

## Functionalized Luminescent Silica Nanoparticles with Chelate Groups on Interface: Synthesis and Characterization

V.A. Burilov<sup>1,2,\*</sup>, A.T. Latypova<sup>1</sup>, A.R. Mustafina<sup>2</sup>, I.S. Antipin<sup>1,2</sup>, A.I. Kononov<sup>1,2</sup>.

<sup>1</sup> Kazan (Volga Region) Federal University, 18, Kremlyovskaya Str., 420088 Kazan, Russian Federation

<sup>2</sup> IOPC KSC RAS, 8, Arbuzov Str., 420088 Kazan, Russian Federation

(Received 19 May 2013; published online 31 August 2013)

Design, synthesis and characterization of luminescent silica nanoparticles with chelate groups on surface as well as the synthesis of new organosilanes with amino and carboxyl groups for silica surface functionalization is presented.

**Keywords:** Silica nanoparticles, Luminescence, Organosilanes.

PACS number: 82.70.Dd

### 1. INTRODUCTION

Currently large attention of researchers is focused on silica nanoparticles, doped with luminescent complexes for the further development of nanotechnological approaches in sensor systems. A promising procedure for the preparation of luminescent silica nanoparticles is the introduction of luminophores inside silica nanoparticles followed by modification of their surface. The choice of lanthanide complexes as luminophores is due to their long lifetimes, considerably exceeding the lifetimes of organic luminophores, narrow lines, and great Stokes shifts. Synthesis of silica nanoparticles can be performed by so called reverse microemulsion method [1]. In this method hydrolysis of tetraethylortosilane (TEOS) with subsequent polycondensation happens around water drop that's why this method is useful for water-soluble luminophores. This method was successfully used in our previous works [2, 3] to obtain monodisperse nanosized luminescent silica nanoparticles with diameter near 150 nm in solution. In presented work design, synthesis of new chelate precursors and subsequent modification of silica surface by them is discussed.

### 2. SYNTHESIS OF TRIALKOXY SILANES WITH CHELATE GROUPS

One of the most effective chelate molecules is well known ethylenediaminetetraacetic acid (EDTA). The shortest way to synthesis trialkoxysilane with similar structure fragment was the reaction of triethoxysilyl propylamine (TESPA) with bromoacetic acid in the presence of base. We made this reaction according to literature method [4] with NaOH in water but observed only polycondensation products according to MALDI TOF and NMR measurements. We modified synthesis using *t*-butylbromoacetate, triethylamine as a base and toluene as solvent in inert atmosphere under reflux and identified product 1 as yellow oil with yield 75 % (Fig. 1). Product obtained was fully characterized by NMR <sup>1</sup>H and GCMS. (<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ 3.76 (6H, (-O-CH<sub>2</sub>-CH<sub>3</sub>)), 3.38 (4H, (-CH<sub>2</sub>COO-*t*-Bu)), 2.67-2.58 (2H, (Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH-)), 1.57-1.48 (2H,

(Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH-)), 1.40 (18H(-*t*-Bu)), 1.16 (9H, (-O-CH<sub>2</sub>-CH<sub>3</sub>)), 0.59-0.51(2H, (Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH-)).

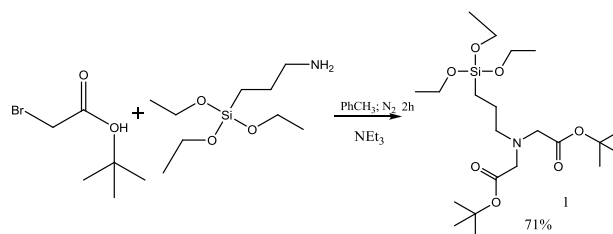


Fig. 1 – Synthetic route for compound 1

In the same manner we synthesized another precursor with four ester groups (Fig. 2). Product 2 as brown-yellow oil with yield 63 % was fully characterized by NMR <sup>1</sup>H. (<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ 3.46 (9H (-O-CH<sub>3</sub>)), 3.36-3.17 (8H (-CH<sub>2</sub>COO-*t*-Bu)), 2.85-2.24 (10H (-CH<sub>2</sub>-NH-)), 1.43 (2H, (Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH-)), 1.36 (36H(-*t*-Bu)), 0.54-0.46 (2H, (Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH-)).

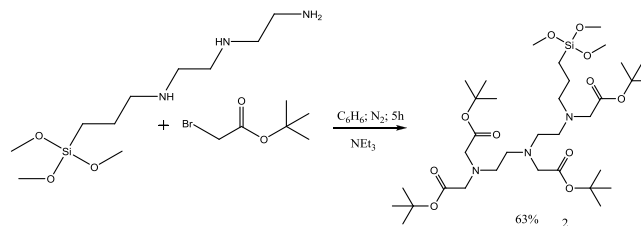


Fig. 2 – Synthetic route for compound 2

### 3. SYNTHESIS OF FUNCTIONALIZED SILICA NANOPARTICLES.

One of the most convenient methods of silica surface modification is step-by-step synthesis, when firstly silica nanoparticles doped with luminophore are obtained and after that polycondensation of trialkoxysilane with the surface -OH groups leads to desired product [4]. In our work we used complex of Tb(III) with p-sulfonatothiocalix[4]arene (TCAS) (Fig. 3) as luminescent dopant.

ultrav@bk.ru\*

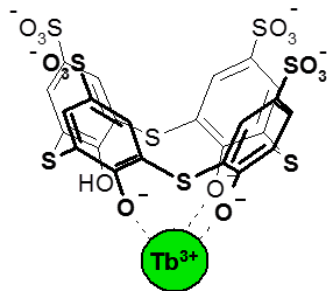


Fig. 3 – Structure of  $Tb^{3+}$ -TCAS complex

The first step of reaction – synthesis of non-functionalized silica nanoparticles – was done similar to literature methodology [5]. Next step of functionalization was performed using TEOS (0.5956 Mmol) and compound 1 at the presence of ammonia. Variation of compound 1 amount allowed us to functionalize a maximum space of silica surface. The most convenient method for surface modification control is measurement of zeta potential – functionalization of nanoparticles should lead to near-zero zeta potential. As we see from table 1, the best result is synthesis 3 with Zeta potential – 0.38 mV and very good PDI 0.087.

## REFERENCES

1. J. Yana, M.C. Estévez, E. Smitha, K. Wangb, X. Heb, L. Wangc, W. Tan, *Nano Today* **2**, 44 (2007).
2. A.R. Mustafina, S.V. Fedorenko, O.D. Konovalova, A.Yu. Menshikova, N.N. Shevchenko, S.E. Soloveva, A.I. Konovalov, I.S. Antipin, *Langmuir* **25**, 3146 (2009).
3. N. Davydov, A. Mustafina, V. Burirov, E. Zvereva, S. Katsyuba, L. Vagapova, A. Konovalov, I. Antipin, *Chem.*

Table 1 – DLS and Zeta potential results.

Concentration of 1, mmol	Zeta potential, mV	Average size, nm	PDI
0.099	– 45,1	134,8	0,102
0.2475	– 25,2	146,2	0,112
0.495	– 0,38	143,1	0,087

According to IR spectroscopy there is a band  $1741\text{ cm}^{-1}$  which is characteristic band for C=O in esters.

## 4. CONCLUSIONS

Summary, two new organosilanes for silica nanoparticles functionalization were obtained. Optimal parameters for functionalization of nanoparticles surface were found.

## ACKNOWLEDGMENTS

We thank RFBR grants №№ 12-03-33122; 13-03-01005 and 13-03-00045 for financial support.

*Phys. Chem.* **13**, 3357 (2012).

4. W.J. Rieter, J.S. Kim, K.M. Taylor, H. An, W. Lin, T. Tarrant, W. Lin, *Angew. Chem. Int. Ed.* **46**, 3680 (2007).
5. R.P. Bagwe, L.R. Hilliard, W. Tan, *Langmuir* **22**, 4357 (2006).