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# Ultrafast Layer-by-Layer Assembly of Thin Organic Films Based on Triazolinedione Click Chemistry

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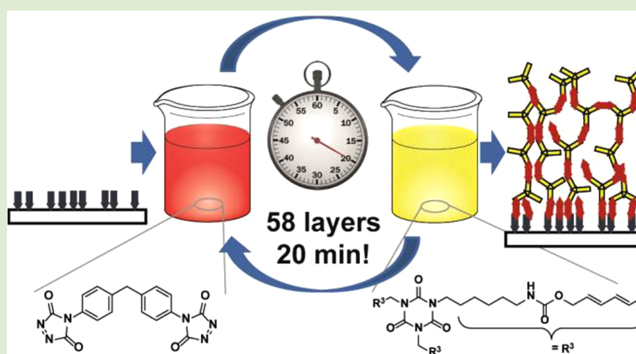
Supporting Information

**ABSTRACT:** Layer-by-layer deposition is a widely used method for surface functionalization. It is shown here that up to 58 covalently linked molecular layers could be assembled in 20 min at room temperature on a silicon wafer by the layer-by-layer click reaction of a divalent triazolinedione and a trivalent diene. The layer growth was found to be linear. The multilayers were analyzed by ellipsometry, atomic force microscopy, and X-ray photoelectron spectroscopy.



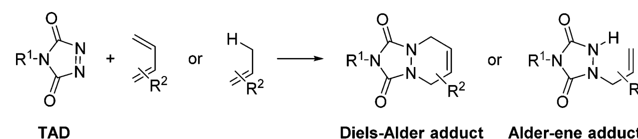

Layer-by-layer (LbL) assembly is a popular and versatile technique for the deposition of thin films of controlled thickness on various substrates.[1−3] It is based on the alternating deposition of mutually attractive molecules. In early examples, researchers made use of polyanions and polycations.[3] Since then, several other interactions such as hydrogen bonding,[4,5] supramolecular interactions,[6,7] and covalent linking[8−17] were utilized. In comparison to noncovalent LbL assemblies, covalently linked multilayers show enhanced stability against solvents and solutions of high ionic strength or extreme pH and are therefore more desirable systems for applications in materials science and coatings.

The main reason for the popularity of the LbL technique is its simplicity, and LbL deposition has found widespread application in the field of functional surfaces. LbL methods have for example been used to assemble stacked graphene anodes for organic solar cells,[18] to build self-healing polymer coatings,[19] and to tune the wettability properties of a surface.[20,21] The multilayers are typically assembled by soaking a surface in two solutions that contain the mutually attractive molecules. The only equipment that is required is a set of tweezers and beakers. Nevertheless, there is one major drawback: the LbL build-up is highly time-consuming, especially for covalently cross-linked multilayers. Dipping times typically range from 20 min to several hours.[9,11,13−16] Thus, assembling 20 layers with 20 min dipping would take 6.5 h, excluding the washing steps in between each layer deposition. Hence, decreasing the time needed for the LbL assembly is of great interest to surface scientists.

One elegant method to speed up the LbL process is spray-assisted LbL deposition.[22−25] Solutions containing molecules with complementary reactive groups are sprayed in a sequential manner on the surface instead of dipping the surface into the solutions. Using the spray method, application times can be decreased to a few seconds. Spin-coating-assisted LbL is another way to speed up the multilayer assembly.[26] However, a drawback of these methods is the inefficient use of adsorbate solutions, which to a large extent are rinsed off the substrate.

Recently, the group of Du Prez demonstrated the high reactivity of triazolinedione (TAD) compounds toward both conjugated dienes and isolated alkenes in a Diels−Alder or an Alder−ene reaction, respectively (Scheme 1).[27,28] Subsequently, we exemplified this high reactivity in the field of polymer conjugation by linking linear polymers with either small molecules or other macromolecules. These reactions

**Scheme 1. Reaction of Triazolinedione (TAD) with Diels−Alder and Alder−Ene Reaction Partners**

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typically are complete within a time scale of seconds, proceed at room temperature without the need of a catalyst, and thus meet the criteria of a click reaction.[29−31] Therefore, this chemistry should be well suited to the assembly of covalently linked multilayers by the traditional dipping method, if adsorbate molecules bearing multiple TAD and diene units, respectively, are reacted to a substrate. The high reaction rate of the TAD click reaction would greatly aid the acceleration of the LbL process, thereby eliminating a major drawback of current LbL systems. To the best of our knowledge, there is only one example in which TAD was reacted with surface-immobilized molecules.[32]

In this contribution, we show that nanoscale films with up to 58 layers can be assembled within 20 min on silicon substrates that were activated with a cyclohexene-terminated monolayer. To this end, the samples were alternatingly dipped into solutions of a divalent TAD and an isocyanurate derivative substituted with three diene moieties, respectively. The application of a divalent TAD and a trivalent diene should guarantee linear layer growth even if some degree of "back-bonding" to the surface cannot be excluded.[9,10,12] The layer thickness was monitored by ellipsometry, and the samples were further analyzed by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

First, silicon wafers were functionalized with a self-assembled monolayer (SAM) of a cyclohexene-terminated silane 1 (Figure 1) to yield surfaces that are reactive toward TAD. The static

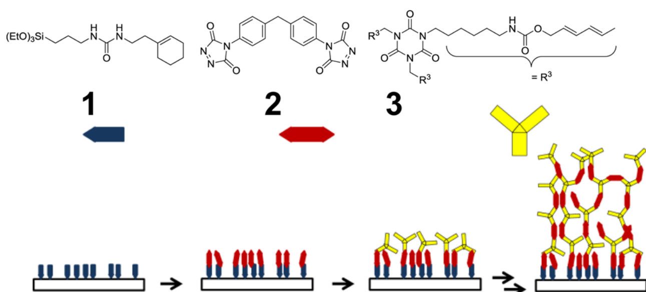


**Figure 1.** Molecular building blocks used in this study and schematic representation of the layer-by-layer process. Silicon wafers were first covered with a layer of cyclohexene silane 1. Multilayers were assembled by soaking the surface in solutions of divalent triazolinedione (TAD) 2 and trivalent diene 3 in an alternating fashion.

contact angle increased from less than 10° for the activated surface to 67° for the coated surface (see Figure S1 in the Supporting Information). This increase in hydrophobicity is initial proof of the deposition of silane 1 on the silicon wafer. Moreover, nitrogen could be detected in the XPS spectrum as expected for a nitrogen-containing coating (Figure S3, Supporting Information). The thickness of the SAM (determined by ellipsometry) was 1.0 nm, while the RMS roughness (determined by AFM) was 0.8 nm. The fact that this value is about half of the length of the grafted molecule (ca. 2 nm) indicates that a reactive coating with a lower density of cyclohexenes was obtained, rather than a tightly packed SAM. This low coverage might be caused by the mild reaction conditions used for the monolayer preparation, i.e., stirring of the activated silicon wafers overnight at room temperature in a 10 mM solution of the corresponding silane 1. Nevertheless, since TAD shows an excellent selectivity toward the alkenes at short reaction times, the surface modification is not hampered by this lower density.[27]

In a second stage, the molecular building blocks for the LbL deposition were readily synthesized from bulk chemicals. TAD 2 was synthesized in 95% yield over three steps without the need of chromatographic purification.[27] However, it must be noted that the stability of TAD against moisture and heat is moderate, while the corresponding urazole precursor is known to be very stable. Thus, we always prepared a fresh batch of TAD for the LbL deposition by oxidation of the urazole precursor. The trifold-substituted isocyanurate derivative 3 was synthesized by reacting hexamethylene diisocyanate isocyanurate trimer with 2,4-hexadien-1-ol and was used without further purification. In general, any molecule that tolerates the reaction conditions and bears more than one diene moiety could be used as a building block for this LbL deposition.

Finally, two solutions were prepared for the LbL deposition. TAD 2 and the diene building block 3 were dissolved in dry THF under an atmosphere of argon at concentrations of 150 and 75 mM, respectively. The coated silicon wafers were first immersed in the solution of TAD 2, in which the cyclohexene on the monolayer reacted to yield a wafer with terminal TAD groups (Figure 1). This layer could then be reacted with the diene building block 3 by immersion in the corresponding solution. These two soaking steps were repeated until the desired number of layers was deposited on the silicon wafer. In between each deposition step, the wafers were rinsed with acetone to remove unreacted molecules and dried in a stream of argon. While optimizing the reaction, we found that soaking the sample for 10 s at each deposition step is sufficient. Longer soaking times for up to 5 min did not lead to an increase in multilayer thickness as determined by ellipsometry.

Figure 2 illustrates the results of ellipsometry measurements of a batch of samples with up to 20 layers. These analyses show

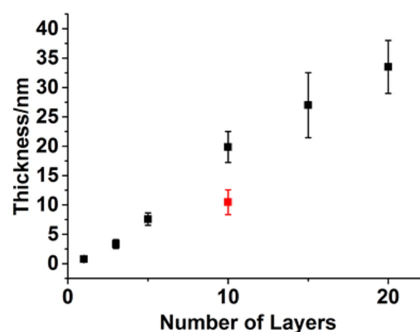


**Figure 2.** Ellipsometry data for multilayer samples bearing up to 20 layers (black squares) show a linear increase with layer number. The red square describes a sample that was passivated after five regular dipping cycles, preventing further deposition of layers. Each sample was measured on ten spots. The error bars represent the standard deviation of these values.

a clear linear correlation between the thickness of the organic multilayer and the layer number with a slope of 1.8 nm/layer. The sample with 10 layers indicated by the red square shows a thickness that is lower than expected for a ten-layer sample because a blocking layer was assembled on this sample after five normal deposition steps. Instead of soaking the sample in a solution of building block 3 to assemble layer six, which could then again react with TAD, the sample was soaked in a solution of 2,4-hexadien-1-ol (500 mM, 5 min) in order to saturate all


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TAD moieties on the surface. Subsequent dipping of this passivated sample four times in solutions of 2 and 3 did not lead to any increase in layer thickness, which proves that the LbL process relies on covalent bonding and not on unspecific adsorption.

Samples with 5 and 15 layers were further analyzed by AFM to study the topography of the multilayer surfaces (Figure 3 and Figure S2A and B, Supporting Information). They both show a granular polymer coating with a root-mean-square roughness of 2 and 5 nm, respectively. Caruso et al., who assembled multilayers of covalently linked polymers by azide–alkyne click chemistry, reported surface roughnesses of 4 and 6 nm for 8- and 16-layer films.[11] This observed increase in surface roughness with layer number can be ascribed to irregularities during the LbL process. Moreover, the multilayer coating was scraped off the silicon wafer with the cantilever, which allowed us to measure the thickness of the multilayer coating by a second analytical method. We measured around 7 nm for the sample with 5 layers and around 27 nm for the sample with 15 layers, which is very close to the thickness measured by ellipsometry (Figure 2) and clearly confirms the linear increase in height with each deposition step.

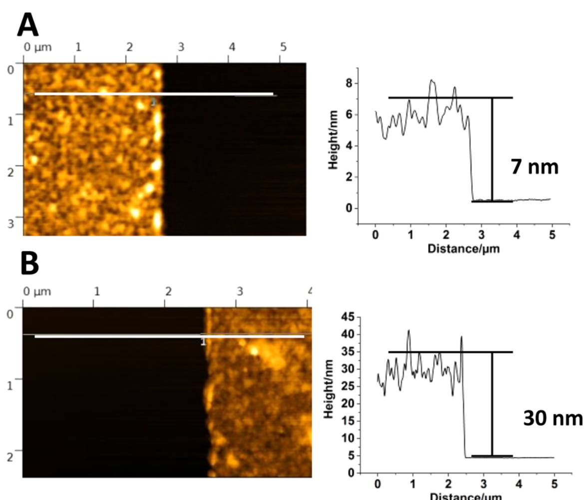


**Figure 3.** AFM images of samples with 5 (A) and 15 (B) layers. Parts of the multilayer coating were removed with the cantilever of the AFM in order to measure the height of the coating. Height profiles are shown on the right side.

The atomic compositions of multilayer samples with up to eight layers were analyzed by XPS. Carbon, nitrogen, silicon, and oxygen can be detected on the surface, which all derive from either the organic multilayer coating or the underlying silicon wafer, which is oxidized under ambient conditions. Survey scans are shown in Figure S4 in the Supporting Information. The intensities of the carbon and nitrogen signals, characteristic for the multilayers, increase with layer number, whereas the signals for silicon show a steady decrease with layer number (Figure 4A and Figure S4, Supporting Information). The overlying organic multilayers prevent the photoelectrons of the silicon wafer from escaping the sample. High-resolution spectra of the carbon signal of a selection of samples are shown in Figure 4B. The monolayer shows the smallest carbon signal with shoulders that can be assigned to higher oxidized carbon atoms, i.e., in the urea group of the silane 1. The intensities increase for the multilayer samples as a result of the larger amount of carbon from the polymer coating. Furthermore, the shoulders are more pronounced as the multilayer samples contain larger amounts of oxidized carbons, stemming from the carbonyl carbon atoms in the TAD 2, carbamate, and isocyanurate functions in diene 3.

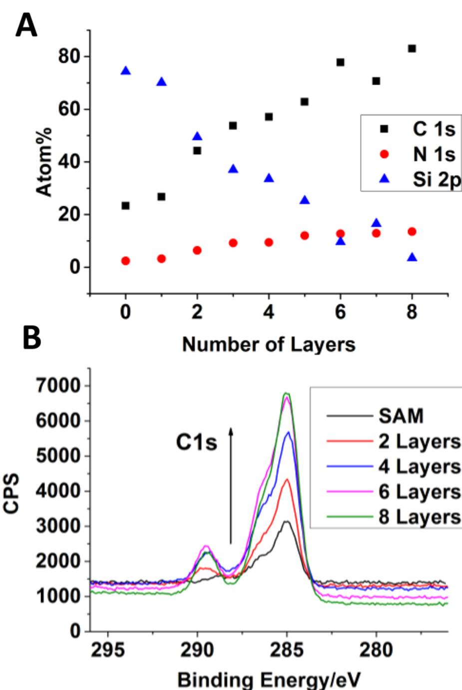


**Figure 4.** XPS measurements. (A) Atomic concentrations of C 1s, N 1s, and Si 2p for samples with up to eight layers. The intensities of the element being characteristic for the multilayer coating increase (C 1s and N 1s), whereas the Si 2p signal of the underlying wafer decreases with layer number. (B) High-resolution scans of C 1s show significant shoulders as a result of higher oxidized carbon species in the molecular building blocks 2 and 3.

Since ellipsometry, AFM, and XPS measurements provided consistent evidence that multilayers can be assembled based on TAD chemistry, it was our next objective to further speed up the LbL process. The rinsing and drying steps in between layer deposition were the remaining bottleneck that slowed down the LbL deposition. Rinsing and drying the sample lasts about 1 min per layer. Nevertheless, it is important to remove unreacted molecules from the surface to prevent cross contamination of the two adsorbate solutions. Thus, the washing steps cannot be skipped. We prepared an additional batch using a simplified washing procedure. Instead of rinsing and drying the sample in between each soaking step, we simply dipped it for 3 s in acetone and THF and immersed it in the other LbL solution. The drying step was thus skipped. Assembling one layer and washing takes around 20 s in total if this dip washing method is used. The increase in thickness determined by ellipsometry is linear too, while the slope remains the same as for the previous batch (Figure 5). The multilayer coatings display also similar roughnesses (Figure S2, Supporting Information). This optimized procedure allows ultrafast LbL assembly without the loss of material that is inevitable in the spray-assisted method.

In conclusion, we presented an ultrafast LbL method utilizing the click reaction between a divalent TAD and a trivalent diene molecule. Using ellipsometry, a linear increase of the layer thickness as a function of the layer number could be proven and



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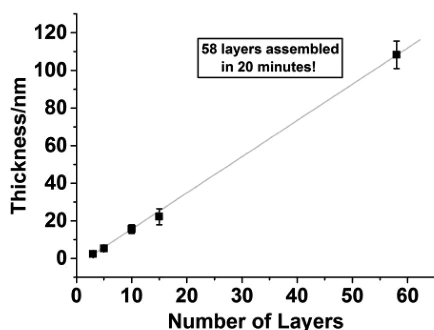


**Figure 5.** Ellipsometry data for multilayers bearing up to 58 layers, prepared by the dip washing method, show the same slope as the batch prepared by the traditional rinsing method (see Figure 2).

further confirmed by AFM and XPS analyses. After optimization of both the deposition and the washing steps, 58 layers could be assembled in merely 20 min. Since the synthesis of the divalent TAD is straightforward and a variety of molecules can be simply substituted with various dienes, we envision that this reaction can find application in numerous LbL systems. Currently, we are expanding the scope of this reaction in the area of surface modifications.

## ■ ASSOCIATED CONTENT

### Supporting Information

Synthetic procedures and description of the LbL deposition. 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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