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研究課題名（英文） Selective separation and extraction of Actinide and Lanthanide group rare earth metals by highly selective amide type novel ligands and nano-adsorbents

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研究成果の概要（和文）：ランタノイドイオン（Ln（Ⅲ））と安定に錯形成する、レアメタル選択的分離のための新しい機能材料を開発した。はじめに、メソ構造材料とＯとＮドナー配位子であるいくつかの異なるPTA誘導体を調整し、そのＰＴＡ誘導体をメソ多孔体上に固定化することに成功した。この配位子を固定化した材料は、そのネットワークサイトへのLn輸送に対し高効率で迅速な応答性示す。興味深いことに、Ln(III)を吸着した配位子－メソポーラス材料のＥＸＡＦＳデータはLn(III)特異的な配位子錯体の結果とよく一致しており、この材料がＬｎ（Ⅲ）イオン回収に特異的な機能を示すメソポーラス個体材料であることを明らかにした。

研究成果の概要（英文）：I have developed some new functional materials which appear through stable complexation with lanthanide (Ln(III)) ions for selective separation of rare metals. I prepared O and N-donor atoms as different PTA ligands. Then the PTA ligands were successfully anchored onto mesoporous ilica. The data also revealed that EXAFS data of specific Ln(III)-ligands complex were the same as Ln(III)-ligands-mesoprous materials which was very interesting and exceptional the solid functional mesoporous materials for Ln(III) ions recovery. The most significant point was: Ln(III) sorption was not affected by the presence of monovalent and divalent of sodium, potassium, calcium, magnesium, chloride, sulfate and nitrate ions due to strong tendency to form stable complexation with trivalent Ln(III). The EXAFS data revealed that O and N donor atoms of the nano-adsorbent were strongly coordinated to Ln(III) ions to form stable complexes.

研究分野： 工学

科研費の分科・細目： 構造、機能材料

キーワード： Nanomaterials　Functional groups　Lanthanide　Coordination　EXAFS

１．研究開始当初の背景

(1) The O and N-donor atoms containing different functional of Lewis base ligands were synthesized and subsequently anchored onto mesoporous silica as hybrid Lewis base adsorbents (HyLBA) for lanthanide (Ln) separation with stable coordination mechanism. The crystallography for the Ln and Lewis base ligands complex suggested that ligands were strongly coordinated to specific Ln with O and N by forming a stable complex with two 5–membered rings. The data clarified that bond lengths (average) between Ln and amide oxygen (2.32 Å) were shorter than Ln–N (2.662 Å) in phenanthroline moiety indicating strong O driven Lewis base ligands.

(2) The Ln coordination was also evaluated by EXAFS. The EXAFS data revealed that O and N-donor atoms of the HyLBA were strongly coordinated to Ln ions to form stable complexes. However, the bond distance of O donor atoms was also shorter than N donor atoms. The results suggested that HyLBA has a good prospect of promising applications for separation and recovery of Ln ions from effluents.

2. 研究の目的

(1) The lanthanide elements are increasingly used in many electronic devices such as lasers, high-intensity lightning, magnetic bubble memory films, refractive index lenses, fiber optics, superconductors, catalysts, polishing compounds and carbon arcs, refining industry and nuclear technology due to their specific properties. However, the source of lanthanide elements is minerals which consist of mixtures of several elements. The price of rare-earth elements increases and it is necessary to recovery them with cost effective materials [**1**]. In nuclear fuel cycle processing, radioactive heavy metals including lanthanide and actinide elements are generated from nuclear fission and multiple neutron capture reaction. Then the removal of these elements prior to geological disposal is really effective for long-term waste management. Therefore, separation, sorption and recovery of lanthanide from nuclear and metal-containing industrial waste streams are important both environmentally and economically. However, it is difficult to separate these elements as they have similar chemical properties.

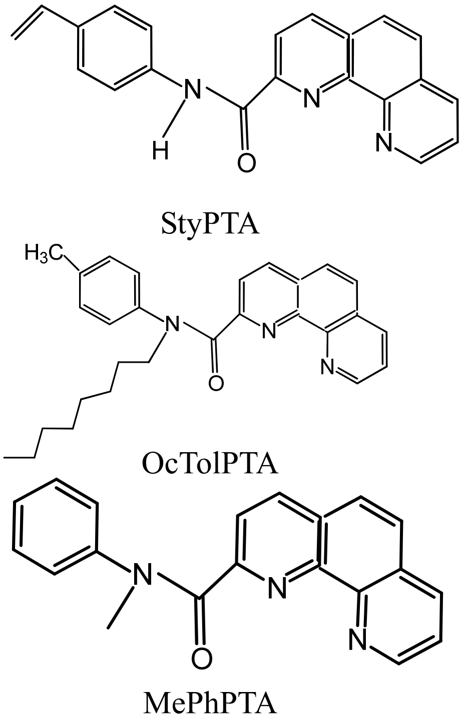
(2) There are various types of processes available such as solvent extraction, membrane separation, chemical absorption, ion exchange adsorbents, biosorption, and distillation to remove or recovery of the lanthanide elements [**2**]. In all the aforementioned literature, the lanthanide metals were successfully separated or adsorbed using either a solvent extraction process, or supported materials as solid-liquid extraction and sorption method. On the other hand, the coordination chemistry of lanthanide with O– and N– donor ligands has advanced due to the fact that steric factors can be optimized with the ligand set lanthanide contraction by choosing the best metal size from the lanthanide.

(3) The promising of O and N– donor ligand anchored adsorbents (HyLBA) for effective coordination ability of O and N–donor atoms with lanthanide are quite interesting aspect for effective stable coordination complexation mechanism during sorption system. Several parameters were investigated, such as O– and N– donor ligand preparation, characterization, mesoporous material processing, pH of the initial solution, sorption capacity, and recovery

by stripping agents. The lanthanide coordination and bonding mechanism were determined from the X-ray crystallography and EXAFS measurement. The lanthanide interaction mechanism in liquid state with O and N– donor ligand are almost the same as lanthanide coordination even at the solid state HyLBA according to EXAFS technique in this study which is very interesting aspect for selective lanthanide sorption and recovery systems [**3**].

3．研究の方法

(1) I have synthesized different functional group containing both O and N donor atoms Lewis base ligands as in **Fig. 1**. In preparation of various ligands, 1,10-phenanthroline-2-carboxylic acid (0.4 g, 1.78 mmol) was refluxed in thionyl chloride (6.35 g, 53.4 mmol) for 24 h, and then residual thionyl chloride was removed by rotary evaporation.



StyPTA

OcTolPTA

MePhPTA

Fig. 1. *Structure of different functional group containing O and N-donor atoms of Lewis base ligands.*

Without isolation and purification, the resulting 1,10-phenanthroline-2-carbonyl chloride was used in the subsequent step.

(2) Mesoporous silica monolith was synthesized by using direct templating method of lyotropic liquid crystalline phase of F108 as template. In typical conditions, the composition mass ratio of F108:TMOS:HCl/H_2O was 1.4:2:1 respectively. Homogeneous sol-gel synthesis was achieved by mixing F108/TMOS in a 200 mL beaker and then shaking at 60 °C until homogeneous. The exothermic hydrolysis and condensation of TMOS occurred rapidly by addition of acidified aqueous HCl (at pH = 1.3) solution to this homogeneous solution. The methanol produced from the TMOS hydrolysis was removed by using a diaphragm vacuum pump connected to a rotary evaporator at 45 °C. After that the materials were dried at 45 °C for 24 h to complete the drying process. The organic moieties were then removed by calcination at 500 °C for 6 h under normal atmosphere [**4**].

(3) The HyLBA was prepared via direct and indirect method. In direct anchored process, the Lewis base ligands (60 mg) were dissolved in *N*, *N*–dimethylformamide (DMF) and mesoporous silica added. After that, the mixture was stirred for 6 h and DMF was removed by evaporation method. In indirect immobilization method, 0.20 M ethanol solution of dilauryl dimethyl ammonium bromide (DDAB) and 1.0 g of mesoporous silica monoliths were immobilized. Then the Lewis base ligands (50 mg) in DMF solution was contacted with 1.0 g DDAB–masoporous silica materials. The immobilization procedure was performed under vacuum at 45 °C until Lewis base ligands saturation were achieved. Then the DMF was

removed by a vacuum connected to a rotary evaporator at 80 °C and the resulting adsorbent was washed with warm water to check the stability and elution of Lewis base ligands from mesoporous silica/DDAB–mesoporous silica. The ligands immobilized materials were dried at 45 °C for 6 h and grinded into fine powder as HyLBA for all experimental works.

4． 研究成果

(1)The crystal structure of the complex formed between Sm(III) and MePhPTA is isostructural as shown in **Fig. 2**. In this crystal complexation, two MePhPTA molecules, one nitrate ion and two water molecules were directly coordinated with Sm(III) to form stable 10–coordinate complex. This coordination number is often found for Sm(III) complexes [**5**]. However, the two nitrate ions and water molecules were in outer sphere in this complex. The MePhPTA molecules coordinated as tridentate ligand with two N atoms in phenanthroline moiety and one O atom in amide group. Moreover, aza–aromatic N donor was a comparatively soft donor, but N donors in MePhPTA molecules coordinated with hard f-element metal ion even in the presence of other hard O donor such as nitrate ions and water molecules. This tendency exhibits due to the presence of amide oxygen in MePhPTA which enhance the binding ability with lanthanide metal ions. The bond lengths between Sm(III) and amide oxygen (2.448 and 2.475 Å) were significantly shorter than Sm(III) and N bonds in phenanthroline moiety (2.609 and 2.662 Å), although the ionic radius of oxygen was not so different from that of nitrogen. The bond length between Sm(III) and amide oxygen is also shorter than Sm(III) and oxygen in the crystal formation of 10–coordinate hydrated complex as reported from Shannon's ionic radii (about 2.52 Å) [**6**].

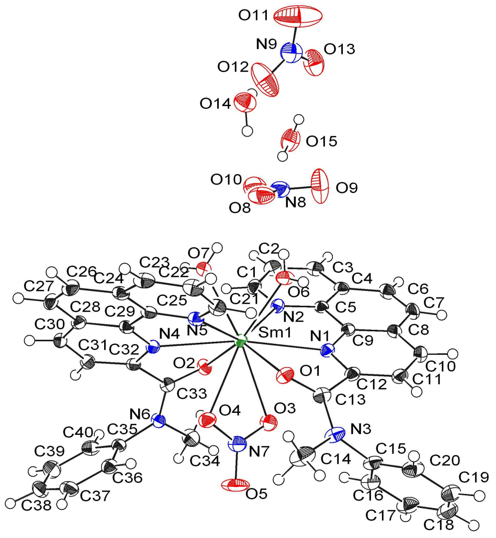


Fig. 2. *ORTEP drawing and numbering of* $Sm[(MePhPTA)NO_3(H_2O)_2](NO_3)_2(H_2O)_2$.

(2) The lanthanide coordination structures of Nd(III), Eu(III) and Yb(III) sorption on HyLBA are successfully investigated. **Fig. 3** shows the extracted EXAFS spectra their Fourier transform magnitude structural functions for lanthanide adsorbed HyLBA samples. All spectra showed a sharped peak at ~2.5 Å in the Fourier transform, which correspond to backscattering contributions from the nearest neighboring oxygen shell. Fitting of the first shell showed that Nd(III), Eu(III) and Yb(III)

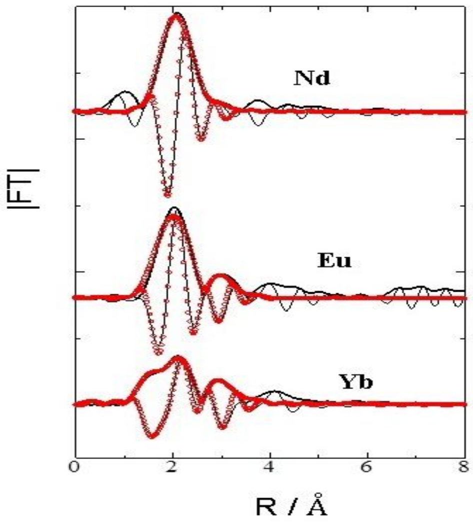


Fig. 3. *The corresponding Fourier transforme EXAFS oscillations of Nd(III), Eu(III) and Yb(III) complexes. The black lines are experimental, and red dotted lines are calculated.*

were coordinated with O and N atoms at specific bond distances. In Nd(III) adsorbed HA sample, the Nd–O bond distance in the first shell was 2.472 Å with 5.4 of O atoms and Nd–N was 2.976 Å with 7.0 of N atoms and the second shell Nd–C was 3.843 Å bond distance with coordination numbers of 11.7 with C atoms. However, the bond length between Ln–O and Ln–N are quite similar to the X–ray crystallographic complexes of Sm(III) with hybrid Lewis base ligand, where two ligand molecules were coordinated to one Sm(III) [**3**]. The FEFF simulation spectrum estimated from the crystal coordination adjacent to real spectrum, the coordination structure shows quite similar to the crystal structure. In the stable complexes of solid samples, the lanthanide and ligand ratio was also 1:2 according to curve fitting analyses. After immobilization of OcTolPTA ligand onto large pore mesoporous silica monoliths, the ligand movability was negligible. On the other hand, the ionic radii of Yb(III) is smaller than Eu(III) or Nd(III). Then, it is estimated that Coulombic interaction between Yb(III) and HyLBA is greater than that in case of Eu(III) or Nd(III), resulting in stronger interaction of Yb(III) with HyLBA than Eu(III) and Nd(III). Therefore, Yb(III) might overcome Eu(III) or Nd(III) in competition sorption operation and exhibited high sorption capacity as already indicated in preceding section.

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５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

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〔図書〕（計　0 件）

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名称：
発明者：
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種類：
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取得年月日：
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