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· Communication

Air-Stable Titanium Alkoxide Based Metal−Organic Framework as an Initiator for Ring-Opening Polymerization of Cyclic Esters

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An air-stable titanium−organic framework, prepared from Ti(O^{i}Pr)$_4$ and 1,4-butanediol, has been characterized via single-crystal X-ray diffraction, revealing a unique supramolecular structure. Its functionality as a highly active initiator for the ring-opening polymerization of cyclic esters is demonstrated. A discrete titanium trimer containing the related ligand (2R,3R)-2,3-butanediol has also been prepared, and it shows analogous activity as a polymerization initiator.

The investigation into metal-coordination polymers has undergone a renaissance in recent years.[1] Typically, organic components are used in conjuction with metals having a known coordination bias, which provides a degree of control over the final structure. Such materials are usually referred to as metal−organic frameworks (MOFs) and can possess well-defined arrays, which often define large pores or channels, akin to zeolites, making them of interest as functional materials.[2] To date, many metal−organic-coordination motifs are known, such as those based on Cd^{2+}, Zn^{2+}, and Ag$^+$.[3−9] Previously, the construction of titanium−organic frameworks and other supramolecular motifs has tended to utilize polyfunctional aryloxides as ligands in order to impart structural rigidity and stability.[10−13] In this Communication, we report the synthesis and characterization of [Ti$_2$L$_3$(LH)$_2$]$_\infty$ (**1**, where LH$_2$ = 1,4-butanediol), a novel titanium-based MOF that utilizes the covalent bonding of a flexible aliphatic alkoxide organic linker. We chose 1,4-butanediol as the logical starting point for such a synthesis because it is predisposed to coordination in two directions and the length of the linker disfavors chelation. The use of 1,4-butanediol as a ligand is rare and unknown for group 4 metals.[14−16]

A metal alkoxide based MOF such as **1** should possess chemical functionality, for example, as a Lewis acid. Given the current interest in ring-opening polymerization (ROP) of cyclic esters catalyzed by a range of metal alkoxides, including titanium alkoxides,[17−22] we anticipated that an air-stable MOF based on titanium alkoxide linkages may prove to be a useful initiator for the ROP of ϵ-caprolactone and rac/L-lactide. The results reported here confirm this is the case. To gain insight into the mode of catalysis, we also report the structure and catalytic activity of a related

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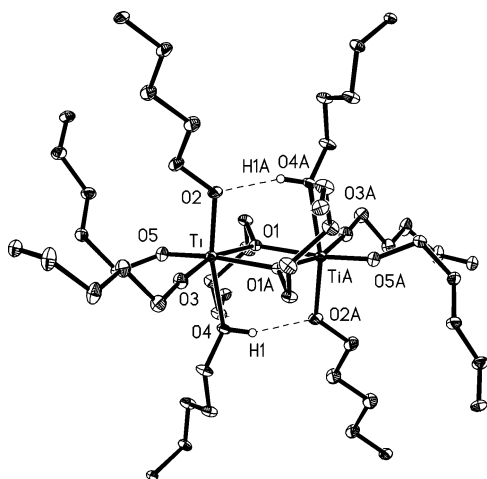
Figure 1. Dimeric building block observed for **1**. The ellipsoids are shown at the 50% probability level. The H atoms not involved in H bonding have been removed for clarity. Selected bond lengths (Å) and angles (deg): Ti−O1 2.004(1), Ti−O1A 2.066(1), Ti−O2 1.887(1), Ti−O3 1.791(1), Ti−O4 2.263(1), Ti−O5 1.819(1); O4−Ti−O2 166.48(4), O1−Ti−O1A 73.91(4), O3−Ti−O5 97.74(5) [O4−H1 0.86(2), H1···O2A 1.92(8), and O4···O2A 2.747(1) Å; O4−H1−O2A 160(2)°.

molecular species $Ti_3L'_4(L'H)_4$ [**2**, where $L'H_2 = (2R,3R)$-2,3-butanediol].

Complex **1** crystallized readily in high yield from a solution of $Ti(O^iPr)_4$ in excess 1,4-butanediol (stoichiometric quantities of the ligand did not yield crystalline material), and a single-crystal X-ray structure was determined (Figure 1). The *pseudo*octahedral Ti centers are associated into a Ti_2O_{10} edge-sharing bioctahedral structural motif via two bridging alkoxide groups. One protonated OH group of a ligand is coordinated to each Ti center and is stabilized via an intradimer O−H···O hydrogen bond in a manner similar to that previously observed within titanium alkoxide dimers.[21] Bond lengths and angles within this structural unit are consistent with literature precedent.[10,12,18,21,23,24]

The three-dimensional structure is built up of these bioctahedral Ti_2O_{10} units linked via the organic spacer. Each bioctahedron represents a node with 10 potential connectors, and in **1**, all of these are utilized, resulting in the polymeric structure shown in Figure 2a. This complete utilization of possible connectors contrasts with previously reported titanium aryloxide MOFs, which contain similar Ti_2O_{10} units but which exhibit a maximum connectivity of eight, leading to different supramolecular structures.[10] The distinction is presumably due to the flexibility of the aliphatic linker in **1**, which allows highly efficient packing to occur. Within the three-dimensional network, three large rings are present, which are shown in Figure 2b.

Complex **1** is colorless, reasonably soluble in most common organic solvents, and, unusual for a titanium alkoxide, is air-stable.[25] These properties suggest this complex as an attractive candidate for commercially relevant polymerization catalysis. **1** was tested for the polymerization
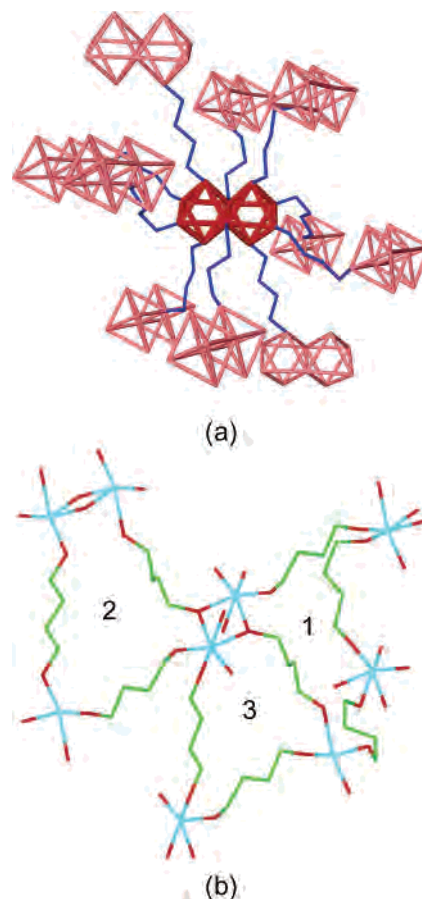

Figure 2. (a) 10-fold connectivity of each bioctahedral node in **1** (Ti_2O_{10} units shown in red; C_4H_8 connectors in blue). (b) Three ring structures present in the crystal structure: **1**, $L_2(LH)_2Ti_4$ ring; **2**, $L_2(LH)OTi_4$ ring; **3**, $L_2(LH)Ti_3$ ring (where $LH_2 = 1,4$-butanediol).

Table 1. Polymerization Results

monomer	initiator	yield[d]	$M_n{}^e$	$M_w{}^e$	PDI[e]
ϵ-caprolactone[a]	**1**	95	21 900	27 100	1.24
L-lactide[b]	**1**	90	7 700	9 500	1.23
rac-lactide[c]	**1**	90	33 700	59 200	1.76
rac-lactide[c]	**2**	85	51 400	73 700	1.43

[a] Toluene, initiator:monomer = 1:100, room temperature, 48 h. [b] Toluene, initiator:monomer = 1:100, 110 °C, 3 h. [c] 130 °C; initiator:monomer = 1:300; time, 2 h; atactic poly(*rac*-lactide) from homonuclear decoupled NMR analysis. [d] Dried isolated yield. [e] Determined from gel permeation chromatography referenced to polystyrene standards.

of ϵ-caprolactone and L/*rac*-lactide (Table 1). The activity of **1** is comparable to that of previously reported molecular titanium alkoxide ROP initiators, and a reasonably low polydispersity index (PDI) for the molecular weight distribution implies that the polymerization is well-controlled.

We are unaware of any previous reports of the use of a MOF material as an initiator for ROP of cyclic esters, and we can only speculate as to the nature of the catalytically active species. In general, the molecular details of the mechanism of well-controlled metal alkoxide catalyzed ROP remain poorly understood,[26] and in the case of **1**, it is unlikely

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(25) Exposing a sample to the atmosphere for 5 days resulted in no change in the Fourier transform IR spectra, and the powder X-ray diffraction pattern was consistent with that calculated from the single-crystal data of **1**, indicating that the bulk sample is unchanged. However, this does not preclude a small amount of surface hydrolysis.

Chart 1. Polymers Produced Using **1** as the Initiator

Polylactide (PLA)

Polycaprolactone (PCL)
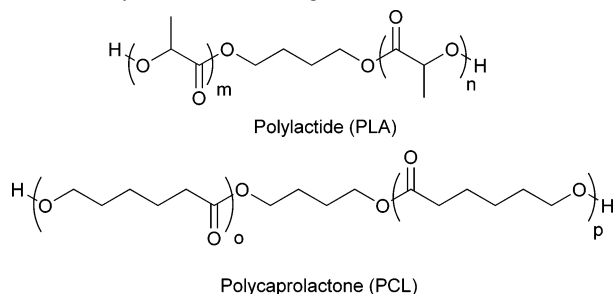
that the active species retains the polymeric structure found in the solid state. However, a number of observations point toward the probable nature of the species involved. First, dissolution of **1** occurs rapidly in toluene/dilactide solutions at 110 °C and somewhat more slowly at room temperature in toluene/ϵ-caprolactone, indicating that the catalysis is homogeneous. This dissolution is presumably a result of deaggregation of **1**, mediated by complexation of the cyclic ester to the metal center. Such complexation is generally accepted as the first step in the coordination−insertion mechanism of metal alkoxide catalyzed ROP.[27] Second, the 1,4-butoxide ligand is apparently retained in this deaggregated initiating species because matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra of the poly(L-lactide) and poly(caprolactone) produced from **1** indicate that this ligand is incorporated in the polymers as a chain extender (Chart 1). Taken together, these observations suggest that, under the conditions employed for polymerization, a discrete molecular titanium alkoxide containing chelating and/or bridging 1,4-butoxide ligands is the likely initiator.

To lend further credence to the identity of the initiator derived from **1**, we synthesized a molecular analogue of **1** using (2*R*,3*R*)-2,3-butanediol as a related ligand, which should favor chelation over polymeric bridging. A similar synthetic methodology was employed, as previously shown for **1**, to afford the discrete titanium trimer complex **2**, which was characterized by X-ray crystallography (Figure 3). On the molecular level, the coordination environment at Ti is similar to that in **1**. The Ti centers have a distorted octahedral geometry, the central Ti is bound to two terminal alkoxides and four bridging alkoxides, whereas the other two Ti centers are bound to three terminal alkoxides, two bridging alkoxides, and one alcohol group. Again, the OH groups of protonated ligands participate in intramolecular H bonding.[28] As a
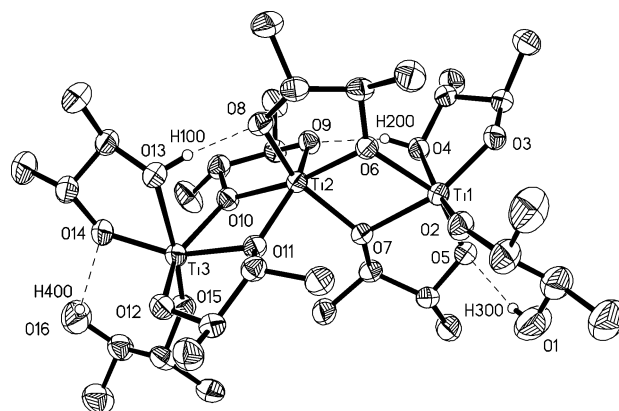

Figure 3. Trimeric molecular structure of **2**. The ellipsoids are shown at the 50% probability level. The H atoms not involved in H bonding have been removed for clarity. Selected bond lengths (Å) and angles (deg): Ti1−O2 1.793(2), Ti1−O3 1.827(2), Ti1−O4 2.229(2), Ti1−O5 1.881(2), Ti1−O6 2.059(2), Ti2−O6 1.981(1), Ti2−O7 1.974(2), Ti2−O8 1.892(2), Ti2−O10 1.987(1), Ti2−O11 1.992(1), O6−Ti1−O5 148.60(6), O6−Ti2−O10 169.16(6).

discrete molecular species, **2** is soluble in organic solvents and ^{1}H and ^{13}C NMR spectra confirm that the solid-state structure remains intact (for example, eight resonances are observed for the eight unique methyl groups expected on the basis of the crystal structure). Polymerization of *rac*-lactide using **2** as an initiator yielded results similar to those obtained for **1** in terms of activity and the degree of control over the molecular weight distribution (Table 1). This suggests that in both cases discrete molecular titanium alkoxides are involved in the ROP of cyclic esters.

In conclusion, a titanium alkoxide, stabilized in the solid state as a polymeric MOF, is activated in the presence of cyclic esters to act as an initiator for the well-controlled ROP of ϵ-caprolactone and lactide. Similar polymerization activity is found for a related molecular titanium alkoxide. We are currently investigating the synthesis of other stable MOFs and their potential utility as ROP initiators.

Supporting Information Available: MALDI-TOF spectra of the polymers produced, powder X-ray diffraction, Fourier transform IR measurements, and full experimental details; crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) We would anticipate a similar structure if (2*S*,3*S*)-2,3-butanediol were employed; attempts to isolate a structure using the (*R*,*S*) diastereomer are ongoing.