

One-pot preparation of surface modified boehmite nanoparticles with rare-earth cyclen complexes†

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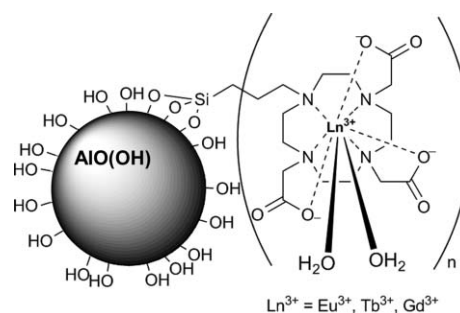
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We report on the one-pot synthetic procedure of cyclen derivatives bearing three acetate groups attached on boehmite nanoparticles, the complexing capabilities of these inorganic–organic hybrid materials with rare earth cations, and the behaviour as contrast agents or fluorescence probes.

There is much interest in the functionalisation of nanoparticles with organic components for a wide variety of goals.¹ The good dispersability in organic media of such surface modified nanoparticles by organic molecules offers many possibilities in important areas of chemistry such as analytical chemistry, catalysis and medical research.² Although a wide variety of nanoparticle supports have been reported, most of these concern silica, gold or II–VI semiconductors.³ We have recently shown the possibilities of new sensing systems based on nano-sized boehmite as support of indole- or naphthalene-polyamines.^{4,5} This type of sensing system is based on the phenomenon of photoinduced electron transfer (PET). Furthermore, the use of boehmite nanoparticles as support presents additional advantages such as, the possibility to make fluorescence emission studies in pure water with little scattering and the recovering of the sensor system after using.

Extraction of rare earth cations from solutions of nuclear fuel wastes are of crucial importance for both the further conversion of the waste into a wasteform by solidification, embedding or encapsulation and for possible reprocessing. The ability of acetates and phosphates side arms in polyazamacrocycles or linear polyamines to bind rare earth metal cations is well known.⁶ However, as far as we know there are no reports using these ligands in a chemical system to extract these radioactive rare earth cations from aqueous solutions and be able to recover the extractor for further reusing. We demonstrate here that the system formed by the cyclen molecule with acetate-containing groups bonded to three nitrogen atoms can be attached by alkoxy silanes to boehmite nanoparticles. This opens up the possibility of the development of rare earth cations extractor chemical devices from aqueous solutions.

Iron oxides such magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃) or other ferrites, which are insoluble in water have been studied as contrast agents for magnetic resonance imaging (MRI). These nanoparticles are coated with polymers such as dextran or carboxydextran.⁷ Due to the low sensitivity of MRI, boehmite nanoparticles may amplify the signal as the carrier can be loaded with contrast agents. To our knowledge, this is one of the first one-pot reported procedures for attaching lanthanide macrocyclic complexes to the surface of boehmite nanoparticles.



Tris-*tert*-butyl ester of DO3A was prepared under mild alkylation conditions according to Parker and co-workers⁸ Reaction of DO3A ester with (3-iodopropyl)trimethoxysilane afforded a mixture of unreacted DO3A triester, functionalized DO3A and (3-iodopropyl)trimethoxysilane. To this mixture of products were added the nanosized particles of boehmite (γ-AlOOH). Supported aluminium-DO3A triester nanoparticles were separated from DO3A by centrifugation. Hydrolysis of the *tert*-butyl groups of DO3A was accomplished using trifluoroacetic acid. Lanthanide complexes were prepared by reaction of the supported ligands with the appropriate chloride salts (see ESI†). The supported complexes were characterized by a variety of experimental analyses. Elemental analysis revealed that boehmite nanoparticles loaded 2.81×10^{-4} , 2.17×10^{-4} and 1.57×10^{-4} moles of gadolinium, terbium and europium per gram of sample. These values are similar to other loadings obtained before for different organic substrates.⁵ These numbers are translated into 800–1500 ions of lanthanide per nanoparticle considering an average diameter of 18 nm per nanoparticle of boehmite.

Fluorescence spectra of colloidal solutions containing Eu³⁺ and Tb³⁺ complexes (Eu–Boeh and Tb–Boeh) grafted in the nanoparticle were recorded upon direct excitation at 396 and 355 nm, respectively. The europium complex supported on boehmite nanoparticles showed the typical transitions of europium complexes, especially intense was the band $\Delta J = 2$ which is particularly sensitive to the chemical environment. The terbium complex in

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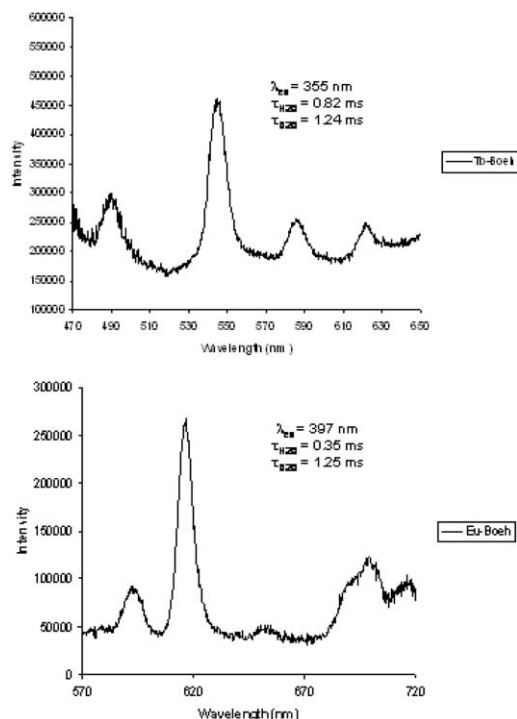


Fig. 1 Emission spectra of Tb-boehmite (top) and Eu-boehmite (bottom) in water.

boehmite shows distinctive luminescence at 480–630 nm consisting of four emission bands, assigned to the respective transitions from 5D_4 state to the ground state 7F_J ($J = 3, 4, 5, 6$) (Fig. 1). The number of coordinated water molecules in Eu-Boeh and Tb-Boeh was assessed by measuring the lifetime of the Eu 5D_0 and Tb 5D_4 excited states in H_2O and D_2O .⁹ Such measurements were done at several pHs with or without NaCl. The results were consistent with the presence of two bound water molecules ($q = 2$). Addition of NaCl to Eu-Boeh or Tb-Boeh at different pHs did not produce any change in the fluorescence intensity. Although LnDO3A derivatives are susceptible to interact with carbonate, titrations of Eu-Boeh nanoparticles with $NaHCO_3$ at pH 7.4 in 0.1 M HEPES resulted in no changes in the $\Delta J = 2/\Delta J = 1$ ratio.¹⁰

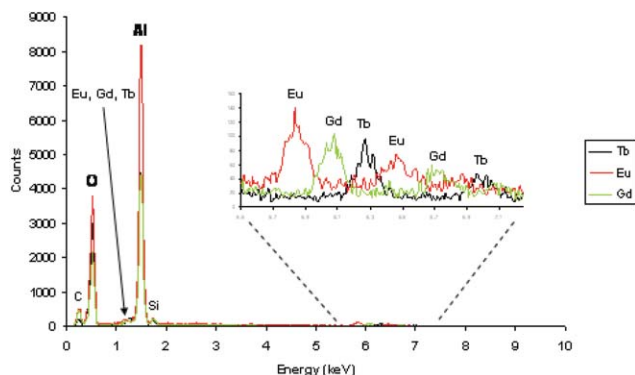


Fig. 2 EDX spectra for the boehmite nanoparticles loaded with Eu, Tb or Gd complexes.

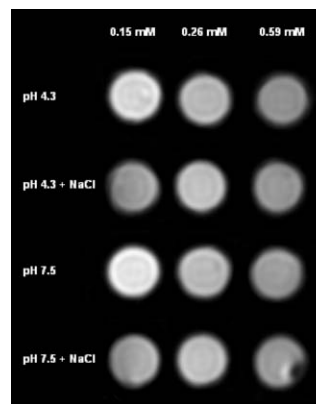


Fig. 3 T_1 map of Gd-boehmite acquired at 1.5 T (TE 8.8 ms, TR 10000 ms, and TI 200 ms) at different pHs.

The energy-dispersive X-ray (EDX) spectra (Fig. 2) of the Eu^{3+} , Tb^{3+} , and Gd^{3+} modified nanoparticles evidence the attachment of the DO3A to the surface.

Using this method, the average qualitative analysis of the samples provided 1 : 1 lanthanide : silicon atomic ratio which supports that all grafted cyclen was complexed to the lanthanides.

Magnetic resonance imaging of the gadolinium sample was performed on a whole body 1.5 T GE Excite MR scanner (63 MHz, 25 °C) (Fig. 3). Inversion–recovery spin echo pulse sequences (TE 8.8 ms/TR 10000 ms/TI 50–4000 ms) were used for T_1 measurements. The values of T_1 were plotted against several gadolinium concentrations obtained by ICP-MS measurements. The relaxivity measured at pH 4.3 and 7.5 provided, values of 1.75 and 1.49 in the absence of NaCl and 1.33 and 1.32 $mM^{-1} s^{-1}$ in the presence of NaCl. These low relaxivities suggest a poor water exchange dynamics, however at pH 2 relaxivity increases to a relatively high value ($11.71 mM^{-1} s^{-1}$) suggesting that the protonation state of the –OH groups at the surface plays an important role in water exchange dynamics. From the same experiment a T_1 value of 1560 ms was measured for boehmite.

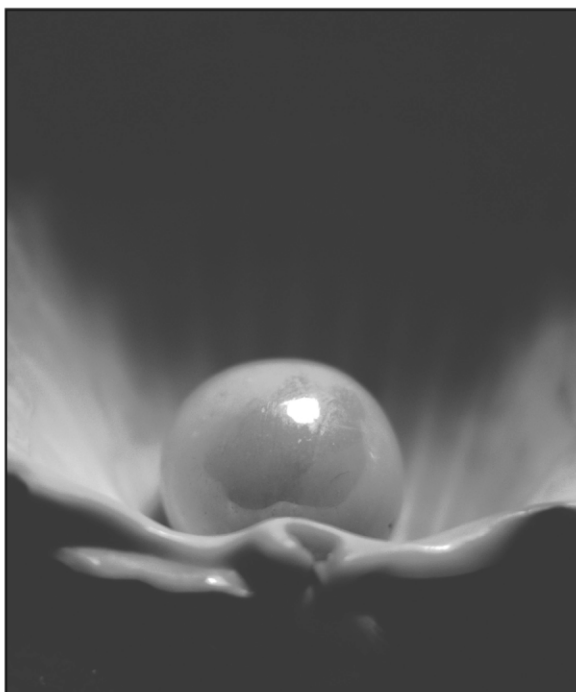
In conclusion, we have modified the surface of boehmite nanoparticles with an easy one-pot reaction by appending a silane that contains a cyclen moiety. These nanoparticles are able to complex lanthanide ions in aqueous solution and hold promise as potential new contrast agent media for MR applications.

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