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Synthesis of carbamoylphosphonate silanes for the selective sequestration of actinides

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The synthesis of carbamoylphosphonate silanes (CMPO analogs) designed for sequestering actinide cations in self-assembled monolayers on mesoporous supports (SAMMS) is described.

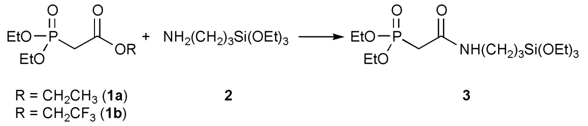
The Cold War resulted in the production of huge nuclear arsenals around the globe. Vast amounts of mixed radioactive wastes were generated as a by-product of this arms race. Uncertain of how these wastes should be treated for long-term or permanent disposition, the decision was made to store these materials in underground tanks until such time as a suitable strategy was identified and put into action. In the United States, the current plan is to mix these wastes with a suitable silica source and then melt the mixture and form it into non-leachable glass logs for permanent disposition in a deep subterranean repository (*e.g.* Yucca Mountain, Nevada). This strategy will not only include all of the non-radioactive components of the waste mixture (the vast majority of the waste components are not radioactive), but also increases the final waste volume by adding a considerable amount of silica to the mix. The cost associated with this clean-up strategy is estimated to be many, many billions of dollars. If the radionuclides could be selectively removed from these complex mixtures, then the volume of waste requiring expensive glassification could be reduced by orders of magnitude and the remaining waste could be treated much more affordably as low-level waste. The time and cost savings of such a strategy are potentially immense.

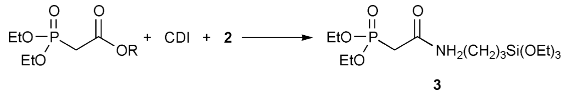
Much effort has been expended over the years in the area of solvent extraction for the separation of actinides, with a particular focus on plutonium specific ligands.[1] One of the more notable classes of ligand to result from this research is the carbamoylphosphine oxide (‘CMPO’) ligand, in which a carbonyl amide and a P=O double bond are arranged in a suitable fashion to chelate the actinide cation.[2]

The synthesis and elaboration of mesoporous ceramics has been the focal point of much research over the last decade. The hexagonal phase of mesoporous silica (named MCM-41 by its inventors) can be thought of as a glass honeycomb with highly uniform, nanometer scale pore diameter and wall thickness.[3] This morphology results in huge amounts of surface area (commonly 900–1000 m^2 g^{-1}) in a very compact volume. Being silica-based, MCM-41 is amenable to vitrification processing. Excellent chemical specificity can be imparted to this interface by coating the glass honeycomb with a suitably functionalized self-assembled monolayer. Self-assembled monolayers on mesoporous supports (SAMMS) have thus proven to be superior sorbent materials for heavy metals, oxometallate anions and caesium.[4] In this manuscript we describe the synthesis of silanes that incorporate the CMPO features, as well as the deposition of monolayers composed of these silanes within mesoporous silica (MCM-41).

Efforts to prepare the desired silane directly *via* amidation of triethylphosphonoacetate (**1a**) with aminopropyltriethoxysilane (**2**) were unsuccessful (the reaction required elevated temperatures and generated multiple side products).

Thus, our focus turned to the trifluoroethyl analog (**1b**). This material was prepared in straightforward fashion by treating diethylphosphonoacetic acid with thionyl chloride, and subsequently with trifluoroethanol.[5] After distillation, the desired trifluoroethyl ester was obtained in 58% yield.[6] Exposure of **1b** to neat **2**, resulted in a moderate exotherm and the clean production of the desired CMPO silane (**3**).[7] Attempts to purify **3** *via* vacuum distillation resulted in partial decomposition of the product. Fortunately, the reaction affording **3** is sufficiently clean as to allow direct usage of the crude product (we simply removed the trifluoroethanol by-product under vacuum).

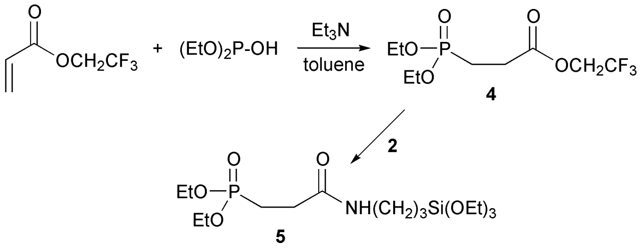




In an effort to increase the overall efficiency of this synthesis, we explored alternate amidation methods. Of the methods tried, the most valuable involved carboxylate activation using carbonyl diimidazole (CDI), as shown below.

This approach was found to be very clean, but separation of the product from the solvent and by-products proved problematic. Ultimately however, it was found that the CMPO silane reaction mixture could be used in the monolayer deposition directly, with no ill side-effects on monolayer quality.

One method for enhancing selectivity for the larger actinide cations over the more common transition metal cations is to enlarge the chelating cavity of the ligand. Thus we also wanted to prepare the corresponding homolog (structure **4**). This was accomplished *via* conjugate addition diethylphosphite to trifluoroethyl acrylate, as shown below. Once again, the trifluoroethyl ester was purified by vacuum distillation in good yield.[9] Mixing **4** with neat **2** resulted in a modest exotherm, and was found to be complete in approximately 100 minutes. Once again, attempted distillation resulted in partial decomposition of the product, so the trifluoroethanol was removed under vacuum and the desired CMPO silane (**5**) used directly.[10]



Formation of CMPO self-assembled monolayers within an MCM-41 matrix occurs without problem in refluxing toluene. Analysis of the propionamide phosphonate SAMMS (derived from **5**) by solid-state ^{13}C and ^{29}Si NMR reveals a surface coverage of approximately 2.1 silanes nm^{-2} and moderately good silane crosslinking using this approach (although a modest number of terminal and isolated silanes are present in these

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monolayers). Evaluation of these nanoporous sorbent materials has revealed excellent selectivity for the actinide cations, as well as rapid sorption kinetics. For example, the phosphonic acid SAMMS derived from **3** display distribution coefficients[11] of approximately 20 000 for Pu(IV) under conditions of pH < 1 and high nitrate concentrations. This means that for a solution to solids ratio of 100, there was 200 times as much Pu(IV) in the SAMMS as was left in the residual supernatant after equilibrium was achieved (which took approximately 1 minute). In other words, under these conditions, approximately 99.5% of the Pu(IV) was removed from solution. Similarly, for the phosphonic acid SAMMS derived from **5**, K_d values of approximately 15 000 were typically observed, indicating approximately 99.2% Pu(IV) removal under these conditions. What makes these observations even more remarkable is the fact that no competition from a wide variety of transition metal cations or complexants was observed.[12] Even EDTA, present in huge excess, does not interfere with the sequestration of Pu(IV) by these sorbent materials. The details of these binding studies will be reported elsewhere.

In conclusion, attempts to prepare these materials from the commercially available ethyl ester were problematic, but the amidation chemistry using the trifluoroethyl ester proceeded smoothly and in high yield. The resulting silanes were found to be unstable at elevated temperatures, as they underwent partial decomposition during attempted vacuum distillation. Fortunately the amidation chemistry is exceptionally clean, and the crude silane can be used directly to prepare highly efficient actinide specific sorbent materials.

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5 A representative procedure for the preparation of **3** involves the dropwise addition of thionyl chloride (2.2 mL, 30 mmol) to diethylphosphonoacetic acid (4.8 mL, 30 mmol). The color of the reaction mixture changed from yellow to orange–red during the 4 h reaction time. Trifluoroethanol (2.2 mL, 30 mmol) was added to the reaction vessel. After stirring for 20 min, the reaction mixture was heated to reflux for 1 h, cooled to ambient temperature and subjected to short-path vacuum distillation (bp 98–102 °C @ 0.40 Torr) to afford 4.8 g (17 mmol) of **1b** as a colorless liquid (58% yield). Conversion to **3** was accomplished by treating neat **1b** with 1 equiv. of **2** (modestly exothermic). The trifluroethanol by-product was removed under vacuum.

6 NMR spectral data for **1b**. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, ppm relative to TMS: 4.51 (q, 2H, -O-CH_2-$\mathrm{CF_3}$, $J_{\mathrm{H\text{-}F}} = 8.4$ Hz), 4.17 (dq, 4H, CH_2-O-P, both J values ($J_{\mathrm{H\text{-}H}}$ and $J_{\mathrm{H\text{-}P}}$) are approximately 7.4 Hz), 3.06 (d, 2H, P(O)-CH_2, $J_{\mathrm{H\text{-}P}} = 21.9$ Hz), 1.34 (t, 6H, CH_3-, $J = 7.0$ Hz). ^{31}P NMR (121.4 MHz, $\mathrm{CDCl_3}$, ppm relative to phosphoric acid): 22.7 m. ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$, ppm relative to TMS): 164.6 (s, -*CO*-), 123.2 (q, -CF_3, $J_{\mathrm{C\text{-}F}} = 291$ Hz), 63.1 (s, -CH_2-O-P(O)), 61.1 (q, O-CH_2-$\mathrm{CF_3}$, $J_{\mathrm{C\text{-}F}} = 36.9$ Hz), 33.9 (d, P(O)-CH_2-CO-, $J_{\mathrm{C\text{-}P}} = 134$ Hz), 16.3 (s, CH_3-$\mathrm{CH_2}$-O).

7 NMR spectral data for **3**. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, ppm relative to TMS): 4.11 (dq, 4H, $\mathrm{CH_3}$-CH_2-O-P(O), both J values ($J_{\mathrm{H\text{-}H}}$ and $J_{\mathrm{H\text{-}P}}$) are approximately 7.4 Hz), 3.80 (q, 6H, Si-O-CH_2-$\mathrm{CH_3}$, $J = 6.9$ Hz), 3.21 (app. q, 2H, -NH-CH_2, $J = 6.4$ Hz), 2.80 (d, 2H, P(O)-CH_2, $J = 20.7$ Hz), 1.61 (p, 2H, $\mathrm{CH_2}$-CH_2-$\mathrm{CH_2}$, $J = 6.4$ Hz), 1.31 (t, 6H, CH_3-$\mathrm{CH_2}$-O-P, $J = 7.2$ Hz), 1.19 (t, 9H, Si-O-$\mathrm{CH_2}$-CH_3, $J = 6.9$ Hz), 0.60 (m, 2H, $\mathrm{CH_2}$-CH_2-Si). ^{31}P $\mathrm{NMR_{3,}}$ ppm relative to phosphoric acid): 28.2 m. ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$, ppm relative to TMS): 164.1 (s, *CO*), 62.8 (s, CH_2-O-P), 58.4 (s, CH_2-O-Si), 42.5 (s, CH_2-N), 35.1 (d, P(O)-CH_2-CO, $J_{\mathrm{P\text{-}C}} = 133$ Hz), 22.8 (s, $\mathrm{CH_2}$-CH_2-$\mathrm{CH_2}$), 18.2 (s, CH_3-$\mathrm{CH_2}$-O-P), 16.2 (s, CH_3-$\mathrm{CH_2}$-O-Si), 7.6 (s, CH_2-Si).

8 A representative procedure for the preparation of **4** begins with the conjugate addition of diethylphosphite (20.4 mL, 158 mmol) to 2,2,2-trifluoroethyl acrylate (24.2 mL, 191 mmol), catalyzed by triethylamine (23.5 mL, 169 mmol) in xylene (100 mL). This mixture was held at reflux for two days. The solvent was removed by distillation and the product distilled to give **4** in 80% yield as a colorless liquid (bp 70–90 °C at 0.001 Torr). Conversion to **5** was once again mildly exothermic when carried out using neat **2**. The trifluoroethanol by-product was once again removed under vacuum.

9 NMR spectral data for **4**. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, ppm relative to TMS): 4.23 (q, 2H, O-$CH_2$$\mathrm{CF_3}$, $J_{\mathrm{H\text{-}F}} = 9$ Hz), 4.05 (m, 4H, PO-CH_2), 2.66 (m, 2H, P-CH_2), 2.04 (m, 2H, -CH_2CO), 1.27 (t, 6H, $\mathrm{POCH_2}$-CH_3, $J = 7$ Hz). ^{31}P NMR (121.4 MHz, $\mathrm{C_6D_6}$, ppm relative to phosphoric acid): 33.5 m. ^{13}C NMR (75.4 MHz, $\mathrm{C_6D_6}$, ppm relative to TMS): 170.9 (d, *CO*, $J_{\mathrm{P\text{-}C}} = 17$ Hz), 124.1 (q, -$\mathrm{CF_3}$, $J_{\mathrm{C\text{-}F}} = 277$ Hz), 61.9 (d, PO-CH_2-, $J_{\mathrm{P\text{-}C}} = 6.1$ Hz), 60.8 (q, -$CH_2$$\mathrm{CF_3}$, $J_{\mathrm{C\text{-}F}} = 36$ Hz), 27.7 (d, CH_2-CO, $J_{\mathrm{P\text{-}C}} = 3.4$ Hz); 21.6 (d, P-CH_2-, $J_{\mathrm{P\text{-}C}} = 145$ Hz), 16.7 (d, $\mathrm{POCH_2}$-CH_3, $J_{\mathrm{P\text{-}C}} = 5.7$ Hz).

10 NMR spectral data for **5**. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, ppm relative to TMS): 4.49 (br s, 1H, *NH*), 4.03 (m, 4H, PO-CH_2), 3.77 (q, 6H, Si-O-CH_2, $J = 6$ Hz), 3.18 (m, 2H, N-CH_2), 2.42 (m, 2H, P-CH_2), 2.04 (m, 2H, -CH_2-CO), 1.57 (m, 2H, C-CH_2-C), 1.27 (t, 6H, $\mathrm{POCH_2}$$CH_3$, $J = 7$ Hz), 1.17 (t, 9H, $\mathrm{SiOCH_2}$$CH_3$, $J = 7$ Hz), 0.61 (m, 2H, CH_2-Si). ^{31}P NMR (121.4 MHz, $\mathrm{C_6D_{6,}}$ ppm relative to phosphoric acid): 36.4. ^{13}C NMR (75.4 MHz, $\mathrm{C_6D_6}$, ppm relative to TMS): 171.5 (d, *CO*, $J_{\mathrm{P\text{-}C}} = 16$ Hz); 62.2 (d, P-O-CH_2, $J_{\mathrm{P\text{-}C}} = 6.5$ Hz), 58.9 (s, SiO-CH_2), 43.0 (s, N-CH_2), 29.4 (d, CH_2-CO, $J_{\mathrm{P\text{-}C}} = 3.5$ Hz), 23.9 (s, C-$\mathrm{CH_2}$-C), 21.8 (d, P-CH_2, $J_{\mathrm{P\text{-}C}} = 143$ Hz), 18.8 (s, $\mathrm{SiOCH_2}$-CH_3), 16.7 (d, $\mathrm{POCH_2}$$CH_3$, $J_{\mathrm{P\text{-}C}} = 6.1$ Hz), 8.8 (s, CH_2-Si).

11 The distribution coefficient (K_d) is simply a mass-weighted partition coefficient, defining the distribution of the target analyte between the solution and SAMMS phases at equilibrium.

12 The transition metals studied in these competition experiments included Fe(III), Al(III), Zr(IV), Ni(II), Ca(II), Mn(II), Mo(VI), Cu(II), Pb(II), Cr(III), and Hg(II), all present at 100 ppm. Complexing anions included phosphate, sulfate, citrate and EDTA, all present at 0.1 M.