5174 *Chem. Mater.* **2010,** *22,* 5174–5178
DOI:10.1021/cm101039k

CHEMISTRY OF MATERIALS
Article

Synthesis, Characterization, and Surface Tethering of Sulfide-Functionalized Ti_{16}-oxo-alkoxy Cages

Salvador Eslava,* Anthoula C. Papageorgiou, Simon K. Beaumont, Georgios Kyriakou, Dominic S. Wright, and Richard M. Lambert*

Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom

Received April 14, 2010. Revised Manuscript Received July 7, 2010

The parent cage $[Ti_{16}O_{16}(OEt)_{32}]$ readily undergoes ligand exchange with a range of primary alcohols to yield species of the type $[Ti_{16}O_{16}(OEt)_{32-x}(OR')_x]$, with $R' = $ Me, *n*-Pr, and *n*-Bu with *x* of up to 8. Attempted ligand exchange using the thiol $[HO(CH_2)_4SH]$ in an attempt to produce functionalized cages suitable for tethering to Au surfaces failed, resulting only in the polymerization of the Ti oxo-cores. However, the use of the thioether $[HO(CH_2)_4SCH_3]$ resulted in successful thio-functionalization and preservation of the Ti_{16} cage core, likely due to methyl protection on the sulfide which precludes further intermolecular reaction with other cage molecules. ESI-MS and NMR showed that the resulting substituted cage $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$ contained eight methylthio-*n*-butoxy ligands in two groups of four pseudoequivalent positions. High resolution XPS and STM demonstrated that this sulfide-functionalized cage underwent covalent tethering to Au surfaces involving five sulfur linkages per cage, forming a monolayer of adsorbed species in which the molecular integrity had been preserved. In contrast, the parent oxo-alkoxy cage underwent extensive decomposition, rendering it useless as a building block for specific surface architectures.

Introduction

Titanium-oxo-alkoxy cages $[Ti_xO_y(OR)_z]$ are complexes consisting of an inorganic titanium oxide core surrounded by an organic shell of alkoxy groups.[1,2] The number of titanium atoms in structurally characterized cages ranges from 3 to 18. Of these, the titanium cage $[Ti_{16}O_{16}(OEt)_{32}]$ (**1**) has been most studied due to its ease of synthesis and its relatively high stability in organic solvents (Figure 1).[2−4] In general, $[Ti_xO_y(OR)_z]$ cages are synthesized by controlled hydrolysis of titanium alkoxides in the presence of water. The peripheral ligands (R) may be substituted by other functional groups, preserving the titanium-oxo cores, by exchanging one alkoxide for another:[2]

$$Ti_xO_y(OR)_z + tHOR' \rightarrow Ti_xO_y(OR)_{z-t}(OR')_t + tHOR \quad (1)$$

By such means, a number of substituted cages have been prepared and characterized by nuclear magnetic resonance (NMR) spectroscopy and single-crystal X-ray diffraction.[2−6] Khitrov et al. and Soloviev et al. have characterized similar species by mass spectrometry.[7,8]

Titanium-oxo-alkoxy cages have been used as nano-building blocks for advanced materials and composites, including hybrid organic−inorganic networks.[1,2,9−11] Photocatalytic, photovoltaic, electrochromic, and sensing applications[12] may also be envisaged, which would involve secure tethering of the cages to metal surfaces in order to harness their properties for such applications.

Here, we describe the electro-spray ionization mass spectrometry (ESI-MS) characterization of a range of alkoxy-substituted Ti_{16} cages derived from the parent $[Ti_{16}O_{16}(OEt)_{32}]$ (**1**) by ligand substitution with a range of alcohols. Ligand substitution using a thiol was not possible due to cage polymerization, but the thioether-containing cage $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$ was successfully prepared, as confirmed by NMR. High resolution X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) showed that this sulfide-functionalized cage could be covalently tethered

---

*Corresponding author. Tel: +44 1223 336467. Fax: +44 1223 336362. E-mails: se296@cam.ac.uk (S.E.), rml1@cam.ac.uk (R.M.L).

(1) Rozes, L.; Steunou, N.; Fornasieri, G.; Sanchez, C. *Monatsh. Chem.* **2006**, *137*, 501.
(2) Fornasieri, G; Rozes, L; Le Calve, S; Alonso, B.; Massiot, D.; Rager, M. N.; Evain, M.; Boubekeur, K.; Sanchez, C. *J. Am. Chem. Soc.* **2005**, *127*, 4869.
(3) Mosset, A.; Galy, J. *C. R. Acad. Sci., Ser. I* **1988**, *307*, 1747.
(4) Schmid, R.; Mosset, A.; Galy, J. *J. Chem. Soc., Dalton Trans.* **1991**, 1999.
(5) Le Calve, S.; Alonso, B.; Rozes, L.; Sanchez, C.; Rager, M. N.; Massiot, D. *C. R. Chim.* **2004**, *7*, 241.
(6) Eslava, S.; Hengesbach, F.; McPartlin, M.; Wright, D. S. *Chem. Commun.* **2010**, *46*, 4701.
(7) Khitrov, G. A.; Strouse, G. F.; Gaumet, J. J. *J. Am. Soc. Mass. Spectrom.* **2004**, *15*, 260.
(8) Soloviev, A.; Søgaard, E. G. *J. Mater. Sci.* **2006**, *41*, 6159.
(9) Rozes, L; Fornasieri, G; Trabelsi, S.; Creton, C.; Zafeiropoulos, N. E.; Stamm, M.; Sanchez, C. *Prog. Solid State Chem.* **2005**, *33*, 127.
(10) Bocchini., S; Fornasieri., G.; Rozes., L.; Trabelsi., S.; Galy, J.; Zafeiropoulos, N. E.; Stamm., M.; Gerard, J. F.; Sanchez, C. *Chem. Commun.* **2005**, 2600.
(11) Trabelsi, S.; Janke, A.; Hässler, R.; Zafeiropoulos, N. E.; Fornasieri, G.; Bocchini, S.; Rozes, L.; Stamm, M.; Gérard, J. F.; Sanchez, C. *Macromolecules* **2005**, *38*, 6068.
(12) Chen, X.; Mao, S. S. *Chem. Rev.* **2007**, *107*, 2891.

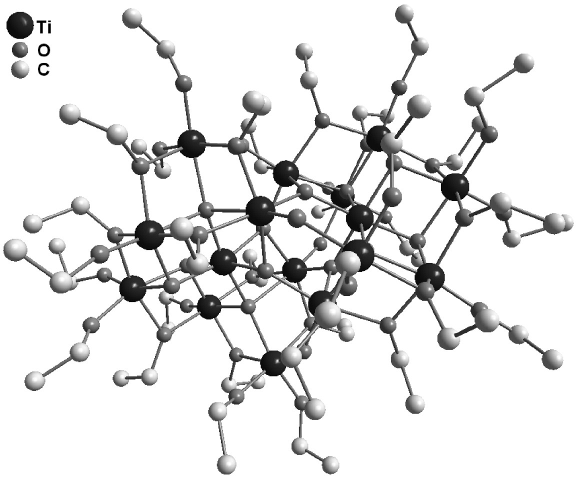

Figure 1. Structure of the cage $[Ti_{16}O_{16}(OEt)_{32}]$ (**1**). H-atoms and the disorder in some of the EtO groups are omitted for clarity.

to Au surfaces, preserving its molecular integrity, in contrast to the parent cage which underwent decomposition.

Experimental Section

Preparation of 1 and Ligand Substitution. The parent cage was prepared by the method described in ref 2. Briefly, under a dry nitrogen atmosphere 7 mL of $Ti(OEt)_4$, 7 mL of anhydrous ethanol, and 300 μL of doubly deionized water were placed in a 25 mL stainless Teflon-lined autoclave and heated to 100 °C for 2 weeks. Subsequent cooling at ~0.2 °C min^{-1} gave (> 1 mm) colorless crystals of **1** (~60% yield). *In situ* substitution reactions in almost quantitative yields were carried out using crystals of **1** dissolved in 2:1 v/v mixtures of toluene and the relevant alcohol (R′OH), with R′ = Me, *n*-Pr, or *n*-Bu. The thiolated cage $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$ was prepared in almost quantitative yields by reaction of **1** with 32 mol equiv of 4-(methylthio)-1-butanol ($[HO(CH_2)_4SCH_3]$, Aldrich 95%) in toluene. Stirring for 20 h under nitrogen at room temperature followed by the removal of the volatile residues under vacuum gave an opaque oil, which was collected and dissolved in a 2:1 vol mixture of toluene/ethanol for the ESI-MS measurements.

ESI-MS and NMR. Mass spectra were recorded in positive ion mode with a Bruker BioApex 4.7e instrument equipped with an ESI source. Typically, the cage samples were introduced into the ESI source as a 2:1 v/v toluene/alcohol mixture at a flow rate of 120 μL min^{-1}. Nitrogen was used as the nebulizing and drying gas, and the cone voltage was varied between 0.5 and 150 V with the capillary voltage set at 3.9 kV. The source and desolvation temperatures were both 150 °C, and the data were processed using Xmass 5.0.10 software. ^{13}C NMR spectra were obtained in d_6-benzene on a Bruker Avance Cryo Ultrashield 500 MHz NMR spectrometer.

Deposition on Au and XPS and STM. Deposition of the parent cage **1** and the sulfide-functionalized cage $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$ on cleaned gold surfaces was carried out by transferring the latter under N_2 to a nitrogen glovebox where they were immersed for 2 h in 1 mL of toluene containing 1.6×10^{-5} mol of either the parent cage **1** or the sulfide-functionalized cage. Samples were then rinsed with 5 mL of toluene before transfer under N_2 to either an Omicron VT-STM UHV instrument or a SCIENTA ESCA300 at NCESS Laboratory, Daresbury, UK, for characterization by STM and high resolution XPS, respectively. STM images were recorded in constant current mode with a chemically etched tungsten tip. High resolution XPS core level spectra were excited using monochromatized Al Kα radiation and recorded at a pass energy of 150 eV. Binding energies are referenced to the Au $4f_{7/2}$ line set at 84.0 eV.

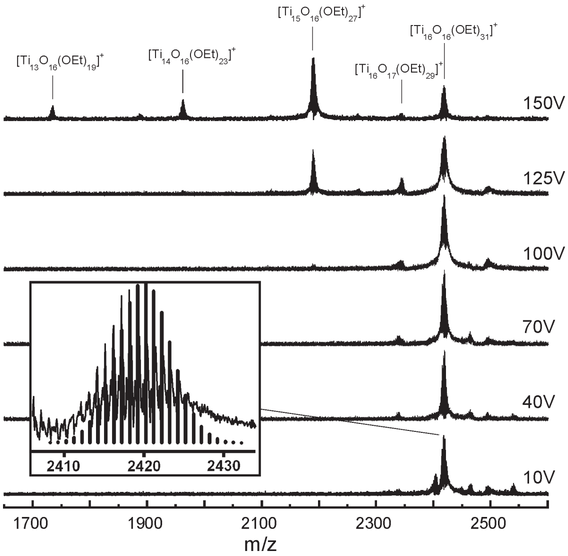

Figure 2. Cone voltage dependence of ESI-MS spectra of $[Ti_{16}O_{16}(OEt)_{32}]$ cages. The inset shows the simulated cage envelope of the principal fragment overlaid on the raw data.

Results and Discussion

ESI-MS Study of Ligand Substitution by OR′ (R′ = Me, ⁿPr, and ⁿBu). Figure 2 shows mass spectra acquired for the parent cage **1** measured with cone voltages, ranging from 10 to 150 V: a cone voltage of 10 V resulted in minimal fragmentation. The spectra exhibit a principal peak at 2419 *m*/*z* attributed to **1** having lost one ethoxy group (i.e., $[Ti_{16}O_{16}(OEt)_{31}]^+$), and the inset shows the calculated effect of the different isotopomers on the ion envelope which is overlaid on the experimental data, the two being in good agreement.[13] Higher voltage produced the fragment $[Ti_{16}O_{17}(OEt)_{29}]^+$, corresponding to the loss of an ethoxy group and a diethylether molecule, Et_2O, the latter being derived from the ethoxy ligands of the cage. The ion $[Ti_{15}O_{16}(OEt)_{27}]^+$ appeared at 100 V cone voltage, corresponding to elimination of an ethoxy group and a $[Ti(OEt)_4]$ unit. Further elimination of $[Ti(OEt)_4]$ units occurred at a cone voltage of 150 V, yielding the fragments $[Ti_{14}O_{16}(OEt)_{23}]^+$ and $[Ti_{13}O_{16}(OEt)_{19}]^+$. The stability of the $Ti_{16}O_{16}$ core is noteworthy: even at 150 V cone voltage, the species $[Ti_{16}O_{16}(OEt)_{31}]^+$ was present in high abundance. The observed fragmentation behavior of **1** is in broad agreement with ESI-MS characteristics reported previously for the cage $[Ti_6O_4(O_2C_4H_5)_8(OCH_2CH_3)_8]$, which shows the loss of similar species from the parent ion.[7]

Figure 3 shows mass spectra resulting from the ligand exchange of **1** using MeOH, ⁿPrOH, and ⁿBuOH; in each case, it is again apparent that the degree of fragmentation increased markedly with cone voltage. After the treatment of **1** with MeOH/toluene, the principal ion detected

---

(13) A low intensity signal at 2404 *m*/*z* that vanished at higher cone voltage could not be assigned.

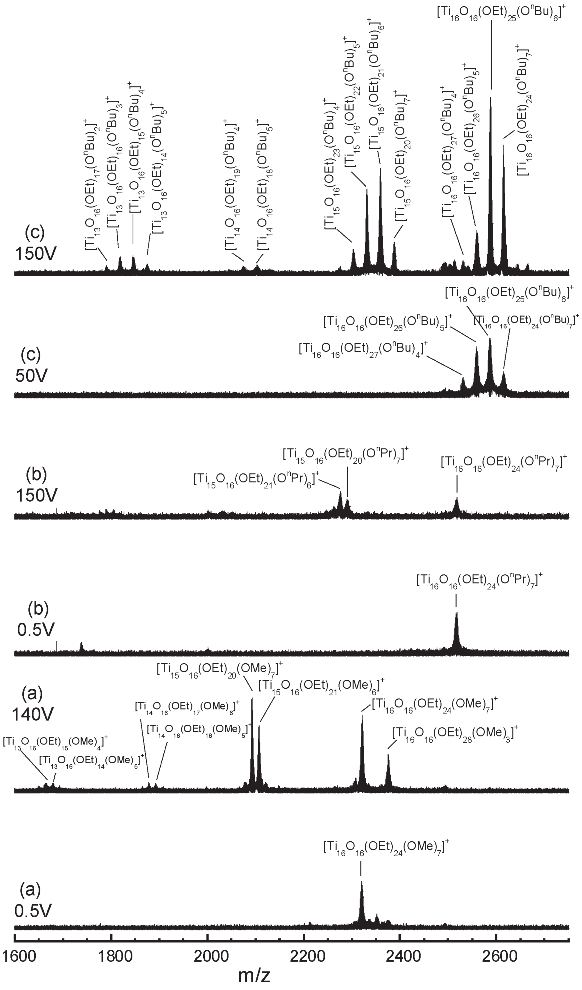

Figure 3. ESI-MS spectra of ligand-exchanged $[Ti_{16}O_{16}(OEt)_{32}]$ cages after treatment with MeOH (**a**), ^{n}PrOH (**b**), and ^{n}BuOH (**c**) as a function of cone voltage.

at low cone voltage was $[Ti_{16}O_{16}(OEt)_{24}(OMe)_7]^+$, confirming that the *in situ* synthetic procedure resulted in the substitution of at least seven EtO groups (Figure 3a). At 140 V cone voltage, extensive fragmentation occurred, and a new ion appeared at the highest *m*/*z* corresponding to $[Ti_{16}O_{16}(OEt)_{28}(OMe)_3]^+$; the other fragments correspond to the elimination of both $[Ti(OEt)_4]$ and $[Ti(OEt)_3(OMe)]$ units from the parent ion $[Ti_{16}O_{16}(OEt)_{24}(OMe)_7]^+$. It is known that the most favored substitutions of **1** are those in which four, eight, or sixteen ethoxy ligands are replaced, resulting in the most symmetric structures.[2] Accordingly, it seems likely that the observed ions $[Ti_{16}O_{16}(OEt)_{24}(OMe)_7]^+$ and $[Ti_{16}O_{16}(OEt)_{28}(OMe)_3]^+$ originate from the cages $[Ti_{16}O_{16}(OEt)_{24}(OMe)_8]$ and $[Ti_{16}O_{16}(OEt)_{28}(OMe)_4]$, respectively, formed in the reaction of **1** with MeOH after ESI loss of a MeO group, although the 8-substituted product is the most abundant.

In contrast to the above behavior, the treatment of **1** with *n*-PrOH/toluene resulted only in the substitution of eight ethoxy groups, the ion $[Ti_{16}O_{16}(OEt)_{24}(O^nPr)_7]^+$ being the principal species observed at low cone voltage (Figure 3b). At 150 V of cone voltage, additional ions resulting from the loss of $[Ti(OEt)_4]$ or $[Ti(OEt)_3(O^nPr)]$ units from the parent ion $[Ti_{16}O_{16}(OEt)_{24}(O^nPr)_7]^+$ were also detected. The treatment of **1** with *n*-BuOH/toluene resulted in a wider range of ligand substitutions, the parent ions observed at 50 V being $[Ti_{16}O_{16}(OEt)_{32-x}(O^nBu)_{x-1}]^+$, where $x = 5-8$. As before, higher cone voltage (150 V) caused the loss of additional $[Ti(OEt)_4]$ and $[Ti(OEt)_3(O^nBu)]$ units.

Ligand Substitution with $[HO(CH_2)_4SH]$ and $[HO(CH_2)_4SCH_3]$. Having shown that ESI-MS characterized the transalcoholysis of **1** producing cages of the type $[Ti_{16}O_{16}(OEt)_{32-x}(OR')_x]$, with R′ = Me, *n*-Pr, and *n*-Bu with *x* of up to 8; depending on the identity of R′, we next studied the possibility of analogous postfunctionalization using a thiol in order to produce cages with the potential for covalent tethering to metal surfaces. Similar procedures have been used for single-molecule magnets consisting of Mn oxo-cages but have not previously been explored for titanium-oxo-alkoxy cages.[14]

Accordingly, ligand substitution of **1** was attempted using the thiol $[HO(CH_2)_4SH]$ and procedures analogous to those described above for alkoxy substitution. However, this resulted in the formation of turbid suspensions, which, upon evaporation of the volatiles under vacuum, led to a solid material that was insoluble in organic solvents, possibly the result of nucleophilic attack by the S atom on the titanium-oxo core, a process likely to result in polymerization. Similar effects have been reported in the modification of manganese cages.[15] However, the use of the thioether 4-(methylthio)-1-butanol $[HO(CH_2)_4SCH_3]$ resulted in successful thio-functionalization and preservation of the Ti_{16} cage core, thanks presumably to the methyl protection on the sulfide which precludes further intermolecular reaction with other molecules of **1**.

Figure 4 shows the mass spectrum of **1** postfunctionalized in this way and dissolved in a toluene/ethanol mixture: the three lightest ions may be assigned to $[Ti_{16}O_{16}(OEt)_{31}]^+$, $[Ti_{16}O_{17}(OEt)_{29}]^+$, and $[Ti_{16}O_{16}(OEt)_{27}]^+$. The heavier ions correspond to cages containing methylthio-*n*-butoxy groups, of formulas $[Ti_{16}O_{16}(OEt)_{32-x}\{O(CH_2)_4SCH_3\}_x]^+$ ($x = 1-6$). Given that the most abundant alkoxy-substituted cages derived from **1** normally correspond to 4-, 8-, or 16-substitutions,[2] the heaviest ions produced in the present case may plausibly be assigned to $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$. NMR data (see below) strengthen this conclusion. Thus, cage **1** may be postfunctionalized according to

$$\begin{aligned} &Ti_{16}O_{16}(OEt)_{32} + 8HO(CH_2)_4SCH_3 \\ &\rightarrow Ti_{16}O_{16}(OEt)_{24}[O(CH_2)_4SCH_3]_8 + 8EtOH \quad (2) \end{aligned}$$

Figure 5a shows the -O-CH$_2$- region ^{13}C NMR spectrum of 4-(methylthio)-1-butanol $[HO(CH_2)_4SCH_3]$, which shows only one signal, as expected. Figure 5b,c shows the spectra of parent cage **1** and $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$, respectively, with the -OCH$_2$- groups

---

(14) Gomez-Segura, J.; Veciana, J.; Ruiz-Molina, D. *Chem. Commun.* **2007**, 3699.

(15) Cornia, A.; Fabretti, A. C.; Pacchioni, M.; Zobbi, L.; Bonacchi, D.; Caneschi, A.; Gatteschi, D.; Biagi, R.; Del Pennino, U.; De Renzi, V.; Gurevich, L.; Van der Zant, H. S. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 1645.

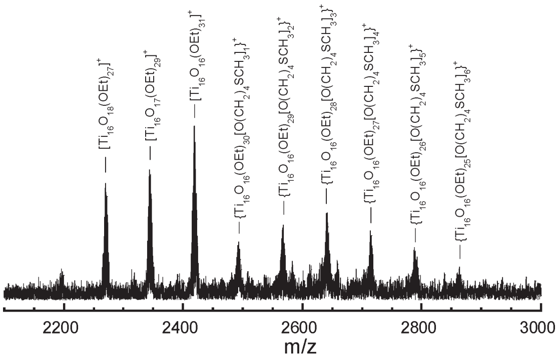

Figure 4. ESI-MS spectra of $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$ cages dissolved in a 2:1 mixture of toluene/ethanol. Cone voltage is 60 V.

resonating at δ 55−80. The ethoxy groups in **1** exhibit eight signals around δ 70 (Figure 5b) since the 32 ethoxy groups in **1** have 8 distinct environments resulting from the 2-fold molecular axis and pseudo 4-fold axis of symmetry within the molecule.[2] Successful postfunctionalization of **1** with the methylthio-*n*-butoxy groups is confirmed by the following features of the ^{13}C NMR spectrum (Figure 5). First, of the eight resonances in the range δ 73−69 assigned to ethoxy groups, only six are kept in the range δ 73−69, and two are very deshielded to ca. δ 75 and 77. These two resonances can be assigned to eight methylthio-*n*-butoxy ligands (in two groups of four pseudoequivalent positions) and the other six resonances to the remaining 24 residual ethoxy groups. Fornasieri et al. observed the same changes in **1** substituted with eight *n*-Pr groups, whereas substitution of only four ligands led to only one resonance deshielded to δ higher than 73.[2] Second, a resonance at δ 58 reveals the presence of free ethanol, resulting from ligand substitution as indicated by eq 2 (the signal at δ ~62 is due to the presence of unreacted 4-(methylthio)-1-butanol, which was used in excess).

Tethering the Thiolated Cages to Gold Surfaces. The thiolated cages were deposited on clean gold surfaces by adsorption from solution after which they were examined by high resolution XPS carried out at NCESS Daresbury Laboratory, UK (see Experimental Section). For reference purposes, the parent cage **1** was similarly deposited on gold, and the results are shown in Figure 6. First, note that in the case of deposited **1**, the Ti 2p intensity is ~2.3 times higher than that found for the sulfide analogue. Given the relatively large escape depth of the Ti 2p photoelectrons (> 5 nm) compared to the cage diameter (~1.5 nm), this is at least consistent with the sulfide-functionalized cage having formed a saturated monolayer, whereas **1** produced two or more layers of deposited material; as we shall see, this is consistent with the STM images.

As can be seen from Figure 6b, the sulfide-functionalized cages exhibit a broad S 2p emission. The resolution of the S 2p XP spectra is limited by the S/N ratio resulting from the low number density of sulfur atoms in the adsorbed layer (~2 atomic %). These data, acquired at a normal photoelectron exit angle, represent the optimum amount of information that could be obtained on a realistic time scale. It is clear that two chemically distinct states of sulfur were present: the breadth of the sulfur 2p envelope is substantially greater than can be accounted for by a single ($2p_{3/2,\ 1/2}$) spin orbit doublet. The important point is that these two sulfur species are visible to XPS and are present in about equal amounts, consistent with a monolayer of cages on the Au surface and in line with the STM results. A multilayer of cages would yield a single S 2p component. The observed S $2p_{3/2}$ binding energies of 163.4 and 164.5 eV correspond to surface-tethered sulfur and sulfur not in contact with the gold surface.[16,17] Quantification of the spectra provides an estimate of the ratio of the surface bound to unperturbed sulfur of 5(±1):3, i.e., about half the sulfide ligands are involved in bonding to the metal surface. The large (1.1 eV) downshift in S 2p binding energy induced by adsorption implies strong electronic interaction with the metal surface involving significant charge transfer from Au to S, as indicated in Figure 6 c. This picture is consistent with a comprehensive survey of dialkyl sulfides adsorbed on Au by Whitesides and co-workers who concluded that dialkyl sulfides anchor to gold surfaces via a gold−sulfur coordinate bond.[18] Note that after correction for photoionization cross-sections,[19] the calculated S:Ti ratio in the adsorbed phase is 1.2 (±0.2):2, consistent with the 1:2 stoichiometry of the sulfide-functionalized cages.

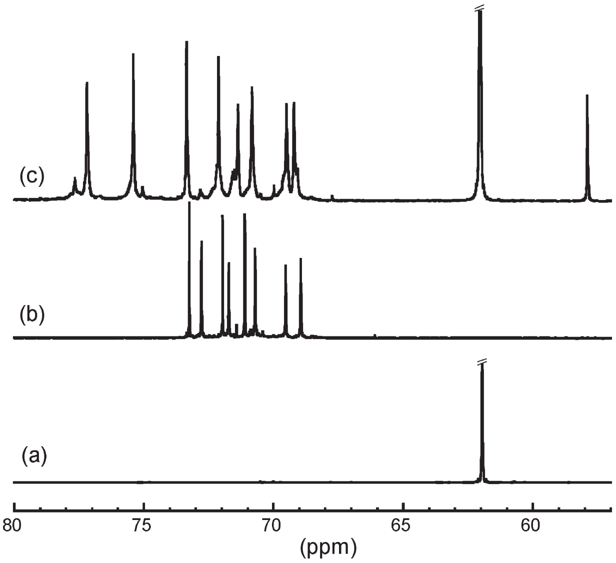

Figure 5. ^{13}C NMR spectra of the -OCH_2- resonance region of (**a**) $[HO(CH_2)_4SCH_3]$, (**b**) $[Ti_{16}O_{16}(OEt)_{32}]$, and (**c**) $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$.

Figure 7a shows an STM image of the clean, herringbone reconstructed Au(111), and Figure 7b illustrates the result of immersing this surface in a solution of Ti_{16} cages (**1**). The latter, in conjunction with the (blue) line scan shown in Figure 7d, indicates ~85% coverage of the Au(111) surface with a contact layer of adsorbed cages

---

(16) Berner, S.; Biela, S.; Ledung, G.; Gogoll, A.; Bäckvall, J.-E.; Puglia, C.; Oscarsson, S. *J. Catal.* **2006**, *244*, 86.

(17) Turner, M.; Vaughan, O. P. H.; Kyriakou, G.; Watson, D. J.; Scherer, L. J.; Davidson, G. J. E.; Sanders, J. K. M.; Lambert, R. M. *J. Am. Chem. Soc.* **2009**, *131*, 1910.

(18) Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365.

(19) Yeh, J. J.; Lindau, I. *At. Data Nucl. Data Tables* **1985**, *32*, 1.

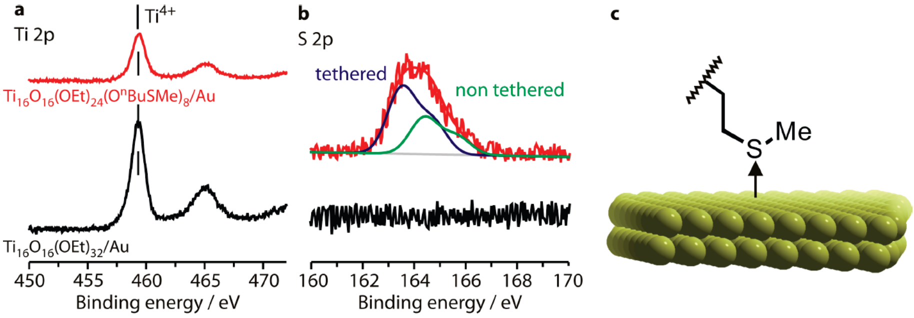

Figure 6. (a) Ti 2p and (b) S 2p XP spectra of the $[Ti_{16}O_{16}(OEt)_{32}]$ and $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$ cages on gold surfaces. (c) Schematic indicating the likely mode of adsorption of dialkyl sulphides when tethered to gold,[18] with the arrow indicating the direction of observed charge transfer.

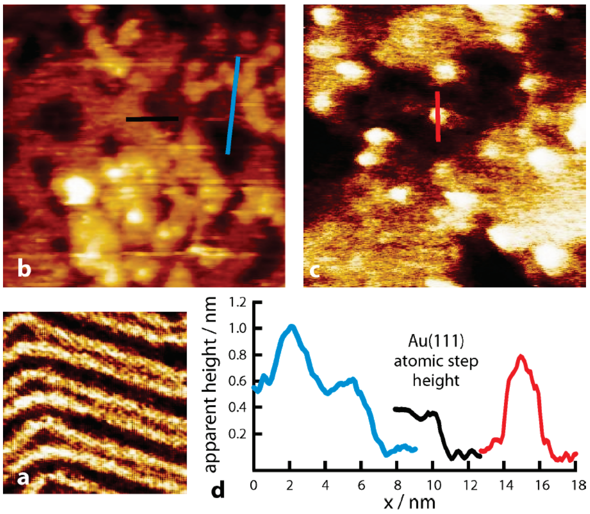

Figure 7. Clockwise from bottom left: STM images of (a) clean, reconstructed Au(111) (25 × 25 nm^2, V_{gap} = 2.41 V, I = 0.21 nA); (b) **1** supported on Au(111) (25 × 25 nm^2, V_{gap} = −1.00 V, I = 0.26 nA) and (c) $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$ supported on Au(111) (25 × 25 nm^2, V_{gap} = −0.62 V, I = 0.33 nA). (d) Line profiles corresponding to the lines drawn in panels b and c showing apparent heights of the film of **1** on Au(111) (blue), Au(111) atomic step height (black), and isolated $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$ on Au(111) (red).

identified by its greater apparent height compared to the Au atomic step height (black line scan). The absence of distinguishable features in this contact layer suggests Au-activated cage condensation. On top of this contact layer, individual features corresponding to the lateral dimensions of the Ti_{16} cages (∼2 nm) are distinguishable.

Exposure of a similarly clean Au surface to a solution containing the same concentration of sulfide-functionalized cages produced images such as that shown in Figure 7c. Here, the cage coverage is in the monolayer range, and individual entities of ∼2 nm diameter in direct contact with Au are seen (red line scan). The lateral dimensions of these entities are consistent with those of an individual cage, and they are accordingly assigned as such. Similar behavior has been reported previously for sulfide-functionalized Mn_{12} cages.[20]

Note that these STM results are in quantitative accord with the XPS data. They show that the parent cage **1** forms a featureless layer in contact with the Au surface on top of which a second layer of cages agglomerates. In contrast, the sulfide-functionalized cages adsorb without decomposition, and uptake ceases at a monolayer or less: the result is a layer of robustly tethered photofunctional molecules in electronic contact with the metal surface. We may propose a tentative explanation for this marked difference in behavior between the parent cage **1** and its sulfide counterpart as follows. The greater linker length of the sulfide ligands which tether the cage to the gold surface prevents their decomposition by the latter. At the same time, the free sulfide ligands (Figure 7c) prevent accretion of higher layers of cages on top of the contact layer.

These are encouraging results, given that in the present case thiol functionalization, a common approach to covalent tethering of adsorbates, is inapplicable. However, sufficiently extended thioether ligands do provide a viable strategy for covalently linking the cages to a metal surface, opening the door to synthesis of purposefully designed building blocks to enable the construction of new types of functional surface architectures.

Conclusions

The titanium-oxo-alkoxy cage $[Ti_{16}O_{16}(OEt)_{32}]$ (**1**) and alkoxy cages derived from it by ligand substitution using primary alcohols are stable in solution. However, the parent cage undergoes extensive decomposition in contact with gold surfaces and cannot therefore be used to photofunctionalize them. Attempts to achieve ligand substitution of **1** by means of the thiol $[HO(CH_2)_4SH]$ so as to create photoactive building blocks capable of linking covalently to a metal surface were unsuccessful due to cage polymerization. The alternative strategy of using the corresponding thio-ether $[HO(CH_2)_4SCH_3]$ prevented polymerization and resulted in successful functionalization yielding the stable cage $[Ti_{16}O_{16}(OEt)_{24}\{O(CH_2)_4SCH_3\}_8]$. Individual cages could be covalently tethered to gold surfaces without decomposition, as demonstrated by STM and XPS, thus providing a viable method for harnessing the properties of titanium oxo-cages to metal surfaces.

Acknowledgment. We acknowledge the financial support under Research Grant EP/F00253X/1 awarded by the UK Engineering and Physical Sciences Research Council. S.K.B. acknowledges financial support from the University of Cambridge; Trinity Hall, Cambridge; and UK Society of the Chemical Industry and the International Precious Metals Institute.

---

(20) Zobbi, L.; Mannini, M.; Pacchioni, M.; Chastanet, G.; Bonacchi, D.; Zanardi, C.; Biagi, R.; Del Pennino, U.; Gatteschi, D.; Cornia, A.; Sessoli, R. *Chem. Commun.* **2005**, 1640.