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Building Layer-by-Layer a Bis(dithiocarbamato)copper(II) Complex on Au{111} Surfaces

Roberto Cao, Jr.,[†] Alicia Díaz,[†] Roberto Cao,*[,†] Antonio Otero,[‡] Raymundo Cea,[§]
María C. Rodríguez-Argüelles,[‖] and Carmen Serra[‖]

Contribution from the Laboratorio de Bioinorgánica, Facultad de Química, Universidad de La Habana, La Habana 10400, Cuba, Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Ciudad Real 13071, España, Instituto de Química, Universidad Nacional Autónoma de México, Circuito exterior, Ciudad Universitaria, México 04510, D.F. México, and Universidade de Vigo, 36200 Vigo, Spain

Received November 21, 2006; Revised Manuscript Received March 20, 2007; E-mail: cao@fq.uh.cu

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Abstract: A bis(dithiocarbamato)copper(II) complex (CuDTC$_2$) was built on Au{111} surfaces (sheets and electrode beads) using different building blocks in a layer-by-layer (LbL) procedure. The process was followed by AFM and cyclic voltammetry. Initially 4-piperidinemethanethiol, which was synthesized here for the first time, was self-assembled on a gold surface and a highly organized array was obtained. The resulting monolayer was treated with CS$_2$ and NH$_3$ to transform the NH groups of piperidine into dithiocarbamate groups (DTC) with the formation of an amphiphilic ligand (DTCpipS) with thiolate and DTC terminal anionic groups. Two reductive desorption peaks were observed in the cyclic voltammogram of self-assembled DTCpipS, a more intense peak at −0.87 V (thiolate group) and a broader, less intense peak at −0.68 V, corresponding to the desorption of the DTC group bound to the gold surface after the ligand made a ∼180° flip on the surface. Copper(II) and the morpholyldithiocarbamate anion were associated with self-assembled DTCpipS in order to complete the formation of the CuDTC$_2$ complex on the gold surface. In the voltammogram of the LbL self-assembled CuDTC$_2$ complex the reductive desorption peak at −0.68 V disappeared and one single peak was observed at −0.85 V. This corresponds to the reorientation of all of the DTCpipS dianions in order to coordinate to copper(II) through the DTC groups, leaving the self-assembly only through the thiolate groups. The complete formation of the LbL self-assembled CuDTC$_2$ complex was confirmed by XPS and ToF SIMS, with a detected fragment corresponding to the whole complex.

Introduction

The formation of self-assembled monolayers of thiols on gold surfaces has been widely studied.[1] However, dithiocarbamate (DTC) monolayers have received much less attention.[2,3] The planar DTC group, NCS$_2^-$, is characterized by π-delocalization over all four atoms. Both sulfur atoms bind to gold surfaces but with lower stability than alkanethiols.[3]

The development of nanosciences has increased with studies on molecular architecture through the formation of several self-assembled monolayers (SAM) on solid surfaces, one over the other, in the so-called layer-by-layer procedure (LbL).[1] When multilayers are self-assembled, more than one functional group can be present on the surface, a situation very beneficial when considering molecular receptors.

A coordination compound can be built LbL on a solid surface using different procedures, including coordination, chemisorption, electrostatic, and supramolecular interactions, among others.[4−8] The reported procedures are generally based on the formation of coordination compounds using only two building blocks: the metal ion and the ligand.

Bis(dithiocarbamato)copper(II) complexes (CuDTC$_2$) are highly stable and can scavenge superoxide and nitric oxide, two radicals of biological importance.[9−15] With this in mind, a

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[†] Universidad de La Habana.

[‡] Universidad de Castilla-La Mancha.

[§] Universidad Nacional Autónoma de México.

[‖] Universidade de Vigo.

(1) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103−1169.

(2) Zhao, Y.; Pérez-Segarra, W.; Shi, Q.; Wei, A. *J. Am. Chem. Soc*. **2005**, *127*, 7328−7329.

(3) Morf, P.; Raimondi, F.; Nothofer, H.-G.; Schnyder, B.; Yasuda, A.; Wessels, J. M.; Jung, T. A. *Langmuir* **2006**, *22*, 658−663.

(4) Wanunu, M.; Popovitz-Biro, R.; Cohen, H.; Vaskevich, A.; Rubinstein, I. *J. Am. Chem. Soc.* **2005**, *127*, 9207−9215.

(5) Hatzor, A.; Moav, T.; Cohen, H.; Matlis, S.; Libman, J.; Vaskevich, A.; Shanzer, A.; Rubinstein, I. *J. Am. Chem. Soc.* **1998**, *120*, 13469−13477.

(6) Hatzor, A.; van der Boom-Moav, T.; Yochelis, S.; Vaskevich, A.; Shanzer, A.; Rubinstein, I. *Langmuir* **2000**, *16*, 4420−4423.

(7) Major, R. C.; Zhu, X.-Y. *J. Am. Chem. Soc.* **2003**, *125*, 8454−8455.

(8) Semenov, A.; Spatz, J. P.; Möller, M.; Lehn, J.-M.; Sell, B.; Schubert, D.; Weidl, C. H.; Schubert, U. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 2547−2550.

(9) Cao, R; Fragoso, A.; Villalonga, R *Monatsh. Chem.* **1996**, *127*, 775−782.

(10) Cao, R.; Travieso, N.; Fragoso, A.; Villalonga, R.; Diaz, A.; Martinez, M. E.; Alpizar, J.; West, D. X. *J. Inorg. Biochem*. 1**997**, *66*, 213−217.

(11) Fragoso, A.; Cao, R.; D' Souza, V. T. *J. Carbohydr. Chem.* **1997**, *16*, 171−180.

(12) Martin, R.; Fragoso, A.; Cao, R. *Supramol. Chem.* **2003**, *15*, 171−175.

(13) Díaz, A.; Ortiz, M.; Sánchez, I.; Cao, R.; Mederos, A.; Sanchiz, J.; Brito, F. *J. Inorg. Biochem.* **2003**, *95*, 283−290.

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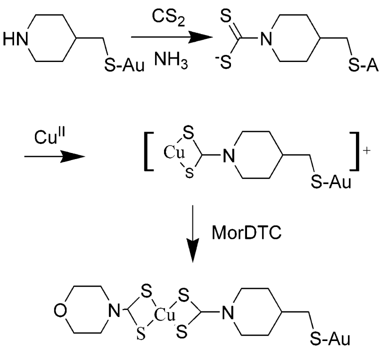
Scheme 1



$CuDTC_2$ complex was built LbL on gold surfaces. In order to achieve this goal, 4-piperidinemethanethiol (pipSH) was synthesized for the first time. It was envisaged that the thiol group would serve to bind pipSH onto gold surfaces. Once this first monolayer was formed, three others would be added LbL (Scheme 1):

- CS_2 to interact with the nitrogen atom of piperidine to form a dithiocarbamate group.
- Copper(II) to coordinate to the resulting DTC group.
- The morpholyldithiocarbamate anion (MorDTC) to complete the coordination sphere of copper(II).

We report here the study of this LbL process on Au{111} surfaces by AFM and cyclic voltammetry using different building blocks. The complete formation of $CuDTC_2$ was confirmed by XPS and ToF SIMS.

Results and Discussion

First Monolayer. The interaction of a 1 mM methanolic solution of pipSH with an Au{111} sheet 20 h led to the formation of a uniform array, as observed by AFM (Figure 1). The observed high level of organization of the array was unexpected due to the short length of the thiol. Nevertheless, this result can be explained by considering the relatively strong interactions that must be present between the wide (when compared with a linear alkanethiol) ring of pipS anion in a chair conformation. In addition, the NH groups of these rings, which point upward from the surface, could form intermolecular hydrogen bonds between the self-assembled pipS units, and this must contribute to the resulting highly organized array.[16,17] Such organization of self-assembled pipS should strongly limit the rotations about the axis of the molecule.[1] When the methanolic solution of pipSH was left to interact with the gold surface for longer periods, especially more than 2 days, less organized arrays were observed by AFM, apparently due to the partial adsorption of islands of pipS through hydrogen bonds.[17]

When pipSH was self-assembled on gold beads and the cyclic voltammogram recorded, a reductive peak at −0.87 V (vs Ag/AgCl) was observed, and this corresponds to the desorption of the pipS monolayer.

Second Monolayer. The Au{111} sheet modified with the pipS monolayer was introduced into a methanolic solution containing CS_2 and NH_3. Dithiocarbamate groups (DTC) (second monolayer) were formed on the piperidine nitrogen atoms pointing up from the monolayer, which were therefore sterically available for covalent interactions with CS_2 in order to form the second monolayer. On the other hand, a bare Au{111} sheet was modified with the ammonium dithiocarbamate of pipSH (DTCpipS), obtained *in situ* in methanol (λ_{max} at 260 and 292 nm, log $\epsilon \sim 4.2$). Both modifications gave very similar AFM micrographs (Figure 2), but these were much less organized than that observed for the pipS monolayer. An important factor in this change is probably the loss of the intermolecular hydrogen bonds once the nitrogen atoms are deprotonated and transformed into DTC groups.

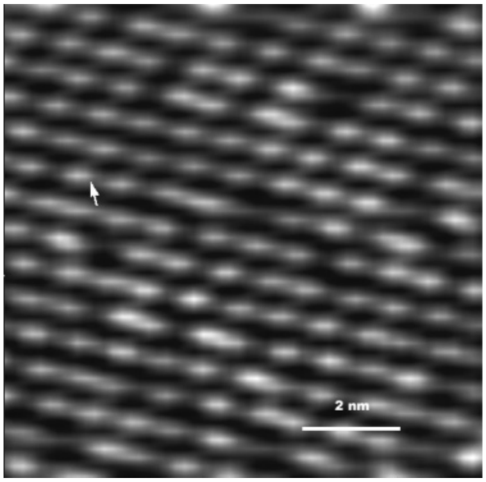


Figure 1. AFM micrograph (10×10 nm^2) of the pipS monolayer on an Au{111} surface.

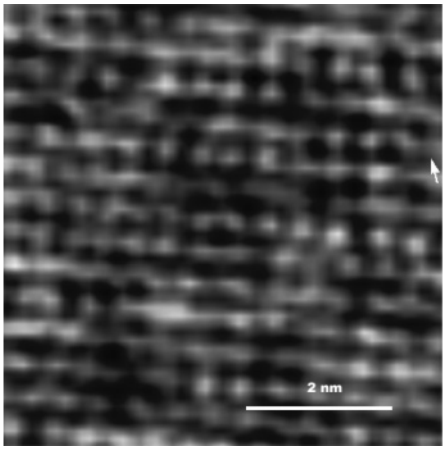


Figure 2. AFM micrograph (6×6 nm^2) of DTCpipS self-assembled in two steps (LbL) on an Au{111} surface.

The DTCpipS dianionic ligand can show amphiphilic behavior due to the two terminal sulfur-containing anionic groups: thiolate and dithiocarbamate. Consequently, the DTCpipS monolayer should actually correspond to a mixture of the amphiphilic ligand chemisorbed either through its thiolate or dithiocarbamate groups. When DTCpipS was formed by the condensation of CS_2 onto the pipS monolayer, a dynamic ~180° flip could have taken place to transform the chemisorption of DTCpipS through the thiolate group to form DTC−Au bonds. This process could also serve to explain the observed irregularity in the self-assembly of DTCpipS by AFM. Whereas the thiolate group of DTCpipS should self-assembly on the surface with a tilt of about a 30° from the surface normal,[1] when chemisorbed through the dithiocarbamate group the angle of tilt is much

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[14] Moncada, S.; Palmer, R. M. J.; Higgs, E. A. *Pharmacol. Rev.* **1991**, *43*, 109−142.
[15] Buttler, A. R.; Williams, D. L. H. *Chem. Soc. Rev.* **1993**, *22*, 233−241.
[16] Johnson, S. R.; Evans, S. D.; Brydson, R. *Langmuir* **1998**, *14*, 6639−6647.
[17] Wang, H.; Chen, S.; Li, L.; Jiang, S. *Langmuir* **2005**, *21*, 2633−2636.

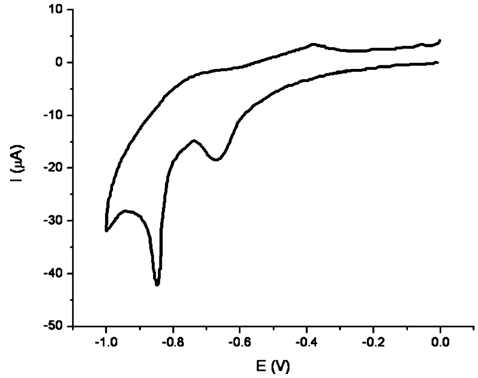

Figure 3. Cyclic voltammogram of the reductive desorption process of DTCpipS self-assembled on a gold electrode recorded at 100 mV·s^{-1} and 5 μA·cm^{-1}.

smaller, with the group standing practically perpendicular to the surface.[3,18] The probability of each of the two processes taking place should be affected by the steric hindrances caused by the two different positions of the chemisorbed molecules relative to the gold surface. About one-third of the molecules were observed in a higher position (brighter spots) in the AFM micrograph (Figure 2), which should correspond to the DTCpipS chemisorbed on the gold surface through the dithiocarbamate groups (smaller tilt, higher position).

The two-step modification was also studied by cyclic voltammetry. A gold electrode modified with pipS was introduced into a methanolic solution containing CS_2 and NH_3, and the reductive desorption process was studied by cyclic voltammetry. Two irreversible reduction peaks were observed at −0.85 and −0.68 V (Figure 3), and these correspond to the desorption of DTCpipS chemisorbed through the thiolate and dithiocarbamate group, respectively. At this point it is important to highlight that the reductive desorption peak of diethyl dithiocarbamate self-assembled on a gold electrode was reported at −0.759 V (vs Hg/HgO).[3] The area under the peak at −0.68 V (vs Ag/AgCl) corresponds to 35% of the peak at −0.85 V. This result could support the interpretation given above for the AFM micrographs of self-assembled DTCpipS. When a second cycle was recorded, the intensity of the desorption peak at −0.68 V decreased while the one at −0.85 V became more intense. In a third cycle the less negative peak was no longer observed, while the other peak increased in intensity. These observations indicate that DTCpipS chemisorbed through the DTC group was completely released from the monolayer and then flipped back to form Au−SR bonds. However, this process was not instantaneous. This flip requires the DTCpipS ligand to move out of the monolayer and then reintroduce itself through the other end (DTC). Desorption and diffusion away from the surface is favored in aqueous solutions by the highly hydrophilic nature of DTCpipS, which has two anionic terminal groups.

An additional experiment was carried out in order to confirm that the less negative peak actually corresponds to the desorption of the dithiocarbamate group. The dithiocarbamate of 4-piperidinemethanol (ammonium salt), DTCpipOH, was obtained *in situ* and self-assembled on the gold electrode. The voltammogram of its desorption process contained a single reductive peak at −0.64 V, which is very similar to that assigned for the desorption of DTCpipS through the DTC group (−0.68 V).

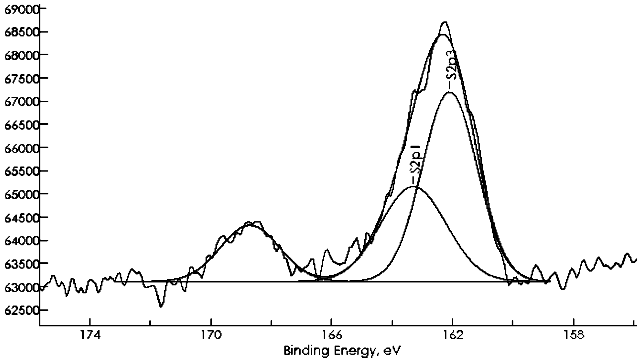

Figure 4. XPS spectrum of $CuDTC_2$ self-assembled on an Au{111} sheet in the S2p region.

When DTCpipS was obtained *in situ* and then self-assembled on a gold electrode, the recorded voltammogram was the same as that obtained in the two-step process (LbL). Therefore, both AFM and cyclic voltammetric studies gave the same results for the chemisorption of DCTpipS, regardless of whether it was obtained in one or two steps.

Third and Fourth Monolayers. It is accepted that copper(II) coordinates more strongly to a dithiocarbamate group than to a thiolate group, which favors its reduction to Cu(I). In order to confirm this criterion for this specific system the interaction of DTCpipSH and DTCpipOH with copper(II) was studied spectrophotometrically. The spectra of both systems were practically the same, with a charge transfer band at 426 nm (log $\epsilon \sim 4.1$), indicating that the coordination only took place through the dithiocarbamate group.[10]

When the fourth monolayer (MorDTC) was self-assembled in order to complete the formation of $CuDTC_2$, which is actually $[Cu(DTCpipS)(MorDTC)]^-$ (Scheme 1), the voltammogram of this modified electrode presented the peaks of the Cu^{II}/Cu^{I} pair at $E_{ox} = -0.35$ V and $E_{red} = -0.38$ V (see S1), which is typical for this type of complex.[10] The reductive desorption peak was observed at −0.85 V. The reductive desorption peak at −0.68 V was absent, indicating that the presence of copper(II) forced the reorientation of all the DTCpipS dianions to leave them only self-assembled through the thiolate groups and with the DTC groups coordinated to copper(II).

An Au{111} sheet modified with the complete LbL formation of $CuDTC_2$ was analyzed by XPS (X-ray photoemission spectroscopy) (Figure 4). The Cu2p3/2 peak at 932.55 eV was identified, indicating the presence of Cu(II). The S2p3/2 peak of DTC was observed at 162.10 eV and the S2p1/2 (DTC) peak at 163.30 eV, which is in agreement with a previous report.[3] The ratio between the intensities of these two peaks should be 1:2, but a value of 1:1.67 was actually observed. This difference should be due to the overlap of the S2p3/2 peak of the DTC groups with the S2p peaks of the thiolate group bound to gold, which appears at 162 eV.[19] In this analysis we took into consideration the fact that there are four coordinated sulfur atoms of the two DTC groups for each thiolate sulfur atom.

A peak at 168.70 eV was also observed (Figure 4), and this is assigned to oxidized thiolate groups with an intensity that is consistent with a previous report.[19] The intensity of this peak

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(18) Weinstein, R. D.; Richards, J.; Thai, S. D.; Omiatek, D. M.; Besel, C. A.; Faulkner, C. J.; Othaman, S.; Jennings, G. K. *Langmuir* **2007**, *23*, 2887−2891.

(19) Schoenfisch, M. H.; Pemberton, J. E. *J. Am. Chem. Soc.* **1998**, *120*, 4502−4513.

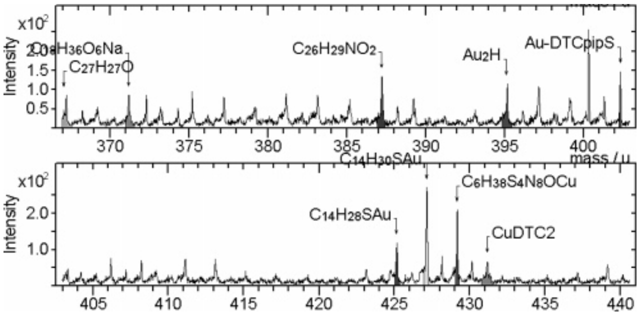

Figure 5. Tof SIMS spectra (*m*/*z* 360−440) of $CuDTC_2$ self-assembled LbL on an Au{111} sheet.

was not observed to increase with time (2 weeks). As expected, the XPS spectrum of $CuDTC_2$ self-assembled as a whole was found to be similar to that shown in Figure 4.

The presence of different positive fragments (CS_2^+ 75.948, Cu^+ 62.933, $AuSC_4H_6^+$ 283.031, etc.), that give information on the composition of the formed multilayer, were detected by ToF SIMS (time-of-flight secondary ion mass spectrometry) (Figure 5). More importantly, positive fragments corresponding to MorDTC (162.015), DTCpipS-Au (402.318) and $CuDTC_2$ itself (431.122) were also detected albeit with lower intensity. These spectra were recorded once $CuDTC_2$ had formed completely (LbL) on an Au{111} sheet and also at times of 1, 4, 7 h and a week later. Significant differences were not observed between these spectra.

Conclusions

To the best of our knowledge, this is the first report on the LbL construction of a coordination compound on Au{111} surfaces using different small molecules as building blocks. A bis(dithiocarbamate)copper(II) complex was built by the initial self-assembly of pipSH, followed by the condensation of CS_2 onto its nitrogen atoms, the coordination of copper(II) to the resulting DTC groups pointing outward from the surface, and finally the additional coordination of MorDTC to complete the coordination sphere of the metal ion. The complete LbL formation of $CuDTC_2$ on Au{111} sheets was confirmed by XPS and ToF SIMS determinations.

It is interesting that cyclic voltammetry showed that some self-assembled DTCpipS amphiphilic ligands, formed after the formation of the second monolayer, flipped on the gold surface to chemisorb through the DTC groups. After repeated voltammometric cycles DTCpipS remained self-assembled only through its thiolate group, which is the most stable mode. The dynamics processes observed for the amphiphilic DTCpipS ligand on gold surfaces could serve to develop other systems with similar characteristics, but under more controlled conditions, that could be capable of rolling over solid surfaces as nanowheels.

Experimental Section

Materials. 4-Piperidinemethanol and sodium sulfide were purchased from Aldrich, and the other reagents, all of analytical quality, from Merck. All chemicals were used without further purification. Sodium morpholyldithiocarbamate (MorDTC) was synthesized as reported elsewhere.[9]

Spectroscopy. The NMR spectra were recorded on a Varian Gemini 400 spectrometer in DMSO-d_6 (125 MHz for ^{13}C). The spectrophotometric determinations were carried out on an Ultrospec 2100 *pro* (Amersham BioSci.) apparatus.

The XPS spectrum was obtained using a VG Escalab 250 iXL ESCA instrument (VG Scientific). The measurements were carried out using monochromatic Al Kα radiation (1486.92 eV). Photoelectrons were collected from a take off angle of 90° relative to the sample surface. The measurement was obtained in a constant analyzer energy mode (CAE) with a 100 eV pass energy for survey spectra and 20 eV pass energy for high-resolution spectra. The binding scale was referenced by setting Au4f7/2 BE at 84.0 eV.

The mass spectra of the samples were recorded on a TOF-SIMS IV instrument from Ion-Tof GmbH Germany. The sample was bombarded with a pulsed gallium ion beam (25 keV) at 45° incidence. The secondary ions generated were extracted with a 10 kV voltage, and their time-of-flight from the sample to the detector was measured in a reflectron mass spectrometer.

Atomic Force Microscopy. AFM determinations were performed on a NanoScope IIIa microscope (Digital Instruments) with a silicon nitride tip. For this, a commercial sheet of mica covered with a thin layer of Au{111} was used. The sheet was introduced into a methanolic solution of the compound to be self-assembled for the appropriate period of time (24 h or less) and then removed, washed with methanol, rinsed, and left to dry at room temperature. The same procedure was used to form the self-assembled monolayer on the gold electrode.

Electrochemical Measurements. Electrochemical determinations were carried out with a Yanaco P-900 cyclic polarograph coupled to a Graphted WX1000 X-Y recorder using a standard three cell holder. A gold bead, Pt, and Ag/AgCl (saturated) were used as working, counter, and references electrodes, respectively. All solutions were previously deoxygenated with nitrogen. KOH (0.5 M) was used as the solvent for all the reductive desorption processes. The voltammograms were recorded at 100 $mV\cdot s^{-1}$ and 5 $\mu A\cdot cm^{-1}$.

The gold electrode was prepared by annealing the tip of a gold wire (1 mm diameter and 5 cm long) (99.99%), which had previously been cleaned overnight with nitric acid (68%). The formed gold bead was electrochemically pretreated in $HClO_4$ (0.1 M) at 2.1 V until gold(III) oxide formation (red color) was observed in order to guarantee the formation of a Au{111} surface.[20] The electrode was then cleaned with HCl (0.1 M) and thoroughly rinsed with doubly distilled water.

PipSH. 4-Piperidinemethanol (0.461 g, 4 mmol) was dissolved in acetonitrile (80 mL), mixed with sodium sulfide (0.390 g, 5 mmol), and stirred at 40−50 °C during 1 h, after which small aliquots (0.1 mL or less) of H_3PO_4 (85%) were added every hour until a slightly acidic medium was achieved, expressed as a change of color from green to yellow. The reaction mixture was stirred overnight. The yellow solution was concentrated to dryness under vacuum to give a yellowish solid to which dry Na_2SO_4 (about 3 g) was added. The resulting mixture was extracted several times with CH_3CN. The extract was dried under vacuum to give a hygroscopic yellowish solid. Yield: 0.325 g (62%). Anal. Calcd for $C_6H_{13}NS$: C, 54.91; H, 9.98; N, 10.67; S, 24.43. Found: C, 54.80; H, 10.15; N, 10.56; S, 24.24. Mp: 90−92 °C. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): $\delta = 1.29-1.38$ (m, 4H), 1.75 (w, H), 2.12 (d, 2H), 2.92 (t, 4H); ^{13}C NMR (125 MHz, DMSO-d_6, 25 °C) $\delta = 25.3, 35.7, 44.1, 65.7$.

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Supporting Information Available: Cyclic voltammogram. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Calvente, J. J.; Kovacová, Z.; Sánchez, M. D.; Andreu, R.; Fawcett, W. R. *Langmuir* **1996**, *12*, 5696−5703.