upon isomerization. Moreover, the cooperativity operative in $\mathbf{2}_{\mathrm{Fe}}$ results from the chiral interactions of one trigonal face predisposing the other toward assembling in an analogous fashion, thus enhancing the same metal chirality.

These results show that the amide proton is an important feature in the stability of metal complexes of enterobactin. The solid- and solution-state CD spectra of $\mathbf{2}_{\mathrm{Fe}}$ in combination with the crystal structure of $\mathbf{2}_{\mathrm{Fe}}$ confirm the Δ chirality for $\mathbf{Ent}_{\mathrm{Fe}}$. Most importantly, we have shown that, in an aqueous environment, complexes of labile metals of defined stereospecificity can be synthesized using simple bidentate ligands, relying solely on weakly polar interactions. Interactions peripheral to the immediate metal coordination environment measurably impact the selectivity and stability of metal complexes, suggesting new avenues in the design of stereospecific metal chelators.

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Supplementary Material Available: Synthetic details and tables of atomic coordinates and thermal parameters for $[\mathrm{Fe(S\text{-}(PhMe)_2TAM)_3}](\mathrm{Me_4N})_3$ and $[\mathrm{Fe(TrenCAM)}]\mathrm{K}_3$ (5 pages). Ordering information is given on any current masthead page.

A New Class of Organized Self-Assembled Monolayers: Alkane Thiols on GaAs (100)

C. Wade Sheen, Jing-Xuan Shi, Jan Mårtensson,[1]
Atul N. Parikh, and David L. Allara*

Department of Materials Science and
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received October 14, 1991

Self-assembled monolayers (SAMs) have been of intense interest in the past few years, but actual examples of highly organized films[2] are limited almost exclusively to those formed on oxide and coinage metal substrates, as shown by the major systems of alkylsiloxanes on natively oxidized $\mathrm{SiO_2}$,[3] *n*-alkanoic acids on natively oxidized Al[4] and Ag,[5] dialkyl disulfides,[6] dialkyl sulfides,[7] and alkanethiols on Au,[8] and alkanethiols on natively oxidized Ag.[9] Since a key potential application of SAMs is in chemically specific electrochemical and electronic devices, as demonstrated by the intense interest in applying the thiol/Au system to modified electrodes and sensors,[8a,b,10] it is notable that no examples of organized SAMs *bonded directly* to a bare semiconductor substrate surface have been reported. We now report the discovery of a new class of organized monolayers derived from the self-assembly of alkanethiols directly onto the bare GaAs (100) surface. That viable S/GaAs chemistry might exist to allow self-assembly has been indicated by current studies which show that room temperature coverage of GaAs by deposits of inorganic sulfide salts,[11] $\mathrm{P_2S_5}$,[12] and simple organothiol compounds (six carbons or less)[13] exerts significant effects on electron–hole pair recombination velocities. We have produced SAMs from alkanethiols, $\mathrm{X(CH_2)}_n\mathrm{SH}$ for $\mathrm{X} = \mathrm{CH_3}$ with $n = 11\text{–}21$ and $\mathrm{X} = \mathrm{CO_2H}$ and $\mathrm{CO_2CH_3}$ with $n = 15$. The bulk of our characterization has been on octadecanethiol (ODT, $\mathrm{X} = \mathrm{CH_3}$, and $n = 17$), and for brevity we focus on these results which show that the monolayer consists of a stable, highly organized assembly of tilted, conformationally ordered alkyl chains, chemically bonded directly to the bare GaAs surface.

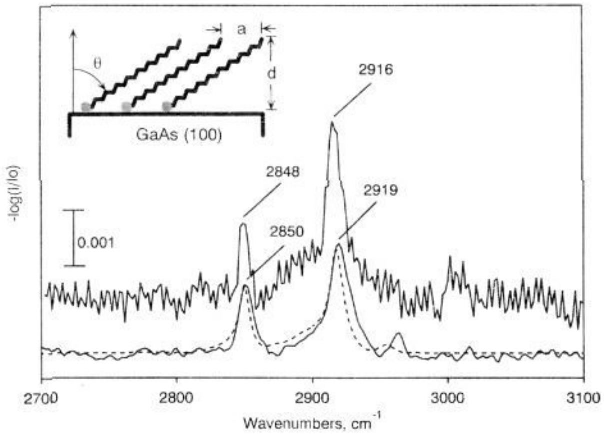

Figure 1. Infrared spectra of the C–H stretching modes for a self-assembled monolayer of ODT formed on both sides of a GaAs wafer with a (100) surface orientation. The lower plot is a transmission spectrum (solid line) and a simulation (dashed line) for an average single-chain structure with a chain tilt of 57° and a twist of 45°. The upper plot is the reflection spectrum taken at a 55° angle of incidence with a p-polarized beam. The intensity scales are in absorbance units for transmitted and reflected power, respectively, ratioed against a film-free sample. The inset at the upper left shows a schematic representation of a self-assembled monolayer of ODT on GaAs (100). The thickness (*d*), chain spacing (*a*), and chain tilt angle (*θ*) dimensions are shown. The balls at the surface represent sulfur.

Semiinsulating (dopant density 10^{15} cm^{-3}) *n*-type GaAs single crystals of (100) orientation and polished on two sides (Macom Co., Boston, MA) were washed with pure ethanol and exposed to UV light and ozone to remove trace organics.[14] The native

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[1] Permanent address: Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping (Sweden).

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surface oxide was stripped with concentrated HCl, to provide an arsenic-covered surface,[15,16] rinsed with pure water, and immediately placed in N_2-purged PTFE containers with enough ODT (Aldrich; recrystallized, mp 29.5–31.0 °C) to cover the wafer after the thiol melted. Heating at 100 °C for 5 h gives good quality monolayers; shorter reaction times or lower temperatures lead to incomplete, disordered monolayers. After extensive solvent (chlorobenzene, ethanol, water) washing the films were analyzed. Contrary to the observation with the Au system,[6] similar processing but with dialkyl disulfide does not result in monolayer formation.

Single-wavelength ellipsometry[4,8a] showed the films to have a reproducible thickness of 14 ± 2 Å. The transmission and reflection (55° angle of incidence, p-polarization) infrared spectra (2-cm^{-1} resolution) of the monolayer sample (Figure 1) show that the symmetric and antisymmetric CH_2 stretching modes are peaked at 2850 (transmission) and 2848 (reflection), and 2919 (transmission) and 2916 cm^{-1} (reflection), respectively. These frequencies strongly indicate a densely packed assembly of rodlike chains with a low degree of gauche defects.[8a,9d,17] When anisotropic (tensor) optical functions[9d,18] determined from crystalline $(C_{18}H_{37}S)_2$ are used, spectral simulations made for a 14-Å film show a best fit (Figure 1) to experiment[19] for an average chain tilt of 57 ± 3° from the surface normal with a chain twist of 45 ± 5°. For a fully extended chain structure of 26-Å chains the ellipsometric data give an average tilt of 57 ± 3°. The inset in Figure 1 shows the approximate configuration of the octadecyl chains as seen looking at a plane perpendicular to the surface and containing the chain. For $\theta = 57°$ the interchain spacing a in Figure 1 is 8 Å.[20]

High coverage of the surface by alkyl groups is evident from the oleophobic character of the surface, demonstrated by the observation of a contact angle (static pendant drop) of hexadecane equal to 41 ± 2°. In comparison, the densely packed films made from adsorption of $C_{18}H_{37}SH$ on Cu, Ag, and Au[9d] and of $C_{18}H_{37}SiCl_3$ on native SiO_2[21] show reported angles of 46° and 43°, respectively.[22]

A comparison of the X-ray photoelectron spectra[23] for a GaAs (100) substrate with native oxide (10 Å), an oxide-stripped surface, and an ODT monolayer stored in air for over 2 days shows that the ODT films impart a significant stability toward oxidation of the GaAs as evidenced by the significant drop in the intensities of the As 3d (45 eV) peak associated with oxide and the O 1s peak (532 eV) in the thiol-treated sample (we estimate less than about 3% of a monolayer of oxide even after the 2-days exposure). It has been shown by Sandroff and co-workers[24] that S–As bonds form as a result of aqueous sulfide ion treatment of the GaAs (100) surface, but even at the resolution of our measurements,[23] because of intrinsic line widths, the S 2p peak (165 eV) overlaps the Ga 3s peak (160 eV), precluding detailed interpretation of the interfacial bonding.[25] We note that the sulfide ion treated surfaces are not very stable toward oxidation.

From the point of view of potential chemical sensor applications, it is extremely important to note that we find, as with Au,[6,8d,26] a variety of functionalized surfaces can be prepared from $X(CH_2)_nSH$, where X is a common functional group such as OH, CO_2CH_3, and CO_2H. For example, for $X = CO_2H$ and $n = 15$ the resultant surface shows a pH-dependent contact angle curve which is qualitatively similar to that reported[27] for the film on Au, with an inflection point at about pH = 6.

Further studies on the structural chemical and electrical[28] aspects of these films are in progress and will be reported elsewhere.

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(19) The transmission experiment was simulated. The reflection experiment was not because of interference effects associated with the two-sided, parallel-face samples (optical cavity effects). However, the spectral peak frequencies are unaffected. Note that the simulated line widths are several wavenumbers less than the experimental, which suggests some subtle differences in chain structure between the monolayer and the bulk crystalline disulfide phase. Exploration of the details of the vibrational spectra are in progress.

(20) This structure is reasonably self-consistent on the basis of chemical bonding of the chains to a fixed As lattice with the tilt angles of the chains adjusting to achieve maximum packing. The lattice constant for the *fcc* zincblende crystal of GaAs is 5.63 Å. Given the 4.5-Å chain diameter, the first regular lattice upon which chains can fit on the (100) surface has first and second nearest neighbor spacings of 5.63 and 7.98 Å, respectively. Tilting of the chains exclusively along each of these two directions yields tilt angles of ~37° and 56°, respectively. The experimental results suggest tilting predominantly along the diagonal (7.98 Å) direction. However, some rotation of alignment toward the nearest neighbor direction is expected in order to maximize chain overlap. In-plane X-ray diffraction experiments are in progress to provide definitive structures.

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Water-Soluble Cyclophane Receptors with Convergent Functional Groups

Daniel R. Carcanague, Carolyn B. Knobler, and
François Diederich*

Department of Chemistry and Biochemistry
University of California at Los Angeles
Los Angeles, California 90024-1569

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During the past decade, we and others have prepared cyclophane receptors with apolar cavities which form stable inclusion complexes with apolar solutes in aqueous solution.[1] Here, we describe a new series of water-soluble cyclophanes featuring carbonyl or hydroxyl residues converging in a precise geometrical array into large apolar binding cavities.[2]

Schemes I and II show the short syntheses of the eight cyclophanes **1–8** via the novel spacers **11–14**.[3,4] In protonated form,

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