

Synthesis, Characterization and Luminescent Properties of New Coordination Polymers Based on *p*-tert-Butylcalix[4]arene-tetracarboxylic acid and Lanthanide cations

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Abstract: A series of new coordination polymers based on *p*-tert-butylcalix[4]arene-tetracarboxylic acid with Eu³⁺ (1a), Tb³⁺ (1b) and Tm³⁺ (1c) were prepared by hydro and solvothermal methods. The obtained solid compounds were characterized by infrared and luminescence spectroscopy, powder X-ray diffraction, scanning electron microscopy and thermogravimetric analysis. The infrared curves and the x-ray diffraction patterns indicate that the same crystalline structure was obtained for all lanthanides.

Introduction

In recent decades the chemistry of calixarenes has been widely investigated due to their possible application in various fields such as: extraction and separation process of heavy metals, extraction of lanthanides ions from nuclear waste, catalysis, gas adsorption, sensors and luminescent devices [1-6].

According to the Pearson theory [7], lanthanide cations are classified as hard acids which may form strong complexes with ligands possessing hard donor sites, like oxygen or nitrogen atoms. Therefore, appropriately modified calixarenes are good candidates for hosting of such cations. Sabbatini *et al.* has shown that Tb³⁺ complex of *p*-tert-butylcalix[4]arene tetraacetamide shows a high luminescence quantum yield (0.2) and a long luminescence lifetime (1.5 ms) [8]. Although host-guest interactions of calixarene derivatives with lanthanide ions have been reported, very little is said about using calixarene derivatives as building blocks to grow extended coordination polymers [9]. Recently, it has been reported that the conformational changes of calixarene derivatives may be controlled by regulating the temperature of solvothermal reaction, what may lead to the generation of various coordination polymers with different poly-dimensional topological structures [10].

In the present work, we used *p*-tert-butylcalix[4]arene tetracarboxylic acid (Fig. 1) as a building block to prepare coordination polymers with lanthanide cations. Two different preparation methods were applied: hydrothermal in the case of Eu³⁺ and Tb³⁺ and solvothermal synthesis with Tm³⁺. Such issue is a great challenge and according to our best knowledge, trials to prepare coordination polymers using the investigated here ligand (1), have never been performed before. The obtained products were characterized by infrared and luminescence spectroscopy, powder X-ray diffraction, scanning electron microscopy and thermogravimetric analysis.

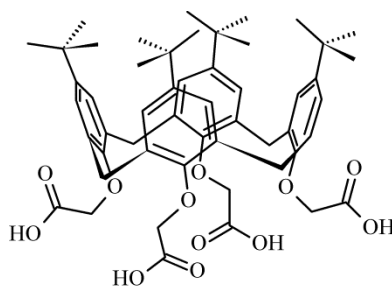


Fig. 1. Chemical structure of 25, 26, 27, 28 tetrakis(hydroxycarbonylmethoxy)-*p-tert*-butylcalix[4]arene (1) used to prepare coordination polymers

Experimental

Materials and Methods

IR spectra were recorded on a Bruker model IF66 using KBr pellets. Thermogravimetric analyses (TGA) were performed at a rate of 5 °C/min under N₂ using a DTG-60H of Shimadzu. Powder X-ray diffraction patterns (XRD) were collected in a Bruker D8 Advance diffractometer with Cu K α radiation (1.5418 Å) operating at 40 kV and 40 mA over the 2 θ range of 5-60°. Scanning electron microscopy (SEM) images were collected on Shimadzu SS-550 with tungsten filament coupled with EDS, working at 15 kV. Luminescent spectra were acquired on ISS PC1 Spectrofluorometer with an excitation monochromator equipped with a 300W xenon lamp. The emission was collected with a monochromator resolution of 0.1 nm equipped with a photomultiplier. All syntheses were carried out in a 23 ml Teflon-lined stainless steel reactor.

High purity TmCl₃.6H₂O was purchased from Aldrich and was used as received. EuCl₃.6H₂O and TbCl₃.6H₂O salts were obtained by treating the respective metal oxides with concentrated HCl. The organic solvents dimethylformamide (DMF) and acetonitrile (CH₃CN) were reagent grade and were used without further purification. Starting material, ligand: 25,26,27,28-tetrakis(hydroxycarbonylmethoxy)-*p-tert*-butylcalix[4]arene (1) was synthesized in the Department of Chemical Technology at GUT according to the procedure described in [11].

Hydrothermal Synthesis

The suspension of *p-tert*-butylcalix[4]arene tetracarboxylic acid (1) (0.3 mmol, 0.2640 g) in 10 mL of water was placed in a 23 mL Teflon-lined stainless steel reactor. After adjusting the pH to 5 using an aqueous 2M NaOH solution, salt of an appropriate lanthanide LnCl₃.6H₂O (Ln = Eu or Tb), (0.3 mmol, 0.1099 g of Eu³⁺ or 0.112 g of Tb³⁺, respectively) was added. The mixture was heated at 120°C for four days. After this time, the reactor was cooled slowly to room temperature. Unfortunately this synthetic method failed in producing good quality crystals suitable for single X-ray diffraction analysis. Powders of products (1a) and (1b) were isolated, collected by filtration, washed with water and dried in air.

Solvothermal Synthesis

In order to obtain crystals of coordination polymers based on calixarene-tetracarboxylic acid and lanthanide cations, the solvothermal reaction described by Lang *et al.* [10] was adopted with thulium cations.

Ligand (1) (0.06 mmol, 0.0528 g) and TmCl₃.6H₂O (0.06 mmol, 0.023 g) were dissolved in 12 mL of a solvent mixture DMF/CH₃CN (1:1) and 1M HCl (4.2 mL) was added. The mixture was heated at 90°C for 1 day. Subsequently, the reactor was left standing in order to cool down to the room temperature. Colorless block crystals of (1c) were collected by filtration, washed with CH₃CN and dried in air. The X-ray crystallographic analysis is currently in progress. For comparison, solvothermal synthesis using Eu³⁺ and Tb³⁺ cations was carried out, however the characterization part is actually in progress.

Results and Discussion

Both methodologies led to the novel coordination polymers based on calix[4]arene-carboxylic acid (1) and lanthanide cations: Eu^{3+} (1a), Tb^{3+} (1b) and Tm^{3+} (1c).

The compounds (1a), (1b) and (1c) show the same profile of thermal decomposition with the first weight loss 4% for (1a) and (1b) and 8% for (1c) corresponding to the coordinated water molecules around 180°C . The second big weight loss is attributed to decomposition of the organic part of the calixarene at about 250°C for (1a) and 300°C for (1b) and (1c).

Infrared spectroscopy

The infrared spectra of (1), (1a), (1b) and (1c) are shown in Fig. 2. The peak at 1742 cm^{-1} in ligand (1) spectrum corresponding to the stretching vibration of C=O carbonyl group is significantly shifted to 1585 , 1605 and 1612 cm^{-1} in structures (1a), (1b) and (1c) spectra, respectively. Therefore, it is assumed that the lanthanide cations are directly bonded to the oxygen carbonyl atoms. Moreover, additional band at 1694 cm^{-1} attributed to stretching vibration of another C=O carbonyl group may be observed in the spectrum of (1b), suggesting that rather unsymmetrical type or a mixture of coordination polymers was formed in this case. It may be supposed that lanthanide cations in all structures are not situated inside the cavity of calixarene as the peaks in the range of $1100\text{--}1200\text{ cm}^{-1}$ corresponding to the stretching vibrations of C-O etheral groups remained unchanged. It may not be excluded that in the case of structures with Eu^{3+} and Tb^{3+} , the unreacted starting material (1) is present in the structure as the residual peak at 1742 cm^{-1} may be visible.

The broad band at 3400 cm^{-1} may corresponds to the stretching vibration of O-H of both coordinated and lattice water molecules.

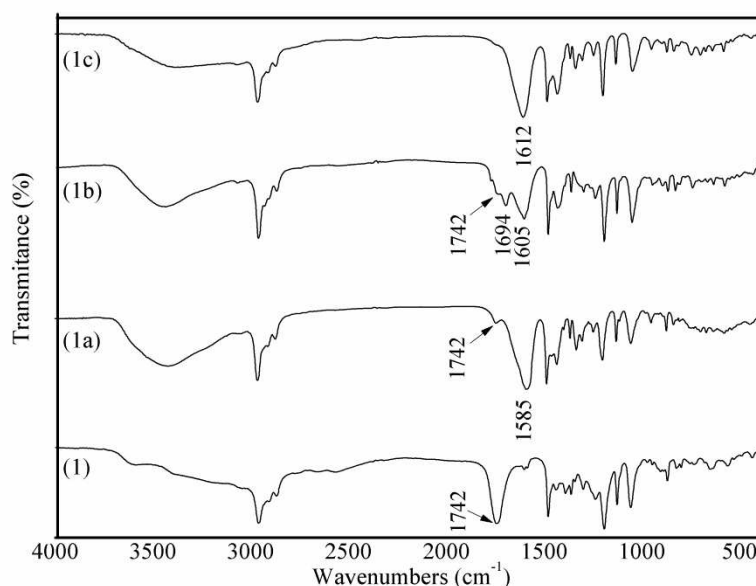


Fig. 2. IR spectra of coordination polymers (1a), (1b), (1c) and of calix[4]arene-acid (1)

Powder X-Ray Diffraction

In spite of different synthetic methods used, the X-ray diffraction patterns of (1a), (1b) and (1c) confirm that novel, similar structures were obtained. New peaks at 10.6 , 22.7 , 24.6 , 29.1 , 35.7 , 39.1 , 42.8 , 47.2 and 48.2 which does not occur in the pattern of (1) may be observed in all samples corresponding to the phase of expected coordination polymers with Eu^{3+} , Tb^{3+} and Tm^{3+} cations (Fig. 3). However, peaks attributed to the starting material (1) are visible in the XRD pattern of (1a) and (1b) what gives confirmation of IR results. Moreover, additional peaks in (1b) pattern probably assigned to another structure formed during the synthesis may be observed.

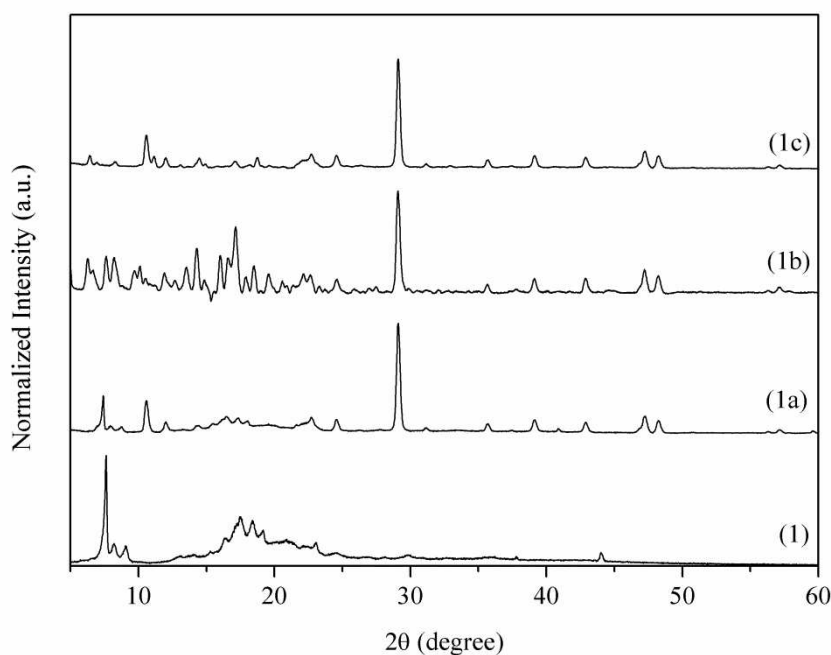


Fig. 3. XRD patterns of (1), (1a), (1b) and (1c)

Luminescent properties

The luminescence of the compounds (1a) and (1b) was investigated in solid state at room temperature. Characteristic emissions of Eu^{3+} (red) and Tb^{3+} (green) were observed when the compounds (1a) and (1b) were excited at 394 nm and 318 nm, respectively (Fig. 4). While (1a) showed intense emission at 616 nm only upon direct excitation of Eu^{3+} ion at 394 nm (level 5L6), (1b) showed strong emission at 545 nm upon ligand excitation at 318 nm. These results suggest that the studied calixarene derivative works as a good antenna for the Tb^{3+} ions. As a result, the emission peaks of the structures correspond to the transitions ${}^5\text{D}_0 \rightarrow {}^7\text{F}_n$ ($n = 0-4$) at 578, 591, 616, 650, 696 nm for Eu^{3+} ion in (1a) and the transitions ${}^5\text{D}_4 \rightarrow {}^7\text{F}_n$ ($n = 6, 5, 4$ and 3) at 490, 545, 585 and 619 nm for Tb^{3+} ion in (1b), respectively. It is well established that the characteristic luminescence of Eu^{3+} ions is slightly influenced by the surrounding ligands. Since the transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ shows three peaks, it is expected that europium ions occupy an environment of low symmetry. Additionally, (1a) and (1b) show short lifetimes of 0.29 and 0.42 ms, respectively. This can indicate that the non-radiative deactivation of the emitting state is more efficient in the compound containing europium.

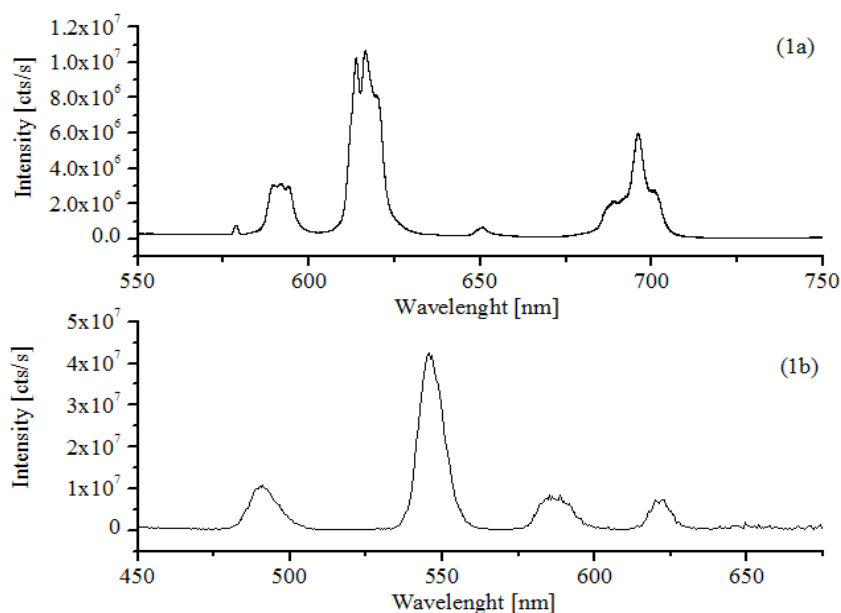


Fig. 4. Emission spectra of compound (1a), λ_{exc} (394 nm) and (1b), λ_{exc} (318 nm)

Scanning Electron Microscopy

The micrographs of (1), (1a), (1b) and (1c) are shown in Fig. 5. It can be seen that the calix[4]arene tetracarboxylic acid shows irregular agglomerates larger than $100 \mu\text{m}$. On the other hand, the samples (1a) and (1b) show a plate-like morphology, while in the sample (1c) no characteristic morphology can be identified. These results can indicate the formation of new structures based on lanthanides and the calix[4]arene tetracarboxylic acid.

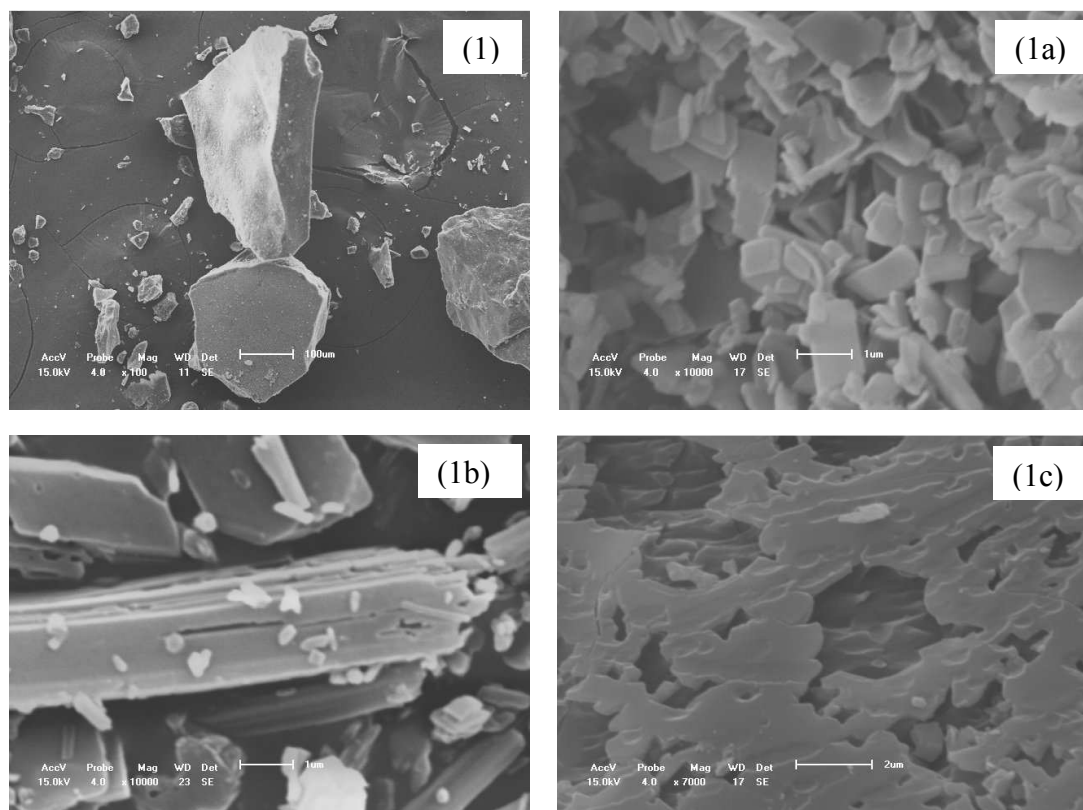


Fig. 5. SEM images of calix[4]arene tetracarboxylic acid (1) and of (1a), (1b) and (1c)

Conclusions

Three novel coordination polymers based on *p-tert*-butylcalix[4]arene-tetracarboxylic acid and lanthanide cations (Eu^{3+} , Tb^{3+} and Tm^{3+}) were prepared and then characterized by IR and luminescence spectroscopy, XRD, SEM and TGA. Structural analysis performed by XRD and Infrared spectroscopy indicates that all compounds show the same crystalline structure. Different synthetic methods were used in order to get suitably large crystals for structure determination by single-crystal x-ray diffraction. We used hydrothermal in the case of (1a) and (1b) and solvothermal reaction for preparation of (1c). The luminescent properties of structures (1a) and (1b) were investigated and strong green emission spectra was observed when exciting (1b) at 318 nm. On the other hand, direct excitation of the Eu^{3+} ion at 394 nm suggest by analyzing the emission lines that in such compounds, lanthanide ions occupied an environment of low symmetry.

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