, 819w, 776w, 738 m, 720 m, 693 m, 632w, 553, 448w.

General Characterization

Elemental analyses were performed in a Perkin-Elmer 240 analyzer. IR spectra were recorded with a Tensor 27 FTIR spectrophotometer (KBr pellets, range in 4,000–400 cm⁻¹). The fluorescence spectrum was tested on an FLS920 fluorescence spectrophotometer at 77 K.

X-ray Diffraction Analysis

The crystallographic data of the complex were collected with a Bruker SMART 1000 CCD diffractometer. The diffractometer is equipped with a graphite monochromator, and Mo K α radiation (λ =0.71073 Å) was used for experiment. The structure was solved by direct methods with the SHELXTL-97 programs [30] and refined by full-matrix least-squares techniques against F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms located and refined isotropically. The crystallographic data and structure refinement parameters for the complex were given in Table 1 and the selected bond lengths and bond angles were listed in Table 2.

Table 2 Selected bond lengths (Å) and bond angles (°) for the complex

Yb(1)-O(14)	2.284(5)	Yb(2)-O(12)	2.199(5)
Yb(1)-O(1)	2.301(5)	Yb(2)-O(5)#3	2.214(5)
Yb(1)-O(9)	2.320(6)	Yb(2)-O(11)#4	2.216(5)
Yb(1)-O(4)#1	2.321(5)	Yb(2)-O(15)	2.278(5)
Yb(1)-O(13)	2.346(6)	Yb(2)-O(3)#5	2.315(5)
Yb(1)-O(7)	2.377(5)	Yb(2)-O(2)#5	2.330(5)
Yb(1)-N(2)	2.410(6)	Yb(2)-N(1)#5	2.423(6)
Yb(1)-O(7)#2	2.418(5)		
O(14)-Yb(1)-O(1)	81.53(19)	O(1)-Yb(1)-O(13)	143.90(18)
O(14)-Yb(1)-O(9)	72.17(19)	O(9)-Yb(1)-O(13)	79.6(2)
O(1)-Yb(1)-O(9)	85.18(18)	O(4)#1-Yb(1)-O(13)	70.94(19)
O(14)-Yb(1)-O(4)#1	78.74(19)	O(14)-Yb(1)-O(7)	149.19(19)
O(1)-Yb(1)-O(4)#1	144.50(18)	O(1)-Yb(1)-O(7)	83.63(17)
O(9)-Yb(1)-O(4)#1	115.81(17)	O(9)-Yb(1)-O(7)	133.15(17)
O(14)-Yb(1)-O(13)	123.4(2)	O(4)#1-Yb(1)-O(7)	98.78(17)
O(13)-Yb(1)-O(7)	83.3(2)	O(15)-Yb(2)-O(3)#5	151.2(2)
O(14)-Yb(1)-N(2)	132.9(2)	O(12)-Yb(2)-O(2)#5	90.53(18)
O(1)-Yb(1)-N(2)	74.16(18)	O(5)#3-Yb(2)-O(2)#5	85.80(18)
O(9)-Yb(1)-N(2)	66.16(19)	O(11)#4-Yb(2)-O(2)#5	149.18(19)
O(4)#1-Yb(1)-N(2)	139.41(18)	O(15)-Yb(2)-O(2)#5	74.8(2)
O(13)-Yb(1)-N(2)	69.75(19)	O(3)#5-Yb(2)-O(2)#5	131.62(19)
O(7)-Yb(1)-N(2)	67.01(19)	O(12)-Yb(2)-N(1)#5	88.3(2)
O(14)-Yb(1)-O(7)#2	82.22(19)	O(5)#3-Yb(2)-N(1)#5	82.8(2)
O(1)-Yb(1)-O(7)#2	76.52(17)	O(11)#4-Yb(2)-N(1)#5	143.95(19)
O(9)-Yb(1)-O(7)#2	150.44(18)	O(15)-Yb(2)-N(1)#5	138.7(2)
O(4)#1-Yb(1)-O(7)#2	71.81(17)	O(3)#5-Yb(2)-N(1)#5	66.33(19)
O(13)-Yb(1)-O(7)#2	128.05(19)	O(2)#5-Yb(2)-N(1)#5	65.32(18)
O(7)-Yb(1)-O(7)#2	68.11(19)	O(12)-Yb(2)-C(8)#5	86.4(2)
N(2)-Yb(1)-O(7)#2	128.21(18)	O(5)#3-Yb(2)-C(8)#5	87.54(19)
O(12)-Yb(2)-O(5)#3	171.1(2)	O(11)#4-Yb(2)-C(8)#5	96.84(19)
O(12)-Yb(2)-O(11)#4	98.1(2)	O(15)-Yb(2)-C(8)#5	165.6(2)
O(5)#3-Yb(2)-O(11)#4	89.14(19)	O(3)#5-Yb(2)-C(8)#5	18.38(19)
O(12)-Yb(2)-O(15)	81.5(2)	O(2)#5-Yb(2)-C(8)#5	113.25(19)
O(5)#3-Yb(2)-O(15)	105.3(2)	N(1)#5-Yb(2)-C(8)#5	47.95(19)
O(11)#4-Yb(2)-O(15)	77.3(2)	O(5)#3-Yb(2)-O(3)#5	90.0(2)
O(12)-Yb(2)-O(3)#5	86.4(2)	O(11)#4-Yb(2)-O(3)#5	78.66(19)

Symmetry transformations used to generate equivalent atoms: #1 x, -y + 1/2, z - 1/2; #2 -x+2, -y, -z; #3 -x+2, y - 3/2, -z+1/2; #4 -x+1, y - 1/2, -z+1/2; #5 x, y - 1, z; #6 x, y+1, z; #7 x, -y+1/2, z+1/2; #8 -x+2, y + 3/2, -z+1/2; #9 -x+1, y+1/2, -z+1/2

Fig. 1 a The ORTEP representation of the complex showing the coordination environment of Yb(III) ions with 30 % probability of thermal ellipsoids. All the hydrogen atoms were omitted for clarity. b Three dimensional networks constructed by pta aions and Yb(III) ions



Crystallographic data for the complex have been deposited at the Cambridge Crystallographic data centre, CCDC Number is 705532. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12



Scheme 1 The two types of coordination modes of pta ligands in the complex

Union Road, Cambridge CB21EZ, U. K.; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Structure Description

In the complex, there are two types of Yb(III) ions with different coordination environment, as shown in Fig. 1a. One (Yb(1)) is eight-coordinated and the other (Yb(2)) seven-coordinated. The pta ligands also show two coordination modes. The ligand connect four Yb(III) ions in each modes, but the coordinated sites of pta are not completely same, as shown in Scheme 1a and b. A 3D framework is constructed with Yb(III) ions and pta ligands, as shown in Fig. 1b.

Fig. 2 The distorted polyhedron formed by the coordination atoms (a eightcoordinated, dicapped trigonal prism; b seven-coordinated, pentagonal bipyramid. Oxygen atoms, red; nitrogen atoms, blue; Yb(III) ions, green)



For Yb(1), five of the coordination oxygen atoms (O(1), O(7), O(9), O(4A) and O(7A)) are from carboxyl groups and the Yb(1)-O bond lengths are 2.301(5), 2.377(5), 2.320 (6), 2.321(5) and 2.418(5) Å, respectively; the other two oxygen atoms (O(13) and O(14)) are from water molecules and the bond lengths are 2.346(6) and 2.284(5) Å, respectively; the bond length of Yb(1)-N is 2.410(6) Å. The bond angles of O-Yb(1)-O range between $68.11(19)^{\circ}$ and 150.44 (18)° and that of O-Yb(1)-N range between $66.16(19)^{\circ}$ and $139.41(18)^{\circ}$.

For Yb(2), five of the coordination oxygen atoms (O (2A), O(3A), O(5A), O(11A) and O(12)) are from carboxyl groups and the Yb(2)-O bond lengths are 2.330(5), 2.315 (5), 2.214(5), 2.216(5) and 2.199(5) Å, respectively; only one coordinated water molecules (O(15)) is on Yb(2) and the Yb(2)-O bond length is 2.278(5) Å. The bond length of Yb(2)-N is 2.423(6) Å. The bond angles of O-Yb(2)-O range between 74.8(2)° and 171.1(2)° and that of O-Yb(2)-N range between 65.32(18)° and 143.95(19)°.

Yb(III) ions have two coordination numbers of 7or 8 for the complex. The coordination atoms form different coordination polyhedron. For eight-coordinated Yb(1) ions, their coordination atoms form a distorted dicapped trigonal prism, shown in Fig. 2a. While for seven-coordinated Yb



Fig. 3 Emission spectum of the complex with the excitation at 310 nm

(2) ions, the coordination atoms form a distorted pentagonal bipyramid, as shown in Fig. 2b. Yb(III) ions are located inside the two polyhedrons.

Photoluminescent Property

The fluorescence spectrum with solid sample for the complex was determined in near-infrared region with the excitation of UV-rays at 77 K, the emission spectra was shown in Fig. 3. The complex display a strong emission band at 990 nm upon the excitation of 310 nm, and it is resulted from the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition [31–33]. Strong luminescence of the complex should be attributed to the high effective energy transfer from pta anion ligand to Yb(III) ions [34, 35]. The mechanism of energy transfer of solid lanthanide complexes has been widely discussed to interpret their luminescent properties [36-38]. When the triplet-state energy of the ligand is greater than or equal to the energy gap between the excited state and ground state of lanthanide ion, efficient luminescence could be obtained. From the results we could conclude that the energy gap of Yb(III) ion is lower than the triplet-state energy of pta ligand.

On the reference [13], the NIR-emitting Ln(III) ions are particularly prone to vibrational deactivation. Species containing high-energy oscillators, such as C-H and O-H bonds are able to quench the lanthanides excited states nonradiatively, leading to the lower NIR-luminescence intensities. In the titled complex, one pta anion ligand has only two C-H bonds, the energy lossed by them is relatively less. It makes the complex emit strong fluorescence. Just like the complex $\{ [Yb(pta)(H_2O)_3] \cdot 4H_2O \}_n$ in previous literature reported by us [27], it is also a complex formed by Yb and pta anion ligand and display strong near infrared luminescence. The H₃pta ligand used in the complex is a stable organic acid (m.p. > 300 °C), and the complex also has high thermal stability (m.p. > 300 °C). It is propitious to be used as near infrared luminescent materials or promising probe for fluoroimmuno-assays.

In summary, we have synthesized a new Yb(III) coordination compound by using 2,4,6-pyridinetricarboxylate anions as the organic linker. The structure is completely different from the reported Yb(III) complex also with 2,4,6pyridinetricarboxylate ligand. It shows the reaction condition have important affect to the structure of complex. The ligand pta³⁻ anion displays two coordination modes. Furthermore, the Yb(III) complex shows its strong characteristic fluorescence in near-infrared region at excitation of UV-rays.

Acknowledgements This work was supported by Scientific Research Foundation of the Education Department of Henan Province (No. 2009B150026) and project of Xuchang Science and technology plans (No. 1101069).

References

- Parkar D (2000) Luminescent lanthanide sensors for pH, pO2 and selected anions. Coord Chem Rev 205:109
- Yang X, Jones RA (2005) Anion dependent self-assembly of "Tetra-Decker" and "Triple-Decker" luminescent Tb(III) salen complexes. J Am Chem Soc 127:7686
- Cui Y, Xu H, Yue Y, Guo Z, Yu J, Chen Z, Gao J, Yang Y, Qian G, Chen B (2012) A luminescent mixed-lanthanide metal-organic framework thermometer. J Am Chem Soc 134:3979
- Xu J, Ma YF, Liu WS, Tang Y, Tan MY (2011) Preparation, crystal structures and luminescent properties of terbium and europium complexes with a new amino-alkenone type ligand. J Fluoresc 21:35
- Li WX, Chai WJ, Sun XJ, Ren T, Shi XY (2010) Synthesis and luminescence properties of Two novel lanthanide (III) perchlorate complexes with Bis(benzoylmethyl) sulfoxide and benzoic acid. J Fluoresc 20:873
- Song HH, Li YJ (2008) Synthesis, crystal structure and luminescence properties of two novel lanthanide coordination polymers containing double chain. Inorg Chim Acta 361:1421
- Zhang HJ, Fan RQ, Zhou GP, Wang P, Yang YL (2012) Syntheses, structures, and luminescent properties of three novel twodimensional lanthanide coordination polymers with mixed aromatic carboxylate ligands. Inorg Chem Commun 16:100
- Cui YJ, Yue YF, Qian GD, Chen BL (2012) Luminescent functional metal–organic frameworks. Chem Rev 112:1126
- Cepeda J, Balda R, Beobide G, Castillo O, Fernandez J, Luque A, Perez-Yanez S, Roman P, Vallejo-Sanchez D (2011) Lanthanide (III)/pyrimidine-4,6-dicarboxylate/oxalate extended frameworks: a detailed study based on the lanthanide contraction and temperature effects. Inorg Chem 50:8437
- Sivakumar S, Reddy MLP, Cowley AH, Butorac RR (2011) Lanthanide-based coordination polymers assembled from derivatives of 3,5-dihydroxy benzoates: syntheses, crystal structures, and photophysical properties. Inorg Chem 50:4882
- Pope SJA (2007) Dual-emissive complexes: visible and nearinfrared luminescence from bis-pyrenyl lanthanide(III) complexes. Polyhedron 26:4818
- White KA, Chengelis DA, Gogick KA, Stehman J, Rosi NL, Petoud S (2009) Near-Infrared Luminescent Lanthanide MOF Barcodes. J Am Chem Soc 131:18069
- Sun LN, Yu JB, Zhang HJ, Meng QG, Ma E, Peng CY, Yang KY (2007) Near-infrared luminescent mesoporous materials covalently bonded with ternary lanthanide [Er(III), Nd(III), Yb(III), Sm(III), Pr(III)] complexes. Micropor Mesopor Mat 98:156
- An J, Shade CM, Chengelis-Czegan DA, Petoud S, Rosi NL (2011) Zinc-adeninate metal-organic framework for aqueous

encapsulation and sensitization of near-infrared and visible emitting lanthanide cations. J Am Chem Soc 133:1220

- Chen XY, Yang X, Holliday BJ (2010) Metal-controlled assembly of near-infrared-emitting pentanuclear lanthanideβ-diketone clusters. Inorg Chem 49:2583
- 16. Jankolovits J, Andolina CM, Kampf JW, Raymond KN, Pecoraro VL (2011) Assembly of near-infrared luminescent lanthanide host (host-guest) complexes with a metallacrown sandwich motif. Angew Chem Int Ed 50:9660
- Driesen K, Deun RV, Gorller RC, Binnemans K (2004) Nearinfrared luminescence of lanthanide calcein and lanthanide dipicolinate complexes doped into a silica-PEG hybrid material. Chem Mater 16:1531
- Ward MD (2007) Transition-metal sensitised near-infrared luminescence from lanthanides in d–f heteronuclear arrays. Coord Chem Rev 251:1663
- Mancino G, Ferguson AJ, Beeby A, Long NJ, Jones TS (2005) Dramatic increases in the lifetime of the Er3+ Ion in a molecular complex using a perfluorinated imidodiphosphinate sensitizing ligand. J Am Chem Soc 127:524
- Bünzli JCG, Piguet C (2005) Taking advantage of luminescent lanthanide ions. Chem Soc Rev 3:1048
- Zhao XQ, Cui P, Zhao B, Shi W, Cheng P (2011) Investigation on structures, luminescent and magnetic properties of Ln(III)-M (M=Fe(HS)(II), Co(II)) coordination polymers. Dalton Trans 40:805
- Zhao XQ, Zuo Y, Gao DL, Zhao B, Shi W, Cheng P (2009) Syntheses, structures, and luminescence properties of a series of Ln(III)-Ba(II) heterometal-organic frameworks. Cryst Growth Des 9:3948
- 23. Lyszczek R (2010) Synthesis, structure, thermal and luminescent behaviors of lanthanide-Pyridine-3,5-dicarboxylate frameworks series. Thermchim Acta 509:120
- 24. Yang AH, Zhao LH, Quan YP, Gao HL, Cui JZ, Shi W, Cheng P (2010) Formation of the water layer in lanthanide coordination polymers with 6-Methyl-2,3,5-Pyridinetricarboxylate as a novel bridging ligand. Cryst Growth Des 10:218
- Wang HS, Ma JG, Zhai B, Liu YY, Cheng P (2007) Syntheses and structures of d⁹ and d¹⁰ metal complexes with 2,3,5-pyridinetricarboxylic acid. J Mol Struct 829:1
- Wang HS, Li GC, Chen Y, Zhang ZJ, Liu ML (2010) Structures and luminescent properties of Sm(III) and Dy(III) coordination polymers with 2,4,6-pyridinetricarboxylic acid. J Coord Chem 63:4068
- 27. Wang HS, Zhao B, Zhai B, Shi W, Cheng P, Liao DZ, Yan SP (2007) Structures and Photoluminescence of 1D Lanthanide Coordination Polymers with 2,4,6-Pyridinetricarboxylic Acid. Cryst Growth Des 7:1851
- Li CJ, Peng MX, Leng JD, Yang MM, Lin Z, Tong ML (2008) Synthesis, structure, photoluminescence and magnetic properties of new 3-D lanthanide-pyridine-2,4,6- tricarboxylate frameworks. CrystEngComm 10:1645
- 29. Syper L, Kloc K, Mlochowski J (1980) Synthesis of ubiquinone and menaquinone analogues by oxidative demethylation of alkenylhydroquinone ethers with argentic oxide or ceric ammonium nitrat. Tetrahedron 36:123
- Sheldrick GM (1997) SHELXL 97, program for the refinement of crystal structures. University of Göttingen, Germany
- Deun RV, Fias P, Nockemann P (2006) Visible-light-sensitized near-infrared luminescence from rare-earth complexes of the 9-Hydroxyphenalen-1-one ligand. Inorg Chem 45:10416
- 32. Shavaleev NM, Accorsi G, Virgili D (2005) Syntheses and crystal structures of dinuclear complexes containing d-block and f-Block luminophores. Sensitization of NIR luminescence from Yb(III), Nd(III), and Er(III) centers by energy transfer from Re(I)-and Pt (II)-Bipyrimidine metal centers. Inorg Chem 44:61

- Ziessel RF, Ulrich G, Charbonnière L (2006) NIR lanthanide luminescence by energy transfer from appended terpyridine–boradiazaindacene dyes. Chem Eur J 12:5060
- Dexter DL (1953) A theory of sensitized luminescence in solids. J Chem Phys 21:836
- 35. Brown TD, Shepherd TM (1973) Factors affecting the quantum efficiencies of fluorescent terbium(III) chelates in the solid state. J Chem Soc Dalton Trans 336
- 36. Supkowski RM, Bolender JP, Smith WD, Reynolds LEL, Horrocks WD (1999) Lanthanide ions as redox probes of

long-range electron transfer in proteins. Coord Chem Rev 185-186:307

- 37. Beeby A, Faulkner S, Parker D, Williams JAG (2001) Sensitised luminescence from phenanthridine appended lanthanide complexes: analysis of triplet mediated energy transfer processes in terbium, europium and neodymium complexes. J Chem Soc Perkin Trans 2:1268
- 38. Zhang ZH, Song Y, Okamura T, Hasegawa Y, Sun WY, Ueyama N (2006) Syntheses, structures, near-infrared and visible luminescence, and magnetic properties of lanthanide-organic frameworks with an imidazole-containing flexible ligand. Inorg Chem 45:2896