Synthesis of a Three-Layer Organic Thin Film Prepared by Sequential Reactions in the Absence of Solvents

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We report the synthesis of a trilayer organic thin film on Au prepared via vapor-phase coupling of surface-confined 11-mercaptoundecanoic acid (MUA), hexamethylenediamine (HMDA), and 4-(trifluoromethyl)benzoyl chloride (TFMBC). The surface is prepared by activating the MUA monolayer with vapor-phase trifluoroacetic anhydride, which yields anhydrides at the solid/vapor interface. Next, the surface is exposed to vapor-phase HMDA to form an amine-terminated bilayer linked to MUA via both covalent amide bonds and electrostatic acid/base interactions. The bilayers are then capped with vapor-phase TFMBC to form a third covalently bound fluorinated layer. The reaction products are confirmed by Fourier transform infrared−external reflection spectroscopy. The spectroscopic data are supported by ellipsometric measurements and contact-angle goniometry, which show modulation in both the film thickness (1.2 to 2.1 nm) and contact angle (15 to 106°) as the film progresses from the MUA monolayer to the final trilayer product. X-ray photoelectron spectroscopic analysis indicates the presence of terminal trifluoromethyl (CF$_3$) functional groups in the final product. Films prepared using the same reactants in organic solvents have properties very similar to those prepared in the vapor phase. Comparison of the C−F stretching regions of trilayer-film spectra with that of a bilayer film prepared using a simple amide-coupling reaction between activated aminothiophenol and TFMBC (which we assume goes to completion) suggests that the trilayer films cover 30−40% of the Au surface.

Introduction

We report the synthesis of trilayer organic thin films prepared using three consecutive vapor-phase reactions carried out in the absence of solvents (Scheme 1).[1] The trilayer structures described here are a significant advance over our previous reports of the vapor-phase synthesis of bilayers,[2−6] because in the present case the second layer is a bifunctional diamine that reacts with the first layer primarily via a single terminal amine group (that is, cross coupling is not the dominant reaction mode). In principle, therefore, this method can be used to prepare organic thin films composed of alternating layers of other bifunctional molecules without the need for protection/deprotection steps.

There are some obvious technological reasons for preparing organic thin films using vapor-phase reactants at or near atmospheric pressure rather than liquid solvents.[7] For example, solvent-free processes lend themselves to automation and eliminate the need for solvent remediation.[6] Vapor-phase reactions can also be used to prepare structures that are unstable in liquids.[3−5] Our principal interest, however, is to begin to develop an understanding the basic rules that govern organic synthetic chemistry performed on solid surfaces in the absence of solvents.

Studies involving vapor-phase assembly of organic multilayers are rather scarce. What literature that does exist can be divided into two groups: reactions occurring under ultrahigh vacuum (UHV) conditions and reactions that take place at or near atmospheric pressure in an inert gas such as N$_2$ or Ar. Several different UHV-based methods have been reported; these include organic molecular beam deposition (OMBD),[8−11] molecular layer deposition (MLD),[12] and the molecular layer epitaxy (MLE) approach recently reported by Yitzchaik and co-workers.[13]

Previously we demonstrated the feasibility of using vapor-phase reactants at atmospheric pressure to synthesize bilayers consisting of self-assembled monolayers[7] (SAMs) and a second layer bound to the SAM by electrostatic,[4,5] hydrogen bonding,[3] or covalent[2,6] interactions. For example, in a very early report we showed that vapor-phase chlorosilanes react quantitatively with hydroxyl-terminated SAMs.[2] More recently we compared the synthesis of bilayer assemblies prepared by ester coupling of several different types of hydroxyl-terminated monolayers with heptanoyl chloride vapor.[6]

In addition to our own work, there have been other studies by Hutt and Leggett,[14] Pan et al.,[15] Duevel and Corn,[16] and Himmel et al.[17] involving alternative approaches for preparing bilayers from ω−functionalized

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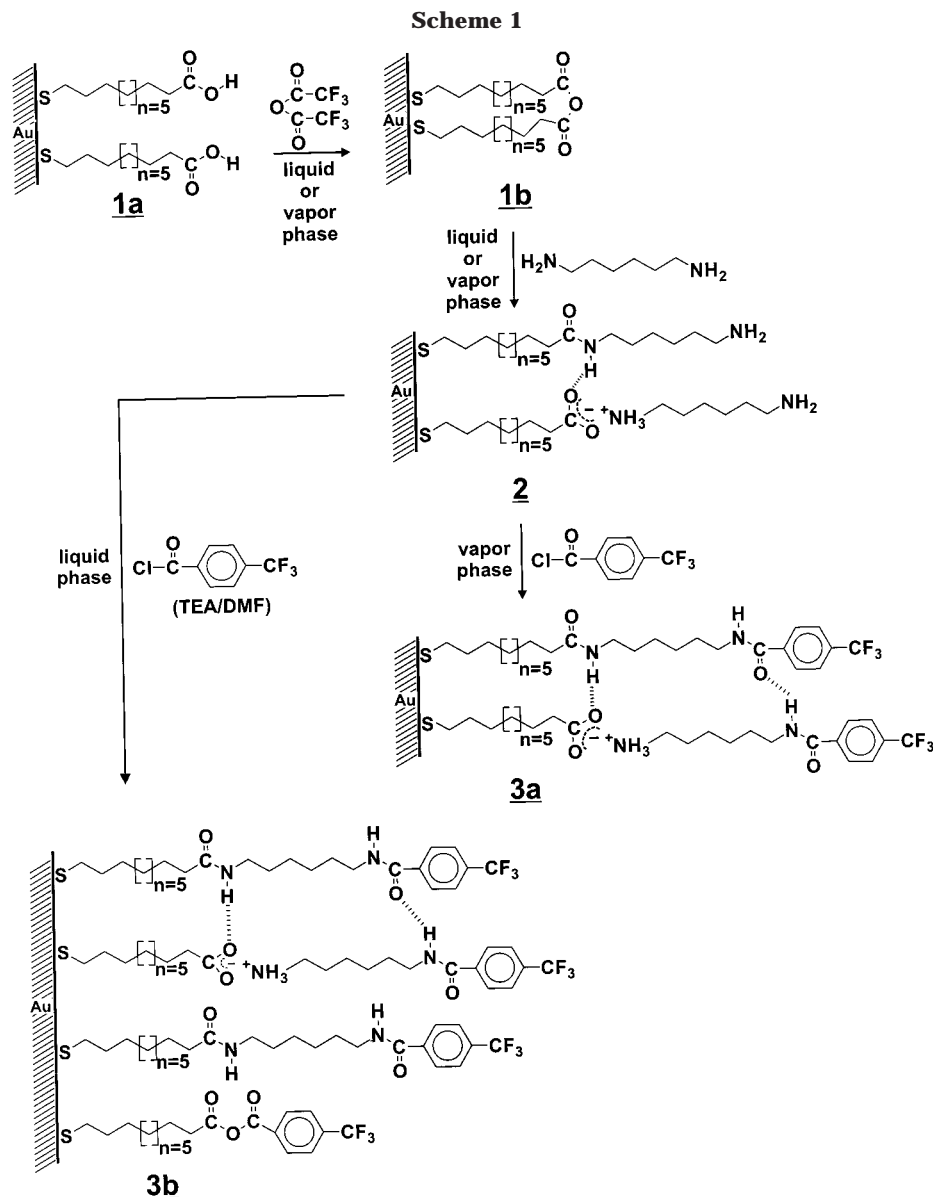(12) Yoshimura, T.; Tatsuura, S.; Sotoyama, W. *Appl. Phys. Lett.* **1991**, *59*, 482.

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Scheme 1

SAMs and vapor-phase reactants. However, we are not aware of any multilayer films having been prepared using vapor-phase reactants. In contrast, the synthesis of multilayer organic thin films using liquid-phase chemistry is well documented. For example, multilayers have been prepared by the Langmuir–Blodgett method,[7,18,19] by the metal–alkylphosphonate self-assembly methods pioneered by Mallouk,[20,21] Katz,[22] and Thompson,[23] by covalent linking of self-assembled multilayers,[24–26] by simple acid–base hydrolytic chemistry,[27–29] and by many other methods.

In the present study, an 11-mercaptoundecanoic acid (MUA) base monolayer (**1a**, Scheme 1) was prepared on a Au substrate and then exposed to trifluoroacetic anhydride (TFAA) vapor, which activates the MUA by forming anhydrides (**1b**, Scheme 1) at the solid/vapor interface.[30–32] Next, the activated MUA surface was exposed to vapor-phase, bifunctional hexamethylenediamine (HMDA), which we anticipated would result in the formation of an amine-terminated bilayer. This second layer links to the first through both amide bonds and electrostatic acid–base interactions (**2**, Scheme 1). Finally, the amine-terminated bilayer was exposed to vapor-phase 4-(trifluoromethyl)benzoyl chloride (TFMBC), which should result in a fluoro-terminated trilayer assembly if the first

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coupling reaction occurs via only one end of the diamine (**3a**, Scheme 1). For comparison, the bilayer and trilayer assemblies shown in Scheme 1 were also prepared in solution, and films prepared by both methods were characterized before and after each reaction using contact-angle goniometry,[33,34] ellipsometry,[35] Fourier transform infrared−external reflection spectroscopy (FTIR−ERS),[36] and X-ray photoelectron spectroscopy (XPS).[33]

Experimental Section

Chemicals. The following chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received: 11-mercaptoundecanoic acid (MUA), 95%; trifluoroacetic anhydride (TFAA), 99+%; hexamethylenediamine (HMDA), 98%; 4-(trifluoromethyl)benzoyl chloride (TFMBC), 97%; 4-aminothiophenol (ATP), 90%; 1-methyl-2-pyrrolidinone (MP), 99.5%; triethylamine (TEA), 99.5%; N,N-dimethylformamide (DMF), 99.8%; dichloromethane (DCM), 99.6%. Absolute ethanol (EtOH) in glass was purchased from Aaper Alcohol & Chemical Co. (Shelbyville, KY) and used as received. N_2 from gas cylinders had a purity of at least 99.995% and was passed through three Drierite gas-drying units (Hammond 26800, Fisher Scientific Co., Pittsburgh, PA) before use.

Substrate Preparation. MUA-modified Au substrates were prepared as described previously.[6] Briefly, all wafers were cleaned in a low-energy ozone cleaner for 10 min (Boekel Industries, Inc., model 135500). Diced wafers (2.6 cm × 1.3 cm) were then rinsed with warm EtOH[37] for 1−2 min and then soaked for >18 h in an ethanolic 1 mM solution of MUA. After removal from the soaking solution, the substrates were rinsed with EtOH, sonicated for 1−2 min in EtOH to remove physisorbed material, rinsed with EtOH again, and then dried in a stream of N_2. The MUA base monolayer on Au was analyzed by contact-angle and ellipsometric measurements, as well as FTIR-ERS, prior to vapor- or liquid-phase functionalization.

Vapor-Phase Functionalization. Immediately after base-monolayer modification, the substrate was transferred to a clean borosilicate glass vial fitted with a Teflon/silicone septum. All vials housing the substrates were purged with dry N_2 for at least 20 min prior to dosing with excess vapor-phase reactants. For example, in the activation step, vapor-phase TFAA was generated by passing N_2 at 0.25 L/min over the headspace of a vial containing neat liquid TFAA. The resulting subsaturated vapor was passed over the MUA monolayer via a 1.5 mm i.d. Teflon tube for 5 min. Longer dosing periods yielded identical results. Excess TFAA was removed from the reaction vial and substrate surface by purging with pure N_2 for 20 min prior to characterization. Bilayer **2** (Scheme 1) was formed in a similar manner by dosing with vapor-phase HMDA for 5−10 min. However, the last vapor-phase reaction involving TFMBC was carried out at a slightly elevated temperature (~40−45 °C, 15−20 min) due to its low vapor pressure (78−79 °C/16 mmHg; Aldrich).

Liquid-Phase Functionalization. Liquid-phase activation of the MUA base monolayer using TFAA and subsequent bilayer formation using HMDA was carried out using a procedure similar to that described by Yan et al.[31,32] Briefly, the surface-confined MUA monolayer was activated by immersion in a solution of 0.1 M TFAA and 0.2 M TEA in anhydrous DMF for 20 min, followed by thorough rinsing in dichloromethane and spectroscopic characterization. Next, the activated MUA monolayer was immersed in a solution of anhydrous MP containing 10 mM HMDA for 30 min, followed by rinsing in dichloromethane. Finally, the bilayer assembly was capped by immersion in a solution of anhydrous DMF containing 10 mM TFMBC and 20
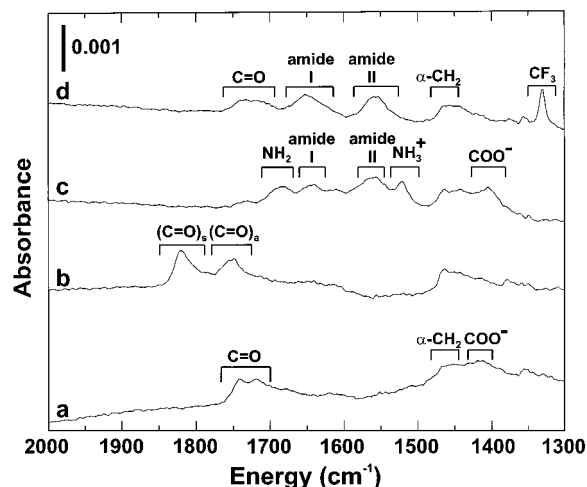

Figure 1. FTIR−ERS spectra of (a) a MUA monolayer on Au,[61] (b) the MUA monolayer after exposure to vapor-phase TFAA, (c) the resulting active surface anhydride after exposure to vapor-phase HMDA, and (d) the amine-terminated bilayer after exposure to vapor-phase TFMBC.

mM TEA for 30 min. The trilayer assembly was rinsed in dichloromethane before characterization.

To estimate the effectiveness of the vapor- and liquid-phase trilayer coupling reactions, we compared the magnitude of the C−F stretching mode peak to that of a simple bilayer prepared by liquid-phase coupling. This bilayer was prepared by immersing a clean Au wafer in an ethanolic solution of ATP (1 mM) for >18 h. The modified Au substrate was rinsed in EtOH and dried in a stream of N_2. Next, the ATP-modified substrate was immersed in a dichloromethane solution of TFMBC (10 mM) and TEA (20 mM) for 30 min. The substrate was rinsed thoroughly in dichloromethane prior to characterization. This bilayer coupling reaction was assumed to go to completion.

Fourier Transform Infrared−External Reflection Spectroscopy (FTIR−ERS) and X-ray Photoelectron Spectroscopy (XPS). FTIR-ERS measurements were made using an FTS-6000 spectrometer (Bio-Rad, Cambridge, MA) equipped with a Harrick Scientific Seagull reflection accessory (Ossining, NY) and a liquid-N_2-cooled narrow-band MCT detector. All spectra were the sum of 256 individual scans and obtained at 4 cm⁻¹ resolution using *p*-polarized light at an 84° angle of incidence with respect to the Au substrate. XPS spectra were acquired using a Perkin-Elmer (PHI) model 5500 spectrometer (Norwalk, CT). XPS data acquisition employed a pass energy of 29.35 eV, a step increment of 0.250 eV, and a Mg anode power of 400 W.[38] The acquisition time for the high-resolution scans was 30 min.

Ellipsometric Thickness Measurements. Ellipsometric measurements were made in air with a Gaertner Scientific (Chicago, IL) model L2W26D ellipsometer using a 70.00 ± 0.02° angle of incidence with 632.8 nm laser light and assuming a film refractive index (n_f) of 1.46. The reported thicknesses are the average of 10 measurements made at five different locations on each of two independently prepared substrates. The estimated error in the thickness measurements is ±0.3 nm.

Contact-Angle Measurements. Advancing water contact angles were measured using a FTA-200 goniometer (First Ten Angstroms, Portsmouth, VA) and doubly distilled water. The stage holding the substrate was housed in a transparent enclosure to minimize exposure of the Au surface to the surroundings. The reported thicknesses are the average of 10 measurements made at five different locations on each of two independently prepared substrates. The estimated contact-angle error is ±5°.

Results and Discussion

Figure 1 shows the FTIR−ERS spectra of monolayers, bilayers, and trilayers corresponding to each step of the reaction sequence outlined in Scheme 1. The spectrum of

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Table 1. Contact-Angle and Ellipsometric Thickness Data for the Vapor- and Liquid-Phase Reactions Discussed in the Text

Au/monolayer	contact angle ($\pm 5°$)[a]		film thickness (± 0.3 nm)[b]	
	vapor	liquid	vapor	liquid
Au/MUA	15	15	1.2	1.2
Au/MUA anhydride	65	72	1.3	1.4
Au/MUA + HMDA	60	80	1.7	1.6
Au/MUA + HMDA + TFMBC	106	108	2.1	2.0
Au/ATP		65		0.5
Au/ATP + TFMBC		115		1.0

[a] Average of five advancing water contact-angle (θ_a) measurements made on each of two independently prepared substrates. [b] Average of five different ellipsometric thickness measurements made at five different locations on each of two independently prepared substrates.

the MUA monolayer (part a of Figure 1) prior to activation reveals two characteristic C=O stretching bands at 1740 and 1720 cm^{-1}, which arise from non-hydrogen-bonded and hydrogen-bonded carboxylic acids, respectively.[3,4,16,36,39–41] Following exposure of the MUA base monolayer to vapor-phase TFAA, the C=O stretching bands are replaced by two new absorption bands at 1820 and 1749 cm^{-1} (part b of Figure 1) that are characteristic of the symmetric and asymmetric C=O stretching modes of a carboxylic anhydride.[31,39–41] Contact-angle measurements of the carboxylic acid and anhydride surfaces indicate an increase in hydrophobicity from 15 to 65°, respectively (Table 1), which is attributed to the lower polarity of the surface anhydride.[31] FTIR–ERS data obtained before and after the contact-angle measurements indicated no detectable hydrolysis of the surface anhydride occurred. On the basis of spectroscopic and contact-angle measurements, we conclude that activation of MUA is complete and that the hydrolysis of the anhydride on the surface is slow.[42,43]

When the anhydride surface (*1b*, Scheme 1) is exposed to the bifunctional, vapor-phase diamine (HMDA), a partial bilayer forms. In principle, 50% of the HMDA should bind to the activated MUA surface via an electrostatic interaction and 50% through covalent amide linkages (*2*, Scheme 1) if there is no cross coupling (that is, as long as only one end of the diamine reacts with the surface). Several new bands in the spectrum obtained following the vapor phase reaction with HMDA (part c of Figure 1) support the model illustrated in Scheme 1. First, the newly formed amide linkages in the bilayer give rise to amide I and II bands at 1640 and 1560 cm^{-1}, respectively.[16,31,39–41,44,45] The presence of a slightly stronger amide II band compared to amide I might suggest that the amide bonds within the mixed bilayer (*2*, Scheme 1) are predominantly in a trans conformation.[32,44,45] Second, evidence for the acid–base interaction (*2*, Scheme 1) comes from the two bands assigned to the NH$_3^+$ and COO$^-$ functionalities (part c of Figure 1). The band at 1520 cm^{-1} can be attributed to the symmetric NH$_3^+$

bending modes,[2,39,40] whereas the band centered at 1410 cm^{-1} arises from the symmetric COO$^-$ stretching modes.[5,39,40,46] The peak at 1680 cm^{-1} is assigned to the bending mode, δ(N–H), of the terminal NH$_2$ groups of the bilayer.[39–41]

Ellipsometric and contact-angle measurements (Table 1) also support the model shown in Scheme 1. Following the reaction with vapor-phase HMDA, there is an increase in the thickness of the thin film (by 0.4 nm) but only a negligible change in the contact angle. The measured advancing contact angle (60°) for the amine-terminated bilayer agrees well with reported contact angles of other amine-terminated SAMs.[47,48] Although the thickness, contact-angle measurements, and, more importantly, the spectral evidence all confirm the proposed mixed amine-terminated bilayer (*2*, Scheme 1), only the successful formation of a third layer through reaction with the free terminal amine (−NH$_2$) groups in the bilayer can confirm this structure. Reaction with 4-(trifluoromethyl)benzoyl chloride (TFMBC) provides a convenient means for analyzing the success of this strategy, because the trifluoromethyl (−CF$_3$) group is easily detected by FTIR–ERS and XPS.

Part d of Figure 1 shows the spectrum obtained after the amine-terminated bilayer is exposed to vapor-phase TFMBC (*3a*, Scheme 1). The presence of a peak at 1330 cm^{-1}, which arises from the symmetric stretching mode of the trifluoromethyl (CF$_3$) group,[49–54] confirms that free amine groups are accessible to TFMBC. The increased height of the amide I and II bands (compared to the corresponding bilayer film, *2*) also confirms the final reaction step shown in Scheme 1. The presence of the C=O stretch is somewhat surprising, and the only explanation we can offer is that his band arises from unreacted MUA.

It was possible to estimate the percentage coverage of the trilayer film by comparing the height of the symmetric CF$_3$ stretching mode (part d of Figure 1) to that of a similar bilayer film prepared using a simple liquid-phase synthesis that goes to completion. The bilayer we chose for this purpose involved an amidation reaction between surface-confined 4-aminothiophenol (ATP) and TFMBC. The spectroscopic data corresponding to this coupling are shown in Figure 2. Prior to amidation, the δ(NH$_2$) bending mode (1621 cm^{-1}) and aromatic ring vibrations (1588 and 1489 cm^{-1}) of ATP are apparent in spectrum a of Figure 2.[2,39–41] The formation of a CF$_3$-terminated amide-coupled bilayer is indicated by the presence of the amide I and II bands at 1675 and 1525 cm^{-1}, respectively, and the symmetric CF$_3$ stretching mode at 1330 cm^{-1} in spectrum b of Figure 2.[39–41,49–54] The near-complete disappearance of the δ(NH$_2$) bending mode in part b of Figure 2 supports the necessary assumption that the reaction goes nearly to completion and thus forms a good standard against

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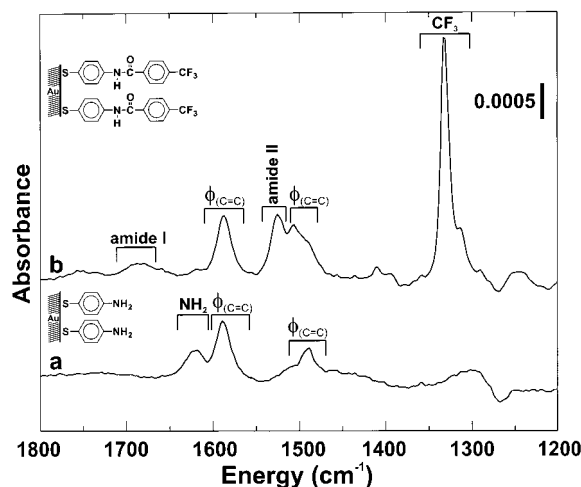
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Figure 2. FTIR−ERS spectra of (a) an ATP monolayer on Au and (b) a trifluoromethyl-terminated amide-coupled bilayer (ATP−TFMBC) prepared by immersing (a) in a TFMBC/TEA/DCM solution.

Figure 3. FTIR−ERS spectra of (a) a MUA monolayer on Au, (b) MUA after immersion in a TFAA/TEA/DMF solution, (c) the active surface anhydride after immersion in a HMDA/MP solution, and (d) the amine-terminated bilayer after exposure to a TFMBC/TEA/DMF solution.

which the success of the vapor-phase trilayer chemistry can be judged.

To estimate the yield of the vapor-phase trilayer reaction, we ratioed the height of the peak corresponding to the symmetric CF_3 group in part d of Figure 1 with that in part b of Figure 2. This simple procedure is only semiquantitative for a number of reasons but especially because of potential differences in the relative average tilt angles of the CF_3 functional groups in the two systems.[54,55] Given this caveat, we estimate that about 30% of the surface prepared via the vapor-phase method (**3a**, Scheme 1) is covered by the fluorinated trilayer. This relatively low coverage is likely due to coupling reaction inefficiencies such as cross coupling of the bifunctional diamine (HMDA) to the activated acid group or the inaccessibility of the free terminal amine ($-NH_2$) groups to TFMBC arising from packing constraints.

The ellipsometric and contact-angle measurements (Table 1) support the spectroscopic data for the vapor-phase trilayer. For example, the reaction with vapor-phase TFMBC results in an additional film thickness of 0.4 nm, which can be compared with an expected thickness increase of 0.6 nm for a complete trilayer thin film.[56] There is also a significant increase in the hydrophobicity of the surface, from 60 to 106°, which is consistent with the transition from primary amine to trifluoromethyl termination of the thin film. For comparison, the contact-angle of the ATP−TFMBC bilayer changed from 65 to 115°, which is consistent with the results obtained from other related trifluoromethyl-terminated SAMs;[33,57] in addition, the ellipsometric thickness of the ATP−TFMBC bilayer also changed from an initial value of 0.5 to 1.0 nm. Consistent with the spectroscopic data, both of these results indicate a higher surface coverage of the trifluoromethyl group for the bilayer.

We prepared a trilayer thin film using a more conventional liquid-phase synthesis so as to compare its physical and chemical properties with those of the film prepared using the vapor-phase approach. Parts a and b of Figure 3 show that the spectra of the MUA base monolayer and
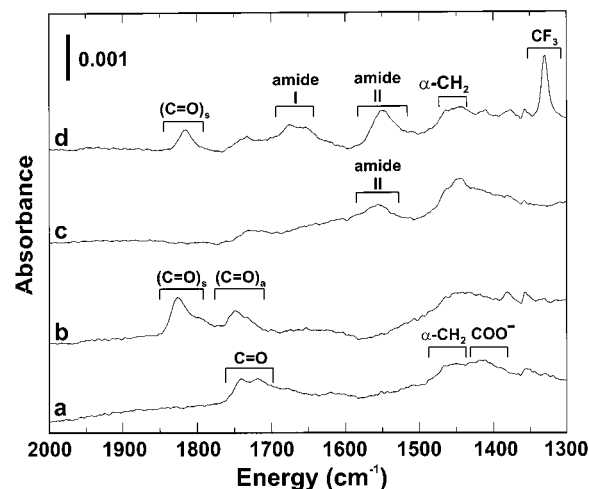
activated MUA are similar to their vapor-phase counterparts shown in parts a and b of Figure 1, and therefore, we conclude that the structure of the activated MUA surface is independent of how it is prepared.[30] However, when HMDA is linked to the activated surface anhydride in solution, the resulting spectrum (part c of Figure 3) is quite different from the analogous vapor-phase spectrum (part c of Figure 1). The only peak that can be clearly associated with the newly formed bilayer is the amide II band at 1559 cm^{-1}.[39-41] The broad band located in the 1400−1500 cm^{-1} region of the spectrum can be assigned to a combination of the $\alpha(CH_2)$ bending, CH_2 bending, and the symmetric COO^- stretching mode.[5,39-41,46] This feature is also present in Figure 1. It is unclear why neither the symmetric NH_3^+ bending modes nor the NH_2 deformation bands are present in part c of Figure 3 as they are in part c of Figure 1. These spectral differences suggest that the solvent plays a key role in determining the final structure (or at least the spectroscopic properties) of the thin films.[6]

Part d of Figure 3 shows the FTIR−ERS spectrum obtained after capping the amine-terminated bilayer (**2**, Scheme 1) with TFMBC in solution. The absorption intensity of the symmetric CF_3 peak at 1330 cm^{-1} is slightly higher compared to the peak found in part d of Figure 1. By comparing the height of this peak with that of the corresponding CF_3 peak in the ATP−TFMBC bilayer spectrum (part b of Figure 2), we estimate that the surface coverage of the fluorinated trilayer thin film prepared in the liquid phase is about 40%. The other vibrational peaks for the trilayer films prepared by liquid- and vapor-phase reactions are also comparable, with one exception. The band located at 1815 cm^{-1} (part d of Figure 3) arises from the carbonyl ($C=O$) stretch of a mixed anhydride that we believe forms between TFMBC and the carboxylate anion in the MUA base monolayer.[39-41] This band is unique to the thin film prepared in the liquid phase (**3b**, Scheme 1), because the displacement of the carboxylate/amine salt from the bilayer thin film cannot occur in the vapor phase.[4] The presence of the anhydride band might also explain why the extent of fluorination of the trilayer thin film prepared in the liquid phase is higher than when the reaction is carried out in the vapor phase. Importantly, the ellipsometric thickness and contact-angle values (Table 1) obtained for the two trilayer films were nearly independent of how they were prepared.

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(56) Molecular dimensions of 4-(trifluoromethyl)benzoyl chloride were estimated using Cerius² 3.0; Molecular Simulations, Inc.: San Diego, CA, **1997**.

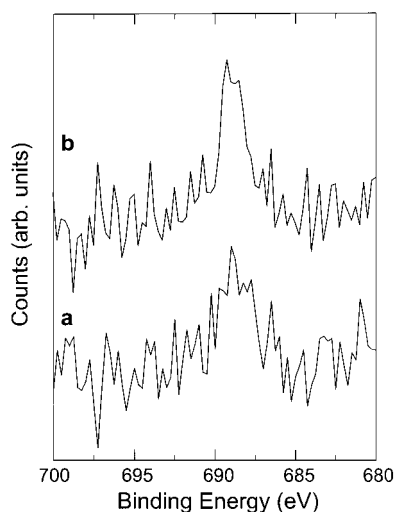(57) Graupe, M.; Takenaga, M.; Koini, T.; Colorado, R., Jr.; Lee, T. R. *J. Am. Chem. Soc.* **1999**, *121*, 3222.

Figure 4. High-resolution XPS spectra in the F(1s) region for the trilayer thin films prepared via the (a) vapor-phase and (b) liquid-phase methods.

XPS analyses carried out on the trilayer thin films confirmed the model shown in Scheme 1. Parts a and b of Figure 4 show high-resolution XPS spectra of the trilayer thin films prepared by vapor- and liquid-phase reactions, respectively. The peak centered around 688.5 eV corresponds to the F(1s) binding energy of the fluorine in the trifluoromethyl (CF_3) group.[58,59] The XPS data were collected over a relatively short period of time (30 min) to minimize damage to the fluorinated organic thin film by the X-ray beam.[60]

Summary and Conclusions

In summary, we have described the formation of trilayer organic thin films on Au using vapor- and liquid-phase

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(61) In this study we did not make an effort to fully protonate the MUA SAMs by acidifying them prior to spectral acquisition. Accordingly, at neutral pH, a fraction of the SAM is deprotonated and in the carboxylate (COO⁻) form as shown in part a of Figures 1 and 3 (see refs 16 and 46). Additionally, we have found that MUA SAMs cannot be activated using vapor-phase TFAA if acidified prior to reaction. This is not the case when the activation step is carried out in the presence of a base in liquid phase (see refs 30 and 31).

synthetic approaches and compared their chemical and physical properties. The spectroscopic characterization of these organic thin films at various stages of preparation has revealed several interesting points. First, the surface coverage of the trilayer prepared via the vapor-phase method (30%) is somewhat lower than the analogous trilayer thin film prepared via the liquid-phase method (40%). This is likely due to the dissociation of the salt thin film in the liquid phase and subsequent coupling to additional TFMBC. However, the important point is that the two methods yield thin films of comparable coverage. Second, we also discovered that there are other more subtle differences in the FTIR−ERS spectra obtained from the two classes of thin films prepared. These are likely a consequence of rather small differences in the average orientation of the thin film components driven by the presence of the solvent. Third, only the coupling reactions carried out in the vapor phase resulted in the formation of both covalent bonds and stable electrostatic interactions. The most significant finding in this study, however, is that it is possible to prepare trilayer thin films in the vapor phase using an intermediate second layer functionalized identically on both ends (the diamine, HMDA). This strategy greatly simplifies the thin film synthesis as it obviates the need for more complex protection/deprotection chemistry.

Although the reaction efficiencies were more-or-less independent of whether the reactions were performed in the vapor or liquid phase, it would be more satisfying if the vapor-phase efficiency more closely approached 100%.[2] Understanding the factors controlling the extent of reactions such as those described here are presently the focus of our work. Note, however, that there are many examples of technological applications where 100% conversion is unnecessary. For example, even though the estimated coupling efficiency of the vapor-phase chemistry is only 30%, we were able to increase the contact angle of the initial thin film (15°) by nearly 90° without using solvents.