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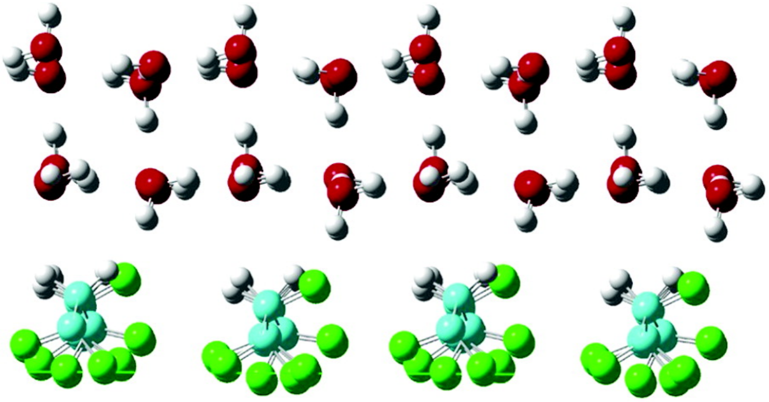

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Crystalline Ice Grown on the Surface of the Ferroelectric Polymer Poly(vinylidene fluoride) (70%) and Trifluoroethylene (30%)

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Abstract: Water ice is observed to order at the copolymer ferroelectric poly(vinylidene difluoride−trifluoroethylene) surface. The successful growth of crystalline thin films of water on these polymer surfaces implicates water to polymer dipole interactions. These ice thin films are sufficiently ordered for experimental identification of the wave vector dependence in the electronic band structure of hexagonal ice. The significant band dispersion, of about 1 eV, suggests strong overlap of molecular orbitals between adjacent water molecules in the ice film. The presence of dipole interactions with adsorbate water is consistent with the possibility of water acting as a spectator to surface ferroelectric transitions in this system.

Introduction

Because of biomedical and polymer electronic devices, studies of adsorbates (in particular water) on polymer surfaces are of considerable interest but are presently quite limited. Detailed studies of adsorbate chemistry on polymer surfaces have proven to be difficult to undertake because of the complexities associated with the ordering of polymer surfaces. Through technical advances in making crystalline polymers, this situation is changing.

Recent studies indicate profound effects on the dielectric properties of the Teflon-like crystalline copolymer poly(vinylidene difluoride) with 30% trifluoroethylene, P(VDF-TrFE 70:30) with the absorption of water.[1] These studies suggest that the dipole of water exhibits a “spectator” behavior[1] to the ferroelectric transition at the surface of P(VDF-TrFE 70:30).[2] Ice and water layer films on such polymers can be perturbed by interactions at the interface with the ferroelectric polymer, particularly if there is an order imposed on water molecules by the polymer surface dipoles.

The electronic structure of ice, while historically of considerable interest,[3−7] has been difficult to study by the standard electron spectroscopies.[7,8] The electronic dispersion (band structure) in ice crystals has been difficult to obtain experimentally because of the absence of periodicity in almost all ice samples making the experimental application of Bloch’s theorem impossible.[7] The success of such measurements depends on the ability to grow a water ice single crystal at a particular surface. While water will adsorb and order for the first layer or two, such as on the surface of NaCl(100),[9] multilayers are typically polycrystalline.[7,9] Theory suggests that it may be possible to grown ordered ice layers, say on the surface of MgO,[10−12] but success has been elusive. In this paper, we present evidence of preferential water molecule ordering and band dispersion for crystalline multilayer thin films of ice, grown at the surface of the well-known ferroelectric copolymer P(VDF-TrFE 70:30) of poly(vinylidene difluoride) (70%) and trifluoroethylene (30%).

Experimental Section

Ultrathin ferroelectric thin films of copolymer 70% poly(vinylidene difluoride) with 30% trifluoroethylene, P(VDF-TrFE 70:30) were fabricated by Langmuir−Blodgett (LB) deposition technique on graphite substrates from the water subphase, which can produce films with

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thickness ranging from 1 monolayer (1 ML, 0.5 nm) to over 500 ML.[2,13] The ice single-crystal films were grown on the polymer surface with a polymer film thickness of 25 Å. The polymer substrate samples 3 and 5 molecular layers thick were prepared in ultrahigh vacuum by annealing at 110 °C, which has proved to be an effective recipe in prior studies.[1,14−20] The sample was cooled by means of a liquid nitrogen-cooled cryostat in ultrahigh vacuum to temperatures of 120−135 K, and its temperature was determined by use of a calibrated chromel−alumel thermocouple.

Angle-resolved photoemission spectroscopy (ARPES) and ultraviolet photoemission spectroscopy (UPS) were undertaken by synchrotron radiation with a 3 m toroidal grating monochromator at the Center for Advanced Microstructure and Devices in Baton Rouge, LA. Electron binding energies were measured with a hemispherical electron analyzer with an angular acceptance of ±1°. Due to the polarized nature of synchrotron radiation, the light polarization photoemission was undertaken by changing the light incident angle, with respect to the surface normal, to obtain photoemission with the vector potential more along the surface normal, that is, p (75° incidence), and more in the plane of the film, that is, s + p (43°) polarized light, while the photoelectrons were collected along the surface normal throughout, preserving the highest point group symmetry.

Theoretical Approaches. For the ice crystal calculations, we applied a plane-wave-based density functional theory (DFT) method within the Perdew−Burke−Ernzerhof (PBE) generalized gradient approximation,[21] which was implemented in the CASTEP computer code (Accelrys Inc. San Diego, CA).[22] The wave functions were expanded in terms of a plane-wave basis set with a kinetic energy cutoff of 300 eV, which with adopted ultra soft pseudopotentials[23] provided good convergence of calculated total energies and atomic forces. The supercell was taken with the dimension 7.544 Å × 10.481 Å × 20.000 Å. The polymer substrate was put on the $x-y$ plane. The semiempirical (with a PM3 parameter set) theoretical calculations of the water ice on PVDF-TrFE were done with the HyperChem package.[15]

Results and Discussion

Water interaction with the crystalline copolymer P(VDF-TrFE 70:30) is largely characterized by an absorbed water phase (water absorbed in the bulk of the polymer film) and ice grown on the surface of the polymer at low temperatures,[14−15] with a transitional water species between ice and absorbed water expected.[15] The different interactions of with P(VDF-TrFE 70:30) result in two thermal desorption features (as shown in Figure 1a), with water desorbing at roughly 160 K, characteristic of ice,[8,14−15,24,25] and desorption of water above room temperature, characteristic an absorbed water phase.[14,15] Only when there is sufficient absorbed water in the near surface region of the PVDF-TrFE copolymer will an ice layer form on the surface of the polymer film.

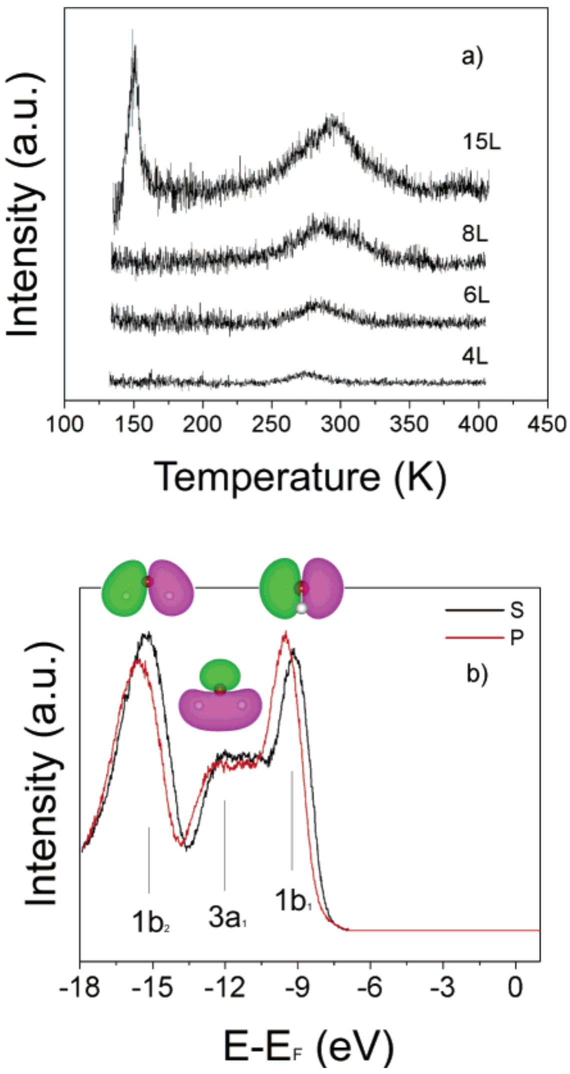

Figure 1. (a) Thermal desorption spectra of water from a thin film of P(VDF-TrFE 70:30) at different water exposures (4−15 L). (b) UPS of ice on the ferroelectric polymer as a function of S (black) and P (red) polarized light.

Preferential Orientation of Water Ice Molecules on P(VDF-TrFE). A thin film of water ice about 50 Å thick, grown at the surface of the P(VDF-TrFE) copolymer, does exhibit a preferential order. The photoemission of the 50 Å thick ice film exhibits three features resulting from the expected occupied molecular orbitals of water: $1b_1$, $3a_1$, and $1b_2$ at binding energies of −9.2, −12, and −15.3 eV, respectively, as seen in Figure 1b. This is consistent with other photoemission studies of adsorbed water and ice.[5,6,9,24,25] We observe that the photoemission spectra of an ice layer this thick contain no contributions from PVDF-TrFE copolymer.[16−18] Semiempirical calculations place the highest occupied $1b_1$ molecular orbital (HOMO) at −9.21 eV, with the $3a_1$ and $1b_2$ molecular orbitals at slightly greater binding energies than observed at −14.56 to 14.85 eV and 17.1 to 17.5 eV, respectively.

The sensitivity of photoemission features induced by specific molecular orbitals to the polarization of the plane-polarized

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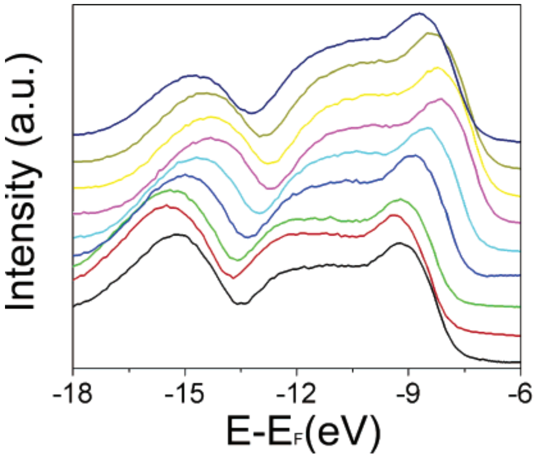

Figure 2. Energy-dependent photoemission spectra of multilayer ice, grown on a thin film of P(VDF-TrFE 70:30), showing evidence of band dispersion. The photoelectrons were collected along the surface normal.

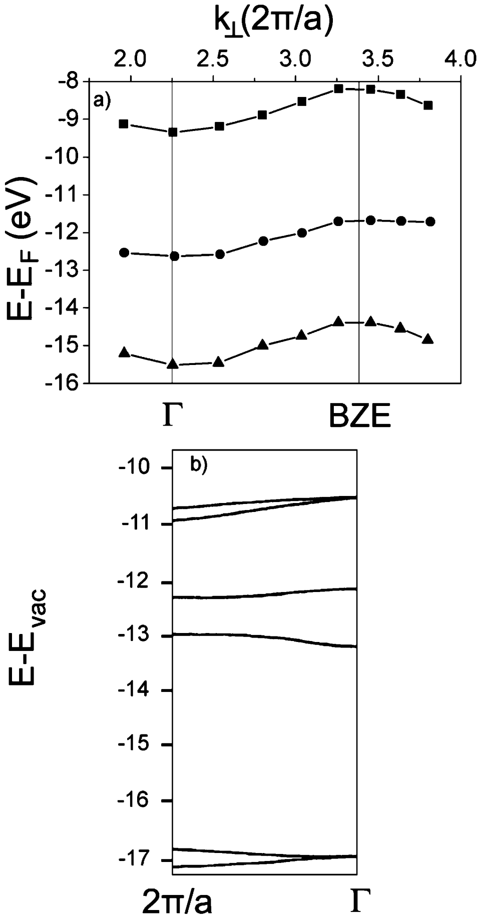

Figure 3. (a) Compilation of the band dispersion as a function of wave vector $k_\perp$, providing an experimental lattice parameter of 2.9 Å along the surface normal. (b) Band structure calculation for cubic ice, adapted with permission from ref 3. Copyright 1973 American Institute of Physics.

incident light indicates a preferential order of the water molecules in our ice film. Symmetry selection rules in photoemission can be used to determine the molecular orbital dipole interaction with plane-polarized light. This light polarization dependence can be used to make some determinations about molecular orientation, as is the case here for water ice on P(VDF-TrFE). The enhancement of the $1b_1$ (−9.2 eV) photoemission feature in more p-polarized light and the enhancement of the $1b_2$ (−15.3 eV) molecular orbital photoemission feature in slightly more s-polarized light indicates that, on average, the majority of water molecules lie with the H−O−H plane parallel with the film (“hands” parallel with the ice to polymer interface). This is because the molecular b_1 orbital must lie largely along the surface normal while the b_2 molecular axis must lie largely in the plane of the film, to provide the observed light polarization dependence observed.

The data imply that not all water molecules lie perfectly in the plane of the film. The difference in the intensities of the $1b_1$ and $1b_2$ molecular orbitals is about 7−13%, while for all the water molecules oriented in the ”perfect” planar configuration, the expected changes in the light polarization-dependent photoemission (in the geometry of our experiment) should be as large as 28−37%. The fact that the observed differences are a quarter (roughly 25%) of the expected values indicates either that the water molecules are tilted by some 20−25° out of plane or that approximately 37−38% of the water molecules adopt a different orientation. Theory, as discussed below, predicts that some 16% of the water molecules in our hexagonal ice adopt an orientation with one hydrogen above the plane and the other below the plane, effectively adopting an orientation where the water is not coplanar with the ice to polymer interface. It is clear that the ice grown on P(VDF-TrFE 70:30), as described here, is not a “perfectly” ordered ice but one with a considerable amount of defects. Nonetheless, this ice is sufficiently ordered to obtain evidence of band structure (that is periodic enough to provide evidence of a conserved electron wave vector).

Band Structure of Ice. There is further evidence of water adopting a preferential order in the ice layers formed on the surface of the P(VDF-TrFE 70:30) copolymer. Energy-dependent photoemission spectra were taken for the thin ice film grown on the PVDF-TrFE polymer surface (Figure 2a), with the photoelectrons collected normal to the surface. In this particular experimental setup, the photon energy dependence of the photoemission spectra (relative to the Fermi level) can be exploited to determine the dispersion (change in binding energy) as a function of wave vector $k_\perp$ (along the surface normal). Such dispersion is observed here (Figure 3) and is a consequence of the hybridization of molecular orbitals of adjacent water molecules fulfilling the criteria of Bloch’s theorem[26] As shown in Figure 2, the photoemission peak binding energies exhibit oscillatory behavior as a function of electron wave vector (proportional to the square root of electron kinetic energy). This is summarized in Figure 3a, where the peak position of each band is plotted against the $k_\perp$ vector.

From this dispersion amplitude of 1 eV, not only is the crystallinity of the ice film evident but also a bulk lattice parameter for along the surface normal can be derived. The positions of the Brillouin zone center and Brillouin zone edge are used, as well as the wave vector difference between the Brillouin zone center and edge according to

$$k_\perp = \sqrt{\frac{2m}{\hbar^2}[E_{\mathrm{kin}}(\cos\theta)^2 + U_{\mathrm{in}}]} \qquad (1)$$

where the value of $k_\perp$ (the wave vector along the surface normal)

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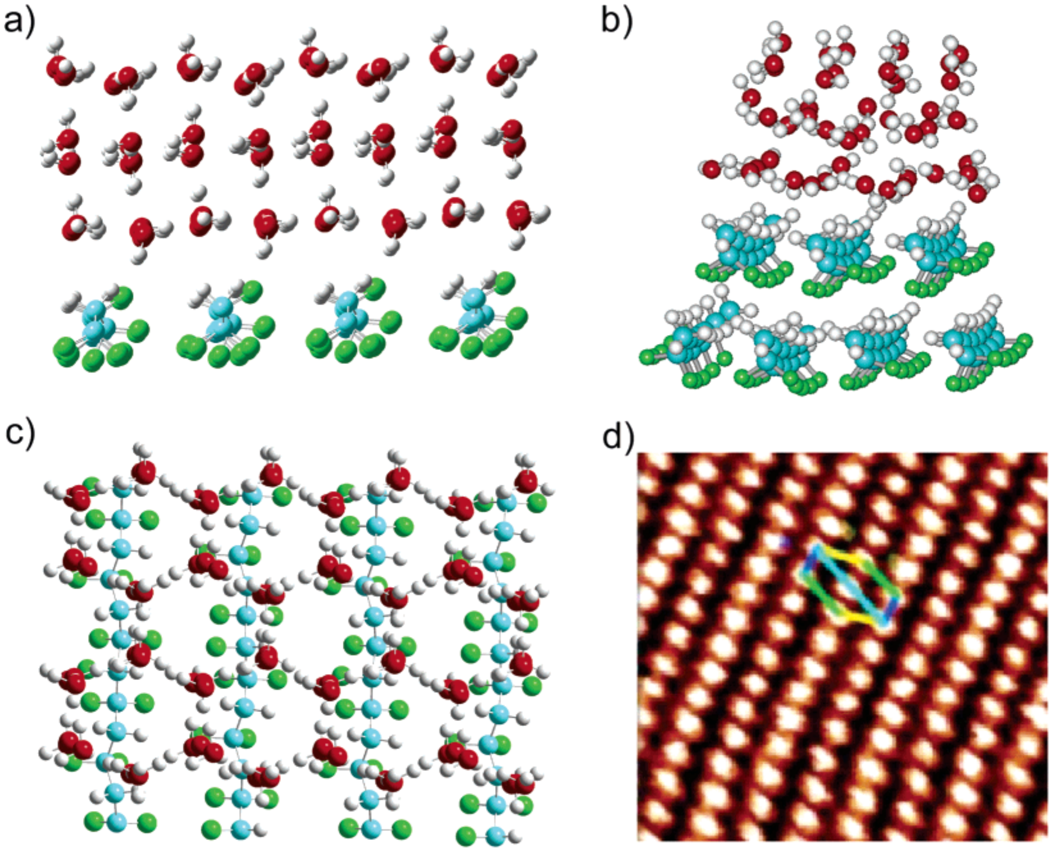

Figure 4. Structure of the ice on PVDF-TrFE predicted by DFT methods at the interface (a) and from the top (c) showing the honeycombed structure. Semiempirical calculations of the ice layer on the ferroelectric polymer (b) result in a similar 2.8 Å lattice spacing along the surface normal for the ice layer. The PVDF-TrFE is well ordered as indicated in panel d from the STM of the ferroelectric polymer surface, adapted with permission from ref 19. Copyright 2003 American Institute of Physics.

can be estimated from the photoelectron kinetic energy (E_{kin}) if some assumptions about the inner potential U_{in} are made, since the emission angle relative to the surface normal (θ) is zero. From these values, we find that single-crystal ice grown here has a crystal layer spacing of 2.9 ± 0.1 Å along the surface normal.

This lattice parameter derived from the band dispersion can be assigned to the calculated value of 2.8 Å for the O−O distances in FCC ice[3−4] and hexagonal ice structures.[10−12] As seen in Figure 3, the experimental dispersion is opposite to band dispersions calculated along the ⟨111⟩ direction (perpendicular to the hexagonal plane) for FCC ice,[3] as seen in Figure 3b. This is consistent with a different molecular orientation for water in our hexagonal ice compared to the expectations for the FCC ice.[3−4]

The expectation that the inner potential U_{in} is negligible in an insulator (like water ice) is not completely borne out by the data. We find some evidence for a small inner potential corresponding to a wave vector of about 0.1 ± 0.3 Å^{-1}, which increases with increasing energy (as is often observed with metals[27]). This corresponds to a very small inner potential energy correction but does tend to suggest that effects from the potential change across the surface boundary cannot be completely neglected.

The electron mean free path at roughly 50 eV kinetic energy is generally accepted to be quite short,[28−31] but as we see from the data here, ice is a wide band-gap insulator; thus plasmon losses do not contribute to reducing the electron mean free path.[30−31] Accordingly, we would expect that the electron mean free path for the photoelectrons in the water ice is much longer than is observed in metals, consistent with the longer mean free paths observed in organic systems.[28] The mean free path is clearly sufficient to observe that Bloch's theorem[26] is fulfilled for the occupied molecular orbitals of water, although we do not observe photoelectrons from the PVDF-TrFE substrate for the ice samples grown here.

Structure of Ice on P(VDF-TrFE). The experimental orientation of the water molecules within our ice films and the lattice constant are consistent with our theoretical expectations. We have calculated the possible structures of ice on a P(VDF-TrFE 70:30) copolymer surface. From both DFT calculations (Figure 4a) and semiempirical calculations (Figure 4b), it is clear that it is energetically favorable for most of the water molecules to lie with the H−O−H plane parallel to the surface. This is consistent with experiment, as noted previously. The apparent differences in the two calculational approaches, represented in Figure 4 panels a and b, is due to the use or absence of periodic boundary conditions. In semiempirical calculations (Figure 4b), a periodic boundary condition was not used.

As a result of interactions with the surface of the ferroelectric polymer, DFT calculations show that the formation of an ice Ih "honeycombed" structure (Figure 4c) is adopted (i.e., a

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hexagonal ice). Both the crystal structure calculations shown in Figure 4a and the semiempirical calculation shown in Figure 4b show the distance between ice layers to be about 3.1−2.8 Å respectively. These two calculated values for layer spacing are, on average (i.e., 2.95 Å), in agreement with our experimental value of 2.9 ± 0.1 Å derived from the band structure.

Given the orientation of water both observed and calculated, the greatest wave function overlap would be with the $1b_1$ molecular orbital, and this molecular orbital should give rise to the largest dispersion among the occupied molecular orbitals of water with changing wave vector along the surface normal, as is indeed observed. We observed the largest dispersion in the $1b_1$ and $1b_2$ molecular orbitals (Figure 3a), and what dispersion appears to occur with the $3a_1$ is quite likely an artifact of changing cross-section between the two branches, that is, a_1 and a_2, of the bands arising from the $3a_1$ molecular orbital,[3,5] as indicated in the theoretical band structure for FCC ice (Figure 3b). This differs from the expectation that the unoccupied $4a_1$ molecular orbital would show 1−2 eV dispersion, while the $3a_1$ molecular orbital would exhibit somewhat less dispersion, with only minimal dispersion shown by the $1b_1$, and $1b_2$ orbitals.[3,5]

Summary

The P(VDF-TrFE 70:30) films are very well ordered,[19] as illustrated in the scanning tunneling microscopy (STM) image in Figure 4d. This, no doubt, aids in the formation of an ordered ice layer. With the formation of an ordered ice layer, details of the electronic structure can now be probed. While some dispersion was observed in prior photoemission studies of ice, also on the order of 1 eV,[5] the results were not very compelling and a preferential orientation of the water molecules was not obtained. This study continues to add to the contention that water, in constrained geometries, will adopt unusual crystallographic order.[32−34]

Theory suggests that it is the dipoles at the P(VDF-TrFE) interface that contribute to order in our ice films: a molecular ordering that propagates as the ice film grows. Certainly, the polar “anchoring” of the water dipole by surfaces has been observed[35] and predicted.[36] Unfortunately, like other ice films, our ice films do contain a considerable number of defects, but these films are sufficiently crystalline to exhibit band structure and are not an amorphous ice.[37]

Because the ordering of ice is intimately connected with the order and dipole orientation at the surface of the PVDF-TrFE film, changes in the surface dipole arrangement of the PVDF-TrFE will affect the structure and electronic properties of the ice layer. There is a surface dipole rearrangement that occurs at temperatures (300 K) well below the bulk ferroelectric transition temperature (350 K),[13,17,20] and condensed water could well be a spectator to this surface dipole ordering transition, as speculated elsewhere.[1]

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE-0415421. X.C.Z. was supported in part by grants from DOE (DE-FG02-04ER46164), NSF (DMII-0210850 and CHE-0427746), and the Nebraska Research Initiative. We thank Christina M. Othon, Kristin Kraemer, and Stephen Ducharme for their assistance.

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