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Creating Monolayers and Thin Films of a Novel Bis(alkyl) Substituted Asymmetrical Polyoxotungstate, $\{[\text{CH}_3(\text{CH}_2)_{11}\text{Si}]_2\text{OSiW}_{11}\text{O}_{39}\}_4$ Using the Langmuir–Blodgett Technique

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Creating monolayers and thin films of a novel bis(alkyl) substituted asymmetrical polyoxotungstate, $\{[\text{CH}_3(\text{CH}_2)_{11}\text{Si}]_2\text{OSiW}_{11}\text{O}_{39}\}^{4-}$ using the Langmuir–Blodgett technique

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A bis(alkyl) substituted, asymmetric polyoxometalate $\{[\text{CH}_3(\text{CH}_2)_3]_4\text{N}\}_4\{[\text{CH}_3(\text{CH}_2)_{11}\text{Si}]_2\text{OSiW}_{11}\text{O}_{39}\}$, was prepared and incorporated into monolayer and multilayer thin films using Langmuir–Blodgett techniques.

Polyoxometalates (POMs) are soluble metal-oxide clusters that display a wide range of physical properties that make them attractive building blocks for supramolecular assemblies and for materials science applications.¹ In particular, due to their tunable redox behavior, distinct spectroscopic states, and high electron densities, POMs have been investigated for applications in catalysis,^{2,3} photo- and electrochromism,⁴ electron microscopy,⁵ and magnetism.⁶ The preparation of organic–inorganic hybrid systems that take advantage of the magnetic, electrochemical, and optical properties of POMs is the focus of much of the recent work.^{3,7–9} Only a few investigations have involved using Langmuir–Blodgett (LB) techniques to prepare hybrid POM materials.^{9,10} In the reported cases, symmetrical Keggin⁹ and Keplerate¹⁰ anions were incorporated into LB films by electrostatic association with amphiphilic dimeric dioctadecylammonium (DODA) cations. In none of the reported cases was the POM species the amphiphile in the organized system. Here we report the synthesis of the first bis(alkyl) substituted, amphiphilic, asymmetrical POM species, a bis(dodecyl) derivative. It yields a LB monolayer at the air–water interface that is stable and forms reversibly as evident by the lack of hysteresis in compression/expansion cycles. The LB monolayers were characterized by their surface pressure vs molecular area (Π/A) isotherms. Preliminary results using FT-IR spectroscopy to study the LB transferred monolayers on ZnSe substrates are also described.

The amphiphilic compound used in this work was prepared by adding two equivalents of dodecyltrichlorosilane in CH_3CN to an aqueous solution of the Keggin lacunary POM precursor $\text{K}_8\text{SiW}_{11}\text{O}_{39}^{8-}$ (Fig. 1) at 50 °C.¹¹ The POM product was isolated and purified as ${}^4\text{Q}_4\{[\text{CH}_3(\text{CH}_2)_{11}\text{Si}]_2\text{OSiW}_{11}\text{O}_{39}\}$, $1\{{}^4\text{Q} = [\text{CH}_3(\text{CH}_2)_3]_4\text{N}^+\}$.¹²

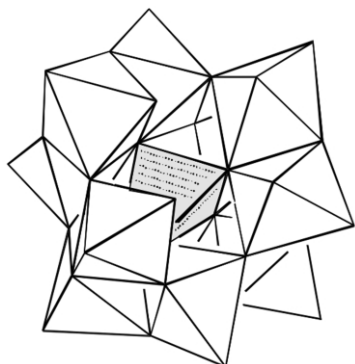


Fig. 1 Polyhedral notation of the Keggin lacunary anion $\alpha\text{-SiW}_{11}\text{O}_{39}^{8-}$. Each octahedron represents a d^0W atom surrounded by six oxide ions. The cross hatched area denotes a tetrahedrally coordinated Si heteroatom.

Langmuir–Blodgett (LB) monolayer and multilayer films were prepared at ambient temperatures using a commercial trough. Pressure isotherms for a monolayer were obtained using 20 to 50 μl of a 0.501 mM DCM solution of **1** on an aqueous subphase at compression speeds ranging from 10 to 150 cm min^{-1} . An evaporation time of 15 min was allowed prior to compression. Multiple layers were deposited onto a ZnSe substrate using the vertical lifting method at a surface pressure of 25 mN m^{-1} , a dipping speed of 5 mm min^{-1} , and a 15 min waiting period above the subphase between dipping cycles.

A representative Π/A isotherm of **1** at a compression speed of 25 cm min^{-1} is shown in Fig. 2. A transition from a liquid expanded phase to a liquid-condensed (LC) phase occurred at a surface pressure of ca. 3 mN m^{-1} . The LC phase was stable until the surface pressure exceeded 34 mN m^{-1} whereupon collapse of the monolayer was observed. A limiting area (A_0) of $197 \pm 10 \text{ \AA}^2 \text{ molecule}^{-1}$ was determined by extrapolating from the linear part of the LC phase. The area per molecule value determined for **1** in this system is much larger than the calculated value of ca. 115 $\text{ \AA}^2 \text{ molecule}^{-1}$ for the potassium salt of the $\text{SiW}_{11}\text{O}_{39}^{8-}$ lacunary anion in a closest packed cubic array.¹³ The difference between the experimental value found for **1** in the LB system and the value for the $\text{K}_8\text{SiW}_{11}\text{O}_{39}$ precursor in a crystal lattice is probably due in part to the presence of much larger ${}^4\text{Q}^+$ counterions. It is interesting to note that the area of the tetraanionic **1** in a LB monolayer is close to the value (ca. 180 $\text{ \AA}^2 \text{ molecule}^{-1}$) that Coronado *et al.* observed for isoelectronic Keggin species.⁹ The values are similar despite the fact that the bulky ${}^4\text{Q}^+$ cations are present in monolayers with **1**, whereas Coronado employed potassium ions.⁹ This suggests that the organizing influence of the LB film is balanced by repulsions between the POM anions. It is clear that stable LB monolayer formation depends on the organosilyl groups on **1** and not on the ${}^4\text{Q}^+$ cations, since tetraalkylammonium surfactants alone do not form stable LB films.⁹

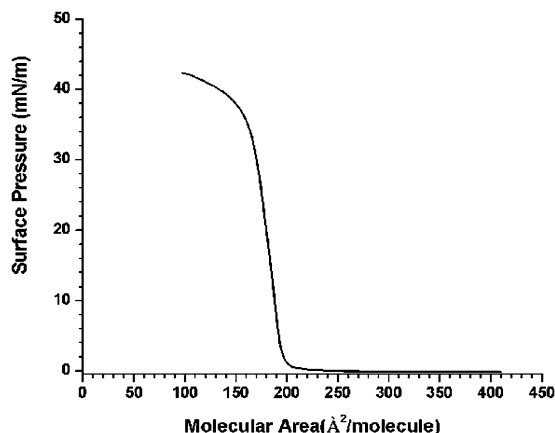


Fig. 2 Π/A isotherm of 20 μl of 0.501 mM solution of **1** at a compression speed of 25 cm min^{-1} ($22 \pm 1 \text{ }^\circ\text{C}$).

Up to ten compression and expansion cycles were performed on monolayers of **1** at the air-water interface to explore the reversibility of the monolayer formation (Fig. 3). The monolayer was compressed at 25 cm min⁻¹ to a maximum surface pressure of 25 mN m⁻¹. During decompression at the same rate, the measured surface pressure closely followed the curve recorded during the compression process. The recompression–expansion curves closely resembled the original compression data, indicating minimal hysteresis.

To further verify the stability of the monolayer formed with **1**, the molecular area was monitored over time at a fixed surface pressure of 25 mN m⁻¹ (Fig. 3, inset). The molecular area decreased < 5% over 20 h. The drop in area can be attributed to minimal reorganization of the molecule under pressure over time and due to the evaporation of the aqueous subphase during the experiment.

We note with interest that **1** forms a stable LB film, even though the POM head group and alkyl tails have similar sizes (*ca.* 10 Å *vs.* *ca.* 15 Å). In addition, in preliminary work, the bis(octadecyl) analogue of **1** forms a stable LB monolayer with a limiting area of *ca.* 200 Å² molecule⁻¹. The longer tail of the bis(octadecyl) compound appears to have little or no effect on the structure of the LB system.

In a related experiment, monolayers of **1** were transferred onto a ZnSe substrate at a surface pressure of 25 mN m⁻¹. Beginning with a down stroke, ten dipping cycles were performed, each cycle consisting of a down stroke and an up stroke. The transfer ratio measures the efficiency with which a LB film is transferred to a substrate. It is the area of monolayer removed from the subphase at constant pressure divided by the area of substrate immersed in the subphase. The transfer ratios for the LB films on the up stroke were fairly consistent and varied between 0.87 and 1.0. However, the transfer ratios for the down stroke decreased nearly monotonically from 0.86 to -0.19 (data not shown). The reduction of transfer during successive down strokes indicates that the interactions between POM-based amphiphiles are not strong enough to promote deposition of a symmetrical bilayer and that the films are most likely X-type overall (one in which the amphiphiles deposit in a head-to-tail fashion, with the head groups generally pointing away from the substrate.)

Transfer of the monolayers and the environment of the POM species were analyzed by infrared spectroscopy. Fig. 4(a) shows the diffuse reflectance IR spectrum for **1** in a KBr matrix and the characteristic POM vibrations are clearly observed below 1000 cm⁻¹. The peak at ~1050 cm⁻¹ is assigned as an asymmetric stretching band for the Si–O–Si bridge of the bis(alkyl) substituted POM.¹¹ Fig. 4(b) shows the IR spectrum for a multilayer film of **1** on a ZnSe substrate. The POM vibrations below 1100 cm⁻¹ and the Si–O–Si stretching band in the LB film IR spectrum clearly indicate that the intact POM species is present in the LB multilayer assembly. In addition, all of the bands attributed to POM vibrations in the LB film are narrower and slightly shifted (1–3 cm⁻¹) to lower frequencies relative to

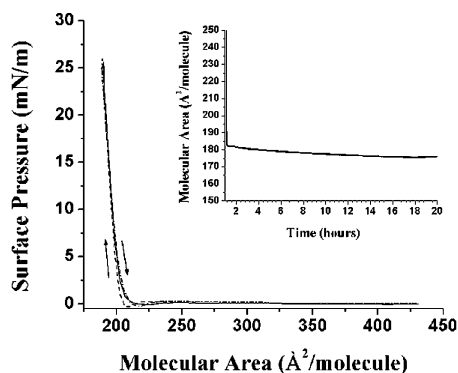


Fig. 3 Successive compression and expansion cycles of a monolayer of **1** (compression speed = 25 cm min⁻¹. Inset: molecular area *vs.* time at a constant surface pressure of 25 mN m⁻¹.

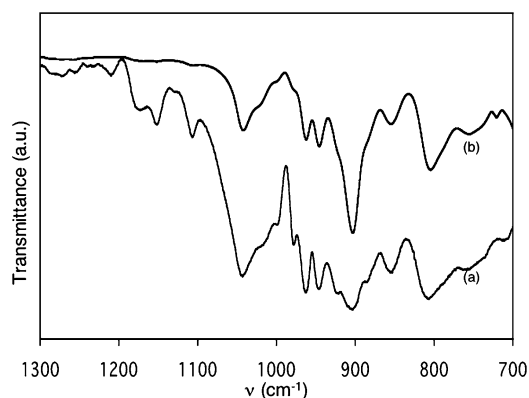


Fig. 4 FT-IR spectra of **1** (a) KBr pellet; (b) LB film (20 layers) on ZnSe.

those in the KBr pellet. Similar changes in band shape and position observed in LB films prepared with the intact Keggin compound H₄SiW₁₂O₄₀ and DODA were attributed to a lower degree of anion hydration and increased organization of the POM in the film.⁹ **1** is dehydrated in KBr as no bands are observed from 3500–3300 cm⁻¹. Consequently, molecular organization of **1** within the LB film is responsible for the changes in the IR spectra.

We have used the LB technique to prepare an organized organic–inorganic hybrid system containing a bis(alkyl) substituted, amphiphilic, asymmetrical POM. We are currently characterizing more fully the structure of the LB system and the electronic and optical properties of the POM within the organized film. We are also preparing related compounds and examining their behavior in LB thin films.

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- 83%; ²⁹Si NMR: δ (DMSO-d₆) -50.3 ppm, -85.4 ppm; Elemental analysis for C₈₈H₁₉₄N₄O₄₀Si₃W₁₁, calculated %: C-26.06, H-4.82, N-1.38, O-15.78, Si-2.08, W-49.87; found %: C-25.05, H-4.57, N-1.38, O-16.49(difference), Si-2.41, W-50.1; IR, cm⁻¹: 2959(s), 2923(s), 2863(s), 1381(w) 1148(w), 1108(w), 1038(m), 964(s), 938(s), 905(vs), 857(m), 806(vs).
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