

# Epitaxial Growth of the Ionic Polymer Fluoroaluminum Phthalocyanine on the Basal Plane of Single Crystal Tin Disulfide

A. Schmidt,<sup>†</sup> R. Schlaf,<sup>‡</sup> D. Louder,<sup>§</sup> L.-K. Chau,<sup>⊥</sup> S.-Y. Chen, T. Fritz,<sup>||</sup>  
M. F. Lawrence,<sup>#</sup> B. A. Parkinson,<sup>‡</sup> and N. R. Armstrong\*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received May 9, 1995. Revised Manuscript Received August 15, 1995<sup>⊗</sup>

The epitaxial growth of fluoroaluminum-phthalocyanine (FAlPc) thin films on the hcp (0001) tin disulfide (SnS<sub>2</sub>) surface is reported. Growth conditions can be achieved that lead to FAlPc films of polymer-like aggregates (FAlPc)<sub>n</sub> with the long axis of the aggregate apparently standing perpendicular to the surface. When the substrate is held at a temperature of 260 °C during deposition, reflection high-energy electron diffraction of the resultant thin films showed that FAlPc grows epitaxially on SnS<sub>2</sub> in a square lattice structure, starting with the first monolayer, with a unit cell dimension of 13.2 ± 0.8 Å. One axis of the resulting FAlPc square lattice overlayer is oriented along the main axis of the basal plane SnS<sub>2</sub>. Scanning tunneling microscopy (STM) showed elongated crystallites growing along the main crystallographic axes of the substrate, and these same STM data indicate that phthalocyanine film growth may be initiated at step sites on the SnS<sub>2</sub> surface. The development of H-aggregate (FAlPc)<sub>n</sub> in these thin films is confirmed by the position of the Q-band absorbance maximum observed for these thin films (642 nm), which is blue-shifted from the monomer absorbance maximum at ca. 675 nm. The Q-band spectrum of the epitaxial film is much narrower (fwhm 28 nm) than comparable spectra from less-ordered thin films of (FAlPc)<sub>n</sub> aggregates deposited on sapphire (fwhm 55 nm). The polarization dependence of these Q-band spectra was consistent with individual FAlPc molecules in these thin films, on average, lying parallel to the surface plane. Dye sensitization/photoelectrochemistry showed photocurrent action spectra that paralleled the absorbance spectra and made possible the characterization of even monolayer-level coverages. Quantum efficiencies for charge injection from the FAlPc aggregates into the SnS<sub>2</sub> conduction band (≤5%) was lower by at least a factor of 10, relative to previously explored phthalocyanine sensitizers which do not form linear cofacial aggregates.

## Introduction

Metal phthalocyanine (Pc) dyes are widely used in established and emerging technologies because of the wide variety of electronic, linear, and nonlinear optical properties obtainable in thin films of these materials.<sup>1</sup> Crystalline Pc's tend to exhibit extensive polymorphism in their packing structures, which is typical for molecular materials held together by relatively weak van der Waals interactions.<sup>1a,2</sup> This polymorphism has hampered investigations of the structure–property relationships for these materials. FAlPc is one of the few Pc's,

however, that can show mainly one packing structure.<sup>3</sup> The large electronegativity of the axial fluorine in these molecules leads to an ionic interaction of the type  $\text{-F}^{\delta-}\text{-Al}^{\delta+}\text{-F}^{\delta-}\text{-Al}^{\delta+}$ , and an ionic “polymer” (FAlPc)<sub>n</sub> can be formed (see Figure 1).<sup>4</sup> The molecules in the polymer are cofacially stacked, with the plane of the molecule perpendicular to the stacking direction, and a separation of the individual FAlPc molecules of 3.66 Å.<sup>3,4</sup> This H aggregation leads to a blue (hypsochromic) shift in the absorbance spectrum of the polymer (FAlPc)<sub>n</sub> ( $\lambda_{\text{max}} = 633$  nm in the solid versus a  $\lambda_{\text{max}}$  of ca. 675 nm in solution).<sup>5</sup> FAlPc is of interest for photonic applications because of its relatively high  $\chi^{(3)}$  value ( $5 \times 10^{-11}$  esu),<sup>6</sup> picosecond excitonic lifetimes,<sup>7</sup> and fast decay times in spectral hole burning (<1 ps)<sup>8</sup> reported in polycrystalline and amorphous films. This molecule is therefore

<sup>†</sup> Present address: Max-Planck-Institut für Polymerforschung, P.O. Box 3148, 55128 Mainz, FRG.

<sup>‡</sup> Hahn-Meitner-Institut, Bereich CG, 14109 Berlin, FRG.

<sup>§</sup> Department of Chemistry, Colorado State University, Ft. Collins, CO 80523.

<sup>⊥</sup> Present address: Department of Chemistry, National Chung-Cheng University, Chia-Yi, Taiwan, 621 R.O.C.

<sup>||</sup> Institut für Angewandte Photophysik, Universität Dresden, 01062 Dresden, FRG.

<sup>#</sup> Department of Chemistry, Concordia University, Montreal, Quebec, Canada.

\* To whom correspondence should be addressed.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, October 1, 1995.

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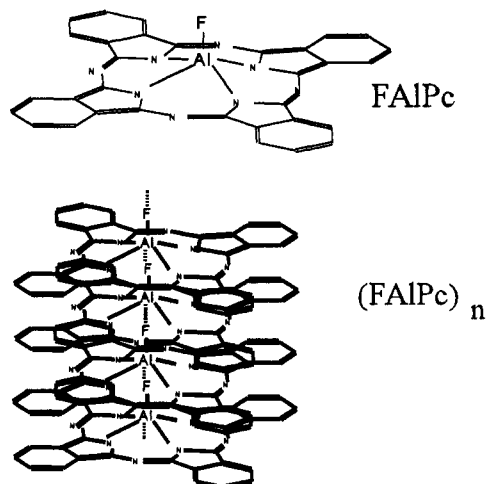
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**Figure 1.** Molecule FAIPc and a schematic of the polymer formed by ionic interaction between the molecules. The repeat distance between Pc rings is 3.66 Å.

an ideal system to examine the influence of packing structures on nonlinear optical properties such as  $\chi^{(3)}$ , and excited state decay times, provided it is possible to grow highly ordered, thin films of FAIPc.

FAIPc has been previously shown to grow epitaxially on single crystal KCl with the polymer axis perpendicular to the substrate surface, while on glass substrates the polymer backbone is generally oriented parallel to the surface.<sup>3b,c</sup> Other divalent, trivalent, and tetravalent metal Pc's have been shown to form well-ordered, epitaxial monolayer or multilayer thin films on single crystal metals,<sup>9</sup> single crystal alkali halide salts,<sup>10</sup> hydrogen terminated silicon,<sup>11</sup> and the hexagonal closest packed (0001) surface planes of layered semiconductors such as MoS<sub>2</sub> and SnS<sub>2</sub>.<sup>12</sup> In all cases, when well ordered thin films are formed, the Pc's tend to orient with the plane of the molecule parallel to the substrate plane. Of these substrates, SnS<sub>2</sub> has been especially attractive because of its large bandgap (ca. 2.2 eV), which makes optical characterization of phthalocyanine

thin films possible, either by transmission through the Pc/SnS<sub>2</sub> thin film or by photoelectrochemical characterization.<sup>13</sup>

It has become of interest recently to determine the conditions under which highly ordered linear aggregates of FAIPc would form using vacuum deposition methods developed previously for other trivalent metal phthalocyanines.<sup>12</sup> The lattice match between the surface unit cell of SnS<sub>2</sub> ( $a_1 = a_2 = 3.64$  Å) and the (FAIPc)<sub>n</sub> long chain axis ( $b_2 = 3.66$  Å) suggested that a type of one-dimensional epitaxy, with the Pc ring lying perpendicular to the substrate plane, would be possible. In the studies reported here surface electron diffraction, STM, and optical/photoelectrochemical characterization experiments show that the substrate temperatures necessary to sustain epitaxy are much higher than previously seen for other phthalocyanines. These studies suggest a packing configuration with Pc rings *parallel*, rather than perpendicular, to the substrate plane of SnS<sub>2</sub>. STM studies also indicate that the strongest interaction of the FAIPc thin films occurs at step sites in the SnS<sub>2</sub> (0001) basal plane, which may therefore be the site for nucleation of the initial Pc deposits. Many of the challenges of using a surface electron diffraction technique, such as RHEED, to unambiguously determine the orientation of thin films of large molecules like the phthalocyanines are also evident from these studies.

## Experimental Section

FAIPc was synthesized from ClAlPc obtained from Kodak, following the method described by Linsky et al.<sup>3a</sup> and subsequently purified by gradient sublimation. Elemental analysis (Desert Analytics, Tucson) proved the material to be at least 98% pure. Subsequent purification was conducted immediately prior to deposition of the Pc thin films (see below). Single crystal tin disulfide (SnS<sub>2</sub>) for photoelectrochemical studies was grown by chemical vapor transport and doped with chlorine to obtain n-type SnS<sub>2</sub> as described elsewhere.<sup>13</sup> The doping density was determined to be ca.  $10^{16}$  cm<sup>-3</sup>.

Sample deposition was carried out in an ultrahigh-vacuum (UHV) system with a base pressure of ca.  $10^{-9}$  Torr. FAIPc was evaporated from a Knudsen cell at 390 °C. The Knudsen cell was held at this temperature for at least 30 min prior to deposition, thus final outgassing and purification of FAIPc preceded the deposition on SnS<sub>2</sub>. The SnS<sub>2</sub> was cleaved immediately before introduction into vacuum and held overnight at 300 °C in vacuum at base pressure. The cleaned hexagonal (0001) surface of tin disulfide was brought down to the deposition temperature immediately before Pc deposition. The rate of deposition was monitored by a quartz crystal microbalance (QCM, 10 MHz) in close proximity to the substrate and was ca. 1 Å/min for all experiments. All coverages have been converted to equivalent monolayer coverage (EQM; 1 EQM = 3.7 Å, the molecular thickness of flat-lying FAIPc).

To monitor the surface structure, reflection high-energy electron diffraction (RHEED) investigations were carried out with grazing incidence 10 kV electrons from a Vacuum Generators L200 electron gun. The RHEED diffraction patterns which appeared on a phosphor screen on the opposite side of the deposition chamber were imaged on a CCD camera (512 × 512 pixel, 8 pixel resolution) and recorded using a computer with a frame grabber (IRIS). Background correction was done by Fourier-filtering the image (IPPLUS image processing software). Subsequent processing of the RHEED data was necessary in order to obtain the reciprocal lattice spacings for the Pc overlayer, at various azimuthal angles, and

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to produce data of adequate quality for reproduction here. This was especially critical in these studies, given the sensitivity of the FAIPc/SnS<sub>2</sub> thin films to electron beam damage, which necessitated extremely short RHEED data acquisition times. At each azimuthal angle the RHEED data obtained by the CCD camera was "binned" along each diffraction streak seen—i.e., the diffraction streak intensity was summed over the entire diffraction streak. This "sum" of diffraction intensity was then plotted as a function of horizontal position on the phosphor screen and used to determine the spacing between diffraction streaks (see text).

Scanning tunneling microscopy (STM) investigations were carried out ex-situ at room temperature with a Nanoscope III STM/AFM system (Digital Instruments). The scan head was housed in a small vacuum chamber (10<sup>-3</sup> Torr) to reduce etching effects. The vacuum chamber was equipped with a liquid N<sub>2</sub> trap to ensure dry vacuum for the STM work.

Mass spectral analysis of the FAIPc vapor was obtained with a Hewlett-Packard 5988A quadrupole mass spectrometer, equipped with a solids probe (electron impact ionization at 70 eV).

The UV-vis absorbance spectroscopy was performed with a HITACHI U-2000 two-beam spectrophotometer. An additional, home-built rotation stage with one polarizer allowed for polarization dependent UV-vis spectroscopy. Thin layers of the SnS<sub>2</sub> crystal were cleaved from the parent crystal, with intact FAIPc layers adequate in thickness to allow transmission spectra to be recorded. The absorbance was measured four different ways. In the first two cases the surface normal was rotated by 45° out of the optical axis and the polarizer set to obtain s- and p-polarized light on the surface (s: polarization parallel to rotation axis of sample, A(45,0); p: polarization perpendicular to rotation axis of sample, A(45,-90)). The second two cases were obtained with the optical axis parallel (0°) to the surface normal and the polarizer set to the two positions as outlined above (A(0,0) and A(0,90)). The ratio between the two absorbances measured under 0° rotation allowed us to determine the in-plane dichroism of the FAIPc thin films.

For photoelectrochemical spectroscopy the SnS<sub>2</sub> crystals were mounted on a metal stub and surrounded with an epoxy shroud. The crystal was cleaved and put into vacuum immediately. The deposition of FAIPc on SnS<sub>2</sub> was done at 10<sup>-6</sup> Torr, with the substrate held at 50 °C. The epoxy shroud did not allow for a higher substrate temperature during deposition. After Pc deposition these photoelectrodes were immediately immersed into the photoelectrochemical cell. The photoelectrochemical studies were conducted in a 0.2 M KHP (pH = 4), and 0.2 M hydroquinone electrolyte. Hydroquinone acted as the regenerating agent (sensitizer) to reduce the photo-oxidized dye. The illumination source was a tungsten halogen lamp (400 W, modulated at 25 Hz) passed through a Jobin-Yvon IR H-10 monochromator, which provided for illumination in the wavelength range 400–1000 nm, with a band-pass of 16 nm. The output of the lamp through the monochromator was determined through the use of a calibrated photodiode. Potential control of the photoelectrode was achieved with a PAR 174 potentiostat. Unless otherwise stated, all potentials for the photocurrent yield spectra were held at ca. +0.5 V vs Ag/AgCl, which is sufficiently positive compared to the flat band potential of SnS<sub>2</sub> so that the photocurrents are nearly independent of potential.<sup>10</sup> The output of the current-to-voltage converter was demodulated with an Ortec-Brookdeal lock-in-amplifier.

In dye sensitization/photoelectrochemistry the photocurrent density,  $j$ , from charge injection from the excited state dye is given by

$$j/(1.602 \times 10^{-19} \text{ C}) = j' = \phi F_A \quad (1)$$

using the quantum yield of carrier generation per absorbed photon,  $\phi$ , and the absorbed photon flux,  $F_A$ . The absorbed photon flux is given by

$$F_A = F_0(1 - e^{-2.3A}) \quad (2)$$

where  $A$  is the absorbance of the dye layer.  $F_0$  is the incident photon flux on the sample surface. The actual measured quantities are the photocurrent intensity,  $I_A$ , and the incident light intensity,  $I_0$ , but a calibrated photodiode allowed determination of the photon flux from the intensity at each wavelength (energy per unit area and time). For very thin films ( $A < 0.5$ ) one can therefore write for the photocurrent density

$$j' \approx \phi F_0 2.3A \quad (3)$$

The quantum yield per incident photon, QYIP (i.e. number of photogenerated electrons per incident photon), is then given by

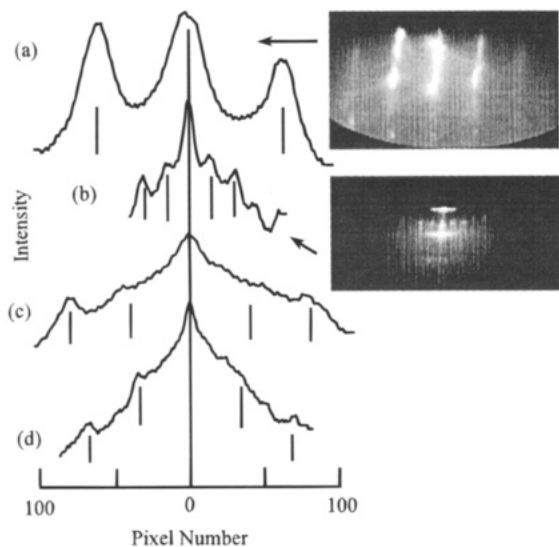
$$\text{QYIP} = j'/F_0 = \phi(1 - e^{-2.3A}) \approx \phi 2.3A \quad (4)$$

For very thin films the quantum yield is expected to follow the absorbance spectrum, if it is assumed that the quantum yield shows no wavelength dispersion.

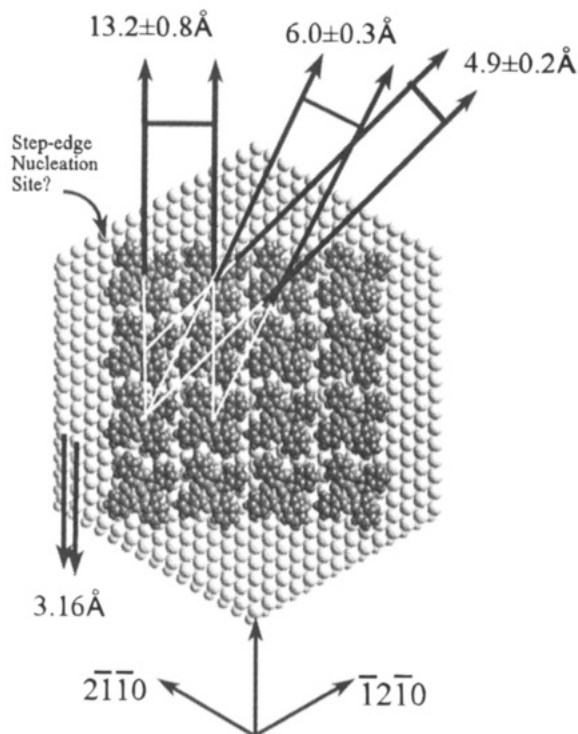
## Results and Discussion

**Surface Electron Diffraction.** When the substrate was held at temperatures below 250 °C during the deposition process, the RHEED data obtained for FAIPc thin films deposited on freshly cleaved SnS<sub>2</sub> indicated an amorphous or polycrystalline structure with no discernible electron diffraction patterns. Raising the substrate temperature to ca. 260 °C during deposition produced a distinct RHEED pattern, developed during growth of the first equivalent monolayer of FAIPc. We have observed that investigation of such crystalline organic thin films by high energy electrons, with the sample maintained at this deposition temperature, causes rapid destruction of the organic surface, and hence degradation of the RHEED pattern. We therefore determined the surface structure *only qualitatively* during the growth of the Pc thin films, by using the RHEED analysis to obtain a single diffraction image frame with the CCD, with only a few seconds exposure of the sample to the electron beam. In this way we could determine whether a distinct RHEED pattern was visible during any stage of growth of the Pc thin film, as an indication that a reasonably ordered film was being created. Probing the order of these thin films by this approach was useful for coverages up to ca. 60 equivalent monolayers. Beyond this coverage the RHEED patterns observed generally indicated that ordered films were no longer being formed (on the coherence length scale of the RHEED experiment, ca. 50–100 nm). By sampling the RHEED data at different coverages in the FAIPc film, we could observe that inelastic electron scattering (background) increased with coverage, and the RHEED streaks became weaker, but the overall diffraction pattern did not change. We conclude therefore that the same overall Pc packing structure is obtained for all coverages up to 60 EQM.

Figure 2 shows the room temperature RHEED diffraction data obtained for a typical FAIPc thin film, at all of the azimuthal angles at which RHEED data was acquired. Figure 3 shows the model which we believe best explains the nucleation of such a thin film. The electron beam damage during RHEED analysis at this substrate temperature still necessitated short exposure times to the electron beam. The signal-to-noise and signal-to-background in these RHEED diffraction images were sufficient to obtain precise measurements of



**Figure 2.** RHEED data for (a) a bare SnS<sub>2</sub> crystal, along a major azimuth (e.g., [11 $\bar{2}$ 0]), and the same surface covered with ca. 50 equivalent monolayers of FAIPc (growth at a substrate temperature of 260 °C, RHEED data acquired at room temperature). (b) Diffraction data taken along the azimuthal direction in (a), (c) diffraction data taken at 45° to the azimuth in (a) and (d) diffraction data taken at 30° to the azimuth in (a). Representative RHEED data are shown to the right of the line scans for (a) and (b) (see text for details).



**Figure 3.** Schematic view of the proposed packing of FAIPc during the formation of the first monolayer, showing the major crystallographic axes of the SnS<sub>2</sub> substrate, the proposed orientation of the FAIPc monolayer with respect to the substrate and the major azimuthal angles along which RHEED characterization in Figure 2 was carried out.

reciprocal lattice spacing from the CRT monitor used to display these images. As shown in Figure 2 integration of all of the RHEED patterns was carried out along each diffraction streak, and those “binned” scans were then used to help measure the reciprocal lattice spacing in the Pc thin film. Only images of the major diffraction

patterns are reproduced here—the diffraction patterns obtained at 30° and 45° azimuths were weak, with the short electron beam exposure times used, and within the limitations of the 8-bit CCD camera technology employed in these experiments, did not have sufficient signal-to-background to allow for adequate reproduction. Because of experimental restrictions within the vacuum chamber, electron diffraction measurements at 90° to the main crystallographic direction of SnS<sub>2</sub> used here were not possible.

Figure 2a represents RHEED data obtained with the electron beam aligned along a main crystallographic axis of bare SnS<sub>2</sub> (e.g., the [11 $\bar{2}$ 0] azimuth). Figure 2b–d shows the RHEED data and/or line scans from that data for a ca. 50 EQM FAIPc/SnS<sub>2</sub> thin film, along the same azimuth as shown in Figure 2a, and at 30° and 45° to that azimuth. The SnS<sub>2</sub> basal plane has hexagonal symmetry with a surface lattice parameter of  $a_1 = a_2 = 3.64$  Å. The row-to-row spacing of SnS<sub>2</sub>, which corresponds to the RHEED streaks in Figure 2a, is hence [ $\sin(60^\circ) \times 3.64$  Å = 3.15 Å]. The reciprocal lattice spacings of the organic overlayer were calibrated by comparison to those diffraction streaks obtained from the bare SnS<sub>2</sub> surface. The diffraction streaks in Figure 2b–d correspond to net plane spacings in the Pc overlayer of  $13.2 \pm 0.8$  Å (0°),  $4.9 \pm 0.3$  Å (45°) and  $6.0 \pm 0.3$  Å (ca. 30°). Table 1 gives further details of the net plane spacings found for each of the azimuthal directions, and a comparison of these spacings with those expected from two different orientations of the Pc overlayer.

The series of Pc overlayer diffraction streaks observed along the main crystallographic axes of SnS<sub>2</sub> confirm that we have achieved epitaxy, i.e., the lattice structure of the FAIPc monolayer  $\rightarrow$  multilayer is dictated by the basal plane lattice of the SnS<sub>2</sub> substrate—in this case the Pc lattice appears to be closely aligned with a major axis of the SnS<sub>2</sub> substrate. The diffraction series shown in Table 1 can be explained as ( $h,0$ ) streaks with a Pc surface unit cell size of  $13.2 \pm 0.8$  Å. This value is within experimental error that expected for the diameter of the flat-lying FAIPc molecule.<sup>3b,c</sup>

We now have to distinguish between two possible FAIPc structures on the SnS<sub>2</sub> surface: (i) a square lattice of flat-lying (FAIPc)<sub>n</sub>, consisting of linear cofacial Pc columns perpendicular to the substrate, with lattice parameter  $b_1 = b_2 = 13.2$  Å, or (ii) a rectangular lattice of (FAIPc)<sub>n</sub> with the cofacial Pc rings perpendicular to the surface plane, with lattice parameters  $b_1 = 13.2$  Å and  $b_2 = 3.6$  Å. Table 1 compares the experimental RHEED data together with the expected net plane spacings for the first case (shown in Figure 3) and for the rectangular lattice.

This comparison shows that the experimental data are best described with a square Pc lattice with lattice parameter  $b_1 = b_2 = 13.2 \pm 0.8$  Å. The (1,1) and (3,3) diffraction streaks expected for this square lattice do not appear in the experimental results for reasons that are not presently clear, but all other net plane spacings agree (within experimental error) with the spacings and orientations expected from a Pc assembly with flat-lying rings. The azimuthal angles in our surface electron diffraction experiments can not be determined better than  $\pm 5^\circ$ , the theoretically expected RHEED streaks for the flat-lying Pc square lattice at 27° are therefore

**Table 1. Experimental (from RHEED) and Theoretical Net Plane Spacings (Å), Order of Reflections, and Angle of Observation vs Main Direction of SnS<sub>2</sub> (in Parentheses)**

	0° along the SnS <sub>2</sub> [1120] azimuth	30° to the SnS <sub>2</sub> [1120] azimuth	45° to the SnS <sub>2</sub> [1120] azimuth
experimental	13.2 ± 0.8 Å 6.3 ± 0.3 Å 4.8 ± 0.3 Å	6.0 ± 0.3 Å 3.6 ± 0.2 Å	4.9 ± 0.2 Å 2.4 ± 0.1 Å
(i) expected for square lattice: $b_1 = b_2 = 13.2$ Å	(1,0): 13.2 Å (2,0): 6.6 Å (3,0): 4.4 Å (4,0): 3.3 Å	(1,2): 5.9 Å (27°) (2,4): 3.0 Å (27°)	(1,1): 9.4 Å (2,2): 4.7 Å (3,3): 3.1 Å (4,4): 2.4 Å
(ii) expected for rectangular lattice: $b_1 = 13.2$ Å, $b_2 = 3.6$ Å	(1,0): 13.2 Å (2,0): 6.6 Å (3,0): 4.4 Å	(0,1): 3.6 Å (from domains rotated by 60° to the main crystal axis of SnS <sub>2</sub> )	(4,1): 2.4 Å (43°)

equivalent in position to the streaks observed at ca. 30°. A rectangular lattice of FAIPc, with the long axis of the aggregate parallel to the substrate, cannot explain the larger RHEED streak spacings at 30° and 45°. Nevertheless, the streaks expected for a rectangular lattice are a subset of the streaks observed for the square Pc lattice. Our RHEED experiments do not, therefore, allow us to completely exclude the possibility of a mixture of crystal orientations in these FAIPc films, with both crystal orientations present. The crystallites grown in these experiments have to be larger than the coherence length of the experimental method, which for RHEED analysis is ca. 50–100 nm. The streak intensity is nearly equal for every order (for a given angle), which indicates that contributions from FAIPc in rectangular surface lattices must be quite small. The presence of a significant fraction of such rectangular lattices would increase the intensity of the high order streaks attributed to the square lattice.

A square lattice, or nearly square lattice, overlayer structure has been found for several different trivalent and tetravalent metal phthalocyanines on metals (Cu(100)),<sup>9,12e,f</sup> alkali halides,<sup>10</sup> van der Waals semiconductors (MoS<sub>2</sub>, SnS<sub>2</sub>),<sup>11,12</sup> and hydrogen-terminated silicon and selenium-terminated GaAs.<sup>11</sup> The lattice parameter is between 13 and 14 Å for all such phthalocyanine thin films and substrates, the azimuthal rotation between substrate and overlayer depends on the actual interaction between them. Chloroindium phthalocyanine (ClInPc) grows on SnS<sub>2</sub> in a square lattice, with  $b_1 = b_2 = 13.4$  Å and a rotation of ±4° to the main crystallographic axis of SnS<sub>2</sub>, as indicated by low energy electron diffraction (LEED).<sup>12</sup> This agrees within experimental error with our results here for FAIPc on SnS<sub>2</sub>, where only RHEED analysis was possible for these samples.

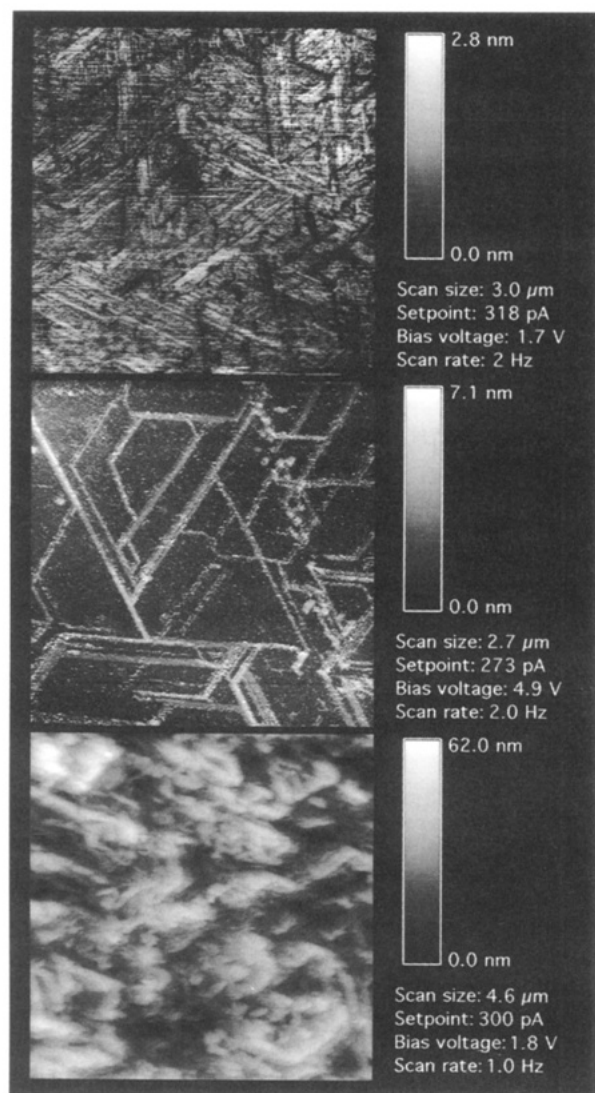
We have hypothesized that one of the major origins for the formation of flat-lying molecular planes is the polarization interaction between the  $\pi$  and nonbonding (bridging nitrogen) orbitals of the Pc ring and the surface atoms of the substrate material.<sup>12d</sup> FAIPc and ClInPc molecules are essentially the same except for the central metal ligand, which causes ClInPc to be more "puckered", with the In atom out of the Pc plane. Purely cofacial linear aggregates of ClInPc are therefore difficult to form, and this molecule prefers a flat-lying orientation in the first monolayer on all substrates investigated to date, when growth conditions for epitaxy are met.

In FAIPc the strong tendency to form the purely linear cofacial aggregate, and the close match between one axis of the unit cell of this aggregate and the unit cell for

the SnS<sub>2</sub> substrate (3.6 Å in the FAIPc lattice versus 3.64 Å along the SnS<sub>2</sub> main direction, 13.2 versus 3.15 Å perpendicular to the main growth direction) made it conceivable that epitaxy of these aggregates perpendicular to the main crystallographic axes of SnS<sub>2</sub> would occur and that the rectangular lattice discussed above would form. The studies discussed here, however, suggest that the van der Waals interactions between the flat-lying adsorbed in the first monolayer, and the SnS<sub>2</sub> surface are more important. At the substrate temperatures necessary to achieve good electron diffraction data, the first arriving FAIPc molecules apparently adopt a flat-lying square lattice configuration, even though the lattice mismatch is large (13.2 versus 3.15 Å in one growth direction and 13.2 versus 3.64 Å along the other growth direction). Starting from the first monolayer of FAIPc the subsequent molecules arriving at the surface appear to form the ionic polymer aggregate already observed in several other studies (see UV-vis results below).<sup>3,4</sup> It may not be surprising that we were able to sustain this ordered film growth up to ca. 60 monolayers—the proposed packing structure of this thin film reflects the bulk structure of FAIPc and little "lattice strain" is expected. The 60 EQM ordered films were still too thin for  $\theta$ - $2\theta$  X-ray diffraction, so we did not obtain complimentary X-ray diffraction data for these materials, which could have further supported this hypothesis.

**Scanning Tunneling Microscopy.** To further explore the growth of FAIPc on SnS<sub>2</sub> we investigated several thin films by STM, after growth in UHV accompanied by RHEED characterization. Large area scans were used to infer macroscopic crystallographic features of these thin films and to examine the degree of long-range order and molecular scale roughness in the  $z$ -axis direction. Higher resolution scans produced too much "etching" of the organic layer by the probe and were generally avoided, except as discussed below.

Figure 4 shows the results for two samples, one with 2 EQM coverage (upper micrograph), which gave a clear RHEED diffraction pattern as described above, and a much thicker film (bottom micrograph), which did not show a discernible diffraction pattern, i.e., was not ordered over a distance scale of ca. 50–100 nm. The micrograph at the top of Figure 4 results from a tip bias voltage of 1.7 V for imaging of the ordered 2 EQM thick FAIPc/SnS<sub>2</sub> surface, over a 3  $\mu\text{m}$   $\times$  3  $\mu\text{m}$  area. Dark streaks are observed in the FAIPc thin film which appear to have the shape, frequency of occurrence, and orientation of steps in the basal plane of the SnS<sub>2</sub> crystal.<sup>14</sup> Some elongated deposits are seen, ca. 40–50 nm in length, which seem to occasionally span over a



**Figure 4.** STM micrographs from FAIPc thin films on SnS<sub>2</sub>. Top micrograph: 3 μm × 3 μm scan of a 2 equivalent monolayer FAIPc film, measured with 1.7 V bias, 318 pA setpoint current. The 6-fold symmetry, caused by the equivalent domains of FAIPc on the surface is visible. Center micrograph: 2.7 μm × 2.7 μm micrograph of the same sample, measured with 4.9 V bias, setpoint current of 273 pA. The FAIPc thin film has now been etched away on the terraces but has remained at the steps. Bottom micrograph: 4.6 μm × 4.6 μm micrograph of a much thicker (ca. 50 EQM) FAIPc film, which showed little order detectable in the RHEED characterization.

whole terrace on the SnS<sub>2</sub> surface (ca. 0.4 μm). The angle between such steps and the long axis of the elongated crystallites is 60°. These films appear to vary in thickness less than 1.4 nm, except in regions of grain boundaries. As we concluded from the surface electron diffraction experiments, growth appears to occur along the principal axis directions of SnS<sub>2</sub> (as shown in Figure 3). On some of the terraces elongated crystallites with different orientations can be recognized, but the angle between the main axes of these crystallites is always

60°. Several nonequivalent domains of FAIPc have to be present, since none of the six main growth directions is favored. Because there was considerable "etching" of these organic layers under conditions necessary to obtain molecular resolution, STM did not aid in determining how the polymer backbone is oriented vs the surface. These crystallites are in the size range necessary to produce adequate RHEED data, i.e., they meet or exceed the coherence length requirements of surface electron diffraction of such organic deposits.<sup>12h</sup>

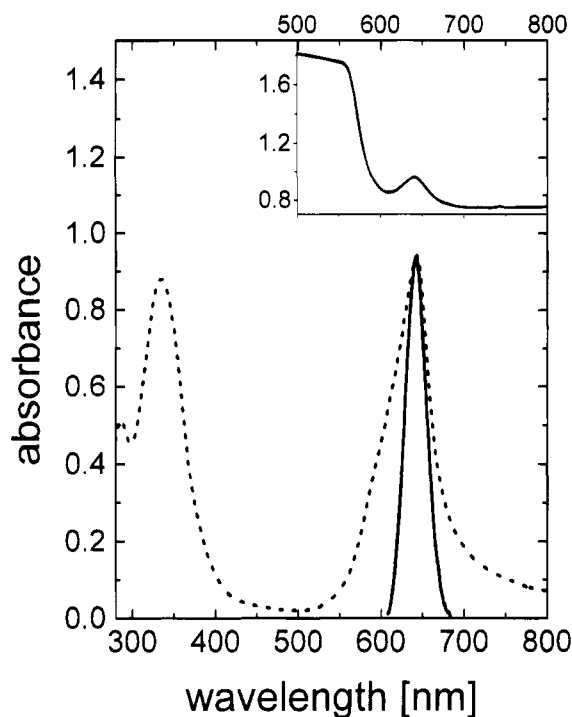
When the tip bias voltage was increased from 1.7 to 4.9 V, the FAIPc thin film was clearly removed from the scanned region, even at these low resolutions, as can be seen in Figure 4, center (same sample, but at a different position, after several scans). The etching of such organic thin films at high tip bias has been repeatedly observed in our STM investigations of these materials.<sup>12c</sup> The SnS<sub>2</sub> terraces appear to be etched clean after a few scans over the same area, while approximately monolayer thickness crystalline deposits appear to remain at the steps in the basal planes of SnS<sub>2</sub>, suggesting that the interaction between FAIPc and the SnS<sub>2</sub> is strongest at these surface steps. This finding, together with the weak van der Waals interaction between FAIPc and SnS<sub>2</sub> and the high substrate temperatures required during growth, leads us to the additional hypothesis that the nucleation of FAIPc occurs at step sites on SnS<sub>2</sub>, as shown schematically in Figure 3. Mass spectroscopy did not reveal oligomers of the type (FAIPc)<sub>n</sub> to be present in the molecular beam emanating from the Knudsen cell. We therefore assume that single FAIPc molecules are deposited on the SnS<sub>2</sub> surface. Each FAIPc molecule apparently is mobile enough on the surface to diffuse along a terrace until it finally binds at a step site with a polymer nucleus or itself forms such a nucleus. Recent AFM/STM studies by Tada and Mashiko suggest that surface diffusion lengths of large aromatic hydrocarbons of up to 1 μm are possible on such van der Waals surfaces, during the initial nucleation of this type of Pc film.<sup>10g</sup> "Topographically directed nucleation" has been observed for other molecular crystalline systems<sup>15</sup> and may play a role in the growth of several other previously investigated phthalocyanine and perylene films on this type of layered material.<sup>12</sup>

Figure 4, bottom, shows a poorly ordered sample (as indicated by the lack of well-defined diffraction streaks in the RHEED data) from a thick (>60 EQM) FAIPc film. The STM picture of a 4.6 μm × 4.6 μm area confirms that this is not a macroscopically ordered film, but the underlying 6-fold symmetry of the substrate still causes some 60 and 120 angles to be visible at the grain boundaries in this textured Pc film.

**Visible Wavelength Spectroscopy and Photoelectrochemistry.** An example of the absorbance spectra of these epitaxially grown FAIPc thin films is shown in the inset of Figure 5. The SnS<sub>2</sub> substrate absorbance begins at ca. 560 nm, corresponding to its bandgap of 2.2 eV,<sup>13,14</sup> and the Q-band for the FAIPc aggregates in the epitaxial thin film gave an absorbance

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**Figure 5.** Inset: UV-vis absorbance spectrum of a 50 EQM epitaxial film of FAIPc on SnS<sub>2</sub>. SnS<sub>2</sub> absorbs light strongly below ca. 560 nm. The absorbance spectrum of epitaxial FAIPc alone is determined by subtracting the absorbance from SnS<sub>2</sub>. The resulting absorbance (—, normalized) is shown below the inset and compared to a 250 EQM less ordered film of FAIPc on sapphire (---, corrected for sapphire absorbance).

maximum at 642 nm. The fwhm of the peak, after correction for absorbance from the SnS<sub>2</sub> background, is 28 nm (solid line in the full spectrum in Figure 5). This blue shift of the maximum absorbance, if compared to the solution spectrum of FAIPc monomer in pyridine, with a maximum at about 675 nm, has been shown to be caused by the linear cofacial aggregation (H aggregate) of eclipsed Pc's in the solid state.<sup>5,16</sup>

For reasons of comparison we also grew a 250 EQM film of FAIPc on a single crystal sapphire substrate at a lower substrate temperature (100 °C) and higher growth rates of 2.5 EQM/min. RHEED characterization showed this film to be disordered on the scale of the RHEED coherence length and is more representative of the type of absorbance spectra expected in the photoelectrochemical experiments described below. The absorbance spectrum of such a film is shown in Figure 5 (dashed line) and compared to the substrate-corrected absorbance of the epitaxial FAIPc film on SnS<sub>2</sub>. Because sapphire is transparent in the whole spectral region the B band of FAIPc is now also visible below 400 nm. The maximum absorbance of the Q-band is at 642 nm, with a fwhm of 55 nm. It is clear that H aggregates of FAIPc are also formed during such a deposition on sapphire, but the Q-band is broader than for the epitaxial film on SnS<sub>2</sub>. In molecular crystals of this type the full hypsochromic shift is achieved if only about 6–10 FAIPc molecules form a linear aggregate.<sup>5</sup> The width of the Q-band peak, however, is a reflection of the degree of heterogeneity of environments of the molecules present in such films and clearly indicates the substantially

**Table 2. Polarization-Dependent UV-vis Absorbance Measured at 641 nm<sup>a</sup>**

	FAIPc on sapphire	epitaxial FAIPc on SnS <sub>2</sub>
A(0,0)	1.016	0.84
A(0,90)	1.016	0.85
in-plane dichroism: $r(0)^\circ = A(0,90)/A(0,0)$	1.00 ± 0.07	1.01 ± 0.14
A(45,90)	0.60	0.92
A(45,0)	0.57	1.0
$r(45^\circ) = A(45,90)/A(45,0)$	0.81 ± 0.06	0.92 ± 0.14
Q (deg)	70 ± 10	59 ± 17

<sup>a</sup> The absorbance is corrected for the substrate and the error is approximately 5%.

enhanced ordering achievable under conditions of epitaxial growth. The narrowness of this spectral response is unprecedented for Q-band spectra of Pc thin films and more closely resembles the kind of spectral response expected from J-aggregate or H-aggregate cyanine dyes, with considerable long range order.<sup>17</sup>

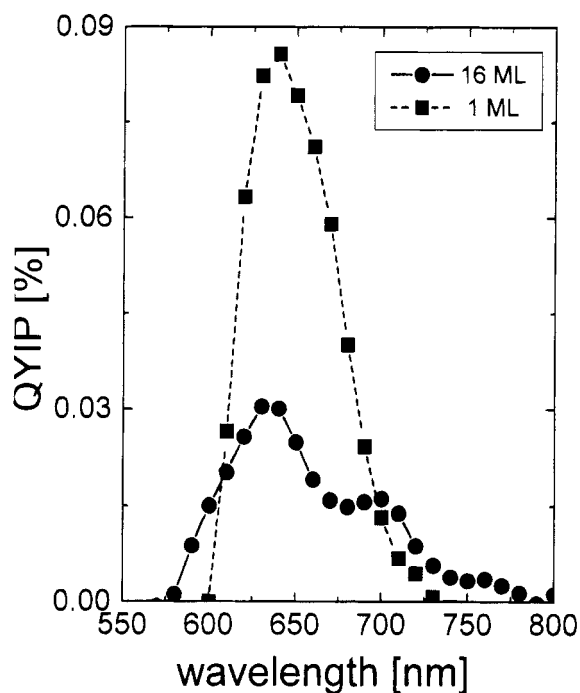
Polarization dependent visible wavelength spectroscopy allows evaluation of the in-plane dichroism of FAIPc/SnS<sub>2</sub> thin films, in the film plane, and the average angle,  $\theta$ , of the transition dipole moment in these FAIPc thin films vs the surface normal. The transition dipole moment of FAIPc is parallel to the molecular plane.<sup>1,5</sup> Table 2 summarizes the absorbances for the different polarization conditions (see Experimental Section) for an epitaxial film on SnS<sub>2</sub> and a less ordered film on sapphire. Both samples (and also the substrates alone) do not show an in-plane dichroism, as expected for amorphous or 4-fold/6-fold symmetric samples. The method for the determination of the angle,  $\theta$ , is described in ref 18. The theory was developed for nonabsorbing substrates, and the results are quite sensitive to absorbance errors (reflections from surfaces and substrate absorbance). For sapphire, which is transparent at 641 nm, the application of this treatment is straightforward, but for the moderately absorbing SnS<sub>2</sub> substrate it can provide only trends in orientation. The best we can determine is whether the orientation on a "control" substrate and on SnS<sub>2</sub> are approximately the same. A value of  $\theta = 70^\circ \pm 10^\circ$  for FAIPc/sapphire indicates that, on average, the Pc adopts a nearly flat-lying orientation on the sample surface. A value of  $\theta = 59^\circ \pm 17^\circ$  on SnS<sub>2</sub> suggests that the molecular planes of FAIPc on SnS<sub>2</sub> may be oriented similarly to orientations seen on sapphire substrates. These data suggest that, on average, the Pc plane may not be perfectly parallel to the SnS<sub>2</sub> surface, which would be difficult to reject from the RHEED data alone. They do, however, eliminate the possibility of having the majority of the Pc rings perpendicular to the substrate plane.

Photoelectrochemical measurements were carried out with FAIPc grown at 50 °C on single-crystal SnS<sub>2</sub>. These films are not well ordered, but it was difficult to prepare crystals that could withstand the temperatures needed for epitaxial layer growth of the Pc thin film and

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**Figure 6.** Quantum yield per incident photon, QYIP, for the photocurrent yield of a 1 EQM and a 16 EQM disordered film of FAIPc on single crystal SnS<sub>2</sub>. The QYIP has a maximum at 640 nm for the 1 EQM film with a fwhm of 55 nm. The QYIP of the 16 EQM film is lower by a factor of 3, with two maxima at 635 and 700 nm.

still hold up to the conditions of photoelectrochemical characterization. Figure 6 compares the action spectrum (i.e., QYIP vs excitation wavelength) of a 1 EQM thick FAIPc film with that of a 16 EQM film, both on SnS<sub>2</sub>. A 1 EQM Pc film is too thin to give a reasonable intensity absorbance peak in transmission spectroscopy of these materials. The 16 EQM film shows an absorbance spectrum equivalent to that seen on the sapphire sample in Figure 5. We conclude that, at 50 °C deposition temperature FAIPc must also grow as a short chain ionic aggregate polymer on SnS<sub>2</sub>.

The action spectrum of Figure 5 follows closely in shape the absorbance spectrum of thicker FAIPc films (Figure 3), as expected from eq 4. Compared to other dye sensitizers<sup>19,20</sup> especially other phthalocyanines on SnS<sub>2</sub>,<sup>13,21</sup> the overall photoelectrochemical efficiency is quite low, the quantum yields per *absorbed* photon, computed for monolayer coverage FAIPc thin films discussed here, were not greater than ca. 5%. Quantum yields per absorbed photon in excess of 50% have been observed for various epitaxially grown Pc thin films on SnS<sub>2</sub> (indium-chloro, gallium-chloro, aluminum-chloro, and vanadium-oxo Pc's). These Pc's all form deposits with the Pc rings parallel to the substrate plane, and with each Pc plane staggered in the *x,y* dimension with respect to the Pc plane below, causing a red-shift of the Q-band spectral response, rather than the blue-shift seen here for the FAIPc thin films.

This difference in efficiency between the two different types of Pc aggregate thin films may be caused by at least three different factors. First, the oscillator strength of (FAIPc)<sub>n</sub> and therefore the absorbance, *A*, in eq 4 is smaller for an equivalent coverage than for other trivalent metal Pcs. Second, the quantum yield for charge injection into the semiconductor substrate, obtained for low coverage oligomers and polymers, is typically lower than for monomers.<sup>22,23</sup> Instead of charge separation of an exciton and transfer of the electron from the monomer to the SnS<sub>2</sub> surface, the exciton may be efficiently transported along the polymer chain in systems such as (FAIPc)<sub>n</sub>. This decreases the rate of injection into the semiconductor, a process summarized recently by Spitler and Parkinson.<sup>19,20a,b</sup> A third reason for the lower efficiency is the likelihood of fast intersystem crossing between the singlet state of FAIPc and its triplet state, caused by the H aggregation.<sup>22</sup> It is not clear at present whether the formation of triplet states, which is favored in such linear cofacial phthalocyanine aggregates, would automatically mean that the photoelectrochemical efficiency of such a dye would be lowered. Some dyes which are known to form triplet states in high yield have nevertheless demonstrated good photoelectrochemical dye sensitization efficiencies.<sup>23</sup> Recent studies of cofacial silicon phthalocyanine dimers, which show many of the same spectral properties as the FAIPc aggregates, have shown that triplet state formation is indeed favored following excitation in the Q-band region, and that the energy of this triplet state is low—less than 1 eV above the ground state energy for the dye aggregate.<sup>24</sup> If we can assume that a similar energetic situation pertains for the FAIPc aggregates, the energy of the triplet states produced at the SnS<sub>2</sub> interface may be insufficient in energy to efficiently inject charge into the conduction band of this semiconductor. Further studies of the spectroscopic states of the FAIPc system are underway.

The 16 EQM thick film of FAIPc on SnS<sub>2</sub> has a photocurrent maximum of 635 nm (Figure 6) which is, within the error of this experiment, identical to the result for the 1 EQM film. There is a second maximum near 700 nm in the photocurrent experiment, which is not recognizable in the absorbance spectra shown above or in other FAIPc spectra acquired on SnS<sub>2</sub> crystals. This second peak may be explainable as arising from the photoelectrochemical activity of monomers (absorbance expected near 675 nm) present on the SnS<sub>2</sub> surface. As explained above, trivalent metal Pc monomers generally show a higher photoelectrochemical charge injection efficiency than oligomer/polymers, therefore even small amounts present in the film may be detected by photocurrent spectroscopy. Photocurrent spectroscopy is a more sensitive tool than absorbance spectroscopy for the determination of defects and alternate forms of dye aggregates on such a surface. These results suggest that, at low coverages (e.g., 1 EQM), FAIPc tends to aggregate at certain nucleation sites on the SnS<sub>2</sub> surface. As coverage increases but before the FAIPc thin film becomes completely continuous (e.g., ca. 16

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EQM), some FAIPc monomers may deposit on surfaces other than the nucleation sites, resulting in the photocurrent peak at 675 nm. The overall quantum yield per incident photon is smaller by a factor of 3 for the 16 EQM thick sample compared with the 1 EQM thick sample. This can be explained by the fact that only photons absorbed within the exciton diffusion length (typically 10–20 EQM)<sup>22</sup> can diffuse to the surface and inject electrons into the SnS<sub>2</sub> substrate. The presence of monomers proves that defects are present in the thick film, which will decrease the effective exciton diffusion length in the film and only a small percentage of the absorbed photons will contribute to the photocurrent. This results in a decrease of the quantum efficiency per incident photon and also per absorbed photon.

### Conclusion

We have shown that it is possible to obtain epitaxial FAIPc thin films on single crystal SnS<sub>2</sub>. The interaction between the flat-lying Pc molecules and the substrate appears to determine the epitaxial packing structure, even if another perpendicular Pc orientation would give a smaller lattice mismatch along one crystal axis. The reasonable ordering in these deposits is supported by STM views of these surfaces. This growth of flat-lying, linear cofacial Pc aggregates may be aided by the fact

that multilayer growth of such aggregates, with their long axis perpendicular to the substrate, does not require a packing architecture significantly different than the known bulk structures for this molecule. We have recently shown that for some phthalocyanines and perylenes, past the first 1–2 monolayers, the departure of the thin film architecture from the bulk packing arrangements of these molecules causes such lattice strain that significant structural rearrangements occur, causing loss of “layer-by-layer” growth conditions.<sup>12e,f</sup> This does not appear to be observed for FAIPc films until considerable thicknesses have been reached. Nonresonant  $\chi^{(3)}$  values and nonlinear optical decay times of such highly ordered thin films, from femtosecond pump–probe experiments, are currently under examination.

**Acknowledgment.** We gratefully acknowledge assistance from M. L. Anderson, P. Lee, M. Neely M. Malcomson, and K. W. Nebesny. A.S. wishes to thank the Alexander von Humboldt foundation (Feodor Lynen fellowship VB2 FLF). This research was partly supported by the National Science Foundation (Chemistry), the Air Force Office of Scientific Research, and the Materials Characterization Program—State of Arizona.

CM950208X