

High-Sensitivity Transmission IR Spectroscopy for the Chemical Identification and Structural Analysis of Conjugated Molecules on Gallium Arsenide Surfaces

Dmitry A. Krapchetov,[†] Hong Ma,[‡] Alex K. Y. Jen,[‡] Daniel A. Fischer,[§] and Yueh-Lin Loo^{*,†}

Chemical Engineering Department and Center for Nano- and Molecular Science and Technology, University of Texas at Austin, Austin, Texas 78712, Materials Science and Engineering Department, University of Washington, Seattle, Washington 98195, and Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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We demonstrate the use of high-sensitivity, off-normal transmission IR spectroscopy with s-polarized light to probe the chemical identity and orientation of quaterphenyldithiol (QPDT) molecular assemblies on GaAs as a function of ammonium hydroxide (NH₄OH) concentration. NH₄OH is added to the assembly solution to convert the thioacetyl groups on the QPDT precursor to thiolates. When assembled at high NH₄OH concentrations, the acetyl groups are completely removed, and QPDT is disordered on GaAs. Assembly at low NH₄OH concentrations, however, results in QPDT assemblies that are preferentially upright. The molecular orientation is further quantified with near-edge X-ray absorption fine structure spectroscopy.

Introduction

Organic thin films, especially conjugated molecular assemblies, have attracted considerable attention as candidates for electrically active components in nanoscale electronic devices. Indeed, this field has seen significant progress; single-molecule nanojunctions¹, nanopores,² and soft-contact³ nanoscale devices have been demonstrated recently. Whereas the device front has seen major advances, the organization of molecules, which is central to device performance,^{4,5} remains poorly understood.

To elucidate the structure of molecular assemblies, high-sensitivity spectroscopic techniques, such as Fourier transform infrared (FTIR) spectroscopy,⁶ Raman spectroscopy,^{7,8} sum frequency generation (SFG) spectroscopy,^{9,10} and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy,^{11,12} have been used. For example, reflection–absorption infrared spectroscopy (RAIRS) has been used to identify the chemical composition and structure of molecular assemblies on metals.^{6,13,14} Much of

the recent focus, however, has been on molecular assemblies on semiconductors, such as thiols on GaAs,^{15–17} or silanes on Si.^{18,19} Because semiconductors are transparent to IR, RAIRS often leads to spectra with low signal-to-noise ratios, even when a heavily doped semiconductor is used.²⁰ Attenuated total reflectance (ATR) IR^{21,22} and off-normal transmission IR^{17,19} with p-polarized light have been demonstrated for probing molecular assemblies on semiconductors. The execution of these experiments, however, is technically challenging. Specifically, ATR experiments are frequently complicated by crystal surface contamination²¹ and the need for precisely beveled semiconductor substrates to guide light,²² whereas transmission IR with p-polarized light requires complex spectral simulations for structural analysis.¹⁷

In this letter, we demonstrate the first use of off-normal transmission IR with s-polarized light for probing the chemical identity and the structure of quaterphenyldithiol (QPDT) adsorbed on GaAs. NEXAFS provided additional quantification of the ensemble-average molecular orientation. QPDT can be structurally disordered or laterally organized on GaAs depending on the assembly conditions. This transmission IR approach is applicable to a wide range of conjugated adsorbates, including *n*-phenyl, *n*-phenyldimethyl²³ and oligo(phenylene-ethyne)¹⁰ on semiconductors, because the IR dipole selection rules for these systems are analogous.

Experimental Section

Monolayer Formation. The assembly of QPDT was carried out according to previously published procedures.¹⁵ In brief, the acetyl-

- * Corresponding author. E-mail: lloo@che.utexas.edu.
[†] University of Texas at Austin.
[‡] University of Washington.
[§] National Institute of Standards and Technology.
 (1) Liang, W.; Shores, M. P.; Bockrath, M.; Long, J. R.; Park, H. *Nature* **2002**, *417*, 725.
 (2) James, D. K.; Tour, J. M. *Chem. Mater.* **2004**, *16*, 4423.
 (3) Tran, E.; Rampi, M. A.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3835.
 (4) Ishida, T.; Mizutani, W.; Liang, T.-T.; Azehara, H.; Miyake, K.; Sasaki, S.; Tokumoto, H. *Ann. N. Y. Acad. Sci.* **2003**, *1006*, 164.
 (5) Seitz, O.; Boecking, T.; Salomon, A.; Gooding, J. J.; Cahen, D. *Langmuir* **2006**, *22*, 6915.
 (6) Tolstoy, V. P.; Chernyshova, I. V.; Skryshevsky, V. A. *Handbook of Infrared Spectroscopy of Ultrathin Films*; John Wiley & Sons: New York, 2003.
 (7) Chu, H.; Yang, H.; Huan, S.; Shen, G.; Yu, R. *J. Phys. Chem. B* **2006**, *110*, 5490.
 (8) Wang, Y.; Chen, H.; Dong, S.; Wang, E. *J. Chem. Phys.* **2006**, *124*, 074709/1.
 (9) Noguchi, H.; Ito, M.; Uosaki, K. *Chem. Lett.* **2005**, *34*, 950.
 (10) Richter, L. J.; Yang, C. S. C.; Wilson, P. T.; Hacker, C. A.; Van Zee, R. D.; Stapleton, J. J.; Allara, D. L.; Yao, Y.; Tour, J. M. *J. Phys. Chem. B* **2004**, *108*, 12547.
 (11) Stohr, J.; Outka, D. A. *Phys. Rev. B* **1987**, *36*, 7891.
 (12) Stohr, J. *NEXAFS Spectroscopy*; Springer: Berlin, 1992.
 (13) de Boer, B.; Meng, H.; Perepichka, D. F.; Zheng, J.; Frank, M. M.; Chabal, Y. J.; Bao, Z. *Langmuir* **2003**, *19*, 4272.
 (14) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927.

- (15) Krapchetov, D. A.; Ma, H.; Jen, A. K. Y.; Fischer, D. A.; Loo, Y.-L. *Langmuir* **2005**, *21*, 5887.
 (16) Shaporenko, A.; Adlkofer, K.; Johansson, L. S. O.; Ulman, A.; Grunze, M.; Tanaka, M.; Zharnikov, M. *J. Phys. Chem. B* **2004**, *108*, 17964.
 (17) Sheen, C. W.; Shi, J. X.; Maartensson, J.; Parikh, A. N.; Allara, D. L. *J. Am. Chem. Soc.* **1992**, *114*, 1514.
 (18) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
 (19) Maoz, R.; Sagiv, J.; Degenhardt, D.; Moehwald, H.; Quint, P. *Supramol. Sci.* **1995**, *2*, 9.
 (20) Brunner, H.; Mayer, U.; Hoffmann, H. *Appl. Spectrosc.* **1997**, *51*, 209.
 (21) Ding, X.; Moumanis, K.; Dubowski, J. J.; Tay, L.; Rowell, N. L. *J. Appl. Phys.* **2006**, *99*, 054701/1.
 (22) Baum, T.; Ye, S.; Uosaki, K. *Langmuir* **1999**, *15*, 8577.
 (23) Tai, Y.; Shaporenko, A.; Rong, H. T.; Buck, M.; Eck, W.; Grunze, M.; Zharnikov, M. *J. Phys. Chem. B* **2004**, *108*, 16806.

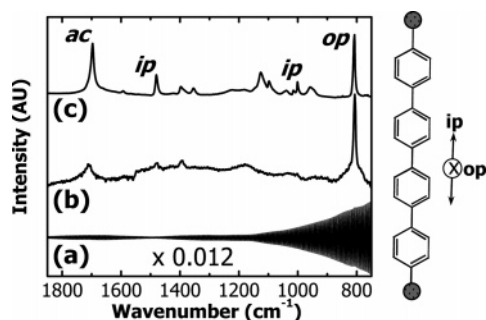


Figure 1. Background-corrected transmission IR spectra of QPDT-10 acquired at $\theta = 45^\circ$ with s-polarized light (a) before and (b) after smoothing. (c) Transmission IR spectrum of the precursor of QPDT dispersed in KBr. The major in-plane (ip), out-of-plane (op), and acetyl (ac) vibrations are labeled. The directions of the vibrations associated with the phenyl backbone are illustrated in the schematic on the right.

protected precursor of QPDT¹⁵ was first dissolved in a cosolvent of ethanol and tetrahydrofuran (3:1 v/v) at 50 μM . Ammonium hydroxide, at either 10 or 160 mM, was then added to the solution to convert the thioacetyl endgroups on the QPDT precursor to thiolates before freshly etched GaAs substrates were submerged for assembly an hour later. We shall refer to the two samples as QPDT-10 and QPDT-160, respectively. Sample preparation took place in a nitrogen glovebox (<0.1 ppm H₂O, <0.1 ppm O₂) over the course of 20–24 h. To etch GaAs, the substrates were soaked in concentrated hydrochloric acid for 1 min, rinsed with deionized water, and dried in a stream of nitrogen.

FTIR. Transmission IR data were acquired with 2 cm^{-1} resolution for 1000 scans using a dry-air-purged Nicolet Magna-IR 860 spectrometer equipped with a liquid-nitrogen-cooled MCT detector. s- and p-polarized light at angle of incidence θ with respect to the substrate normal were used. This was accomplished experimentally by twisting the sample so that the substrate normal is θ away from the incident irradiation. Undoped, double-side-polished (100) GaAs wafers from AXT were used as substrates. For all transmission IR studies, we used sulfur-passivated GaAs as the background. Sulfur-passivated GaAs specimens were prepared by first etching the substrates in concentrated hydrochloric acid for 1 min, rinsing in deionized water, and then immediately immersing the etched substrates in a solution of ammonium sulfide in water (20% v/v, Aldrich) for 10 min.²⁴ This procedure results in a stable overlayer of sulfur that prevents surface oxidation and reduces hydrocarbon adsorption.²⁴ The background-corrected spectra were smoothed using conventional 12-point fast Fourier transform (FFT) smoothing²⁵ in Origin commercial software to remove periodic interference.^{6,19} (See Figure 1a,b for representative spectra before and after smoothing.) A multipoint baseline correction was applied in GRAMS/AI commercial software to all spectra. The transmission 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. A transmission IR spectrum of the powder of the acetyl-protected precursor of QPDT dispersed in KBr (1:150 mg) was also acquired for comparison.

NEXAFS. NEXAFS experiments were carried out on beamline U7A at the National Synchrotron Light Source at Brookhaven National Laboratories.²⁶ A detailed description of the setup can be found elsewhere.¹⁵ Carbon-edge NEXAFS spectra were collected at angles of incidence ranging from 20 (grazing) to 75° (near-normal). The angle-dependent NEXAFS data were analyzed according to the building block (BB) model^{27,28} to quantify the ensemble-average molecular orientation of the assemblies. The π^* resonance at

285 eV, the most intense spectral feature, was used for quantitative analysis of the molecular orientation.¹⁵

Results and Discussion

Figure 1a contains a background-corrected transmission IR spectrum of QPDT-10 acquired at an IR angle of incidence of $\theta = 45^\circ$ away from the substrate normal with s-polarized light. The interference fringes that result from the back-reflection of the double-side-polished GaAs wafer are periodic⁶ and therefore can be easily removed by Fourier smoothing²⁵ to yield the spectrum in Figure 1b. The resulting spectrum is consistent with that of the acetyl-protected precursor of QPDT dispersed in KBr, shown in Figure 1c. Specifically, we observe resonances associated with the phenyl backbone of QPDT, including the in-plane (ip par; 1475 and 1001 cm^{-1}) and out-of-plane (op; 807 cm^{-1}) phenyl ring vibrational modes.¹³ The resonances at 1706 and 1353 cm^{-1} are associated with C=O and CH₃-CO vibrations^{13,29} of the acetyl protecting group, respectively (the removal of acetyl groups is incomplete during assembly).¹⁵ Additionally, a weak ip perp¹³ ring vibration appears at 1398 cm^{-1} . In addition to chemical identification, we are able to infer the molecular orientation of QPDT with transmission IR. The features that provide insight into the molecular orientation are the strong ip ring vibration (1475 cm^{-1}), with a dipole moment along the molecular axis, and the strong op ring vibration (807 cm^{-1}), with a dipole moment perpendicular to the molecular axis and out of the phenyl ring plane. We used s-polarized, rather than p-polarized, light for the examination of molecular orientation because s-polarized light is selective for components of the dipole moment that are parallel to the substrate. As a result, an unambiguous selection rule for the phenyl backbone with respect to the substrate can be defined. In contrast, p-polarized light is selective for a mixture of dipole moments depending on the angle of incidence of the irradiation; the determination of orientation with transmission IR spectra obtained using p-polarized light thus requires rigorous spectral simulations.¹⁷

The presence of a unique dipole selection rule in experiments with s-polarized light is best illustrated in Figure 2a where a molecular assembly with an azimuthally averaged backbone tilt, ρ , away from the substrate normal can be represented by an orientation cone. This orientation cone can be characterized by a dipole moment coordinate system in which the z axis is oriented along the symmetry axis. The electric field vectors for s- and p-polarized light are also illustrated in Figure 2a. For a QPDT assembly on GaAs that is positioned with its substrate normal parallel to the IR incidence (as sketched in Figure 2b), the ip vibrations of QPDT (1475 and 1001 cm^{-1}) are characterized by dipole moments along the z axis, whereas the op vibration (807 cm^{-1}) is characterized by a dipole moment along the x or y axis. For a specific vibrational mode to absorb energy, the dipole moment of that particular bond must be collinear with the electric field vector of the incident polarized light. The op vibration with a dipole moment along the y axis absorbs s-polarized light and maintains a constant sampling cross section independent of θ (Figure 2b,c). For a given sample, the intensity of the op vibration is thus constant. Accordingly, the ip intensity is also independent of θ when the experiment is carried out with s-polarized light. It follows that an examination of the op/ip ratio, which is independent of θ in experiments with s-polarized light, should provide an indication of the orientation of the molecular assembly.

(24) Lebedev, M. V.; Mayer, T.; Jaegermann, W. *Surf. Sci.* **2003**, *547*, 171.

(25) Cranston S. D.; Ombao, H. C.; von Sachs, R.; Guo, W.; Litt, B. *IEEE Trans. Biomed. Eng.* **2002**, *49*, 988.

(26) For detailed information on the NIST/Dow Soft X-Ray Materials Characterization Facility at NSLS BNL, see <http://www.nsls.bnl.gov/newsroom/publications/newsletters/1996/96-nov.pdf>.

(27) Kinzler, M.; Schertel, A.; Haehner, G.; Woell, C.; Grunze, M.; Albrecht, H.; Holzhueter, G.; Gerber, T. *J. Chem. Phys.* **1994**, *100*, 7722.

(28) Outka, D. A.; Stoehr, J.; Rabe, J. P.; Swalen, J. D. *J. Chem. Phys.* **1988**, *88*, 4076.

(29) Niklewski, A.; Azzam, W.; Strunskus, T.; Fischer, R. A.; Woell, C. *Langmuir* **2004**, *20*, 8620.

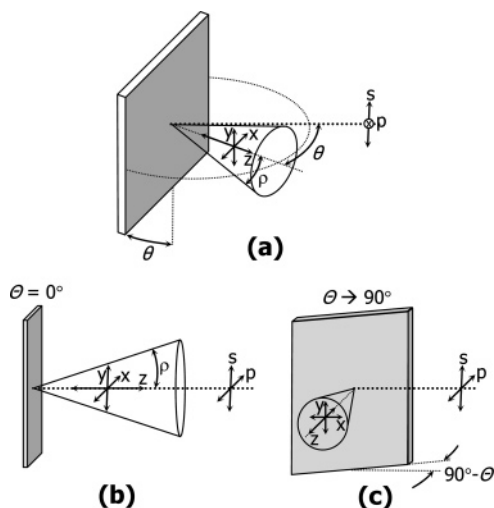


Figure 2. (a) Schematic of the transmission IR setup with the substrate twisted θ relative to the IR incidence. The orientation cone of a molecule tilted ρ away from the substrate normal with its corresponding dipole coordinate system is included. (b) Experimental setup at $\theta = 0^\circ$. (c) Experimental setup as $\theta \rightarrow 90^\circ$.

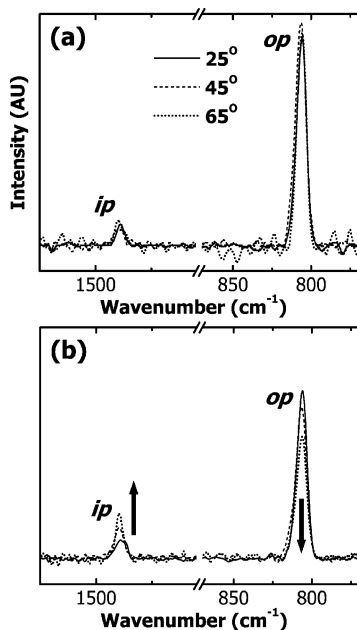


Figure 3. Transmission IR spectra of QPDT-10 acquired at various angles of incidence using (a) s- and (b) p-polarized light.

Experiments with p-polarized light, however, are dramatically different. When $\theta = 0^\circ$ (Figure 2b), the op vibration with a dipole moment along the x axis has the largest sampling cross section for p-polarized light. This sampling cross section, however, decreases as the specimen is twisted away from the IR incidence (increasing θ). When $\theta \rightarrow 90^\circ$ (Figure 2c), the ip vibration with a dipole moment along the z axis has the largest sampling cross section for p-polarized light. This sampling cross section in turn decreases with decreasing θ . As a consequence, op/ip from experiments with p-polarized light reflects not only the molecular orientation but also changes in the sampling cross sections of the two dipole moments. As such, the op/ip ratio varies with the IR angle of incidence. Figure 3 contains transmission IR spectra of QPDT-10 acquired with (a) s- and (b) p-polarized light at $\theta = 25^\circ, 45^\circ,$ and 65° . As expected, the op/ip ratio remains constant with θ when s-polarized light is used. With p-polarized light, however, the op/ip ratio varies dramatically with θ (Figure 3b). Given the differences in the experimental setup, we are able to

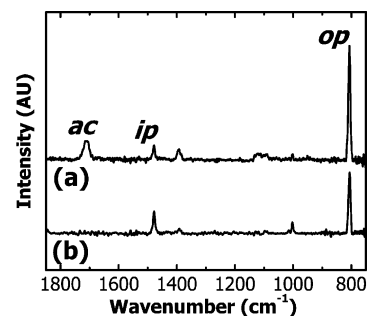


Figure 4. Transmission IR spectra of (a) QPDT-10 and (b) QPDT-160. The spectra were collected using s-polarized light at $\theta = 30^\circ$.

infer the orientation of the molecular assembly directly from data acquired with s-polarized light, whereas orientation analysis with p-polarized light requires additional spectral simulations to decouple the orientation contribution from changes in the sampling cross section in the signal.

Figure 4 contains background-corrected and baseline-corrected IR spectra of QPDT-10 and QPDT-160 collected with s-polarized light at $\theta = 30^\circ$.³⁰ To examine the orientation of the two samples, we employed an orientation ratio, or OR,

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

where $(\text{op/ip})_{\text{assembly}}$ and $(\text{op/ip})_{\text{powder}}$ are the op/ip ratios for the molecular assembly of QPDT on GaAs and the powder of the QPDT precursor, respectively. OR thus effectively compares the orientation of the molecular assembly on GaAs to that of the isotropic powder of the QPDT precursor. Given the dipole selection rules established for s-polarized light above, $\text{OR} > 1$ indicates that the molecular assembly is preferentially upright, and $\text{OR} < 1$ indicates that the molecules within the molecular assembly are “lying down”. Accordingly, $\text{OR} \sim 1$ indicates that the molecular assembly does not exhibit any preferential orientation. Comparing the two spectra in Figure 4 reveals dramatic differences between QPDT-10 and QPDT-160. Although the resonance associated with the acetyl protecting groups at 1706 cm^{-1} is present in the QPDT-10 spectrum, it is completely absent in the QPDT-160 spectrum, indicating that the thioacetyl groups have been completely converted to thiolates in the presence of 160 mM NH_4OH . More importantly, we observe that the relative intensities of op and ip ring vibrations are markedly different in the two spectra. In Figure 4a, the op ring vibration is significantly stronger than the ip ring vibration; the comparison of the op/ip ratio to that of the isotropic QPDT powder indicates an $\text{OR} \gg 1$. QPDT-10 is thus preferentially oriented upright. OR for QPDT-160 in Figure 4b is ~ 1 . This comparison suggests that the orientation of QPDT-160 is not significantly different from that of the isotropic powder of the QPDT precursor (Figure 1c) and implies that QPDT-160 is disordered. That the structure of QPDT on GaAs is highly dependent on the details of assembly is not surprising. Previously, we reported a strong solvent dependence of the assembly process¹⁵ where QPDT assembled from an ethanol-rich solution is preferentially upright with a backbone tilt, ρ , of 28° from the substrate normal and QPDT assembled from tetrahydrofuran, a solvent commonly used for assembling conjugated molecules on gold^{13,23} and GaAs,^{31,32} is disordered.

(30) We empirically found $\theta = 30^\circ$ to be the optimal angle for these experiments because the exact position of the specimen depends on a balance between increasing interference at lower θ and decreasing substrate transmissivity at higher θ .

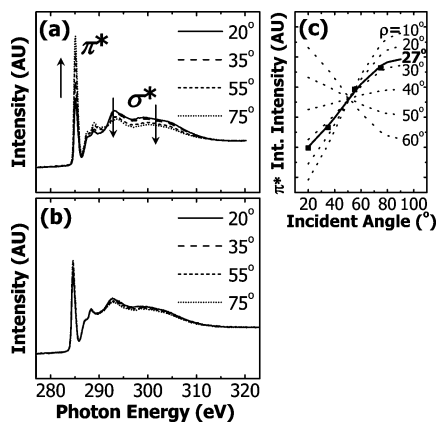


Figure 5. C 1s pre- and post-edge normalized NEXAFS spectra of (a) QPDT-10 and (b) QPDT-160 as a function of the X-ray angle of incidence. (c) Integrated π^* intensities as a function of the angle of incidence for QPDT-10 and the corresponding theoretical fits to obtain the average molecular tilt, ρ , away from the substrate normal.

To quantify the ensemble-average molecular orientation of QPDT-10 and QPDT-160 further, we carried out NEXAFS experiments on beamline U7A at the National Synchrotron Light Source at Brookhaven National Laboratories. The pre- and post-edge normalized spectra obtained at the C edge for QPDT-10 and QPDT-160 as a function of the X-ray angle of incidence are shown in Figure 5. The spectral features are identified in Figure 5a; we observe that the π^* resonance at 285 eV grows while the σ^* resonances (at 293 and 303 eV) diminish with increasing

X-ray angles of incidence. This phenomenon, commonly known as dichroism, indicates that QPDT-10 is preferentially oriented.^{12,15} The NEXAFS spectra for QPDT-160 at varying angles of incidence are shown in Figure 5b. The spectra show very little angular dependence and, consistent with the IR results presented in Figure 4b, suggest a disordered molecular assembly. To quantify the ensemble-average molecular tilt of QPDT-10, we plotted the integrated π^* intensity as a function of the angle of incidence in Figure 5c. Fitting the data in Figure 5c to the BB model^{27,28} yields an average backbone tilt of $\rho = 27 \pm 3^\circ$ from the substrate normal.

Conclusions

The development of high-sensitivity transmission IR has provided us a routine, in-house means of characterizing conjugated molecular assemblies on GaAs. In addition to chemical identification, transmission IR with s-polarized light provided insight into the molecular orientation. The quality of the final assembly is sensitive not only to the assembly solvent¹⁵ but also to the amount of ammonium hydroxide added to convert the thioacetyl end groups to thiolates. Because the organization of molecules can dramatically impact charge transport,^{4,5,33} the ability to elucidate the molecular structure prior to nanoscale device fabrication and characterization is crucial. The transmission IR experiments described above provide a straightforward and convenient means of doing so.

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(31) Allara, D. L.; Dunbar, T. D.; Weiss, P. S.; Bumm, L. A.; Cygan, M. T.; Tour, J. M.; Reinert, W. A.; Yao, Y.; Kozaki, M.; Jones, L., II. *Ann. N. Y. Acad. Sci.* **1998**, *852*, 349.

(32) Jiang, W.; Zhitenev, N.; Bao, Z.; Meng, H.; Abusch-Magder, D.; Tennant, D.; Garfunkel, E. *Langmuir* **2005**, *21*, 8751.

(33) Kim, Y.-H.; Jang, S. S.; Goddard, W. A., III. *J. Chem. Phys.* **2005**, *122*, 244703/1.