drimers, protons closer to the center of the molecule resonate downfield of those further away.[4] We have further characterized 2-4 by ^{13}C NMR spectroscopy, elemental analysis, and gel permeation chromatography. Gel permeation chromatograms of the dendrimers demonstrate their high purity and the smooth progression of retention times with molecular weight.

These materials are all white microcrystalline or glassy solids that are highly soluble in organic solvents such as dichloromethane, chloroform, THF, ethyl acetate, and toluene. Despite the fact that the molecular weight of **46** is nearly 10 times larger than that of **4**, their melting points differ very little. Compound **46** melts from 192-203 °C and does not readily flow in its molten state, whereas **4** melts sharply at 176-178 °C. We are pursuing the synthesis of higher generations of these dendrimers in order to establish the limits of this approach and are characterizing the thermal and light-scattering properties of the present materials.

Registry No. **1**, 135340-02-2; **3**-OSi, 135340-03-3; **3**-OH, 135340-04-4; **4**, 7383-70-2; **7**-OSi, 135340-05-5; **7**-OH, 135340-08-8; **10**, 135340-09-9; **15**-OSi, 135340-06-6; **15**-OH, 135340-07-7; **22**, 135340-10-2; **46** (homopolymer), 135426-00-5; phenol, 108-95-2; 1,3,5-benzenetricarbonyl trichloride, 4422-95-1.

Synthesis and Polymerization of Propargylamine and Aminoacetonitrile Intercalation Compounds

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Layered inorganic solids (e.g., $M(O_3POH)_2$, MX_2, MOCl, MO_3; M = transition metal, X = chalcogenide) can intercalate organic guest molecules and ions to form layered solids with alternating inorganic and organic layers.[1] Alkylamines intercalate as bilayers between adjacent inorganic host layers. Interaction of the intercalated guest with the host can alter the optical, electronic, or magnetic properties of both the host and guest.[2] Pyrrole, 2,2'-bithiophene,[3] aniline,[4] acrylonitrile,[5] and diene[6] guests have been polymerized in intercalation compounds under suitable conditions. Day[7] and Tieke[8] demonstrated that diacetylenic guest molecules between MX_4^{2-} layers (M = Cd, Mn; X = halide) can be polymerized when irradiated with UV light or γ-rays, giving a material with alternating inorganic and polydiacetylene layers. While the orientation of the diacetylenic molecules in these materials allowed solid-state polymerization to occur, similar materials with monoacetylenic guest molecules did not polymerize. We report herein the intercalation and subsequent polymerization of propargylamine and aminoacetonitrile into $M(O_3POH)_2 \cdot H_2O$ (M = Zr, Sn).

The acetylenic intercalation compounds were prepared by adding neat propargylamine to a slurry of the host, α-$M(O_3POH)_2 \cdot H_2O$ (M = Zr, Sn), suspended in water and stirring for 2 days at room temperature. Both the Zr and Sn compounds are colorless and show only a single phase in their powder X-ray diffraction patterns (interlayer spacings of 16.2 and 16.5 Å, respectively). The observed stoichiometries from thermogravimetric analysis in an oxygen atmosphere[9] are $Zr(O_3PO^-)_2(HC{\equiv}CCH_2NH_3^+)_2 \cdot H_2O$, Zr-CC, and $Sn(O_3PO^-)_2(HC{\equiv}CCH_2NH_3^+)_2 \cdot H_2O$, Sn-CC. The water found in these materials is presumably in the hexagonal holes of the host phosphate, similar to α-$Zr(O_3POH)_2 \cdot H_2O$.[10] The aminoacetonitrile intercalates were prepared by adding a 20-fold excess of aminoacetonitrile hydrochloride to a slurry of $M(O_3PO^-Na^+)_2 \cdot 3H_2O$ in water and stirring for 6 days at room temperature to yield grey blue solids. The zirconium aminoacetonitrile compound, Zr-CN, obtained is biphasic with interlayer spacings of 12.9 and 12.0 Å and a stoichiometry of less than two amines per formula unit, $Zr(O_3PO^-)_{1.7}(N{\equiv}CCH_2NH_3^+)_{1.7}(O_3POH)_{0.3} \cdot H_2O$. The tin aminoacetonitrile compound, Sn-CN, was single phased (14.7 Å) with a stoichiometry of $Sn(O_3PO^-)_2(N{\equiv}CCH_2NH_3^+)_2 \cdot H_2O$. These propargylamine and aminoacetonitrile intercalation compounds were characterized by powder X-ray diffraction, elemental analysis, and TGA, as well as FTIR and ^{13}C CPMAS NMR spectroscopies. All of the spectroscopic and analytical data are given in the supplemental material (see paragraph at end of paper).

The intercalation compound Sn-CC prepared in this study is normally an opaque powder. We have found however that a clear crystalline film of Sn-CC can also be prepared. If $Sn(O_3POH)_2 \cdot H_2O$ (0.75 g) is added to 5.5 mL of a 60% (w/w) aqueous solution of propargylamine and heated at 50 °C for 2 weeks the solid tin phosphate dissolves to give a transparent solution. Mixing an equal volume of water with this mixture, centrifuging, and decanting off the liquid from the top, leaves a clear viscous red liquid which when evaporated on a glass slide gives a clear yellow film. This film is stable in chloroform but irreversibly disintegrates in water to give an opaque suspension. The interlayer separation of this film is 15.3 Å, and its IR and ^{13}C CPMAS NMR spectra are very similar to that of powdered Sn-CC. In a related system, Alberti has demonstrated that α-$Zr(O_3POH) \cdot H_2O$ can be exfoliated in a 0.1 M propylamine solution.[11] What has presumably happened in the case of Sn-CC is that the $Sn(O_3POH)_2 \cdot H_2O$ exfoliated in the original solution and, on evaporation of the water and excess propargylamine the tin phosphate plates settled to give the observed thin film. This thin film does not give the expected ratio of 2 amines per host formula unit but gives 2.3 amines per formula unit,

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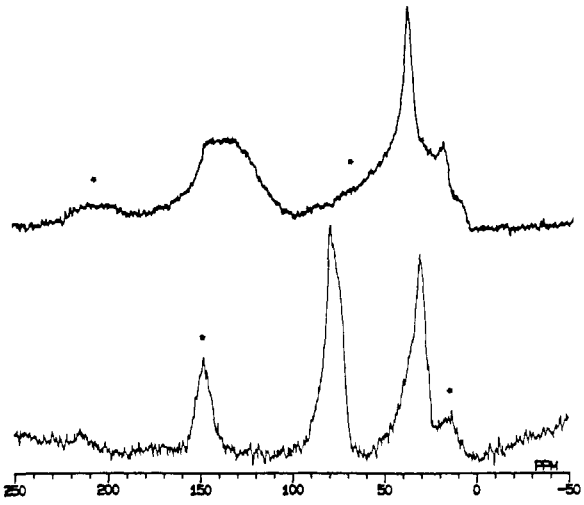

Figure 1. ^{13}C CPMAS spectra of Sn-CC (bottom) and Sn-CC 180 °C 24 h (top); the asterisks designate spinning sidebands.

$Sn(O_3PO^-)_2(HC{\equiv}CCH_2NH_3^+)_2(HC{\equiv}CH_2NH_2)_{0.3}$. The H_2O found in the powdered samples is not present in this material, which may account for the reduced interlayer spacing of the film as compared to the bulk powder.

UV irradiation or heating of Zr-CC or Sn-CC leads to changes in their NMR and IR spectra consistent with the polymerization or oligomerization of the intercalated guest monomers. Thermal treatment (24 h, 150–180 °C, in air) of Zr-CC or Sn-CC converts the white powdered starting materials into copper colored solids. The ^{13}C CPMAS NMR spectra of unpolymerized Zr-CC and Sn-CC show a single resonance for the acetylenic carbons at 79 ppm and resonance for the methylene carbon at 32 ppm, Figure 1. In the ^{13}C CPMAS NMR spectra of the thermally treated solids, Zr-CC (150 °C) and Sn-CC (180 °C), the resonance due to the acetylenic carbons is completely absent and a new broad peak at 130 ppm has grown in, characteristic of sp^2 olefinic carbons in aromatic and polyacetylenic materials.[12] Photolysis (11 days, 550-W medium pressure Hg lamp) of Zr-CC and Sn-CC also resulted in copper-colored solids. The ^{13}C CPMAS NMR spectra of the photolyzed materials showed that the acetylenic resonance at 79 ppm was still prominent in both spectra while the 130 ppm resonance was weak in Zr-CC and completely absent in Sn-CC. On the basis of these spectra the degree of polymerization of the exhaustively photolyzed Zr-CC and Sn-CC materials was estimated to be 30% and <1%, respectively. Both Zr-CN and Sn-CN give a ^{13}C nitrile resonance at 118 ppm and a methylene resonance at 29 ppm. After thermal treatment (150 °C, 24 h) the nitrile resonance disappears and is replaced by resonances at 140 and 169 ppm similar to those found in thermally polymerized polyacrylonitrile.[13,14] While the broadening in the ^{13}C spectra of Zr-CC (150 °C), Sn-CC (180 °C), Zr-CN (150 °C), and Sn-CN (150 °C) could be due to a dispersion of local environments, a portion of the broadening probably also comes from the paramagnetic nature of the solids. These thermally annealed materials give ESR spectra with g values ranging from 2.002 to 2.003 and line widths between 6 and 14 G.[15] These values are similar to those observed in other types of thermally treated polymers.[16]

Photolysis of these intercalation compounds did not significantly alter their powder X-ray diffraction patterns. Thermal treatment of these materials, however, leads to reductions in their crystallinity and observed interlayer spacings: Zr-CC (150 °C), 12.5 Å;[17] Sn-CC powder (180 °C), 9.9 Å; Sn-CC thin film (180 °C), 9.9 Å; Zr-CN (150 °C), 11.5 Å; Sn-CN (150 °C), 13.1 Å. Zr-CC and Sn-CC have a $\nu_{C\equiv C}$ stretch at 2138 cm^{-1} which disappears on thermal or photochemical treatment while a new band assigned to the allylic methylene of the proposed polymer[18] at 1447 cm^{-1} appears. In a deuterated sample of Zr-CC, $Zr(O_3PO^-HC{\equiv}CCH_2ND_3^+)_{1.7}(O_3POD)_{0.3}{\cdot}D_2O$,[19] a sharp band at 3251 cm^{-1} is observed, which we assign to the acetylenic ν_{CH}. Upon photolysis the acetylenic ν_{CH} decreases and is replaced by a broad band centered at 3112 cm^{-1}, characteristic of an olefinic ν_{CH}. Zr-CN and Sn-CN show a weak $\nu_{C\equiv N}$ stretch at 2277 cm^{-1} which disappears on heating, while a new band between 1680 and 1610 cm^{-1} grows in, similar to that found in thermally treated polyacrylonitrile polymers.[20,21]

Thermogravimetric analysis of Zr-CC and Sn-CC was carried out at a heating rate of 10 °C/min in air. The TGA of Zr-CC was difficult to obtain since upon heating to 170 °C the solid turns brown and bumps, ejecting solid from the balance pan. This type of intumescence has also been observed in other thermally treated acetylenic materials.[22] If Zr-CC is first thermally annealed at temperatures between 110 and 150 °C, it turns to a copper color with an observed weight loss of 8%. The copper colored solid can then be heated in air to 1000 °C, without bumping to give the pyrophosphate, $Zr(O_3POPO_3)$. Sn-CC does not bump solid from the balance pan on heating but shows a similar weight loss. Mass spectral analysis of the gas being given off during the initial heating shows that monomeric propargylamine is given off. TGA analysis of propylamine intercalates of $M(O_3POH)_2{\cdot}H_2O$ suggest that the water present in these materials is also lost below 150 °C.[23] The 8% weight loss occurring between 110 and 150 °C, prior to bulk polymerization, is composed of both free propargylamine and water.

The ^{13} CPMAS NMR and FTIR show that thermal treatment of these materials results in polymerization of the guest molecules. Powder X-ray diffraction demonstrates that the materials remain layered upon polymerization, with interlayer spacings larger than that of α-$Zr(O_3POH){\cdot}H_2O$, suggesting that the polymerization occurs within the interlayer space. Photolysis can initiate polymerization to give products similar to the thermally treated materials, based on their IR and ^{13}C CPMAS NMR

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spectra. However, the extent of the photochemical reaction is limited, as observed by ^{13}C CPMAS NMR spectroscopy. The polymeric intercalation compounds Zr-CC, Sn-CC, Zr-CN, and Sn-CN are insulators as pressed powder pellets ($\sigma < 10^{-8}\ \Omega^{-1}\ cm^{-1}$). Heating these compounds to 300 °C in argon turns them black and decreases their ESR line widths but does not increase their conductivity. Heating to > 750 °C does not alter the physical appearance of these materials but increases their conductivity to between 10^{-2} and 1 $\Omega^{-1}\ cm^{-1}$. This graphitization reaction as well as the conducting and nonlinear optical properties of these materials are currently under investigation and will be the subject of future reports.

Supplementary Material Available: Analytical and spectroscopic data (powder X-ray diffraction, elemental analysis, thermogravimetric analysis, FTIR, and ^{13}C CPMAS NMR) for all of the intercalation compounds described in this paper as well as the synthesis of $Zr(O_3PO^-HC{\equiv}CCH_2ND_3^+)_{1.7}(O_3POD)_{0.3}\cdot D_2O$ (3 pages). Ordering information is given on any current masthead page.

Building Block Approach to $CdNb_2O_6$: Synthesis, Molecular Structure, and Hydrolysis of $CdNb_2(\mu\text{-}OAc)_2(\mu\text{-}O\text{-}i\text{-}Pr)_4(O\text{-}i\text{-}Pr)_6$

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A large variety of advanced materials are based on multicomponent oxides. Many of these materials involve large transition metals such as titanium, niobium, or tantalum. The latter two for instance allow the obtaining of high-permittivity ceramics such as $Cd_2Nb_2O_7$, $CdNb_2O_6$, $Pb(Nb_{2/3}Mg_{1/3})O_3$ (PNM), $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT), or $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT),[1] some being of interest as microwave dielectric resonators. Sol–gel processing is a popular and versatile method for the preparation of ceramics in various shapes, fine powders, fibers, or coatings. The first step in the sol–gel process is the preparation of a solution containing the requisite metal cations in the appropriate stoichiometry. Metal alkoxides $M(OR)_n$ or oxo alkoxides $MO(OR)_n$ are versatile molecular precursors of metal oxides.[2] The solutions used for the obtaining of the materials are commonly comprised of a metal alkoxide, the other precursors being—depending generally on commercial availability—alkoxides, carboxylates, or more ionic precursors such as nitrates or hydroxides.[3] The structure and composition of precursors formed in soluton should be characterized in order to get a better understanding of the hydrolysis–polycondensation reactions and thus a better control of the final properties in the gel and the resulting ceramic.

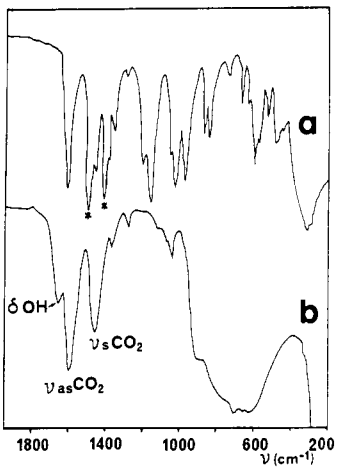

Figure 1. Infrared spectra (a) of $CdNb_2(\mu\text{-}OAc)_2(\mu\text{-}O\text{-}i\text{-}Pr)_4(O\text{-}i\text{-}Pr)_6$ (Nujol mulls) and (b) of the hydrolysis product **2** of **1** (KBr pellet).

We report here the results obtained in the case of the Nb–Cd system. The reaction between niobium isopropoxide and cadmium acetate offers the heterometallic compound $NbCd_2(\mu\text{-}OAc)_2(\mu\text{-}O\text{-}i\text{-}Pr)_4(O\text{-}i\text{-}Pr)_6$, which has been structurally characterized. Hydrolysis and thermal treatment of the resulting derivative offer a molecular route to $CdNb_2O_6$ in mild conditions (~600 °C).

Multicomponent oxide materials involving cadmium display attractive photoconductivity or dielectric properties. Cadmium(II) alkoxides remain limited. The reaction between $Cd[N(SiMe_3)_2]_2$ and various alcohols offers a selective high-yield route to a large variety of Cd(II) alkoxides.[4] The solubility of these alkoxides is governed by the steric bulk and/or the polydentate behavior of the alkoxide ligand. Their poor solubility can be overcome by the formation of soluble heterometallic alkoxides[5,6] in the case of multicomponent oxides. Their major drawback is thus a limited stability, probably as a result of β-elimination reactions.[2]

We thus turned to the use of cadmium acetate as a cadmium precursor. Anhydrous $Cd(OAc)_2$ dissolves readily in toluene or in hexane in the presence of niobium isopropoxide at room temperature according to

$$Cd(OAc)_2 + 2Nb(O\text{-}i\text{-}Pr)_5 \xrightarrow{25\ °C} CdNb_2(OAc)_2(O\text{-}i\text{-}Pr)_{10}$$

No reaction is observed between $Cd(OAc)_2$ and niobium pentaethoxide $[Nb(OEt)_5]_2$ even after 24 h in refluxing toluene, thus suggesting that the reaction proceeds via monomeric $Nb(OR)_5$ fragments. Indeed, the addition of small amounts of ethanol, which is known to form the $Nb(OEt)_5(EtOH)$ monomer, allows a reaction to occur even at room temperature.

The heterometallic species $CdNb_2(OAc)_2(O\text{-}i\text{-}Pr)_{10}$ (**1**) has been characterized by microanalysis, ^1H, ^{13}C, and ^{113}Cd NMR, and infrared spectroscopy.[7] The infrared (IR)

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