

Self-Assembled Hybrid Bilayers of Palladium Alkanethiolates

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Octane (C_8), dodecane (C_{12}), and hexadecane (C_{16}) thiolates of palladium, as well as their binary mixtures covering the entire range of compositions, have been prepared from organic media and characterized using powder X-ray diffraction (XRD), infrared spectroscopy (FTIR), and scanning tunneling microscopy (STM). All thiolates—mono as well as mixed—adopt bilayered lamellar structures as evidenced by XRD and STM. In monothiolates, the thickness of the bilayer as measured by the d_{001} spacing is governed by the length of the alkyl chain, while in hybrid bilayers, the thickness depends on the binary composition as well. In C_8 – C_{12} and C_{12} – C_{16} bilayers, in which the difference in the chain lengths of the constituent thiols is four methylene units, the thickness varies nearly proportionally to the weighted average of the chain lengths. In contrast, the C_8 – C_{16} system shows a steplike behavior with only a few compositions (C_8 , 60–80%) exhibiting intermediate d values. The alkyl chains are in all-trans conformation in monothiolates, while in hybrid bilayers, especially in C_{12} – C_{16} , gauche defects are observed, their concentration being the highest around 50:50 composition. Interestingly, these hybrid thiolates seem to provide adequate free volume to entrap small molecular species.

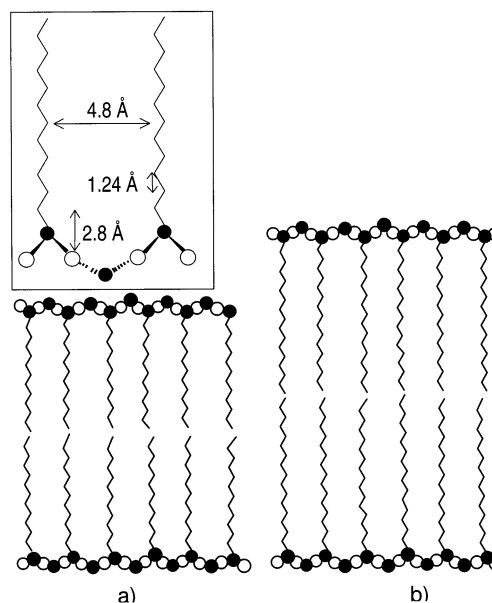
Introduction

Layered metal organics, more popularly known as “covalent soaps” have attracted wide attention since the first report on long-chain silver thiolates.^{1,2} Alkylthiolates of silver^{1–5} and copper,⁶ as well as carboxylates of silver,⁷ have been prepared as precipitates from organic solvents. They are layered structures (see Scheme 1) similar to lipid membrane bilayers. In all cases, simple linear relations have been derived between the layer thickness and the alkyl-chain length. On the basis of X-ray diffraction and IR spectroscopy, it has been well established that the hydrocarbon chains in these mesostructures adopt a fully extended all-trans conformation similar to the monolayers of alkane thiols on Au surfaces.^{8,9} The mesogenic thermotropic behavior of the metal thiolates have also been well established.²

Unlike the thiolates and the carboxylates mentioned above, long-chain palladium thiolates reported by us¹⁰ are unique among alkanethiolates in that they self-assemble in organic medium and remain soluble. The other known bilayer systems in organic media are perfluoroalkyl systems¹¹ and halo-bridged platinum composites¹² linked to long-chain phosphates. The hydrophobic interactions, which are the driving forces for the self-assembly of hydrocarbon chains in aqueous medium are absent in organic media because the chains are completely soluble in the latter. The organizations in organic media are, therefore, considered to be driven by enthalpy rather than entropy.¹³ With this knowledge, we considered it interesting to investigate the nature of the organization that would result when alkane chains of different lengths are introduced during the synthesis. While it is naive to expect a disordered structure, we thought that the self-assembling process may still be influential enough to bring together an organization that is hybrid yet crystalline.

A few mixed bilayers such as fullerene–lipid bilayer films¹⁴ and asymmetric phosphatidylcholines¹⁵ with two different acyl

SCHEME 1: A Schematic Illustration of the Structure of Palladium Alkanethiolates (a) C_{12} and (b) C_{16} ^a



^a Alkane chains of the thiols arrange themselves in all-trans conformation into bilayer structures separating rows of sulfur (●)-bridged Pd atoms (○). The bilayer thickness is estimated on the basis of the known thickness of the C–μS–Pd motif and the number of methylene units assuming no interdigitation of the chains. The inset shows one structural motif. Only long-chain thiols ($>C_4$) tend to form such lamellar structures. Butanethiolate complex remains amorphous, while shorter chain thiolates crystallize out into hexameric ring structures.¹⁰

chains are known. On the other hand, there have also been several investigations on mixed hydrocarbon systems in the form of self-assembled monolayers on metal surfaces and two-dimensional condensates. For example, Whitesides and co-workers^{16–19} obtained mixed monolayers of alkane thiols on

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gold and characterized them by X-ray photoelectron and infrared spectroscopy, as well as by contact angle measurements. They found preferential adsorption of the longer chain thiols, an observation that goes well with the strong tendency of the longer chains to self-assemble. Some evidence for the aggregation of individual component thiols on a molecular scale was found although a clear phase segregation into macroscopic islands was not observed. In regions where the two thiols coexisted, the terminal portion of the longer chain that extends beyond the terminus of the shorter chain was found to be disordered. The authors suggested that, by using chains of different lengths, it is possible to control the degree of disorder in the monolayers and to introduce free volume in the outer part of the monolayers, where the chains are disordered. The adsorption behavior of binary mixtures of *n*-alkanes of different chain lengths on graphite surface has been studied by calorimetric and neutron scattering measurements.^{20,21} Generally, the two alkanes were found to be phase-separated except in the case of a mixture of octane and nonane molecules at low coverages, which formed a mixed solid monolayer. In an interesting report on the formation of a mesoporous silica, Ulagappan and Rao²² used a template consisting of supramolecular organization of alkanes and a surfactant, hexadecyltrimethylammonium bromide, in which the alkane molecules containing 8–14 methylene units formed a core surrounded by a layer of the surfactant molecules with a one-to-one alignment of the alkane chain and the surfactant tail.

In this paper, we report the results of our investigations on the structure of palladium thiolate containing two different alkane chains, based on powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning tunneling microscopy (STM) measurements. Three binary alkane thiol systems, octane–dodecane (C_8 – C_{12}), dodecane–hexadecane (C_{12} – C_{16}), and octane–hexadecane (C_8 – C_{16}), were studied covering the entire composition ranges. Our study has shown that crystalline mesostructures ascribable to hybrid bilayers are formed with no phase separation into individual thioliates.

Experimental Section

The procedure adopted here for the synthesis of mixed palladium thioliates is similar to the one reported for the monothioliates.¹⁰ A toluene solution (5 mM) containing the desired molar ratio of the two alkane thiols was added to a toluene solution of palladium acetate (4.5 mM, 5 mg in 2 mL of toluene). The resulting solution was stirred for a few minutes. Following the reaction, the solution became viscous and the yellow color deepened to orange yellow. The acetic acid released was washed away with water, and the organic layer was dried over $MgSO_4$. Various binary combinations—10:90, 20:80, 30:70, 40:60, and 50:50—of octane (C_8), dodecane (C_{12}), and hexadecane (C_{16}) thioliates were prepared. The obtained thioliates were freely soluble in organic solvents such as toluene, methanol, and heptane.

X-ray diffraction patterns were obtained using Siemens Seifert 3000TT diffractometer employing $Cu\ K\alpha$ radiation. A film obtained by evaporating a few drops of the toluene solution on the glass slide and subsequently annealing at 60 °C for 30 min was used for XRD measurements. Fourier transform infrared measurements were done using an IFS66v/s Bruker spectrometer with a resolution of 2 cm^{-1} . Samples for infrared measurements were prepared by evaporating a few drops of the thiolate solution in toluene on a dry KBr pellet. Scanning tunneling microscopy was carried out using a Digital Instruments Quadrex Multimode microscope attached to a Nanoscope-IV SPM controller.

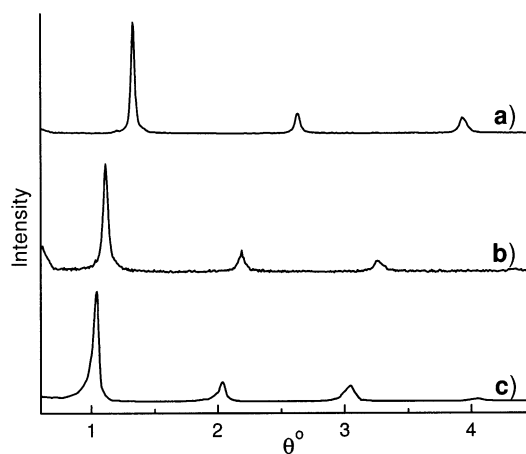


Figure 1. XRD patterns of the palladium thioliates: (a) C_{12} monothiolate; (b) C_{12} – C_{16} (50:50) mixed thiolate; (c) C_{16} monothiolate.

Samples for imaging were prepared by depositing a droplet of the dilute thiolate dispersion on a freshly cleaved highly oriented pyrolytic graphite (HOPG) surface.

Results and Discussion

In Figure 1, we show the X-ray powder diffraction pattern obtained with $Pd-(C_{12})_{0.5}(C_{16})_{0.5}$ mixed thiolate, along with those of dodecane and hexadecane monothioliates. Here, it is appropriate to discuss the structure of the monothioliates in some detail. The *d* spacings of the Bragg peaks vary as 1:2:3 and so on. For example, the pattern obtained from dodecanethiolate (Figure 1a) exhibits peaks with *d* values of 34.11, 17.11, and 11.04 Å corresponding to the (001), (002), and (003) reflections, respectively. The (001) reflection, which is a direct measure of the bilayer thickness,^{1,10} increases from 34.11 Å in case of dodecanethiolate to 44.03 Å in the case of hexadecanethiolate. The increase is linear with a slope of 2.48 Å per methylene unit and an intercept of 5.62 Å. The values of the slope reported previously for silver thioliates and carboxylates are 2.42 and 2.50 Å, respectively.^{1,7} The structure of the headgroup is ascertained from the intercept. Based on a search through the Cambridge structural database²³ for unstrained sulfur-bridged Pd motifs containing C–S bonds (including palladium ethylthiolate and *n*-propylthiolate), we obtained the length of the C– μ S–Pd motif along the C–S bond as 2.79 Å, which compares well with one-half of the experimental intercept (5.62 Å). The van der Waals radius of the methyl end group is taken to be 1.69 Å.¹ Thus, the calculated projected lengths of octane-, dodecane-, and hexadecanethioliates are 11.94, 16.90, and 21.86 Å, respectively. The observed layer thickness may differ slightly from the estimated value because of small interdigitation of the hydrocarbon chains up to 0.5 Å.⁷ Besides, the layer thickness is also sensitive to the annealing conditions; a variation up to 1 Å has been observed routinely by us. A schematic illustration of the structure of the monothiolate is given in Scheme 1.

It is interesting that the mixed thiolate shows a progression of intense reflections similar to monothioliates with their *d* spacings varying as 1:2:3. The diffraction peaks, therefore, correspond to (001), (002), and (003) reflections of a lamellar mesophase, involving two chains per diffracting unit. The d_{001} spacing is found to be 39.7 Å in the case of the mixed thiolate C_{16} – C_{12} , 50:50. It nearly corresponds to the mean value of the d_{001} spacings of the individual monothioliates, 34.11 (C_{12}) and 44.03 Å (C_{16}). The subsequent reflections, d_{002} and d_{003} of the mixed thiolate, also follow a similar trend. Thus, the intermediary *d* spacings and their intensity patterns indicate the presence

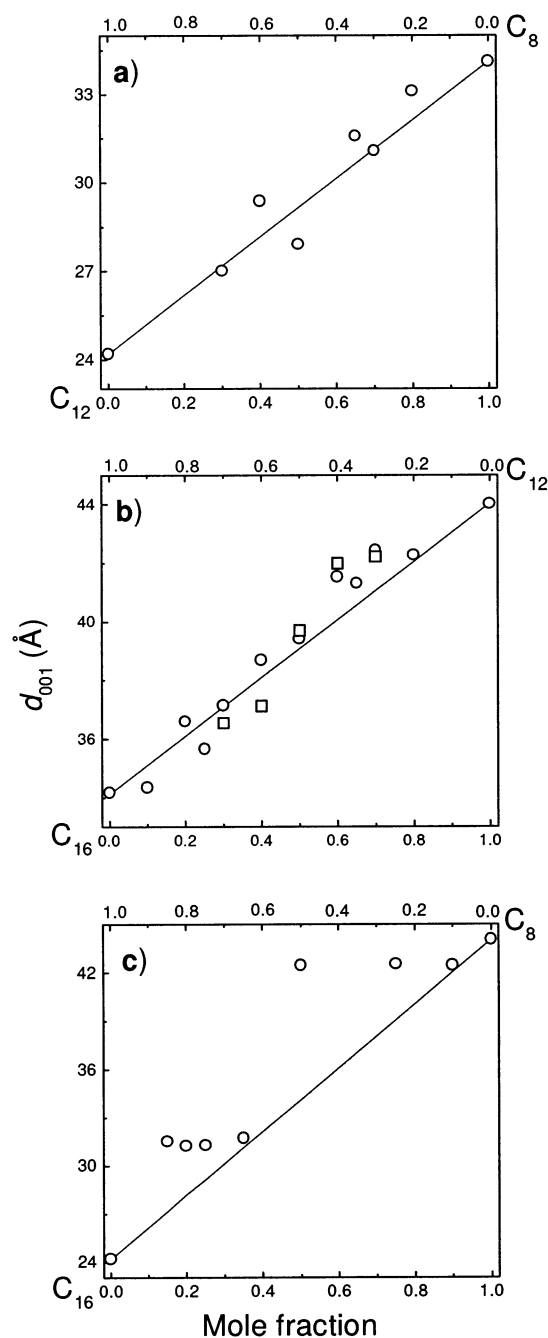
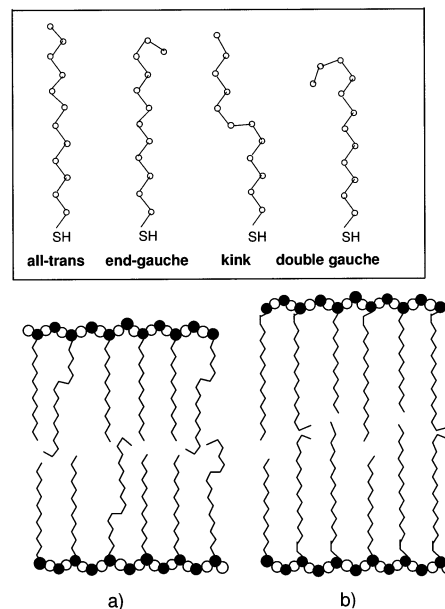


Figure 2. Variation in the d_{001} spacing for the three mixed thiolates with composition (a) C_8-C_{12} , (b) $C_{12}-C_{16}$, and (c) C_8-C_{16} . Circles denote the experimental data points. The straight lines represent hypothetical bilayers with d_{001} spacings obtained as weighted averages of the chain lengths of the two constituent thiols plus the $C-\mu S-Pd$ layer thickness. To ascertain the reproducibility in experiments, a few compositions of $C_{12}-C_{16}$ were repeated (squares).

of a true hybrid phase. We have been successful in preparing hybrid thiolates with various compositions of $C_{12}-C_{16}$ thiols, as well as by employing C_8-C_{12} and C_8-C_{16} thiol mixtures. It is noteworthy that the hybrid thiolates, when prepared using the toluene solution, contained no noticeable trace of the constituent monothiolate phases. But in highly polar solvents such as acetonitrile, palladium thiolates are insoluble and the XRD patterns from the precipitates showed broad features and even peaks corresponding to monothiolates. Thus, it appears that the solubility of the thiolate plays an important role in determining the formation of hybrid nanocomposites.

SCHEME 2: A Schematic Illustration of the Structures of Mixed Palladium Thiolates of the $C_{12}-C_{16}$ System, (a) C_{12} -rich and (b) C_{16} -rich^a



^a Here, the bilayer thickness corresponds to the weighted average of the chain lengths of the component thiols plus the $C-\mu S-Pd$ layer thickness. The C_{16} chain adopts disordered conformations to self-assemble into a hybrid bilayer. The C_{12} chain remains defect-free. The inset shows the various defective conformations of the alkyl chains.

Figure 2 shows the variation in the d_{001} spacing with the thiol composition for the three binary systems, C_8-C_{12} , $C_{12}-C_{16}$, and C_8-C_{16} . The first two systems, in which the constituent thiols differ by four methylene units, the d spacing increases gradually as the mole fraction of the longer chain thiol increases. This behavior may be compared with an "ideal" situation in which the two types of molecules organize cooperatively incorporating several defects (Scheme 2), such that the resulting bilayer thickness is simply an average of the chain lengths of the two molecules weighed with composition, plus a $C-\mu S-Pd$ layer thickness of 5.62 Å. We see from Figure 2a,b that within the experimental uncertainty, the experimental values more or less follow "ideal", except at higher concentrations of the longer thiol, where the values are slightly on the higher side. This deviation may be due to the reluctance of the longer chain to accommodate a larger number of defects, especially when their population is high. Yet, it is interesting that both systems show a clear tendency to self-assemble, a behavior that is typical of long thiols.⁹ The C_8-C_{16} system, however, behaves somewhat differently (see Figure 2c). The d value shows a steplike variation and reaches saturation at 50:50 composition, closely matching that of the C_{16} monothiolate. Intermediate d spacings are seen only in C_8 -rich compositions (>60%), beyond which the C_{16} thiol dominates the bilayer organization. It is possible that higher disparity in the chain lengths (8 methylene units) and the relatively lower tendency of the C_8 thiol to self-assemble may be the cause of such a behavior.

STM imaging revealed a large number of string-like features generally in bunch, four or five, extending a few tenths of nanometers in both mono and mixed thiolates. As examples, we show the images obtained with C_{12} thiolate and a mixed thiolate ($C_{16}-C_{12}$, 50:50) in Figure 3. The typical width of the strings of the C_{12} thiolate (Figure 3a) was measured to be ~ 34 Å, closely matching with the bilayer thickness found by XRD. Scanning in smaller regions showed that each string consisted

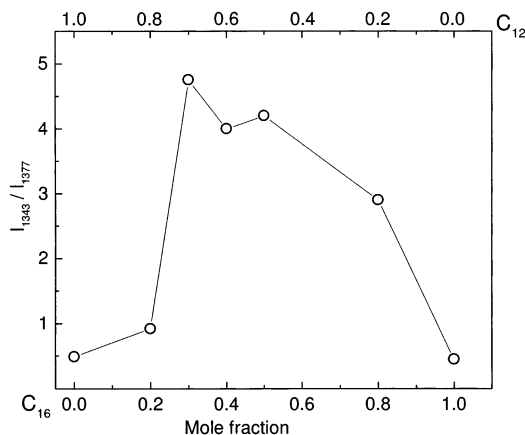


Figure 5. Variation in the ratio of the intensities of the end gauche mode (1343 cm^{-1}) and the methyl umbrella mode (1377 cm^{-1}) with the composition of the C_{12} – C_{16} mixed thiolate.

thiol that accommodates these defects to form crystalline mesophases with intermediate layer thicknesses. At higher proportions of C_{16} , for which the layer thickness approaches that of the C_{16} monothiolate, the defect concentration also decreases gradually. Apart from the above wagging modes, the spectra also exhibit weak bands at 1301 and 1365 cm^{-1} due to W_{g-t-g} ,^{8,28–30} indicating the presence of a very small population of kinks in the chain.

A series of peaks observed between 1000 and 1150 cm^{-1} are assigned to the skeletal $C-C-C$ vibrational modes (R_x), while the progression bands in the region 700 – 980 cm^{-1} are assigned to the rocking modes (P_x) of the methylene chains.³² The main band at 720 cm^{-1} is the head band of the rocking progression. This band is present in all of the cases, whereas the progression series gets diminished in the case of mixed thiolates. A weak peak observed at 646 cm^{-1} is assigned to the $C-S$ stretch to an adjacent gauche methylene unit, $\nu(C-S)_g$.³ The $\nu(C-S)_t$, which is expected at 719 cm^{-1} , is obscured by the rocking head band.

An interesting observation that follows from the infrared spectra of the C_{12} – C_{16} system (see Figure 4) is the existence of a strong peak at 1577 cm^{-1} in the spectra of mixed thiolates (spectra g, h, and i) that is absent in the case of the monothiolates (spectra f and j). The peak at 1577 cm^{-1} is assignable to the antisymmetric stretching of acetate groups.^{32,33} Further evidence for the presence of an acetate group in the mixed bilayer is drawn from the observation of a distinctly high-intensity region around 1420 cm^{-1} , which is unusual for methylene deformation (which occurs at around the same position). This is taken to correspond to the symmetric stretching of the acetate group. The extra features at 682 and 620 cm^{-1} in the case of mixed thiolate are assignable to the bending modes of the acetate group. These infrared signatures are clearly not due to the liberated acetic acid, for it was carefully washed away while depositing the bilayer film. Moreover, the $C=O$ stretching band of free acetic acid, if present, would appear at 1730 cm^{-1} , distinctly different from the observed bands.³² The presence of acetate groups amidst the crystalline bilayers is indeed surprising. It arises possibly because of the incomplete displacement of the acetate groups of the palladium acetate by thiols. However, this is not the case with compositions rich in C_{12} ($>70\%$). The spectrum of the C_{12} – C_{16} 80:20 thiolate shown in Figure 5 is completely devoid of the acetate modes. Such is the case with all compositions of the other two (C_{12} – C_8 and C_8 – C_{16}) mixed thiolate systems (see Figure 6).

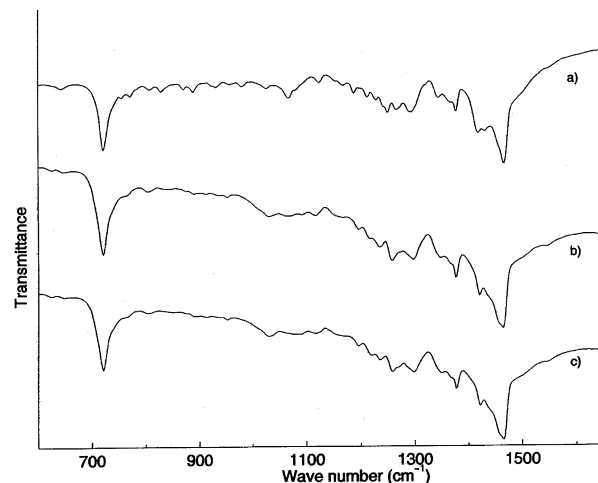


Figure 6. FTIR spectra of mixed palladium thiolates: (a) C_{12} – C_{16} (80:20); (b) C_8 – C_{12} (50:50); (c) C_8 – C_{16} (65:35). Spectra b and c are only representative; indeed all compositions of C_8 – C_{12} and C_8 – C_{16} systems showed no modes corresponding to the acetate group.

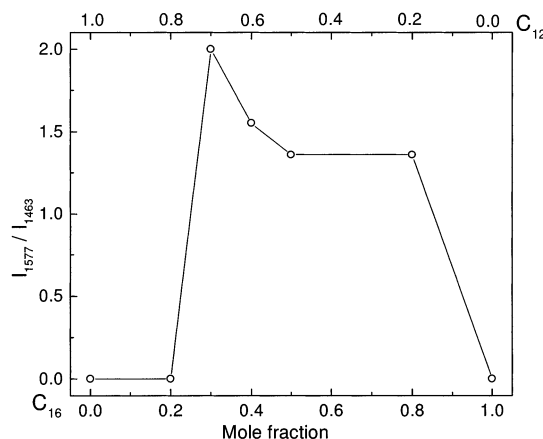


Figure 7. Variation in the ratio of the intensities of antisymmetric stretching mode of the acetate group (1577 cm^{-1}) and the methyl scissoring mode (1463 cm^{-1}) with the composition of the C_{12} – C_{16} mixed thiolate. This is taken as a measure of the relative population of undisplaced acetate groups that are present in the bilayer.

On the basis of the above observations and in the absence of any kinetic or mechanistic details of the reaction, we speculate that following the palladium acetate and thiol reaction, some sort of rudimentary assembly builds up spontaneously in solution in which some acetate groups from the palladium acetate precursor may get trapped and become inaccessible for further reaction (even after refluxing the toluene solution of thiolate for extended hours). The population of the undisplaced acetate groups for different compositions of the C_{12} – C_{16} system was calculated from the intensity ratio I_{1577}/I_{1463} (Figure 7). It is remarkable that the acetate group population nearly mimics the population of the end gauche defects (compare Figures 5 and 7). The amount of acetate retained by the structure depends on the composition of the C_{12} – C_{16} mixed thiolate; those containing the C_{16} thiol at 30% or greater carry a relatively higher population of the acetate. In contrast, monothiolates of C_{12} and C_{16} , as well as their mixed thiolates rich in C_{12} ($>70\%$), fail to accommodate the acetate groups in the bilayer structure (see Figures 4, 6, and 7). Thus, the two factors—readiness to assemble and adequate disorder leaving some free volume—seem to be important in providing shelter to the acetate groups. The C_{16} thiol in combination with small amounts of C_{12} does it well. It has been suggested in the literature^{1,19} that it may be

possible to trap solvent molecules in the voids between alkyl chains of thiolates. The mixed thiolates presented above provide excellent experimental evidence.

In summary, our study has shown that palladium thiolates self-assemble into hybrid bilayered mesophases when a mixture of thiolates is employed. The hybrid thiolates are crystalline and consist of layered structures of which the thicknesses, as measured by the d_{001} spacings, are intermediate to the corresponding monothiolates. The bilayer thickness and the internal structure depend on the chain lengths of the constituent thiols and more so on the difference in the chain lengths. When the difference is four methylene units as in C_8-C_{12} and $C_{12}-C_{16}$ systems, the bilayer thickness varies continuously with the composition of the thiol mixture. The layer thicknesses closely follow the estimated values, obtained as the weighted averages of the thicknesses of the corresponding monothiolates. When the disparity of the thiol chain lengths is high, as in the case of the C_8-C_{16} system (eight methylene units), bilayers with intermediate layer thicknesses were found only with C_8 -rich (>60%) compositions. Below 60%, the layer thickness was nearly equal to that of the C_{16} monothiolate. STM images of both mono- and mixed thiolates showed string-like features extending to tens of nanometers, the widths matching closely the layer thickness obtained from XRD. The monothiolates consist of highly ordered chains in a fully extended all-trans conformation. All of the hybrid structures, in contrast, consist of disordered chains with fair amounts of gauche defects and kinks. The concentration of defects varies with the composition of the thiol mixture. At a few specific compositions, the $C_{12}-C_{16}$ bilayers incorporate acetate groups in an unusual environment. Thus, the composition and the disparity in the chain lengths of the constituent thiols are the important experimental parameters that govern the structure of the resulting hybrid bilayer.

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