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Langmuir, 1997, 13 (21), 5602-5607 • DOI: 10.1021/la970493u

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Self-Assembly of Photoluminescent Copper(I)–Dithiol Multilayer Thin Films and Bulk Materials

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Received May 12, 1997. In Final Form: August 4, 1997[®]

Self-assembled multilayer thin films have been prepared on Au and mercaptosilanized glass substrates by alternate surface derivatization with Cu²⁺ ion and alkanedithiols. The films deposited on glass show intrinsic orange-red photoluminescence and were studied by fluorescence spectroscopy. A strongly photoluminescent solid was also obtained by reaction of 1,6-hexanedithiol with cupric perchlorate in ethanolic solution. Multilayer structures on Au were studied by ellipsometry and X-ray photoelectron spectroscopy (XPS). Both in the solid material and in the self-assembled thin films, XPS measurements suggest Cu is present in the +1 oxidation state. This was also confirmed by cyclic voltammetry of Cu ion adsorbed to a self-assembled monolayer of 1,6-hexanedithiol on gold. Metal–metal interactions in the form of clustering might contribute to the unusual photophysical properties observed in both types of materials.

Introduction

Self-assembled monolayers (SAMs) of organic thiols on Au have been studied extensively over the past 14 years,¹ while considerably less work has been reported on the self-assembly of multilayer thin films. Such systems are of particular interest for their potential applications in nonlinear optics² and molecular electronics, since complicated structures can be designed and prepared with molecular precision. Among the different approaches leading to well-defined multilayer assemblies,³ methods based on the ionic interaction between the constituents have resulted in particularly stable and easy to prepare systems. Mallouk and co-workers developed this construction strategy by exploiting the strong ionic binding between zirconium ion and organic phosphonates.^{3b,c} Their method leads to successive multilayer formation simply by alternate immersion of a suitably functionalized substrate in solutions containing ZrOCl₂ and a bis-(phosphonic acid), respectively. Several different systems based on this principle have since been reported. A recent variation on this theme consists of multilayer self-assembly by alternate derivatization of an amino-functionalized silicon surface with cobalt ion and diisocyanobenzene.^{3g}

The findings reported in this paper are closely related to the work of Ulman and co-workers,⁴ who described a method for multilayer formation based on the interaction of Cu²⁺ ion with carboxylic acids and thiols. In their work, bifunctional compounds containing both a thiol and a

carboxyl group were attached to a Au substrate via their thiol functionality, followed by reaction with a solution containing Cu²⁺ ion to form a Cu carboxylate at the surface of the SAM. A subsequent layer of bifunctional molecules is then formed with preferential attachment to the Cu carboxylate via the thiol functionality, thus resulting in multilayer structures of Cu sites sandwiched between the carboxyl and the thiol groups of the bifunctional molecules (Figure 1). The question of whether Cu is present in the +1 or +2 oxidation state has been controversial, but the more recent work suggests the +1 state.^{4b} We address this problem again and, as shown below, suggest that Cu ion is adsorbed to the carboxyl surface as Cu(II) but is subsequently reduced to Cu(I) upon binding to the thiol. A detailed XPS study also shows that reduction of Cu(II) can occur to a substantial extent in the X-ray beam during the examination of the sample by XPS.

The main result we report here is that multilayer thin films are also formed on Au and mercapto-functionalized glass surfaces when dithiols instead of mercaptoalkanoic acids are used (Figure 2) and that the films deposited on glass exhibit orange-red photoluminescence which is visible with the naked eye. While the incorporation of fluorescent dyes in LB multilayer systems of molecular dimensions has been studied, particularly in the pioneering work of Kuhn et al.,⁵ the intrinsic photoluminescence of a self-assembled multilayer thin film has, to our knowledge, not been reported before. These thin film structures were studied by ellipsometry, X-ray photoelectron spectroscopy (XPS), and fluorescence spectroscopy, and monolayer samples of Cu ion adsorbed to SAMs of 3-mercaptopropionic acid and 1,6-hexanedithiol on gold were examined by cyclic voltammetry. A bulk material which shows strong solid state photoluminescence and is probably structurally similar to the multilayers was obtained as an insoluble yellow precipitate by reaction of Cu²⁺ ion with dithiols in ethanolic solution.

Experimental Section

Thin Film Preparation. Glass microscope slides (Corning, USA) were derivatized with (3-mercaptopropyl)trimethylsilane following the method described by Goss et al.⁶ The dry, silanized substrates were immersed in a 50 mM aqueous solution of Cu-

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[®] Abstract published in *Advance ACS Abstracts*, September 15, 1997.

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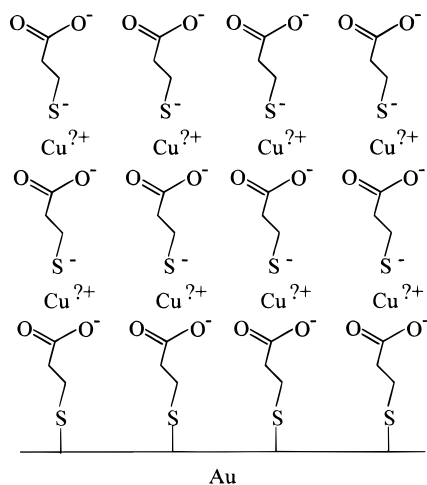


Figure 1. Schematic diagram of the multilayer structure obtained by alternate deposition of SAMs of mercaptoalkanoic acids (here C₃ for simplicity) and Cu²⁺ ion.⁴ Note that the oxidation state of Cu is undefined, as is the tilt angle of the dithiol molecules.

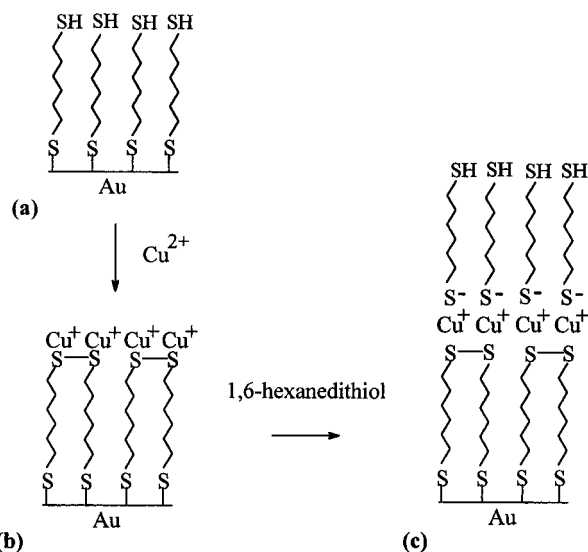


Figure 2. Scheme of multilayer formation by alternate surface derivatization with dithiols and Cu²⁺ ions. (a) SAM of 1,6-hexanedithiol on Au. (b) Attachment of Cu to the surface of the SAM and oxidation of vacant thiol groups to disulfides. The Cu is present as Cu(I) as shown by XPS. (c) Formation of a subsequent dithiol layer on the Cu(I)-derivatized surface.

(ClO₄)₂ for at least 1 h followed by thorough rinsing with water and 2-propanol and immersion in a 10 mM solution of 1,6-hexanedithiol in 2-propanol for 10–15 h. Alternate repetitions of these procedures led to the formation of photoluminescent thin film structures.

Multilayer thin films on Au were constructed by the same method, but starting with a SAM obtained by immersion of the Au substrate in a 10 mM solution of dithiol in 2-propanol for 10–15 h. Dithiols used were 1,6-hexanedithiol and 1,9-nonanedithiol. Mixed monolayer samples were prepared using a derivatizing solution containing both 1,6-hexanedithiol (1 mM) and *n*-pentanedithiol (20 mM) in 2-propanol. Attachment of Cu to the thiol sites on the derivatized surface was carried out as above, followed by further derivatization with *n*-pentanedithiol. Monolayers of 3-mercaptopropanoic acid were prepared analogously and were further derivatized with Cu²⁺ ion and *n*-pentanedithiol. Au substrates were prepared by sputtering Au films of ca. 300 nm thickness on glass microscope slides. Prior to Au deposition, a thin film of Cr (10–30 nm) was sputtered onto the glass surface to promote the adhesion of the Au. The substrates were used immediately after sputtering. Their quality was controlled by ellipsometry, giving values of $\Delta = 110 \pm 0.5$

and $\Psi = 43.5 \pm 0.3$, which are typical for freshly prepared clean Au surfaces.^{1a}

Bulk Material Preparation. One gram (2.7 mmol) of Cu-(ClO₄)₂·6H₂O was dissolved in 50 mL of ethanol and an equimolar amount of 1,6-hexanedithiol (406 mg) was added while stirring. The pale yellow precipitate was collected in a Büchner funnel, thoroughly washed with ethanol, and dried under reduced pressure. Washing with diethyl ether prior to drying resulted in a partial color change to olive green, and hence was avoided. Elemental analysis (Galbraith Laboratories, Inc.) gave C, 32.63% (34.04%); H, 5.27% (5.67%); S, 29.88% (30.26%); and Cu, 31.61% (30.02%). The numbers in parentheses are the theoretically expected values for an endless polymeric structure of $-(\text{Cu}-\text{S}-\text{C}_6\text{H}_{12}-\text{S}-)$ units. No detectable amount of oxygen was found in the analysis. The yield of 555 mg is practically quantitative for the elemental product composition found. The IR spectrum (KBr pellet) of the material was the same as that of 1,6-hexanedithiol, except for the absence of the S–H stretching mode at 2550 cm⁻¹. The product was insoluble in common solvents such as water, alcohols, hexane, toluene, chloroform, and DMF. X-ray powder diffraction gave a featureless spectrum typical of amorphous polymeric materials. As discussed below, XPS analysis showed that Cu is present in the +1 oxidation state and confirmed a S to Cu atomic ratio of 2:1, as found by elemental analysis.

Ellipsometry. A Rudolf 2000FT automatic ellipsometer with a He/Ne laser as light source (632.8 nm) was used to monitor multilayer self-assembly on Au substrates. The angle of incidence in all studies was 70°, and commercial software was used to interpret the data. Ellipsometry could not resolve reliably the formation of these types of ultrathin films on glass substrates, because the refractive indices of substrate and film are very similar.

XPS. X-ray photoelectron spectra were obtained with a Physical Electronics 5700 monochromatic XPS system. The Al anode (1486.7 eV) was operated at 300 W with a 2 mm filament (24 mA emission) to produce a $\sim 1.5 \times 0.6$ mm X-ray spot at the sample. Samples were mounted with a spring clip so that the Au film supporting the SAM was at electrical ground. All binding energies were referenced to the Au 4f_{7/2} transition at 84.0 eV.

Electrochemistry. Cyclic voltammetry experiments were carried out in a 0.1 M aqueous K₂SO₄ solution using a CH Instruments (Memphis, TN) Model 660 electrochemical work station and a three-electrode electrochemical cell with a saturated calomel reference electrode (SCE), a platinum flag counter electrode, and a gold disk working electrode of 0.008 cm² surface area. The electrolyte solution was deaerated with argon prior to each experiment. All potentials are quoted with respect to SCE.

Fluorescence Spectroscopy. All spectra were recorded on a Spex Fluorolog DM 3000 luminescence spectrophotometer operating in the front-face mode (22.5° angle between excitation beam and emission detection). Solid-state powder samples were investigated as thick films loosely attached as an ethanolic suspension to a black cardboard substrate and dried before measurement.

Materials. All chemicals used were of highest possible purity grade and used as received from Fluka and Aldrich.

Results and Discussion

Film Growth. The growth of dithiol–Cu multilayer thin films on Au was followed by ellipsometry. Figure 3 shows the increase in ellipsometric thickness upon deposition of layers of 1,9-nonanedithiol and Cu. The slope of this line gives an average monolayer (S–C₉H₁₈–S–Cu–) thickness of approximately 10 Å. As expected, a slightly smaller slope is observed if 1,6-hexanedithiol was used instead (~ 8 Å per layer). The refractive index assumed for the thin film material was 1.45, in accordance with previous ellipsometric studies of alkanethiol layers on Au.⁷ The thicknesses determined are consistent with

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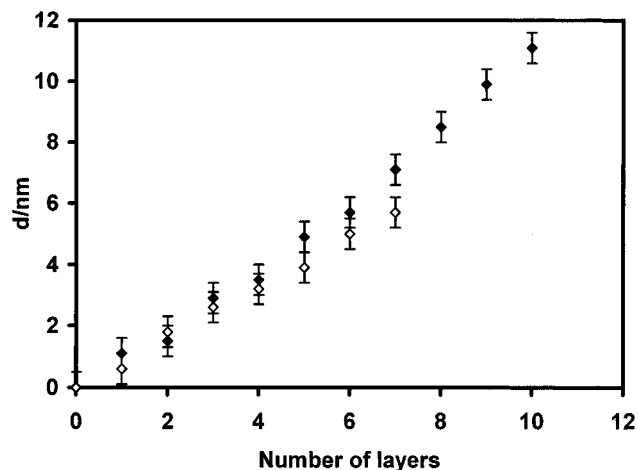


Figure 3. Ellipsometric thickness of dithiol/Cu multilayer thin films on Au as a function of the number of dithiol depositions: (◆) 1,9-nonanedithiol and (◇) 1,6-hexanedithiol.

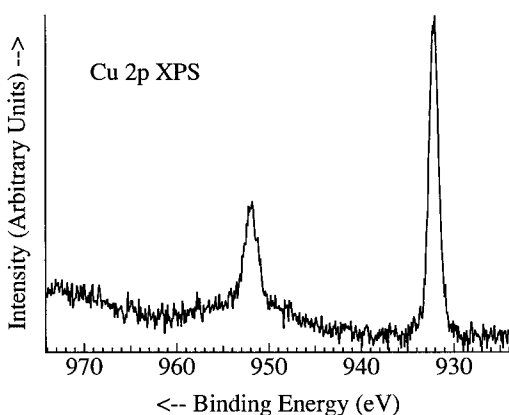


Figure 4. XPS spectrum of the Cu 2p region of a sample comprising 25 layers of 1,6-hexanedithiol/Cu deposited on Au. The peaks at 951.9 and 932.1 eV are characteristic of Cu(I). No evidence for the presence of Cu(II) is seen.

what can be expected for multilayer growth of the dithiols used,⁷ and within the accuracy of the measurement, regular layer-by-layer growth is suggested. An important question is to what extent looping of dithiol molecules (i.e., attachment via both -SH groups) occurs. Our results do not indicate that such structures, which would significantly impede regular multilayer formation, play an important role in the systems studied. In a previous study, no looping was found for rigid conjugated dithiols,⁸ and recent STM work by Nakamura et al.⁹ indicates that even relatively long-chain (C_{12}) α,ω -alkanedithiols are attached to the Au surface via only one thiol functionality.

XPS Measurements. The bulk material and different thin film preparations on Au were examined by XPS to establish the oxidation state of Cu in the respective systems. Figure 4 shows the XPS spectrum in the Cu 2p region of a multilayer sample comprising 25 layers of 1,6-hexanedithiol/Cu. Peaks at 932.1 eV (Cu 2p_{3/2}) and 951.9 eV (Cu 2p_{1/2}) and the absence of satellites (shake-up lines) characteristic of Cu(II) give clear evidence that Cu is present in the +1 oxidation state.^{4b,10} Qualitatively, the same spectrum was obtained for the corresponding bulk material and for multilayer thin films of 1,9-nonanedithiol

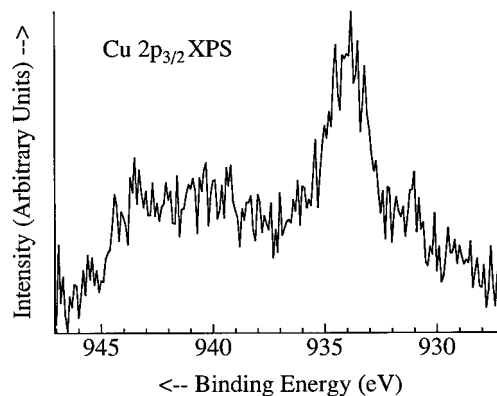


Figure 5. XPS spectrum of a submonolayer of Cu²⁺ ions attached to a mixed SAM of 1,6-hexanedithiol and *n*-pentanethiol on Au prepared by using a 20-fold excess of the monothiol. The spectrum shown is the sum of 10 spectra, each recorded during 1 min at different spots of the sample, to minimize the effect of reduction due to prolonged X-ray exposure. The peak at 933.9 eV is characteristic of Cu(II).

on Au. The existence of Cu in the +1 state is counter-intuitive if one imagines that each Cu atom is coordinated to two thiolate ligands, as suggested from the elemental analysis of the bulk material and from the successive layer by layer growth of the thin films. To elucidate at which stage of multilayer self-assembly the reduction of Cu(II) to Cu(I) occurs, the sample was examined by XPS after the first monolayer of Cu ions had been adsorbed to the dithiol functionalized Au surface. Surprisingly, Cu was found to be already present in the +1 oxidation state with no evidence for the presence of Cu(II). The Cu²⁺ ion is known to react with thiols giving disulfides and Cu⁺.¹¹ Since the only thiol groups available for the reduction of Cu²⁺ ions are confined to the surface of the Au substrate, the Cu(II) reduction step probably occurs with -SH oxidation and leads to the formation of surface bound disulfides, as illustrated in Figure 2. This assumption is supported by an experiment where the free thiol groups on the surface were diluted with *n*-pentanethiol to such an extent that disulfide formation becomes improbable (assuming no phase segregation of the two thiols). With an *n*-pentanethiol:1,6-hexanedithiol ratio of 20:1, the submonolayer of Cu attached to the surface remained in the +2 oxidation state, as seen in the XPS spectrum in Figure 5, with a Cu 2p_{3/2} binding energy of 933.9 eV.¹⁰ The weaker signal in the 937–945 eV range is attributable to shake-up lines associated with Cu(II). A small amount of Cu(I) is visible (931.1 eV). Further immersion in an *n*-pentanethiol solution led to reduction of the surface bound Cu(II) to Cu(I).

The ability to distinguish between Cu(II) and Cu(I) in monolayer and submonolayer systems motivated us to re-examine the oxidation state of Cu in Cu-mercaptoalkanoic acid systems.⁴ In our study, 3-mercaptopropanoic acid was used as the bifunctional building unit and only the first monolayer of adsorbed Cu ions was examined, while Ulman and co-workers⁴ used more complex and longer chain mercaptoalkanoic acids and studied multilayer thin films. In accordance with their second paper,^{4b} we found that Cu is present as Cu(I) in these assemblies. However, in contrast to the reaction scheme on fully dithiol derivatized surfaces, the Cu sites in the first monolayer

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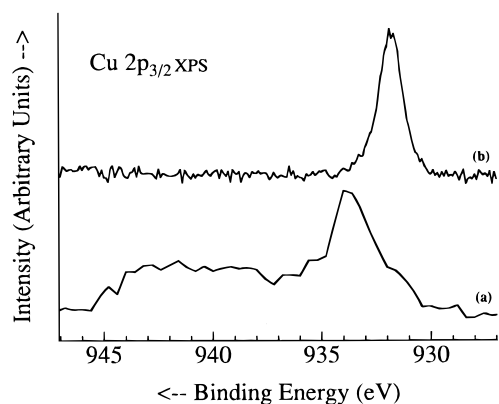


Figure 6. XPS spectrum of a Cu monolayer adsorbed to a SAM of 3-mercaptopropionic acid on Au (a) before and (b) after further derivatization with *n*-pentanethiol. Cu(II) is reduced to Cu(I) upon formation of the subsequent thiol layer.

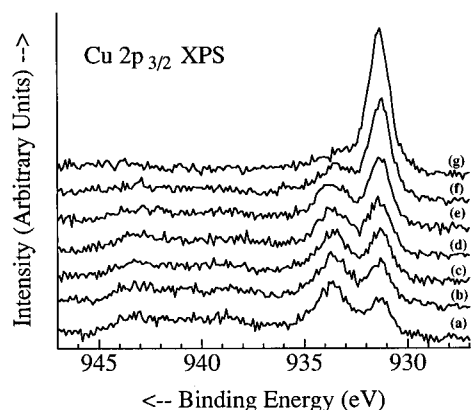


Figure 7. Series of spectra of a Cu monolayer adsorbed to a SAM of 3-mercaptopropionic acid on Au showing the conversion from Cu(II) to Cu(I) with X-ray exposure. Each spectrum was acquired during 1 min. X-ray exposure times were (a) 1–2, (b) 5–6, (c) 10–11, (d) 15–16, (e) 26–27, (f) 55–56, and (g) 155–156 min.

bound to the surface-confined carboxylic acid function remain at first in the +2 oxidation state and are reduced only upon the formation of a further thiol layer, as seen in the XPS spectra in Figure 6. This result is consistent with the fact that Cu(II) cannot be reduced by carboxylic acids and confirms that XPS can distinguish unambiguously between the oxidation states of Cu in the systems under investigation. Note, however, that reduction of Cu(II) also occurs upon prolonged exposure of the monolayer sample to the X-ray beam during XPS examination. Figure 7 shows a series of spectra of the same monolayer as in Figure 6a after different exposure times. The gradual conversion to Cu(I) is apparent from the increase of the peak at 931.3 eV and a corresponding decrease of the peak at 933.7 eV. Such autoreduction of Cu(II) has previously been observed in Cu-doped zeolites¹² and can lead to misinterpretations of the spectra. This must be considered as a possible artifact when Cu oxidation states are determined by XPS. For this reason, special care was taken to avoid prolonged beam exposure of a single spot of our samples.

Cyclic Voltammetry. The electrochemistry of the multilayer structures prepared is complicated and is characterized by ill-defined and poorly reproducible features. Most likely, both oxidation and reduction of the Cu(I) sites lead to the irreversible destruction of the layered assemblies. For this reason, we discuss only the

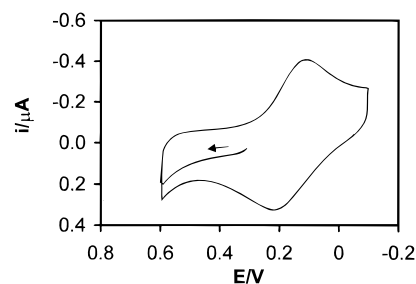


Figure 8. Cyclic voltammogram of Cu ions adsorbed to a SAM of 3-mercaptopropionic acid on a gold disk electrode (0.008 cm²) in 0.1 M aqueous K₂SO₄ solution. The potential sweep begins at the open circuit potential of 300 mV vs SCE in the direction of the arrow. Sweep rate was 0.1 V s⁻¹.

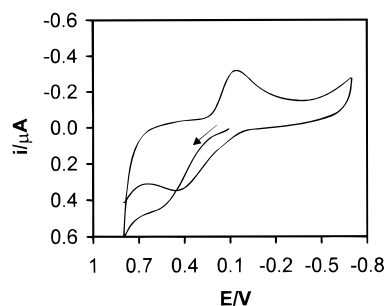


Figure 9. Cyclic voltammogram of Cu ions adsorbed to a SAM of 1,6-hexanedithiol on a gold disk electrode (0.008 cm²) in 0.1 M aqueous K₂SO₄ solution. The potential sweep begins at the open circuit potential of 100 mV vs SCE in the direction of the arrow. Sweep rate was 0.1 V s⁻¹.

electrochemical behavior of the first monolayer of Cu ions adsorbed to a SAM of 3-mercaptopropionic acid and 1,6-hexanedithiol. The conclusions from XPS regarding the oxidation state of Cu in these two different systems are confirmed by cyclic voltammetry. Figure 8 shows a typical cyclic voltammogram of a SAM of 3-mercaptopropionic acid on gold after the adsorption of Cu²⁺ ions. The first anodic sweep starting from the open circuit potential at 300 mV shows no oxidation peak, i.e., Cu is present in the +2 oxidation state, as expected, and cannot be further oxidized. The cathodic sweep is characterized by a reduction peak at 120 mV representing the reduction of surface bound Cu(II) to Cu(I), which is reoxidized during the subsequent anodic sweep with a peak potential of 220 mV. Repeated cycling does not lead to a significant loss of signal, which indicates that Cu remains strongly adsorbed in both oxidation states within the potential range of the experiment. In accordance with XPS, the voltammetric behavior of the 1,6-hexanedithiol/Cu system is different (Figure 9). The first anodic sweep shows the oxidation of Cu(I) to Cu(II) as a shoulder at 550 mV. This confirms that Cu²⁺ ion is reduced upon adsorption to the dithiol SAM. The sloping anodic background current is typical for dithiols adsorbed on the electrode surface and probably represents the slow electrochemical oxidation of the remaining free -SH groups. Subsequent cycles do not show the same behavior. The reduction of Cu(II) to Cu(I) occurs at 50 mV, and all following anodic sweeps now show an oxidation peak at 450 mV. If the first potential sweep is cathodic and is carried out toward negative potentials (not shown in Figure 9) no reduction peak is observed, which also confirms the initial +1 oxidation state of Cu. Unlike the mercaptopropionic acid system, some loss of signal is observed upon repeated cycling, which is probably due to the desorption of Cu²⁺ ion at positive potentials. Both monolayer systems show a further reduction wave at very negative potentials close to solvent decomposition. This is due to the reduction of

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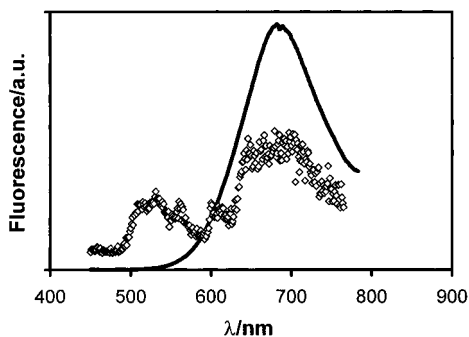


Figure 10. Photoluminescence emission spectrum of the bulk material obtained by reaction of 1,6-hexanedithiol with Cu^{2+} (solid line) and of the corresponding multilayer thin film (\diamond) prepared on mercaptosilanized glass (25 layers). The spectra are not plotted on the same Y scale. The emission intensity of the multilayer sample was approximately 4 orders of magnitude weaker. The excitation wavelength employed was 400 nm.

Cu(I) to Cu(0) , which should be accompanied by nucleation of clusters of metallic Cu . This is important to note since XPS cannot distinguish between Cu(I) and hypothetically present Cu(0) . After sweeping to such negative potentials, the systems are destroyed and their electrochemistry becomes complicated and irreproducible. Electrochemical experiments were carried out here to complement the XPS studies and to provide an independent way to determine the oxidation state of Cu in these systems. Electrochemical studies can also yield precise information on the degree of surface coverage and help to determine changes that accompany the redox switching of the surface species. This is currently being investigated.

Luminescence Studies. Both the multilayer thin films and the bulk material prepared using 1,6-hexanedithiol exhibit interesting photophysical properties. The dry bulk material shows an intense orange-red photoluminescence upon illumination with UV light (ca. 360 nm). With prolonged exposure to air, the emission became faint and the material changed color to pale olive green. After several days of storage in air at room temperature, emission was no longer detected. This decomposition is probably caused by oxidation of the Cu(I) sites in the material. Multilayer thin films on Au did not show detectable photoluminescence, probably because of quenching by the metallic surface,¹³ but the same systems grown on mercaptosilanized glass (10–30 layers) emit light of the same color as the bulk material. This film emission is faint but still visible to the naked eye. No fluorescence was seen in films prepared using 3-mercaptopropanoic acid⁴ instead of dithiols, nor do bulk reaction products of Cu^{2+} ion with 3-mercaptopropanoic acid show any visible emission. The fluorescence emission spectra of the 1,6-hexanedithiol– Cu(I) bulk material and the corresponding multilayer thin film on glass are shown in Figure 10. Both systems are characterized by a broad emission peak centered at 680 nm. The thin film sample shows an additional smaller peak at 525 nm, indicating some structural differences between the bulk material and the multilayer system. The excitation wavelength, 400 nm, corresponded approximately to the maximum in the excitation spectrum, which means that these materials show a large Stokes shift. The fluorescence intensity of the 1,9-nonanedithiol material was of the same color but significantly weaker and was not investigated in detail.

While Cu(I) has long been known as an activator in ZnS phosphors, leading to complex emission patterns across

the visible spectrum,¹⁴ and the photoluminescence of Cu(I) sites in ion exchanged zeolites is well-established,¹⁵ only a few isolated reports describe the photoluminescence of organic copper thiolates in solution or in the solid state.¹⁶ The earlier studies are rather qualitative, and the precise origin of the light emission remains unclear. For example, the reaction product of Cu^{2+} ion and propylthiouracil shows a strong solid-state photoluminescence which has been exploited to detect trace amounts of Cu .^{16a} Similarly, some Cu , Au , and Ag thiolates were found to exhibit orange-red solid-state photoluminescence of unknown origin.^{16b} The solid-state and solution photoluminescence of a self-assembled Cu(I) cyclophane, which comprises copper thiolate moieties, has been reported recently and was tentatively attributed to metal-to-ligand charge-transfer transitions and $\pi \rightarrow \pi^*$ transitions of the aromatic ligands.^{16d} Sabin et al.^{16c} studied the photophysical properties of hexanuclear Cu(I) clusters with di- n -propylmonothiocarbamate as a ligand and observed emission spectra very similar to those shown in Figure 10. Their spectra also showed the large Stokes shift observed here. From theoretical considerations, and by comparison with the corresponding Ag(I) complexes and other luminescent Cu(I) compounds containing halogenide and amine ligands, the emission is thought to be related to a mixed excited state composed of cluster-centered $d \rightarrow s$ and ligand-to-metal charge-transfer transitions. To account for the large Stokes shift, strong metal–metal interactions have been assumed with a significant distortion of the molecular structure in the excited state. From the similarity of their luminescence spectra, both our bulk material and the multilayer thin films probably involve metal–metal interactions with the copper sites probably part of a polynuclear cluster, so that the systems are somewhat more complicated than those suggested in the drawing in Figure 2. This conclusion is also supported by the observation that the photoluminescence of the corresponding 1,9-nonanedithiol material is much weaker than that for the 1,6-hexanedithiol, even taking into account the lower concentration of Cu sites. Although both the IR spectrum and the elemental analysis of the bulk material are consistent with an endless polymeric structure of Cu ions and dithiol molecules, given the enormous structural diversity of copper thiolates,¹⁷ this is an oversimplification, since one would expect a +2 oxidation state for a Cu ion sandwiched between two thiolate groups. Further studies are needed to determine the structure of these species. Powder diffraction data show no signs of crystallinity, and attempts to obtain more structural information by mass spectrometry have so far been unsuccessful.

Conclusions

Self-assembled multilayer thin films showing intrinsic visible photoluminescence have been prepared by repeated alternate adsorption of Cu^{2+} ion and an alkanedithiol on a mercapto-functionalized glass surface. Likewise, a photoluminescent solid was obtained, which is probably structurally similar to the thin films but requires further

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characterization. XPS and cyclic voltammetry show that Cu is present in the +1 oxidation state in these materials. From comparison with the fluorescence of polynuclear Cu(I) clusters, metal-metal interactions probably play an important role in governing the photophysical properties of these novel materials. There are many possible applications of luminescent thin films of molecular dimensions. For example, materials with similar properties may be useful in miniature optoelectronic devices such as optical switches or wavelength converters. The more immediate importance of the materials described could be their use as easily prepared and variable systems for studying the photophysical properties of metal ions in layered assemblies, which might lead to a better understanding of the electronic transitions involved in the light

emitting process and hence to a more rational approach for the design of new luminescent thin film structures.

Acknowledgment. The authors thank Professor Stephen E. Webber, Steven M. Savoy, and Dr. Ti Cao for their help in obtaining the fluorescence spectra, the University of Texas Science and Technology Center for Synthesis, Growth and Analysis of Electronic Materials for the use of the X-ray photoelectron spectrometer, and Sandra Whaley for sputtering the gold films. Financial support from the National Science Foundation (CHE-9423874) and the Robert A. Welch Foundation is gratefully acknowledged.

LA970493U