

Dibenzo Crown Ether Layer Formation on Muscovite Mica

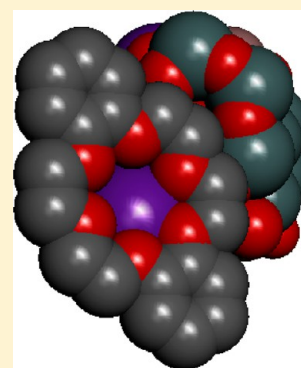
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S Supporting Information

ABSTRACT: Stable layers of crown ethers were grown on muscovite mica using the potassium–crown ether interaction. The multilayers were grown from solution and from the vapor phase and were analyzed with atomic force microscopy (AFM), matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, and surface X-ray diffraction (SXRD). The results show that the first molecular layer of the three investigated dibenzo crown ethers is more rigid than the second because of the strong interaction of the first molecular layer with the potassium ions on the surface of muscovite mica. SXRD measurements revealed that for all of the investigated dibenzo crown ethers the first molecule lies relatively flat whereas the second lies more upright. The SXRD measurements further revealed that the molecules of the first layer of dibenzo-15-crown-5 are on top of a potassium atom, showing that the binding mechanism of this layer is indeed of the coordination complex form. The AFM and SXRD data are in good agreement, and the combination of these techniques is therefore a powerful way to determine the molecular orientation at surfaces.



1. INTRODUCTION

Cleaved (001) muscovite mica ($a = 0.51906$ nm, $b = 0.9008$ nm, $c = 2.0047$ nm, $\alpha = \gamma = 90^\circ$, $\beta = 95.757^\circ$, space group $C2/c$, chemical formula $KAl_2(Si_3Al)O_{10}(OH)_2$ (Figure 1)) is atomically flat,¹ which makes it a suitable material for the self-assembly of molecular layers.^{2,3} Many self-assembled layers are stabilized by alkyl chain–alkyl chain interactions, hydrogen bonding, π – π stacking, van der Waals interactions, covalent bonds, or a combination of these interactions.^{4–7} Crown ether-based molecules are known to bind specifically to alkali and other metal ions, where the specificity is controlled by the sizes of the ion and the crown ether ring.^{8–10} Muscovite mica has potassium ions present on its (001) surface, which might be able to form a coordination complex with crown ether-based molecules. Furthermore, the potassium ions at the muscovite mica surface can be exchanged (e.g., for sodium, cesium, or manganese ions),^{11,12} which opens the way to modify the surface's affinity for differently sized crown ethers. These versatile properties make the muscovite mica/crown ether combination an interesting candidate for the growth of (ordered) molecular layers. Crown ethers can be tailored and functionalized at will; therefore, these ordered molecular layers could be used as a template for other crystal structures.

In previous research, muscovite mica has been used as a support for crown ether-based polymer and nanoparticle structures.^{13,14} The stability of crown ether-based polymers attached to ground muscovite flakes has also been investigated,¹⁵ but to the best of our knowledge, no attempts have been made to produce ordered crown ether-based molecular layers on muscovite mica.

In this article, the formation of molecular layers of three different crown ethers (dibenzo-15-crown-5 (DB15C5), dibenzo-18-crown-6 (DB18C6), and dibenzo-24-crown-8 (DB24C8) (Figure 2)) on potassium- and sodium-terminated muscovite mica is described. The layers were prepared using two different techniques, that is, vapor deposition and submersion in a solution of crown ether. The stability and formation of the layers were investigated with the help of atomic force microscopy (AFM) and in a solution with in situ AFM, respectively. The presence of the crown ether at the surface was verified with the help of matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. Finally, layers of the three different crown ethers were investigated using surface X-ray diffraction (SXRD) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

2. EXPERIMENTAL SECTION

2.1. Specimen Preparation. Muscovite mica (quality grade ASTM-V1) was obtained from S&J Trading Inc. (Glen Oaks, NY, USA); the dibenzo-15-crown-5 (purity 97%) and dibenzo-24-crown-8 (98%) were purchased from Sigma-Aldrich, and the dibenzo-18-crown-6 (98%) was purchased from Acros Organics. All crown ethers were used without further purification. Solutions of $(1.0 \pm 0.3) \times 10^{-4}$ M crown ether were prepared by dissolving the crown ether in ethanol (absolute, Emsure, ACS, ISO, Reag. Ph. Eur. obtained from Merck). These solutions were left for 2 to 7 days at room temperature to equilibrate prior to use.

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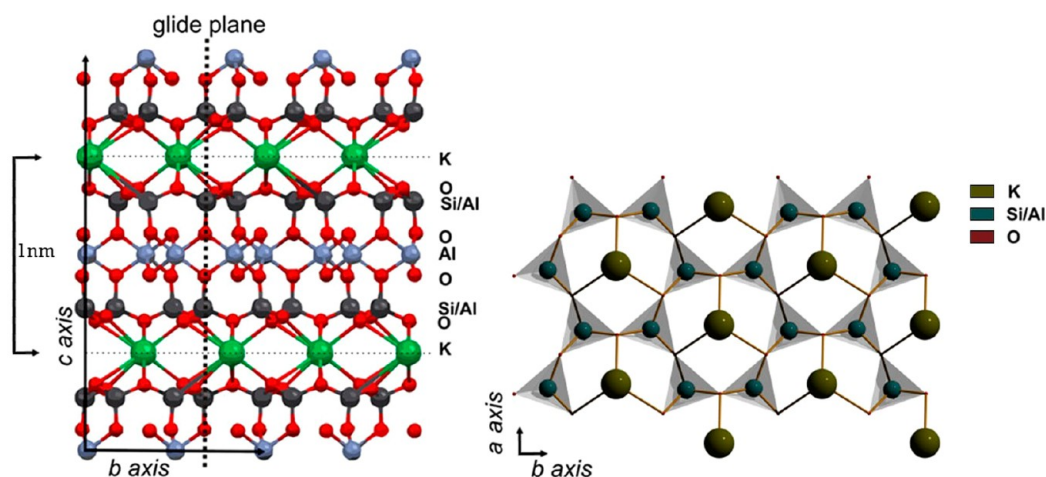


Figure 1. (Left) Side-view, ball-and-stick model of the atomic structure of muscovite mica; the surface after cleavage corresponds to the horizontal dotted line through the potassium atoms. The arrows on the left indicate the $1/2c^*$ (or 1 nm) single step height of the muscovite mica crystal. (Right) Top-view, schematic structure of a muscovite mica (001) surface. On the vertices of the tetrahedra are oxygen atoms, at their center is a silicon (75%) or aluminum (25%) atom, and at the center of the hexagons are potassium ions. A cleaved muscovite mica surface contains half of the number of potassium ions shown, at random positions in order to preserve charge neutrality.



Figure 2. (Left to right) Chemical structures of dibenzo-15-crown-5, dibenzo-18-crown-6, and dibenzo-24-crown-8.

In the submersion method, a freshly cleaved 1 cm^2 piece of muscovite mica was submerged in a solution of $(1.0 \pm 0.3) \times 10^{-4} \text{ M}$ crown ether for 10 s. The muscovite mica was then slowly removed from the solution in approximately 20 s and dried for 2 min in a vertical position and at least 1 hour in a horizontal position under a gentle nitrogen gas flow. If the sample was washed with water (ultrapure, $18.2 \text{ M}\Omega/\text{cm}$ resistance, and $<3 \text{ ppb}$ organic content (MQ)), this was done immediately after the removal from the crown ether solution by subsequent submersion in water for 10 s and removal and drying as described previously.

In the case of vapor deposition, a freshly cleaved 1 cm^2 piece of muscovite mica was attached to the bottom of a crystallizer (beaker) using double-sided adhesive tape. The beaker was then turned upside down onto a glass plate, effectively making a glass container. This container contained crown ether powder and was heated at the base to $85 \pm 5^\circ \text{C}$, leading to a temperature of $35 \pm 5^\circ \text{C}$ at the position of the muscovite mica, located 7 cm above the heat source. The muscovite mica was exposed for at least 1 h to the crown ether vapor.

The ion exchange of the potassium for sodium ions on the surface was performed by submerging freshly cleaved muscovite mica samples in a 10^{-2} M solution of NaCl (Emsure, ACS, ISO, Reag. Ph. Eur. obtained from Merck) in water (MQ) for at least 1 h. The muscovite mica was then removed and washed twice in water (MQ). The muscovite mica was dried in a vertical position for 2 min and in a horizontal position for at least 1 h under gentle nitrogen gas flow. The molecular layers were then prepared as described above without further cleaving.

Glassware was cleaned vigorously, first using soap and a bristle brush for the persistent tarnish and subsequently rinsed 10 times with water (MQ) and 3 times with ethanol (Emsure etc.) to ensure that as little contamination as possible was present.

2.2. Surface Characterization. AFM was performed on dry samples and in a liquid environment (in situ). AFM was applied in intermittent contact mode (Dimension 3100) with NSG 10 golden silicon probes from NT-MDT. In situ measurements were performed using a Nanoscope IV (multimode) with SNL probes from Veeco. A

liquid cell was used for the in situ measurements, where a rubber O-ring connects the sample with the cell and prevents the liquid from evaporating.

MALDI-TOF measurements were performed using a Biflex III MALDI-TOF MS in reflectron mode, with an α -cyano matrix (20 mg of α -cyano-hydroxy cinnamic acid in 0.5 mL of acetonitrile and 0.1% trifluoroacetic acid, which results in a saturated solution). Mica samples were fixed to an MTP adapter for a prespotted anchor chip with double-sided conducting adhesive stickers (originally intended for SEM) and were spotted with $0.5 \mu\text{L}$ of matrix solution.

SXRD was performed at beamline ID03 of the ESRF using a vertical z -axis diffractometer equipped with a 2D detector in stationary geometry.¹⁶ The momentum transfer in the X-ray diffraction experiments is denoted by $\vec{Q} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$, with \vec{a}^* , \vec{b}^* , and \vec{c}^* being the reciprocal lattice vectors and (hkl) being the diffraction indices. The diffraction rods are oriented along the l direction. The experiment was performed using a 15 keV beam having a 1 mm horizontal width and $20 \mu\text{m}$ vertical width, with an incoming angle of 0.6° for nonspecular data; this led to a footprint of $1 \times 2 \text{ mm}^2$. Structure factors from several crystal truncation rods (CTRs) were derived from the detector images using MATLAB code written for this purpose. Fitting of the SXRD data was carried out using the ROD program.¹⁷

The surface termination was characterized prior to the full data acquisition by measuring the (111.4) and $(\bar{1}\bar{1}1.4)$ reflections for a large part of the surface to make sure that measurements were carried out on a single-terminated muscovite mica surface.¹ The measurements were performed under dry conditions by placing the samples in a cell with a constant nitrogen flow. For the SXRD experiments, a layer of DB15C5 was prepared by submerging a freshly cleaved piece of muscovite mica into a solution of saturated DB15C5 in ethanol for 2 h, which was then removed and dried as discussed previously. The DB18C6 layer was prepared by submerging a freshly cleaved piece of muscovite mica in a saturated DB18C6 in ethanol solution for 2 h, which was removed from the solution in 20 s and then washed by submersion in ethanol for 10 s.

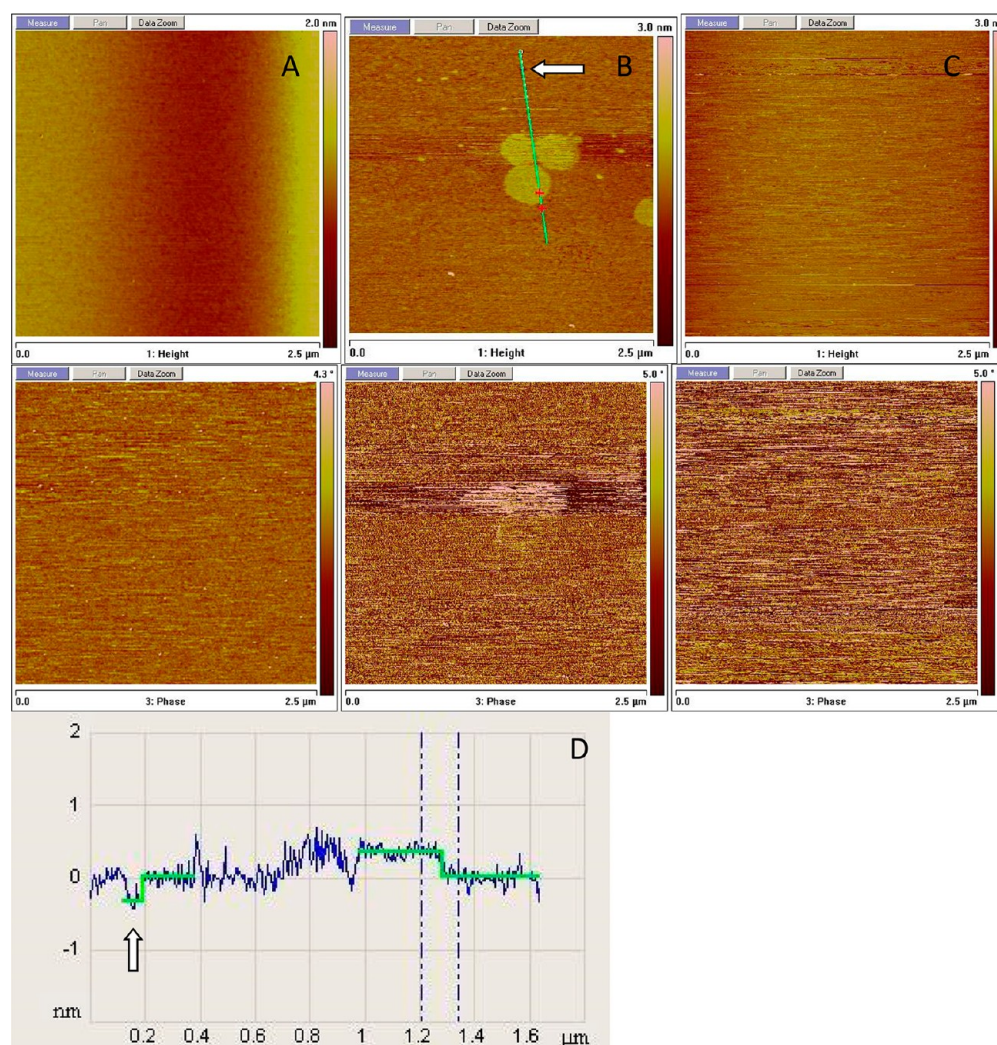


Figure 3. AFM height (top) and phase (bottom) images of (A) DB15C5, (B) DB18C6, and (C) DB24C8 layers on muscovite mica (001). (D) Height profile of the cross-section from panel B, showing that both the hole (indicated by the arrow) and the patches are 0.4 ± 0.15 nm high.

The sample was then removed and dried as discussed previously. The DB24C8 layer was prepared by submerging a freshly cleaved piece of muscovite mica in a 9.1×10^{-5} M solution for 2 h, which was then removed and dried as discussed above.

A model was developed to fit the data and includes the bulk and a surface unit cell of muscovite mica and a specified number of crown ether molecules. The fit parameters are the occupancy, location, and orientation of the molecules and the atomic Debye–Waller parameters. All CTRs (eight different ones were measured) are sensitive to the presence of crown ether molecules in the model.

3. RESULTS AND DISCUSSION

3.1. Molecular Layer Formation. Layers of the three crown ethers (DB15C5, DB18C6, and DB24C8) were prepared on a muscovite mica surface by the submersion method (Experimental Section). After subsequent washing in water, the samples were analyzed using AFM (Figure 3). Of these three crown ethers, DB18C6 is expected to bind the strongest to the muscovite mica because a geometry with the potassium ion in the center of the crown ether ring is energetically most favorable.¹⁸ The potassium ion fits into its crown ether ring of DB18C6, whereas the ring of DB15C5 is too small and the ring of DB24C8 is too large.⁹ From calculations, it is also known that DB18C6 bonds more strongly to potassium ions in methanol than do DB15C5 and DB24C8.⁸ Potassium ions are present on the

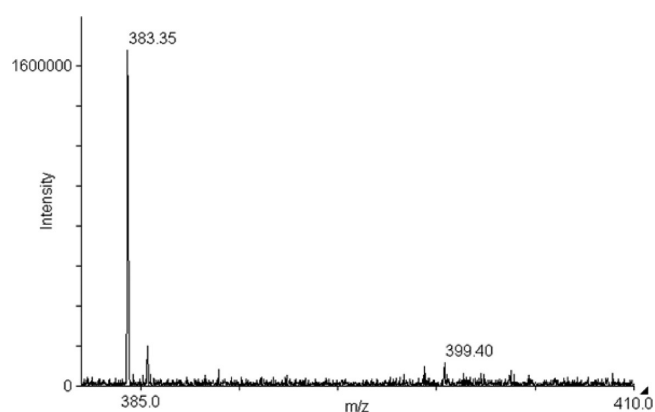


Figure 4. MALDI-TOF mass spectrum of the DB18C6 layer on muscovite mica, with the peak at 383 amu corresponding to the $[\text{DB18C6-Na}]^+$ complex and that at 399 amu corresponding to the $[\text{DB18C6-K}]^+$ complex.

surface of untreated muscovite mica; therefore, it is expected that DB18C6 binds better than the other crown ethers. However, the results may be different from this expectation because the experiments are not performed in methanol but in ethanol.

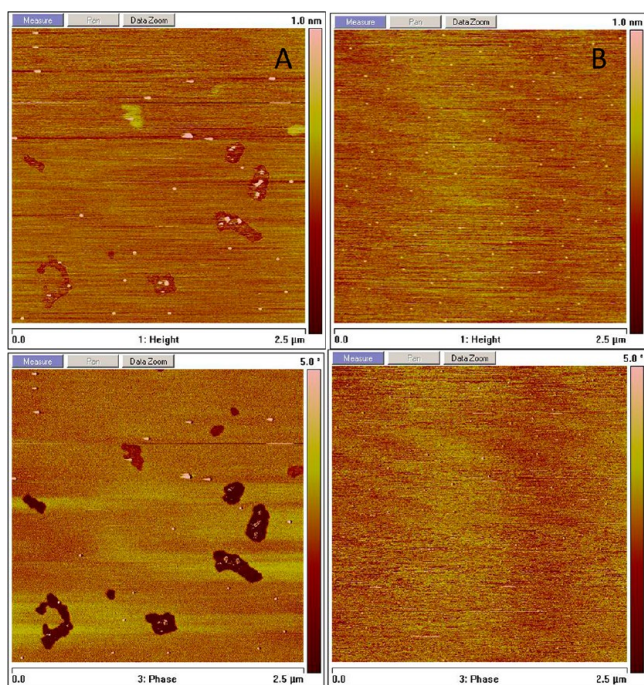


Figure 5. AFM height (top) and phase (bottom) images of the result of DB18C6 vapor deposition on muscovite mica after (A) 1 h of exposure (holes are 0.2 ± 0.1 nm deep) and (B) 17 h of exposure to the vapor.

AFM height and phase images of the three crown ether molecular layers on a muscovite surface are depicted in Figure 3A–C. Multiple patches of a second layer are visible in the height image of Figure 3B. The absence of a phase difference between the patches and the layer underneath indicates that they consist of material with the same physical properties. In the same height

image, a small, dark spot is visible above the patches, which is a hole in the first layer. The height of the islands is 0.4 ± 0.15 nm, and the hole is also 0.4 ± 0.15 nm deep. This height indicates that the crown ether molecules are lying relatively flat on the surface (a perfectly flat layer would be 0.3 nm high). It is expected that the apolar benzene rings will bend away slightly from the polar surface, which will lead to a slightly larger layer thickness than when the molecules would lie perfectly flat.

The multilayers of DB18C6 were investigated with the help of MALDI-TOF mass spectrometry in order to prove that the material on the muscovite mica indeed consisted of these molecules (Figure 4). The peaks at 383 and 399 atomic mass units (amu) originate from the DB18C6 molecule, complexed with a sodium or potassium ion, respectively. The sodium ions might originate from several sources, e.g., (air) contaminants or impurities in the muscovite mica or from the matrix solution that was used in MALDI-TOF. The observed peaks, however, prove that molecules of DB18C6 are indeed present on the surface. The MALDI-TOF spectra of the layers of DB15C5 and DB24C8 on muscovite mica can be found in Supporting Information S1 and S2 and confirm the presence of these molecules as well.

Considering the observed full coverage of the surface, all three crown ethers seem to attach well to the muscovite mica. This can be explained by looking at their binding constant to potassium ions. The binding constants of potassium ions in a solution with the three crown ethers are of the same order of magnitude ($\log K$ values larger than 3, where K is the equilibrium binding constant to the metal ion).⁹ Therefore, it is likely that the crown ethers behave similarly.

It is expected that crown ether molecules interact more strongly with available ions in the supernatant solution because a geometry in which the potassium ion is at the center of the crown ether ring is energetically most favorable,¹⁸ which is not possible at the muscovite mica surface. The potassium ions are located on

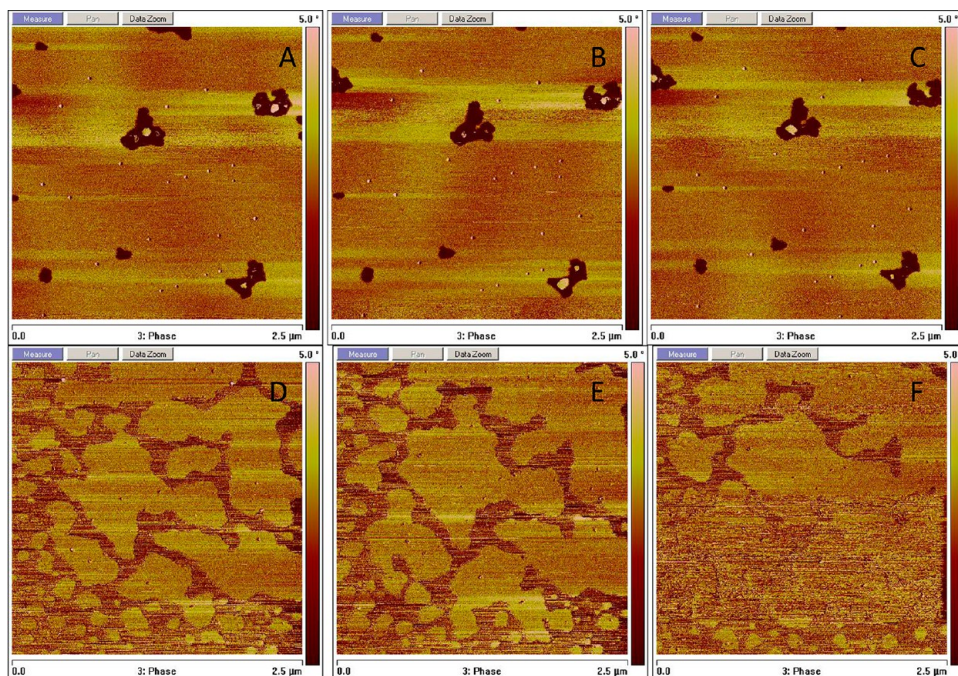


Figure 6. (A–C) Subsequent AFM phase images of an incomplete layer of DB18C6 on muscovite mica, obtained by vapor deposition, showing some change in the surface morphology over time, which indicates a slight mobility of the first layer. (D–F) Subsequent AFM phase images of an incomplete second layer of DB18C6 on muscovite mica, produced with the submersion technique. The images show a rapidly changing surface morphology, indicating a highly mobile second layer. The time interval between the images is 9 min.

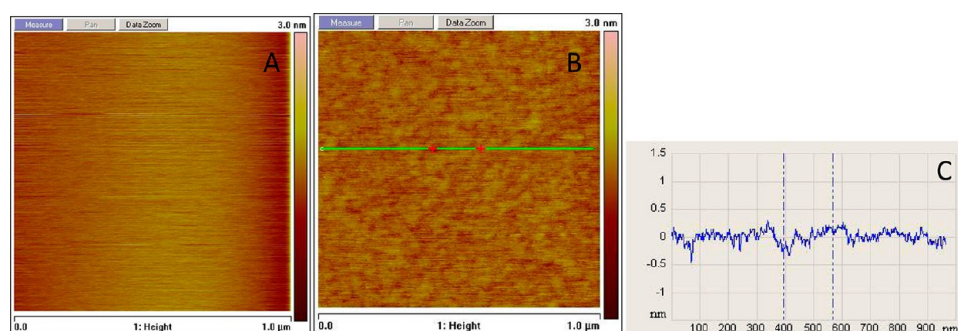


Figure 7. AFM height images of (A) a DB18C6 layer and (B) the same layer after exposure to a 10^{-2} M KCl solution and washing with water. (C) Cross section from panel B, in which the height of the partial layer is 0.2 ± 0.1 nm.

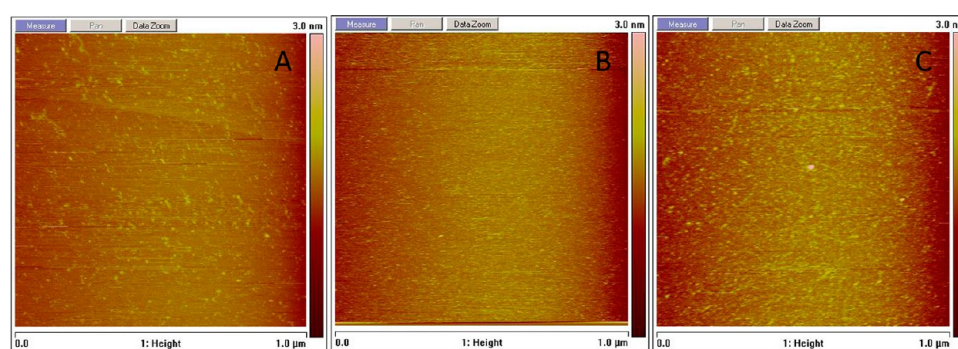


Figure 8. Consecutive in situ AFM height images of (A) ethanol on mica. (B, C) Subsequent measurements of 2×10^{-5} M DB18C6 in ethanol solution. The time interval between images is 9 min.

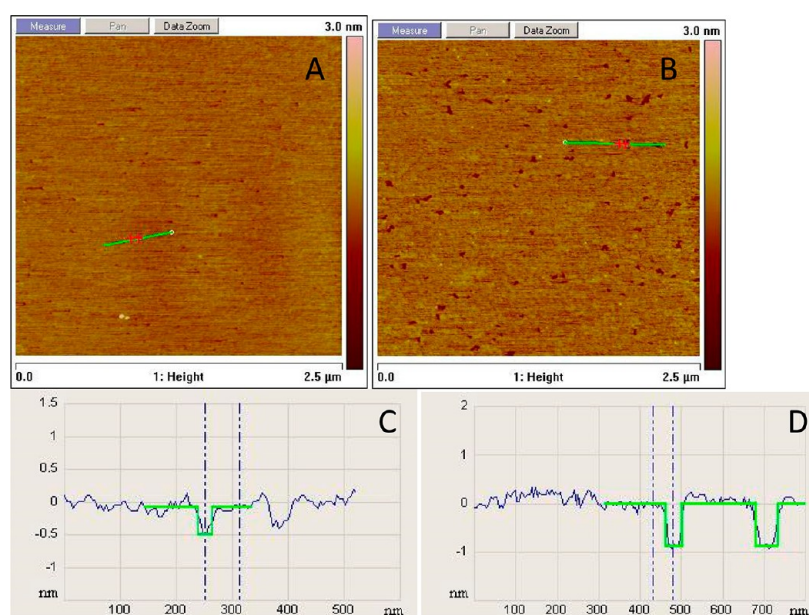


Figure 9. AFM height images of a layer of (A) DB24C8 and (B) a bilayer of DB15C5 on sodium-exchanged muscovite mica. (C) Cross-section from panel A, showing two holes with a depth of 0.4 ± 0.1 nm. (D) Cross-section from panel B, showing two holes with a depth of 0.8 ± 0.2 nm.

the muscovite surface, and on the basis of our observations, the crown ethers are still able to bind to the potassium ions. Therefore, the potassium ions stabilize the first molecular layer. The second molecular layer is expected to be less stable.

3.2. Stability and Mobility of the Crown Ether Layers.

The vapor deposition technique (Experimental Section) also produces molecular layers, but the submersion method was the fastest method for obtaining molecular layers. However, the

vapor deposition technique was superior in obtaining a partial first layer (Figure 5).

Figure 5 depicts AFM height and phase images of an incomplete layer of DB18C6 after 1 h of exposure and a complete molecular layer after 17 h of exposure to the DB18C6 vapor. This means that the surface of muscovite mica becomes saturated after a couple of hours. The phase image of the incomplete molecular layer in Figure 5A clearly shows a large phase difference between the holes and the material on top.

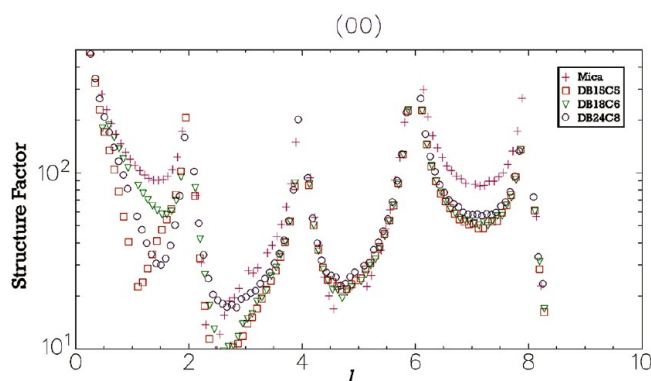


Figure 10. SXR D specular data of muscovite mica (magenta plusses), DB15C5 (red squares), DB18C6 (green triangles), and DB24C8MLs on muscovite mica (blue circles).

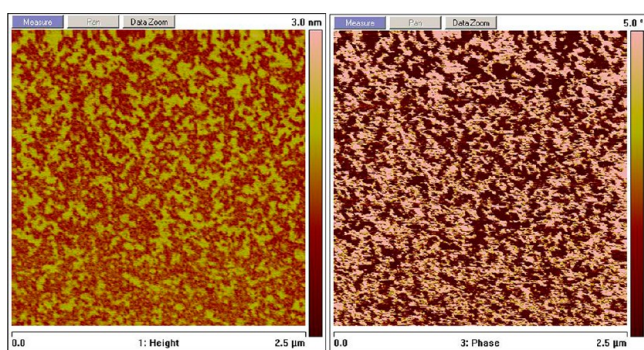


Figure 11. AFM height (left) and phase (right) images of a dry layer of DB15C5. The height of the layer is 0.8 ± 0.2 nm.

Therefore, the lower-lying material is expected to be the muscovite mica whereas the material on top is DB18C6, whose presence was confirmed by MALDI-TOF (Supporting Information Figures S3 and S4).

A second molecular layer of DB18C6 can be obtained via the submersion method by excluding the washing step with water. Although the first layer of DB18C6 seems quite immobile, because it changes its appearance only slightly during subsequent AFM scans (Figure 6A–C), the second layer shows high mobility (Figure 6D–F). Its higher mobility can be explained by a relatively weak interaction with the first molecular layer of DB18C6, and the first molecular layer attaches more strongly to the potassium ions of the muscovite mica substrate.

A similar high mobility of the second layer was observed for DB15C5 and DB24C8 on muscovite mica (Supporting Information Figures S5 and S6).

Leaving a DB18C6 layer exposed to water for 20 h did not remove the crown ether material from the surface; a complete layer remained. To investigate if the crown ether layer can be

removed with a solution containing potassium ions, a layer of DB18C6 on muscovite mica was exposed to a solution of 10^{-2} M potassium chloride in water for 10 s and then washed twice in pure water to prevent the crystallization of the potassium chloride on the surface. As can be seen in Figure 7, less material is present on the substrate after exposure to the potassium chloride solution. MALDI-TOF showed that crown ether material was still present on the muscovite mica surface (Supporting Information Figure S7). From this observation, it follows that the formation of the DB18C6 crown ether layer is reversible and that a 10 s washing step in a solution containing potassium ions can wash away a significant amount of DB18C6. However, it is not possible to say if the first or the second layer has been partially removed. The preferred location of the potassium ions in the center of the crown ether ring cannot be achieved on the muscovite mica surface, and the number of free ions exceeds that of available potassium ions on the muscovite mica, which can explain the decrease in surface coverage.

3.3. In Situ Measurements. The formation process of the crown ether layer of DB18C6 on muscovite mica has been investigated using in situ AFM (Figure 8).

Figure 8A shows a reference measurement of muscovite mica in ethanol. Figure 8B,C shows in situ AFM images with the DB18C6 solution added to the ethanol (DB18C6 concentration of 2×10^{-5} M). The difference in time between each image is approximately 9 min. The standard deviation of the z values (R_q) increased from 0.12 to 0.18 nm after DB18C6 was added. However, no significant other change was observed in the AFM images, which might be the result of a fast adsorption of DB18C6. Alternatively, it is possible that the crown ether layer is very mobile when it is in contact with a solvent. A third possibility is that there is no DB18C6 layer at all. It is not possible to make a distinction among these three possibilities on the basis of the in situ AFM data. In situ studies in previous research on layer formation of a phthalocyanine with eight triether tails on muscovite mica showed similar results.¹⁹

The preparation of the film, however, provides additional clues. When a multilayer is prepared, the muscovite mica is submerged in a crown ether solution and then immediately rinsed with water, with the surface still wet. If no layer was formed in the solution, then the water rinse should remove all of the crown ether through dilution. This is not the case; therefore, we conclude that a stable layer has formed in situ.

3.4. Sodium-Terminated Muscovite Mica. The potassium ions on the muscovite mica were exchanged for sodium ions to examine their effect on the formation of layers of dibenzo crown ethers (Figure 9). On the basis of work by Xu and Salmaron²⁰ and Osman et al.,¹¹ it is expected that the ion-exchange procedure exchanges all of the surface potassium ions with sodium. AFM measurements revealed similar results as in the case of potassium-terminated muscovite mica. All three crown

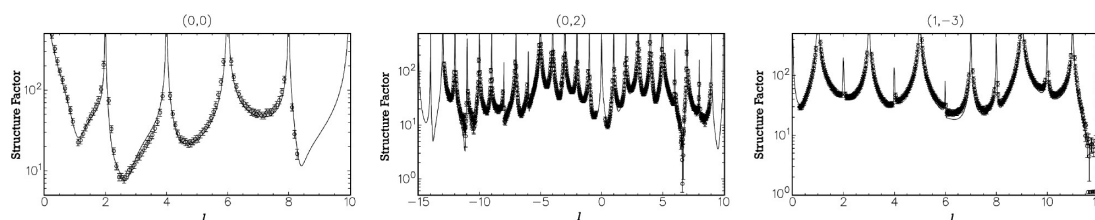


Figure 12. SXR D data rods (dots) and fit (curves) of the DB15C5 layers on muscovite mica. The y axis depicts the structure factor amplitude, and the x axis depicts the l value. The labels above each graph indicate the h and k values for the specific crystal truncation rod.

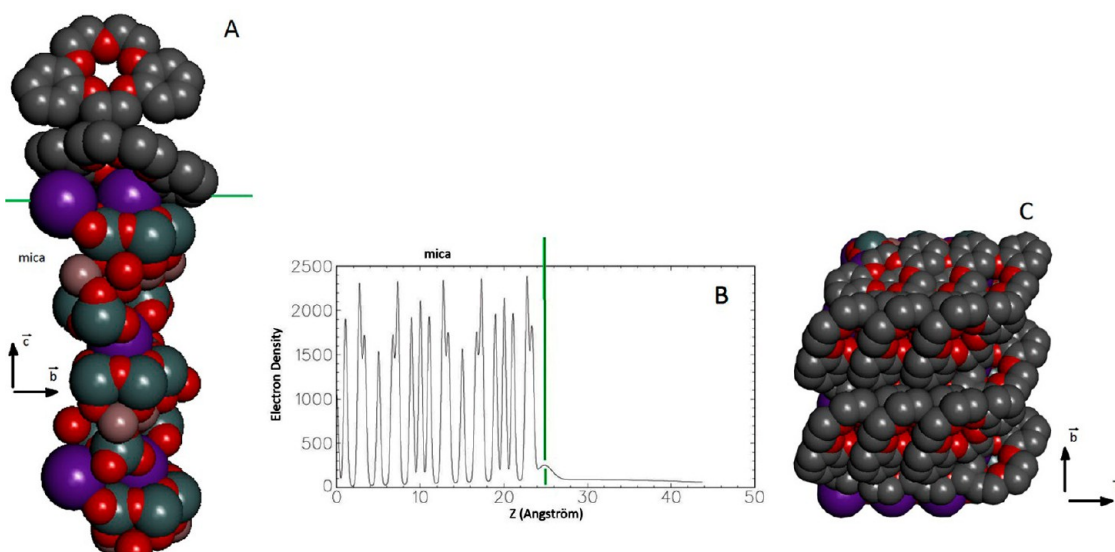


Figure 13. (A) Unit cell of the model that was used to fit the DB15C5 dry layers on muscovite mica. (B) *z*-density plot in the (00) direction. (C) Top view of 3 × 3 muscovite mica unit cells with the DB15C5 molecules on top. The top three molecules at the top of the image are edited out for clarity.

ethers formed stable layers, and also the second layers showed mobility. However, the amount of material deposited on the surface seemed consistently larger. Figure 9B shows a nearly complete bilayer of DB15C5, as judged from the height of the layer, whereas for the potassium-terminated muscovite mica, holes with a depth of 2 MLs were never observed.

Both AFM measurements depicted in Figure 9 were performed on a sample that was submerged in a solution of the specified crown ether in ethanol ($(1.0 \pm 0.3) \times 10^{-4}$ M) and subsequently washed with water. In Figure 9A, a complete layer of DB24C8 has formed with a height of 0.4 ± 0.2 nm, and Figure 9B depicts a double layer of DB15C5 of 0.8 ± 0.1 nm in height.

The calculated stability constants of all three crown ethers with the potassium ion complex in methanol are of the same order of magnitude, which explains the similarity among the three different crown ether MLs. The stability constants of the crown ether with potassium ion are also of the same order of magnitude as for the crown ether with the sodium ion complex.⁸ This can explain the similarity between the crown ether layers on K-terminated muscovite mica and on Na-terminated muscovite mica.

3.5. Surface X-ray Diffraction. The goal of using SXRD was to investigate possible in-plane order in the crown ether layers and to establish where the crown ether molecule is in relation to the unit cell of muscovite mica. SXRD data were acquired on samples of potassium-terminated muscovite mica with a dry layer of DB15C5, DB18C6, and DB24C8, which were imaged using AFM prior to the SXRD measurement. The measurements of the DB18C6 and DB24C8 layers are discussed in the Supporting Information (Figures S8 and S9) because of the similarity among the three molecules. Figure 10 depicts the specular data obtained from muscovite mica and the three crown ethers. Clear differences between the reference and the data with crown ethers on muscovite mica and between individual crown ethers on muscovite mica can be observed. Both this and the AFM data indicate that there are layers of crown ether present on the muscovite mica surface.

The necessary number of crown ether molecules was determined by the quality of the resulting fit. For all three crown ethers, the data could be fit better with two molecules than

with one molecule. In the case of DB15C5, three molecules in the model yielded worse fits than when two molecules were used (or the occupancy of the third molecule refines back to zero). Furthermore, fits with models that included only one molecule yielded unrealistic results, for example, an occupancy value of the molecule that was larger than one. The occupancy of the topmost potassium layer of the muscovite mica was fixed at 0.5.

In the case of DB15C5, the obtained data on most CTRs can be fitted with just muscovite mica in the model. However, the specular rod, which gives the out-of-plane information, cannot be fitted with this model. This means that the surface contains a flat film, which is in agreement with the AFM measurements (Figure 12). Changes in all CTRs are observed when a molecule is added to the model. This means that the in-plane position of the molecule(s) is determined by the data. That is, the molecules have to be in the depicted position (Figure 13) for the fit to follow the data and cannot deviate in their in-plane or out-of-plane position without changing the quality of the fit.

Some CTRs are depicted in Figure 13 (the others can be found in Supporting Information Figure S10), and the fit has $\chi = 3.3$.

A unit cell of the resulting fit is depicted in Figure 13, together with the *z*-projected charge density and a top view.

The molecule closest to the surface of muscovite mica is tilted by approximately 30° with respect to the plane of the muscovite mica surface. This molecule lies on top of a potassium atom and has an occupancy of 0.70, and the second molecule is tilted by approximately 55° and has an occupancy of 0.48 molecule per unit cell. The surface area of the DB15C5 molecule was estimated to be 80 Å² using Spartan '08 V1.2.0 software in order to estimate the surface coverage. From this, the surface coverage can be calculated for the first layer to be 1.0, and for the second molecular layer, it can be calculated to be 0.5. Thus, Figure 10 shows 1.5 molecular layers. The surface area occupied by one DB24C8 molecule in its crystal structure ((CSD entry DOHBOC01) area of 116 Å²) compares well with the estimation made using Spartan (121 Å²), showing that the estimations are valid.

The resulting fit also provide heights for the two layers: for the first layer, it is 0.4 nm, and for the second layer, it has a height of 0.6 nm. The Debye–Waller parameters for the layers are 46 for

the first and 43 for the second, which means that the position of the molecules in both layers may vary by 0.5 Å. The height for the second DB15C5 layer and its coverage are close to what is observed in Figure 12 using AFM, which validates the results from the SXRD model.

SXRD measurements reveal that for DB18C6 and DB24C8 the first molecule also lies relatively flat whereas the second lies more upright (Supporting Information Figures S8 and S9).

4. CONCLUSIONS

Layers of DB15C5, DB18C6, and DB24C8 crown ethers were produced on muscovite mica by two different techniques: crown ether vapor deposition on muscovite mica and the submersion of muscovite mica in a solution of crown ether. The submersion method was the fastest in producing the layers. AFM images show that the first crown ether layer is relatively stable when compared to the mobile second layer, as a result of a stronger interaction of the first layer with the substrate.

Molecular layers similar to those on a potassium-terminated substrate were formed on a sodium-terminated muscovite mica substrate. All dibenzo crown ethers had a stable first layer and a mobile second layer on potassium- and sodium-terminated muscovite mica. SXRD measurements revealed that for all three investigated crown ethers the first molecule lies flat and the second lies more upright. We found excellent agreement between AFM and SXRD data, which makes it a powerful combination for determining the orientation of molecular layers.

A novel interaction between molecules and a substrate has been used to produce molecular layers. Owing to the nature of the binding, however, these layers are not stable in ionic (and especially K^+ -containing) solutions. The described method provides a route to forming flat, self-assembled monolayers with different surface properties because it can be implemented with a wide variety of crown ethers.

■ ASSOCIATED CONTENT

Supporting Information

MALDI spectra. AFM height images. SXRD results on DB24C8 layers, SXRD measurements on DB18C6 layers, and SXRD CTRs of DB15C5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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