

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

Highly luminescent lanthanide complexes with novel bis- β -diketone ligand: Synthesis, characterization and photoluminescent properties

Hong-Feng Li, Guang-Ming Li, Peng Chen, Wen-Bin Sun, Peng-Fei Yan*

Key Laboratory of Functional Inorganic Material Chemistry (Heilongjiang University), Ministry of Education, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, PR China

HIGHLIGHTS

- ► A bis-β-diketone ligand BPB has been prepared.
- A series of BPB lanthanide complexes have been prepared and characterized.
- The photoluminescent behaviors of BPB lanthanide complexes are investigated.
- Bis-β-diketone is more efficient to sensitize lanthanide than the monoβ-diketone.

ARTICLE INFO

Article history: Received 24 February 2012 Received in revised form 18 May 2012 Accepted 29 May 2012 Available online 8 June 2012

Keywords: Lanthanides Bis-β-diketone Ligand design Triple-stranded dinuclear structure Photoluminescence

G R A P H I C A L A B S T R A C T



ABSTRACT

A biphenyl-linked bis- β -diketone ligand, 3,3'-bis(3-phenyl-3-oxopropanol)biphenyl (BPB) has been prepared for the syntheses of a series of dinuclear lanthanide complexes. The ligand bears two benzoyl β -diketonate sites linked by a 3,3'-biphenyl spacer. Reaction of the doubly negatively charged bis-bidenate ligand with lanthanide ions forms triple-stranded dinuclear complexes Ln₂(BPB)₃ (Ln = Nd (1), Sm (2), Eu (3), Yb (4) and Gd (5)). Electrospray mass spectrometry is used to identify the formation of the triple-stranded dinuclear complexes 1–5, which have been further characterized by various spectroscopic techniques. The complexes display strong visible and NIR luminescence upon excitation at ligands bands around 360 nm, depending on the choice of the lanthanides, and the emission quantum yields and luminescence lifetimes of 2–3 have been determined. It shows that the biphenyl-linked ligand BPB is a more efficient sensitizer than the monodiketone ligand DBM (dibenzoylmethane), through the comparisons of Ln₂(BPB)₃ and Ln(DBM)₃ on their photoluminescent properties.

Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.

Introduction

On account of the unique optical properties of lanthanide (Ln) ions, lanthanide complexes with organic ligands continue to receive increasing attention because of their potential application in disparate fields such as optoelectronic device [1], telecommunication [2], bioassays [3], and sensors [4]. The luminescence from Ln(III) ions is featured by high color purity, long-lived excited lifetimes and the emission ranges from ultraviolet to visible and near

* Corresponding author. E-mail address: yanpf@vip.sina.com (P.-F. Yan).

1386-1425/\$ - see front matter Crown Copyright @ 2012 Published by Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.saa.2012.05.078

infrared light (0.3–3 μ m). However, suitable sensitizer is required as the antenna to excite the lanthanide center, in respective to the fact that 4f-4f transitions in lanthanide ions are spin- and parity-forbidden [5].

The β -diketone is one of the most studied ligands due to their chemical stability, highly molar extinction coefficiency and high energy transfer efficiency from the ligand to the Ln(III) ions [6]. Up to date, hundreds of different β -diketone ligands have been documented, among which dibenzoylmethane (DBM) and its derivatives are extensively studied due to their strong absorption and high ligand-to-metal energy transfer efficiency [7]. The triplet energy level of DBM is 20300 cm⁻¹ [8], which is 3050 cm⁻¹ higher

E-mun uuuress. yanpi@vip.sma.com (F.-r. Tan).

than the ${}^{5}D_{0}$ energy level of Eu(III) ion (17250 cm⁻¹). According to theoretical calculations and experimental data [9], it is widely accepted that energy transfer could take place effectively if the triplet energy level of ligand is 2000–5000 cm⁻¹ higher than the ⁵D₀ resonance level of the Eu(III) ion. Thus the ligand DBM has suitable energy level for sensitizing the luminescence of Eu(III) ion. Indeed, many DBM Eu(III) complexes and related electroluminescent devices have been studied extensively [10]. For example, Huang and coworkers reported a Eu(III) complex Eu(DBM)₂(c-DBM)(bath) as the electroluminescent material and its maximum luminance was found to be 2797 cd m^{-2} at 14 V [11]. However, the energy gap between the triplet energy level of DBM and the excited state level of NIR-emissive Ln(III) ion (such as Nd, Er, Yb) is too large to make the energy transfer efficient. One feasible approach that can decrease the energy gap is to incorporate a conjugated group into the phenyl of DBM. Several Nd(III). Er(III), and Yb(III) complexes with DBM containing condensed aromatic group or a conjugated polyene chain have been reported with excellent NIR luminescence [12].

Recently, lanthanide complexes of bis-β-diketones have attracted attention due to their highly efficient photoluminescence, visible light sensitization and chirality as well [13,14]. Pikramenou et al. have reported a dinuclear samarium complex based on a bis-β-diketone ligand 1,3-bis(3-phenyl-3-oxopropanoyl)benzene which could be seen as a derivative of DBM. The photoluminescent studies show that luminescence signal is more intense (about 11 times) than the corresponding DBM complex, although the two ligands possess the similar triplet state levels [13b]. The increase of the luminescence quantum yields of the dinuclear complexes was attributed to the effect of an additional Ln(III) lumophore in the dinuclear complexes. Recently, we have reported a series of triple-stranded dinuclear complexes Ln₂(BTB)₃ assembled about a bis-β-diketone ligand 3,3'-bis(4,4,4-trifluoro-1,3-dioxobutyl) biphenyl (BTB) which bears two trifluoroacetyl β-diketonate sites linked by a 3,3'-biphenyl spacer [15]. The complex Eu₂(BTB)₃ displays 1.33 times luminescence signal intensity than the mononuclear complex Eu(BTFA)₃. The result prompts us to synthesize a new bis- β -diketone ligand 3.3'-bis(3-phenvl-3-oxopropanol) biphenyl (BPB) which could be looked upon as coupling of the two mono- β -diketone DBM at the *meta*-position of benzene ring (Scheme S1). The triplet state energy levels of BPB should be close to those of DBM, because the meta-connection could interrupt the π -electron conjugation of two DBM which makes the triple state localized at each structure [16]. The synthesized ligand has been utilized for the syntheses a series of lanthanide complexes Ln₂(BPB)₃ (Ln = Nd (1), Sm (2), Eu (3), Yb (4) and Gd (5)). To examine the effect of the bis-β-diketone ligand on sensitizing the luminescence of Ln(III) ions, the photoluminescent properties of the lanthanide complexes are compared with the corresponding Ln(DBM)₃ complexes.

Experimental

Materials and instruments

The commercially available chemicals were analytical reagent grade and used without further purification. $LnCl_3 \cdot 6H_2O$ was prepared according to the literature by dissolving 99.99% oxide in a slight excess of hydrochloric acid. The solution was evaporated and the precipitate was recrystallized from water. 3,3'-diacetylbiphenyl was prepared according to the process described in the literature [15].

Elemental analyses were performed on an Elementar Vario EL cube analyzer. FT-IR spectra were obtained on a Perkin-Elmer Spectrum One spectrophotometer by using KBr disks in the range of 4000–370 cm⁻¹. UV spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer. The ¹H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer in CDCl₃ solution. Electron ionization (El) and Electrospray TOF (ESI–TOF) mass spectra were recorded on Agilent 5973 N and Bruker maXis mass spectrometers, respectively. Excitation and emission spectra were measured with an Edinburgh FLS 920 fluorescence spectrophotometer. Luminescence lifetimes were recorded on a single photon counting spectrometer from Edinburgh FLS 920 fluorescence spectrophotometer with microsecond pulse lamp as the excitation. The data were analyzed by software supplied by Edinburgh Instruments. Luminescence quantum yields for Eu(III) and Sm(III) complexes were measured according to the method reported by Nakamura using [Ru(2,2'–bipyridyl)₃]Cl₂ (Φ = 0.028 in aerated H₂O) as a standard [17].

Syntheses of 3,3'-bis(3-phenyl-3-oxopropanol)biphenyl, BPB

A solution of 3,3'-diacetylbiphenyl (1.0 g, 4.2 mmol) in 20 mL ethyl benzoate was added dropwise to a stirred suspension of NaH (60% dispersion in mineral oil) (0.336 g, 8.4 mmol) in 20 mL methyl benzoate at 60 °C. The reaction mixture was stirred at 60 °C for 2 h, and then kept overnight at room temperature (Scheme S2). The resulting yellow precipitate was filtered and washed thoroughly with toluene. The powered solid was suspended in 30 mL glacial acetic and stirred for 2 h. The product was filtered and washed with water, and recrystallization from acetone gave white needle crystals (0.6 g, 32%). Anal. Calc. for C₃₀H₂₂O₄: C, 80.70; H, 4.97; O, 14.33. Found: C, 80.65; H, 5.05; O, 14.28. IR (KBr, cm⁻¹): 3427, 3059, 1600, 1541, 1478, 1421, 1318, 1286, 1261, 1229, 1218, 1065, 999, 892, 753, 683, 618. ¹H NMR (CDCl₃, 400 MHz): 15.01 (s, 2H, Hi), 8.26 (t, *J* = 1.6 Hz, 2H, Ha), 8.03-8.05 (m, 6H, Hd, Hf), 7.86 (d, J = 8 Hz, 2H, Hb), 7.51-7.66 (m, 8H, Hh, Hc, Hg), 6.95 (s, 2H, He). ESI-MS m/z 469 $[M + Na]^{+}$.

Syntheses of the complexes Ln₂(BPB)₃

A solution of LnCl₃·6H₂O (2.0 mmol) in 20 mL MeOH was added dropwise to a stirred solution of BPB (1.34 g, 3.0 mmol) in 50 mL CHCl₃, resulting in a pale yellow solution. A solution of NEt₃ (0.61 g, 6.0 mmol) in 5 mL MeOH was added dropwise to this solution and stirred overnight at room temperature. The product was filtered and washed with CHCl₃ (2 × 10 mL), MeOH (2 × 10 mL), H₂O (2 × 10 mL) and dried under vacuum to give the desired product Ln₂(BPB)₃ (Ln = Nd, Sm, Eu, Gd, and Yb) (yields 48–65%). Ln(DBM)₃ complexes were prepared according to the process described in the literature [18].

Results and discussion

¹H NMR spectrum

The ¹H NMR spectrum of BPB obtained at 400 MHz in CDCl₃ is shown in Fig. 1. The observed broad single peak, 2H at δ 15.01 shows the characteristic H^{enol} protons (Hi), and the singlet, 2H at δ 6.95 is assigned to methine H^{keto} protons (H_e). By integrating the areas corresponding to both species, it is found that the ligand exists completely in the enolic form in CDCl₃. A single peak, 2H observed at δ 8.26 is assigned to the protons Ha due to the absence of direct coupling with neighboring protons. Doublet, 2H, Hb is observed at δ 7.86 due to the coupling of Hc protons. Protons Hd, Hf appear as two unresolved doublet peaks at δ 8.03–8.05 and correctly integrate for six protons. Multiple signals in the range of δ



Fig. 1. 400 MHz ¹H NMR spectrum of BPB in CDCl₃.

7.51–7.66 are attributed to the methine protons Hh, Hc, Hg, integrating for eight protons.

ESI-TOF mass spectrum

The mass spectra and elemental analysis data of the complexes are summarized in Table 1. In view of the soft ionization of the sample provided by ESI–TOF mass spectrometry, which avoids destructive fragmentation of the complexes, we have resorted to this technique to ascertain the formation of the dinuclear complexes. The patterns of mass spectra show characteristic mass distribution of the complexes 1-5. Taking **3** as an example (Fig. 2), the peak centered at m/z 1659.24 is attributed to [Eu₂(BPB)₃ + Na]⁺, confirming its formation. The results of elemental analyses are in agreement with the calculated values from molecular formulae assigned to these complexes.

IR spectra

The characteristic FT-IR spectral data of the ligand and their corresponding Ln(III) complexes are given in Table 2. The IR spectral data of the ligands are compared with those of the lanthanide complexes in order to ascertain the formation of the complexes. The broad bands at 3559–3144 cm⁻¹ are ascribed to the presence of the intra-molecular H-bondings in ligands (enol forms) and intermolecular H-bondings in the complexes (solvent molecules). The free ligand shows a strong band at 1600 cm⁻¹, which is the characteristic frequency of the diketone $v_{C=0}$ stretching vibrations. The $v_{C=0}$ bands are shifted to the lower frequency and appear around 1592–1596 cm⁻¹ in all the complexes, indicating the coordination of the oxygen atoms to the lanthanide ions. This coordination is further supported by the appearance of bands in the range of 431–439 cm⁻¹ due to v_{Ln-O} stretching vibrations. The ligand is indicated to be in the enolic form by the presence of a band at 1421 cm⁻¹ of a $v_{C=C=O}$ stretching vibration, which is shifted to

Table 1

Elemental analysis and mass spectrum data of Ln(III) complexes of BPB.



Fig. 2. Expanded regions of the ESI-TOF-MS of Eu₂(BPB)₃ in acetone.

1395–1412 cm⁻¹ in complexes **1–5**. Moreover, the absorbance frequency due to $v_{C=C}$ of benzene rings at 1540, 1465 cm⁻¹ of the ligands are split into two peaks at 1514–1553 cm⁻¹ and 1451–1484 cm⁻¹, respectively, in the complexes.

UV-Vis and phosphorescent spectra

UV-Vis absorption spectra of the ligands DBM, BPB and their corresponding Eu(III) complexes in acetone are shown in Fig. 3. The maximum absorption bands at 342 and 348 nm for DBM and BPB are attributed to the singlet–singlet π - π * electronic transition in the diketones. The absorption maxima is slightly red-shifted about 10 nm and 12 nm in complexes Eu(DBM)₃ and Eu(BPB)₃ compared with the free ligands, as a result of the enlargement of the conjugate structure of the ligand subsequent to coordination to the Eu(III) ions. In comparison with DBM, the maximum absorption peak is red-shifted about 5 nm for BPB, indicating a slight increase of conjugation of the ligand. The spectral patterns of Eu(III) complexes in acetone are similar to that of the free ligands, indicating that the coordination to the lanthanide ions do not significantly influence the energy of the singlet states of the diketone. The single state energy $({}^{1}\pi - \pi^{*})$ levels of DBM and BPB can be estimated by referring to their wavelengths of UV-Vis absorbance edges, which are 26110 cm^{-1} (383 nm) and 25773 cm^{-1} (388 nm), respectively.

It is well-known that the energy-level match between the triple states of the ligand and excited levels of Ln(III) ions in lanthanide complexes plays an important role in determining the luminescent properties of the lanthanide complexes. On account of the difficulty in observing the phosphorescence of the ligand, the emission spectrum of the Gd(III) complex at 77 K is used to estimate the triplet state energy level, because the lowest excited energy level of Gd³⁺ ion ($^{6}P_{7/2}$) is too high to accept energy from the ligand [19]. As shown in Fig. 4, the triplet energy levels of DBM and BPB, which correspond to their lower wavelength emission, are 20300 cm⁻¹ (492 nm) and 20000 cm⁻¹ (500 nm), respectively.

Complex	Mw. (M – solvent + Na) found (cal.)	Elemental analysis found% (cal.%)			
		С	Н	0	
$Nd_2(BPB)_3(CH_3OH)_2(H_2O)_2$ (1)	1643.52 (1644.91)	64.22(64.17)	4.20(4.21)	14.77(14.87)	
$Sm_2(BPB)_3(CH_3OH)_2(H_2O)_2(2)$	1657.24 (1657.14)	63.80(63.71)	4.08(4.18)	14.75(14.76)	
$Eu_2(BPB)_3(CH_3OH)_2(H_2O)_2$ (3)	1659.24 (1660.35)	63.68(63.60)	4.09(4.18)	14.61(14.73)	
$Yb_2(BPB)_3(CH_3OH)_2(H_2O)_2(4)$	1702.36 (1702.53)	62.14(62.09)	4.01(4.08)	14.36(14.38)	
Gd ₂ (BPB) ₃ (CH ₃ OH) ₂ (H ₂ O) ₂ (5)	1671.13 (1670.92)	63.15(63.21)	4.15(4.15)	14.72(14.64)	

Table 2

Characteristic IR bands (cm⁻¹) of the ligand and the corresponding complexes.

Compounds	<i>v</i> (O—H)	v(C==0)	ν(C=C)	ν(C=C)	v(C=C-O)	v(Ln—O)
BPB	3427	1600	1541	1478	1421	-
$Nd_2(BPB)_3(CH_3OH)_2(H_2O)_2$ (1)	3414	1592	1552/1514	1483/1451	1410	431
$Sm_2(BPB)_3(CH_3OH)_2(H_2O)_2$ (2)	3414	1592	1550/1515	1482/1451	1411	431
$Eu_2(BPB)_3(CH_3OH)_2(H_2O)_2$ (3)	3415	1592	1552/1515	1484/1452	1412	432
$Yb_2(BPB)_3(CH_3OH)_2(H_2O)_2$ (4)	3414	1590	1552/1517	1483/1452	1411	435
$Gd_2(BPB)_3(CH_3OH)_2(H_2O)_2$ (5)	3412	1593	1553/1515	1484/1452	1410	432



Fig. 3. UV–Visible absorption spectra of DBM, BPB and complexes ${\rm Eu}({\rm BPB})_3$ and ${\rm Eu}({\rm DBM})_3$ in acetone.



Fig. 4. Phosphorescence spectra of Gd(DBM)₃ and Gd₂(BPB)₃ at 77 K.

The triplet energy level of BPB is 300 cm^{-1} lower than that of DBM, which indicates that the coupling of the two DBM moieties at the *meta*-position of the benzene ring does not significantly affect the triple state of the ligand.

Luminescence properties

The excitation and emission spectra of the isoabsorptive solutions of complexes **1–4** and the corresponding DBM complexes in acetone are shown in Fig. 5. All the complexes show characteristic Ln(III) emission upon excitation under the absorbance wavelengths of the ligands. The excitation spectra of Eu(III) and Sm(III) complexes are recorded by monitoring the strongest emission bands of their corresponding lanthanide ions in each case. They all show a broad bands between 260 nm and 430 nm with an excitation maximum at approximately 360 nm, which can be assigned to the π - π * electronic transition of the ligands. The emission spectra

of the complexes Eu(BPB)₃ and Eu(DBM)₃ are shown in Fig. 5a, which display a series of characteristic narrow band emission of Eu(III) ion at 579, 593, 612, 650, and 693 nm, corresponding to the ${}^{5}D_{0} \rightarrow {}^{7}F_{I}(J = 0-4)$ transitions. Among them, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at $\lambda = 612$ nm is the most strong transition that is an induced electric dipole transition, whose intensity is sensitive to the coordination environment [20]. Instead, the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is a magnetic dipole transition whose intensity is independent of the coordination environment [21]. Thus, the intensity ratio of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition (I_{7F2}/I_{7F1}) reflects the nature and symmetry of the first coordination sphere. The intensity ratios of I_{7F2}/I_{7F1} are 21.4 and 17.4 for complexes Eu(BPB)₃ and Eu(DBM)₃, respectively revealing the decrease of the symmetry around Eu(III) ion in complex Eu(BPB)₃ by the formation of triple-stranded dinuclear structure. The luminescence lifetimes of complexes Eu(BPB)₃ and Eu(DBM)₃ in acetone are determined at room temperature under direct intra-4f⁶ excitation by monitoring the emission decay curves within the ${}^5D_0 \to {}^7F_2$ transition at 612 nm. Each of the decay curves is well-reproduced by singleexponential functions, which suggests that only one species exists in the excited state in the two complexes. The lifetimes observed for complexes Eu(DBM)₃ and Eu(BPB)₃ are 238 µs and 284 µs, respectively. In addition to the lifetime measurements, the luminescence quantum yields of the complexes in acetone are also measured to be 1.1% and 1.8% for Eu(DBM)₃ and Eu(BPB)₃, respectively.

The excitation and emission spectra of complexes Sm(BPB)₃ and Sm(DBM)₃ in acetone are shown in Fig. 5b. Upon excitation at 360 nm, complexes Sm(BPB)₃ and Sm(DBM)₃ show characteristic narrow band emissions of Sm(III) ion corresponding to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{J}$ (J = 5/2, 7/2, 9/2, 11/2) transitions. The four expected peaks for the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2-11/2}$ transitions are well resolved. The most intense peak is the hypersensitive transition ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ at 648 nm. The quantum yields of Sm(BPB)₃ and Sm(DBM)₃ are measured to be 0.026% and 0.015% and their lifetimes are found to be 18.7 µs and 7.6 µs, respectively.

Considering the higher triple state energy of the ligands than the energy levels of Nd(III) (${}^{4}F_{3/2}$, 11527 cm⁻¹) and Yb(III) (${}^{2}F_{5/2}$, 10000 cm⁻¹) luminescent excited state, the suitability of the ligands as a sensitizer for Nd(III) and Yb(III) luminescence are examined. As shown in Fig. 5c, the emission spectra of complexes Nd(BPB)₃ and Nd(DBM)₃ consist of three bands at 873, 1057, and 1330 nm, which are attributed to the *f*-*f* transitions ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$, ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{13/2}\text{,}$ respectively. For complexes Yb(BPB)₃ and Yb(DBM)₃, the emission spectra contain one band corresponding to the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition (Fig. 5d). This band is split into two components that the strongest is centered at 972 nm and a shoulder at 1002 nm. The luminescent intensities of the dinuclear complexes Nd(BPB)₃ and Yb(BPB)₃ are 1.8 and 2.4 times higher than that of mononuclear complexes Nd(DBM)₃ and Yb(DBM)₃ in the isoabsorptive solutions. It proposes that BPB could be a better candidate on sensitizing luminescence of the Ln(III) ions than DBM, which might be attributed to the rigidity of the triple-stranded helicate. The rigid structure restricts the thermal vibration of the ligands and reduces the energy loss by the radiativeless decay.



Fig. 5. Excitation and emission spectra of isoabsorptive solutions (A = 0.1) of complexes 1-4 and corresponding complexes Ln(DBM)₃ in acetone.

Conclusion

In summary, we have reported a novel bis- β -diketone, 3,3'bis(3-phenyl-3-oxopropanol)biphenyl (BPB) featured by the coupling of two mono- β -diketone dibenzoylmethanate (DBM) at the *meta*-position of the benzene ring. The reaction of BPB with Ln(III) ions in a 3:2 ratio results in the formation of triple-strand dinuclear complexes. The lower triple state energy level enables BPB to sensitize the metal-centered luminescence of Nd(III), Sm(III), Eu(III) and Yb(III) ions. Notably, the luminescence quantum yield experiments show that dinuclear complexes have higher luminescent intensities than that of corresponding mono- β -diketone complexes. Better photoluminescent behavior of Ln₂(BPB)₃ complexes ensures their potential applications as emitting layers in lightemitting diodes.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (Nos. 21072049 & 21072050 & 51102081 & 21102039), Heilongjiang Province (No. 2010td03) and Heilongjiang University (2010hdtd-08 and 2010hdtd-11).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.05.078.

References

- [1] (a) C. Piguet, J.-C.G. Bünzli, Chem. Soc. Rev. 34 (2005) 1048-1077;
- (b) J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357–2368;
 (c) K. Kuriki, Y. Koike, Y. Okamoto, Chem. Rev. 102 (2002) 2347–2357;
 (c) K. Kuriki, Y. Koike, Y. Okamoto, Chem. Rev. 102 (2002) 2347–2357;
- (d) J.-C.G. Bünzli, Chem. Rev. 110 (2010) 2729–2755.
- [2] S.I. Klink, L. Grave, D.N. Reinhoudt, F.C.J.M. Van Veggel, M.H.V. Werts, F.A.J. Geurts, J.W. Hofstraat, J. Phys. Chem. A 104 (2000) 5457–5468.
- [3] J.-C.G. Bünzli, S.V. Eliseeva, Chem. Soc. Rev. 39 (2010) 189-227.
- [4] (a) M. Montalti, L. Prodi, N. Zaccheroni, L. Charbonnière, L. Douce, R. Ziessel, J. Am. Chem. Soc. 123 (2001) 12694–12695;
 (b) H. Tsukube, S. Shinoda, Chem. Rev. 102 (2002) 2389–2403.
- [5] Y. Ma, Y. Wang, Coord. Chem. Rev. 254 (2010) 972–975.

- [6] (a) K. Binnemans, Chem. Rev. 109 (2009) 4283-4374;
 (b) G.F. De Sa, O.L. Malta, C. De Mello Donegá, A.M. Simas, R.L. Longo, P.A.
- Santa-Cruz, E.F. Da Silva, Coord. Chem. Rev. 196 (2000) 165–195.
 [7] K. Binnemans, Handbook on the Physics and Chemistry of Rare Earths, Elsevier, Amsterdam, 2005. vol. 35, Chapter 225, pp 107–185.
- [8] W. Sager, N. Filipescu, F. Serafin, J. Phys. Chem. 69 (1965) 1092–1100.
- [9] M. Latva, H. Takalo, V.-M. Mukkala, C. Matachescu, J.C. Rodriguez-Ubis, J. Kankare, J. Lumin. 75 (1997) 149–169.
- [10] (a) Z.Q. Bian, K.Z. Wang, L.P. Jin, Polyhedron 21 (2002) 313–319;
 (b) M.R. Robinson, M.B. O'Regan, G.C. Bazan, Chem. Commun. (2000) 1645–1646;
 (c) H. Xin, F.Y. Li, M. Guan, C.H. Huang, M. Sun, K.Z. Wang, Y.A. Zhang, L.P. Jin, J. Appl. Phys. 94 (2003) 4729–4731;
 (d) M. Sun, H. Xin, K.Z. Wang, L.P. Jin, C.H. Huang, Chem. Commun. (2003) 702–703.

(e) F.S. Liang, Q.G. Zhou, Y.X. Cheng, L.X. Wang, Chem. Mater. 15 (2003) 1935– 1937.

- [11] C.H. Huang, Z.Q. Bian, M. Guan, F.Y. Li, H. Xin, China Patent, (2003) Appl. 03142611.5.
- [12] (a) L.F. Yang, Z.L. Gong, D.B. Nie, B. Lou, Z.Q. Bian, M. Guan, C.H. Huang, H.J. Lee, W.P. Baik, New J. Chem. 30 (2006) 791–796;
 (b) M.D. Seltzer, S. Fallis, R.A. Hollins, N. Prokopuk, R.N. Bui, J. Fluoresc. 15 (2005) 597–603.
- [13] (a) J. Yuan, S. Sueda, R. Somazawa, K. Matsumoto, K. Matsumoto, Chem. Lett. 32 (2003) 492–493;

(b) A.P. Bassett, S.W. Magennis, P.B. Glover, D.J. Lewis, N. Spencer, S. Parsons, R.M. Williams, L. De Cola, Z. Pikramenou, J. Am. Chem. Soc. 126 (2004) 9413–9424;

(c) M. Albrecht, S. Schmid, S. Dehn, C. Wickleder, S. Zhang, A.P. Bassett, Z. Pikramenou, R. Fröhlich, New J. Chem. 31 (2007) 1755–1762;

(d) Y.M. Luo, Z. Chen, R.R. Tang, L.X. Xiao, H. Peng, J. Spectrochim. Acta, Part A 69 (2008) 513–518;

- (e) S.G. Liu, P. He, H.H. Wang, J.X. Shi, M.L. Gong, Inorg. Chem. Commun. 12 (2009) 506–508.
- [14] (a) P. He, H.H. Wang, S.G. Liu, J.X. Shi, G. Wang, M.L. Gong, Inorg. Chem. 48 (2009) 11382–11387;
 (b) P. He, H.H. Wang, H.G. Yan, W. Hu, J.X. Shi, M.L. Gong, Dalton Trans. 39
- (2010) 8919–8924. [15] H.F. Li, P.F. Yan, P. Chen, Y. Wang, H. Xu, G.M. Li, Dalton Trans. 41 (2012) 900–
- 907. [16] (a) Y.C. Chen, G.S. Huang, C.C. Hsiao, S.A. Chen, J. Am. Chem. Soc. 128 (2006) 8549-8558;
- (b) W. Zhang, P.C. Huang, Mater. Chem. Phys. 96 (2006) 283-288.
- [17] K. Nakamura, Bull. Chem. Soc. Jpn. 55 (1982) 2697–2705.
- [18] R.G. Charles, A. Perroto, J. Inorg. Nucl. Chem. 26 (1964) 373-375.
- [19] Y.W. Wang, Y.L. Zhang, W. Dou, A.J. Zhang, W.W. Qin, W.S. Liu, Dalton Trans. 39 (2010) 9013–9021.
- [20] G. Zucchi, V. Murugesan, D. Tondelier, D. Aldakov, T. Jeon, F. Yang, P. Thuéry, M. Ephritikhine, B. Geffroy, Inorg. Chem. 50 (2011) 4851–4856.
- [21] Y.B. Wang, X.J. Zheng, W.J. Zhuang, L.P. Jin, Eur. J. Inorg. Chem. (2003) 1355-1360.