# Tailoring of Organically Modified Silicas for the Solid−Liquid Extraction of Actinides

Stéphane Bourg,† Jean-Charles Broudic,† Olivier Conocar,† Joël J. E. Moreau,*,‡
Daniel Meyer,† and Michel Wong Chi Man‡

*CEA Valrho, DCC/DRRV/SPHA, Atalante, BP 171, 30207 Bagnols sur Cèze Cedex, France,
and Laboratoire de Chimie Organométallique, CNRS UMR 5076, ENSCM,
8 Rue de l'Ecole Normale, 34296, Montpellier Cedex 5, France*

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Hybrid materials with complexing properties toward lanthanides(III), americium(III), and plutonium(IV) are described. These new silica-based materials, containing malonamide ligands, have been prepared by sol−gel hydrolysis and condensation of a silylated tetraethylmalonamide in the presence of tetraethoxysilane (TEOS). A family of these hybrid materials was obtained by varying the amount of TEOS, the catalyst, and the $R_w$ ratio (amount of water added per Si−O bonds). The porous hybrids exhibited BET surface areas up to 300 $m^2\ g^{-1}$ with the average pore diameter ranging from 30 to 90 Å. The new hybrids were used as solid phase extractants in batch experiments for the extraction of americium and plutonium from high-level liquid wastes. The hybrids were shown to be highly efficient materials in solid−liquid extraction, exhibiting distribution coefficients up to $10^4$ and loading capacities up to 0.46 mequiv/g. They compared favorably to related silica-based material containing malonamide immobilized by classical techniques. The sol−gel approach allows one to adjust the ligand loading and to achieve some control and some tuning of the ligand environment since the oxide matrix is built around the complexing moieties. The use of templating techniques was also studied to enhance the extracting properties.

## Introduction

Sol−gel chemistry[1] is an important and versatile route for the synthesis of organically modified silicas.[2−7] Hybrid materials, prepared by sol−gel hydrolysis and condensation of alkoxy-silylated organic molecules, consist of a mixed three-dimensional network with a regular distribution of the organic fragment attached to the inorganic network. The incorporation of functionalized ligands opens interesting possibilities for metal complexation.[8,9]

The mild reaction conditions of this process allow the tailoring of the materials properties. The sol−gel approach also allows one to adjust the ligand loading and build the oxide matrix around the complexing moieties. Moreover, the complexing sites will be homogeneously distributed throughout the material. The drawback of the method is that, despite a high specific surface area and porosity, some of the ligands may not be accessible in the matrix. The choice of the complexing fragment and of the condensation conditions (dilution factor, amount of water, catalyst) should, however, allow one to achieve some control and some tuning of the ligand environment.

On the other hand, a better arrangement of the complexing fragments within the materials may result from using template-based approaches.[10] Imprinting methods have been used in cross-linked polymers as well as in silica gels[11−13] to prepare polymeric supports possessing solid-state organized structures. Molecular and supramolecular templating have been used to synthesize a broad range of organic and inorganic materials (Figure 1).[14−16] Recently, the extraction of uranyl ions from aqueous solutions using imprinted silicas was also

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* To whom correspondence should be addressed. Tel.: 04 67 14 72 11. Fax: 04 67 14 72 12. E-mail: jmoreau@cit.enscm.fr.

† CEA Valrho.

‡ ENSCM.

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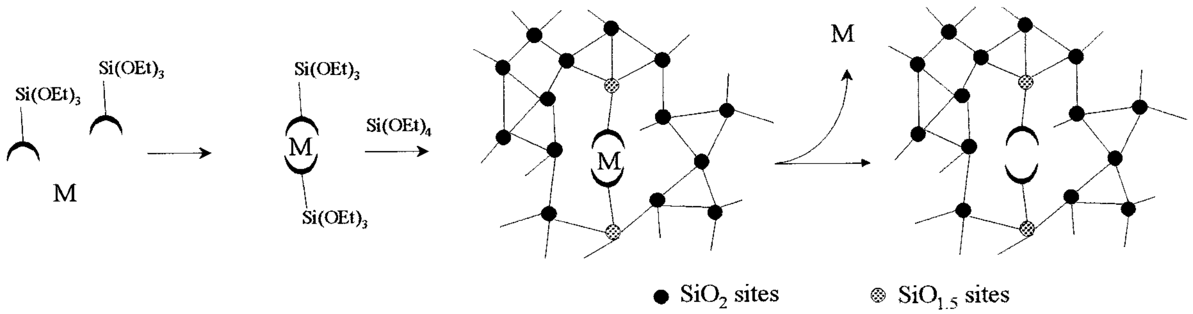
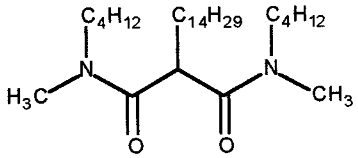


**Figure 1.** General synthetic route for imprinted materials.

described.[17,18] Therefore, if such a process is used with hybrid organic–inorganic gels, a predetermined arrangement of the potential ligands could be obtained if the ligand is also a complexing agent of the metal template. This organization of the ligands could increase the complexing ability of organically modified silicas. Such materials are of interest in heterogeneous catalysis[19] and as solid supports in extraction chromatography.

One potential application of this chemistry is the elaboration of new specific solid extractants for the treatment of the acidic aqueous high-level liquid waste (HLLW) produced by the nuclear industry and research. In the field of spent nuclear fuel reprocessing, liquid–liquid extraction and the use of organic extractants such as tributyl phosphate (TBP),[20] carbamoylmethylphosphine oxide (CMPO),[21] or malonamide derivatives improved radionuclides separation performances. However, the high diversity of the HLLW arising from the retreatment was hardly accommodating with the use of liquid–liquid extraction techniques. In the field of solid–liquid extraction, ion exchange chromatography using resins such as DIPHONIX [22] (sulfonic and diphosponic resin, which extracts valence III, IV, and VI actinides) or Reillex HPQ [23] (a polyvinylpyridine-based resin, which is Pu(IV) selective) were then investigated. In those cases, the major problem arose from the aging of the resins, which accumulate nuclides, leading to a potential risk of criticality. The organic extractants, previously developed for liquid–liquid chromatography, can be impregnated on an organic or an inorganic support to avoid the anion exchange extraction (for example, CMPO on organic resin[24] or on silica for Pu and U extraction[25]). Malonamide bidentate ligands, which complex actinides (III, IV, and VI) and lanthanides,[26,27] are of particular interest because they can be totally incinerated and are relatively stable under ionizing irradiations and strong acidic conditions.[28,29] A lot of work was carried out to optimize the formula of the diamide, leading for example to compound **1** (Figure 2), which exhibits enhanced extraction properties.[30,31]



**1**

**Figure 2.** *N*,*N*′-Dimethyl-*N*,*N*′-dibutyltetradecylmalonamide (DMDBTDMA).

Our current interest in silica-based organic–inorganic hybrids led us to study these materials for the extraction of Pu(IV) and Am(III) from HLLW. Complexation of these radionucleides by functionalized silicas seemed of interest for a solid–liquid separation technique and also for the confinement of these elements since vitrification or ceramization of the complexed silica-based materials can be achieved. We were interested in exploring the preparation of hybrid materials with complexing properties toward actinides upon hydrolysis and condensation of alkoxide ligands, which can be obtained by introduction of $Si(OR)_3$ groups. Only a few examples of the extraction of lanthanides and actinides with hybrid materials are described in the literature.[32,33] We studied the preparation of new hybrid materials containing malonamide ligands. Our initial results showed that the presence of the malonamide functionality on the surface of the hybrid material led to nearly quantitative extraction of the target metal ions.[34] Distribution coefficients, $K_d$, as high as $10^4$ and loading capacities up to 0.6

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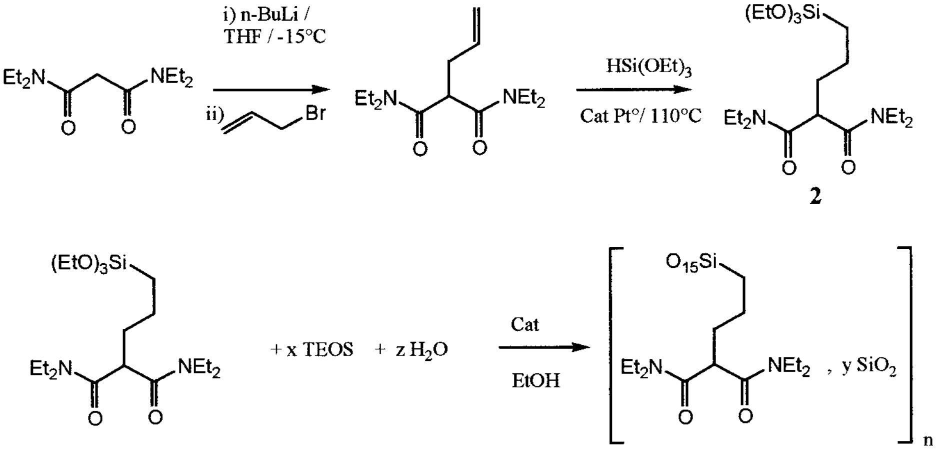
**Scheme 1. Synthesis of Precursor 2 and of the Hybrid Silicas 3, 4, 5, 6a−c, and 7a−c**



2

**3**, x=2, z=5.5, cat:$NH_4F$
**4**, x=3, z=7.5, cat:$NH_4F$
**5**, x=4, z=9.5, cat:$NH_4F$
**6a-c**, x=5, z=11.5, 23, 46, cat: $NH_4F$
**7a-c**, x=5, z=11.5, 23, 46, cat: $HNO_3$

mequiv/g were observed. We have focused here on the preparation of hybrids based on silylated malonamide **2** for the extraction of Pu(IV), Am(III), and Ln(III) from acidic aqueous waste. Moreover, compared to primary amides, we can expect malonamide such as **2** to exhibit a more lipophilic behavior. Malonamide **2** was chosen because its immobilization offers a possible comparison with known materials containing the noncovalently attached compound **1**.

In the first part of this study, materials were prepared by varying the experimental conditions of the synthesis: the influence of dilution rate of the precursor in tetraethoxysilane $Si(OEt)_4$ (TEOS), the influence of the amount of water per Si−O bond ($R_w$ ratio), and the nature of the catalyst (nucleophilic or acidic) are studied. All these parameters can greatly influence the properties of the materials. We also synthesized templated materials to examine the effect on the extracting properties of a pre-organization of the ligand by metal ion templates before the sol−gel condensation. In the second part of this study, the extraction properties of all materials are discussed and the results are compared with those obtained with related impregnated and grafted materials.

## Results and Discussion

**Synthesis of Organically Modified Silicas.** Synthesis of Precursor **2.** The malonamide precursor **2** was obtained in two steps from *N*,*N*,*N*,*N*-tetraethylmalonamide by alkylation at the central carbon with allylbromide, followed by hydrosilylation with triethoxysilane in the presence of a platinum catalyst (Scheme 1).

*Synthesis of Hybrid Silicas **3**−**7**.* To study the influence of the dilution rate on the extraction properties, the hydrolysis and condensation of precursor **2** were performed in the presence of 2, 3, 4, and 5 molar equivalents of tetraethoxysilane: TEOS. The reaction was performed in ethanol with the concentration of **2** varying from 0.16 to 0.33 mol/L and that of TEOS from 0.66 to 0.84. $NH_4F$ ($5 \times 10^{-5}$ mol) was used as the catalyst. The amount of water per Si−O bond, $R_w$ ratio, was fixed at 50% (Scheme 1). Gelation occurred in 4−12 h. After aging for 1 week, the materials were then powdered and washed with acetone and diethyl ether to give xerogels **3**−**6a**.

**Table 1. Main Molar Ratio[a] of Hybrid Silicas 3, 4, 5, 6a−c, 7a−c, 10a−c, and 11a−c**

| gel | N/Si found | N/Si calcd | *y*[b] | *x*[c] | C/Si found | C/Si calcd | H/Si found | H/Si calcd |
|---|---|---|---|---|---|---|---|---|
| **3** | 0.41 | 0.67 | 3.3 | 2 | 3.18 | 3.26 | 6.93 | 6.28 |
| **4** | 0.35 | 0.5 | 4.3 | 3 | 3.24 | 2.64 | 6.37 | 5.09 |
| **5** | 0.29 | 0.4 | 5.5 | 4 | 2.26 | 2.15 | 5.23 | 4.15 |
| **6a** | 0.24 | 0.33 | 6.9 | 5 | 2.18 | 1.77 | 4.77 | 3.42 |
| **6b** | 0.14 | 0.33 | 13.1 | 5 | 1.09 | 1.77 | 2.72 | 3.42 |
| **6c** | 0.19 | 0.33 | 9.3 | 5 | 1.41 | 1.77 | 3.21 | 3.42 |
| **7a** | 0.25 | 0.33 | 7.0 | 5 | 1.82 | 1.77 | 4.54 | 3.42 |
| **7b** | 0.24 | 0.33 | 7.5 | 5 | 1.98 | 1.77 | 4.32 | 3.42 |
| **7c** | 0.30 | 0.33 | 5.6 | 5 | 2.08 | 1.77 | 4.94 | 3.42 |
| **10a** |  | 0.33 |  | 5 |  | 1.77 |  | 3.42 |
| **10b** | 0.20 | 0.33 | 5.72 | 5 | 2.05 | 1.77 | 5.15 | 3.42 |
| **10c** | 0.22 | 0.33 | 8.02 | 5 | 1.54 | 1.77 | 3.78 | 3.42 |
| **11a** | 0.18 | 0.33 | 9.79 | 5 | 1.91 | 1.77 | 4.76 | 3.42 |
| **11b** |  | 0.33 |  | 5 |  | 1.77 |  | 3.42 |
| **11c** | 0.27 | 0.33 | 6.20 | 5 | 1.93 | 1.77 | 4.64 | 3.42 |

[a] Determined on the basis of elemental analysis (cf. Experimental Section). [b] Silicate vs silsequioxane ratio (cf. Scheme 1) calculated on the basis of N and Si elemental analyses. [c] Moles of TEOS used (cf. Scheme 1).

The resulting solids were analyzed and the results are presented in Table 1. Elemental analyses show that, on the basis of the N/Si molar ratio, only 70% of the malonamide moieties remained in the material. The composition silicate vs silsesquioxane ratio, *y*, differs somewhat from initial stoichiometry, *x*, in the initial reaction mixture (Scheme 1). It probably arises from a slower hydrolysis and condensation of precursor **2** compared to those of TEOS. The C/Si and H/Si values are higher than the expected values for a silsesquioxane stoichiometry and account for an incomplete hydrolysis of the precursors and the presence of residual uncondensed Si−O−Et and Si−OH groups in the hybrid network.

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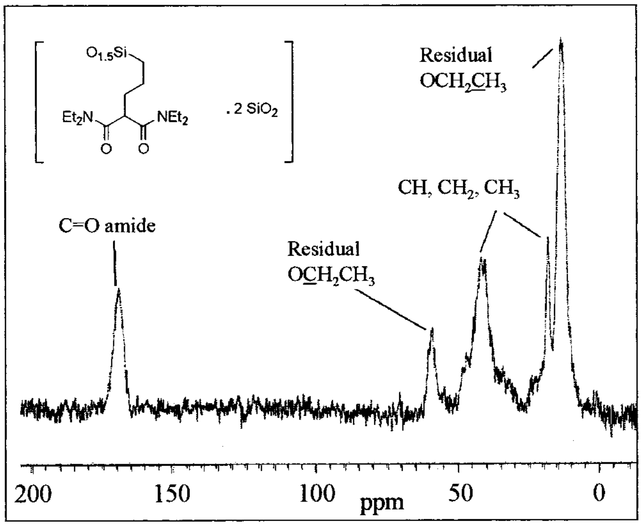

**Figure 3.** $^{13}$C CP-MAS NMR spectrum of hybrid silica **3**.

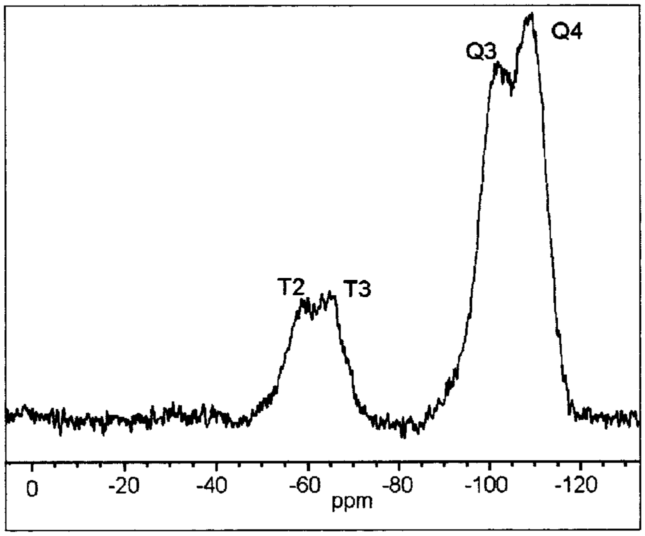

**Figure 4.** $^{29}$Si CP-MAS NMR spectrum of hybrid silica **3**.

The infrared spectra were very similar for all the hybrid materials **3**−**6a**, whatever the dilution factor. They exhibit specific vibration frequencies at 1640 cm$^{-1}$ ($\nu_{C=O}$) and 950 cm$^{-1}$ ($\delta_{Si-OH}$). The $^{13}$C solid state NMR spectra clearly show the presence of the amide groups with resonances at 170 ppm (C=O) and at 60 and 15 ppm (residual OEt groups) as shown in Figure 3. The $^{29}$Si NMR spectra show the expected resonance lines indicative of the presence of T, $CSiO_3$ substructures in the region −60 to −70 ppm, and also the resonances arising from the presence of Q, $SiO_4$ substructures. The $^{29}$Si NMR spectra were similar for all the gels and the spectrum of the gel **3** is given as an example (Figure 4). Although the $^{29}$Si NMR measurements using CP-MAS cannot be analyzed on a quantitative basis, the obtained spectra exhibiting high intensities for $T^3$ lines are consistent with a high degree of condensation of the organic subunit in the material.[4,6]

We studied the surface and porosity properties of the xerogels by using nitrogen sorption experiments according to BET and BJH calculations.[35−37] A priori, the specific surface area can influence the percentage of accessible complexing sites and then the distribution coefficients and the capacities whereas the pore distribution has an influence on the extraction kinetics. Results on the total pore volumes, BET surface areas, and average pore diameters of the gels are given in Table 2. Gels **3**, **4**, and **5** were nonporous with respect to $N_2$ and showed low BET surface areas (2−3 m$^2$/g). For gel **6a**, prepared with 5 equiv of TEOS, the surface area increased to 234 m$^2$/g for a total porous volume of 0.54 mL/g and an average pore diameter of 90 Å. The adsorption−desorption isotherm of gel **6a** belongs to class IV according to the Brunauer classification.[38] The type E hysteresis, according to the De Boer classification,[39,40] arises from the presence of bottleneck shape mesopores. The pore size distribution, obtained by BJH calculation, was quite large and bimodal, ranging from 50 to 150 Å. Scanning electron microscopy (SEM) of the hybrid silicas gave some information on the macroporosity. An SEM photo of gel **6a** showed a granular surface. Some 0.1-$\mu$m-diameter pores were observed. These observations are in agreement with the above porosity results.

**Table 2. Textural Characterization of Hybrid Silicas 3, 4, 5, 6a−c, 7a−c, 10a−c, and 11a−c**

| gel | catalyst | template | $R_w$ ratio[a] (%) | BET surface (m$^2$/g) | pore volume (mL/g) | pore diameter[b] (Å) |
|---|---|---|---|---|---|---|
| **3** | $NH_4F$ | none | 50 | 2 | n.p.[c] | |
| **4** | $NH_4F$ | none | 50 | 3 | n.p. | |
| **5** | $NH_4F$ | none | 50 | 2 | n.p. | |
| **6a** | $NH_4F$ | none | 50 | 234 | 0.54 | 92 |
| **6b** | $NH_4F$ | none | 100 | 290 | 0.5 | 69 |
| **6c** | $NH_4F$ | none | 200 | 315 | 0.4 | 51 |
| **7a** | $HNO_3$ | none | 50 | <0.1 | n.p. | |
| **7b** | $HNO_3$ | none | 100 | <0.1 | n.p. | |
| **7c** | $HNO_3$ | none | 200 | <0.1 | n.p. | |
| **10a** | $HNO_3$ | $Nd(NO_3)_3$ | 50 | 7 | n.p. | |
| **10b** | $HNO_3$ | $Nd(NO_3)_3$ | 100 | 6.5 | n.p. | |
| **10c** | $HNO_3$ | $Nd(NO_3)_3$ | 200 | 10 | n.p. | |
| **11a** | $HNO_3$ | $Eu(NO_3)_3$ | 50 | 3 | n.p. | |
| **11b** | $HNO_3$ | $Eu(NO_3)_3$ | 100 | 5 | n.p. | |
| **11c** | $HNO_3$ | $Eu(NO_3)_3$ | 200 | 7 | n.p. | |

[a] Amount of water per Si−O bonds. [b] Calculated with the formula: $Ø_p = [V_p(mL/g)/S(m^2/g)] \times (4 \times 10^4)$, assuming a cylindrical shape of the pores. [c] Nonporous.

To complete the set of extracting materials, we also synthesized hybrid silicas **6** and **7** by varying either the nature of the catalyst or the $R_w$ ratio. The TEOS dilution factor was then fixed to 5 (Scheme 1). Elemental analyses also showed in these cases that the malonamide ligands were not totally incorporated into these hybrid silicas (Table 1). The hydrolysis of **2** partly formed poorly condensed species, which were eliminated upon washing of the gel. Silicas **6a**−**c** were obtained from ethanol solutions containing 1 equiv of precursor

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**2** (0.16 M in EtOH), 5 equiv of TEOS (0.84 M in EtOH), and 11.5, 23, or 46 equiv of water in the presence of 5 × $10^{-5}$ mol of $NH_4F$ as the catalyst. Gelation occurred in <12 h. Gels were aged for 1 week. These materials were mesoporous, with BET surface areas between 235 and 315 $m^2/g$ (Table 2). The increase of the $R_w$ ratio had very little influence on the BET surface area but lead to a decrease of the average pore diameters from 90 to 50 Å. Silicas **7a**−**c** were obtained from ethanol solutions containing 1 equiv of precursor **2** (0.16 M in EtOH), 5 equiv of TEOS (0.84 M in EtOH), and 11.5, 23, or 46 equiv of water. $HNO_3$ (5 × $10^{-5}$ mol) was added as the catalyst. The gels formed in <24 h at 50 °C and were then aged for 1 week. Gels **7**, resulting from acid catalysis, had porosity properties quite different from those of gels **6**. The materials **7** were nonporous with respect to $N_2$ and showed BET surface areas lower than 0.1 $m^2/g$ (Table 2).

We also prepared related silica-based materials **8** and **9** for comparison. Silica **8** was prepared by noncovalent impregnation of silica with *N,N′*-dimethyl-*N,N′*-dibutyltetradecyl malonamide **1**.[41] The surface-silylated silica **9** was prepared according to a classical procedure first by activating silica[42] and then refluxed with precursor **2** in toluene.[43] The solids **8** and **9** exhibited BET surface areas (300 $m^2/g$) similar to those of gel **6a**.

*Synthesis and Characterization of Templated Materials **10** and **11**.* Imprinting techniques were investigated with the aim of improving the properties of these materials. We studied the use of metal ion as temporary templates in the synthesis of the hybrid materials. It was not possible to synthesize imprinted materials using $NH_4F$ as the catalyst, owing to a ligand exchange reaction between $Ln(NO_3)_3$ and the catalyst, leading to a precipitate. We then chose $HNO_3$ as the acidic catalyst to reproduce the media of the HLLW. Templated silicas **10a**−**c** and **11a**−**c** were synthesized like the previous gels, from EtOH solutions, with 1 equiv of precursor **2** (0.16 M in EtOH), 5 equiv of TEOS (0.84 M in EtOH), 11.5, 23, or 46 equiv of water and by addition of 0.5 equiv of $Ln(NO_3)_3$ (**10a**−**c**; Ln = Nd; **11a**−**c**, Ln = Eu); $HNO_3$ (5 × $10^{-5}$ mol) was also added as the catalyst. The molar ratio precursor **2**/$Ln(NO_3)_3$ corresponds to the common stoichiometry of a diamide/lanthanide(III) complex. Gelation occurred in <24 h at 50 °C. Gels were aged for 1 week. The lanthanide was then removed by washing the gels with a 0.01 M $HNO_3$ solution. More than 80% of the metal was extracted. Main molar values resulting from elemental analyses are given Table 1. All the templated materials exhibited low porosity with respect to $N_2$ and low BET surface areas: between 3 and 10 $m^2/g$ (Table 2); nonetheless, these materials exhibit BET surface areas 100 times higher than those of the nontemplated materials.

**Extraction Properties of the Hybrid Silicas for Ln(III), Am(III), and Pu(IV).** For all the synthesized silicas, distribution coefficients and capacities were determined for Ln(III), Am(III), and Pu(IV) in batch extraction experiments. Typically, a known quantity of gel was added to a known volume of a solution containing Am, Ln, or Pu. After being stirred for 2 h, the solutions were centrifuged and filtered. Kinetic measurements showed that, for all the silicas, after 2 h, equilibrium was reached. An example of the extraction kinetics for the gel **6a** is shown in Figure 5. The maximum was reached within 20 min.

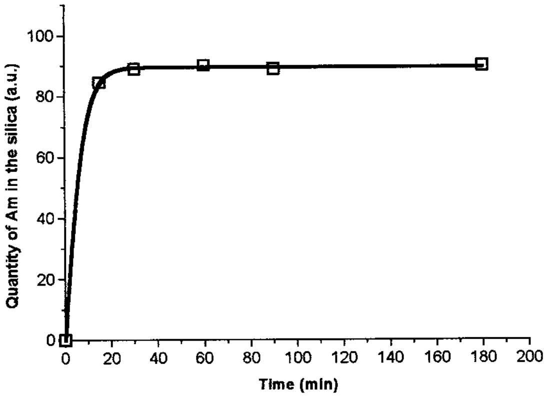

**Figure 5.** Kinetic of extraction of Am(III) for hybrid silica **6a**.

**Table 3. Extraction Properties for Hybrid Silicas 3, 4, 5, 6a−c, 7a−c, 10a−c and 11a−c**

| | $K_d$ (mL/g)[a] | | | | capacity (mequiv/g)[b] | | |
|---|---|---|---|---|---|---|---|
| gel | Nd | Eu | Am(III) | Pu(IV) | Nd | Eu | Pu(IV) |
| **3** | | | 380 | 1800 | | | 0.04 |
| **4** | | | 320 | 1900 | | | 0.02 |
| **5** | | | 170 | 1150 | | | 0.01 |
| **6a** | 100 | | 140 | 3900 | 0.06 | | 0.46 |
| **6b** | 90 | | 140 | 9100 | 0.03 | | 0.31 |
| **6c** | 150 | | 160 | 3250 | 0.04 | | 0.38 |
| **7a** | 5 | 10 | 40 | 30 | <0.01 | <0.01 | 0 |
| **7b** | 50 | 60 | 110 | | <0.01 | <0.01 | |
| **7c** | 100 | 100 | 250 | 8400 | 0.08 | 0.07 | 0.01 |
| **10a** | 40 | 80 | 20 | 1100 | <0.01 | <0.01 | 0.02 |
| **10b** | 100 | 330 | 240 | | 0.27 | 0.28 | |
| **10c** | 440 | 670 | 1160 | 12300 | 0.12 | 0.11 | 0.06 |
| **11a** | 50 | | 90 | 5400 | 0.01 | <0.01 | 0.02 |
| **11b** | 290 | 210 | 450 | | 0.23 | 0.12 | |
| **11c** | 500 | 390 | 770 | 6800 | 0.14 | 0.11 | 0.01 |

[a] The measurements of the distribution coefficients were performed under conditions where the metal is in very low concentration, using 1−4 mL of an aqueous nitric acid solution: $[HNO_3]$ = 3.5 M, $[M]_o$ = 4 × $10^{-5}$ M, and 25 mg of hybrid gel. [b] Capacities were measured at $[HNO_3]$ = 3.5 M.

*Distribution Coefficients ($K_d$).* In solid−liquid extraction, the distribution coefficient $K_d$ is defined as the ratio of the number of moles in the solid phase (in mol/g) by the number of moles in the liquid phase (in mol/mL) at equilibrium. The measurements were made under conditions where the metal is in very low concentration in an aqueous nitric acid 3.5 M solution. The distribution coefficients of Ln(III), Am(III), and Pu(IV) are given in Table 3 for the **3**−**7** silicas. Whatever the material, the $K_d$ values of Pu(IV), 1000−9000 mL/g, are 1−2 orders of magnitude higher than those of Ln(III) and Am(III), 100−400 mL/g. The coordination chemistries of Am and Pu are different. For Am(III), species of type Am(malonamide)$_x$H$_y$(NO$_3$)$_{(3-y)}$, with an *x* value up to 5, and for Pu(IV), species of type Pu(malonamide)$_2$(NO$_3$)$_4$ were characterized in malonamide liquid solution.[26,27] Therefore, the complexation sites of these metals in the solid material may be different. This would result in different $K_d$ values for these metals, which can vary according to the nature of the solid material.

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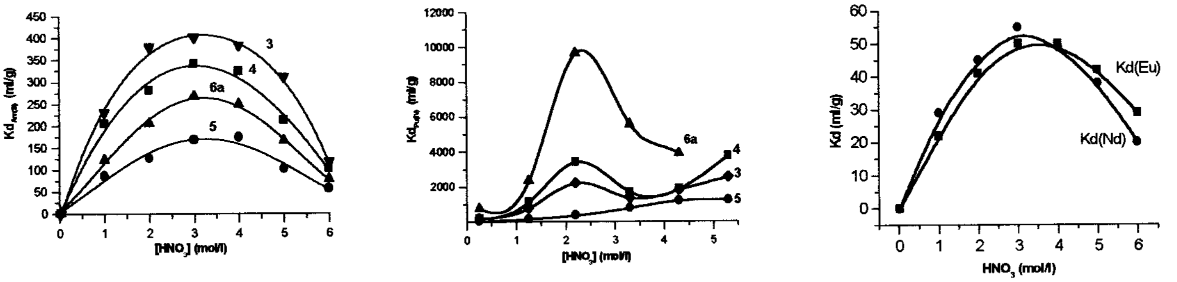
(42) Ave, W. A.; Hastings, C. R. *J. Chromatogr.* **1969**, *42*, 319.
(43) Carpino, L.; Knapczyk, J.; Mansour, E. M. E. *J. Org. Chem.* **1983**, *48*, 5.



(a) (b) (c)

**Figure 6.** $K_d$ values for Am (a) and Pu (b) vs [HNO$_3$] for hybrids **3**, **4**, **5**, and **6a** and $K_d$ values for Nd and Eu (c) vs [HNO$_3$] for hybrid **7b**.

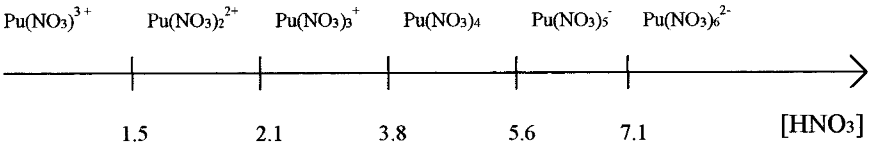


**Figure 7.** Pu(IV) speciation established by Lipis et al.[44]

For the extraction of Am(III), the increase of the TEOS dilution factor from 2 to 5 (materials **3**, **4**, **5**, and **6a**) leads to a decrease of the $K_d$ values, whatever the specific surface area. This is consistent with the decrease of the number of complexing sites per gram of solid, due to the dilution. The nature of the catalyst used to synthesize the hybrid silicas can influence their properties. Regarding the $K_d$ values, with the exception of **7a**, the materials **6a**–**c** and **7b,c** showed similar distribution coefficients. The $R_w$ ratio has no effect on the $K_d$ values of Am(III) and Ln(III) with materials **6a**–**c**. However, for materials **7a**–**c**, an increase of the $R_w$ ratio leads to an increase of these $K_d$ values. For the extraction of Pu(IV), the surface area seems to influence the $K_d$ values to a larger extent than the dilution factor.

Interestingly, the $K_d$ values depend on the concentration of the aqueous nitric acid solution, as shown in Figure 6. The $K_d$ of Am, Nd, and Eu reach a maximum for a 3.5 M HNO$_3$ concentration, whereas the maximum $K_d$ value of Pu appears at 2.5 M HNO$_3$ concentration. This observation is of great interest in a fixation–elution process. At [HNO$_3$] = 3.5 M, the nuclides are fixed on the materials, whereas at [HNO$_3$] = 0.01 M, they are eluted. This behavior can be explained by the nature of the Am(III) or Pu(IV) complexes in solution, which depends on the concentration of nitric acid. In the case of Am(III), an extraction competition between Am(III) and HNO$_3$ leads to a decrease of the $K_d$ values of Am for a nitric acid concentration over 4 M.[27] The chemistry of Pu(IV) is more complex since Lipis et al. showed that at least six Pu(IV) complexes can exist as a function of the acidity (Figure 7).[44]

**Table 4. Comparison of Extraction Properties for Hybrid Silica 6a and Silicas 8, 9**

| extracting material | extractant content | $K_d$ Am(III) (mL/g)[a] | $K_d$ Pu(IV) (mL/g)[a] | capacity Pu(IV) (mequiv/g)[b] |
|---|---|---|---|---|
| **6a** | 1.38 | 230 | 3900 | 0.46 |
| **8** | 0.46 | 10 | 2980 | 0.29 |
| **9** | 0.42 | 30 | 560 | 0.21 |

[a] The measurements of the distribution coefficients were performed under conditions where the metal is in very low concentration, using 1–4 mL of an aqueous nitric acid solution: [HNO$_3$] = 4 M, $[M]_0 = 8.5 \times 10^{-5}$ M, and 30–50 mg of hybrid gel. [b] Capacities were measured at [HNO$_3$] = 4.7 M.

*Capacities.* In solid–liquid extraction, the capacities are defined as the quantity of metal (in mg or in mequiv) extracted in the mass unit of solid phase (in g). The measured capacities of hybrid silicas **3**–**7** are given Table 3. Calculated maximum capacities of the hybrid materials can be deduced from the analysis results. They showed a malonamide content varying from 0.9 to 2 mequiv/g (cf. Experimental Section). Assuming a 1:2 metal–ligand stoichiometry, the maximum capacities of gels **3**–**11** should vary between 0.45 and 1 mequiv/g. Materials **3, 4, 5,** and **7a**–**c**, with no specific surface area, have very low Pu(IV) capacities, whereas these values in the case of gels **6a**–**c** respectively reach 0.46, 0.31, and 0.38 mequiv/g. The respective calculated maximum capacities are 1.38, 0.92, and 1.18 mequiv/g. In all cases, Ln(III) capacities are very low, between 0.04 and 0.1 mequiv/g. Clearly, the number of accessible sites is much higher when the material has a high surface area. It may indicate that the ligand lay at the surface of the solid, whereas for materials with low porosity, the ligands may be embedded in the silica matrix.

*Comparison of Hybrid Material **6a** with Related Impregnated Silica **8** and Grafted Silica **9**.* Table 4 summarizes the main characteristics of the extracting materials **6a**, **8**, and **9**. Compared to those of **8** and **9**, higher distribution coefficients were observed with the hybrid **6a** both for Am(III) and Pu(IV). Also, a higher capacity was measured for Pu(IV), 0.46 mequiv/g vs 0.29 and 0.21 mequiv/g respectively for **8** and **9** at 4.2 M HNO$_3$ (Table 4). Moreover, the analyses of **6a** showed a malonamide content of 1.38 mmol/g in the material. The loading values determined for **8** and **9** were lower, 0.46 and 0.42 mmol/g, respectively. It is interesting to note that the measured capacity in Pu(IV) with **6a** assuming a 1:2 Pu(IV)/malonamide complex was about 60% of its potential value with respect to the total malonamide content. Therefore, the complexing sites in **6a** are not all accessible to the metal ion. A tuning of the pore structure of this material should allow an

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[44] Lipis, L. V.; Pozharrskii, B. G.; Fomin, V. V. *J. Struct. Chem. USSR* **1960**, *1*, 125.

**Table 5. Separation Factors Am/Ln (Ln = Nd, Eu) for Gels 7a−c, 10a−c, and 11a−c**

| | gel | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **7a** | **7b** | **7c** | **10a** | **10b** | **10c** | **11a** | **11b** | **11c** |
| α(Am/Nd) | 10.8 | 2.2 | 2.5 | 0.5 | 2.4 | 2.6 | 1.7 | 1.6 | 1.5 |
| α(Am/Eu) | 5.4 | 1.7 | 2.5 | 0.2 | 0.7 | 1.7 | | 2.2 | 2.0 |

increase of the number of accessible malonamide complexing groups. Therefore, it may allow an increase of the Pu(IV) loading capacities of these materials.

*Templated Materials.* The distribution coefficients and capacities of the imprinted silicas **10a−c** and **11a−c** were measured for Am(III), Ln(III), and Pu(IV), under the same conditions as those for the previous materials and are shown in Table 3. Interestingly, very high $K_d$ values of Am(III) can then be obtained, 4 times higher than the best result obtained with the nontemplated materials. The $K_d$ values of Pu(IV) remained in the same range as those of the previous materials. In all the cases, the increase of the $R_w$ ratio leads to an increase of the $K_d$ values. Concerning the $K_d$ values of Eu(III) and Nd(III), differences are observed according to the nature of the metal ion used as the template. This is not related to the differences in selectivities. In fact, the templating metal could not be completely removed upon washing of the templated materials; consequently, the equilibrium between the liquid and solid phases can be modified.

The separation factors α, defined as the ratio of $K_d$(Am) to $K_d$(Ln), are given in Table 5. The values obtained with the imprinted materials **10−11** are lower than those of the nonimprinted ones, **7**, showing a small increase in the affinity of the materials for the metal template. Ln(III) and Pu(IV) capacities were measured for the imprinted materials **10a−c** and **11a−c** (Table 3). Pu(IV) capacities are very low, whatever the $R_w$ ratio, in agreement with the low porosity of the materials. Therefore, although gel **7a** exhibits a high separation factor, it is of poor interest in extraction chromatography due to its very low capacity.

Surprisingly, capacities of Ln(III) can reach relatively high values, for **10b** and **11b** corresponding to a 100% $R_w$ ratio (0.28 mequiv/g for the best value). Such values were never obtained with nontemplated materials, even with materials having high specific surface areas. This indicates that the use of a template during the synthesis induces more favorable organization of the complexing sites, which remains after the removal of the template.

## Conclusion

A large variety of organically modified silicas were synthesized by varying the dilution rate of the precursor in TEOS, the nature of the catalyst, and the $R_w$ ratio and with or without a template effect. The use of sol−gel techniques leads to higher loading of extracting groups in the materials than classical postfunctionalization techniques. The nucleophilic catalysis leads to porous materials, whereas the acidic catalysis leads to nonporous ones. Therefore, materials with specific surface areas from 0 to 300 m$^2$/g, total porous volume from 0 to 0.55 mL/g, and average pore diameters from 30 to more than 90 Å were used in batch extraction experiments.

Templated hybrid silicas were synthesized with $HNO_3$ as the catalyst. More than 80% of the template can be easily removed by washing with low acid solutions. Templated materials have higher $K_d$ values, for Ln(III), Am(III), and Pu(IV), than the related nontemplated materials. Ln(III) capacities also increase upon templating, reaching 0.28 mequiv/g. The use of a template during synthesis induces organization of the complexing sites, which remains effective after the removal of the template and increases the extraction properties of nuclides analogous to the template.

## Experimental Section

All the experiments were carried out under a nitrogen atmosphere. The solvents were dried by distillation over drying agents—EtOH over magnesium, $Et_2O$ and THF over sodium benzophenone, and $CH_2Cl_2$ over calcium hydride—and freshly distilled under a nitrogen atmosphere before use. Infrared spectra were recorded on a Perkin−Elmer FT 1000. Liquid $^1$H, $^{13}$C NMR studies were realized on a Bruker AC 200 and the liquid $^{29}$Si NMR on a Bruker AC250. Solid-state NMR were performed on a FTAM 300, with a $^{29}$Si frequency of 59.62 MHz, an acquisition delay of 10 s, a rotation speed of 5000 Hz, and from 300 up to 18 000 scans. Chemical shifts $\delta$ were in ppm with TMS as the internal reference. Mass spectra were recorded on a JEOL JMS-DX 300. UV−visible spectra were obtained on a Shimadzu UV-3101 PC. α spectroscopy was realized on a Canberra model 7401. ICP-AES analyses were obtained with a Perkin−Elmer 2000 ICP-AES. Elemental analyses were carried out by the "Service Central d'Analyse du CNRS" in Vernaison, France. Porosity results were obtained either on a Micromeritics 2375 or on a Coulter SA 3100 apparatus.

***N,N,N′,N′*-Tetraethyl-1,3-diamidepropane**. Diethylamine (127 g,1.74 mol) in 200 mL of dichloromethane was placed in a 1-L three-neck flask equipped with a dropping funnel, a mechanical stirring rod, and a thermometer. The temperature was decreased to −15 °C and 52.7 g (0.37 mol) of malonyl dichloride diluted in 100 mL of dichloromethane was added by the dropping funnel. The temperature was maintained under −5 °C. After the addition was completed, the mixture was warmed to room temperature and was then refluxed for 1 h. The solution was filtered, washed with water, and dried over magnesium sulfate. Dichloromethane was removed under vacuum and the residue purified by distillation to give *N,N,N′,N′*-tetraethyl-1,3-diamidepropane, 19.6 g (yield 32%). $Eb_{0.015} = 110$ °C. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 1.14 ($CH_3$, 12H, m), 3.43 ($C-CH_2$, 2H, s), 3.38 ($NCH_2$, 8H, m). $^{13}$C NMR ($CDCl_3$, $\delta$ ppm): 12.7 and 14.0 ($NCH_2CH_3$), 40.1 and 42.4 ($NCH_2CH_3$), 40.4 ($CH_2$), 166.2 (C(O)). IR ($CCl_4$, cm$^{-1}$): $\nu_{C(O)}$ 1636. MS (EI$^+$, *m*/*e*, relative intensities): 214 (10, M$^+$), 215 (20, M + 1$^+$), 72 (100, $NEt_2^+$); 142 (20, M−$NEt_2^+$). Anal. Calcd for $C_{11}H_{22}N_2O_2$: C, 61.65; H, 10.35. Found C, 61.26; H, 10.68.

***N,N,N′,N′*-Tetraethyl-2-allyl-1,3-diamidepropane.** The above malonamide (11.26 g, 52.6 mmol) in 250 mL of THF was placed in a three-neck flask equipped with two dropping funnels and a thermometer. The temperature was lowered to −80 °C, and then 33 mL of a 1.6 M hexane solution of *n*-butyllithium (53 mmol) and 6.5 g of allyl bromide (53.7 mmol) in 27 mL of THF were added simultaneously by the two dropping funnels under magnetic stirring. The temperature was maintained under −50 °C during the addition. After the addition was completed, the mixture was warmed to room temperature and stirred for 3 h. THF was then removed under vacuum. The residue was dissolved in dichloromethane, washed with water, and dried over magnesium sulfate. The solvent was removed under vacuum. The compound was purified by column chromatography on silica with ethyl acetate as the eluent ($R_f = 0.55$). Eight grams of the allyl amide was obtained (yield 60%) as a colorless solid. $F = 30-32$ °C. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 1.13 ($CH_3$, 12H, t, 5,5 Hz), 2.64($C-CH_2$, 2H, t, 6 Hz), 3.35 ($NCH_2$, 8H, m), 3.63 (CH, 1H, d, 6 Hz), 5.06

($\mathrm{CH{=}CH_2}$, 2H, m). $^{13}$C NMR ($\mathrm{CDCl_3}$, $\delta$ ppm): 12.6 and 14.0 ($\mathrm{NCH_2CH_3}$), 33.9 ($\mathrm{CH_2CH{=}CH_2}$), 40.2 and 41.4 ($\mathrm{NCH_2CH_3}$), 49.6 (CH), 116.3 ($\mathrm{CH{=}CH_2}$), 136.1 ($\mathrm{CH{=}CH_2}$), 168.1 (C(O)). IR ($\mathrm{CCl_4}$, cm$^{-1}$): $\nu_{\mathrm{CO}}$ 1633. MS (EI$^+$, *m/e*, relative intensities): 255 (15, M$^+$), 72 (100, $\mathrm{NEt_2^+}$); 182 (10, M$-\mathrm{NEt_2^+}$). Anal. Calcd for $\mathrm{C_{14}H_{26}N_2O_2}$: C, 66.11; H, 10.30. Found: C, 65.94; H, 10.51.

***N*****,*****N*****,*****N*****′,*****N*****′-Tetraethyl-2-triethoxysilylpropyl-1,3-diamidepropane (2).** The above allyl malonamide (5.84 g, 23 mmol), triethoxysilane (4.71 g, 28.7 mmol), and 92 mg of a 10.7% Karstedt platinum catalyst were placed in a tube. A magnet was added and the tube was sealed under reduced pressure. The tube was then heated at 120 °C for 12 h. The compound **2** was purified by distillation (yield 80%) to give a pale yellow viscous liquid. $\mathrm{Eb}_{0.01} = 140$ °C. $^1$H NMR ($\mathrm{CDCl_3}$, $\delta$ ppm): 0.64 ($\mathrm{CH_2Si}$, 2H, t), 1.06 ($\mathrm{CH_3}$, 21H, m), 1.40 ($\mathrm{CH_2CH_2CH_2}$, 2H, m), 1.84 ($\mathrm{CHCH_2}$, 2H, m), 3.37 ($\mathrm{NCH_2}$, 8H, q, 5.5 Hz), 3.45 (CH, 1H, t, 6 Hz), 3.72 ($\mathrm{OCH_2}$, 6H, q, 8 Hz). $^{13}$C NMR ($\mathrm{CDCl_3}$, $\delta$ ppm): 10.3 ($\mathrm{CH_2Si}$), 12.6 and 14.0 ($\mathrm{NCH_2CH_3}$), 18.2 ($\mathrm{OCH_2CH_3}$), 21.7 ($\mathrm{CH_2CH_2CH_2}$), 32.7 ($\mathrm{CHCH_2}$), 40.2 and 41.4 ($\mathrm{NCH_2CH_3}$), 50.2 (CH), 58.2 ($\mathrm{OCH_2}$), 168.6 (C(O)). IR ($\mathrm{CCl_4}$, cm$^{-1}$): $\nu_{\mathrm{Si-O}}$ 1081, $\nu_{\mathrm{Si-C}}$ 1381, $\nu_{\mathrm{CO}}$ 1630. MS (EI$^+$, *m/e*, relative intensities): 419 (40, M$^+$), 163 (40, $\mathrm{Si(OEt_3)^+}$), 72 (100, $\mathrm{NEt_2^+}$); 346 (25, M$-\mathrm{NEt_2^+}$). Anal. Calcd for $\mathrm{C_{20}H_{42}N_2O_5Si}$: C, 57.38; H, 10.11; N, 6.69. Found: C, 57.46; H, 9.98; N, 6.77.

**Hybrid Silicas 3, 4, 5, and 6a−c.** The hybrid silicas were prepared according to the same general procedure: in a Schlenck tube, the precursor **2** (1 mmol) and TEOS (2, 3, 4, or 5 mmol) were dissolved in dry ethanol, at a 1 M concentration with respect to the number of molar equivalents of silicon atom. The concentration of **2** in EtOH varied from 0.16 to 0.33 mol/L and that of TEOS from 0.66 to 0.84. Then, 50 $\mu$L of a 1 M solution of $\mathrm{NH_4F}$ ($5 \times 10^{-5}$ mol) in water and the total added water were adjusted to the desired amount: $R_{\mathrm{w}} = 50\%$ from 5.5 to 11.5 mmol; $R_{\mathrm{w}} = 100\%$, 23 mmol; $R_{\mathrm{w}} = 200\%$, 46 mmol. The solution was stirred for a few minutes and then allowed to stand. The gels formed within 12 h and were aged at room temperature for 1 week. The material was then collected, powdered, and dried under vacuum. It was washed with acetone and diethyl ether and dried again under vacuum at 80 °C for 24 h. The procedure is detailed in the case of hybrid silica **3** as a typical example.

**Hybrid 3**. In a Schlenck tube, 418 mg of **2** (1 mmol) and 416 mg of TEOS (2 mmol) were dissolved in 1.5 mL of dry ethanol. To the solution was then added 50 $\mu$L of a 1 M solution of $\mathrm{NH_4F}$ ($5 \times 10^{-5}$ mol) in water and 50 $\mu$L of water. The mixture was allowed to stand for 7 days at room temperature. The gel was then powdered, filtered, washed with acetone and diethyl ether, and dried again under vacuum at 80 °C for 24 h. The material was collected as a pale yellow powder. IR (KBr, cm$^{-1}$): $\nu_{\mathrm{Si-O}}$ 1078, $\nu_{\mathrm{O-H}}$ 3401, $\nu_{\mathrm{C=O}}$ 1641, $\nu_{\mathrm{C-H}}$ 2939 and 2979. $^{13}$C NMR CP-MAS ($\delta$, ppm): 13.6 ($\mathrm{NCH_2CH_3}$), 18.2 ($\mathrm{OCH_2CH_3}$ residuals), 41.9 ($\mathrm{NCH_2CH_3}$), 58.8 ($\mathrm{OCH_2CH_3}$ residuals), 169.1 (C(O)). $^{29}$Si NMR CP-MAS ($\delta$, ppm): −60.9 (T$^2$), −65.5 (T$^3$), −102.7 (Q$^3$), −110.3 (Q$^4$). BET: $S \approx 2$ m$^2$/g. Anal. Calcd for $\mathrm{C_{4.67}H_9N_{0.67}O_{2.5}Si}$ (assuming complete condensation of the silica network): C, 39.33; H, 6.36; N, 6.55; Si, 19.7%. Found: C, 31.19; H, 5.71; N. 4.7; Si, 22.95. Malonamide content in the solid: 1.98 mequiv/g.

**Hybrid 4**. It was obtained as above using 3 mmol of TEOS and 2 mL of EtOH and a total amount of water of 135 $\mu$L. IR (KBr, cm$^{-1}$): $\nu_{\mathrm{Si-O}}$ 1078, $\nu_{\mathrm{O-H}}$ 3401, $\nu_{\mathrm{C=O}}$ 1644, $\nu_{\mathrm{C-H}}$ 2939 and 2980. $^{13}$C NMR CP-MAS ($\delta$, ppm): 13.6 ($\mathrm{NCH_2CH_3}$), 17.9 ($\mathrm{OCH_2CH_3}$ residuals), 41.6 ($\mathrm{NCH_2CH_3}$), 59.1 ($\mathrm{OCH_2CH_3}$ residuals), 168.9 (C(O)). $^{29}$Si NMR CP-MAS ($\delta$, ppm): −58.6 (T$^2$), −65.7 (T$^3$), −103.4 (Q$^3$), −109.9 (Q$^4$). BET: $S = 3$ m$^2$/g. Anal. Calcd for $\mathrm{C_{3.5}H_{96.75}N_{0.5}O_{2.38}Si}$ (assuming complete condensation of the silica network): C, 34.48; H, 5.58; N, 5.74; Si, 23.04. Found: C, 32.42; H, 5.35; N, 4.08; Si, 23.40. Malonamide content in the solid: 1.78 mequiv/g.

**Hybrid 5**. It was obtained as above using 4 mmol of TEOS and 2.5 mL of EtOH and a total amount of water of 171 $\mu$L. IR (KBr, cm$^{-1}$): $\nu_{\mathrm{Si-O}}$ 1077, $\nu_{\mathrm{O-H}}$ 3430, $\nu_{\mathrm{C=O}}$ 1646, $\nu_{\mathrm{C-H}}$ 2939 and 2982. $^{13}$C NMR CP-MAS ($\delta$, ppm): 13.62 ($\mathrm{NCH_2CH_3}$), 17.82 ($\mathrm{OCH_2CH_3}$ residuals), 41.24 ($\mathrm{NCH_2CH_3}$), 59.63 ($\mathrm{OCH_2CH_3}$ residuals), 168.31 (C(O)). $^{29}$Si NMR CP-MAS ($\delta$, ppm): −58.9 (T$^2$), −64.8 (T$^3$), −102.1 (Q$^3$), −109.4 (Q$^4$). BET: $S \approx 2$ m$^2$/g. Anal. Calcd for $\mathrm{C_{2.8}H_{5.4}N_{0.4}O_{2.3}Si}$ (assuming complete condensation of the silica network): C, 30.7; H, 4.97; N, 5.11%; Si, 25.64. Found: C, 25.17; H, 4.88; N, 3.71; Si, 26.00. Malonamide content in the solid: 1.56 mequiv/g.

**Hybrid 6a**. It was obtained as above using 5 mmol of TEOS and 3 mL of EtOH and a total amount of water of 207 $\mu$L. IR (KBr, cm$^{-1}$): $\nu_{\mathrm{Si-O}}$ 1079, $\nu_{\mathrm{O-H}}$ 3420, $\nu_{\mathrm{C=O}}$ 1635, $\nu_{\mathrm{C-H}}$ 2980. $^{13}$C NMR CP-MAS ($\delta$, ppm): 13.5 ($\mathrm{NCH_2CH_3}$), 17.5 ($\mathrm{OCH_2CH_3}$ residuals), 44.2 ($\mathrm{NCH_2CH_3}$), 59.3 ($\mathrm{OCH_2CH_3}$ residuals), 170.4 (C(O)). $^{29}$Si NMR CP-MAS ($\delta$, ppm): −59 (T$^2$), −64.2 (T$^3$), −102.6 (Q$^3$), −108.9 (Q$^4$). BET: $S = 236$ m$^2$/g, $V_{\mathrm{p}} = 0.54$ cm$^3$/g, $\phi_{\mathrm{p}} = 91$ Å. Anal. Calcd for $\mathrm{C_{2.33}H_{4.5}N_{0.33}O_{2.25}Si}$ (assuming complete condensation of the silica network): C, 27.66; H, 4.48; N, 4.6; Si, 27.75. Found: C, 25.92; H, 4.75; N, 3.4; Si, 27.66. Malonamide content in the solid: 1.38 mequiv/g.

**Hybrid 6b**. **6b** was prepared as above, but the total amount of water used was 414 $\mu$L. Anal. Calcd for $\mathrm{C_{2.33}H_{4.5}N_{0.33}O_{2.25}Si}$ (assuming complete condensation of the silica network): C, 27.66; H, 4.48; N, 4.6; Si, 27.75. Found: C, 14.87; H, 3.08; N, 2.24; Si, 31.7. Malonamide content in the solid: 0.92 mequiv/g.

**Hybrid 6c**. **6b** was prepared as above, but the total amount of water used was 828 $\mu$L. Anal. Calcd for $\mathrm{C_{2.33}H_{4.5}N_{0.33}O_{2.25}Si}$ (assuming complete condensation of the silica network): C, 27.66; H, 4.48%; N, 4.6; Si, 27.75. Found: C, 18.3; H, 3.47; N, 2.93; Si, 30.3. Malonamide content in the solid: 1.16 mequiv/g.

**Hybrid Silicas 7a−c**. The hybrid silicas, obtained using acid catalysis, were prepared according to the same general procedure: in a Schlenck tube, the precursor **2** (1 mmol) and TEOS (5 mmol) were dissolved in 3 mL of dry ethanol. Then, while stirring, the corresponding amount of water (190 $\mu$L, $R_{\mathrm{w}} = 50\%$; 397 $\mu$L, $R_{\mathrm{w}} = 100\%$; 811 $\mu$L, $R_{\mathrm{w}} = 200\%$) and 50 $\mu$L of $\mathrm{HNO_3}$ (65% in water) were added. It was then allowed to stand. The gels formed within 12 h and were aged at room temperature for 1 week. The material was then collected, powdered, and dried under vacuum. It was washed with acetone and diethyl ether and dried again under vacuum at 80 °C for 24 h.

**Hybrid 7a**. It was obtained as above using a total amount of water of 207 $\mu$L. Anal. Calcd for $\mathrm{C_{2.33}H_{4.5}N_{0.33}O_{2.25}Si}$ (assuming complete condensation of the silica network): C, 27.66; H, 4.48; N, 4.6; Si, 27.75. Found: C, 21.62; H, 4.46; N, 3.28; Si, 27.5. Malonamide content in the solid: 1.38 mequiv/g.

**Hybrid 7b**. It was obtained as above, using a total amount of water of 414 $\mu$L. Anal. Found C, 23.64; H, 4.3; N, 3.28; Si, 27.9. Malonamide content in the solid: 1.32 mequiv/g.

**Hybrid 7c**. It was obtained as above, using a total amount of water of 828 $\mu$L. Anal. Found C, 23.18; H, 4.6; N, 3.97; Si, 26.05%. Malonamide content in the solid: 1.56 mequiv/g.

**Hybrid Silicas 10a−c and 11a−c**. *General Procedure.* In a Schlenck tube, 0.5 mmol of $\mathrm{Ln(NO_3)_3}$ was dissolved in 2 mL of dry ethanol. After dissolution, 1 mmol (418 mg) of **2** and 5 mmol (1040 mg) of TEOS in 1 mL of EtOH were added. Then, 10 min later, the corresponding amount of water (190 $\mu$L, $R_{\mathrm{w}} = 50\%$; 397 $\mu$L, $R_{\mathrm{w}} = 100\%$; 811 $\mu$L, $R_{\mathrm{w}} = 200\%$) and 50 $\mu$L of $\mathrm{HNO_3}$ (65% in water) were added. The stirring was stopped. The gelation occurred in 24 h at 50 °C. After an aging period of 1 week, the solid was dried under vacuum at 80 °C, powdered, washed with acetone and diethyl ether, and again dried under vacuum at 80 °C for 24 h. The solid as a suspension in 25 mL of a 0.01 M $\mathrm{HNO_3}$ solution was stirred for 2 h at room temperature to extract the lanthanide. The solution was eliminated by filtration and the solid collected. The procedure was repeated eight times and then the final solid was washed again with acetone and diethyl ether and dried under vacuum at 80 °C for 24 h. ICP-AES analysis showed that 80−95% of the lanthanide salt was eliminated.

**Hybrid 10b**. Anal. Calcd for $\mathrm{C_{2.33}H_{4.5}N_{0.33}O_{2.25}Si}$ (assuming complete condensation of the silica network): C, 27.66; H, 4.48; N, 4.6; Si, 27.75. Found: C, 22.37; H, 4.67; N, 3.78; Si, 25.4. Malonamide content in the solid: 1.54 mequiv/g.

**Hybrid 10c**. Anal. Found: C, 17.85; H, 3.71; N, 3.05; Si, 27.5. Malonamide content in the solid: 0.64 mequiv/g.

**Hybrid 11a**. Anal. Found: C, 22.21; H, 4.64; N, 2.53; Si, 27.3. Malonamide content in the solid: 0.56 mequiv/g.

**Hybrid 11b**. Anal. Found: C, 21.36; H, 4.26; N, 3.57; Si, 25.7. Malonamide content in the solid: 1.48 mequiv/g.

**Batch Extraction Experiments**. The nitric acid solutions were prepared with commercial 65% $HNO_3$. $^{241}$Am(III) solutions were obtained by dilution of an original solution of 35 mg of $AmO_2$ (CEA) in 10 mL of 4 M $HNO_3$ solution. Am(III) solutions were characterized by UV−visible spectroscopy (504 and 814 nm) and by α spectroscopy. Pu(IV) solutions were prepared by dilution of a Pu solution (CEA) purified by ion exchange chromatography on Reillex HPQ columns. Pu(IV) is selectively fixed on the column at 6 M $HNO_3$ and eluted with a 0.5 M $HNO_3$ solution. The oxidation state of Pu was verified by UV−visible spectroscopy (831 nm). Experiments were realized in 2-mL microtubes containing 25−50 mg of hybrid silica and 2 mL of a Am, Ln, or Pu solution. Tubes were stirred for 2 h and centrifugated. The solution was filtered on a 0.45−$\mu$m microfilter. Ln solutions were analyzed by ICP-AES whereas Am or Pu solutions were analyzed by alpha counting.

In solid−liquid extraction, distribution coefficients ($K_d$) are defined as the ratio of the concentration of the metal in the solid to the concentration of the metal in the solution at equilibrium, if the concentration of the extracting group in the solid is assumed to be constant. This is achieved by using initial concentrations of metal around 0.1% of the total amount of extracting group in the solid. The initial and final concentrations of metal in solution were determined by alpha counting for Am(III) and Pu(IV) or ICP-AES measurements for Ln(III). $K_d$ is given by the following formula,

$$K_d\ (\mathrm{mL/g}) = \frac{(A_o - A)}{A}\,\frac{v_{\mathrm{solution}}\ (\mathrm{mL})}{m_{\mathrm{gel}}\ (\mathrm{g})}$$

where $A_o$ and $A$ are the activity of the solution before and after extraction in the case of Am(III) and Pu(IV) or the intensity of the characteristic emission ray measured by ICP-AES in the case of Ln(III). From 3 up to 5 batch experiments were done for one $K_d$ measurement.

Capacities are defined as the quantity of metal extracted by the mass unit of gel and are given by the formula

$$\text{capacity (mequiv/g)} = [(m_o - m)\ (\mathrm{mg})/\text{molar mass(g/equiv)}]/m_{\mathrm{gel}}\ (\mathrm{g})$$

The initial and remaining masses of metal in solution were determined by alpha counting for Pu(IV). If $A$ is the activity of the solution and $A_M$ the intrinsic activity of the metal in $B_q$/g, then $m_M = A/A_M$.

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