

Supplementary Materials

Electrochemical Characterization of Self-Assembled Monolayers on Gold Substrates Derived from Thermal Decomposition of Monolayer-Protected Cluster Films

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Contents:

- ▶ NMR and TEM characterization of as prepared $\text{Au}_{140}\text{C}_{653}$ and carboxylic acid functionalized MPCs.
- ▶ Synthesis details of 6-mercaptohexanoic acid (MHA) including NMR, IR, and MS characterization of MHA product.
- ▶ Digital photographs of functionalized (silanized) glass slide, MPC film assembly before and after thermal decomposition, and evaporated gold substrates.
- ▶ Additional tables of data including capacitance, linear sweep voltammetric desorption, and redox probing of SAMs on gold films created from thermal decomposition of Zn^{2+} M-L MPC films.
- ▶ Double layer capacitance trends of methyl terminated SAMs in two different electrolytes at evaporated gold and Cu^{2+} M-L MPC gold.
- ▶ Background cyclic voltammetry and UV-Vis spectroscopy of a MPC film assembly before and after soaking in pure ethanol to remove excess metal ions.
- ▶ Example voltammograms and linear sweep data for MHDA SAMs on M-L Zn^{2+} films with and without extraction of excess metal ions with ethanol soaking.

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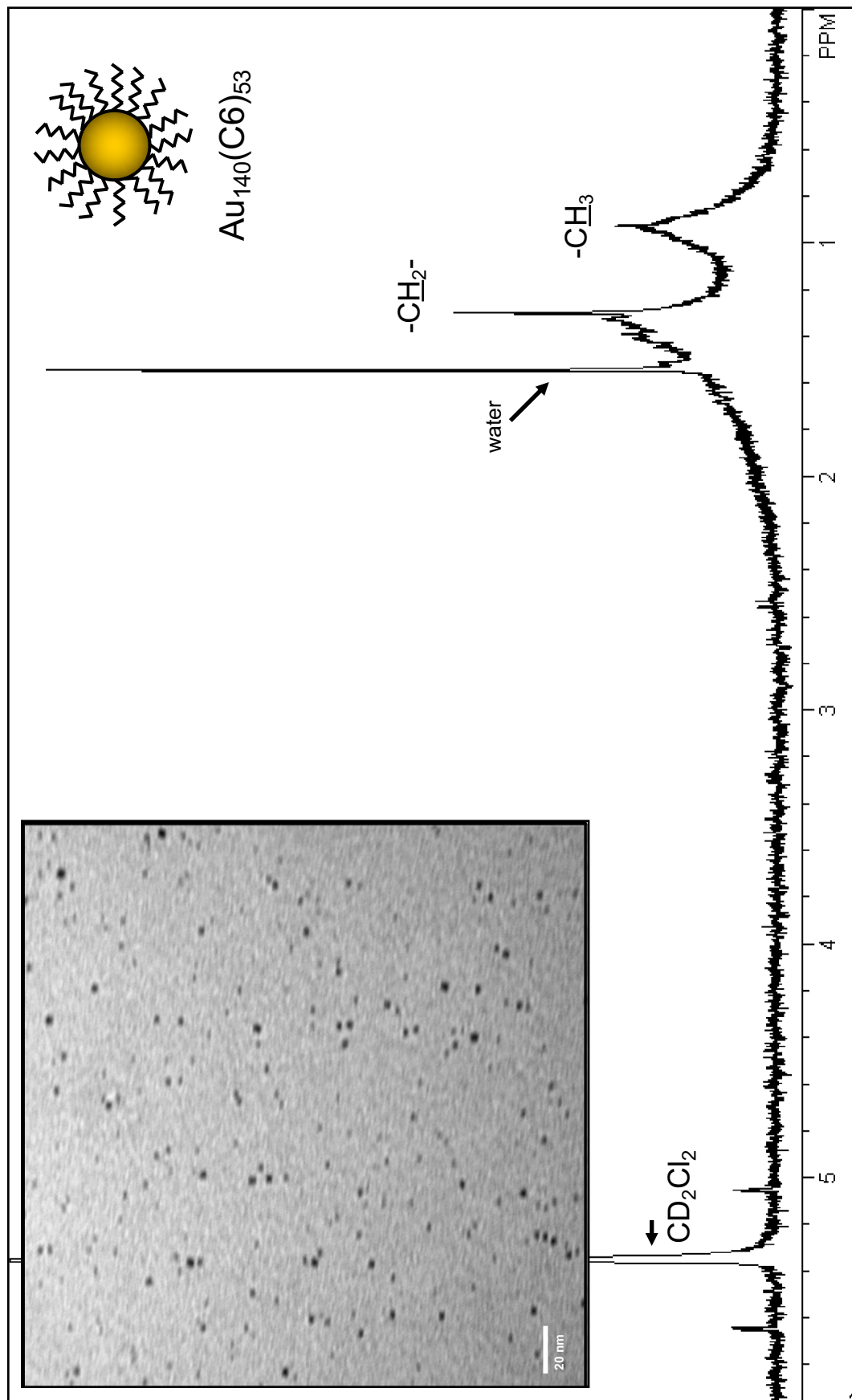


Figure SM-1. A) Typical ^1H NMR spectrum of hexanethiolate MPC in CD_2Cl_2 . Peaks are characteristically broadened with the presence of the gold cores. Residual water is present in the sample (~ 1.6 ppm). INSET: TEM image of hexanethiolate MPCs.

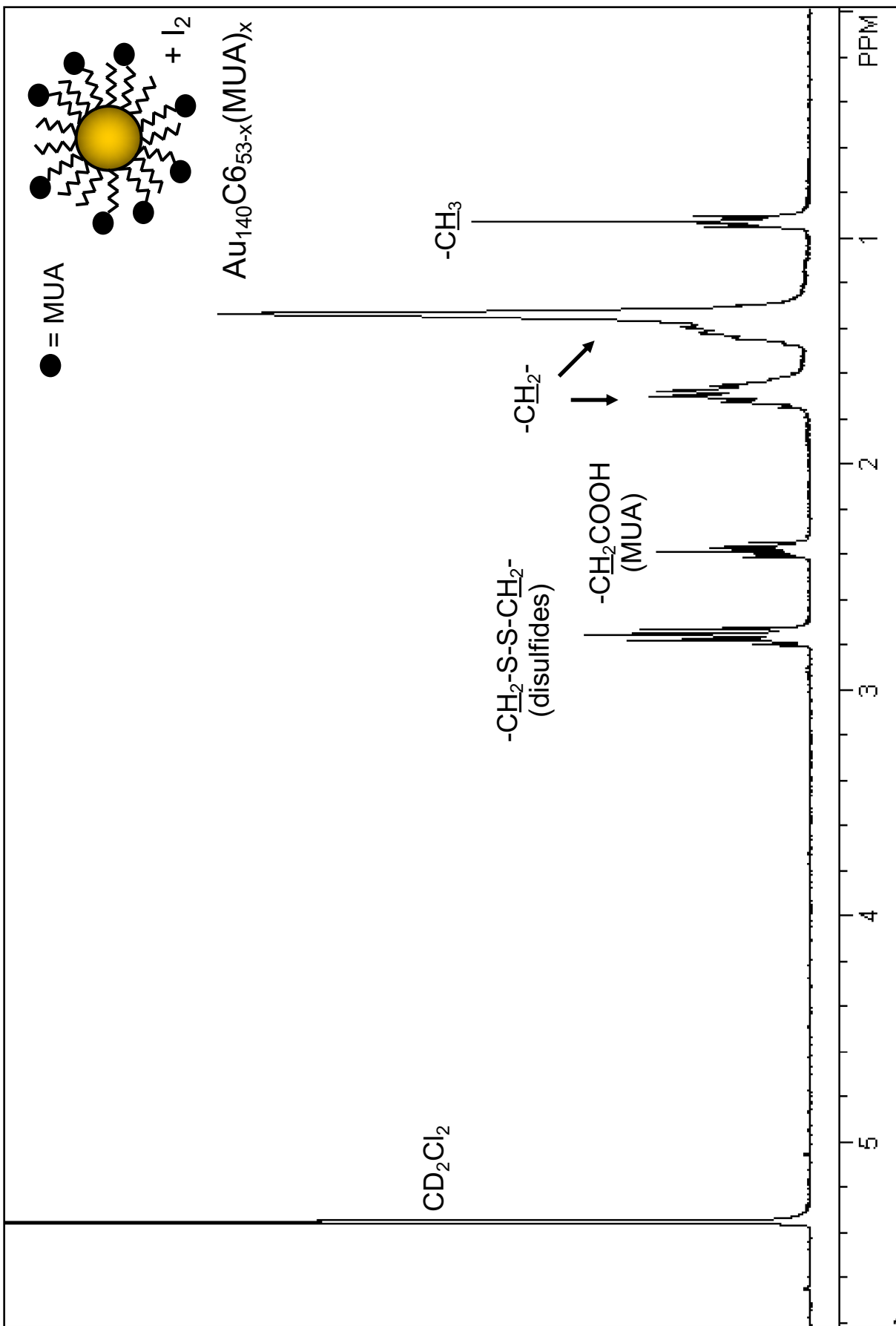
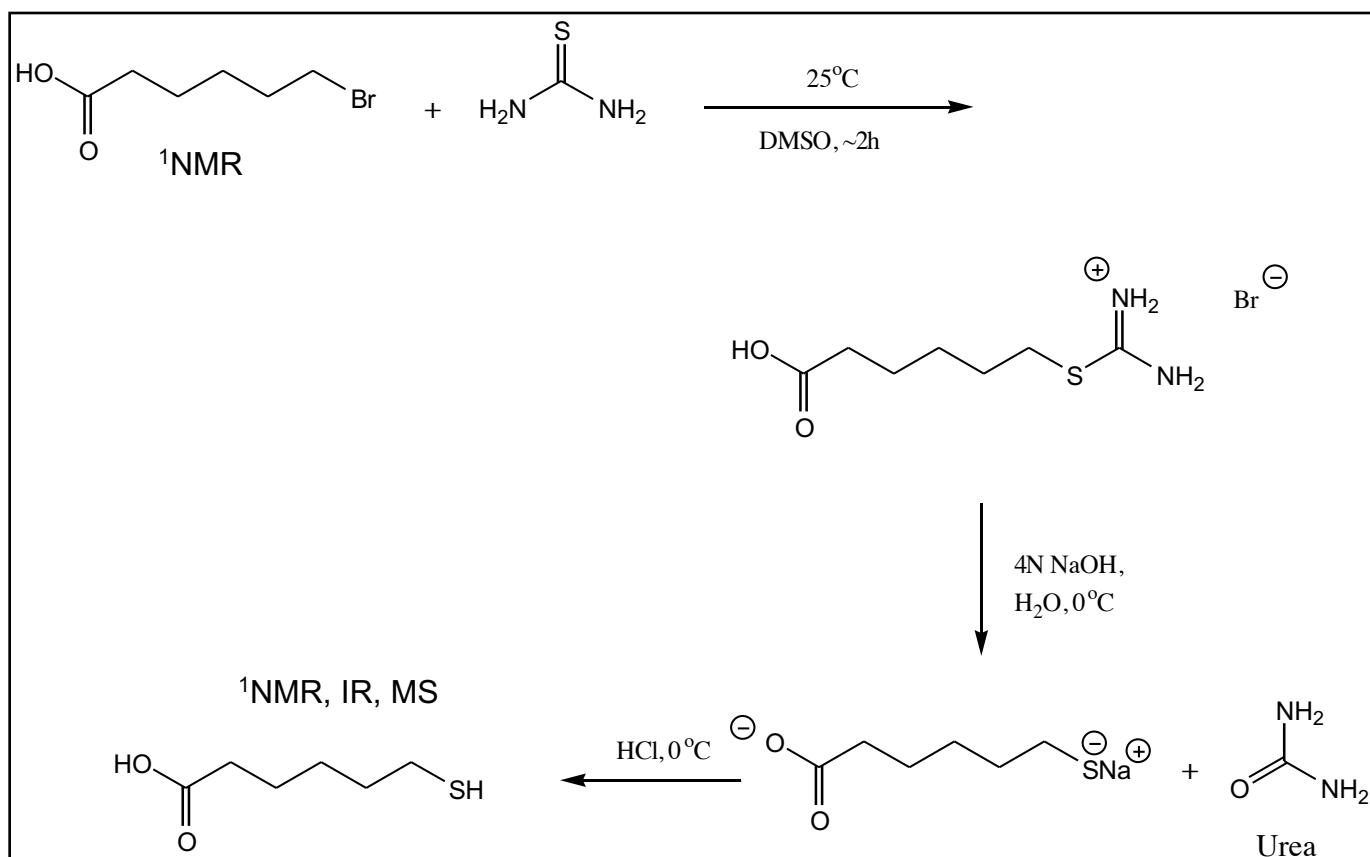


Figure SM-2. Typical ^1H NMR spectrum of MUA place-exchanged MPC after oxidative decomposition with iodine to liberate the peripheral ligands as disulfides. Ratio of MUA to hexanthiolate ligands was determined by integrating the methyl peaks at ~ 1.0 ppm to the signal from the methylene adjacent to the carboxylic acid at ~ 2.4 ppm. On average due to the inherent and well-documented polydispersity of the synthetic procedure, x was determined to be, on average, between 20-25.

Synthesis of 6-mercaptohexanoic acid (MHA). 6-mercaptohexanoic acid (MHA) was synthesized according to published procedures from Olah and Olah,* and following the reaction mechanism shown below in **Scheme SM-I**. Briefly, the starting material (6-bromohexanoic acid) was dissolved in DMSO prior to adding thiourea in a 1:1 mole ratio. A ^1H NMR of BHA is shown as **Figure SM-3**, with a notable peak representing the protons on the methylene unit next to the bromine at 3.45 ppm. This reaction mixture was allowed to stir under a nitrogen environment for 2-6 hours at room temperature before a chilled (0°C) solution of 4N NaOH was added with continuous stirring. Over the next 30 minutes, the reaction mixture was slowly acidified with the addition of chilled (0°C) 4 N HCl until a pH of ~ 2 was achieved and a white precipitate was formed. The slurry was then filtered with the white product washed several times with CH_2Cl_2 . The product was checked with thin-layer chromatography before being purified on with silica gel column chromatography. Fractions were collected, rotary evaporated and characterized via ^1H NMR (**Figure SM-4**), infrared spectroscopy (**Figure SM-5**), and GC-mass spectrometry (**Figure SM-6**). The NMR spectrum of the final product lacks the aforementioned peak at 3.45 ppm representing the methylene protons next to the bromine and a peak at 2.5 ppm, consistent with methylenes next to free thiol is now observed. A small amount of disulfide is also present but should be inconsequential for our experiments. IR spectroscopy confirms the presence of the carboxylic acid and the mass spectrometry verifies the product as well, with a significant percentage of the product as disulfide.



Scheme SM-I. Synthetic scheme for the synthesis of 6-mercaptohexanoic acid (MHA) from 6-bromohexanoic acid.

*G.A. Olah, O. Farooq, S. Morteza, F. Farnia, J.A. Olah, *J. Am. Chem. Soc.* **1998**, *110*, 2560.

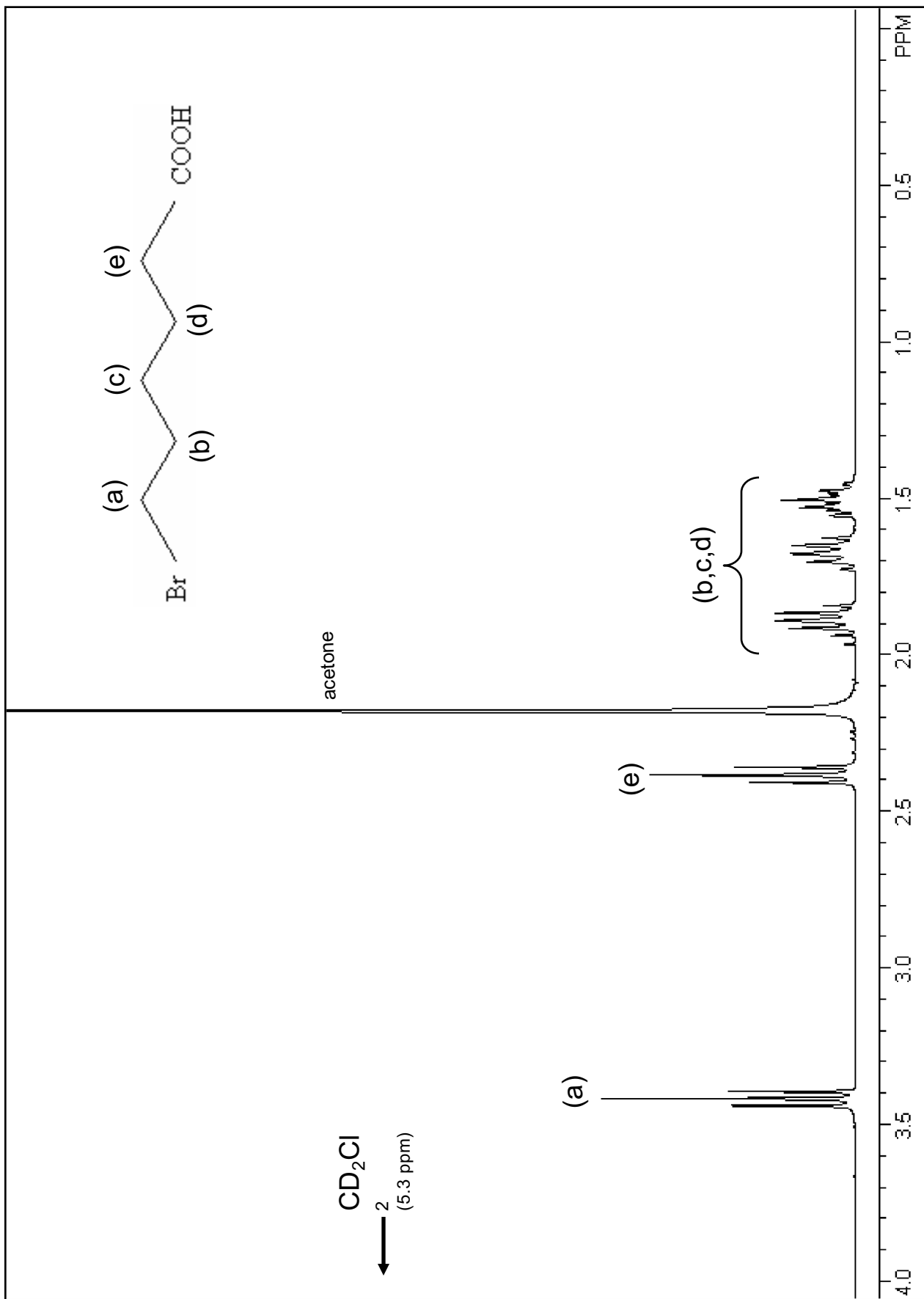


Figure SM-3. ^1H NMR spectrum of starting material, 6-bromohexanoic acid, for the synthesis of 6-mercaptohexanoic acid (MHA).

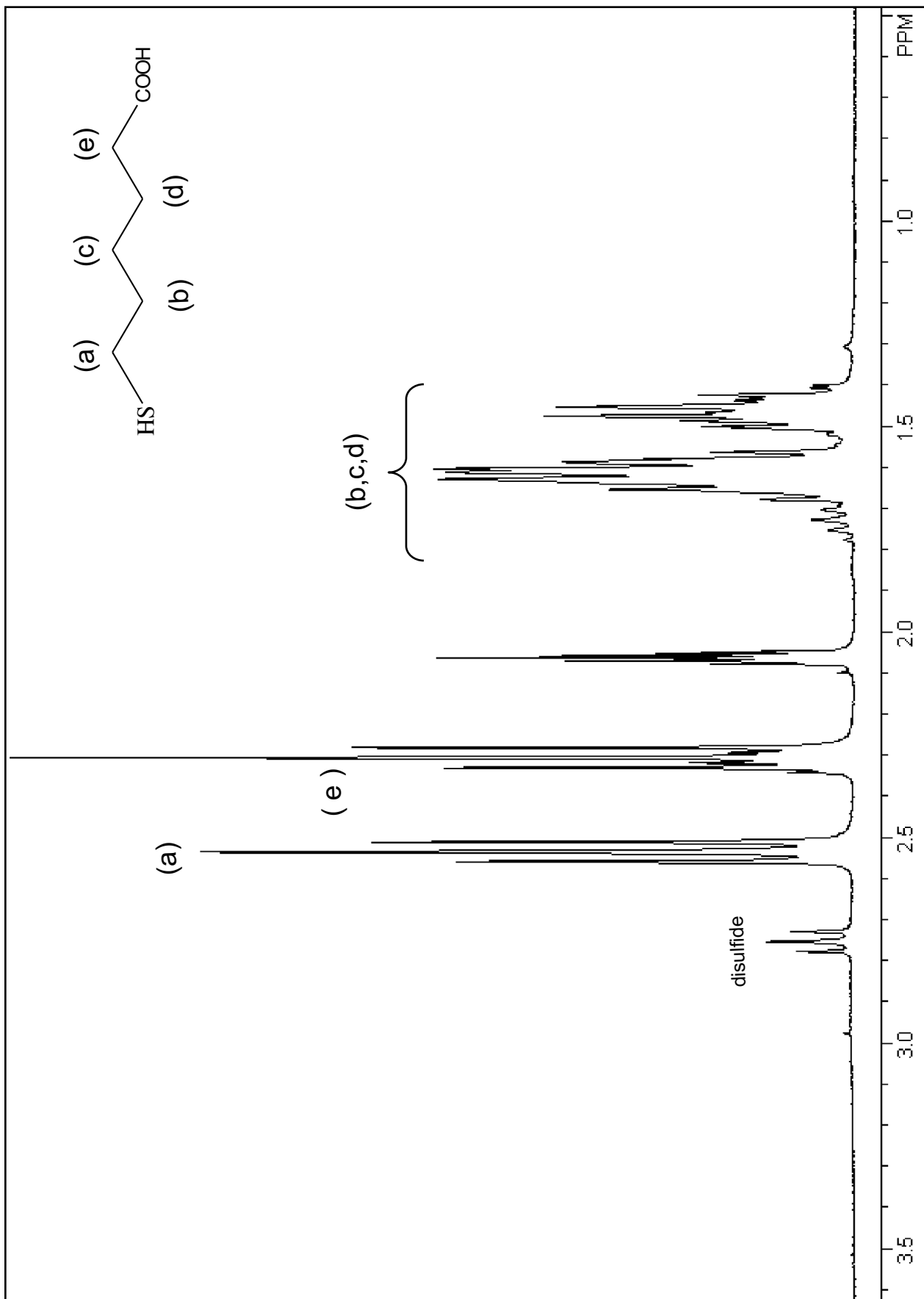
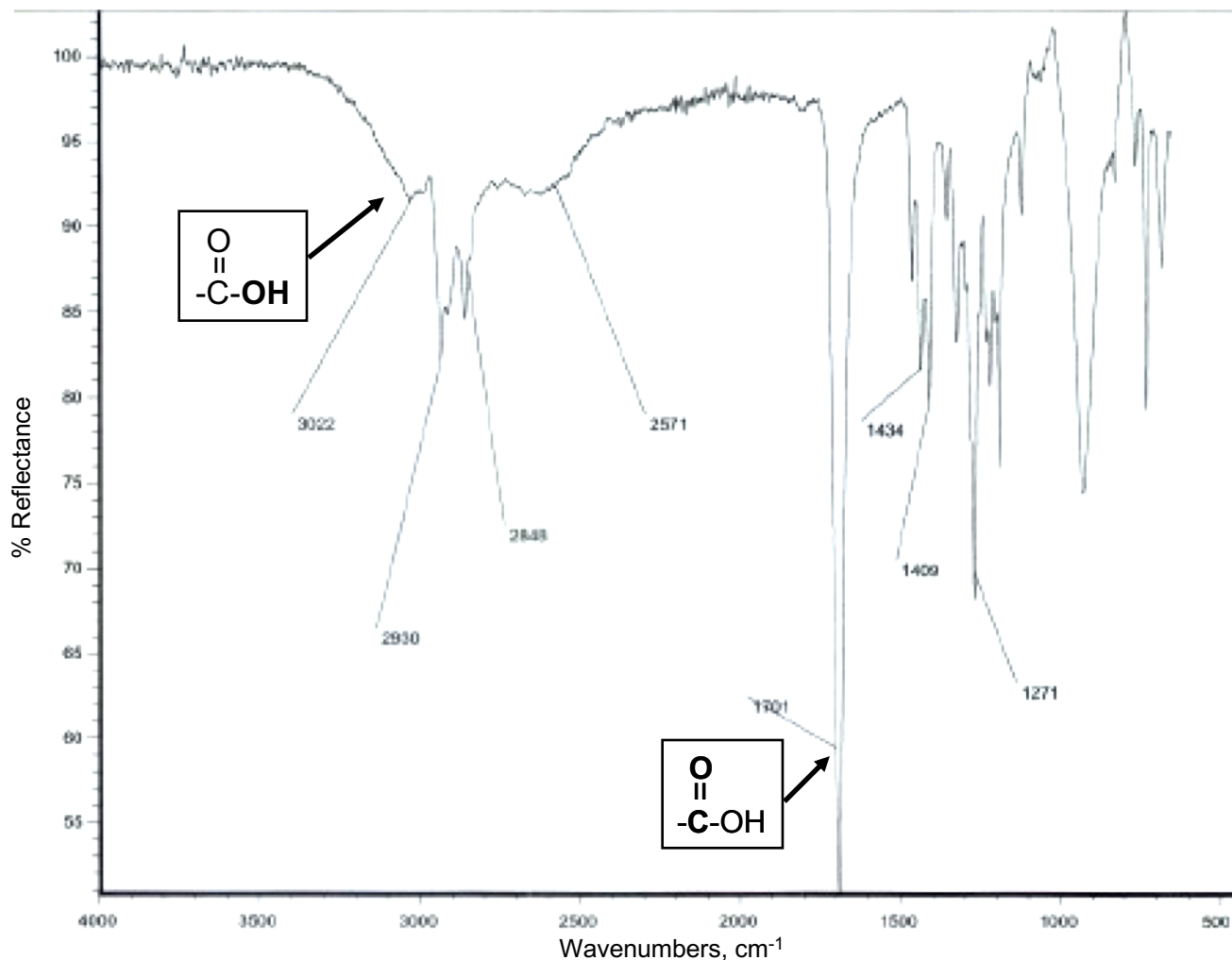
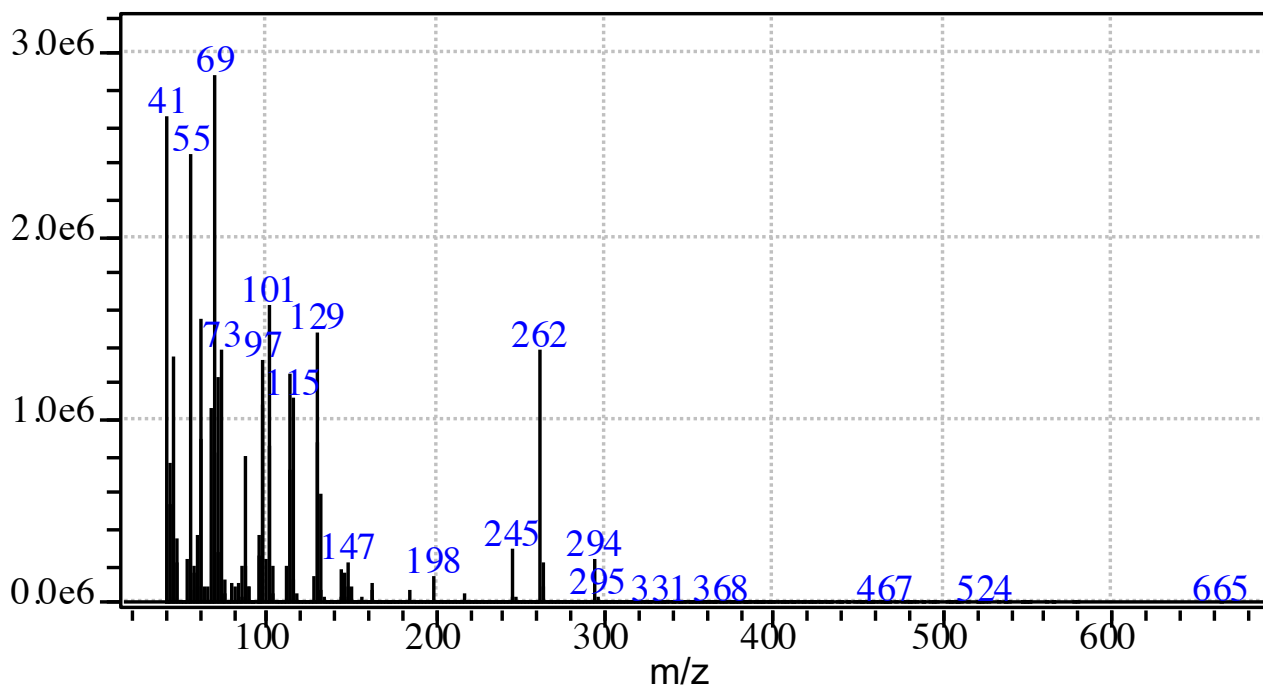


Figure SM-4. ^1H NMR spectrum of product from synthesis of MHA.



Scheme SM-5. IR spectrum for product of MHA synthesis.



Scheme SM-6. GC-MS spectrum for the product of MHA synthesis (thiol, 147; disulfide, 294).

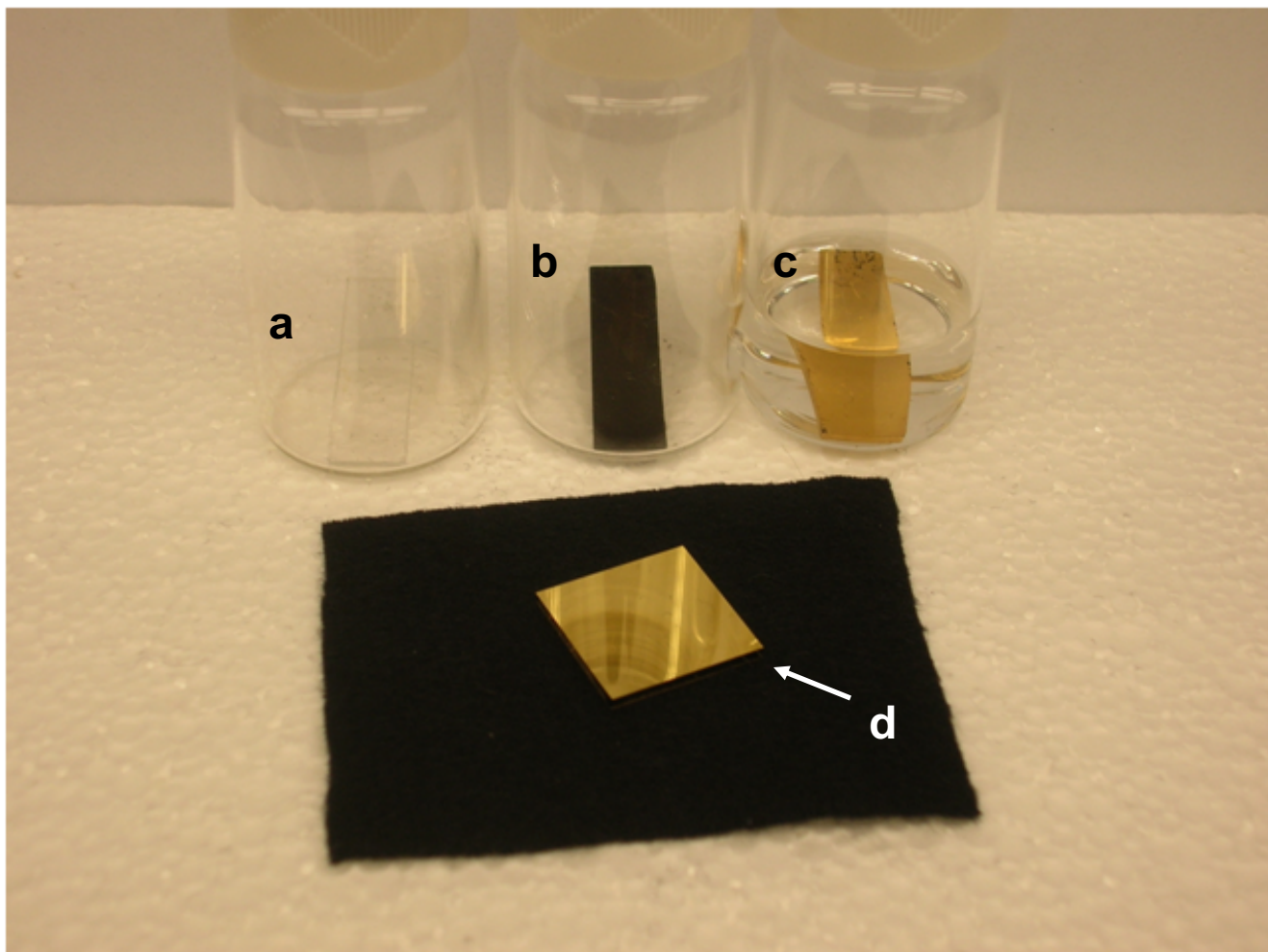


Figure SM-7. Digital photographs of a silanized glass slide (a), an assembled MPC film on glass (b), an MPC film after thermolysis into a thin gold coating (c), and a purchased evaporated gold film on glass (d).

Table SM-1. Double Layer Capacitance Measurements for SAMs at Evaporated Gold Substrates vs. Gold Substrates from Thermolyzed, Metal-Linked MPC Films

SAM	Endgroup	Total Number Carbons	Evaporated Gold ($\mu\text{F}/\text{cm}^2$)	M-L MPC Gold (Cu^{2+}) ($\mu\text{F}/\text{cm}^2$)	M-L MPC Gold (Zn^{2+}) ($\mu\text{F}/\text{cm}^2$)
BT	CH_3	4	16.9(± 8.4) n=10	655.5(± 290.8) n=4	615.0 (± 73.8) n=2
OT	CH_3	8	5.4(± 1.9) n=9	359.1(± 125.2) n=3	354.7 (± 79.6) n=3
DDT	CH_3	12	2.7(± 1.2) n=14	272.2(± 91.0) n=7	244.7 (± 95.0) n=2
MHA	COOH	6	15.9(± 4.3) n=4	1704.2(± 453.6) n=2	279.6 (± 175.1) n=5
MUA	COOH	11	7.2(± 2.05) n=11	1410.7(± 548.3) n=5	173.6 (± 96.4) n=8
MHDA	COOH	16	3.9(± 1.7) n=6	207.7(± 8.2) n=3	180.1 (± 44.3) n=8
MHOL	OH	6	15.9(± 7.8) n=8	179.5(± 39.4) n=2	274.7 (± 43.6) n=4
MUD	OH	11	6.6(± 2.1) n=8	172.7(± 69.3) n=3	106.3 (± 66.4) n=4

Note: Uncertainty () and number of measurements, n, indicated above. Experimental conditions: sweep rate of 100 mV/sec from 0.1 to 0.4V in a solution of 1.0M KCl. Current measured at 250 mV.

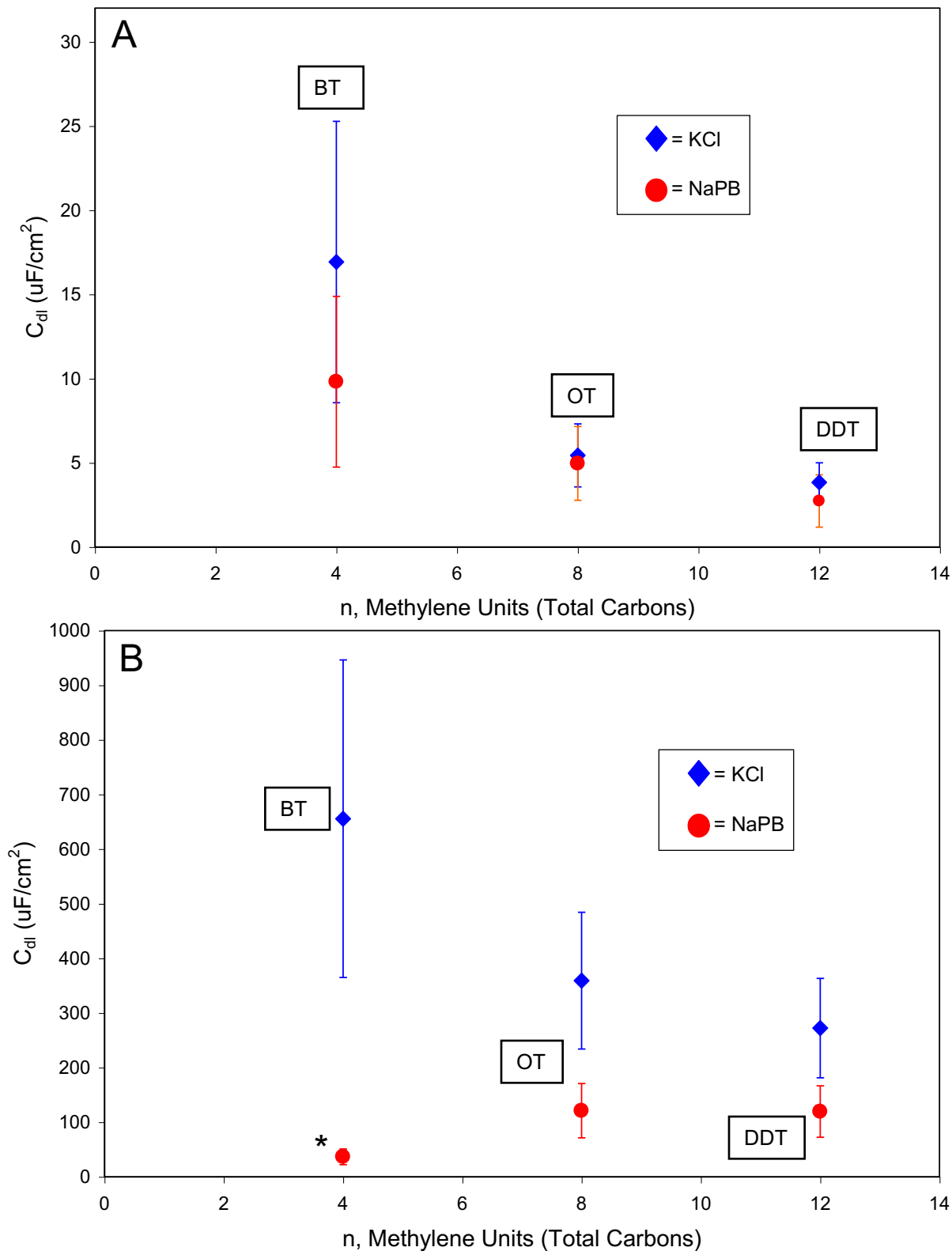


Figure SM-8. **A**) C_{dl} trends of methyl terminated SAMs of varying chainlength (n) on evaporated gold measured in 1.0 M KCl and sodium phosphate buffer (pH=7). **B**) C_{dl} trends of methyl terminated SAMs of varying chainlength (n) on Cu^{2+} MPC gold measured in 1.0 M KCl and sodium phosphate buffer (pH=7). [50]

*BT SAMs have been extensively tested and found to exhibit a high degree of variability in our measurements (shown above). The short chains and lack of intermolecular interaction in this SAM contributes to a lack of structure that can vary per experiment and over time. Erratic results for BT SAMs have been observed throughout the literature as well (e.g., Kolb, et al., Lang. 19 (2003) 830-834; Fawcett, et al., Lang. 18 (2002) 9342-9349; Creager, et al. Lang. 10 (1994) 1186-1192.)

Table SM-2. Desorption Potentials of SAMs at Evaporated Gold Substrates vs. Gold Substrates from Thermolyzed, Metal-Linked MPC Films

SAM	Endgroup	Total Carbon Number	Evaporated Gold (Volts vs. RE)	M-L MPC Gold (Cu ²⁺) (Volts vs. RE)	M-L MPC Gold (Zn ²⁺) (Volts vs. RE)
BT	CH ₃	4	-0.93(±0.04) n=6	-0.63(±0.06) n=3	-0.96 (±0.02) n=2
OT	CH ₃	8	-1.12(±0.03) n=3	-0.66(±0.03) n=2	-0.97 (±0.02) n=3
DDT	CH ₃	12	-1.21(±0.04) n=9	-0.81(±0.10) n=9	-0.91 (---) n=1
MHA	COOH	6	-0.81(±0.01) n=3	-0.72(±0.03) n=3	-0.89(±0.02) n=4
MUA	COOH	11	-1.11(±0.02) n=7	-0.88(±0.07) n=4	-1.02(±0.03) n=9
MHDA	COOH	16	-1.13(±0.04) n=4	-0.90(±0.17) n=7	-0.99(±0.03) n=7
MHOL	OH	6	-1.17(±0.01) n=4	-0.81(±0.05) n=3	-0.97(±0.04) n=3
MUD	OH	11	-1.19(±0.01) n=3	-0.96(±0.14) n=3	-1.02(±0.18) n=4

Note: Uncertainty () and number of measurements, n, indicated above. Experimental conditions: solutions thoroughly deaerated with nitrogen and linear sweep voltammetry performed from -0.3 to -1.5V at 100 mV/sec.

Table SM-3. Difference in Peak Potential Splitting (ΔE_p values) for K₄Fe(CN)₆ Redox Probing of SAMs at Evaporated Gold Substrates vs. Gold Substrates from Thermolyzed, Cu²⁺ Metal-Linked MPC Films

SAM	Endgroup	total carbon	ΔE_p Evaporated Gold (Volts vs. RE)	ΔE_p M-L MPC Gold Cu ²⁺ Linked (Volts vs. RE)	ΔE_p M-L MPC Gold Zn ²⁺ Linked (Volts vs. RE)
BT	CH ₃	4	AN [0.49] n=4	AN [0.34] n=5	AN [0.32] n=1
OT	CH ₃	8	NP n=3	0.098(±0.008) n=2	AN [0.27] n=2
DDT	CH ₃	12	NP n=3	0.124(±0.045) n=3	NP n=5
MHA	COOH	6	AN [0.51] n=4	- ^a	AN [0.26] n=3
MUA	COOH	11	NP n=4	NP n=2	NP n=5
MHDA	COOH	16	NP n=3	NP n=2	NP n=12
MHOL	OH	6	0.25(±0.01) n=5	- ^a	NP n=3
MUD	OH	11	NP n=4	0.131(±0.050) n=3	NP n=7

Note: Uncertainty () and number of measurements, n, indicated above.

^{AN} Indicates the SAM was sufficiently blocking enough toward K₄Fe(CN)₆ that only an anodic peak was observed with the average anodic peak potentials, $E_{p,a}$, shown in brackets.

^{NP} Indicates that the SAM was sufficiently blocking enough toward K₄Fe(CN)₆ that no peaks were observed.

^a SAMs of MHA and MHOL at Cu²⁺ linked MPC gold were not measured since diffusional K₄Fe(CN)₆ voltammetry was previously observed for those specific films on evaporated gold.

Experimental conditions: 2mM K₄Fe(CN)₆ in 0.5 M KCl, cycled from 0 to 0.6 V at 100 mV/sec.

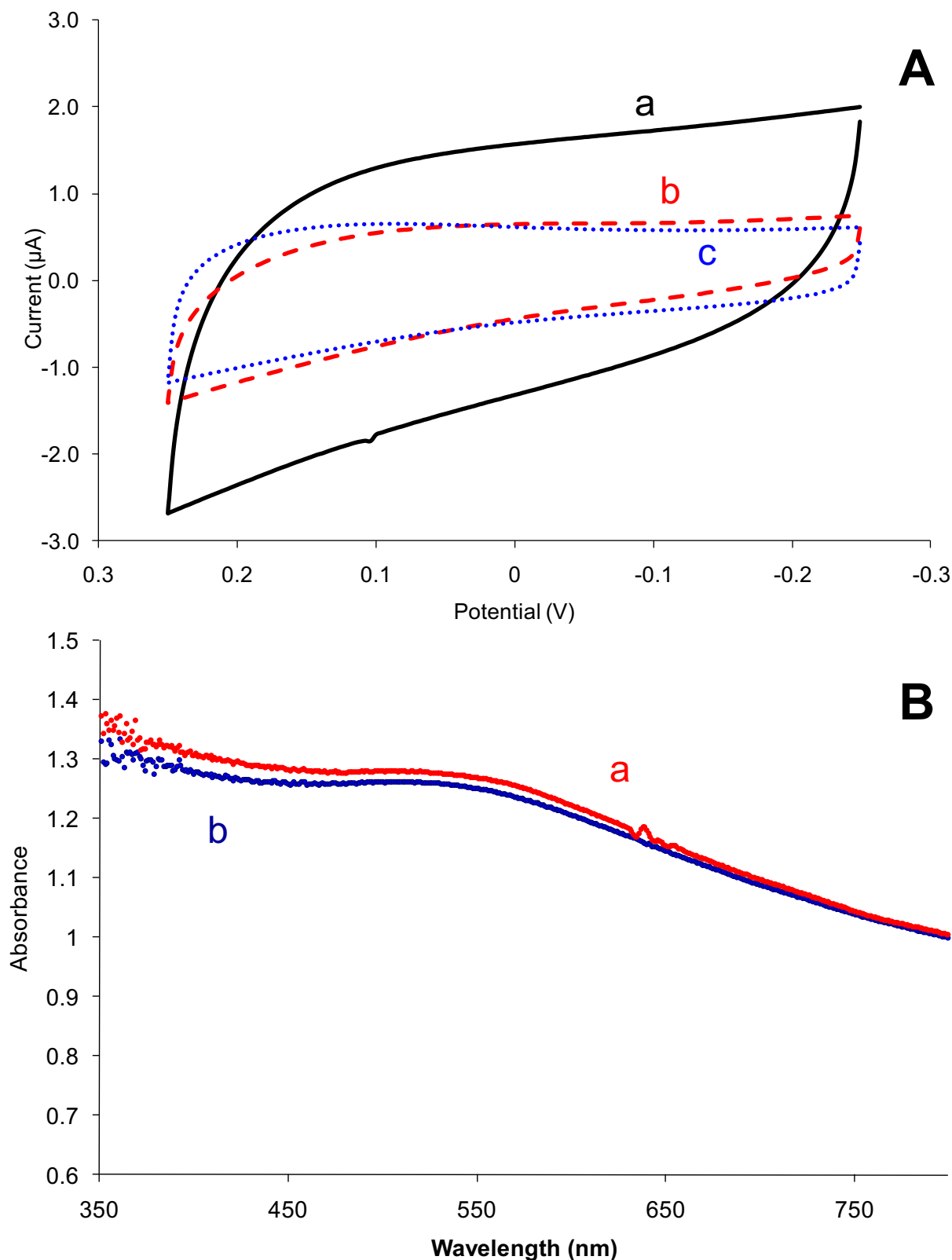


Figure SM-9. **A**) Cyclic voltammetry of a MPC film assembly (a) as prepared with Zn^{2+} -carboxylate linkages, (b) after 10 minutes of soaking in ethanol to extract excess metal ions, and (c) after 20 minutes of soaking in ethanol to extract excess metal ions. **B**) UV-Vis spectroscopy of the Zn^{2+} M-L MPC film assembly (a) before and (b) after 40 minutes of metal ion extraction with pure ethanol. The maximum absorbance and surface plasmon band of the nanoparticle film, centered at ~ 550 nm, are unchanged indicating that there are no changes in film thickness or interparticle distances.

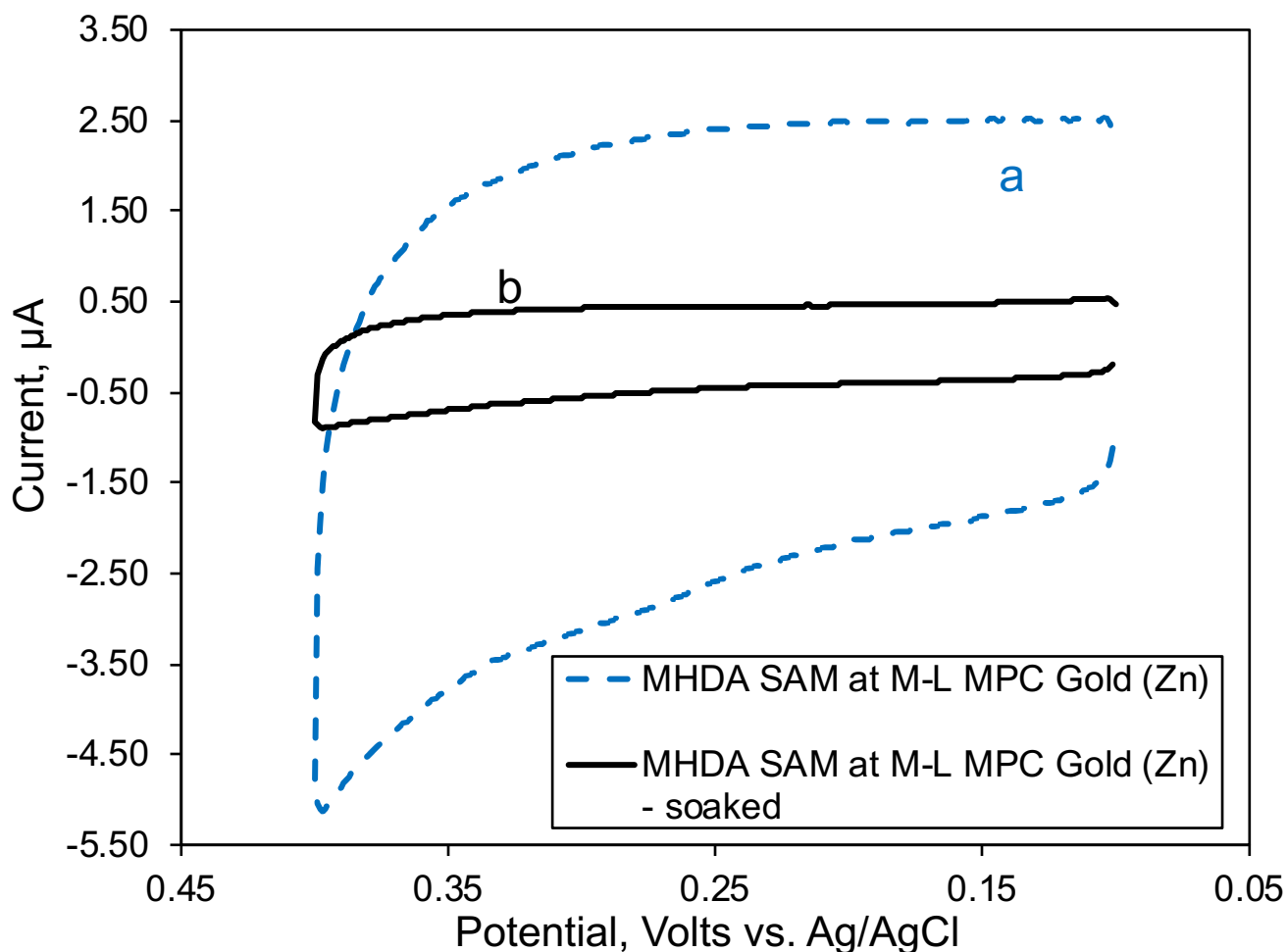


Figure SM-10. Cyclic voltammetry for C_{dl} measurements of MHDA SAMs at gold substrates formed from the thermal decomposition of (a) Zn^{2+} M-L MPC films and (b) Zn^{2+} M-L MPC films after being soaked (metal extracted) with ethanol for 45 minutes. A numerical comparison of both C_{dl} and desorption potential is included in **Table SM-4** below.

Table SM-4. C_{dl} and Desorption Potentials of MHDA SAMs at Thermolyzed M-L (Zn^{2+}) MPC Films With and Without Extraction of Metal Ions During Assembly

SAM	Pretreatment	C_{dl} ($\mu F/cm^2$)	LSV (volts)
MHDA	No metal Extraction	$180.1_{(\pm 44.3)} \quad n=8$	$-0.99_{(\pm 0.03)} \quad n=7$
MHDA	Metal- Extracted	$39.7_{(\pm 12.5)} \quad n=3$	$-1.08_{(\pm 0.04)} \quad n=3$

Note: Uncertainty () and number of measurements, n, indicated above.
Experimental conditions described in Tables 1 and 2.