Synthesis of Luminescent Lanthanide-based MCM-41 Mesoporous Material by a Novel Route

Li Chen, Jingwen CHEN, Jinhui YAN, Yishan SONG[*, a], Jianfeng XU[*, b]

[1]Department of Chemistry,College of Food Science & Technology, Shanghai Ocean University, Shanghai, 201306,P.R. China

[a]email: yssong@shou.edu.cn, [b]email: jfxu@shou.edu.cn

Keywords: Lanthanide; Mesoporous material; Luminescence

Abstract. A novel route was developed to construct luminescent lanthanide-based mesoporous materials. Ligand 2-(2-hydroxyethyl)carbamoyl-benzoic acid (L = HCBC) was synthesized by modification of phthalic acid, and then was introduced into a preparing MCM-41 host by the reaction between the hydroxyl group and active Si-OH. The forming intermediate then reacted with $EuCl_3$ to obtain luminescent mesoporous material Eu-HCBC-MCM-41. The Eu-HCBC-MCM-41 was characterized by UV, small-angle X-ray diffraction (SAXRD) patterns, nitrogen adsorption/desorption isotherms and fluorescence spectra, and the results indicate that ligand and lanthanide ions had been introduced into the MCM-41 host, and the mesoporous material Eu-HCBC-MCM-41 exhibits characteristic luminescence of Eu^{3+}.

Introduction

In luminescent materials, trivalent lanthanide complexes have aroused great interest of many researchers because of their attractive features such as sharp emission spectra for high color purity, broad emission bands covering the ultraviolet–visible–near infrared region, a wide range of lifetimes from the microseconds to seconds level. These properties have attracted much attention for a wide variety of applications in the fields of diagnostic tools, sensors, optical fiber lasers and amplifiers, and electroluminescent materials [1][2]. Meanwhile, lanthanide-based organic–inorganic hybrid materials have been becoming the focus since the materials integrate the respective characteristics of inorganic and organic parts. In the hybrid system, the lanthanide complexes' mechanical strength, acid and alkali resistance, and thermal stability could be improved because of the stability of the inorganic rigid matrix such as SiO_2, TiO=, and so on [3] .

Mesoporous silica materials (MCM-41, MCM-48, SBA-15, SBA-16, and so on) have interesting unique properties, such like ordered pore structure, high surface area, varying morphology, and potentially are excellent host for lanthanide complexes to form functional mesoporous materials [4][5]. Recently, lanthanide-based luminescent mesoporous materials have been reported [6][7][8][9]. To prepare the mesoporous materials with covalent bonds between lanthanide complexes and mesoporous host, silane coupling agents are widely used. Silane coupling agents have Si-OR group which is easy to form strong Si-O-Si bond with etraethoxysilane during a hydrolysis process. However, Si-OR group is not stable because of its hyper-moisture sensitive, and as a result, the intermediate ligands modified by silane coupling agents are hard to purify. Therefore, the purity of the lanthanide complexes and the final mesoporous materials cannot be guaranteed.

On the other hand, hydroxyl is a functional group that can react with active Si-OH to form a covalent C-O-Si bond [10][11][12].   Based on this kind of reaction, the luminescent Eu-containing mesoporous material Eu-HCBC-MCM-41 (HCBC = 2-(2-hydroxyethyl)carbamoyl-benzoic acid) was prepared in this work. The hydroxyl group in the structure of HCBC can anchor the ligand to the forming MCM-41 host, and the HCBC ligand can form a stable chelating structure with lanthanide ions. In the synthesis process, no silane coupling agent was used, which is superior to the reported method since the intermediate ligand can be purified and then ensure the purity of product.

Experimental

Materials: The lanthanide oxide Eu_2O_3 was converted to its chloride by the treatments with concentrated hydrochloric acid. Other chemicals were obtained from commercial sources and used without further purification.

Synthesis of Phthaloyl dichloride: To a mixture of phthalic acid (1.66 g, 10 mmol) in DMF (0.05 mL) was added $SOCl_2$ (15 mL). The mixture was refluxed under stirring for 4 h, during which time the powder gradually dissolved. The excess amount of $SOCl_2$ was then removed under reduced pressure by adding a small amount of toluene, and yellowish product (1.99 g) was obtained. The resulting solid was used for further reaction directly without purification.

Synthesis of 2-(2-hydroxyethyl)carbamoyl-benzoic acid: To a ice-cooled solution of phthaloyl dichloride (1.99 g, 10 mmol) in dichloromethane (20 mL) was added a solution of 2-aminoethanol (0.61 g, 10 mmol) and triethylamine (3 mL, 20 mmol) in dichloromethane (20 mL) over 30 min. The solution was stirred at RT overnight, and then concentrated to be about 5 ml. The resulting deep purple solution was added 1Mol/L HCl 20 ml and then stirred for 2h. The resulting mixture was extracted with 15 ml dichloromethane once and 20 ml dichloromethane twice. The organic phase was combined and then washed with saturated sodium hydrogen carbonate solution (30 mL×2), and brine (30 mL), dried with sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography [silica gel 200-300, dichloromethane/ methanol, 90:10] to get product (0.98 g, 47%). ^{1}H NMR (400 MHz, DMSO): δ = 7.94–7.85 (m, 4 H), 3.94 (t, 2 H), 3.86 (t, 2 H) ppm.

Preparation of MCM-41 host: In a typical synthesis process, cetyltrimethylammoniumbromide (CTAB) was used as a template. 1.0 g CTAB was first dissolved in 40 g of deionized water under heating at 60 ˚C. After the solution turned clear, then added subsequently 11 ml of $NH_3•H_2O$ and 5 ml of tetraethylorthosilicate (TEOS). The solution was further stirred for 3 h, and then was placed in a Teflon-lined vessel and heated at 110 ˚C for 120 h. The resulting white powder was filtered, thoroughly washed with deionized water and dried. CTAB surfactant molecules were then removed by calcination of the resulting white powder at 600 ˚C in air for 6 h.

Preparation of Eu-HCBC-MCM-41: Ligand 2-(2-hydroxyethyl)carbamoyl-benzoic acid was first dissolved in 20 ml ethanol / 3 ml H_2O / 0.1 ml HCl, and then MCM-41 was added (HCBC:MCM-41 = 1:10). The mixture was stirred for 24 hours, and then filtered, washed by Soxhlet extraction with ethanol under reflux for 6 h to remove unreacted ligand. The resulting white solid was re-dispersed in 15 ml ethanol, and then added a small amount of 0.1 Mol/L NaOH, and followed a solution of $EuCl_3•6H_2O$ (HCBC:Eu^{3+} = 3:1) in 5ml 95% ethanol. The mixture was refluxed for 6 h, and then filtered, washed with H2O to remove access $EuCl_3$ and NaCl in the system. The powder of product was dried at 60 ˚C, and this mesoporous material containing Eu^{3+} was denoted as Eu–HCBC–MCM-41.

Measurements: ^{1}H NMR spectra were recorded in DMSO on an INOVA2 400 spectrometer with tetramethylsilane (TMS) as internal reference. Ultraviolet absorption spectra of these powder samples ($5×10^{-4}$ mol/L, DMSO solution) were recorded with an Agilent 8453 spectrophotometer. The X-ray powder diffraction (XRD) patterns of all samples were performed on a Rigaku D/max-rB diffractometer equipped with a Cu anode in a 2θ range from 0.6° to 5.994°. Surface areas and total pore volumes were performed on Quantachrome autosorb-iQ, and the instrument of N_2 adsorption/desorption isotherms using the BET and BJH methods. The luminescence (excitation and emission) spectra and lifetime for the solid sample were determined with a HORIBA FluoroMax-4 spectrophotometer.

Results and discussion

Ligand 2-(2-hydroxyethyl)carbamoyl-benzoic acid (HCBC) was synthesized by modification of phthalic acid molecule. In the structure of HCBC, there is one functional hydroxyl group which is useful to construct mesoporous hybrids. As the previous reports, the hydroxyl group can react with active Si-OH or Si-OR to form a covalent C-O-Si bond under weak acidic addition, and this kind of

reaction has been used to prepare lanthanide organic-inorganic hybrid materials [18][19][20]. In this work, MCM-41 mesoporous host was prepared by typical synthesis process, and on the surface of the SiO_2 network, there are amounts of Si-OH. So HCBC ligand can be introduced into the preparing MCM-41 host by the reaction between the hydroxyl groups from HCBC and Si-OH from MCM-41. In addition, HCBC ligand has good soluble ability in ethanol due to the hydroxyl group, and then Soxhlet extraction technique was applied to remove unreacted HCBC in the system by using ethanol as solvent.

The above resulting intermediate was donated as HCBC-MCM-41. Fig. 1 shows the ultraviolet absorption spectra (5×10^{-4} mol/L DMSO solution) of free HCBC ligand and the intermediate. It can be observed almost the same absorption band of the major π-π* electronic transitions of HCBC and HCBC-MCM-41, they all exhibit two large broad absorption band and the maximum absorption peaks are located at around 225, 242 and 290 nm. The results indicate that the HCBC ligand had been introduced into the mesoporous host successfully.
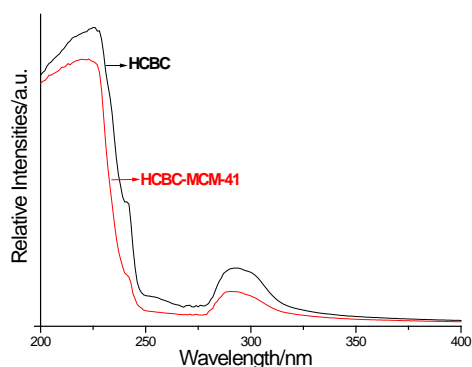

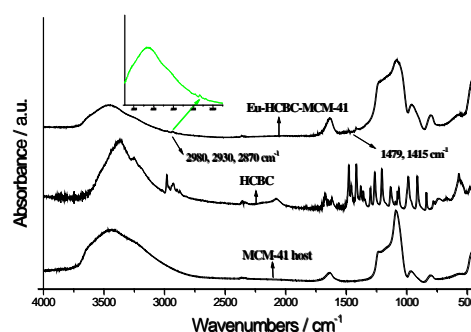Fig. 1 UV spectra of L and HCBC-MCM-41   Fig. 2 IR spectra of L, MCM-41 and HCBC-MCM-41

Fig. 2 shows the IR spectra of HCBC, MCM-41 host and the intermediate HCBC-MCM-41. MCM-41 host exhibits peaks at 3435 cm^{-1}, 1642 cm^{-1}, 1082 cm^{-1}, 958 cm^{-1}, 796 cm^{-1}, 552 cm^{-1}, 458 cm^{-1}, respectively. Among, the peak at 1082 cm^{-1} originate from the antisymmetric stretching vibration of Si-O-Si bonds; the peak at 458 cm^{-1} originates from the symmetrical stretching vibration of Si-O bonds; the peak at 1642 cm^{-1} originates from the bending vibration of H-O-H; the peak at 958 cm^{-1} originates from the bending vibration of Si-OH. HCBC-MCM-41 shows the similar infrared absorption bands except shoulders peak at 2980, 2930, 2870 cm^{-1}, which are the absorption bands of -CH$_2$-CH$_2$- from HCBC comparing with IR of HCBC, indicating that ligand has been been grafted onto the wall of MCM-41. The absorption band of Si-O-C should appear in the 1000–1100 cm^{-1} range, however, it is covered by the absorption band of Si-O-Si bonds.
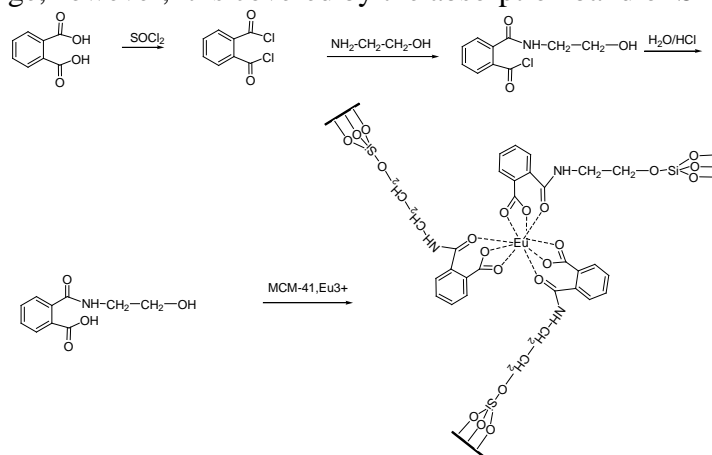

Fig. 3 Synthesis of ligand and mesoporous materials

After grafted into MCM-41 host, there are numbers of coordination sites remained in the structure of HCBC: oxygen atoms and one nitrogen atom. As the reports, the phthalic acid and its

derivatives usually exhibit multi-dentate coordination modes toward metallic ions, and lanthanide ions prefer O- to N- donors [13]. As a result, it's easy for grafted HCBC ligand to capture Eu^{3+} ions to form a complex component in the mesoporous material system, and then the luminescent mesoporous hybrid material Eu-HCBC-MCM-41 was obtained. Fig. 3 shows the synthesis process of HCBC and the mesoporous material Eu-HCBC-MCM-41.

It's worthy to point out that in the preparation process of the Eu-HCBC-MCM-41 mesoporous material, no silane coupling agent was used, and this is a novel synthesis route for the preparation of lanthanide-based mesoporous material. Compared with reported methods — using silane coupling agents to connect lanthanide complex and mesoporous host, the intermediate ligand can be purified, and then the purity of the mesoporous material can be guaranteed in the preparation process.

To characterize highly ordered mesoporous material with hexagonal symmetry of the space group *p6mm*, the small-angle X-ray diffraction (SAXRD) patterns and nitrogen adsorption/desorption isotherms are popular and efficient methods. The SAXRD patterns of preparing MCM-41 host and Eu-HCBC-MCM-41 are presented in Fig. 4. For MCM-41 host, the pattern shows three distinct Bragg peaks in the 2θ range of 0.6–6°, which can be indexed as (100), (110), and (200) reflections and is the character of MCM-41-type two-dimensional hexagonal. The Eu-HCBC-MCM-41 shows similar curve with that of MCM-41 host, indicating that the ordered hexagonal mesoporous structure retained after the introduction of organic component. Furthermore, compared the preparing MCM-41 host, the intensity of the characteristic diffraction peaks of Eu-HCBC-MCM-41 is lower, and the reason is that the presence of organic complex moieties inside the pore channels decreased the crystallinity of the MCM-41 host [14].
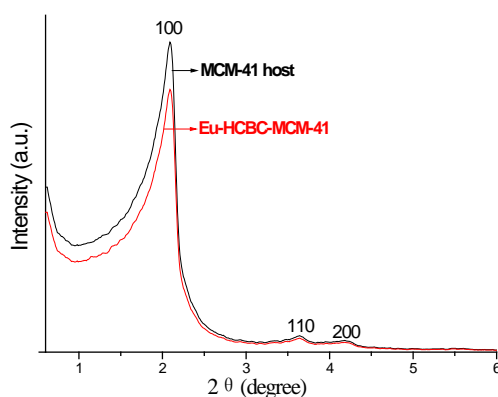

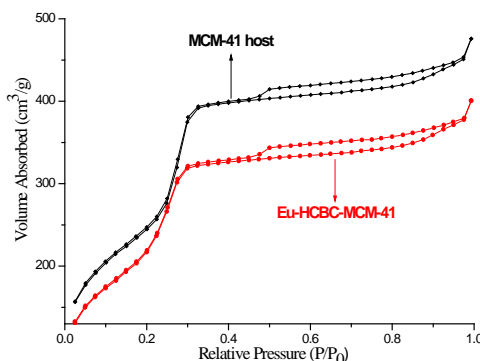Fig. 4 SAXRD of MCM-41 and Eu-HCBC-MCM-41

Fig. 5 N_2 adsorption/desorption isotherms of MCM-41 and Eu-HCBC-MCM-41

Fig. 5 shows the N_2 adsorption–desorption isotherm for MCM-41 host and Eu-HCBC-MCM-41. The two curves are quite similar and display Type IV isotherms with H1-type hysteresis loops at high relative pressure in accordance with the IUPAC classification, indicate that both of them possess a well-defined structure array of regular mesoporous. In addition, it also can be concluded

that the introduction of Eu-HCBC complexes didn't destroyed the mesoporous structure of the preparing MCM-41 host, which coincides with the SAXRD results. By using BET and BJH methods, the surface area and the pore volume of MCM-41 host were calculated to be 754.1 m^2g^{-1} and 0.736 cm^3g^{-1}, and the surface area and the pore volume of Eu-HCBC-MCM-41 were calculated to be 677.4 m^2g^{-1} and 0.62 cm^3g^{-1} which are lower compared with that of MCM-41 host. The decrease is a further evidence for the presence of Eu-HCBC complexes in the channels of the preparing mesoporous MCM-41 host [15].

Fig. 6 shows the excitation (inner) and emission spectra of mesoporous material Eu-HCBC-MCM-41. The excitation spectrum of Eu-HCBC-MCM-41 monitored at 615 nm is dominated by one broad band with the main peak at around 342 nm and with a shoulder at 281 nm. Upon excitation at 342 nm, the characteristic emission peaks of Eu^{3+} $^5D_0 \rightarrow {}^7F_j$ (j = 1, 2) transitions at 592 and 615 nm are observed, among the red luminescent intensity of $^5D_0 \rightarrow {}^7F_2$ transition is stronger.
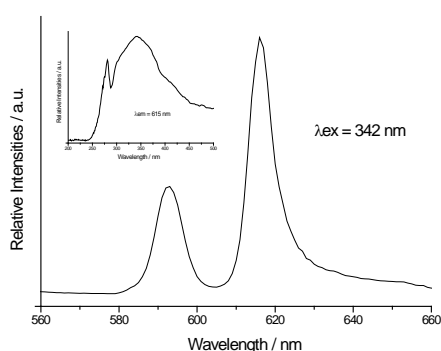

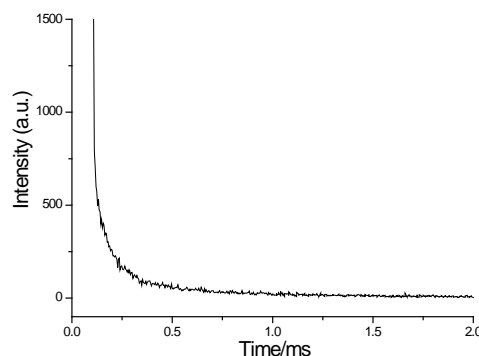Fig.6 Luminescence of Eu-HCBC-MCM-41 Fig.7 Decay curve for Eu-HCBC-MCM-41

Fig.7 presents the luminescence decay curve of $^5D_0$ level for the mesoporous material Eu-HCBC-MCM-41 by monitoring the emission at 615 nm at room temperature. The lifetime value for the emission was obtained to be 0. 153 ms from fittings of the decay curve.

On the basis of the emission spectra and lifetimes of the $^5D_0$ emitting level, the emission quantum efficiency (η) of the $^5D_0$ level can be calculated. The lifetime (s), radiative transition rate (Ar), and nonradioactive transi-tion rate (Anr) are related through the following equation [14][16] [17]: $\eta = Ar/(Ar+Anr)$

Ar can also be obtained by summing over the radiative rates A_{0J} for each $^5D_0 \rightarrow {}^7F_J$ (J = 0-2) transitions of Eu^{3+}: $Ar = \sum A_{0J} = A_{00} + A_{01} + A_{02} + A_{03}$. The $^5D_0 \rightarrow {}^7F_{3,4,5,6}$ transitions should be neglected because of their weak intensities in the spectrum. The magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition is relatively insensitive to the chemical environments around the Eu^{3+} ions, so A_{01}, which could be equal to 50 s^{-1}, as the Einstein coefficient can be considered as a reference for the whole spectrum. A_{0J} can be calculated according to the equation: $A_{0J} = A_{01}(I_{0J}/I_{01})(\upsilon_{01}/\upsilon_{0J})$

Here, I_{01} and I_{0J} are the integrated intensities of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0-2) with υ_{01} and υ_{0J} ($\upsilon_{0J} = 1/\lambda J$) energy centers respectively. υ_{0J} refers to the energy barrier and can be determined from the emission bands of Eu^{3+}'s $^5D_0 \rightarrow {}^7F_1$ emission transitions. The emission intensity, I, taken as integrated intensity of the $^5D_0 \rightarrow {}^7F_J$, J = 0-2 emission curves. On the basis of reference, the value of $A_{01} \approx 50$ s^{-1} and the lifetime (τ), radiative (Ar), and nonradiative (Anr) transition rates are related through the following equation: $Atot = 1/\tau s = Ar + Anr$

On the basis of the above discussion, the quantum efficiencies of Eu-HCBC-MCM-41 can be determined to be 2.6%.

Conclusions

In conclusion, the modification of phthalic acid, results in a ligand HCBC with a functional –OH group, which is useful to introduce its lanthanide complexes to the forming MCM-41 host. The prepared mesoporous material Eu-HCBC-MCM-41 was characterized by UV, IR, SAXRD and N_2 adsorption/desorption isotherm. The results indicate that ligand was introduced into the MCM-41 host, and Eu-HCBC-MCM-41 exhibits characteristic luminescence of Eu^{3+}. In addition, there is no silane coupling agent in the preparation, which is superior to the reported method since the intermediate ligand can be purified and then ensure the purity of product.

Acknowledgement

References

[1] Bunzli Jean-Claude G, Lanthanide luminescence for biomedical analyses and imaging. Chemical Reviews, 2010 110(5) 2729-2755.

[2] Eliseeva, Svetlana V, Buenzli, Jean-Claude G, Lanthanide luminescence for functional materials and bio-sciences. Chemical Society Reviews, 2000 39(1) 189–227.

[3] Binnemans Koen, Lanthanide-based luminescent hybrid materials. Chemical Reviews, 2009 109(9) 4283-4374.

[4] Hoffmann Frank, Cornelius Maximilian, Morell Jurgen, Froeba Michael, Silica-Based Mesoporous Organic–Inorganic Hybrid Materials. Angewandte Chemie International Edition, 2006 45(20) 3216-3251.

[5] Deng Yonghui, Wei Jing, Sun Zhenkun, Zhao Dongyuan, Large-pore ordered mesoporous materials templated from non-Pluronic amphiphilic block copolymers. Chemical Society Reviews, 2013 42(9) 4054-4070.

[6] Feng Jing, Zhang Hongjie, Hybrid materials based on lanthanide organic complexes: a review. Chemical Society Reviews, 2013 42(1) 387-410.

[7] Yan Bing, Recent progress in photofunctional lanthanide hybrid materials. RSC Advances, 2012 2(25) 9304-9324.

[8] Carlos Luis D, Ferreira Rute A S, Bermudez Veronica de Zea, Lanthanide-containing light-emitting organic-inorganic hybrids: a bet on the future. Advanced Materials, 2009 21(5) 509-534.

[9] DeOliveira Edimar, Ner, Claudio R, Serra, Osvaldo A., Antenna Effect in Highly Luminescent Eu^{3+} Anchored in Hexagonal Mesoporous Silica. Chemistry of Materials, 2007 19(22) 5437-5442.

[10] Armelao Lidia, Bottaro Gregorio, Quici Silvio, Cavazzini Marco, Raffo Maria Concett, Barigelletti, Francesco, Photophysical properties and tunable colour changes of silica single layers doped with lanthanide(III) complexes. Chemical Communications, 2007 28 2911-2913.

[11] Quici Silvio, Cavazzini Marco, Raffo Maria Concett, Armelao Lidia, Bottaro Gregorio, Accorsi Gianluca, Sabatinic Cristiana, Barigelletti Francesco, Highly homogeneous, transparent and luminescent SiO_2 glassy layers containing a covalently bound tetraazacyclododecane-triacetic acid-Eu(III)-acetophenone complex. Journal of Material Chemistry, 2006 16(8) 741-747.

[12] Armelao Lidia, Bottaro Gregorio, Quici Silvio, Cavazzini Marco, Scalera Chiara, Synthesis and photophysical characterization of highly luminescent silica films doped with substituted 2-hydroxyphthalamide (IAM) terbium complexes. Dalton Transactions, 2011 40(43) 11530-11538.

[13] Yan Bing, Song Yishan, Chen Zhenxia, A novel quaternary dinuclear luminescent terbium complex $Tb_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4$: hydrothermal synthesis, crystal structure and photophysics. Journal of Molecular Structure 2004 694(1-3) 115-120.

[14] Li Ying, Yan Bing, Hybrid materials of MCM-41 functionalized by lanthanide (Tb^{3+}, Eu^{3+}) complexes of modified meta-methylbenzoic acid: Covalently bonded assembly and photoluminescence. Journal of Solid State Chemistry, 2008 181(5) 1032-1039.

[15] Hu Qingyuan, Hampsey J Eric, Jiang Nan, Li Chaojun, Lu Yunfeng, Surfactant-templated organic functionalized mesoporous silica with phosphino ligands. Chemistry of Materials 2005 17(6) 1561-1569.

[16] Werts Martinus H V, Jukes Ronald T F, Verhoeven Jan W, The emission spectrum and the radiative lifetime of Eu^{3+} in luminescent lanthanide complexes. Physical Chemistry Chemical Physics, 2002 4(9) 1542-1548.

[17] Malta Oscar L, Batista Helcio J, Carlos Luis D, Overlap polarizability of a chemical bond: a scale of covalency and application to lanthanide compounds. Chemical Physics, 2002 282(1) 21-30.