

# Deprotecting Thioacetyl-Terminated Terphenyldithiol for Assembly on Gallium Arsenide

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We characterize the assembly of terphenyldithiol (TPDT) on gallium arsenide (GaAs) from ethanol (EtOH) and tetrahydrofuran (THF) as a function of ammonium hydroxide (NH<sub>4</sub>OH) concentration. NH<sub>4</sub>OH facilitates the conversion of thioacetyl end groups of the TPDT precursor to thiolates in the assembly solution. The final structure of TPDT assembled on GaAs is sensitive not only to the assembly solvent but also to NH<sub>4</sub>OH concentration. In the presence of low concentrations of NH<sub>4</sub>OH (1 mM), TPDT assemblies from EtOH are oriented upright. The same assemblies are less upright when adsorption is carried out at higher NH<sub>4</sub>OH concentrations. In THF, TPDT does not adsorb significantly on GaAs at low NH<sub>4</sub>OH concentrations. The surface coverage and structural organization of these assemblies improve with increasing NH<sub>4</sub>OH concentrations, although these assemblies are never as organized as those from EtOH. The difference in the final structure of TPDT assemblies is attributed to differences in the thiolate fraction in the assembly solution at the point of substrate immersion.

## Introduction

The drive to create nanoscale electronics<sup>1</sup> with active components composed of single molecules or molecular layers has prompted strong interest in molecular assembly. Thiols, in particular, have been shown to chemically attach to metals (Au,<sup>2–5</sup> Ag,<sup>3,5,6</sup> Ni,<sup>7</sup> Pt,<sup>8</sup> etc.) and semiconductors (GaAs<sup>3,9–13</sup>). Conjugated thiol chemistries with rigid backbones have thus played a central role as model systems for molecular wires,<sup>14</sup> switches,<sup>15</sup> rectifiers,<sup>16</sup> and diodes.<sup>17</sup> To this end, charge transport in these systems is governed not only by the chemical structure of the molecule but also by the way the molecules are organized and attached to the electrode surface.<sup>18,19</sup> High-quality and well-

characterized self-assembled monolayer (SAM) structures are thus prerequisites for reliable charge transport studies.<sup>18</sup> Much of the recent attention has focused on the assembly of thiols on GaAs,<sup>12,13,20,21</sup> including the use of dithiols to form GaAs–molecule–metal junctions.<sup>22–24</sup> The understanding of how conjugated dithiols assemble on GaAs surfaces, however, is limited. In light of this, we have chosen to investigate the assembly of a model conjugated dithiol molecule, thioacetyl-protected terphenyldithiol (TPDT), on GaAs.

As-synthesized, conjugated dithiols are usually protected with thioacetyl groups because free thiols have a tendency to oxidize<sup>14</sup> and dimerize.<sup>14,25</sup> The thioacetyl groups are converted in situ to thiolates with the addition of ammonium hydroxide (NH<sub>4</sub>OH) during assembly.<sup>14,26</sup> The assembly of such systems on GaAs is nontrivial and is highly sensitive to the conditions at which the molecules adsorb. For instance, we have shown that the assembly of terphenyl- and quaterphenyldithiols on GaAs is strongly affected by the solvent quality.<sup>20</sup> Here, we report how the concentration of the deprotecting agent, NH<sub>4</sub>OH, in the assembly solution affects the final structure of TPDT assembled from EtOH and THF on GaAs. Specifically, adsorption from EtOH at low NH<sub>4</sub>OH concentrations results in dense TPDT assemblies with

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molecules that are preferentially upright. The same assemblies become less upright when TPDT is adsorbed from EtOH at high  $\text{NH}_4\text{OH}$  concentrations. In contrast, TPDT does not adsorb significantly on GaAs from THF at low  $\text{NH}_4\text{OH}$  concentrations. These assemblies exhibit improved surface coverages and organization when increased  $\text{NH}_4\text{OH}$  concentrations are used. These differences in the assembly behavior of TPDT on GaAs are attributed to differences in the thiolate fraction in the solutions at the point of substrate immersion. Our results demonstrate that a proper concentration of the deprotecting agent—in addition to the appropriate assembly solvent—is essential for achieving high-quality TPDT assemblies on GaAs.

### Experimental Section

**Molecular Assembly Formation.** SureSeal-grade solvents from Aldrich were used as-received to assemble the molecules on GaAs. To remove the native oxide layer from GaAs, the substrates were etched in concentrated hydrochloric acid (HCl) for 30 s and then in concentrated  $\text{NH}_4\text{OH}$  for 30 s. This procedure was repeated again. The substrates were rinsed with EtOH and dried with a stream of nitrogen following the first three etch steps. After the fourth and last etch step in  $\text{NH}_4\text{OH}$ , the substrates were rinsed with deionized water and dried with a stream of nitrogen. The etched substrates were then immediately transferred into a glovebox (MBraun, <0.1 ppm  $\text{O}_2$ , <0.1 ppm  $\text{H}_2\text{O}$ ) and immersed in the assembly solutions. Single-side-polished Si-doped (100) GaAs (AXT) was used for near-edge X-ray absorption fine structure (NEXAFS) spectroscopy; double-side-polished undoped (100) GaAs (AXT) was used for transmission Fourier transform infrared (FTIR) spectroscopy.

The thioacetyl-protected precursor of terphenyldithiol (TPDT) was synthesized according to previously described procedures.<sup>20</sup> Assembly solutions were prepared by dissolving the precursor at 250  $\mu\text{M}$  in either EtOH or THF.  $\text{NH}_4\text{OH}$  at 1, 10, 30, and 160 mM was then added to the assembly solutions to facilitate the conversion of the thioacetyl end groups of the TPDT precursor to thiolates ( $\text{S}^-\text{NH}_4^+$ ).<sup>14</sup> After the addition of  $\text{NH}_4\text{OH}$ , the solutions were left for an hour at 55 °C before freshly etched GaAs substrates were immersed for 18–24 h. The assembly was carried out at 55 °C. Upon removal from the assembly solution, the GaAs wafers were thoroughly rinsed with EtOH, sonicated in a 2 mM solution of tri-*n*-butylphosphine (TBP) in EtOH for 15 min, and left immersed for 40 min in the same TBP solution to remove any extraneous disulfides that may have formed during the assembly.<sup>25</sup> After TBP treatment, the substrates were thoroughly rinsed with EtOH and dried in a stream of nitrogen.

**UV–Vis–NIR.** We employed a Varian Cary 500 UV–vis–NIR spectrophotometer and Starna Cells Q6 quartz UV–vis cuvettes with a path length of 1 mm to examine the deprotection reaction of TPDT in solution. The spectra of neat solvents were used for baseline correction. Each spectrum was collected with 1 nm resolution and a scan rate of 600 nm/min.

**FTIR.** Fourier transform infrared (FTIR) spectroscopy experiments were carried out using a dry-air purged Nicolet Magna-IR 860 spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The TPDT assemblies on GaAs were characterized in transmission mode with an incident angle of 30° relative to the substrate normal using s-polarized light.<sup>27</sup> All transmission spectra were recorded with a 2  $\text{cm}^{-1}$  resolution for 1000 scans. We used the spectrum of sulfur-passivated GaAs as background.<sup>27</sup> Sulfur-passivated GaAs was prepared by etching the substrate using the procedure described above, rinsing with deionized water, and immediately immersing the substrate in an aqueous ammonium disulfide solution (20% v/v, Aldrich)<sup>28</sup> for several hours. This procedure yields a stable sulfur overlayer that prevents oxide growth and reduces hydrocarbon adsorption.<sup>28</sup> The background-corrected spectra were smoothed using conventional 12-point fast Fourier

transform smoothing routine in Origin 6.1 to remove the periodic interference.<sup>27</sup> A multipoint baseline correction was applied to all spectra using GRAMS/AI 7.01. For reference, we acquired a transmission IR spectrum of the thioacetyl TPDT precursor powder dispersed in KBr (1:150 mg).<sup>27</sup> All transmission IR spectra are reported in absorbance units,  $A$ , where  $A = -\log R/R_0$ ,  $R$  is the power reflectivity of the IR beam, and  $R_0$  is the reflectivity of a reference sample.

**NEXAFS.** Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy experiments were carried out at the NIST/Dow soft X-ray materials characterization facility located at beamline U7A at the National Synchrotron Light Source at Brookhaven National Laboratories.<sup>29</sup> The setup is described in detail elsewhere.<sup>20</sup> Carbon-edge NEXAFS spectra were acquired at X-ray incident angles of 20° (grazing), 35°, 50°, and 75° (near-normal). The compilation of angle-dependent data allowed us to assess the ensemble-average orientation of TPDT on GaAs.<sup>20</sup> We scanned in increments of 0.1 eV in the region of interest (280–300 eV) and in increments of 0.5 eV at the pre-edge (250–280 eV) and post-edge (300–330 eV) regions. To compare the surface coverage between samples, polarization-independent spectra acquired at an incident angle of 50° were used. With a polarization factor of 85%, this angle corresponds to the “magic angle”,<sup>30</sup> where spectral details do not depend on the details of the molecular orientation.

### Results and Discussion

**Assembly Solution.** To understand how  $\text{NH}_4\text{OH}$  affects the final structure of TPDT assemblies, we first examined the deprotection reaction in the assembly solvents. More specifically, we characterized the assembly solutions at the point of substrate immersion, i.e., 1 h after  $\text{NH}_4\text{OH}$  was added to the solution. Despite the fact that the assembly takes place over the course of 18–24 h, we assumed that the initial solution conditions have the most dramatic impact on the structure of the final assembly because the adsorption of sulfur on GaAs<sup>28,31</sup> and thiolates on gold<sup>32,33</sup> is known to occur very fast, typically within the first few minutes of immersion. Figure 1a contains the UV–vis spectra of TPDT in EtOH 1 h after the addition of  $\text{NH}_4\text{OH}$  at varying concentrations. A spectrum of the acetyl-protected TPDT precursor in EtOH prior to the addition of  $\text{NH}_4\text{OH}$  is also provided for reference (solid line). The acetyl-protected precursor exhibits an absorption band with a peak maximum at 298 nm. With the addition of  $\text{NH}_4\text{OH}$ , a new absorption band is evident at 345 nm. We attribute this new absorption to deprotected TPDT terminated with thiolates ( $\text{S}^-\text{NH}_4^+$ ). This absorption is associated with thiolates, and not thiols ( $-\text{SH}$ ), because thiol-terminated molecules, obtained either by direct synthesis<sup>20</sup> or by deprotecting acetyl-protected TPDT precursor with sulfuric acid,<sup>34,35</sup> absorb at 302 nm in EtOH. The intensity of the thiolate absorption band at 345 nm increases with increasing  $\text{NH}_4\text{OH}$  concentrations while the intensity of the thioacetyl absorption band at 298 nm decreases. This trend indicates an increase in the thiolate fraction in the assembly solution with increasing  $\text{NH}_4\text{OH}$  concentration. We observe a complete disappearance of the thioacetyl absorption band at 298 nm within 60–70 min after the addition of 160 mM  $\text{NH}_4\text{OH}$ , indicating complete conversion of TPDT from its thioacetyl to thiolate form within this time period.

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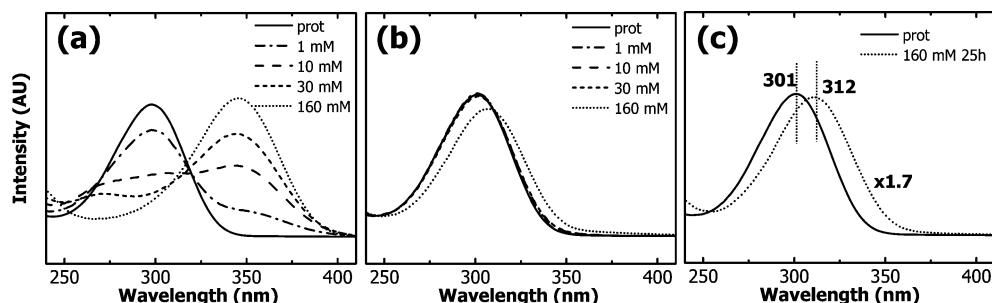
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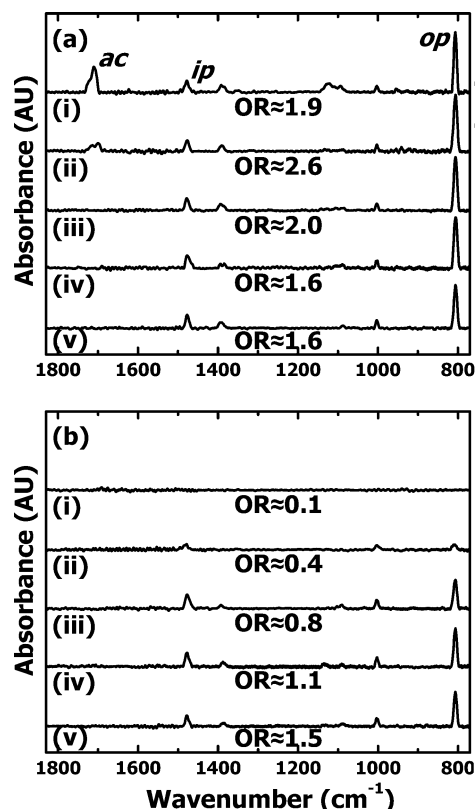
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**Figure 1.** UV-vis NIR spectra of TPDT dissolved in (a) EtOH and (b) THF as a function of  $\text{NH}_4\text{OH}$  concentration 1 h after injection. Spectra of acetyl-protected precursor of TPDT in EtOH and THF are included for reference (solid line). Panel (c) contains UV-vis NIR spectra of acetyl-protected TPDT precursor and TPDT dissolved in THF 25 h after the addition of 160 mM  $\text{NH}_4\text{OH}$ . The latter spectrum was scaled for illustration purposes.

Figure 1b contains the UV-vis spectra of TPDT in THF 1 h after the addition of  $\text{NH}_4\text{OH}$  at varying concentrations. An absorption band attributed to the acetyl-protected precursor is observed at 301 nm<sup>36</sup> (solid line). With the addition of  $\text{NH}_4\text{OH}$ , we observe an absorption shoulder around 330 nm. We attribute this shoulder to the presence of thiolate-terminated TPDT. To quantitatively determine the position of the thiolate absorption band in THF, we examined the UV-vis spectrum of TPDT in THF 25 h after the addition of 160 mM  $\text{NH}_4\text{OH}$  (Figure 1c); from this point forward the time-resolved UV-vis spectra remain unchanged (because the deprotection reaction is complete). From this spectrum, we determine the position of the thiolate absorption band in THF to be 312 nm. Although the UV-vis data of TPDT in EtOH (Figure 1a) suggest complete conversion of TPDT from thioacetyl to thiolate end groups 1 h after the addition of 160 mM  $\text{NH}_4\text{OH}$ , the same reaction in THF appears to be significantly slower. Based on changes in relative intensities of the thioacetyl and the thiolate peaks in Figures 1a and 1b, we estimate less than 50% of thioacetyl end groups are converted to thiolates 1 h after the addition of 160 mM  $\text{NH}_4\text{OH}$  (Figure 1b) in THF. At 1 mM  $\text{NH}_4\text{OH}$ , only  $\approx 1\%$  of the thioacetyl groups are converted to thiolates in THF as compared to  $\approx 25\%$  conversion in EtOH after 1 h. The concentration of  $\text{NH}_4\text{OH}$  drastically affects the fraction of thiolates in the solution at the point of assembly, which necessarily affects the final structure of TPDT on GaAs. In this paper, we examine and elucidate the differences in the chemical composition and the ensemble-average orientation of these assemblies by FTIR and NEXAFS.

**FTIR.** Figure 2a contains transmission IR spectra of TPDT assemblies from EtOH on GaAs at various  $\text{NH}_4\text{OH}$  concentrations. Resonances originating from the phenyl backbone of TPDT include the in-plane, “ip” (1475 and 1001  $\text{cm}^{-1}$ ), and the out-of-plane, “op” (807  $\text{cm}^{-1}$ ), phenyl ring vibrational modes.<sup>36</sup> Additionally, a weak ip perp<sup>36</sup> ring vibration appears at 1398  $\text{cm}^{-1}$ . A feature associated with the C=O vibration<sup>36,37</sup> of the acetyl protecting groups is observed at 1707  $\text{cm}^{-1}$  in assemblies with lower  $\text{NH}_4\text{OH}$  concentrations. It is interesting to note that the thioacetyl TPDT precursor can directly adsorb on GaAs from EtOH without any prior deprotection with  $\text{NH}_4\text{OH}$ , as evident from the FTIR spectrum in Figure 2a-i. The spontaneous adsorption of the thioacetyl precursor has previously been observed on metals,<sup>14,17,38</sup> where the acetyl protecting group



**Figure 2.** Transmission IR spectra of TPDT assembled on GaAs from (a) EtOH and (b) THF with the addition of  $\text{NH}_4\text{OH}$  at (i) 0 mM, (ii) 1 mM, (iii) 10 mM, (iv) 30 mM, and (v) 160 mM.

spontaneously cleaves near the substrate, forming a sulfur-substrate bond. With an absence of thioacetyl end groups at the molecule-substrate interface, the C=O resonance (1707  $\text{cm}^{-1}$ ) we observe in Figure 2a-i must originate from thioacetyl groups located at the molecule-air interface. The intensity of the C=O vibration signal at 1707  $\text{cm}^{-1}$  decreases with increasing  $\text{NH}_4\text{OH}$  concentration, suggesting a corresponding decrease in the concentration of thioacetyl groups at the molecule-air interface. Examination of the overall intensity suggests that the surface coverage is comparable in all these assemblies. Since our UV-vis experiments indicate that both thiolate- and thioacetyl-terminated TPDT are present in the assembly solution at the point of substrate immersion, and the thiolate fraction increases with increasing  $\text{NH}_4\text{OH}$  concentration, our FTIR results suggest that both thiolate- and thioacetyl-terminated TPDT must adsorb on GaAs.

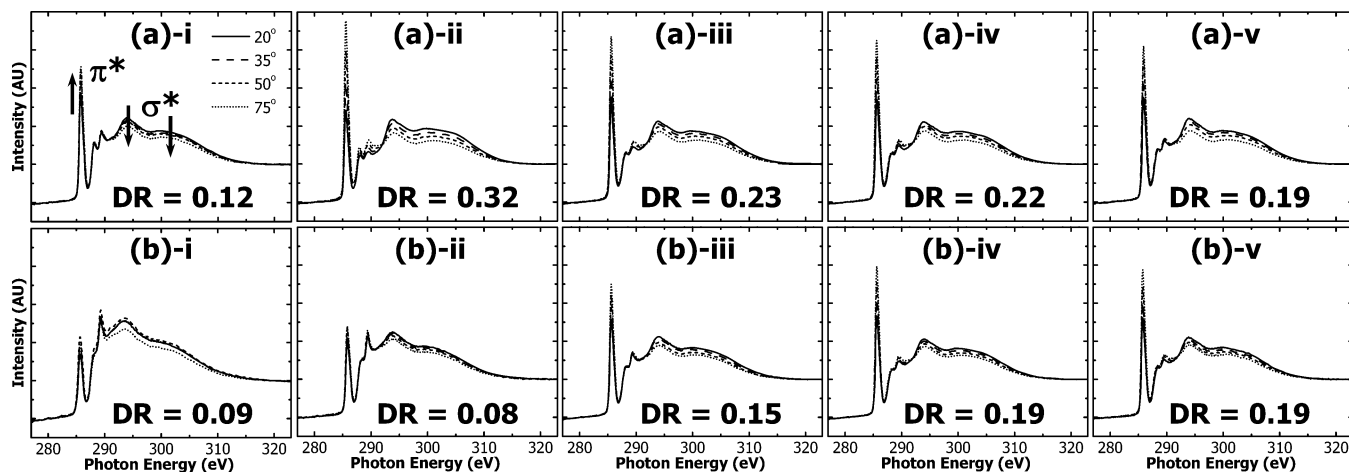
Because we carried out the transmission IR studies using s-polarized light,<sup>27</sup> the electric field vector of the incident

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**Figure 3.** C 1s angle-dependent, pre- and post-edge normalized NEXAFS spectra of TPDT assembled on GaAs from (a) EtOH and (b) THF with the addition of  $\text{NH}_4\text{OH}$  at (i) 0 mM, (ii) 1 mM, (iii) 10 mM, (iv) 30 mM, and (v) 160 mM. The dichroic ratios derived from each set of spectra are included.

irradiation is parallel to the substrate surface, providing selectivity for components of the dipole moments that are parallel to the substrate surface. We can therefore assess the average molecular orientation given the directions of the transitional dipole moments of the adsorbed molecules and the spectrum obtained from an isotropic sample.<sup>27</sup> The spectra in Figure 2a reveal variations in the intensities of the ip and op resonances, indicating that the structure of the final assemblies is strongly dependent on the  $\text{NH}_4\text{OH}$  concentration. Specifically, the phenyl ring ip bands at 1475 and 1001  $\text{cm}^{-1}$  exhibit a dipole moment in the direction parallel to the long molecular axis, while the op mode near 807  $\text{cm}^{-1}$  vibrates in the direction normal to the phenyl backbone plane. We can thus quantify the molecular orientation of TPDT assembled on GaAs by examining changes in the intensity ratios of the mutually orthogonal ip and op resonances.<sup>27</sup> To do so, we employed an orientation ratio (OR),<sup>27</sup>

$$\text{OR} = \frac{(\text{op/ip})_{\text{assembly}}}{(\text{op/ip})_{\text{powder}}} \quad (1)$$

where  $(\text{op/ip})_{\text{assembly}}$  and  $(\text{op/ip})_{\text{powder}}$  are the op/ip intensity ratios of TPDT assembled on GaAs and that of TPDT precursor powder in KBr, respectively. If the molecules are oriented upright, the op/ip intensity ratio of the assembly should be greater than that of TPDT powder. OR should thus be  $> 1$ . On the other hand, if the molecules are “lying down”, the op/ip intensity ratio of the assembly should be less than that of TPDT powder, so  $\text{OR} < 1$ . Finally, if the assembly is disordered, the op/ip intensity ratio should be comparable to that of TPDT powder, so  $\text{OR} \approx 1$ . Orientation ratios extracted from each transmission IR spectrum are included in Figure 2.

When the TPDT assembly is carried out in EtOH with 1 mM  $\text{NH}_4\text{OH}$ ,  $\text{OR} \approx 2.6$ . We observe from Figure 2a-i that the thioacetyl precursor (so in the absence of  $\text{NH}_4\text{OH}$ ) can also spontaneously adsorb from EtOH on GaAs, although its final structure is less upright ( $\text{OR} \approx 1.9$ ) compared to that of TPDT assembled from EtOH at 1 mM  $\text{NH}_4\text{OH}$  (Figure 2a-ii). Further comparison of Figures 2a-ii–v shows that OR decreases with increasing  $\text{NH}_4\text{OH}$  concentration in the assembly solution, suggesting correspondingly less upright molecular orientation. When TPDT is assembled from EtOH at the highest  $\text{NH}_4\text{OH}$  concentration (160 mM),  $\text{OR} \approx 1.6$  (Figure 2a-v). Since the thiolate fraction at the point of substrate immersion is directly related to the  $\text{NH}_4\text{OH}$  concentration in the solution, there appears to be an optimal thiolate fraction in the assembly solution that

results in a dense TPDT assembly that is most oriented. Given that the thiolate fraction is different during the assembly of these samples, it is not surprising that the final structure of the resulting assemblies have different orientation. We speculate that this observation stems from differences in the adsorptivity of thioacetyl- and thiolate-terminated molecules on GaAs. First, the chemical reactivity of thioacetyl and thiolate end groups on GaAs may be different. Not only will this difference in chemical reactivity result in differences in the overall structure of the assembly, it will likely result in differences in composition between the assembly and the solution from which the molecules adsorb. Further, the thioacetyl end group is significantly different in size compared to the thiolate end group. This end group size difference will undoubtedly impact the way the molecules arrange on GaAs.

Transmission IR spectra of TPDT on GaAs assembled from THF at various  $\text{NH}_4\text{OH}$  concentrations are shown in Figure 2b. These spectra are drastically different from those of TPDT assemblies from EtOH. Specifically, the spectra of these assemblies are significantly weaker in overall intensity, especially at lower  $\text{NH}_4\text{OH}$  concentrations. We thus infer that the surface coverage is significantly reduced in these assemblies compared to those from EtOH. When TPDT is assembled from THF without any  $\text{NH}_4\text{OH}$  (Figure 2b-i), very little adsorption occurs. This observation contrasts that of the corresponding assembly from EtOH and indicates that while thioacetyl-terminated TPDT spontaneously adsorbs on GaAs from EtOH, they do not do so from THF. Comparing the remaining spectra in Figure 2b reveals that the overall intensity increases with increasing  $\text{NH}_4\text{OH}$  concentration, indicating an increase in surface coverage. Concomitantly, the OR extracted from the spectra increases to  $\text{OR} \approx 1.5$  at 160 mM  $\text{NH}_4\text{OH}$  (Figure 2b-v). Unlike adsorption from EtOH, our IR experiments suggest that only thiolate-terminated TPDT adsorbs significantly on GaAs when the assembly is carried out in THF. We thus have to assemble TPDT at high  $\text{NH}_4\text{OH}$  concentrations in THF to obtain decent surface coverage. These assemblies, however, are never as ordered as TPDT on GaAs assembled from EtOH.

**NEXAFS.** We carried out NEXAFS experiments on the TPDT assemblies from EtOH and THF. Figure 3a contains pre- and post-edge normalized angle-dependent NEXAFS spectra of TPDT assembled from EtOH at various  $\text{NH}_4\text{OH}$  concentrations. The major spectral features are identified in Figure 3a-i; a pronounced resonance at 285.5 eV is attributed to the  $\text{C } 1s \rightarrow \pi^*_{\text{C}=\text{C}}$  transition<sup>39</sup> in TPDT; broad resonances at 293 and 303 eV are attributed to

the C 1s  $\rightarrow \sigma_1^*$  and  $\sigma_2^*$  transitions,<sup>39</sup> respectively; the features at 287.4 and 288.8 eV are assigned to the R\*/C–S\* and the  $\pi_2^*$  transitions.<sup>39</sup>

To elucidate the structural difference between the different assemblies of TPDT, we examined the angular dependence of the NEXAFS spectra. We can quantify the ensemble-average molecular orientation of TPDT using dichroic ratio (DR),<sup>40</sup>

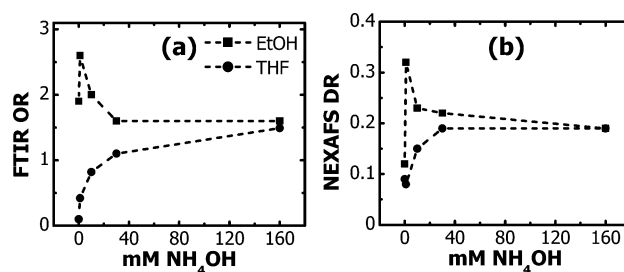
$$DR = \frac{I(75^\circ) - I(20^\circ)}{I(75^\circ) + I(20^\circ)} \quad (2)$$

where  $I(\theta)$  represents the integrated intensity of the  $\pi_1^*$  resonance at 285.5 eV obtained at an X-ray incidence angle of  $\theta$  with respect to the substrate surface. DR is a measure of the level of anisotropy in the molecular assembly. According to the NEXAFS dipole selection rules,<sup>20,40</sup> DR > 0 indicates an ensemble-average molecular orientation that is preferentially upright, while DR < 0 indicates a preferentially “lying down” ensemble-average molecular orientation. Correspondingly, DR  $\approx$  0 indicates the absence of any preferential orientation. Dichroic ratios derived from each set of NEXAFS spectra are included in Figure 3.

When TPDT is assembled from EtOH, we observe a maximum DR = 0.32 when the assembly is carried out with 1 mM of NH<sub>4</sub>OH (Figure 3a-ii). As a point of reference, a DR of 0.32 corresponds to TPDT assemblies with an ensemble-average backbone tilt of  $27 \pm 3^\circ$  away from the substrate normal<sup>41,42</sup> and compares well with the most oriented TPDT assembly in the literature.<sup>20</sup> Consistent with what was observed by FTIR, the thioacetyl TPDT precursor spontaneously adsorbs from EtOH on GaAs (Figure 3a-i), although its final assembly structure is less upright (DR = 0.12) compared to that of TPDT on GaAs assembled from EtOH with 1 mM NH<sub>4</sub>OH (DR = 0.32; Figure 3a-ii). Further comparison of Figures 3a-ii–v shows that DR decreases with increasing NH<sub>4</sub>OH concentration, with DR = 0.19 at 160 mM NH<sub>4</sub>OH (Figure 3a-v). These observations are, again, consistent with the FTIR results shown in Figure 2a.

Figure 3b contains pre- and post-edge normalized NEXAFS spectra acquired at varying X-ray incident angles for assemblies of TPDT from THF as a function of NH<sub>4</sub>OH concentration. From Figure 3b-i, we observe that the integrated  $\pi^*$  intensity, a measure of surface coverage,<sup>20</sup> is low, indicating negligible adsorption of the thioacetyl TPDT precursor from THF. That TPDT does not adsorb significantly from THF was also observed by FTIR. Further comparison of the data sets in Figures 3b-ii–v reveals that the integrated  $\pi^*$  intensity increases with increasing NH<sub>4</sub>OH concentrations, suggesting an increase in the surface coverage. Consistent with IR data, we also observe a moderate increase in DR to DR = 0.19 at 160 mM NH<sub>4</sub>OH (Figure 3b-v), suggesting improved surface organization. A DR of 0.19 corresponds to TPDT assemblies with an ensemble-average backbone tilt of  $34 \pm 3^\circ$  away from the substrate normal. A summary of the ORs and DRs extracted from the FTIR and NEXAFS spectra, respectively, at various NH<sub>4</sub>OH concentrations is presented in Figure 4.

It is interesting to note that thioacetyl precursors of conjugated molecules have been reported to adsorb on gold from both EtOH and THF.<sup>14,17,38</sup> This phenomenon, however, is not the case on GaAs. Rather, we observe that thioacetyl precursors only adsorb



**Figure 4.** Orientation parameters and dichroic ratios from (a) IR and (b) NEXAFS spectra, respectively, for TPDT assembled on GaAs from EtOH and THF as a function of NH<sub>4</sub>OH concentration.

on GaAs when the assembly is carried out in EtOH. Two possible reasons can account for this difference in the adsorption behavior of thioacetyl-terminated TPDT. First, it is known that the affinity of sulfur to gold is very strong, with thiolate exothermic adsorption (0.3–0.5 eV)<sup>43,44</sup> on gold resulting in a covalent sulfur–gold bond of  $\sim 1.3$  eV.<sup>3,45</sup> In contrast, the sulfur–GaAs bond is a weaker semi-ionic interaction of  $\sim 0.81$  eV.<sup>45</sup> Given the weaker molecule–substrate interaction, any solvent effect would be more pronounced on GaAs than on gold. Second, the differences in the tendency for molecules to adsorb from EtOH and THF may be explained on the basis of solvent quality. Specifically, in the case of GaAs, protons are thought to heavily participate in sulfur passivation reactions<sup>46–49</sup> by accelerating electron transfer at the semiconductor/solution interface, and increased proton concentration in polar amphiprotic solvents (water and alcohols) has been shown to result in faster and more effective sulfur passivation of GaAs.<sup>50</sup> The use of apolar, aprotic solvents, such as THF, on the other hand, can result in weaker sulfur–substrate interaction at the GaAs/solvent interface, leading to reduced adsorption.

## Conclusions

We report the effects of NH<sub>4</sub>OH concentration on the final structure of TPDT assembled from EtOH and THF on GaAs. The final structure of TPDT on GaAs is sensitive not only to the solvent quality but also to NH<sub>4</sub>OH concentration used during assembly. Specifically, TPDT assemblies carried out in EtOH at low (1 mM) NH<sub>4</sub>OH concentrations are characterized by a generally upright average molecular orientation. These assemblies become less upright when increased NH<sub>4</sub>OH concentrations are used. TPDT assemblies carried out in THF at low NH<sub>4</sub>OH concentrations exhibit negligible surface coverage, in contrast to the corresponding assemblies from EtOH. The surface coverage and structural organization of TPDT assemblies from THF improve with increasing NH<sub>4</sub>OH concentrations. We relate the differences in TPDT adsorption behavior to thiolate fraction in the assembly solution at the point of substrate immersion. Our results demonstrate that the structure of TPDT assemblies on GaAs is extremely sensitive to the assembly conditions. It is therefore essential to select not only the proper assembly solvent but also the proper concentration of the deprotecting agent to achieve assemblies of desired quality.

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