Inorganic Chemistry
Article
pubs.acs.org/IC

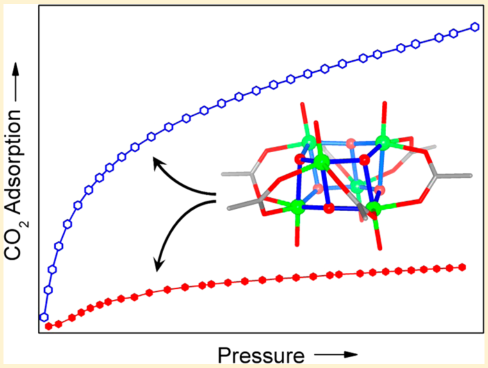
Robust Molecular Crystals of Titanium(IV)-oxo-Carboxylate Clusters Showing Water Stability and CO_2 Sorption Capability

Keunil Hong, Woojeong Bak, and Hyungphil Chun*

Department of Applied Chemistry, College of Science and Technology, Hanyang University, 55 Hanyangdaehak-ro, Ansan 426-791, Republic of Korea

Ⓢ *Supporting Information*

ABSTRACT: A series of new Ti(IV)-oxo clusters supported by carboxylate ligands are synthesized by solvothermal reactions, and their crystal structures and gas sorption properties are studied in detail. Depending on the reaction medium, two types of Ti_6O_6 clusters are formed with benzoate-derived ligands whose 2- or 4-position is substituted by a hydrophobic moiety. The molecular packing structures of these Ti clusters are found stable against water- and heat-treatments. Gas sorption studies reveal that a dense-packed Ti-carboxylate cluster can adsorb almost the same number of CO_2 molecules as the one with considerable intermolecular voids in the packing structure. The effect of benzoate substituents on the gas sorption behavior is discussed.



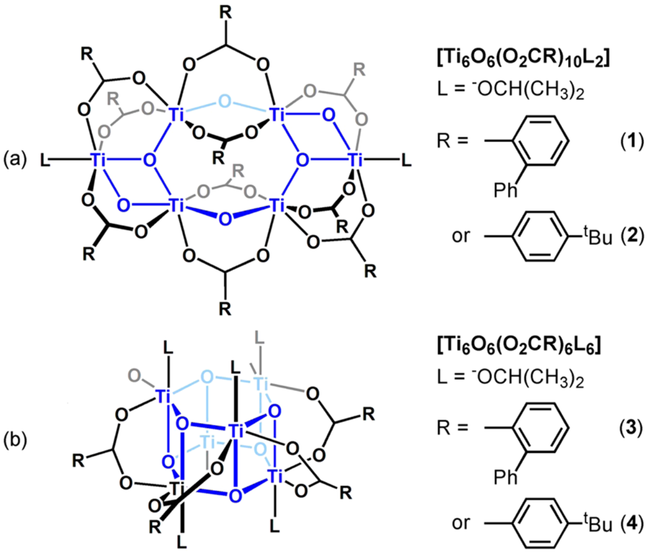
■ INTRODUCTION

Titanium(IV) carboxylate clusters are an important subclass of polyoxotitanates that provide structural and spectroscopic insights for surface properties of bulk TiO_2 phases.[1] The multinuclear molecules have been widely studied as catalysts[2] or as building blocks for various inorganic and organic–inorganic hybrid materials having network structures.[3] A metal–organic framework based on Ti_8-carboxylate secondary building unit has also been reported.[4] Recently, we discovered hitherto unknown properties of Ti-carboxylate compounds and reported that nonporous Ti-carboxylate clusters can selectively adsorb carbon dioxide even in amorphous state.[5]

Inorganic molecular solids showing reversible gas sorptions are very rare,[6] and those without an apparent intrinsic void are especially so.[7] One of the reasons why "porous" inorganic molecules are so rare may be because gas adsorption has not been the most important motivation for synthesizing molecular solids in this area. Nevertheless, it is a highly interesting phenomenon that dense-packed molecular solids can display reversible adsorption behavior, and it even carries some practical implications when the adsorption of carbon dioxide is concerned.[8] Therefore, we decided to systematically investigate the relationship between structures and gas sorption properties of Ti-carboxylate clusters.

As shown in Scheme 1, two benzoate ligands either with a phenyl group on the 2-position or with a *tert*-butyl group on the 4-position are used to build two different types of Ti_6O_6 clusters. Our hypothesis was that in biphenyl-2-carboxylate (2-bpyc), unlike in 4-*tert*-butylbenzoate (4-tbbz), the phenyl group on the 2-position of the benzoate backbone would effectively occupy the interligand space within a titanium cluster, resulting in the removal of potential void where the adsorption of CO_2 can occur. Meanwhile, a bulky substituent, such as *tert*-butyl group, on the 4-position of benzoate would preserve the space between ligands in the rigid polyoxo cluster. The synthesis, structural features, and gas sorption properties of the four new Ti-carboxylate clusters are reported herein.

Scheme 1. Four Ti(IV)−Carboxylate Clusters Synthesized in This Work



Received: March 18, 2014
Published: June 30, 2014

dx.doi.org/10.1021/ic500629y | *Inorg. Chem.* 2014, 53, 7288−7293

Table 1. Summary of Crystal Data and Structure Refinements for 1−4

	1·(CH$_3$CN)$_2$	2	3	4
formula	C$_{140}$H$_{110}$N$_2$O$_{28}$Ti$_6$	C$_{116}$H$_{144}$O$_{28}$Ti$_6$	C$_{96}$H$_{96}$O$_{24}$Ti$_6$	C$_{84}$H$_{120}$O$_{24}$Ti$_6$
FW	2555.70	2273.71	1921.13	1801.20
T (K)	100	100	100	195
λ (Å)	0.710 73	0.700 01	0.659 99	0.649 99
crystal system	triclinic	triclinic	triclinic	cubic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$Pa\bar{3}$
a (Å)	13.167(2)	13.124(3)	12.152(2)	21.821(3)
b (Å)	14.326(2)	14.948(3)	13.180(3)	21.821(3)
c (Å)	17.744(2)	15.715(3)	15.218(3)	21.821(3)
α (deg)	71.689(4)	81.56(3)	96.18(3)	90
β (deg)	70.189(4)	88.73(3)	110.66(3)	90
γ (deg)	87.272(4)	73.82(3)	92.05(3)	90
V (Å^3)	2983.1(6)	2928(1)	2260.2(8)	10390(2)
Z	1	1	1	4
ρ_{calc} (g/cm^3)	1.423	1.289	1.411	1.152
μ (mm^{-1})	0.462	0.442	0.456	0.381
F(000)	1320	1196	996	3792
crystal size (mm^3)	0.20 × 0.17 × 0.08	0.16 × 0.09 × 0.03	0.13 × 0.10 × 0.03	0.20 × 0.20 × 0.10
reflections	137 821	38 632	33 759	122 467
independent (R_{int})	32150 (0.0806)	19364 (0.0173)	16944 (0.0184)	7824 (0.0676)
$T_{\mathrm{max}}/T_{\mathrm{min}}$	0.9640/0.9132	0.9869/0.9326	0.9865/0.9432	0.9629/0.9277
data/restraints/parameters	32150/18/802	19364/12/731	16944/96/651	7824/42/185
GOF on F^2	1.025	1.100	1.089	1.085
R_1, wR_2 [$I > 2\sigma(I)$]	0.0569, 0.1132	0.0625, 0.1860	0.0463, 0.1366	0.0550, 0.1818
R_1, wR_2 (all data)	0.1219, 0.1350	0.0774, 0.2033	0.0517, 0.1412	0.0685, 0.1905
extinction coefficient		0.094(4)	0.075(3)	0.012(2)
largest diff. peak/hole (e/Å^3)	1.212/−0.951	0.914/−0.962	0.914/−0.978	0.810/−0.932

■ EXPERIMENTAL SECTION

All the reagents and solvents were commercially available and used as received. All manipulations were carried out under ambient conditions. The synthetic parameters were optimized to obtain the products as single crystals and are highly reproducible. Thermogravimetric analysis (TGA) data were obtained on a TA Q500 instrument with the heating rate of 10 °C/min under a constant flow of N$_2$ gas (Supporting Information, Figure S1). Fourier transform infrared (FT-IR) spectra were recorded on KBr pellets using a Varian FTS 1000 instrument (Supporting Information, Figures S2 and S3).

[Ti$_6$O$_6$(2-bpyc)$_{10}$(O^{i}Pr)$_2$] (1). A pale yellow solution containing 2-bpycH (161.2 mg, 0.81 mmol) and Ti(O^{i}Pr)$_4$ (60.2 μL, 0.20 mmol) in CH$_3$CN (6.00 mL) was stirred for 30 min and then sealed in a glass vial with a Teflon-lined screw cap. The solution was heated to 60 °C for 20 h, 80 °C for 24 h, and 100 °C for 24 h to produce colorless plate-type crystals. The product was collected, washed thoroughly with CH$_3$CN, and then heated to 100 °C under vacuum for 8 h (55.4 mg, 67%). Anal. Calcd for C, 66.04; H, 4.24; N, 0.00. Found: C, 65.61; H, 4.32; N, 0.36%. The detected nitrogen is probably due to a residue of CH$_3$CN trapped in the crystal lattice. The sample for gas sorption studies was therefore activated by different processes. See below for details.

[Ti$_6$O$_6$(4-tbbz)$_{10}$(O^{i}Pr)$_2$] (2). To a solution containing 4-tbbzH (173.3 mg, 0.97 mmol) in a CH$_3$CN−tetrahydrofuran (THF) mixture (3:1, 3.0 mL), Ti(O^{i}Pr)$_4$ (36.0 μL, 0.12 mmol) was added. After it was stirred for 30 min, the solution was sealed in a glass vial and then heated to 60 °C for 16 h and to 70 °C for 36 h. The product obtained as colorless rod-shape crystals was collected, washed thoroughly with CH$_3$CN, and then heated to 100 °C under vacuum for 8 h (30.1 mg, 65%). Anal. Calcd for C, 61.28; H, 6.38; N, 0.00. Found: C, 61.09; H, 6.50; N, 0.00%.

[Ti$_6$O$_6$(2-bpyc)$_6$(O^{i}Pr)$_6$] (3). A clear solution containing 2-bpycH (206.8 mg, 1.04 mmol) and Ti(O^{i}Pr)$_4$ (31.0 μL, 0.10 mmol) in ^{i}PrOH (3.00 mL) was stirred for 2 h, sealed in a glass vial, and then heated to 80 °C for 12 h, 90 °C for 24 h, and 110 °C for 24 h. Colorless, square plate-type crystals were collected, washed thoroughly with ^{i}PrOH, and then heated to 100 °C under vacuum for 8 h (23.4 mg, 70%). Anal. Calcd for C, 60.02; H, 5.04; N, 0.00. Found: C, 59.40; H, 5.16; N, 0.00%.

[Ti$_6$O$_6$(4-tbbz)$_6$(O^{i}Pr)$_6$] (4). To a solution containing 4-tbbzH (170.1 mg, 0.95 mmol) in an ^{i}PrOH−THF mixture (3:1, 3.0 mL), Ti(O^{i}Pr)$_4$ (35.4 μL, 0.12 mmol) was added. After it was stirred for 30 min, the solution was sealed in a glass vial and then heated to 60 °C for 24 h and to 70 °C for 24 h. Yellow octahedral crystals were obtained, washed thoroughly with ^{i}PrOH, and then heated to 100 °C under vacuum for 8 h (22.9 mg, 64%). Anal. Calcd for C, 56.02; H, 6.72; N, 0.00. Found: C, 56.45; H, 7.17; N, 0.00%.

Gas Sorption Studies. Gas sorption isotherms were measured with a Belsorp Mini-II at 77 (liquid nitrogen) or 195 K (slush bath of dry ice−^{i}PrOH). The gases used were of the highest quality available (N50 for CO$_2$ and N$_2$, and N35 for CH$_4$). Typically, 100−200 mg of the as-synthesized sample was vigorously stirred in water with a small amount of methanol added to disperse the solids. After 12 h, the solid was collected by centrifugation, loaded into the sample cell, and then heated to 120 °C under dynamic vacuum for 10 h before gas sorption measurements were made. The equilibrium criteria were set consistent throughout all the measurements (change in adsorption amounts less than 0.1 cm^3/g within 180 s).

Powder X-ray Diffractions. Powder X-ray diffraction patterns (PXRD) of as-synthesized samples were recorded at the 2D SMC beamline of the Pohang Accelerator Laboratory, Korea. Crystalline samples were thoroughly ground in an agate mortar and packed in a capillary tube (0.3 mm diameter). Debye−Scherrer diffraction data were collected on an ADSC Quantum-210 detector with a fixed wavelength (λ = 1.2004 Å for **1** and **2**, and 1.2002 Å for **3** and **4**) and an exposure of 60 s. The ADX program[9] was used for data collection, and the Fit2D program[10] was used to convert the two-dimensional (2D) patterns to one-dimensional (1D) ones. The PXRD patterns for samples after water treatment and gas sorption measurements were recorded on a Rigaku D/MAX-2500/PC equipped with a Cu sealed tube (λ = 1.541 78 Å).

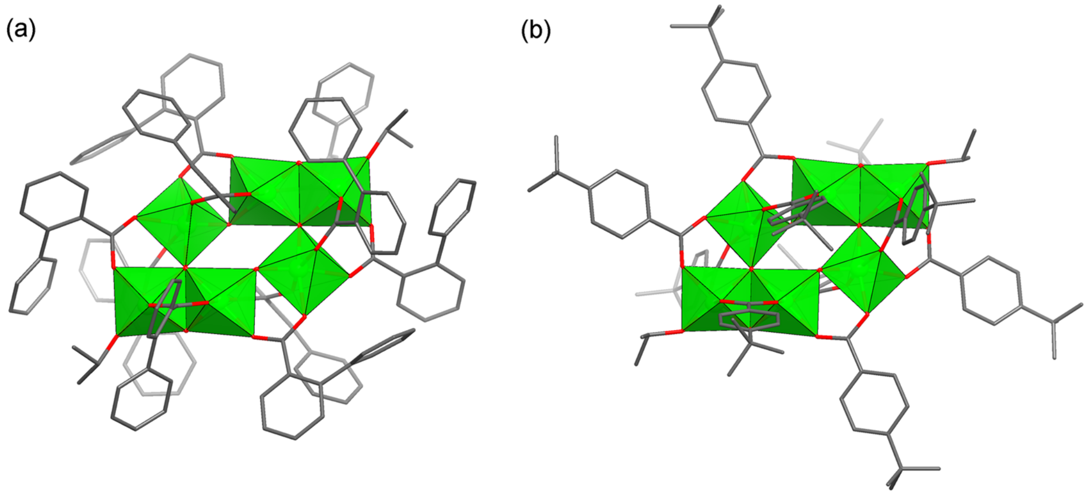


Figure 1. X-ray structures of clusters **1** (a) and **2** (b). TiO_6 units are shown as green octahedra. Hydrogen atoms are omitted for clarity.

X-ray Crystallography. Single crystals of **1**−**4** were directly picked up from the mother liquor with a cryoloop attached to a goniohead and transferred to a cold stream of liquid nitrogen (−173 °C for **1**−**3** and −78 °C for **4**). For **1**, the data were collected on a Bruker D8 Venture diffractometer equipped with a PHOTON 100 CMOS detector using Mo Kα radiation and were processed with APEX2 software. For **2**−**4**, the data collection was carried out using synchrotron X-ray on a ADSC Quantum 210 CCD detector with a silicon (111) double-crystal monochromator at 2D SMC beamline of the Pohang Accelerator Laboratory, Korea. The ADSC Quantum-210 ADX program[9] was used for data collection, and HKL3000sm (Ver. 703r)[11] was used for cell refinement, data integration, and absorption correction. For **2** and **3**, multiple sets of data were collected by manually changing the orientation of mounted crystals, and the individual sets of data were merged using HKL3000sm software. This was necessary because the instrumental setup at the beamline allows only a one-circle rotation of ω, resulting in a poor completeness for low-symmetry structures, such as triclinic. After space group determination, the structures were solved by direct methods and subsequent difference Fourier techniques (SHEXLTL).[12] For **1**, all the non-hydrogen atoms including those of free solvent molecule were refined anisotropically. The coordinated isopropoxide ligand is disordered over two positions. For **2**, all the non-hydrogen atoms were refined anisotropically. Some of the *tert*-butyl moieties are rotationally disordered and refined using a split-atom model. For **3**, all the non-hydrogen atoms were refined anisotropically. Some of the coordinated isopropoxide ligands and phenyl group are disordered over two positions. For **4**, the coordinated isopropoxide and *tert*-butyl moieties are found extensively disordered resulting in unusually large thermal ellipsoids. Residual electron densities were found from the difference maps in intermolecular voids; however, the extensive disorder in the cluster part prohibited a proper modeling or refinements of the partially occupied solvent regions. The diffused electron densities were then removed from the reflection data using the SQUEEZE routine of PLATON.[13] The results of the SQUEEZE process were attached to the CIF file. In all cases, the hydrogen atoms were added to their geometrically ideal positions. Crystallographic restraints were applied to the anisotropic thermal parameters of disordered ligand atoms using the SHELX command ISOR and/or SIMU. But some of the disordered atoms of terminal *tert*-butyl or isopropyl groups still display rather large and distorted thermal motions. The thermal ellipsoid plots of the asymmetric units are shown in Supporting Information, Figure S4. The crystal data and results of structure refinements are summarized in Table 1.

■ RESULTS AND DISCUSSION

The title compounds are readily synthesized in highly crystalline forms when titanium(IV) isopropoxide reacts with an excess amount of carboxylic acids under solvothermal conditions.[14] These reactions can be safely carried out under an ambient condition without the use of extra-dry solvents. All four compounds are obtained in a high yield (>60%) and are stable not only in air but also in aqueous solutions. In gravimetric analysis, the onset of thermal decomposition is observed between 250 and 280 °C and proceeds in two or more steps (Supporting Information, Figure S1). Elemental analysis and PXRD prove that the bulk products are analytically and crystallographically pure (see below). The choice of solvents appears to be a key factor in the synthesis, and thus two types of clusters could be successfully obtained using both biphenyl-2-carboxylic acid and 4-*tert*-butylbenzoic acid. In acetonitrile, a centrosymmetric Ti_6O_6 core is formed (Scheme 1a) in which only two Ti(IV) centers carry an isopropoxide ligand each. The general formula for these clusters is $[Ti_6O_6(O_2CR)_{10}L_2]$, where L is the anion of isopropyl alcohol and RCO_2^- is the carboxylate (2-bpyc for **1** and 4-tbbz for **2**). When isopropyl alcohol is used as the main solvent, a hexagonal column-shaped Ti_6O_6 cluster is obtained with all Ti(IV) centers retaining one isopropoxide ligand each (Scheme 1b). These clusters are formulated as $[Ti_6O_6(O_2CR)_6L_6]$, where RCO_2^- is 2-bpyc for **3** and 4-tbbz for **4**.

The molecular structures of **1** and **2** determined by single-crystal X-ray diffractions are shown in Figure 1. They are based on Ti_6O_6 core in which two $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O)$ subunits are joined by two μ_2-O bridges with a center of inversion symmetry. Of the 10 carboxylate and two isopropoxide ligands that support the Ti_6O_6 core, four carboxylate and the two isopropoxide ligands are arranged on the same plane as the six Ti atoms. The remaining six carboxylates are positioned above and below the plane. This type of geometry is not unknown in Ti-carboxylate clusters;[15] however, all the known examples contain a Ti_6O_4 core rather than Ti_6O_6 as in **1** and **2**. The distances between Ti and μ_3- and μ_2-O atoms are not uniform and show large variations between 1.708(1) and 2.109(1) Å for **1** and between 1.725(1) and 2.068(1) Å for **2**. The distances between Ti and carboxylate O atoms are relatively longer (>2.0 Å) and homogeneous in both **1** and **2**. The isopropoxide ligands are strongly bound with the Ti−O distances of 1.750(1) and 1.784(1) Å for **1** and **2**, respectively. Cluster **1** crystallizes in space group $P\bar{1}$ with two lattice CH_3CN molecules per Ti_6

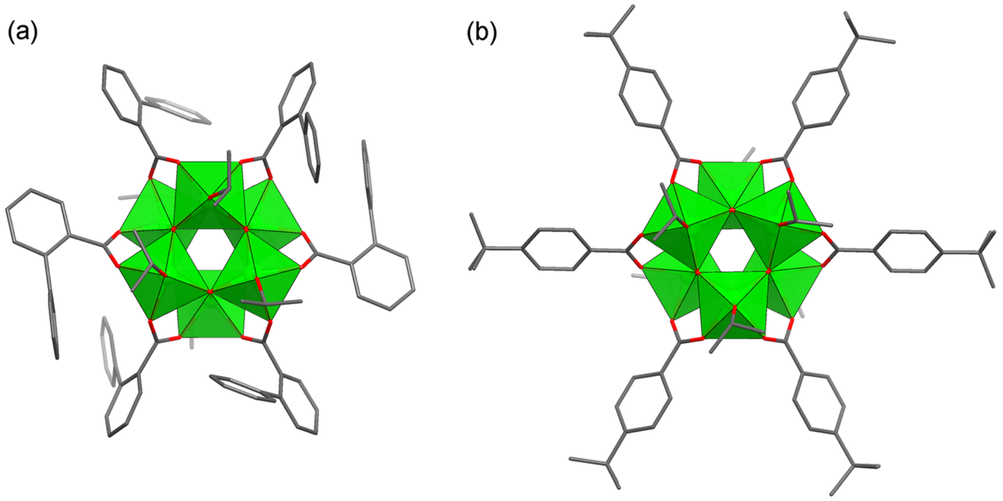


Figure 2. X-ray structures of clusters **3** (a) and **4** (b). TiO_6 units are shown as green octahedra. Hydrogen atoms are omitted for clarity.

cluster. Cluster **2** forms a dense-packed structure without any void or crystallization solvent molecule in space group $P\bar{1}$.

The X-ray structures of clusters **3** and **4** are compared in Figure 2. The hexagonal column-shaped core is built by stacking two Ti_3O_3 hexagons with alternate orientations so that it possesses an ideal S_6 point group symmetry. The μ_3-O atoms are unevenly bound to three Ti atoms, and the "axial" Ti−O distances are significantly longer (>2.1 Å) than the "equatorial" Ti−O distances (≤1.9 Å) in both **3** and **4**. Other Ti−O distances of **3** and **4** show similar characteristics to those in **1** and **2**. Overall, the clusters are supported by six carboxylate ligands positioned around the horizontal plane of the hexagonal column. Each Ti center carries one isopropoxide ligand pointing outward in vertical directions. Cluster **3** forms a dense-packed structure in space group $P\bar{1}$, while cluster **4** crystallizes in cubic space group $Pa\bar{3}$ with 16% of the total crystal volume occupied by disordered solvent molecules (see below).

As one can readily notice, all four clusters do not possess a particular functional group that can interact strongly to guide the packing of molecules. The nonspecific van der Waals contacts, which are responsible for the molecular packing of **1**−**4**, are found surprisingly sturdy, and thus vacuum-dried solids of **1**− **4** display PXRD patterns that closely match the ones simulated from the single-crystal X-ray structures (Figure 3).

Furthermore, the diffraction patterns do not significantly change or deteriorate even after stirring the powder in a water−methanol mixture overnight and subsequently heating it to 120 °C under vacuum for 10 h for a series of gas sorption measurements. Only the experimental patterns for **1** and **2** show slightly reduced intensities and small shifts in the diffraction angles, respectively, after the pretreatments and gas sorption experiments. The stability of the chemical bonds in **1**−**4** in aqueous solutions is also confirmed by the almost identical FT-IR spectra measured before and after the water treatments (Supporting Information, Figures S2 and S3). The surprising water resistance of **1**−**4** owing to their hydrophobic substituents is in good contrast to similar Ti-carboxylate clusters reported earlier by our group. Ti_6O_6 and Ti_8O_{10} clusters supported by 4-aminobenzoate ligands turned completely amorphous when treated with water, although their gas sorption properties do not change upon amorphization.[5]

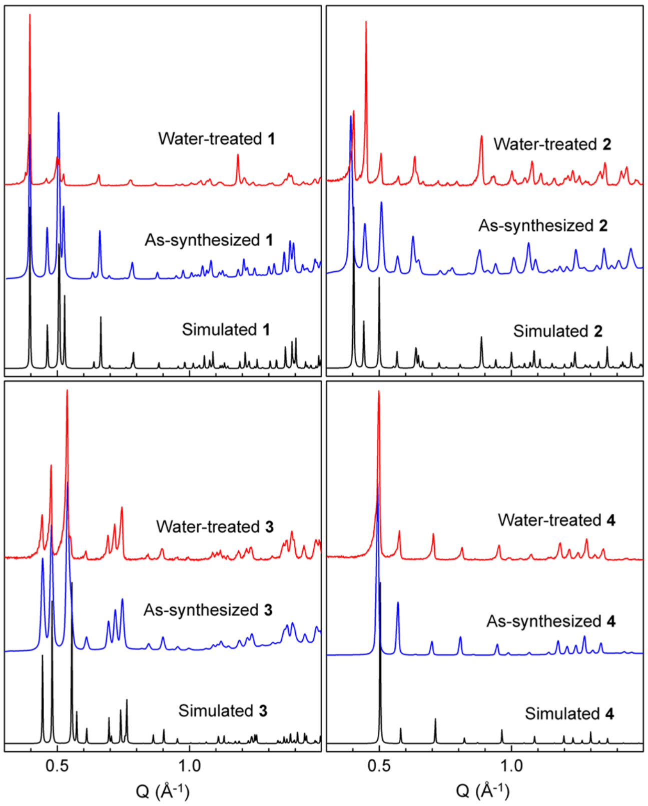


Figure 3. Powder X-ray diffraction patterns for **1**−**4**.

The water- and heat-treated samples of **1**−**4** were subject to gas sorption analysis, and the results are shown in Figure 4. For **1**−**3**, no adsorption of N_2 was observed at both 77 and 195 K. In case of **4**, only a limited amount (10−20 cm^3/g) of N_2 is adsorbed at 77 K, and the adsorption is reduced to an almost negligible level at 195 K. This indicates that **1**−**3** are completely nonporous, and **4** has a very limited porosity, which is probably related to the intermolecular voids. We note that the behavior of **4** with respect to N_2 sorption is opposite to the case of $[Ti_8O_8(benzoate)_{16}]$ that possesses a permanent inner void of 4 Å width. The wheel-shaped cluster shows a significant increase of N_2 uptake on going from 77 to 195 K because the adsorptive

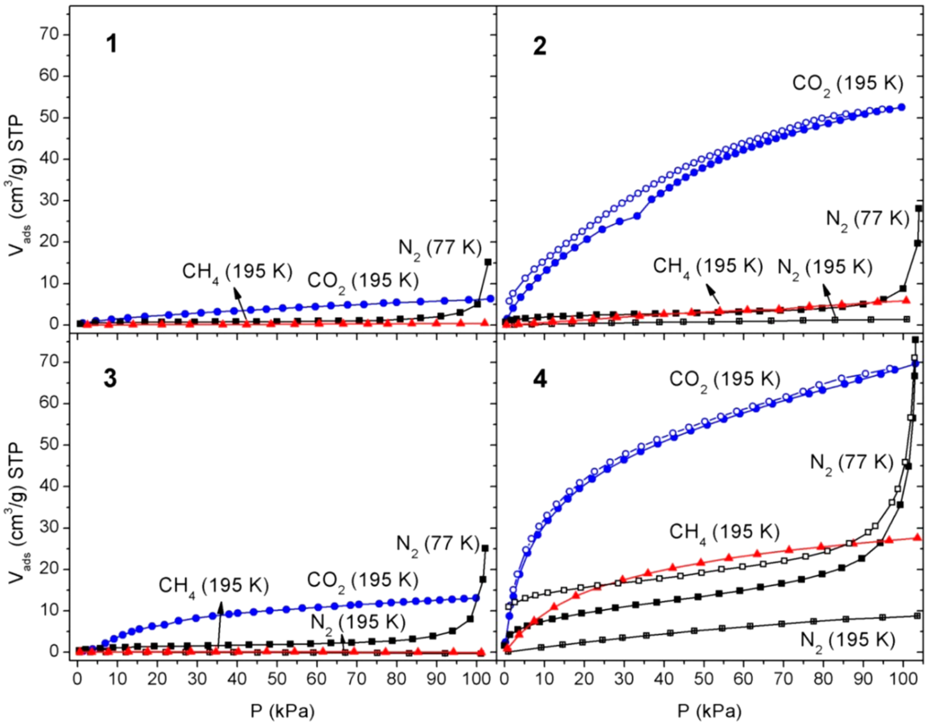


Figure 4. Gas sorption isotherms for **1**−**4**. Filled and open symbols denote adsorption and desorption, respectively.

gas molecules can overcome the kinetic barrier of narrow openings at higher temperature.[5]

Similar to N_2, the adsorption of CH_4 at 195 K was observed only in **4**, albeit to a small extent (27 cm^3/g at 1 bar). The higher volume uptake of CH_4 compared to N_2 at the same temperature is a general phenomenon that originates from the greater polarizability of CH_4 (2.59 vs 1.74 Å^3) leading to stronger interactions with solids.[16]

The most dramatic difference in the sorption behavior of the four clusters was observed for CO_2 at 195 K. As expected, clusters **1** and **3** with 2-substituted benzoate ligand show very limited or no adsorption, while **2** and **4** with 4-substituted benzoate display a significant amount of CO_2 uptake at the same temperature. Considering the discrete molecular nature of the title compounds, it would be more informative to present the sorption data as the number of adsorbed CO_2 molecules per Ti_6 cluster (Figure 5).

It is clear from Figure 5 that clusters **2** and **4** can adsorb almost the same number of CO_2 molecules (~5.5/cluster) despite their differences in geometry and packing structures. Clusters **1** and **3**, which possess the same core geometry as **2** and **4**, respectively, are limited to a maximum uptake of about one CO_2 molecule per cluster. Therefore, these results appear to verify our original hypothesis that substituents on the carboxylate ligands of Ti clusters play an important role in the adsorption of CO_2. It is particularly interesting that the adsorption of CO_2 by the densely packed molecular cluster **2** parallels that of **4** having a relatively large portion of intermolecular voids. The different shapes of the CO_2 adsorption isotherms for **2** and **4** may be related to their packing structures (Figure 6).

In **4**, the adsorption can occur in the intermolecular voids of 4−5 Å width without significantly disturbing the molecular arrangements, and a typical type I curve is observed without a hysteresis between adsorption and desorption. In the densely packed structure of **2**, however, the adsorption of guests can occur only with the expansion of the molecular packing. The structural changes are believed to be responsible for the distinct step in the adsorption branch of CO_2 for **2**. Such a stepped adsorption has also been observed in the case of a nonporous Ti_8O_{10} cluster reported earlier by our group.[5]

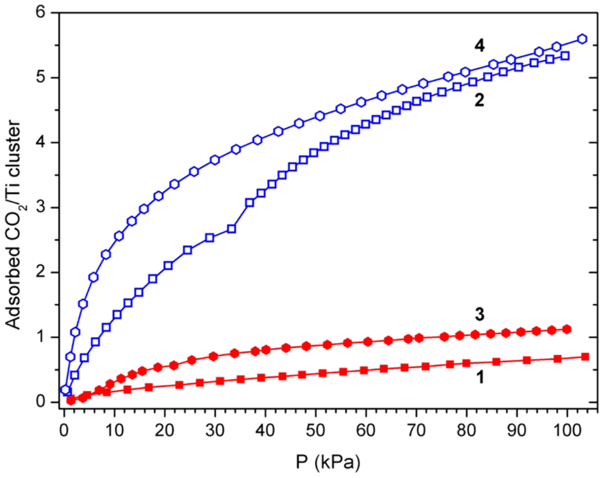


Figure 5. CO_2 sorption data for **1**− **4** plotted as the number of adsorbed molecules per Ti_6 cluster.

In summary, facile synthetic methods were established to obtain two types of carboxylate clusters having a Ti_6O_6 core. Decorating exteriors of the clusters with hydrophobic groups yielded molecular crystals stable after water and heat treatments. Gas sorption studies using N_2, CH_4, and CO_2 reveal that nonporous Ti-carboxylate clusters may show selective adsorption of CO_2 at 195 K depending on the geometry of the carboxylate residue. Our next goal is to elucidate the nature of the interactions between CO_2 and metal cluster molecules so that new materials with an improved CO_2 sorption capacity can be designed and synthesized.

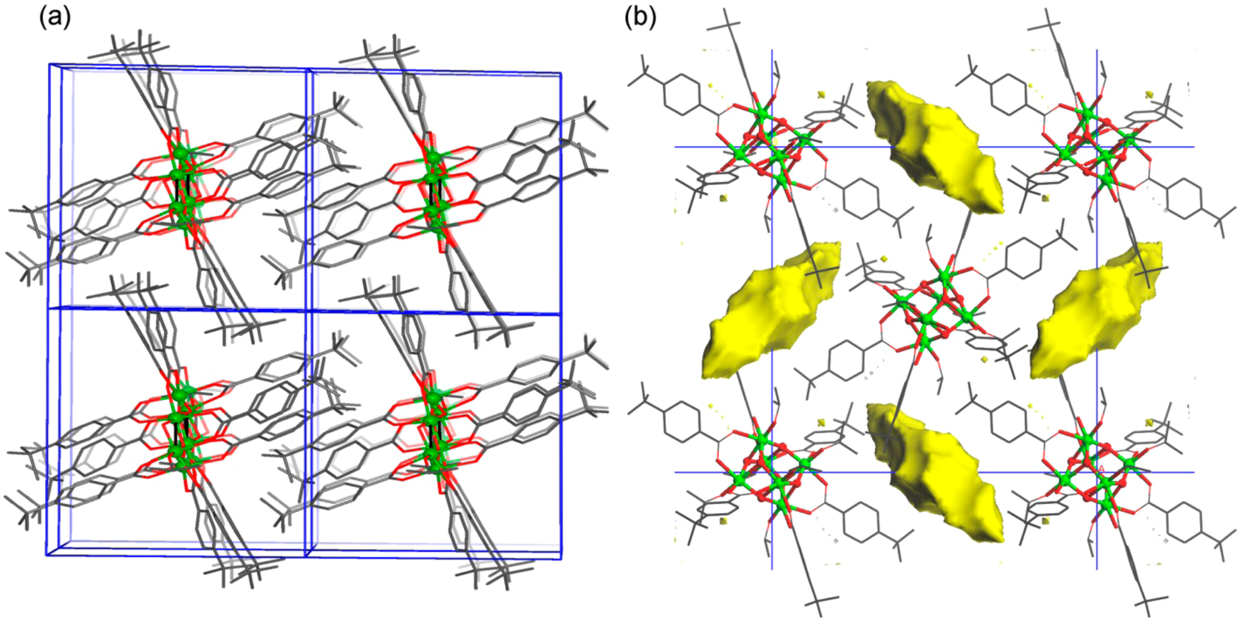


Figure 6. Molecular packing of **2** (a) and **4** (b) shown without the hydrogen atoms. The intermolecular voids occupied by disordered solvent molecules in **4** are highlighted as yellow surface.[17]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

FT-IR spectra, TGA data, and the plots of the crystallographic asymmetric units for **1**−**4**. The crystallographic information file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hchun@hanyang.ac.kr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (2012R1A1A2004333). We thank Dr. D. Moon and Pohang Accelerator Laboratory of Korea for help in collecting X-ray data at the beamline (2013-third-2D-M001). H.C. thanks Prof. K. Kim (POSTECH, Korea) for allowing access to X-ray diffractometer.

■ REFERENCES

(1) (a) Benedict, J. B.; Freindorf, R.; Trzop, E.; Cogswell, J.; Coppens, P. *J. Am. Chem. Soc.* **2010**, *132*, 13669−13671. (b) Benedict, J. B.; Coppens, P. *J. Am. Chem. Soc.* **2010**, *132*, 2938−2944. (c) Macyk, W.; Szaciłowski, K.; Stochel, G.; Buchalska, M.; Kuncewicz, J.; Łabuz, P. *Coord. Chem. Rev.* **2010**, *254*, 2687−2701.

(2) Finn, M. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 113−126.

(3) Rozes, L.; Sanchez, C. *Chem. Soc. Rev.* **2011**, *40*, 1006−1030.

(4) Dan-Hardi, M.; Serre, C.; Frot, T.; Rozes, L.; Maurin, G.; Sanchez, C.; Férey, G. *J. Am. Chem. Soc.* **2009**, *131*, 10857−10859.

(5) Hong, K.; Chun, H. *Inorg. Chem.* **2013**, *52*, 9705−9707.

(6) (a) Duriska, M. B.; Neville, S. M.; Lu, J. Z.; Iremonger, S. S.; Boas, J. F.; Kepert, C. J.; Batten, S. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 8919−8922. (b) Ni, Z.; Yassar, A.; Antoun, T.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 12752−12753. (c) Jung, H.; Moon, D.; Chun, H. *Bull. Korean Chem. Soc.* **2011**, *32*, 2489−2492.

(7) Allison, S. A.; Barrer, R. M. *J. Chem. Soc. A* **1969**, 1717−1723.

(8) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724−781.

(9) Arvai, A. J.; Nielsen, C. *ADSC Quantum-210 ADX Program;* Area Detector System Corporation: Poway, CA, USA, 1983.

(10) Hammersley, A. *Fit2D program;* ESRF: Grenoble CEDEX 9, France, 2004.

(11) Otwinowski, Z.; Minor, W. *Methods in Enzymology;* Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997, Vol. *276*, part A, pp 307.

(12) Sheldrick, G. M. *SHELXTL-PLUS, Crystal Structure Analysis Package;* Bruker Analytical X-Ray: Madison, WI, USA, 1997.

(13) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.

(14) Frot, T.; Cochet, S.; Laurent, G.; Sassoye, C.; Popall, M.; Sanchez, C.; Rozes, L. *Eur. J. Inorg. Chem.* **2010**, 5650−5659.

(15) (a) Heinz, P.; Puchberger, M.; Bendova, M.; Baumann, S. O.; Schubert, U. *Dalton Trans.* **2010**, *39*, 7640−7644. (b) Pandey, A.; Pandey, A.; Singh, S.; Mayer, P.; Parak, W. J. *Z. Naturforsch., B: Chem. Sci.* **2010**, *65*, 147−151. (c) Gao, Y.; Kogler, F. R.; Peterlik, H.; Schubert, U. *J. Mater. Chem.* **2006**, *16*, 3268−3276. (d) Ammala, P. S.; Batten, S. R.; Kepert, C. M.; Spiccia, L.; van den Bergen, A. M.; West, B. O. *Inorg. Chim. Acta* **2003**, *353*, 75−81. (e) Kickelbick, G.; Holzinger, D.; Brick, C.; Trimmel, G.; Moons, E. *Chem. Mater.* **2002**, *14*, 4382−4389. (f) Boraru, B.; Husing, N.; Kickelbick, G.; Schubert, U.; Fratzl, P.; Peterlik, H. *Chem. Mater.* **2002**, *14*, 2732−2740. (g) Steunou, N.; Robert, F.; Boubekeur, K.; Robit, F.; Sanchez, C. *Inorg. Chim. Acta* **1998**, *279*, 144−151. (h) Schubert, U.; Arpac, E.; Glaubitt, W.; Helmerich, A.; Chau, C. *Chem. Mater.* **1992**, *4*, 291−295. (i) Laaziz, I.; Larbot, A.; Guizard, C.; Durand, J.; Cot, L.; Joffre, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *46*, 2332−2334. (j) Doeuff, S.; Dromzee, Y.; Taulelle, F.; Sanchez, C. *Inorg. Chem.* **1989**, *28*, 4439−4445. (k) Gautier-Luneau, I.; Mosset, A.; Galy, J. *Z. Kristallogr.* **1987**, *180*, 83−85.

(16) Webster, C. E.; Cottone, A., III; Drago, R. S. *J. Am. Chem. Soc.* **1999**, *121*, 12127−12139.

(17) The graphic was generated using *Materials Studio,* v. 4.3; Accelrys Software, Inc.: San Diego, CA, USA, 2008.