Characterization of Self-assembled Monolayers from Lithium Dialkyldithiocarbamate Salts

Randy D. Weinstein*† and Joshua Richards

Department of Chemical Engineering, Villanova University, Villanova, Pennsylvania 19085

Susan D. Thai, Donna M. Omiatek, and Carol A. Bessel

Department of Chemistry, Villanova University, Villanova, Pennsylvania 19085

Christopher J. Faulkner, Siti Othman, and G. Kane Jennings*‡

Department of Chemical Engineering, Vanderbilt University, Nashville, Tennessee 37235

Received October 3, 2006. In Final Form: December 5, 2006

We report the formation of self-assembled monolayers (SAMs) onto gold substrates by exposure to lithium dialkyldithiocarbamate salts ([Li^+(R_2DTC^-)], where R = -propyl, -butyl, -octyl, -decyl, -dodecyl, or -octadecyl) in ethanol or methylene chloride. The crystallinity and composition of the monolayers were assessed by polarized modulation infrared reflection spectroscopy (PM-IRRAS). Wettability was characterized by contact angles of water and hexadecane, thickness was measured by spectroscopic ellipsometry, and barrier properties determined by electrochemical impedance spectroscopy. While the shorter R_2DTC^-‘s formed monolayers with liquid-like packing, monolayers prepared from the longest R_2DTC^- (where R = -octadecyl) exhibit similar thickness, crystallinity, wettability, and capacitance as monolayers prepared from n-octadecanethiol. The hydrocarbon chains within the monolayers prepared from (C_{18}H_{37})_2DTC^- are less canted on average than those prepared from n-octadecanethiol. Nonetheless, the (C_{18}H_{37})_2DTC^- SAM exhibits an order of magnitude lower resistance against the penetration of redox probes, which is attributed to a higher density of pinhole defect sites.

Introduction

Monolayer films on gold surfaces have been used to control protein adsorption, mediate electron transfer, initiate polymer film growth, and modulate friction coefficients. These monolayers are most often prepared from alkanethiols due to the commercial availability of many n-alkanethiols and o-terminated alkyl thiols, the synthetic ease of preparing many others, and the well-characterized assemblies and structures that the thiols afford. Monolayers on gold can also be prepared from other sulfur-containing molecules including dialky derivatives, dialky sulfides, dithiocarboxylic acids, Bunte salts, and di- and tridentate thiols. The advantages of employing different head groups in the formation of SAMs include the abilities to prepare films with different structures, packing densities, electron-transfer properties, and thermal stabilities.

Dialkyldithiocarbamates are another class of ligands that spontaneously adsorb to gold surfaces to form monolayers (Figure 1). The recent work of Wei and co-workers showed that several n-alkane, branched-alkane, aromatic, and ring substituted dithiocarbamates could adsorb onto gold surfaces and particles upon exposure to CS_2 and the appropriate secondary amine. These ligands offer some advantages over their traditional thiol counterparts. First of all, R and R’ groups can be independently selected, which enables surfaces to be coated with films that contain a variety of structures and packing densities. Dialkyldithiocarbamates also have interatomic distances between the two sulfur atoms at almost the perfect distance for placing each of the two sulfur atoms on adjacent gold atoms and providing for two-point ligation with resonance generated between the two sulfur atoms. The resonant bidentate structure of the anchored dithiocarbamate has been shown to produce a characteristic different molecule—metal coupling compared to n-alkanethiols, which is believed to make these ligands applicable for molecular electronics. The resonance structure can incorporate both of the sulfur—carbon bonds as well as the carbon—nitrogen bond due to the free electron pairs on the sulfur.

* Authors to whom correspondence should be addressed.
† E-mail: randy.weinstein@villanova.edu. Fax: (610) 519-7354.
‡ E-mail: kane.g.jennings@vanderbilt.edu. Fax: (615) 343-7951.
§ E-mail: randy.weinstein@villanova.edu. Fax: (610) 519-7354.
* Authors to whom correspondence should be addressed.

and nitrogen atoms. Recently, Li and Kosov\textsuperscript{18} computationally showed that a dithiocarbamate used to anchor molecular wires to gold electrodes exhibited improved electron transport properties with strong molecule-electrode coupling, which allowed for enhanced electrical conductance, most likely due to the resonance and availability of the free electrons.

Monolayers formed with these two-point attachments with resonance are, in some cases, more robust to temperature, solvents, and exchanges with other ligands than single attached ligands such as n-alkanethiols. Dimethyl- and diethyl-dithiocarbamate monolayers on gold were shown to be stable in water for longer than a week over the pH range of 1–12 while the same monolayers also showed negligible exchange with solutions of dodecanethiol in ethanol at room temperature for a 1 week exposure.\textsuperscript{14} The monolayer formed from dibutylidithiocarbamate showed stability up to 85 °C in water for 12 h.\textsuperscript{14} Computational studies have also predicted that monolayers generated from several dithiolidithiocarbamates would be excellent wear inhibitors for engines, creating and sustaining monolayers on the iron oxide surfaces even when exposed to high temperatures.\textsuperscript{19} Dithiocarbamates have also been used to stabilize nanoparticles.\textsuperscript{14,20}

In this article, we describe SAMs prepared from lithium dithiolidithiocarbamate salts through characterization of crystalinity and composition by polarized modulation infrared reflection absorption spectroscopy (PM-IRRAS), wettability by contact angle, thickness by spectroscopic ellipsometry, and barrier properties by electrochemical impedance spectroscopy. As the R\textsubscript{2}DTC\textsuperscript{–} adsorbates must be synthesized, we have limited our analysis to those chain lengths in which starting materials are commercially available. We compare the properties of the most crystalline SAM formed from a LiR\textsubscript{2}DTC salt (Li(C\textsubscript{15}H\textsubscript{31})DTC) with those of a SAM prepared from octadecanethiol. Our work demonstrates that R\textsubscript{2}DTC\textsuperscript{–} anions of short to moderate chain length form SAMs that are a less crystalline alternative to thiolate SAMs but that a SAM prepared from (C\textsubscript{18}H\textsubscript{37})DTC\textsuperscript{–} is comparable to a SAM prepared from C\textsubscript{18}H\textsubscript{37}SH in thickness, wettability, and crystallinity.

**Experimental Section**

**Materials.** Gold shot (99.99%) and silicon(100) wafers were obtained from J&J Materials and Montco Silicon, respectively. Chromium-coated tungsten rods were obtained from R.D. Mathis. Octadecanethiol (Sigma-Aldrich), isooctane (Fisher), and 100% ethanol (AAPER) were all used as received while deionized water (16.7 MΩ) was purified with a Modu-Pure system. The working electrode in contact with the aqueous solution was a confined circle with an area of 1 cm\textsuperscript{2}. The differential reflection spectra (DRS) were calculated from the S- and p-polarized signals simultaneously collected by a lock-in-amplifier. All reported IR spectra were repeated at least twice using independent sample preparations. The estimated error in reported spectra based on the standard deviations of band absorbances measured after these independent preparations was less than 10%.

**Electrochemical Impedance Spectroscopy (EIS).** Electrochemical impedance measurements of SAM-coated gold samples were performed with a CM5300 Electrochemical Impedance System (Gamry Instruments) interfaced to a personal computer. A Teflon cell equipped with a gold-coated silicon counter electrode and a Ag/AgCl/saturated KCl reference electrode contained an aqueous solution of 0.1 M Na\textsubscript{2}SO\textsubscript{4}, 1 mM K\textsubscript{3}Fe(CN)\textsubscript{6}, and 1 mM K\textsubscript{4}Fe(CN)\textsubscript{6}/3H\textsubscript{2}O. The working electrode in contact with the aqueous solution was a confined circle with an area of 1 cm\textsuperscript{2}. The measurements were made at the open circuit potential with a 5 mV ac perturbation that was controlled between 50 MHz and 20 kHz. Film resistance and capacitance values were determined by fitting the EIS data with a Randles model equivalent circuit\textsuperscript{22} using software provided by Gamry.

**Spectroscopic Ellipsometry.** Ellipsometric thicknesses were determined from a J.A. Woollam M-2000DI variable angle spectroscopic ellipsometer. Thicknesses were fit to data taken at 75° from the surface normal over wavelengths from 400 to 700 nm using a refractive index of 1.45 at all wavelengths. Optical constants of the underlying gold used in the preparation of each sample were taken prior to monolayer deposition and used as a baseline for thickness measurements. Reported thickness values and errors

of 2924 SAMs with liquid-like packing, as evidenced by the positions of the methylene stretching mode for the most crystalline SAM shown ([(C18)2DTC–]).

represent the averages and standard deviations, respectively, from at least three independently prepared samples.

Contact Angles. A Rame-Hart contact angle goniometer with a microliter syringe was used to measure advancing and receding contact angles on static drops of water and hexadecane on the monolayer surfaces. The needle tip of the syringe remained inside the liquid drop while measurements were taken on both sides of ~5 μL drops. Reported values and ranges represent the average and standard deviation of values obtained from at least six independent sample preparations.

Results and Discussion

SAMs were prepared by exposure of gold substrates to 1 mM solutions of the LiR2DTC salt in ethanol or dichloromethane. Both solvents produced similar results. Water was also used as a solvent but did not yield crystalline SAMs with reproducible properties.

Figure 2 shows PM-IRRA spectra for SAMs prepared from R2DTC–’s with different n-alkyl chain lengths (3, 4, 8, 10, 12, and 18). The IR spectra for SAMs prepared from R2DTC– with short chain lengths (3 and 4) show broad methyl stretching peaks at 2966 cm−1 ($\nu_\text{a}(\text{CH}_3)$), 2937 cm−1 ($\nu_\text{a}(\text{CH}_3)$-Fermi resonance), and 2879 cm−1 ($\nu_\text{s}(\text{CH}_3)$) and a weak methylene stretching peak at ~2925 cm−1 ($\nu_\text{a}(\text{CH}_2)$). The peak widths and positions of these modes are consistent with a liquid-like packing of the adsorbed molecules on the substrate, as is generally observed when SAMs are prepared from shorter chained adsorbates.

R2DTC–’s of moderate chain lengths (8, 10, and 12) also yield SAMs with liquid-like packing, as evidenced by the positions of 2924–2926 cm−1 ($\nu_\text{a}(\text{CH}_3)$) and ~2853 cm−1 ($\nu_\text{s}(\text{CH}_3)$). The full-width at half-maximum (fwhm) for the methyl peaks is still broad (~14 cm−1 for $\nu_\text{a}(\text{CH}_3)$), suggesting heterogeneous orientations of the terminal methyl groups. The advancing water ($\theta_\text{ad}(\text{H}_2\text{O})$) and hexadecane ($\theta_\text{ad}(\text{HD})$) contact angles for these SAMs increase with chain length from 8 to 12 and indicate that the longer chains can more effectively form a lower energy surface (Table 1). The advancing hexadecane contact angles are still well below 45°, indicating that the hydrophobic surface formed is not a homogeneous methyl surface, but rather a mixture of $-\text{CH}_3$ and $-\text{CH}_2-$ groups, in agreement with the broadness of the methyl stretching peaks in Figure 1. In general, these films are less crystalline and possess more hydrophilic and oleophobic surface properties as compared with SAMs formed by n-alkanethiols of similar carbon chain length. 2

In contrast to monolayers from short and moderate chain lengths, monolayers prepared from (C18)2DTC− exhibit crystalline hydrocarbon packing, as evidenced by the methylene stretching peaks at 2919 cm−1 ($\nu_\text{a}(\text{CH}_3)$) and 2851 cm−1 ($\nu_\text{s}(\text{CH}_3)$) as well as narrowed peak widths for the methyl modes (fwhm = 12 cm−1 for $\nu_\text{a}(\text{CH}_3)$). Advancing water (114°) and hexadecane (48°) contact angles are both consistent with a dense sheet of methyl functionality at the surface of the SAM, which is compatible with the sharper methyl modes in the PM-IRRA spectra. The disparity in crystallinity between SAMs prepared from (C18)2DTC− and those prepared from R2DTC− (R = octyl, decyl, and dodecyl) reveals the importance of alkyl chain length in the formation of a crystalline assembly. In comparison, single-chained aliphatic dithiocarbamoylic acids have a head group similar to a R2DTC− yet exhibit oleophobic surfaces for all chain lengths (10–19) reported by Colorado et al. 10 The effect we observe here is attributed to the dichained hydrocarbon structure of the R2DTC− adsorbate, which creates additional constraints in packing and impedes the filling of defect sites of molecular dimension.

Electrochemical impedance spectra accumulated in an aqueous solution containing redox probes, K3Fe(CN)6 and K4Fe(CN)6, provide further evidence of monolayer properties as chain length is altered. Defects within SAMs allow penetration of the probe molecules to the proximity of the gold surface for rapid electron transfer. SAMs prepared from Li(C18)2DTC exhibit an order of magnitude higher charge-transfer resistance ($R_\text{ct}$) against electron transfer to the probe molecules than monolayers prepared from Li(C16)2DTC or Li(C10)2DTC, reflecting the greater crystallinity and lower defect density of the long-chained SAM. The SAM prepared from Li(C18)2DTC does not provide significant resistance against electron transfer, which is consistent with its thinness and noncrystalline structure. The capacitances ($C$) of these SAMs decrease as chain length is increased, consistent with a Helmholtz model where capacitance is inversely proportional to film thickness.

Comparison of SAMs Prepared from C18SH versus (C18)2DTC−. The favorable crystallinity and wetting properties of the (C18)2DTC− derived SAM warrant comparison with a SAM prepared from octadecanethiol (C18SH). Figure 3 shows both the high and low wavenumber regions of PM-IRRA spectra for SAMs prepared from a 16 h immersion in 1 mM ethanolic solution of C18SH or Li(C18)2DTC. In the low wavenumber region (Figure 3b), the R2DTC− and thiolate SAMs generally exhibit the same absorbance peaks due to their similar hydrocarbon composition. One distinct mode that identifies the R2DTC− SAM is the C=O stretching from 1410 to 1440 cm−1. 25 The asymmetric (2918 cm−1) and symmetric (2850 cm−1) methylene stretching positions in Figure 3a indicate primarily trans-extended, crystalline packing for both the thiol- and DTC-derived SAMs with few gauche conformers. Within the hydrocarbon stretching region, the spectra show two important.

Table 1. Effect of R2DTC− Chain Length on the Advancing Water and Hexadecane Contact Angles, the Charge-transfer Resistances, and Capacitances of the SAMs

<table>
<thead>
<tr>
<th>chain length</th>
<th>$\theta_\text{ad}(\text{H}_2\text{O})$ (deg)</th>
<th>$\theta_\text{ad}(\text{HD})$ (deg)</th>
<th>$R_\text{ct}$ (kΩ cm²)</th>
<th>$C$ (μF/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>114</td>
<td>48</td>
<td>26</td>
<td>1.1</td>
</tr>
<tr>
<td>12</td>
<td>108</td>
<td>34</td>
<td>4</td>
<td>2.9</td>
</tr>
<tr>
<td>10</td>
<td>104</td>
<td>25</td>
<td>3.5</td>
<td>3.2</td>
</tr>
<tr>
<td>8</td>
<td>98</td>
<td>&lt;15</td>
<td>1</td>
<td>4.8</td>
</tr>
</tbody>
</table>


differences between the R₂DTC⁻ and thiolate SAMs. First, the asymmetric methylene stretching absorbance, and also the ratio of absorbances between the asymmetric and symmetric methylene modes (the dichroic ratio), are reduced for the R₂DTC⁻ SAM as compared with the thiolate SAM. Reduced methylene intensities in the IR spectra of similar monolayers have been correlated to higher average chain densities caused by altered binding sites of the chemisorbed head groups on the substrate surfaces or by fewer defects that can contribute to highly cant adsorbates locally within a SAM. Second, the ratio of the asymmetric methyl stretching mode at 2965 cm⁻¹ to the symmetric methyl stretching mode at 2880 cm⁻¹ is ~40% greater for the R₂DTC⁻ SAM as compared with the thiolate SAM, reflecting an altered orientation of the terminal methyl groups. These two observations are consistent with an altered structure of the hydrocarbons within the R₂DTC⁻ and thiolate SAMs. To determine whether such structural distinctions are caused by different optical constants of the two molecules, we accumulated transmission infrared spectra of both Li(C₁₈)₂DTC and C₁₈SH in an isotropically oriented state by dispersion in a KBr matrix (see Figure S1 in Supporting Information). The spectra for isotropically oriented Li(C₁₈)₂DTC and C₁₈SH appear similar, other than a 10% lower dichroic ratio for the dithiocarbamate, in contrast to a 40% lower dichroic ratio for the (C₁₈)₂DTC monolayer as compared with that for the thiolate monolayer. The transmission spectra indicate no strong optical differences between these molecules, and thus, the observed differences in the monolayer spectra (Figure 3) are attributed to different chain orientations. The net lower methylene intensity suggests that the DTC hydrocarbons are, on average, in a less canted state than the ~30° cant reported for alkanethiolate SAMs.²⁶ The average adsorbate cant results from a complex interplay of head group—substrate interaction, interchain interactions, and adsorbate molecular size. Here, the combined influence of the larger DTC head group and the two n-octadecyl substituents must lead to binding of adsorbates on different sites on the gold surface as compared to thiol assembly, but still yielding a crystalline monolayer with relatively dense packing.

As shown in Table 2, the advancing contact angle for the (C₁₈)₂DTC⁻ derived SAM (48°) is consistent with a dense methyl surface but is measurably lower than that obtained on the C₁₈SH-derived SAM (51°). The hexadecane contact angle is known to fluctuate within 3−5°, depending on the orientation of the terminal methyl group.¹⁰ Alkanethiols and aliphatic dithiocarboxylic acids with an odd number of carbons generally form SAMs that exhibit lower hexadecane contact angles than do those with an even number of carbons. This effect has been attributed to the orientation of the terminal methyl group away from the surface normal in an odd-chained alkanethiolate SAM, which places the contacting liquid closer to the higher energy methylene groups beneath the methyl—liquid interface. In the case of the (C₁₈)₂DTC⁻ SAM, the ratio of asymmetric to symmetric methyl stretching absorbances (2.2) is higher than the same ratio in the C₁₈S/Au SAM (1.6). This higher ratio suggests that the terminal methyl groups are oriented more away from the surface normal in the R₂DTC⁻ SAM, and similar to wetting properties on odd-chained n-alkanethiols on gold, a reduced hexadecane contact angle is also observed here.

Table 2 also shows that the thicknesses of the (C₁₈)₂DTC⁻ (25 Å) and C₁₈SH (24 Å) derived SAMs are similar. The similarity in thicknesses of the two SAMs is in agreement with the similar crystalline structures as surmised from the PM-IRRA spectra. The measured 1 Å difference may reflect the greater length of the R₂DTC⁻ adsorbate, given the extra C—N functionality as compared with an alkanethiol, but we caution that this slight difference is within the margin of error.

We have examined the barrier properties of (C₁₈)₂DTC⁻ and C₁₈SH SAMs in the presence of aqueous solutions containing K₃Fe(CN)₆ and K₄Fe(CN)₉ with electrochemical impedance spectroscopy (EIS). Figure 4 shows impedance spectra in the form of Bode plots for the two SAMs. At high frequencies, the impedance modulus is independent of frequency and is caused by the resistance due to solution. At moderate frequencies, the log of the impedance modulus increases linearly with decreasing log frequency and exhibits a slope of −1. This behavior indicates that the capacitances of the SAMs dominate the overall impedance, such that the SAM functions as a physical dielectric, separating the conductive substrate from the ion-containing solution. At low frequencies, the impedance modulus is once again independent of frequency, indicating the resistance that the SAM provides against electron transfer to the redox species. The lower impedance of the R₂DTC⁻ SAM at low frequencies indicates that redox probes more easily penetrate within that SAM as compared to the alkanethiolate SAM. To quantify this difference in barrier properties, we have fit the impedance spectra with a Randles model equivalent circuit that is commonly used for highly blocking SAMs with only pinhole defects. Fits of the spectra enable the quantification of film resistance, capacitance, and solution resistance (Table 2). The capacitances of the R₂DTC⁻ and thiolate SAMs are similar, reflecting their similar thicknesses. However, the resistance against electron transfer is an order of magnitude lower for the thiolate SAM compared to the DTC SAM.

---

magnitude greater for the thiolate SAM as compared with the R_2 DTC^- SAM. The lower resistance of the R_2 DTC^- SAM is attributed to defects within the SAM that enable penetration by the redox probes. Using a microelectrode array model and a resistance for uncoated gold of 200 Ωcm^2, we estimate that the fractional surface area available for electrochemical reactions is 8 × 10^-4 for the thiolate SAM and 8 × 10^-3 for the dithiocarbamate SAM. These small fractional areas (<1%) and the general shape of the impedance spectra are consistent with pinhole defects scattered throughout the SAM. Thus, while the hydrocarbon within the (C_18) JsonObject2 DTC^- SAM is in a crystalline state, as confirmed by PM-IRRA spectra, the larger size of the (C_18)JsonObject2 DTC^- adsorbate as compared with C_18 SH may sterically limit its ability to adsorb to the gold surface and quench defects of roughly molecular scale.

As a further test of pinhole defects within the (C_18)JsonObject2 DTC^- SAM, we exposed a SAM prepared by 24 h exposure to 1 mM (C_18)JsonObject2 DTC^- to 1 mM C_18 SH for another 24 h. The SAM exposed to C_18 SH exhibited a much higher charge-transfer resistance, by factors of ~60 and ~50, respectively, than those of SAMs prepared by 24- and 48-h exposures to 1 mM (C_18)JsonObject2 DTC^-.

The smaller size of the C_18 SH adsorbate enables the filling of defect sites within the (C_18)JsonObject2 DTC^- monolayer with negligible displacement of the original monolayer, as verified by PM-IRRA spectra that show no diminution of the C–N (resonance) stretching from 1410 to 1440 cm^-1 after exposure to C_18 SH for up to 1 week.

**Conclusions**

Dialkylthiodicarbamates adsorb to gold to form monolayer films in which the properties of the SAM depend on the hydrocarbon chain length of the R_2 DTC^- adsorbate. R_2 DTC^-s with short and moderate hydrocarbon chain length yield noncrystalline SAMs that are more liquid-like than are alkane-thiolate SAMs of similar hydrocarbon chain length. In contrast, (C_18)JsonObject2 DTC^- adsorbs to gold to produce a SAM that exhibits similar thickness, wettability, capacitance, and crystallinity as a SAM prepared from C_18 SH. The hydrocarbon within the C_18 DTC^- derived SAM exhibits a less canted structure than that in the C_18 S/Au monolayer and a less normal orientation of the terminal methyl group. The (C_18)JsonObject2 DTC^- derived SAM exhibits an order of magnitude lower resistance than the C_18 S/Au SAM against electron transfer from the underlying electrode to solution-phase redox probes. This lower resistance for the (C_18)JsonObject2 DTC^- SAM is due to pinhole defects, which can be filled by the smaller C_18 SH to enhance the resistance dramatically.

**Acknowledgment.** This material is based upon work supported by the National Science Foundation under Grant No. CHE-0416040 (C.A.B.) and the National Research Initiative of the USDA Cooperative State Research, Education and Extension Service, Grant No. 2005-35603-15303 (G.K.J.). This material is also based upon work supported while serving at the National Science Foundation (C.A.B.). Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation. We would like to thank Mr. Riffard Jean-Gilles for his assistance in making some of the dialkylthiodicarbamate ligands. We would also like to thank Mr. Dongshun Bai for initial characterization of the monolayers.

**Supporting Information Available:** Transmission infrared spectra for Li(C_18)JsonObject2 DTC and C_18 SH dispersed in a KBr matrix, as well as experimental description of the KBr pellet-making process. This material is available free of charge via the Internet at http://pubs.acs.org.

Table 2. Comparison of Contact Angles (Water and Hexadecane), Charge-Transfer Resistances, Capacitances, and Thicknesses for SAMs Prepared on Gold from Li(C_18)JsonObject2 DTC and C_18 SH

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>θ_H2O (deg; adv, rec)</th>
<th>θ_HD (deg; adv)</th>
<th>R_t (kΩ cm^2)</th>
<th>C_t (μF/cm^2)</th>
<th>thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_18)JsonObject2 DTC</td>
<td>114 ± 2, 108 ± 3</td>
<td>48 ± 1</td>
<td>26 ± 7</td>
<td>1.1 ± 0.1</td>
<td>25 ± 1</td>
</tr>
<tr>
<td>C_18 SH</td>
<td>115 ± 2, 107 ± 2</td>
<td>51 ± 1</td>
<td>250 ± 60</td>
<td>1.0 ± 0.1</td>
<td>24 ± 1</td>
</tr>
</tbody>
</table>

* ± values represent standard deviations obtained from at least four independent sample preparations.