Chemical Papers 66 (3) 221–225 (2012)
DOI: 10.2478/s11696-011-0123-1

ORIGINAL PAPER

From a Tb^{3+} chelated compound to a hybrid material: selective emission responses to anions

Zheng-Yang Zhang, Qian-Ming Wang*, Jian-Zhong Wu, Wei-Sheng Cai, Yi-Fei Yu

School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

Received 19 August 2011; Revised 10 November 2011; Accepted 12 November 2011

A novel terbium 2-hydroxymethyl-benzoimidazole-6-carboxylic acid complex has been designed and unique emission changes to fluoride anions in comparison with HSO_4^-, AcO^-, Cl^-, Br^-, and I^- were observed. Then, the complex was encapsulated into an inorganic matrix. The novel hybrid material, with strong green emission was successfully synthesized as an anions receptor in water. More importantly, this hybrid material not only gave luminescence response to F^-, but also to HSO_4^-. Spectroscopic studies demonstrated that the recognition process for fluoride ions can be mainly ascribed to its hydrogen bonding interactions with hydrogen bond donor units (NH and OH). In case of hydrogen sulfate, the sensing effects can be probably attributed to its acidity instead of hydrogen bonding interactions.

Keywords: sensor, luminescent, terbium, fluoride, hydrogen sulfate

Introduction

During the past two decades there has been considerable interest in the recognition of specific anions due to their essential role in both biological systems and environmental chemistry (Gale et al., 2008; Kavallieratos et al., 1999). Especially, the luminescent sensor is an attractive application in the detection processes, achieving fast responses and effects easy to be detected by naked eyes (Sambrook et al., 2005; Santacroce et al., 2006).

Although a variety of methods have been employed to design fluorescent materials endowed with anion recognition properties, lanthanide luminescent complexes have recently received increased attention in anion sensing due to their special photophysical performances such as long lifetime, sharp emission peaks, and large Stokes shifts (Bünzli & Piguet, 2005; Parker & Yu, 2005; Gunnlaugsson et al., 2006; Wang et al., 2010; Zhang et al., 2011). However, instability of luminescent complexes in aqueous media seriously restricts their practical use in real life.

Lanthanide luminescent-based hybrid materials have been widely investigated over the last decades (Dong et al., 2000). We have discovered that the incorporation of lanthanide complexes can enable their emission in aqueous media (Tan et al., 2010). More significantly, some of them have displayed highly selective and sensitive interactions toward anions through hydrogen bond donor moieties. In this research, we focused on the differentiation between the complex and hybrid material during the anion sensing process. Accordingly, a novel terbium 2-hydroxymethyl-benzoimidazole-6-carboxylic acid (**a**) complex ($Tb(\mathbf{a})_3$) has been prepared and a novel hybrid material (H_a) was obtained by encapsulating it into an inorganic matrix (tetraethoxysilane, TEOS) (Fig. 1). Both of them, as sensing species, have intense green luminescence and their sensing abilities toward anions were investigated in solutions.

A point worth emphasizing is that the hybrid material still retains striking luminescence even in pure water. It is interesting to find that luminescence of the complex can be quenched by fluoride ions. For the hybrid material, both fluoride and hydrogen sulfate anions can induce smart emission changes. Spectro-

---

*Corresponding author, e-mail: qmwang@scnu.edu.cn

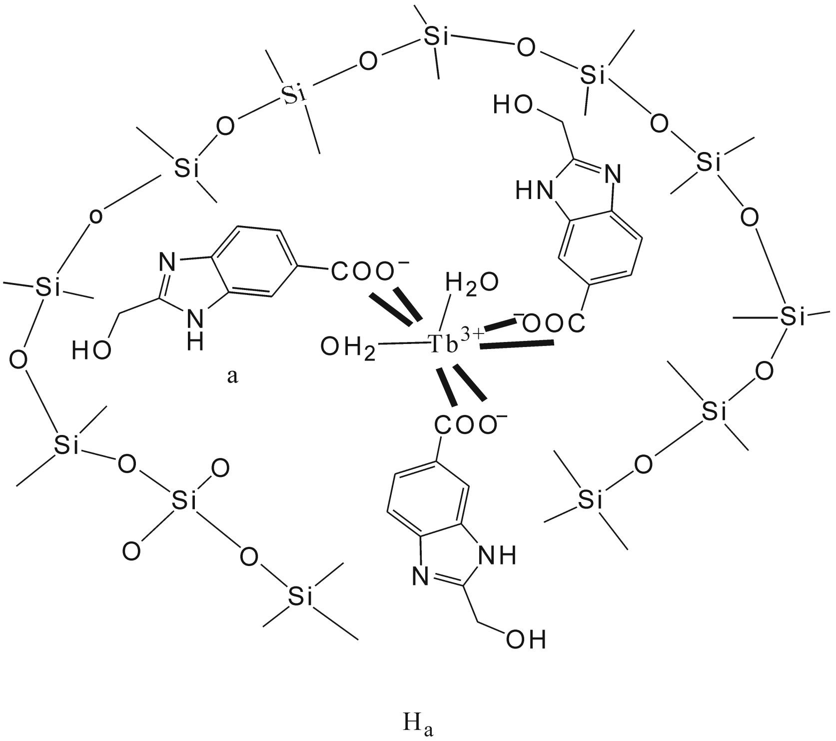

Fig. 1. Scheme of predicted structure of terbium complex ($Tb(\mathbf{a})_3$) and hybrid material (H_a).

scopic studies indicated that for fluoride ions, hydrogen bonding interactions with the imidazole-NH (or hydroxyl OH) resulted in quenching effects. Unlike the fluoride ions, we believe that the recognition process was caused by the acidity of hydrogen sulfate. In addition, the hybrid material presented higher stability than its complex.

Experimental

All starting materials were obtained from commercial suppliers and used as received. ^{1}H NMR spectra were recorded at 293 K using a Varian 400 (400 MHz) with TMS as an internal standard (Varian, Palo Alto, CA, USA). LC-MS was measured by a Thermo Finnigan LCQ Deca XP Max (Thermo Finnigan, San Jose, CA, USA) Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer with a 150 W xenon lamp as the light source. The scan speed was fixed at 300 nm min^{-1}. Both excitation and emission slit widths were 2.5 nm (Hitachi, Tokyo, Japan). Thermogravimetric analysis was carried out using a STA409PC under air at the rate of 10 °C min^{-1} (Netzsch, Selb, Germany). IR spectra were measured by a Varian 660-IR (Varian, Palo Alto, CA, USA). The fluorescence images were taken using a Nikon Eclipse TS100 inverted fluorescence microscope system equipped with a 50 W mercury lamp source (Nikon, Japan).

2-Hydroxymethyl-benzoimidazole-6-carboxylic acid (**a**) was prepared according to literature (Thakurdesai et al., 2007). A mixture of 3,4-diaminobenzoic acid (456 mg, 3 mmol) and glycolic acid (228 mg, 3 mmol) was stirred at 120 °C for 8 h in hydrochloric acid (4 M, 5 mL). The mixed solution was cooled to room temperature and the precipitate was filtered off, washed with water followed by acetonitrile and ether to yield the product as a brown solid. Yield: (486 mg, 71 %). ^{1}H NMR (DMSO-d_6) δ: 8.27 (1H, s, H_1), 8.07 (1H, d, J = 8.4 Hz, H_2), 7.84 (1H, d, J = 8.0 Hz, H_3), 5.02 (2H, s, H_4); MS (LC-MS) found: m/z 191.3 $[MH]^-$.

Preparation of $Tb(\mathbf{a})_3$ was described as follows (Tan et al., 2010): 2-hydroxymethyl-benzoimida-zole-6-carboxylic acid (115.2 mg, 0.6 mmol) was dissolved in 5 mL of ethanol in a 50 mL round bottom flask. $Tb(NO_3)_3 \cdot 6H_2O$ (90.6 mg, 0.2 mmol) dissolved in 5 mL of ethanol and ammonia (1 mL) was added into the flask. The mixture was stirred under 90 °C for 1 h. Crude product was washed with ethanol and water then dried in vacuo overnight and the titled complex (169 mg) was obtained as a brown powder $Tb(\mathbf{a})_3 \cdot 2H_2O$. Elemental analysis (EA), w_i/mass % (found), revealed: C, 42.27; H, 3.38; N, 10.88; (calc) for $C_{27}H_{25}N_6O_{11}Tb$: C, 42.20; H, 3.28; N, 10.94.

Preparation of H_a was realized as follows: 2-hydroxymethyl-benzoimidazole-6-carboxylic acid (115.2 mg, 0.6 mmol) was dissolved in 5 mL of water in a 50 mL beaker. TEOS (416 mg, 2 mmol) and $Tb(NO_3)_3 \cdot 6H_2O$ (90.6 mg, 0.2 mmol) dissolved in 10 mL water were added into the beaker, ammonia (5 mL) was added into the solution. The mixture was

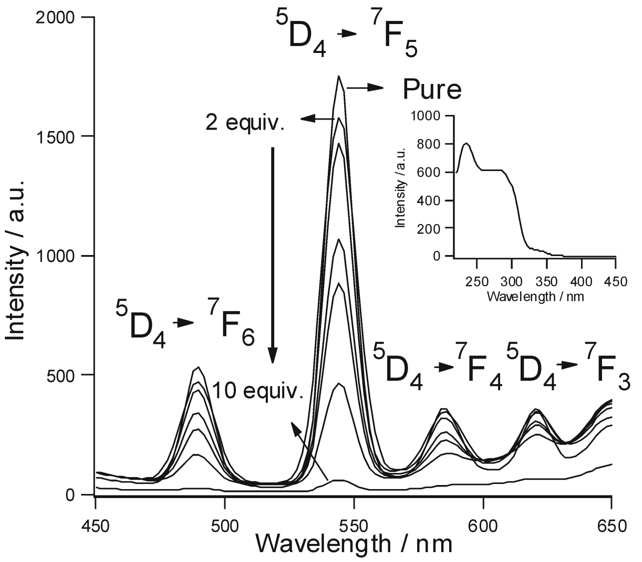

Fig. 2. Emission spectra of Tb(**a**)$_3$ (10^{-5} M in acetonitrile, λ_{ex} = 284 nm) upon addition of 0–10 equivalents of [Bu$_4$N]F. Insert: excitation spectra of Tb(**a**)$_3$ (10^{-5} M in acetonitrile, λ_{em} = 544 nm).

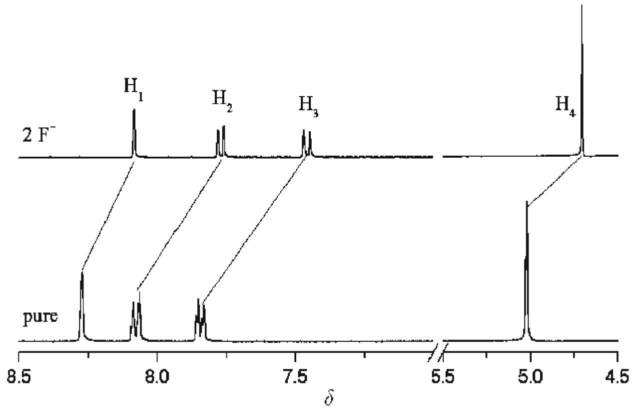

Fig. 3. ^{1}H NMR spectra measured by titration of a DMSO-d_6 solution of pure **a** (1 mM) with two equivalents of [Bu$_4$N]F.

stirred under room temperature for around 5 h, dried at 80 °C for 24 h, and the resulting product (364 mg) was obtained as a brown powder.

Results and discussion

IR spectra of ligand **a** (a), terbium complex Tb(**a**)$_3$ (b), and hybrid material H$_a$ (c) are shown in Fig. S1. The band at 3384 cm^{-1} is due to the –NH stretching vibrations. The broad band located around 2814 cm^{-1} can be ascribed to the intra-molecular hydrogen bonding and molecular packing (Fig. S1a). In Fig. S1b, the coordination interaction between the carboxylate and the terbium ion is supported by the bands located at 1562 cm^{-1} and 1386 cm^{-1}, which are induced by the asymmetric (ν_{as}) and symmetric (ν_{s}) stretching vibrations of carboxylate. Moreover, spectra of the hybrid material (Fig. S1c) show the formation of an Si—O—Si framework, which is evidenced by the broad bands located at 1102 cm^{-1} (ν_{as}, Si—O), indicating the success of hydrolysis and polycondenzation (Dong et al., 2000).

As shown in Fig. S2, terbium complex Tb(**a**)$_3$ with strong green luminescence shows characteristic terbium ion emission. Its excitation spectrum is represented by a broad band ranging from 230 nm to 370 nm with the maximum at 245 nm (Fig. S2). The overall quantum yield was measured as 4.2 % in pure DMSO.

Tb(**a**)$_3$ was dissolved in acetonitrile (10^{-5} M) and its sensing abilities towards anions were studied by fluorescence spectroscopy. The excitation spectrum of Tb(**a**)$_3$ was obtained by fixing the emission wavelength of Tb^{3+} at 544 nm; it exhibited a broad band ranging from 220 nm to 300 nm (insert in Fig. 2). Narrow emission bands with maxima at 488 nm, 544 nm, 583 nm, and 621 nm were recorded. These bands were ascribed to the ^{5}D$_4$ →^{7}F$_6$, ^{5}D$_4$ →^{7}F$_5$, ^{5}D$_4$ →^{7}F$_4$, and ^{5}D$_4$ →^{7}F$_3$ transitions of Tb^{3+} ions, respectively. However, upon addition of fluoride ions from 10^{-5} mol L^{-1} to 10^{-4} mol L^{-1}, the emission of terbium ions gradually decreased and totally disappeared. Therefore, significant changes can be observed by naked eye under the excitation by ultraviolet light (insert in Fig. S3). Similar fluorescence experiments were done by titration of ten equivalents of HSO$_4^-$, AcO$^-$, Cl$^-$, Br$^-$, and I$^-$ corresponding [Bu$_4$N]$^+$ salts (Fig. S4). All these anions caused only minor changes to the luminescence of Tb(**a**)$_3$.

In order to determine the interaction between the complex and anions, the same species were also characterized by UV-VIS spectrum. Tb(**a**)$_3$ in acetonitrile (1 × 10^{-5} M) gave a broad band ranging from 205 nm to 240 nm (Fig. S3). Its absorption significantly increased when the concentration of fluoride anions increased from two to ten equivalents. Continuous addition of fluoride caused no changes in the spectrum. Hydrogen bonds between the fluoride anions and the ligand were assumed to induce the absorption changes. In an analogous fashion, the binding behavior of HSO$_4^-$, AcO$^-$, Cl$^-$, Br$^-$, and I$^-$ anions were also detected. Almost no changes could be observed, showing that there is not enough binding to generate changes in the absorption region (Fig. S3).

To study the interaction between anions and ligand **a** more clearly, ^{1}H NMR spectroscopy was used to investigate the binding affinity of anions to **a** (Fig. 3). The addition of two equivalents of fluoride ions in DMSO-d_6 into **a** generated an upfield shift (from 8.27, 8.07, 7.84, and 5.02 to 8.08, 7.76, 7.45, and 4.70) of the protons of **a** (H$_1$, H$_2$, H$_3$, and H$_4$, respectively). Changes of these proton signals were caused by the co-contribution of hydrogen bonding interactions with

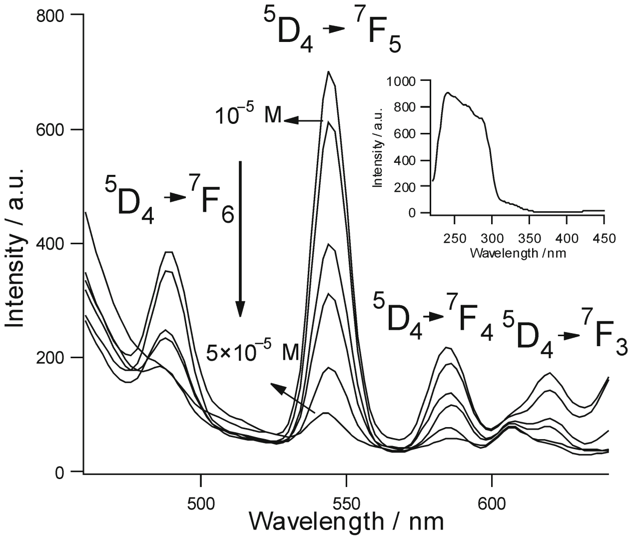

Fig. 4. Emission spectra of H_a (0.5mg mL^{-1} in water, λ_{ex} = 290 nm) upon addition of 0–5×10^{-5} M $[Bu_4N]HSO_4$. Inset: Excitation spectra of H_a (0.5 mg mL^{-1} in water, λ_{em} = 544 nm).

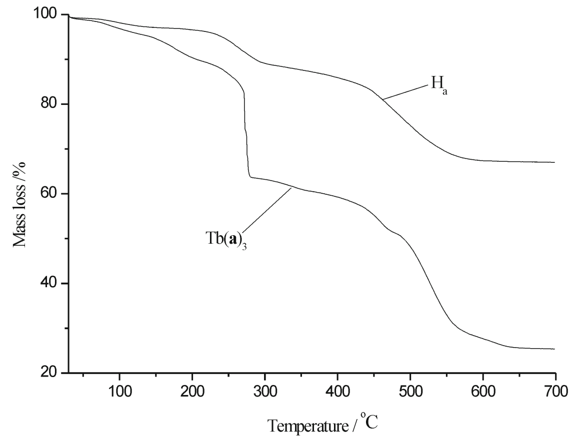

Fig. 5. Thermogravimetric analysis of $Tb(\mathbf{a})_3$ and H_a.

fluoride between the imidazole ring NH and the hydroxyl (OH) proton of $\mathbf{a}^-$. Analogous NMR experiments using HSO_4^-, AcO^-, Cl^-, Br^-, and I^- were done but **a** did not give signal changes with each proton (data not shown).

However, to dissolve $Tb(\mathbf{a})_3$ in an aqueous solution was attempted and it was discovered that the emission of the terbium ion is quenched in the presence of water. It was found that the introduction of a lanthanide complex into a silica matrix enables emissions even in pure water. Consequently, $Tb(\mathbf{a})_3$ was encapsulated into an inorganic host (TEOS) and a novel hybrid material (H_a) with intense green emission was developed as a luminescent receptor in water. Its excitation spectrum exhibits a sharp peak at 248 nm and its emission spectra show characteristic terbium emission, which can be interpreted as follows: excited $^5D_4 \rightarrow ^7F_J$ transitions demonstrate four main components for $J = 6$, 5, 4, and 3, respectively (Fig. S5).

As described in Fig. 4, the ability of H_a to recognize anions was also studied using emission spectroscopy in water. H_a was dispersed in water in the concentration of 0.5 mg mL^{-1}. When the solution was irradiated with light of 290 nm, narrow emission peaks were observed and assigned to the transitions between the excited $^5D_4$ level and various J-levels of the ground state ^7F_J ($J = 6$, 5, 4, and 3) at 490 nm ($^5D_4 \rightarrow ^7F_6$), 544 nm ($^5D_4 \rightarrow ^7F_5$), 584 nm ($^5D_4 \rightarrow ^7F_4$), and 620 nm ($^5D_4 \rightarrow ^7F_3$). For the excitation spectra, a broad band ranging from 220 nm to 300 nm was observed when the emission wavelength was fixed at 544 nm (insert in Fig. 4). Luminescence of H_a decreased gradually and was almost quenched at last upon the addition of hydrogen sulfate ions from 10^{-5} mol L^{-1} to 5×10^{-5} mol L^{-1}. The recognition process in complex was not observed probably because HSO_4^- was not hydrolyzed in the organic solvent (CH_3CN), showing no acidity in CH_3CN. The quenching effect can be also observed upon the titration of fluoride ions from 5×10^{-5} mol L^{-1} to 10^{-4} mol L^{-1} (Fig. S6). Hence, significant changes can be observed by naked eye under the excitation by ultraviolet light (Fig. S7).

In analogous experiments, AcO^-, Cl^-, Br^-, or I^- and 10^{-3} mol L^{-1} titration of corresponding $[Bu_4N]^+$ salts were measured by emission spectroscopy (Fig. S6). Almost no changes could be observed in their luminescence. Accordingly, it is proposed that the target material can be applied as a potential luminescent receptor for recognition of HSO_4^- as well as F^- in water. This hybrid material is a little more sensitive to hydrogen sulfate anions than to the fluoride ones.

We believe that there are hydrogen bonding interaction between the imidazole ring NH/hydroxyl OH and fluoride anions as evidenced by the NMR and UV spectra above. In terms of fluoride ions, their hydrogen bonding interactions with the ligand resulted in the disappearance of the luminescence of the complex as well as that of the hybrid material (Santacroce et al., 2006). However, for HSO_4^-, we are convinced that the coordination interaction between the ligand and terbium were disrupted by its acidity; also, the released protons were combined by carboxylate (COOH formed again), which terminated the energy transfer between them. In this way, recognition effects observable by naked eye occurred.

Moreover, thermal stability of $Tb(\mathbf{a})_3$ and H_a were studied by thermogravimetric analysis (TGA). At temperatures lower than 250 ℃, H_a has relatively higher thermal stability in comparison with the terbium complex (Fig. 5). Therefore, incorporation of the terbium complex into the silica matrix can significantly enhance its thermal stability and increase its decomposition temperature.

From the fluorescence microscopy image (Fig. S8) can be clearly seen that the prepared hybrid material is homogeneously dispersed on the glass surface and displays strong green emission with the diameter about of 10∼30 μm. Besides, formation of large aggregates with the diameter of about 50 μm was clearly observed.

Conclusions

In summary, a novel terbium complex and its hybrid material were prepared as sensing materials. Both of them can quench luminescence of fluoride ions through hydrogen bonding interactions. However, emission of the hybrid material can also be terminated by an addition of hydrogen sulfate anions. Additionally, the complex enables recognition in organic solvents whereas the hybrid material can be used in pure water. More importantly, the hybrid material exhibits higher thermal stability than the complex. These fundamental results show great potential of the hybrid material for future tailored recognition of target ions in practical aqueous systems.

Acknowledgements. Qian-Ming Wang appreciates support of the National Natural Science Foundation of China (21002035) and the Start Fund of Guangdong Talents (C10208).

Supplementary data

Supplementary data associated with this article can be found in the online version of this paper (DOI: 10.2478/s11696-011-0123-1).

References

Bünzli, J. C. G., & Piguet, C. (2005). Taking advantage of luminescent lanthanide ions. *Chemical Society Reviews*, *34*, 1048–1077. DOI: 10.1039/b406082m.

Dong, D. W., Jiang, S. C., & Men, Y. F., Jiang, S. (2000). Nanostructured hybrid organic–inorganic lanthanide complex films produced in situ via a sol-gel approach. *Advanced Materials*, *12*, 646–649. DOI: 10.1002/(SICI)1521-4095(200005)12:9<646::AID-ADMA646>3.0.CO;2-W.

Gale, P. A., García-Garrido, S. E., & Garric, J. (2008). Anion receptors based on organic frameworks: highlights from 2005 and 2006. *Chemical Society Reviews*, *37*, 151–190. DOI: 10.1039/b715825d.

Gunnlaugsson, T., Glynn, M., Tocci, G. M., Kruger, P. E., & Pfeffer, F. M. (2006). Anion recognition and sensing in organic and aqueous media using luminescent and colorimetric sensors. *Coordination Chemistry Reviews*, *250*, 3094–3117. DOI: 10.1016/j.ccr.2006.08.017.

Kavallieratos, K., Bertao, C. M., & Crabtree, R. H. (1999). Hydrogen bonding in anion recognition: A family of versatile, nonpreorganized neutral and acyclic receptors. *Journal of Organic Chemistry*, *64*, 1675–1683. DOI: 10.1021/jo982382l.

Parker, D., & Yu, J. H. (2005). A pH-insensitive, ratiometric chemosensor for citrate using europium luminescence. *Chemical Communications*, *2005*, 3141–3143. DOI: 10.1039/b502553b.

Sambrook, M. R., Beer, P. D., Wisner, J. A., Rowena, L., Cowley, A. R., Szemes, F., & Drew, M. G. B. (2005). Anion-templated assembly of pseudorotaxanes: Importance of anion template, strength of ion-pair thread association, and macrocycle ring size. *Journal of the American Chemical Society*, *127*, 2292–2302. DOI: 10.1021/ja046278z.

Santacroce, P. V., Okunola, O. A., Zavalij, P. Y., & Jeffery, T. D. (2006). A transmembrane anion transporter selective for nitrate over chloride. *Chemical Communications*, *2006*, 3246–3248. DOI: 10.1039/b607221f.

Tan, C. L., Wang, Q. M., & Ma, L. J. (2010). Fluorescent-based solid sensor for HSO_4^- in water. *Photochemistry and Photobiology*, *86*, 1191–1196. DOI: 10.1111/j.1751-1097.2010.00795.x.

Thakurdesai, P. A., Wadodkar, S. G., & Chopade, C. T. (2007). Synthesis and anti-inflammatory activity of some benzimidazole-2-carboxylicacids. *Pharmacologyonline*, *1*, 314–329.

Wang, Q. M., Tan, C. L., Chen, H. Y., & Tamiaki, H. (2010). A new fluoride luminescence quencher based on a nanostructured covalently bonded terbium hybrid material. *Journal of Physical Chemistry C*, *114*, 13879–13883. DOI: 10.1021/jp105035v.

Zhang, Y. Y., Xue, Y. N., & Yu, M. (2011). Hydrothermal synthesis of core-shell structured PS@GdPO(4):Tb^{3+} /Ce^{3+} spherical particles and their luminescence properties. *Chemical Papers*, *65*, 29–35. DOI: 10.2478/s11696-010-0088-5.