

HREELS Study of Self-Assembled Monolayers of Alkylthiols Functionalized with Oligothiophene Moieties: Extreme Surface Analysis and Evidence for Intermolecular Interactions

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SAMs (self-assembled monolayers) of alkanethiols functionalized by α -terthienyl (3T-SAMs) and α -quaterthienyl (4T-SAMs) were formed on a gold surface presenting (111) terraces and studied by high-resolution electron energy loss spectroscopy (HREELS). The angular width of the elastic peak leads to a domain size of ca. 90 Å, comparable to that of the Au(111) terraces of the substrate. Enhancement of the spectral resolution by using a new generation spectrometer enables the improvement of the spectral analysis in the energy range of the vibrational losses. A detailed analysis of the differential cross sections of the different vibrational peaks indicates the nature of their mechanisms: impact mechanisms show that the extreme surface of the monolayers is mainly constituted by thienyl moieties with the thienyl density in 3T-SAMs higher than that in 4T-SAMs; dipolar mechanisms show that molecules are standing up slightly tilted on the substrate; a resonance via a negative ion formation was detected around 4.5 eV. On the other hand, the electronic excitation domain leads to excitonic gap values of 2.62 ± 0.08 and 2.90 ± 0.08 eV for 4T-SAMs and 3T-SAMs, respectively. A sharp feature located at 0.28 ± 0.08 above the electronic threshold was detected in the 3T-SAM spectra. This feature, also appearing in the spectra of the α -oligothiophene evaporated films, is here assigned to a vibronic excitation. Its intensity is always related to the organization degree of the SAMs. An additional band without equivalence in the optical spectra appearing in the 4T-SAM and 3T-SAM HREELS spectra with thresholds at 3.58 ± 0.08 and 4.15 ± 0.08 eV, respectively, is assigned to the electronic gap. The values of the excitonic and electronic gaps are well correlated with those found in the corresponding spectra of evaporated α -quaterthiophene, α -quinquethiophene, and α -sexithiophene films formerly studied. These results lead to the conclusion that thienyl functionalities present strong intermolecular interactions.

Introduction

A modern way of inserting particular chemical groups onto a surface is the use of the self-assembled monolayer (SAM) methodology.¹ In this technique, specific functions are previously incorporated in a molecule provided with a reactive anchorage group (thiols are commonly used) and an alkyl spacer to enable the self-organization of the monolayer. Typical examples are alkylthiols containing aliphatic chains terminated by a specific functionality, which can assemble on different substrates (Au, Ag, Pt, GaAs, etc.) to form densely packed, well-oriented monolayers. The new properties of the functionalized surface will essentially depend on the chemical nature, the orientation, and the intermolecular interactions existing at the extreme surface. The self-assembling process is at variance with the spontaneous entanglement of the alkyl

chain spacers, so that a few hours are needed for the molecules to self-organize. Recently, SAMs of α -quaterthiophene-terminated thiols on gold were studied.² The formation of such assemblies was followed by various techniques of analysis including high-resolution electron energy loss spectroscopy (HREELS). After a long adsorption step of about 12 h, during which molecular arrangement takes place, well-assembled monolayers exposing the thienyl groups at the extreme surface of the ultrathin film could be obtained. This kind of system can be considered as a good model to test the capabilities of HREELS as a method to analyze functionalized surfaces and particularly SAMs. In fact, the analysis of such assemblies is not easy because the quantity of material involved is quite small. Thus, surface analysis techniques can give a good contribution to the study of SAMs whereas traditional methods requiring a more significant amount of matter are quite inefficient. In the last years, HREELS has been revealed as an exceptionally useful tool for this kind of investigation.³ Being one of the most surface sensitive spectroscopic techniques,⁴ HREELS can respond to the SAM analysis requirements: chemical nature of the functionalized surface (chains versus thienyl moieties); molecular orientation; organized domain size; surface electronic excitations.

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In a typical HREELS experiment, a monokinetic electron beam probes the surface region exciting vibrational modes⁴ and electronic states⁵ or even ionizing the molecular film.⁶ The electron backscattering may be described by three specific interactions: dipolar, impact, and resonance:

The dipolar mechanism involves long-range interactions between the incident electron and the transition dipoles present at the surface. Typical distances range from a few tens to a few hundreds of angstroms. Provided that the energy and momentum transfers are small compared to the energy and momentum of the incident electron, the process is very similar to those observed in optical spectroscopy. Backscattered electrons are only slightly deviated from the specular direction. Consequently, when applied to monolayers on conducting surfaces, the selection rules are quite similar to those of RAIRS (reflection-absorption infrared spectroscopy): only modes having transition moments with components perpendicular to the substrate can be excited. Thus, dipolar interactions give information on the orientation of molecular groups in the monolayer.

In contrast, the impact mechanism, which occurs typically at distances of the order of a few angstroms, privileges the sensitivity to the first molecular groups directly exposed to the film-vacuum interface.⁷ The short-range character of the interaction results in a quasi-isotropic backscattering with an information depth of the analysis lower than 10 Å.⁸ Impact energy losses, fundamentally occurring at the extreme surface of the film, enable the analysis of its chemical composition, enhancing the modes of the bonds that are preferentially exposed to the vacuum.

Resonances are a particular case of impact backscattering, where the short-range interaction leads to the creation of a transient negative ion.

Thus, energy losses induced by dipolar and impact interactions furnish different kinds of information about the surface of the organic monolayers, namely, the chemical nature of the extreme surface or the orientation of the molecules or more specifically of the moieties included. Therefore, one needs to determine the nature of the corresponding electron interaction mechanisms. This task is simple with ordered surfaces covered by small molecules where dipole interactions give rise to narrow intense angular lobes centered on the specular direction, whereas those produced by impact are isotropically backscattered.⁴ Unfortunately, SAMs are fundamentally constituted by long molecules distributed in ordered and disordered domains, these latter scattering electrons out of the specular direction. The angular lobes of the electrons

elastically backscattered by SAMs are consequently broadened. In fact, SAM domain sizes have been estimated from this typical angular broadening.⁹ Moreover, the transition dipoles of the moieties at the extremity of the long molecules can be sufficiently far from their images in the metal substrate to invalidate the selection rules for dipolar interaction. Therefore, geometrical considerations may lead to erroneous conclusions when used to distinguish long- and short-range backscattering mechanisms. An alternative methodology consists of analyzing the dependence of the differential cross section (DSCS) on the energy of the incident electron, E_p . As described in the literature,⁴ the DSCS follows a $(E_p)^\delta$ law with $\delta = -1$ for the dipolar mechanism and $\delta = 1$ for the impact mechanism. Explicitly, the DSCS of dipolar processes decreases with the incident electron energy E_p , while that of impact scattering increases. Resonance processes have Lorentzian dependences.⁴ Hybrid situations also exist, where the excitation of a vibrational mode can be induced by both dipolar and impact interactions. In this case, the DSCS has an intermediate dependence.¹⁰

For higher energy losses, involving few electronvolts, electronic excitations are produced by impact scattering, since both energy and momentum transfers represent a large part of the energy and momentum of the incident electron. Furthermore, in short-range interactions, the incident electron can cause distortions of the molecular orbital or suffer electron exchange processes enabling the observation of dipolar forbidden transitions. This has been observed in HREELS spectra of various polymer films such as polystyrene,¹⁰ polyphenylsilanes, and polyphenylsiloxanes,¹¹ where triplet and singlet states of the benzene pendant groups appear through a sequence of peaks roughly 0.5 eV wide. In this case, where individual electronic excitations of the phenyl groups are detected, we may consider that these chemical groups are dispersed and are not interacting with each other. In addition to this individual behavior, these data also proved that incident electrons are capable of promoting electronic interband transitions typical of the solid state. As a result, values of the energy gap of these polymer films were evaluated from the HREELS spectra. In contrast, spectra recorded with evaporated oligothiophene films (nT , n standing for the number of cycles) do not exhibit this individual character of the aromatic cycles. Instead, they are dominated by wide bands with thresholds corresponding to the gap values^{12–15} revealing, in comparison to the pendant groups above mentioned, strong crystalline effects. These values are in agreement with those obtained by optical methods on single crystals.¹⁶ As a result, HREELS can be expected to help for a detailed description of the electronic structure of a surface modified by a specific

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functionalization. In particular, this enables determination of whether the functional groups are submitted to strong or weak intermolecular interactions.

Recently, it was shown that in 12 h adsorbed SAMs of α -quaterthienylalkanethiol, most of the thienyl groups are assembled at the extreme surface.² The choice of this polyene analogue was driven by the fact that electron transitions in the oligothiophene family have been the subject of many experimental and theoretical studies over the last 15 years. To account for data on isolated molecules, various quantum mechanical approaches have been used: semiempirical calculations (AM1 and ZINDO/S,¹⁷ CNDO/S),¹⁸ intermediate neglect of differential overlap (INDO) with a multireference double configuration interaction (MRD-CI),¹⁹ ab initio at the complete active space self-consistent field approximation,²⁰ and time-dependent density-functional theory (TDDFT).²¹ These calculations were compared to UV/vis absorption data in the gas phase²² and in solution in various solvents such as dioxane,^{18,23,24} dichloromethane,²⁵ *n*-hexane,²⁶ benzene,²⁷ cyclohexane, ethanol, and water.²⁸ On the other hand, oligothiophenes were also studied through UV/vis absorption and fluorescence spectroscopy using both thin films and single crystals.^{16,29,30} Theoretical calculations helped in elucidating the nature of the lowest excited state by estimating a Davydov splitting, DS, thus emphasizing the crucial role of intermolecular interactions. DS values recently reported in the literature for 4T single crystals range from 0.3³¹ to 1.1 eV.³² Charge transfer states were also invoked to account for electroabsorption spectroscopy data,³³ although such an explanation still remains controversial.^{30a}

The present study deals with the HREELS characterization of the electronic structure of Au(111) surfaces

covered with SAMs of α -terthienylhexanethiol (3T-SAMs) and α -quaterthienyldodecanethiol (4T-SAMs) and, more precisely, with the interaction among the thienyl functionalities placed at the film–vacuum interface. Both vibrational and electron transitions are studied and compared to the optical and HREELS spectra of α -oligothiophene (*n*T) evaporated thin films previously studied.^{12–14} It is shown that the energy thresholds of electronic excitations of these *n*T-SAMs exhibit a similar dependence versus the conjugated chain length of the oligothiophenyl moieties. The role of intermolecular interactions is discussed.

Experimental Section

Samples. Synthesis of α -thiophene derivatives (12-(2,2':5',2'':5'',2'''-quaterthien-5-yl)-dodecanethiol and 6-(2,2':5',2'':5'',2'''-terthien-5-yl)-hexanethiol) and the preparation of 4T-SAMs were described elsewhere.^{2,34,35} Gold substrates ca. 100 nm thick were supplied by Metallhandel Schröer GmbH and flame annealed to obtain Au(111) terraces. STM (scanning tunneling microscopy) and grazing incidence X-ray diffraction (GIXRD) studies of such substrates show that hydrogen flame annealing produces terraces of (111) having a mean linear dimension around 80 Å. 4T-SAMs and 3T-SAMs were prepared by immersion of the substrates in the corresponding 1 mM solutions of thiols in pure dichloromethane for 12 h and then rinsed in an ultrasonic bath for 2 min. As concluded before,² after a 12 h adsorption, the extreme surface of 4T-SAMs is nearly completely covered (>99.5%) by the thienyl moieties with their axes standing slightly tilted relative to the substrate.^{34,36} For the 3T-SAMs, the coverage is 99.5% after 2 h.³⁷ To avoid surface contamination, freshly prepared samples were then sealed in an argon atmosphere and introduced into the HREELS ultrahigh vacuum (UHV) chamber under a nitrogen flux.

Apparatus. Two different HREELS spectrometers were used: HREELS vibrational spectra were recorded using a LK Technologies ELS3000 spectrometer for 3T-SAMs and an ELS22 Leybold-Heraeus spectrometer for 4T-SAMs. A specular geometrical arrangement was employed with incidence and analysis angles of 60°. The primary electron energy, E_p , ranged from 1.5 to 5 eV, and the analyzer acceptance angle was $\pm 1.5^\circ$. In this case, resolution was of the order of 3 meV taken as the full width at half-maximum (fwhm) of the elastic peak after reflection on the sample.

Electron energy losses corresponding to electronic transitions were recorded using a LK2000R spectrometer. E_p ranged from 0 to 10 eV. Sweeping steps were smaller than 4 meV for all spectra. Spectral resolution was around 13 meV for all samples. Considering the spectral analysis, one can expect the threshold measurement uncertainty to be contained in ± 0.08 eV.

Vacuum was better than 10^{-9} mbar. No irradiation damage was observed during the measurements.

Results and Discussion

Elastic Peak and Local Order. From the intense elastic peaks of the HREELS spectra, one can infer that surfaces of the SAMs are particularly smooth. In fact, for smooth ordered surfaces, the elastic backscattered electrons are mostly contained within a narrow solid angle of a few degrees. In HREELS, the elastic electron scattering

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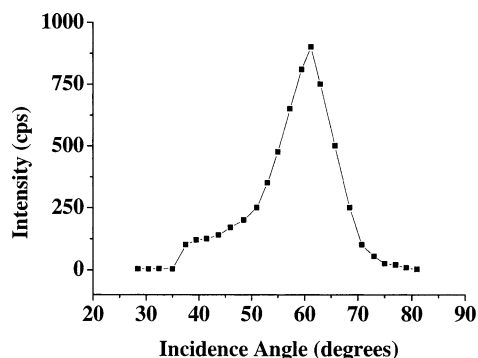


Figure 1. HREELS angular dependence of the elastic peak backscattered from a 3T-SAM using $E_p = 5$ eV incident electron energy.

engenders a sharp Bragg diffraction at an ordered surface and a more diffuse elastic intensity distribution if the surface is disordered. A quantitative estimation of the surface roughness can be associated to a coherent characteristic length evaluated from the HREELS experimental parameters.³⁸ This length was later related to the grain size of the monolayer by Pireaux et al. who correlated widths of the angular lobes to structural characteristics of the SAMs and, namely, to the size of the molecular domains.⁹ The mean diameter D of the domains for different SAMs has then been estimated from the angular dispersion $\Delta\theta$ of the elastic peak.⁹

$$D \cong \lambda/2 \Delta\theta \cos \theta$$

where λ is the wavelength of the incident electron, θ is the incidence angle, and $\Delta\theta$ (expressed in radians) is the fwhm of the angular dispersion of the elastic peak after subtraction of the spectrometer angular dispersion.

The angular dependence of the elastic peak backscattered from 3T-SAMs using $E_p = 5$ eV is presented in Figure 1. In this case, the $\Delta\theta$ of elastic peak angular dispersion is about 10° , leading to domain sizes around 90 Å, which are just about the dimensions of the gold (111) terraces. This value is also of the same order of magnitude as those obtained for similar systems.⁹ In summary, one should expect the existence of dense molecular packing of oligothiophene SAMs in local ordered domains with $D = 90$ Å mean size.

Vibration Losses. The 3T-SAM and 4T-SAM vibrational spectra recorded with $E_p = 5$ eV are displayed in Figure 2. Note that the spectrum of 3T-SAM was recorded with a new generation apparatus, LK3000. This resulted in a noticeable improvement of the resolution, 17.8 cm^{-1} , as compared to that of 4T-SAM, around 116 cm^{-1} . Accordingly, more than 15 bands could be detected on the 3T-SAM spectrum, while 4T-SAM exhibits only 9 assignable bands. Table 1 compares the positions of the main features appearing in both HREELS spectra to those of the Raman and infrared spectroscopy of oligothiophenes and thiophene³⁹ and those of the infrared spectrum of 3T-SAMs.^{36d} The aliphatic chain contributions⁴⁰ are indicated in bold.

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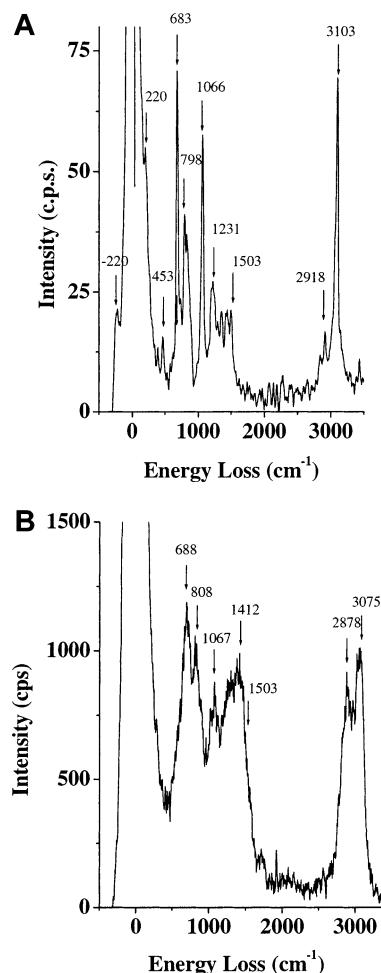


Figure 2. Vibrational HREELS spectra recorded with $E_p = 5$ eV for incidence and analysis angles of 60° : (a) 3T-SAMs recorded with a resolution of 2.32 meV (17.8 cm^{-1}); (b) 4T-SAMs recorded with a resolution of 14.5 meV (116 cm^{-1}).

Table 1. Assignment of HREELS Peaks of 3T-SAMs and 4T-SAMs by Comparison with Those Found in Infrared and Raman Spectroscopy (in cm^{-1}) (References 36d and 39)^a

HREELS				assignments
3T-SAM	4T-SAM	IR	Raman	
220				ν S–Au, stretching (refs 41, 42)
453		450		ring deformation
683	688	688	695	ω_2 C α –H, out-of-plane deformation
734		720		aliphatic CH₂ rocking
				twisting
798	808	791		ω_3 C β –H, out-of-plane deformation
831	825	832	833	C–S, stretching
862		852		ν_8 C α –H, bending + C α –S, deformation
1066	1067	1066		ν_6 C α –H + C α –H, bending
				aliphatic ν C–C stretching
1231		1216	1218	ν_4 C β –H, bending
1358	1307	1378	1367	ν_3 C α =C β , symmetric stretching
1419	1412	1425		ν_2 C α =C β –H, symmetric stretching
1440		1450	1449	ν_2 C α =C β –H, symmetric stretching
				aliphatic ν CH₂, scissoring
1503	1503	1503		ν_1 C α =C β –H, asymmetric stretching
2843	2878	2851		ν_s aliphatic CH₂, stretching
2918		2920	2920	ν_{as} aliphatic CH₂, stretching
3067	3075	3073	3071	ν_0 C β –H, stretching
3103		3105		ν_0 C α –H, stretching

^a Peak positions corresponding to the vibration modes of the aliphatic chain (ref 40) are indicated in bold.

In the 3T-SAM spectrum, one can clearly observe a weak energy loss and the corresponding energy gain located around 220 cm^{-1} . These features have been assigned in

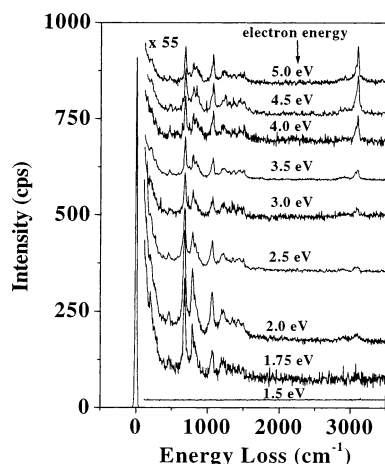


Figure 3. Vibrational HREELS spectra of 3T-SAMs at increasing E_p , recorded for incidence and analysis angles of 60° . For a better observation, the intensity in the loss region was magnified by a factor of 55 and a setoff was introduced to separate the different spectra. Note that the improved resolution of the 3T-SAM spectrum results from the use of a new generation spectrometer.

the literature to the stretching mode of the S–Au bond.^{41,42} As this interfacial bond is buried in the monolayer, we can conclude that Au–S mode excitation is produced by a dipolar interaction mechanism of the incident electron with the transition dipole of the bond. This energy loss is not visible in 4T-SAMs veiled by the extended tails of the elastic peak, probably due to the longer spacer of the molecule.

For higher energy losses, thiophene C–H bonds in α positions possess characteristic intense peaks more precisely around 683 and 3103 cm^{-1} assigned to the out-of-plane (oop) C–H deformation and C–H stretching modes, respectively; those corresponding to β positions are located around 798 and 3067 cm^{-1} , respectively.⁴³ The chain contributions, namely, those of the C–H stretching region around 2900 cm^{-1} , are very weak in 3T-SAMs but stronger in the 4T-SAMs. Globally, both spectra are mostly dominated by important energy losses associated with the thienyl functions, while peaks corresponding to the alkyl chain are comparatively weaker.

Figure 3 displays a series of vibrational HREELS spectra of 3T-SAMs recorded with E_p ranging from 1.5 to 5 eV in specular geometry. One can observe the evolution of the intensity of the different peaks versus the energy of the incident electrons. No energy losses appear for $E_p = 1.5\text{ eV}$, showing that this energy stays below any vibrational excitation threshold.

Considering the length of the SAM molecules, we can expect the transition dipole and its image in the metallic substrate to be far away from each other, invalidating the selection rules for dipolar interaction. Consequently, near the specular direction, electrons having suffered impact interactions may be predominant, broadening the angular lobe. In the present case, the fwhm of the angular lobe is $\Delta\theta = 10^\circ$. This is a good reason for performing an energy analysis instead of using geometrical arguments.

The DSCS values of the C–H out-of-plane deformations (683 and 798 cm^{-1}) and C–H stretching at 3103 cm^{-1} , taken as the ratio between the intensity of the loss peak

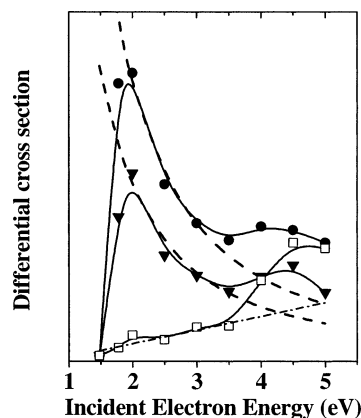


Figure 4. Cross sections for vibrational losses of 3T-SAMs as a function of the incident electron energy of 683 cm^{-1} (●) and 798 cm^{-1} (▼) C–H out-of-plane deformations and 3103 cm^{-1} (□) C–H aromatic stretching superposed to a $1/E_p$ (dashed line) and an E_p linear (dotted line) function, respectively.

and that of the elastic peak, are displayed in Figure 4 as a function of E_p . The experimental points are fitted by a cubic B-spline function for guiding the eye and compared with $1/E_p$ and E_p functions. One can observe that the DSCS associated with the C–H stretching always increases with E_p . Moreover, a Gaussian-like contribution appears centered between 4 and 5 eV with a maximum at $\sim 4.5\text{ eV}$ and a fwhm of $\sim 2\text{ eV}$, typical of a resonance mechanism via a transient negative ion created by the incident electron capture.³⁸ In fact, for aromatic systems temporary negative ions have been observed in this energy domain.⁴⁴ This analysis confirms the strong short-range character existing in the C–H stretching region, revealed by the linear dependence on E_p . In contrast, the DSCS of the oop C–H deformation modes for values of E_p far from the threshold decreases with $1/E_p$, also presenting the same resonance described above. This shows that a marked dipolar character is associated with the C–H oop deformation modes below 3 eV , while a hybrid interaction appears at higher values. Focusing attention on the spectral domain of the ν C–H stretching region of Figure 2a with a maximum at 3103 cm^{-1} , one can observe a strong signal proportional to the mean surface density of thienyl C–H bonds present at the extreme surface of the monolayer. This corroborates other results previously published for 4T-SAMs² consistent with an assembly process with a fast and blocking adsorption, followed by a slow assembling of the 4T moieties at the surface with a high coverage after a 12 h adsorption. As a matter of fact, it was observed in spectra of 4T-SAMs, for increasing adsorption times, that thienyl stretching peaks increase, whereas those of the aliphatic chain decrease, proving that thienyl groups gradually emerge at the extreme surface of the film from the inner layer with their long axes standing up on the substrate, covering the aliphatic spacers. Similarly, in the 12 h adsorption 3T-SAMs analyzed here, thienyl groups mostly cover the extreme surface of the monolayer. Anyhow, a tiny contribution of the aliphatic chain is detected in the HREELS spectra. Moreover, the intensity ratio between thienyl and methylene stretching peaks, markedly much larger than the stoichiometric ratio in the case of 3T-SAMs, indicates a higher surface density of the thienyl moieties relative to that of 4T-SAMs. Besides, as in Figure 2a, the most intense stretching peak located at 3103 cm^{-1} is associated to $C_\alpha\text{--H}$,³⁹ and one must

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Table 2. Intensity of C α -H and C β -H oop Peaks Normalized to That of C-H Stretching^a

samples	C-H out-of-plane deformation contributions			
	683 cm ⁻¹ C α -H	793 cm ⁻¹ C β -H	sum C α -H + C β -H	ratio, <i>r</i> C α -H/C β -H
3T-SAM	0.92	0.20	1.12	4.60
4T-SAM	0.95	0.27	1.22	3.52
6T/Au	0.67	0.24	0.91	2.79
6T/HOPG	2.84	4.23	7.07	0.67

^a Their corresponding sums and ratios are also indicated.

conclude that molecules are preferentially assembled with their extremities pointing at the vacuum interface.

Concomitantly, molecular orientation can also be inferred from the intensity of the different oop C-H deformation peaks. This is clear from the analysis of Table 2, where relative intensities of the C α -H and C β -H oop deformation modes of the 3T-SAMs and 4T-SAMs are compared with those obtained in previous studies on sexithiophene evaporated films on gold (6T/Au) and highly oriented pyrolytic graphite (HOPG).^{43,45} In fact, C-H stretching vibrations are induced by pure impact interactions (see Figure 4), and their intensity can be assumed to be proportional to the density of thienyl groups at the surface. All data are obtained from spectra recorded with the same spectrometer (ELS 22) using the same experimental conditions. With HOPG, it has been shown that 90–95% of the molecules have their axes parallel to the surface, whereas on gold presenting aliphatic hydrocarbon contamination, 6T molecules are expected to be nearly normal to the substrate. This latter case is consistent with substrates having weak interactions with the π electrons. Contributions due to oop C-H deformation energy losses were evaluated using a Gaussian profile for fitting and normalizing to those of thienyl C-H stretching intensities. All data are obtained from spectra recorded with the same spectrometer (ELS 22) using $E_p = 5$ eV and the same geometrical configuration. It is noticeable that the values corresponding to 3T-SAMs and 4T-SAMs are manifestly weaker than those of 6T/HOPG but of the same order of magnitude as those of 6T/Au, excluding a preferential orientation of the thienyl groups parallel to the substrate. This is consistent with perpendicular components of the momentum transfer that are much smaller in the case of both SAMs than those corresponding to the 6T films on the HOPG substrate. Consequently, as the transition moments are perpendicular to the plane of the molecules, one must conclude that 3T-SAMs and 4T-SAMs are standing up on the substrate. This is coherent with RAIRS measurements in the region of the C=C stretching leading to values around between 15° and 20° for 4T-SAMs⁴⁶ and 14° for 3T-SAMs.^{36d}

Furthermore, Table 2 also shows that excluding the films of 6T/HOPG the relative intensity for oop C α -H deformation energy losses is always higher than for C β -H, despite the higher number of C β -H bonds. This corroborates the hybrid character of the interaction with a short-range component, so that C α -H bonds, closer to the vacuum interface, are preferentially probed rather than the more buried C β -H bonds. This conclusion substantiates the above analysis of the stretching regions confirming the presence of C α -H bonds in the vacuum interfacial region. In contrast, an inverse situation occurs

for 6T/HOPG films, where the high component of the transition dipole moment, perpendicular to the surface, strongly responds to the electron interaction, independently of the C-H position. In this case, the peak corresponding to the oop C β -H deformation is more intense, because C β -H bonds are more numerous.

Finally, taking into account the sum of oop C-H deformation contributions one should still conclude that thienyl moieties are more tilted in 4T-SAMs than in 3T-SAMs and less tilted in any of the SAMs than in 6T/Au. Moreover, the ratio between C α -H and C β -H oop energy loss intensity, excluding the case of 6T/HOPG, is always higher than 1 (Table 2). These observations are coherent with molecules standing up on the substrate in the case of the 3T-SAMs, 4T-SAMs, and 6T/Au and lying flat in the case of 6T/HOPG. As the oop transition moments of C α -H and C β -H are comparable and the ratio of the corresponding peak intensities ($r = C_{\alpha\text{-H}}/C_{\beta\text{-H}}$) is very different from the ratio between the number of oscillators, an important short-range contribution (as is also shown from the cross section analysis) must exist. This also reveals the presence of C α -H at the extreme surface of SAMs, as the incident beam probes preferentially the most exposed bonds and less the more buried ones. One should also conclude that r will increase when the longitudinal molecular axis is more perpendicular to the substrate and decrease when it is more parallel. For example, in the case of 6T/HOPG, the fact that r is lower than 1 corresponds to molecules lying flat. In this case, all oscillator transition moments are perpendicular to the substrate and the interaction in specular geometry has a strong dipolar character. The peak intensity mainly depends on the number of oscillators. Consequently, it is expected that $r < 1$, as experimentally observed.

In conclusion, the analysis of the 3T-SAM and 4T-SAM HREELS spectra in the vibrational range shows the following:

A strong supremacy of energy loss peaks corresponding to the thienyl functionalization exists relative to those of alkyl chains of thiols, which are less intense.

3T-SAM and 4T-SAM spectra exhibit strong energy losses characteristic of oop C-H deformation and stretching modes of the thiophene C-H groups.

Taking into account the nature of the high surface sensitivity of the impact interactions and the relative intensity of the alkyl and thienyl C-H stretching, one must conclude that thienyl groups constitute to a great extent the extreme surface of the 3T-SAMs and to a lesser extent that of the 4T-SAMs.

The molecular orientation deduced from oop C-H deformation bands, by comparison with those of evaporated *n*T films, is compatible with thienyl moieties standing up and slightly tilted relative to the substrate.

Electronic Losses. Figure 5 compares two complete spectra of the electrons backscattered by an evaporated film of 4T on gold (4T/Au) and a 4T-SAM sample. Both spectra were recorded using $E_p = 5$ eV and incidence and analysis angles of 60° and 30°, respectively. The intensity axis is normalized to the elastic peak and represented in a logarithmic scale. The exponential tail below 2 eV results from multiple scattering events in the surface region superposed with the individual vibrational losses analyzed above.

At higher energy loss, the first striking feature of the 4T-SAM spectrum emerging with a threshold **G**₄ at 2.62 ± 0.08 eV fits well with that observed in the HREELS spectra of 4T/Au.¹³ In these former studies, **G**₄ was

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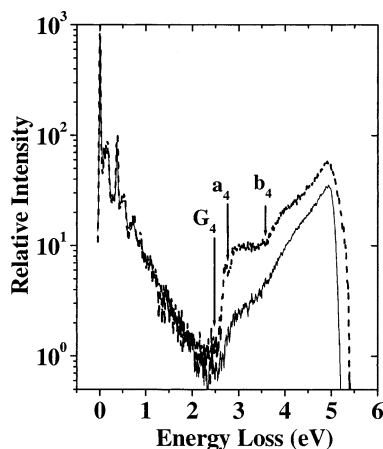


Figure 5. Complete HREELS spectra for 4T-SAMs (solid line) compared to 4T thin film (dashed line) obtained using $E_p = 5$ eV with an incidence angle of 60° and an analysis angle of 30° . The intensity axis is represented in a logarithmic scale. Arrows indicate the position of excitation threshold G_4 located at 2.62 ± 0.08 eV, the feature a_4 at 0.20 ± 0.08 eV from G_4 , and the secondary emission threshold b_4 at 3.58 ± 0.08 eV.

assigned to the excitonic gap, which means that 2.62 ± 0.08 eV is the minimal energy necessary to create an exciton.

That the values of the excitonic gap are identical, within the experimental error, in the 4T/Au and in the 4T-SAMs is not surprising, owing to the reported DS values, S , which range from 0.3 to 1.1 eV as cited above. According to GIXRD measurements, the mean average intermolecular distance found in 4T-SAMs is 10.8% larger than that found in the 4T single crystal.⁴⁶ The corresponding decrease of the Davydov splitting, ΔS , can be evaluated from the electrostatic dipole–dipole interaction,⁴⁷ given by

$$\Delta S = 3S \Delta r/r$$

where r is the intermolecular distance. Therefore, one can expect a total change of DS varying from 0.09 to 0.3 eV. Given the asymmetry of the splitting, larger for the upper state than for the lower one, less than half of the total splitting is expected for the lower level deviation, which is of the same order of magnitude as the measurement accuracy.

Since the excitation of the lower Davydov component is optically forbidden but is observed in HREELS, the electron interaction mechanism must necessarily contain a strong impact character. Such an interpretation is also confirmed by the good superposition of G_4 on the energy loss of the very low intensity peak, corresponding to the forbidden transition and barely observed in the UV/vis absorption spectra of single crystals at low temperature.^{30b} As a matter of fact, electronic transitions induced by electrons, transferring large amounts of momentum compared to the initial ones, as is here the case, are predominantly created by an impact mechanism.

In the 4T/Au HREELS spectrum, the band with threshold G_4 exhibits a sudden rise of intensity followed by a plateau, which may be attributed to a relatively uniform density of states. In contrast, the 4T-SAM spectrum presents a gradual rise, without a plateau. This may be associated with the existence of domains with different sizes, resulting in a rather heterogeneous density of states.

The fact that the 4T-SAM signal is weaker than that of the evaporated film can be in part explained by the lower density of the oligothiophene moieties in the surface region. Moreover, the contribution of impact scattering from the more internal thienyl moieties in the evaporated film could explain, at least partly, the higher intensity in the 4T/Au than in the SAMs. In fact, multiple short-range scattering occurring in the surface region of the film implies a penetration process followed by escape, both involving roughly exponential laws. This contribution from the inner layers was confirmed in previous studies, where the impact mechanism was the predominant process, either in the vibrational⁴⁸ or in the electronic domain.⁴⁹

The narrow peak a_4 , observed in the 4T/Au spectrum around 0.20 ± 0.08 eV above G_4 , does not appear in the 4T-SAM spectrum. Similar structures were also observed in the 5T/Au and 6T/Au spectra,¹³ as well as in the 6T/Au UV/vis absorption spectra,¹⁴ and were assigned to the upper Davydov component, that is, to $1a_g \rightarrow b_u$.¹³ The DS value is, anyhow, quite controversial, and theoretical calculations are still in progress.⁵⁰ Besides, it is also hard to understand why in 4T-SAMs, the lowest level of DS (excitonic gap) is not changed, while the highest level of DS disappears. Equivalent fine structures are well-known from UV/vis spectroscopy. For instance, the precipitation of soluble poly(3-alkylthiophenes) with alkyl side chains longer than butyl is accompanied by the growth of some sharper (fine structure) peaks in the UV/vis spectra. Given their sharpness, these peaks were interpreted as a vibronic coupling between the $\pi-\pi^*$ electronic transition and C=C stretching mode located at 1503 cm^{-1} (~ 0.19 eV), the latter known to occur in well-ordered poly(3-alkylthiophenes).⁵¹ It is then more tempting to assign the narrow peak a_4 to a vibronic structure rather than to the highest DS level transition. Anyhow, the presence of this feature in the HREELS spectra is always correlated to a high degree of molecular order, which is demonstrated by the vibrational analysis described above. In fact, in a disordered system, the large number of defects broadens the distribution of the electronic states hiding the vibronic structure.⁵² Therefore, the absence of this feature in the 4T-SAMs should imply a lower degree of organization, suggesting that intermolecular interactions among thienyl groups are weaker than those in the evaporated film or even in 3T-SAMs, as will be shown below. This is in agreement with the GIXRD measurements,⁴⁶ implying a lower molecular density of the thienyl moieties in the outermost region of the 4T-SAMs than that found in 4T/Au. Thus the intermolecular interaction among the thienyl moieties on the surface of 4T-SAMs becomes about 60% of that of the single crystal, according to the van der Waals interaction dependence on the sixth power of the distance. Nonetheless, this decrease of the intermolecular interaction does not affect the HREELS spectra, since both the ground and excited electronic levels may be affected by an energy deviation of the same order of magnitude.

A third feature, with a threshold located at b_4 , appears for energy losses above 3.58 ± 0.08 eV. This new threshold was assigned to the electronic gap corresponding to the minimum energy necessary to ionize an exciton.¹³ However, a transition to the upper Davydov component could

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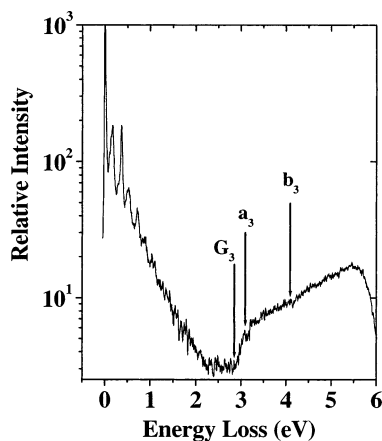


Figure 6. Complete HREELS spectrum of 3T-SAMs (solid line) obtained using $E_p = 6$ eV. The intensity axis is represented in a logarithmic scale with an incidence angle of 60° and an analysis angle of 30° . Arrows indicate the position of the excitation threshold at $G_3 = 2.90 \pm 0.08$ eV and the feature a_3 at 0.28 ± 0.08 eV from G_3 followed by a second threshold b_3 at 4.13 ± 0.08 eV.

also be possible. This feature arising at b_4 is present both in 4T/Au and in the 4T-SAM spectra.

Figure 6 displays a HREELS spectrum of 3T-SAMs using $E_p = 6$ eV. No comparison with 3T-evaporated films is possible because the vapor pressure of 3T is too high to stand under UHV. 4T-SAMs and 3T-SAMs present strong similarities, namely, the existence of an excitonic gap, the narrow peak in the rising part of the band and the electronic gap. In the case of 3T-SAMs, G_3 is located at 2.90 ± 0.08 eV and a_3 at 0.28 ± 0.08 eV above G_3 . If a_3 corresponds to the vibronic feature, its appearance also discloses, as discussed above, a high molecular organization comparable to that of the crystalline phase. Finally, the electronic gap, b_3 , appears at 4.13 ± 0.08 eV.

The above considerations sustained for 4T-SAMs can also be raised for 3T-SAMs and point to a higher degree of molecular organization in this system. Measuring the intensity of the electronic transition in the spectra of 3T-SAMs (Figure 6) and 4T-SAMs (Figure 5), we observe that they are more intense in the 3T-SAM than in the 4T-SAM spectrum but weaker than those appearing in the 4T/Au spectrum. Assuming that the DSCS values are not very different, one should conclude that the average intermolecular distance should be smaller in 3T-SAMs than in 4T-SAMs, but larger than in the 4T/Au. The more intense and well-resolved thienyl bands, compared to those of the aliphatic chain, found in the vibrational HREELS spectra of 3T-SAMs also support a better organization of the 3T-SAMs, when compared with 4T-SAMs. This results likely from the different length of the aliphatic spacer (longer in 4T-SAMs). This conclusion is in opposition with the formation of methyl-terminated SAMs, where the role of the aliphatic chain is crucial, as the intermolecular force is proportional to the chain length.⁵³ In the present case, the 4T-SAM, which has the longest chain, is less organized than the 3T-SAM. This leads us to the conclusion that van der Waals interactions deriving from the aliphatic chain are not crucial in the arrangement of the functionalized layer.

As neither single crystals nor 3T evaporated films could be studied by HREELS, linearity of the excitonic and of the electronic gaps versus the inverse of the ring number ($1/n$) will be analyzed. In Figure 7, three straight lines A,

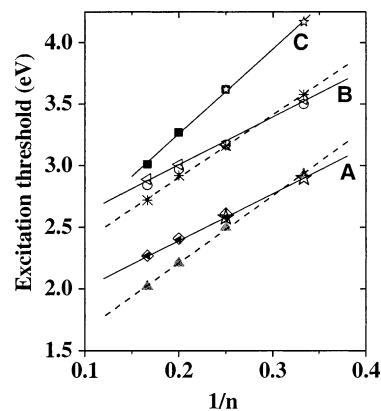


Figure 7. Electronic excitation thresholds of oligothiophenes as a function of the inverse of the number of rings $1/n$: (A) Excitonic threshold energy of condensed oligothiophenes calculated by TDDFT ($\blacktriangle$) [ref 21] and measured from UV/vis absorption of the single crystal ($\diamond$) [ref 30], from HREELS spectra of evaporated thin film (left-pointing solid triangles) [ref 13] and from 3T-SAM and 4T-SAM samples (stars). (B) Electronic excitation threshold of the isolated molecule calculated by INDO/MRD-CI ($*$) [ref 19] and measured from UV/vis absorption spectra in dioxane solution ($\circ$) [refs 18, 23, and 24] and in benzene solution (left-pointing open triangles) [ref 27]. (C) Electronic threshold energy from HREELS spectra of evaporated thin film ($\blacksquare$) previously published [ref 13] and from 3T-SAM and 4T-SAM samples (stars).

B, and C summarize the main results obtained concerning the thresholds of the main electronic excitations found for n T isolated molecules, films, and single crystals compared with those found for 3T-SAMs and 4T-SAMs.

A. Excitonic gaps in the solid phase calculated by TDDFT (π),²¹ measured from UV/vis absorption of the single crystal,³⁰ from HREELS spectra of evaporated thin film,¹³ and from 3T-SAM and 4T-SAM samples. Linear fitting yields the equation

$$y = 5.46/n + 1.12$$

with a correlation coefficient $r = 0.9995$.

B. Electronic excitation thresholds of isolated molecules of α -oligothiophene calculated by INDO/MRD-CI¹⁹ and measured from UV/vis absorption spectra in dioxane^{18,23,24} and benzene solutions.²⁷ Linear fitting for HREELS data versus $1/n$ yields the equation

$$y = 5.10/n + 1.88$$

with a correlation coefficient $r = 0.9994$.

C. Electronic gaps from HREELS spectra of evaporated thin films previously published.¹³ Thresholds of electronic transition in the solid film, comprising the values already obtained for excitonic and electronic gaps and those of the isolated molecules, are displayed versus the inverse of the number of rings. Linear fitting for HREELS data versus $1/n$ yields the equation

$$y = 6.92/n + 1.87$$

with a correlation coefficient $r = 0.9994$.

Comparing these values, one must conclude that measured thresholds for the α -oligothiophene moieties in 3T-SAMs and 4T-SAMs are well correlated with those of the 4T, 5T, and 6T solid films and single crystals. Consequently, one can conclude that in the 3T-SAMs and 4T-SAMs the moieties interact in a similar way as those in the solid phase showing strong intermolecular interactions in 3T-SAMs and 4T-SAMs, but stronger in 3T-SAMs than in 4T-SAMs.

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In summary, the examination of the HREELS spectra in the electronic transition range shows the following:

There is a strong similitude between the SAMs studied and evaporated films of the corresponding oligothiophenes.

4T-SAM spectra exhibit an important threshold at 2.62 ± 0.08 eV, located at the same position as in the 4T evaporated film, which is assigned to the excitonic gap between the ground state and the lowest Davydov level. This observation indicates the existence of strong intermolecular interactions of the same magnitude as those existing in the polycrystalline films. For 3T-SAMs, the threshold observed at 2.90 ± 0.08 eV is in agreement with the value expected from a threshold variation versus $1/n$ (n being the number of thiophene rings in the molecule or thienyl group).

The 3T-SAM spectrum also presents a very sharp feature appearing at 3.17 ± 0.08 eV, which is here assigned to a vibronic transition. This transition, also present in evaporated films, had been differently assigned in previous works to a transition to the upper Davydov component, that is, to a $^1a_g \rightarrow b_u$ transition. Its absence in 4T-SAM spectra combined with an observed excitonic gap in agreement with those of the oligothiophene films favors the "vibronic hypothesis". Whatever the origin of the hump and taking into account that this feature is not clearly present in the spectrum of the 4T-SAMs, one must conclude that the moieties' organization is weaker in SAMs than in the evaporated film and is weaker in 4T-SAMs than in 3T-SAMs.

The 4T-SAM spectra exhibit a much weaker cross section for the first exciton transition than that observed in the evaporated polycrystalline thin films, whereas the 3T-SAM spectra present an intermediate magnitude. This last observation corroborates the conclusions concerning the density of thienyl functions in n T-SAMs inferred from the vibrational HREELS analysis.

Conclusions

Surfaces functionalized by SAMs of thiols containing α -oligothiophene moieties (3T and 4T) were studied using HREELS and exploiting the complete domain of energy loss of the backscattered electrons. The analysis of the elastic peak angular dispersion confirms a local organization with mean domain sizes comparable to the terrace

dimensions of about 90 Å. Dipolar and impact losses coexisting in the vibrational domain of the spectra were identified. The information extracted from impact losses appearing in the vibrational spectra shows that thienyl groups constitute to a great extent the extreme surface of the 3T-SAMs. In contrast, the 4T-SAM spectra exhibit a stronger contribution of the aliphatic chain at the surface, but still inferior to that of the thienyl moieties. On the other hand, an orientation of the thienyl moieties standing up slightly tilted on the substrate could be extracted from the analysis of the dipolar losses. This orientation is consistent with the values found in the literature.

The analysis of the energy range of electronic losses shows that the 4T-SAM has excitonic and electronic gap values equal to those previously found for the corresponding evaporated film on gold (4T/Au). The intensity of these bands is of the same order of magnitude, showing that the analyzed depth is comparable in both systems. The 3T-SAMs also exhibit the same bands with thresholds matching those found from the extrapolation for oligothiophene films. 3T-SAM spectra also reveal a sharp structure formerly observed in n T evaporated films, which is assigned here to a vibronic transition. The absence of this transition in the 4T-SAMs means a lower degree of SAM organization in agreement with the conclusions from vibrational energy losses.

In summary, we can conclude that SAMs are constituted by a monolayer of thienyl groups formed by nanometric organized domains, where intermolecular interactions are similar to those of the solid state, separated by disordered zones. These organic semiconducting monolayers separated by an insulating spacer from the metal substrate seem thus to be good models for organic-inorganic electronic devices. As a final point, this study also corroborates the richness and the capabilities of HREELS in the analysis of organic monolayers and specifically of SAMs.

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