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Dipole-induced structure in aromatic-terminated self-assembled monolayers: A study by near edge x-ray absorption fine structure spectroscopy

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The structure of self-assembled monolayers presenting aromatic rings at a surface is studied by near edge x-ray absorption fine structure spectroscopy (NEXAFS). Fluorine substitution at asymmetric positions in the aromatic rings is used to generate a layer of dipoles at the surface of the monolayer. We find that fluorine substituted aromatic rings are more ordered than unsubstituted aromatic rings by a factor of two based on the polarization dependence of the lowest C 1s to π^* transition, which is associated with transitions from phenyl carbons attached to hydrogens. This result is consistent with the influence of dipole–dipole interactions and quadrupolar interactions between the aromatic groups due to the substitution of fluorine atoms. The work also serves to illustrate how subtle variations in the orientation of an end group of a self-assembled monolayer can be determined by using NEXAFS. © 2004 American Institute of Physics. [DOI: 10.1063/1.1737303]

I. INTRODUCTION

Self-assembled monolayers (SAMs) of alkanethiols on gold substrates form the basis of an important tool for investigations of surface-driven phenomena in a range of disciplines. Examples include control of the orientations of liquid crystals on SAMs supported on obliquely deposited gold films,¹ control of crystallographic orientations of inorganic crystals by using various functional groups tethered to SAMs,² protein immobilization³ and chemical sensing.⁴ The versatility of these experimental systems is largely due to the well-organized structure of the SAM on a gold substrate.⁵ Because of the close packing of the alkanethiols on gold substrates, the functional groups presented by SAMs are typically oriented.⁶ In order to tailor the structures and chemical properties of SAMs, it is important to decipher the intermolecular interactions that govern the ordering and to find ways to enhance the order.

Several past examples demonstrate that it is possible to design the structure and properties of SAMs via specification of the chemical functionality of the molecules used to form the SAMs.⁷ Langer and co-workers introduced bulky groups that protect acids at the terminus of SAMs to prevent the close packing of the monolayer via steric hindrance.⁸ This surface, upon deprotection, forms a loosely packed mono-layer that reversibly reorganizes under the influence of an electric field. Hutchison and co-workers demonstrated the formation of thermally stable SAMs by introducing a three-

dimensional hydrogen bond network into the monolayer.⁹ Abbott and co-workers reported on structural differences between SAMs formed from semifluorinated alkanethiols as compared to alkanethiols, and the impact of these structural difference on the anchoring of liquid crystals.¹⁰

Noncovalent interactions between aromatic groups are known to impact a wide variety of phenomena in chemistry and biology.^{11,12} A classic example is the stabilization of the DNA duplex due to the stacking of the nucleotide bases. The stacking of the nucleotide bases is due to interactions of π orbitals between the bases.¹³ Similar stacking interactions between aromatics are also believed to contribute substantially to the stabilization of the tertiary structure of proteins.14 Whereas considerable effort has been dedicated to the study of aromatic stacking in naturally occurring systems, there is growing interest in the use of non-natural aromatic stacking for the design of materials,¹⁵ for use in supramolecular chemistry¹⁶ and for biological applications.¹⁷ One of the most notable examples of such non-natural aromatic stacking arises in systems containing perfluorosubstituted aromatic rings.^{18,19} While it is known that benzene in the solid state adopts an edge-to-face structure, it has been found that a one-to-one mixture of benzenehexafluorobenzene adopts a face-to-face π stacking of alternating molecules of benzene and hexafluorobenezene.¹⁸ This unique arrangement of aromatic molecules in the solid state reflects molecular interaction arising from the electric quadrupole moments of substituted aromatic rings.¹⁹

In this work, we report on the organization of SAMs, as influenced by the dipole moments and quadrupole moments of fluorine-substituted aromatic groups that are tethered to

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FIG. 1. Self-assembled monolayers formed from alkanethiols 1 and 2. The arrows represent the dipole moments of the aromatic rings. The orientations and magnitudes of the dipoles change when three hydrogen atoms are replaced by fluorine atoms.

the SAMs. The polarization dependence of near edge x-ray absorption fine structure (NEXAFS) spectra is used to study the organization and orientation of the terminal aromatic groups. The structural order of the monolayers induced by fluorine-substitution in the aromatic terminal groups are measured and compared to unsubstituted aromatic terminal groups. We also present a specific model that describes the ordering quantitatively. Our work complements previous NEXAFS by Buck and co-workers, which focused on the role of the substrate-thiol bond and chain length effects on the orientation. The nature of the aromatic end group was not changed by the authors.²⁰

In this paper, we report the use of alkanethiols 1 and 2 to present 2, 3, 4 fluoro-substituted phenoxy groups or unsubstituted phenoxy groups at a surface (Fig. 1). Substitution of fluorine atoms in the aromatic rings causes minimal perturbation to steric interactions between the aromatic terminal groups. However, partial substitution of fluorine atoms at asymmetric positions of an aromatic ring induces a strong dipole moment due to the electron withdrawing effects of the fluorine atoms.^{11,17} This dipole lies across the fluorophenyl group and perpendicular to the alkyl chain, whereas the dipole moment in alkanethiol 2 lies orthogonal to that of alkanethiol 1 (Fig. 1). Furthermore, the electron withdrawing effect of the fluoro groups perturbs the electron density of the p electrons and thus reduces the molecular electric quadrupole moments in the aromatic ring of 1 to a great extent. As a result, when assembled on a gold substrate, SAMs formed from 1 or 2 present a layer of aromatic rings on the surface with arrays of dipole moments that are in orthogonal orientations and with substantially different quadrupole moments. In contrast to the dipole of the unsubstituted SAM, the dipole of the fluorine-substituted SAM can rotate with angle β and thus optimize dipole-dipole coupling by forming an antiparallel arrangement.

II. EXPERIMENT

The compounds **1** and **2** were prepared by a common 3-step route of organic synthesis (Fig. 2). The syntheses started with S_N^2 alkylation of undecenyl bromide with phenol or 2, 3, 4-trifluorophenol to afford the alkylated aromatics. The terminal alkenes were converted to the corresponding thioester by treatment with thiol acetic acid and AIBN under photolytic conditions.²¹ Acidic hydrolysis under reflux afforded the desired aromatic-terminated alkanethiols **1** and **2**.²¹



FIG. 2. Synthesis of phenyl-terminated alkanethiols.

11-Undec-enyloxy-benzene (**A**) To a solution of 0.257 g of phenol (2.735 mmol, 2 eq.) and 66 mg of NaH (60% dispersion) in 15 ml DMF stirred for 20 min, 0.3 ml of 11-bromo-1-undecene (1.367 mmol, 1 eq.) was added. The solution mixture was stirred for 5 h, and then mixed with 50 ml hexane–ether, 50 ml water. The aqueous phase was then extracted three times with hexane; the combined organic phases was dried with MgSO₄, concentrated *in vacuo* and purified by flash chromatography (1% ethyl acetate–hexane) to give 246 mg olefin **A** (0.998 mmol, 73%) as a clear oil: ¹H NMR (250 MHz, CDCl₃) δ 1.26–1.29 (br s, 10H), 1.53–1.58 (qui, 2H), 1.67–1.75 (br s, 2H), 2.00–2.04 (dd, 2H), 3.96–4.00 (t, 2H), 4.88–4.96 (m, 2H), 5.74–5.84 (m, 1H), 6.81–6.98 (m, 3H), 7.2–7.26 (m, 2H).

11-Undecenyloxy-trifluorobenzene (C): ¹H NMR (250 MHz, CDCl₃) δ 1.26–1.29 (br s, 10H), 1.53–1.58 (qui, 2H), 1.67–1.75 (br s, 2H), 2.00–2.04 (dd, 2H), 3.96–4.00 (t, 2H), 4.88–4.96 (m, 2H), 5.74–5.84 (m, 1H), 6.55–6.68 (br m, 1H), 6.78–6.79 (q, 1H).

Thioacetic acid S-(11-phenoxy-undecyl) ester (B) A solution of olefin A (0.41 g, 1.664 mmol) in dry THF (25 ml) containing thiolacetic acid (0.33 ml, 1.96 mmol) and AIBN (32.5 mg, 0.193 mmol) was irradiated in a photochemical reactor (Rayonet reactor lamp, Southern New England Ultraviolet Co., model no. RPR-100) for 5 h under nitrogen (~1 atm). Concentration of the reaction mixture *in vacuo*, followed by flash chromatography (3% ethyl acetate–hexane) gave 483 mg of **B** as a clear oil (1.498 mmol, 90%): ¹H NMR (250 MHz, CDCl₃) δ 1.29–1.33 (m, 14H), 1.55–1.64 (br m, 4H), 2.33 (s, 3H), 2.85–2.90 (t, 2H), 3.96–4.00 (t, 2H), 6.81–6.98 (m, 3H), 7.2–7.26 (m, 2H).

Thioacetic acid S-[11-(2,3,4-trifluoro-phenoxy)undecyl] ester (D): ¹H NMR (250 MHz, CDCl₃) δ 1.29– 1.33 (m, 14H), 1.55–1.64 (br m, 4H), 2.33 (s, 3H), 2.85– 2.90 (t, 2H), 3.96–4.00 (t, 2H), 6.55–6.68 (br m, 1H), 6.78– 6.79 (q, 1H).

11-Phenoxy-undecane-1-thiol (1) To a solution of thioacetate **B** (53 mg, 0.164 mmol) in MeOH (15 mL) was added 5 drops of HCl (12 N), and refluxed under nitrogen for 3 h. The residue product was concentrated *in vacuo* followed by purification of the residues by flash chromatography on silica gel to give 37 mg of the desired thiol **1** (0.131 mmol, 80%). ¹H NMR (250 MHz, CDCl₃) δ 1.33–1.43 (m, 14H), 1.50– 1.66 (br m, 4H), 2.45–2.46 (tt, 2H), 3.96–4.00 (t, 2H), 6.81– 6.98 (m, 3H), 7.2–7.26 (m, 2H).

11-(2,3,4-Trifluorophenoxy)-undecane-1-thiol (2): ¹Η NMR (250 MHz, CDCl₃) *δ*1.33–1.43 (m, 14H), 1.50–1.66

(br m, 4H), 2.45–2.46 (tt, 2H), 3.96–4.00 (t, 2H), 6.55–6.68 (br m, 1H), 6.78–6.79 (q, 1H).

A. Deposition of gold films and preparation of SAMs

Gold films with thicknesses of ~1000 Å were deposited onto silicon wafers (test grade, Silicon Sense Connecting Technologies, NH) mounted on rotating planetaries by using an electron beam evaporator (VES-3000-C manufactured by Tek-Vac Industries, Brentwood, NY). The rotation of the substrates on the planetaries ensured that the gold was deposited without a preferred direction of incidence. A layer of titanium (thickness ~100 Å) was used to promote adhesion between the silicon wafer and the gold film. The rates of deposition of gold and titanium were ~0.2 Å/s. The pressure in the evaporator was less than 5×10^{-7} Torr before and during each deposition. Self-assembled monolayers (SAMs) of alkanethiols **1** or **2** were formed on gold films by immersing the films in ethanolic solutions containing 2 mM of either alkanethiol for 6 h.

B. NEXAFS spectroscopy

Near edge x-ray absorption fine structure (NEXAFS) spectroscopy allows the direct characterization of the chemical properties and orientations of molecules bound to surfaces.²² Electrons in occupied core level states are promoted to empty valence orbitals by absorption of polarized soft x-rays. Each absorption event produces Auger and secondary electrons. The number of detected electrons is approximately proportional to the number of core holes, as long as the escape depth is small compared to the absorption length.²² The effective absorption depth changes somewhat with the polar angle of incidence.²³ However, this effect is identical for the fluorinated and nonfluorinated molecules. The electrons yield provides a convenient measure of the absorption coefficient. By utilizing tunable photons from a synchrotron, the photon energy is scanned across the C 1s absorption edge.

NEXAFS spectroscopy was performed at the Synchrotron Radiation Center (SRC) on the HERMON beam line using secondary electron detection. A load lock was used to introduce the samples into the measurement chamber, which was maintained at a base pressure of less than 10^{-10} Torr. The photon energy interval from 275 to 325 eV was chosen to completely span the C 1s absorption edge and all of the π^* and σ^* transitions. The x-rays were >90% linearly polarized. For each sample, scans were taken at angles of the polarization vector with respect to the sample normal between 85° (near normal incidence) and 20° (near grazing incidence), as indicated in Fig. 3. The position of the light spot on the sample was moved every few scans to prevent extended exposure of the SAMs to photons and radiation damage. Spectra were normalized to a gold film evaporated in situ on silicon to remove the transmission function of the optics. To account for angle-dependent changes of the absorption path and the collection efficiency, we normalized the spectra such that they coincide for photon energies far below and far above the C 1s absorption edge. This procedure effectively normalizes the signal to the number of car-



FIG. 3. Definition of the angles α , β , and χ that characterize the orientation of the aromatic rings on SAMs. α is the tilt angle of the phenyl ether bond with respect to the surface normal. β is the angle of rotation of the aromatic ring around the phenyl ether bond. θ is the angle of the electric field vector, with respect to the normal (which is equal to 90° minus the angle of incidence from normal). χ is the rotation of the phenyl endgroup around the O-alkane bond. Because the O-alkane bond is nearly perpendicular to the normal, χ has little effect on the orientation of the plane of the phenyl ring with respect to the surface normal.

bon atoms sampled in the experiment. The scale given for the absorption in Fig. 4 refers to the pre-edge background.

III. RESULTS AND DISCUSSION

Figure 3 defines the parameters used to describe the structure and order of the terminal aromatic rings of the SAMs. We define α to be the polar angle of the phenyl ether tether with respect to the normal, and β to describe the orientation of the aromatic ring around the ether bond. The tilt angle of the alkanethiols is largely determined by the packing of SAMs on the (1,1,1) gold.²⁴ Because the gold film was deposited on rotating planetaries, we do not expect there to be a macroscopic azimuthal preference of the tilt direction of the alkanethiols.²⁵

The bond angle of the phenyl ether linkage (α) is determined by the electronic structure of the molecule ($\sim 130^{\circ}$).²⁶ Thus, we expect little variation in the angle of α in the SAMs formed from both **1** and **2**, where α approximately equals to 70°. Because of the trans-conformation of the methylene units along the alkyl chain, each alkanethiol occupies an area of about 24 Å² (5.6 Å in diameter).²⁷ Since the longest distance across the facet of a benzene ring is about 5.0 Å, we assume that the aromatic rings experience little steric hindrance from neighboring alkanethiol molecules in the SAM, and hence possess a high degree of rotational freedom (rotation about β).

The positions and intensities of peaks measured in NEX-AFS provide chemical fingerprints of specific moieties in the SAM molecules. Their assignment is based on a combination of the core level shift induced by electronegative neighbors such as oxygen and fluorine and the energetic position of unoccupied molecular orbitals, such as the π^* orbitals of the



FIG. 4. NEXAFS spectra at the C 1s edge as a function of different polarization angles (85° to 25° from the sample normal) for SAMs formed from (A) alkanethiols 1, and (B) alkanethiols 2. A strong polarization dependence of the C 1s-to- π^*, σ^* transitions is observed [peaks (a)–(f)]. The angle is between the electric field vector E and the sample normal (θ in Fig. 3).

aromatic ring. Figure 4 shows the polarization dependence of the C 1*s* NEXAFS absorption spectra of SAMs formed from alkanethiols **1** and **2**. The spectra are normalized below and above the absorption edge $(h\nu = 280 \text{ and } 320 \text{ eV})^{28}$ and the assignments of the resonances for the SAMs formed from alkanethiols **1** and **2** are tabulated in Table I. Because the

core-to-valence electronic excitations are sensitive to the bonding environment, the NEXAFS resonances are governed by the effects of chemical substitutents, and thus the location of atoms within the molecule.^{22,29} Each SAM is characterized by six core-to-valence transitions of the C 1s into the corresponding anti-bonding orbitals. Peak "a" corresponds to the transition of C 1s of the aromatic carbons tethered with hydrogen to the π_1^* anti-bonding orbitals in SAMs prepared from both alkanethiols 1 or 2. Peak "b" corresponds to the transition of C 1s of the aromatic carbons tethered with fluorine/oxygen (SAM prepared from alkanethiols 1) or with just oxygen (SAM prepared from alkanethiols 2) to the π_1^* anti-bonding orbitals in both SAMs prepared from alkanethiols 1 or 2.²⁹ Peak "c" corresponds to the transition of C 1s of the aliphatic carbons to the C-H* anti-bonding orbitals (Rydberg resonance) in both SAMs prepared from alkanethiols 1 or 2.³⁰ Peaks "d" and "e" correspond to the same transitions as peaks "a" and "b," respectively, except the final anti-bonding orbital is the higherlying π_2^* . Peak "f" corresponds to the transition of C 1s of the aliphatic carbons to the C–C σ^* anti-bonding orbitals in both SAMs prepared from alkanethiols 1 or 2.³¹ Substitution of electronegative atoms of fluorine and oxygen on aromatic rings induces a partial positive charge on the carbon. which increases the binding energy of the C 1s level.²⁹ Thus, the transition of the C 1s of a carbon bonded to a fluorine atom and the C 1s of a carbon bonded to a oxygen atom to both π_1^* and π_2^* anti-bonding orbitals are not resolved for SAMs prepared from alkanethiols 1. Furthermore, the shift in the transition energy of the C 1s to π^* anti-bonding orbitals (peak "b") due to fluorine and oxygen substitution also causes an overlap of peak "b" with the C 1s to C-H* transition (peak "c").

Inspection of Fig. 4 indicates two characteristic differences between the transition intensities of SAMs prepared from alkanethiols 1 and 2 that reflect the substitution of fluorine on the aromatic rings on SAMs. First, because the substitution of the fluorine atoms eliminates three C–H bonds, the intensity of the transition from C 1s (aromatic carbon

TABLE I. Assignment of reso	nances for the NEXAFS spectra	of SAMs formed from	alkanethiols 1 and 2.
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SAMs formed from alkanethiol 1 (fluoro-substituted phenyl)		SAMs formed from alkanethiol 2 (phenyl)			
Peak	Assignment	Photon energy (eV)	Peak	Assignment	Photon energy (eV)
а	C=C π_1^* (neighboring C-H)	284.9	а	C=C π_1^* (neighboring C-H)	284.9
b1	C=C π_1^* (neighboring C-F)	287.3 ^a			
b2	C=C π_1^* (neighboring C-O)	287.3	b2	C=C π_1^* (neighboring C-O)	287.5
с	C-H* (alkyl, phenyl)	287.0	с	C-H* (alkyl, phenyl)	287.0
d	C=C π_2^* (neighboring C-H)	288.7	d	C=C π_2^* (neighboring C-H)	288.3
e1	C=C π_2^* (neighboring C-F)	$\sim 290^a$	•••		
e2	C=C π_2^* (neighboring C-O)	$\sim 290^{a}$	e2	C=C π_2^* (neighboring C-O)	Unresolved
f	C–C σ^* (alkyl)	292.9	f	$C-C \sigma^*$ (alkyl)	292.9

^aThe π_2 *C-F/O resonances are masked by the C 1s absorption edge of c, d, or f making an accurate determi-

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tethering hydrogen) to π_1^* anti-bonding orbitals (peak "a") on the fluorophenyl rings (SAM prepared from 1) is significantly smaller than that of the phenyl rings (SAM prepared from 2). Second, the intensity missing from peak "a" is transferred to peak "b" when the ring is substituted with fluorine, because the transition from C 1s to π_1^* is shifted up in energy by the fluorine-induced C 1s core level shift.

The probability of core-level to anti-bonding electronic transitions depends on the angle between the polarization vector of the light and the anti-bonding *p*-orbitals in the molecules. For C 1s excitations, the transition probability is a maximum when the polarization vector is parallel to the orbital, and the transition intensity is dipole-forbidden when the polarization vector is perpendicular to the orbital (follows a $\cos^2 \theta$ law). Thus, by using the linearly polarized synchrotron x-rays, the orientation of the π^* orbitals of the aromatic end groups can be extracted. The excitation of the core electrons to the anti-bonding orbitals in NEXAFS spectroscopy depends strongly on the orientation of the bonding geometry relative to the polarization of the incident x-ray. Figure 4 reveals a similar angular dependence of the intensity of absorptions within each SAM prepared from either 1 or **2**. For absorptions related to the aliphatic chains of both SAMs, the intensity of transitions associated with the σ -bond skeleton (C 1s to C-C σ^* , peak "f") increases with increase in the grazing angle, θ , of the incident polarized x-rays. However, the intensity of transitions associated with the methylene groups (C 1s to C–H*, peak "c") decrease with increase in the grazing angle (Fig. 4). Because the maximum excitation of NEXAFS occurs when the electric field vector E is parallel to the molecular orbital of excitation,²² this result is consistent with the σ bond (C–C) being tilted closer to the normal of the surface whereas the C-H bonds in the methylene groups are oriented towards the parallel to the surface. This type of angular dependence is a general characteristic of SAMs formed from alkanethiols on gold.28

While the structures of the two SAMs seem qualitatively similar, a quantitative comparison of the angular dependence of the intensity of the π_1^* resonance of the aromatic rings does reveal significant differences between the structures of the two SAMs. Figure 5 shows the angular dependence of the intensity of the π_1^* resonance (at 285 eV) of SAMs prepared from 1 and 2 at different angles of incidence of the polarized x-rays. We focused on the π_1^* resonance for a detailed quantitative analysis because it is the best resolved resonance in the C 1s absorption edges. After normalizing the intensity of the π_1^* resonance at $\theta = 90$ degrees for both SAMs, the SAMs with the fluorine-substituted aromatic rings clearly show a stronger angular dependence than the SAMs with unsubstituted rings (Fig. 5). The modulation of the intensity of the fluorine-substituted SAMs is almost twice as large as the unsubstituted SAMs (0.51 versus 0.27, see the)full and dashed fit curves).

Next, we examine the π_1^* resonance at 287.3 eV (peak b1), which is expected to exhibit the same polarization dependence as peak a. The analysis of peak b1 is complicated by an overlap with the C–H resonance (peak c) For a more quantitative analysis we take the difference of the NEXAFS



FIG. 5. Polarization dependence of absorption for the lowest π^* transition of the H-bonded C atoms in the phenyl rings (peak a in Fig. 4). Fluorophenyl (full circles) exhibits stronger polarization dependence than phenyl (open circles) indicating better ordering. Solid (fluorophenyl) and dashed (phenyl) lines show fits to the data of the form A+B cos² θ .

spectra at each angle, SAM 2 minus SAM 1, as shown for $\theta = 55$ degrees in Fig. 6. Thereby, the contribution from peaks c is removed to first order. Gaussian fits to the main peaks confirm the π_1^* resonances at 284.9 and 287.3 eV. An additional weak feature at 287.0 eV indicates a small residual of the C–H resonance, possibly due to the extra C–H bonds in the phenyl of molecule 2. The residual C-H peak does not have any angular dependence, which shows that there is no significant difference in the orientation of the alkane backbone between the two SAMs.. A further complication arises from the presence of two components of peak b (b1 and b2) associated with transitions from carbon atoms neighboring fluorine (b1) and oxygen (b2) in the phenyl rings. However, both transitions have the same ${\pi_1}^*$ final state, have initial state chemical shifts that are nearly identical, due to the similar electronegativity of F and O, and should exhibit the ori-



FIG. 6. Analysis of higher transitions using difference spectra. (a) The NEXAFS spectrum for fluorinated phenyl rings subtracted from those without fluorine substitution at an angle of θ =55°. Similar difference spectra at other polar angles yield (b) the polarization dependence for the π^* transition of the F/O-terminated C atoms (open circles, peak b in Fig. 4) in the phenyl rings and for the C–H bond (filled circles, peak c in Fig. 4). The calculated curve for the higher π^* transition is derived from the fits in Fig. 5, indicating the same polarization dependence as for the lower π^* transition.

entation dependence of the planar phenyl rings. As a result peak b can be analyzed without treating the C–O and C–F components independently.

The areas of the peaks in the difference spectra enable a quantitative analysis of the angular dependence of the π^* resonance at 287.3 eV, as shown in Fig. 6(b). The area as a function of angle is described by the relationship

Area=
$$(A+B\cos^2\theta), -(C+D\cos^2\theta),$$

where the coefficients A,B are for endgroups of SAM 2, with only oxygen and C,D of SAM 1, with both oxygen and fluorine. The coefficients are explicitly calculated using (1) the ratios of B/A and D/C as determined from fits to the π^* peaks in Fig. 5, (2) the relative concentrations of carbon atoms neighboring fluorine (b1) and oxygen (b2) in the endgroups of SAMS 1 and 2 and (3) a normalization to the difference intensity at the magic angle θ =54.7° where the intensity is independent of the molecular orientation.²² The calculated curve [solid line Fig. 6(b)] is in excellent agreement with the experimental data, thus corroborating our finding for the 285 eV resonance that the modulation of the intensity of the fluorine-substituted SAMs is almost twice as large as the unsubstituted SAMs.³²

The above described result leads us to the general conclusion that the distribution in the orientation of the aromatic rings is substantially narrower for the fluorine-substituted aromatic rings than for unsubstituted rings. If perfect order existed (i.e., all phenyl rings stacked parallel to each other and oriented perpendicular to the plane of the surface), the π_1^* intensity in Fig. 5 would change between 0 and 1 with change in polarization of the incident x-rays. The magnitude of the modulation in the π_1^* intensity decreases with increase in the spread of orientations of the phenyl rings. Because the electric field vector cannot be perpendicular to all the phenyls at any angle of incidence, the baseline in Fig. 5 will increase from zero to a finite value when a spread in orientations of the phenyl groups is present. There are several specific models that can be used to describe the orientational disorder of the phenyl groups, such as disorder in the twist angle β (e.g., oscillations around the symmetric positions $\beta = 0^{\circ}$ and 90°), disorder in the oxygen-phenyl bond direction, both in-plane and out-of-plane, symmetry breaking by a fixed angle β between 0° and 90°, and the coexistence of several domains with different azimuthal orientations of the tilted alkyl chains. In this paper, we do not attempt to employ specific models to describe the orientations of the phenyl groups. Instead, we emphasize the change in the overall orientational order of the phenyl rings, defined as the spread in the orientation of the phenyl rings, averaged over all domains as dictated by the substitute of fluorine atoms into the aromatic groups of the SAMs. Explicit calculations for the symmetric geometries $\beta = 0^{\circ}$ and $\beta = 90^{\circ}$ show that the $\beta = 0^{\circ}$ is much closer to the experimental situation, i.e., the planes of the phenyl rings are almost perpendicular instead of parallel to the surface of the gold film.

Strong molecular interactions within SAMs, such as hydrogen bonding, have been shown in past studies to confer additional stability on SAMs,³³ as well as to increase the rate of electron transfer across SAMs.³⁴ Subtle changes in the

orientational order of organic surfaces have also been demonstrated to impact the alignment of liquid crystals at the macroscopic level.^{1,35} Because an anti-parallel alignment is energetically preferred for the dipole-dipole interactions, the small spread in the β angle of the fluorine-substituted aromatic ring likely underlies the high order in the measured NEXAFS signal of the C 1s to π^* transition for the fluorinesubstituted monolayers. Furthermore, because the intensity of the π transition was measured to increase with increase in the angle of incidence of the x-rays, the planes of the aromatic rings containing the π orbitals are tilted perpendicular rather than parallel to the surface (see above). These orientational organizations are consistent with a head-to-tail arrangement of dipoles as well as the interactions of the molecular quadrupolar moments between the fluoro-substituted aromatic rings.¹⁹ For SAMs with aromatic groups that have no fluorine substitution, the interactions of the dipole moment of the aromatic groups are not facilitated by a preferred value of β , thus likely resulting in the less ordered assembly of phenyl rings on the surface. These results, when combined, demonstrate that dipole moment interactions and the molecular quadrupolar effects of aromatic rings can be used to guide subtle variations in the structure of SAMs. We demonstrate in this work that subtle changes in the organization of SAMs due to fluorine-substitution of aromatic groups can be probed by using NEXAFS.

IV. CONCLUSION

To conclude, we used NEXAFS to study the orientations of aromatics groups presented at the outer surfaces of SAMs supported on films of gold. Asymmetric substitution of aromatic end groups with fluorine is used to influence the ordering of the SAMs via electrostatic dipole interactions. The polarization dependence of the NEXAFS signal corresponding to the C 1s to π^* transition in the phenyl groups is found to increase by a factor of 2 with fluorine substitution of the phenyl groups, thus indicating a higher degree of orientational order in the presence of the fluorine-substituted aromatic groups. This observation is consistent with stabilization of the orientational order via the dipole-dipole and the molecular quadrupolar interactions between the aromatic rings in the monolayer. Because the substitution of fluorine atoms does not usually cause additional steric hindrance, we conclude that weak intermolecular interactions due to fluorine substitution of aromatic groups can be used to control the details of the structure of the SAMs.

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