

# Electronic supporting information

## Carboxybetaine modified interface for electrochemical glycoprofiling of antibodies isolated from human serum

*Tomas Bertok<sup>1,#</sup>, Alena Šedivá<sup>1,#</sup>, Jaroslav Filip<sup>1</sup>, Marketa Ilcikova<sup>2</sup>, Peter Kasak<sup>2</sup>, Dusan Velic<sup>3,4</sup>, Eduard Jane<sup>4</sup>, Martina Mravcová<sup>5</sup>, Jozef Rovenský<sup>6</sup>, Pavol Kunzo<sup>7</sup>, Peter Lobotka<sup>7</sup>,  
Vasilij Šmatko<sup>7</sup>, Alica Vikartovská<sup>1</sup>, Jan Tkac<sup>1,\*</sup>*

<sup>1</sup> Department of Glycobiotechnology, Institute of Chemistry, Slovak Academy of Sciences, Dubravská cesta 9, Bratislava, 845 38, Slovak Republic

<sup>2</sup> Center for Advanced Materials, Qatar University, P.O. Box 2713, Doha, Qatar

<sup>3</sup> Department of Physical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynska Dolina, Bratislava, 842 15, Slovak Republic

<sup>4</sup> International Laser Center, Ilkovičova 3, Bratislava 841 04, Slovak Republic

<sup>5</sup> Laboratory of Human Endocrinology, Institute of Experimental Endocrinology, Slovak Academy of Sciences, Vlarska 3, Bratislava, 833 06, Slovak Republic

<sup>6</sup> National Institute of Rheumatic Diseases, Nábřežie I. Krasku 4, 921 12 Piešťany, Slovak Republic

<sup>7</sup> Department of Sensors and Detectors, Institute of Electrical Engineering, Slovak Academy of Sciences, Dubravská cesta 9, Bratislava, 841 04, Slovak Republic

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# These authors contributed equally to this work.

\* Corresponding author. Tel.: +421 2 5941 0263. E-mail: [Jan.Tkac@savba.sk](mailto:Jan.Tkac@savba.sk)

## 1. Synthesis

The synthesis of 2-((11-mercaptoundecyl)dimethylammonio)acetate **1**, which was utilized for SAM formation, was performed in 4 steps. Quarterisation of *N,N*-dimethyl glycine ethyl ester with BDU yielded **2**, which was hydrolysed with basic ionic exchange resin to **3**. Addition on the terminal double bond of **3** was performed with thioacetic acid with catalytic amount of AIBN under inert condition to **4** and the final product **1** was obtained after acidic hydrolyses under inert condition.

The synthesis of **1** was carried out as follow:

### 1.1. Materials

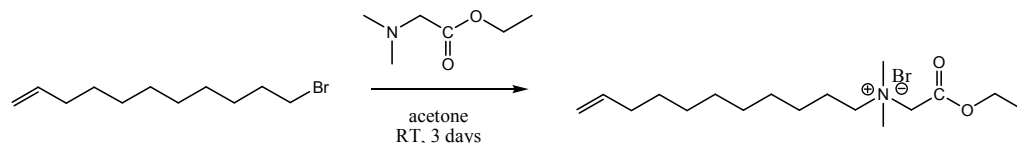
11-bromo-1-undecene (BDU), ethanol, NaOH, *N,N*-dimethyl glycine ethyl ester, diethyl ether, methanol, azobisisobutyronitrile (AIBN), thioacetic acid, acetone, hydrochloric acid and amberlite IRA-400 chloride form were purchased from Aldrich as used as received. Ultrapure water was obtained from Millipore system.

### 1.2. Characterization

<sup>1</sup>H NMR spectra were recorded on a Varian 400 MR spectrometer instrument at 298 K. Chemical shifts are reported in ppm downfield to solvent standard. The solvent was used as a reference. Working frequency was 400 MHz. Coupling patterns were designated as s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet. Concentration of samples was around 10 mg of sample dissolved in 0.7 mL of solvent.

ATR-FTIR data were recorded FTIR 760 (Nicolet) Infrared Spectrophotometer with 32 scans. The spectra were characterized in wavenumbers.

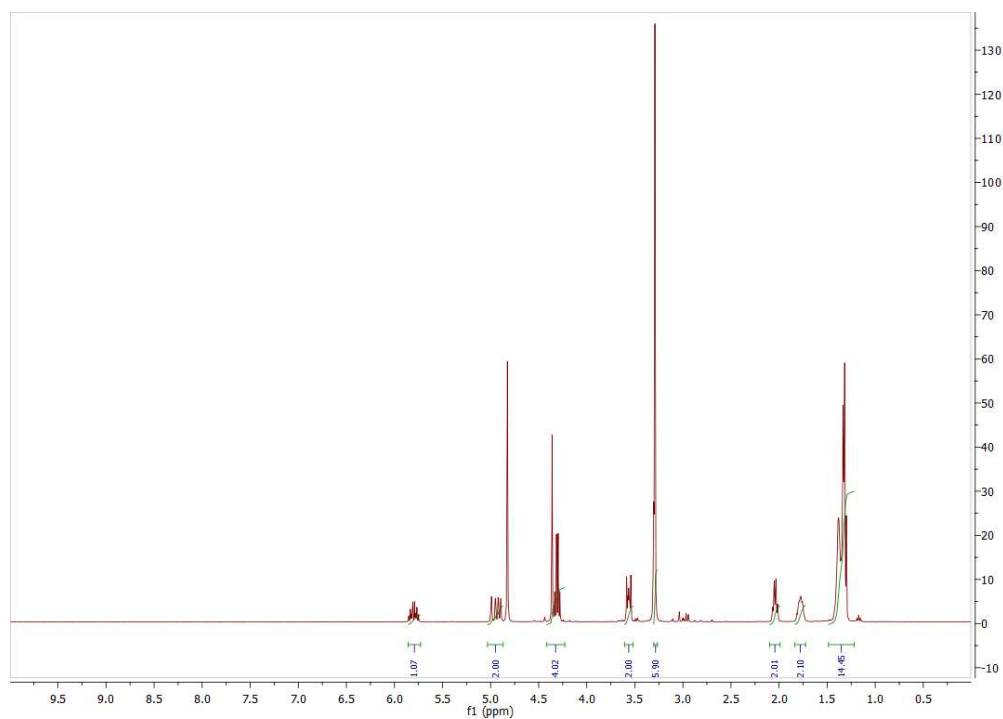
### 1.3. *N*-(2-ethoxy-2-oxoethyl)-*N,N*-dimethylundec-10-en-1-aminium bromide (**2**)



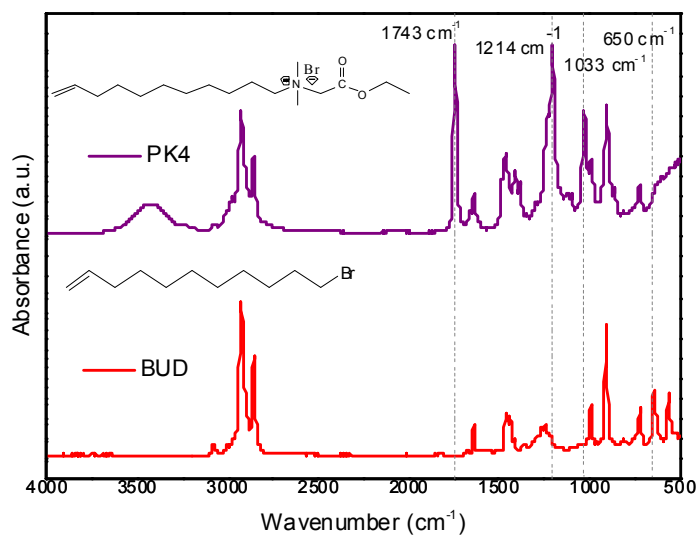
The BDU (0.624g, 2.7 mmol) and *N, N*-dimethyl glycine ethyl ester (8 mmol, 1.14 mL) was stirred in 0.5 mL acetone at ambient temperature for three days. Then the solvent was evaporated and the product was purified by three times re-precipitation into diethyl ether (12 mL) and dried in high vacuum to obtain product in form yellowish oil (0.6813g, 69 %).

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD): δ 5.74-5.86 (m, 1H, H<sub>2</sub>C=CH-CH<sub>2</sub>), 4.88-5.0 (m, 2H, H<sub>2</sub>C=CH), 4.38 (s, 2H N<sup>+</sup>-CH<sub>2</sub>-CO), 4.30 (q, 2H O-CH<sub>2</sub>-CH<sub>3</sub>), 3.53-3.6 (m, 2H, CH<sub>2</sub>-N<sup>+</sup>), 3.24-3.36 (s, 6H, N<sup>+</sup>-Me<sub>2</sub>), 2.00-2.10 (m, 2H, =CH-CH<sub>2</sub>), 1.70-1.84 (m, 2H, CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>), 1.28-1.50 (m, 12H, -CH<sub>2</sub>-and 3H, CH<sub>2</sub>-CH<sub>3</sub>).

**IR (ATR):** cm<sup>-1</sup> 3435, 3078, 2925, 2851, 1743, 1642, 1470, 1409, 1211, 1033, 907, 719.

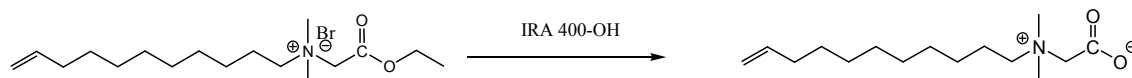


**Figure S1:** <sup>1</sup>H NMR spectrum of **2**



**Figure S2:** Comparison of FTIR spectra for BUD and **2**

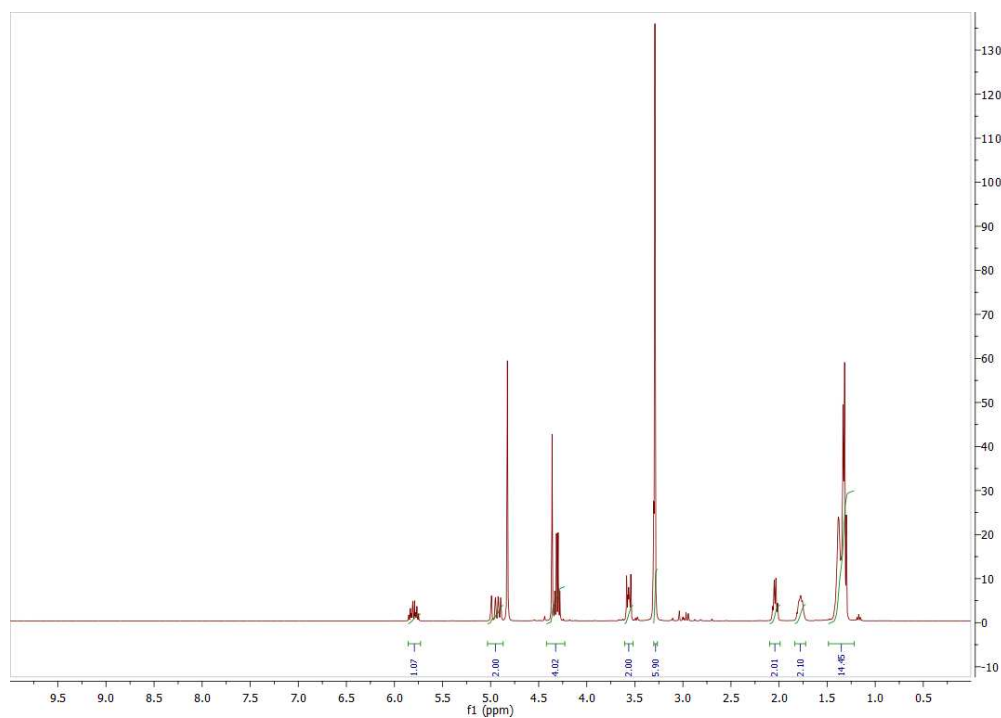
**1.4. Synthesis of 2-(dimethyl(undec-10-enyl)ammonio)acetate (3)**



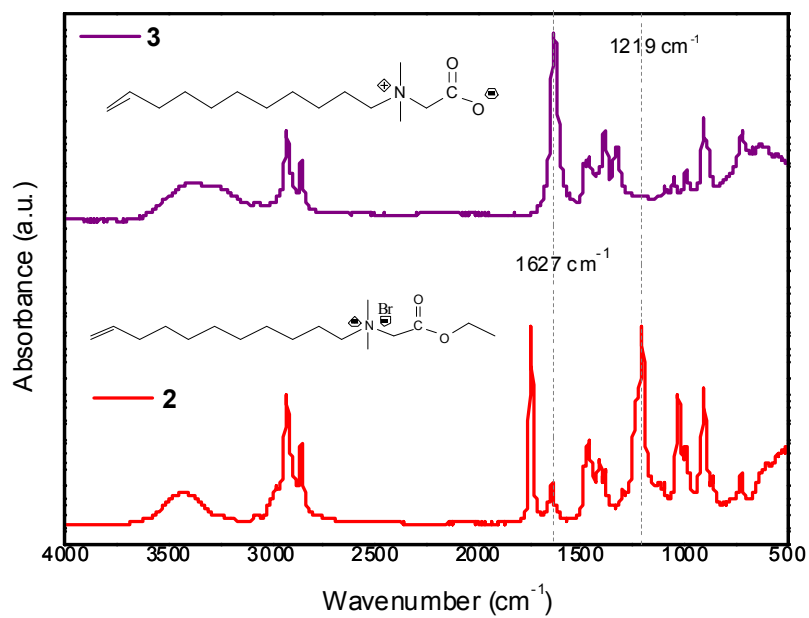
0.6201 (1.7 mmol) g of **2** was dissolved in ultrapure water (5 mL) and passed through amberlite IRA 400 column activated by 0.1 M NaOH (100 mL). The solvent was evaporated, dried in high vacuum and the product **3** was obtained in form of dark orange oil (0.3805g, 98 %).

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD): δ 5.74-5.86 (m, 1H, CH<sub>2</sub>=CH), 4.88-5.01(m, 2H, CH<sub>2</sub>=CH), 3.77 (s, 2H, N<sup>+</sup>-CH<sub>2</sub>), 3.50-3.60 (m, 2H, CH<sub>2</sub>-N<sup>+</sup>), 3.21 (s, 6H, N<sup>+</sup>-Me<sub>2</sub>), 2.00-2.08 (m, 2H, CH<sub>2</sub>=CH-CH<sub>2</sub>), 1.68-1.80 (m, 2H, CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>), 1.28-1.45 (m, 12H, -CH<sub>2</sub>)

**IR (ATR):** cm<sup>-1</sup> 3425, 3075, 2928, 2851, 1743, 1639, 1467, 1409, 1377, 1208, 1030, 907, 716

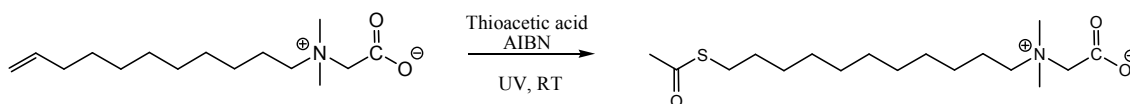


**Figure S3:** <sup>1</sup>H NMR spectrum of **3**



**Figure S4:** Comparison of FTIR spectra for **2** and **3**

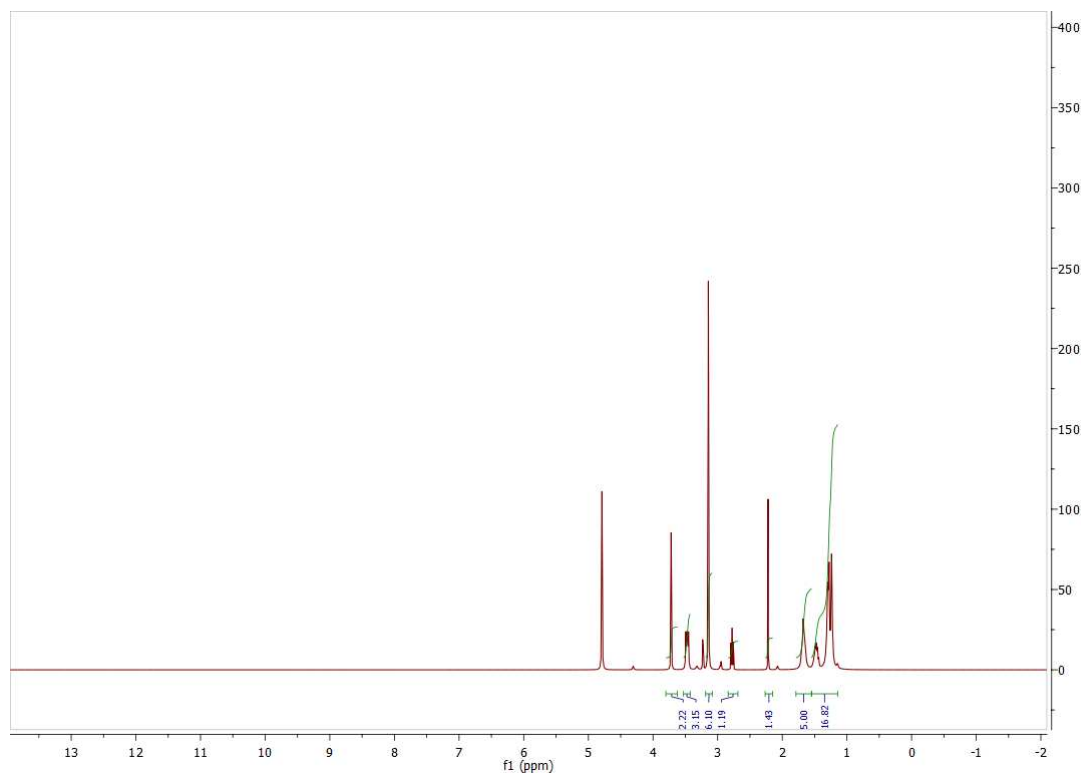
**1.5. Synthesis of 2-((11-(acetylthio)undecyl)dimethylammonio)acetate (4)**



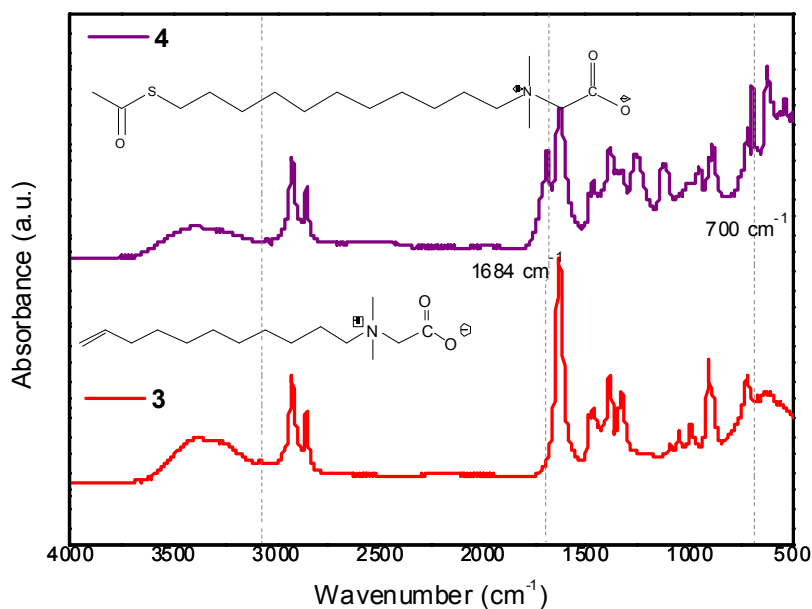
0.3632 g (1.4 mmol) of **3** was dissolved in methanol (0.7 mL) degassed rigorously with nitrogen and thioacetic acid (0.4 mL, 6 mmol) and catalytic amount of AIBN was added. The reaction mixture stirred at ambient temperature overnight while irradiated by UV lamp under nitrogen atmosphere. Then the solvent was evaporated and the product was purified by three times re-precipitation into diethyl ether (12 mL) and dried in high vacuum to obtain product **4** in the form of yellowish oil (0.3039 g, 65 %).

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD): δ 3.78 (s, 2H, N<sup>+</sup>-CH<sub>2</sub>), 3.50-3.60 (m, 2H, CH<sub>2</sub>-N<sup>+</sup>), 3.22 (s, 6H, N<sup>+</sup>-Me<sub>2</sub>), 2.75 (t, 2H, S-CH<sub>2</sub>), 2.22 (s, 3H, CH<sub>3</sub>-CO-S), 1.70-1.80 (m, 2H, CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>), 1.32-1.62 (m, 14H, CH<sub>2</sub>)

**IR (ATR):** cm<sup>-1</sup> 3395, 2922, 2848, 1691, 1629, 1470, 1380, 1250, 1121, 958, 878, 700, 615 cm<sup>-1</sup>.

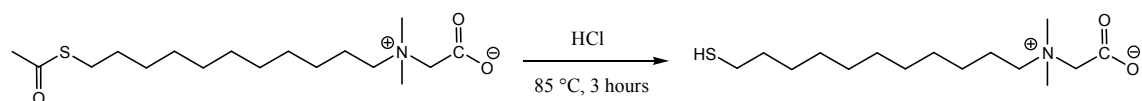


**Figure S5:** <sup>1</sup>H NMR spectrum of **4**.



**Figure S6:** Comparison of FTIR spectra for **3** and **4**

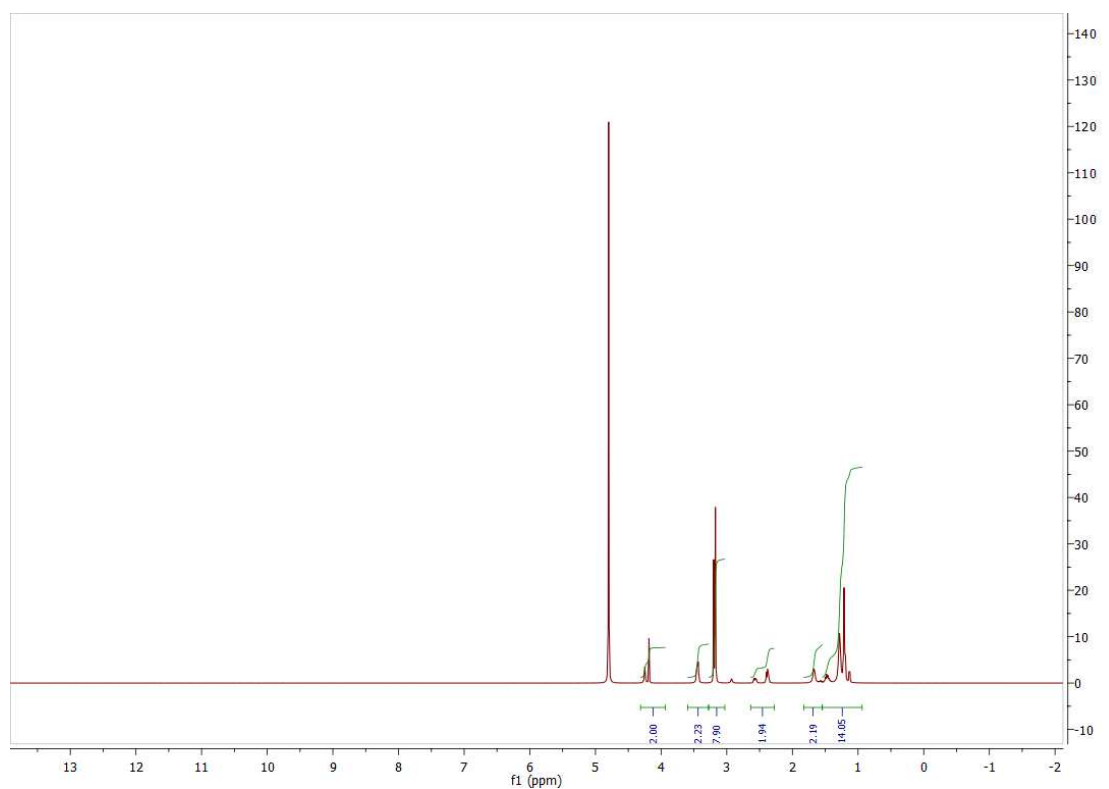
**1.6. 2-((11-mercaptoundecyl)dimethylammonio)acetate (1)**



0.2001 g (0.6 mmol) of **3** was dissolved in ethanol (0.8 mL) and 0.3 mL of concentrated HCl was added and reaction mixture was rigorously filled with nitrogen atmosphere. The reaction mixture was stirred for 3 hour in nitrogen atmosphere at 85 °C. then the solvent was evaporated and the product was purified by re-precipitation into diethyl ether (2 x 14 mL) and dried in high vacuum. The product was obtained in form of orange dense oil (0.1081g, 0.4 mmol, 62 %).

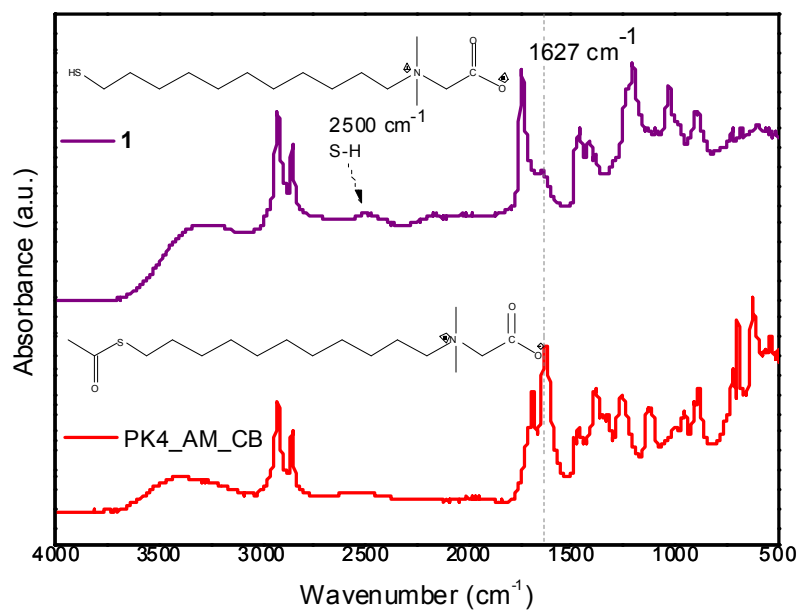
$^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  4.32 (s, 2H,  $\text{N}^+-\text{CH}_2\text{CO}$ ), 3.55-3.65 (m, 2H,  $\text{N}^+-\text{CH}_2$ ) 3.28 (s, 6H,  $\text{N}^+-\text{Me}_2$ ), 2.38 (t, 2H,  $-\text{CH}_2-\text{SH}$ ) 1.74-1.82 (m, 2H,  $\text{CH}_2-\text{CH}_2-\text{N}^+$ ), 1.6-1.2 (m, 14H,  $\text{CH}_2$ ).

**IR (ATR):**  $\text{cm}^{-1}$  3292, 2919, 2851, 2501, 1627, 1464, 1406, 1204, 1024, 893.



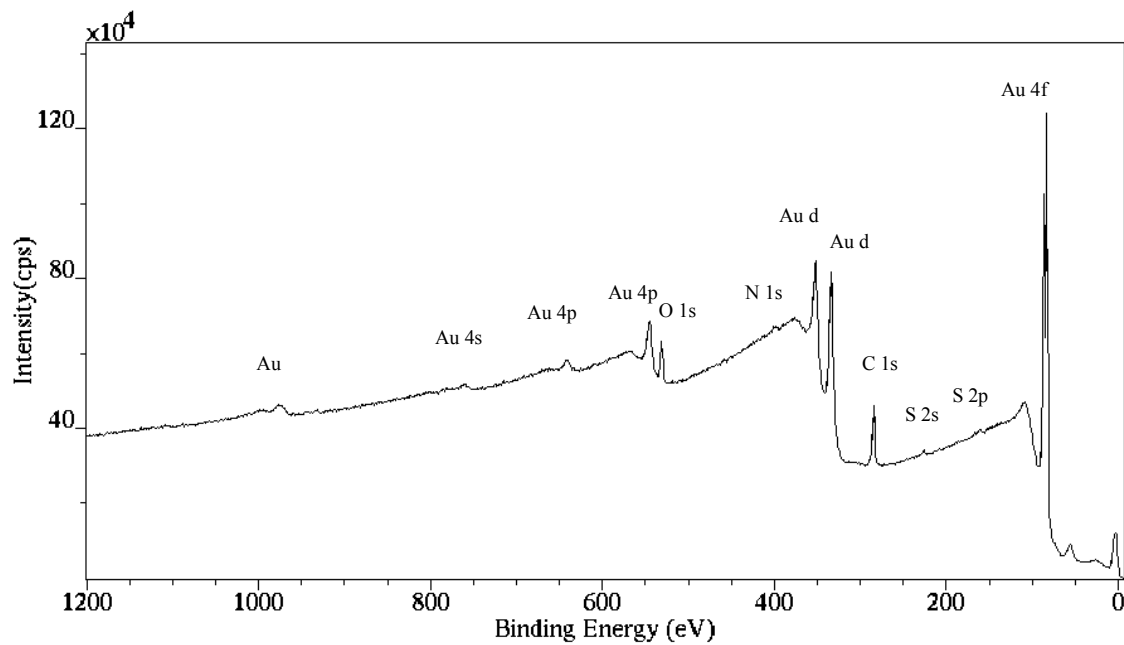
**Figure S7:**  $^1\text{H}$  NMR spectrum of **1**.





**Figure S8:** Comparison of FTIR spectra for **4** and **1**.

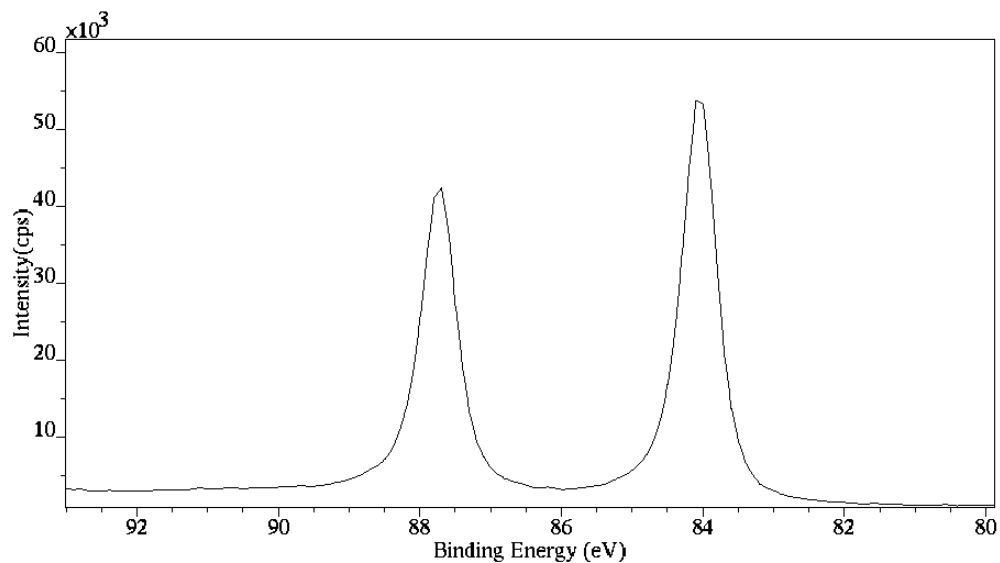
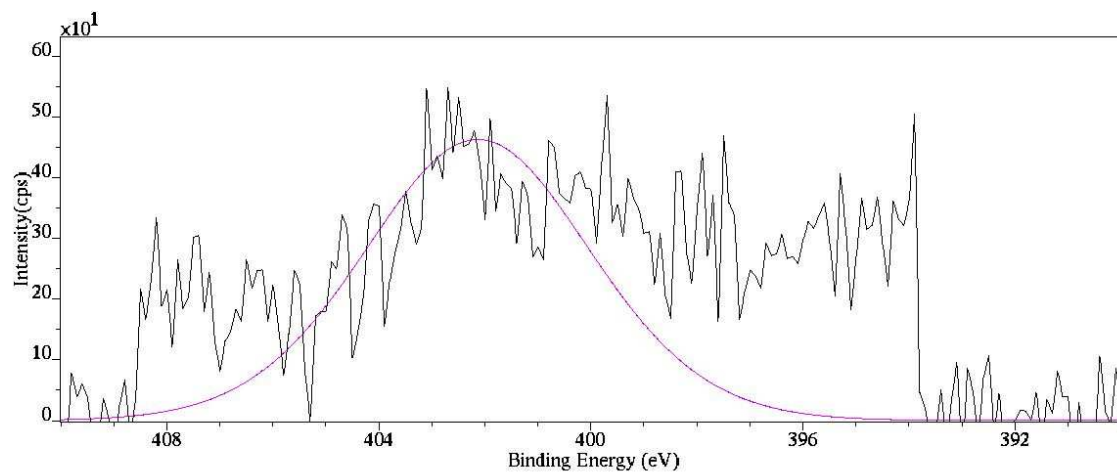
**1.7. XPS analysis**

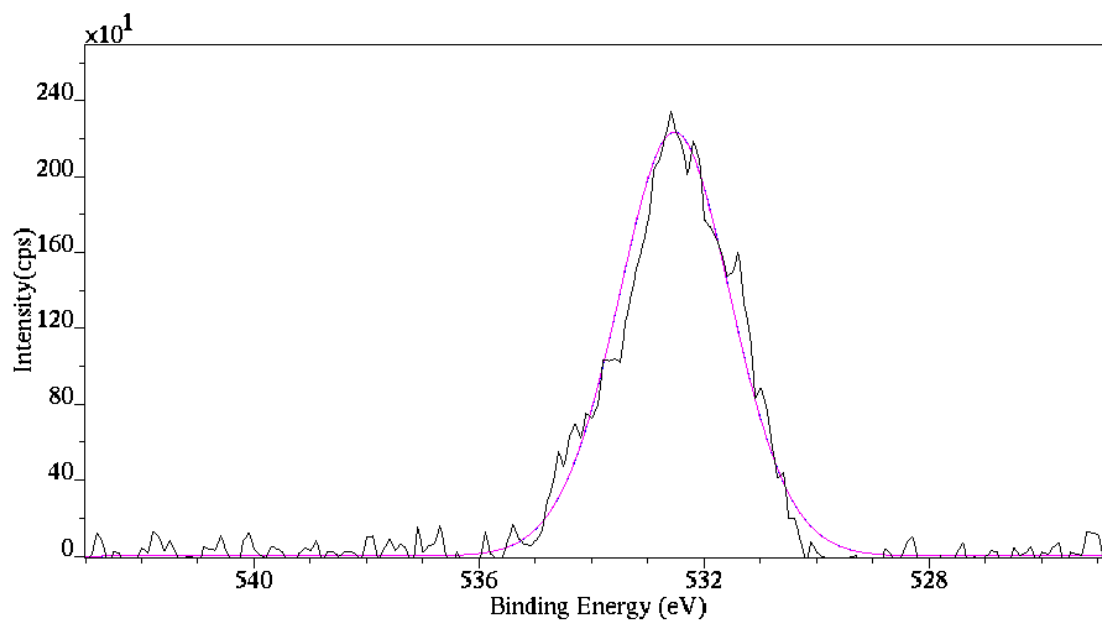


**Figure S9:** XPS wide survey scan

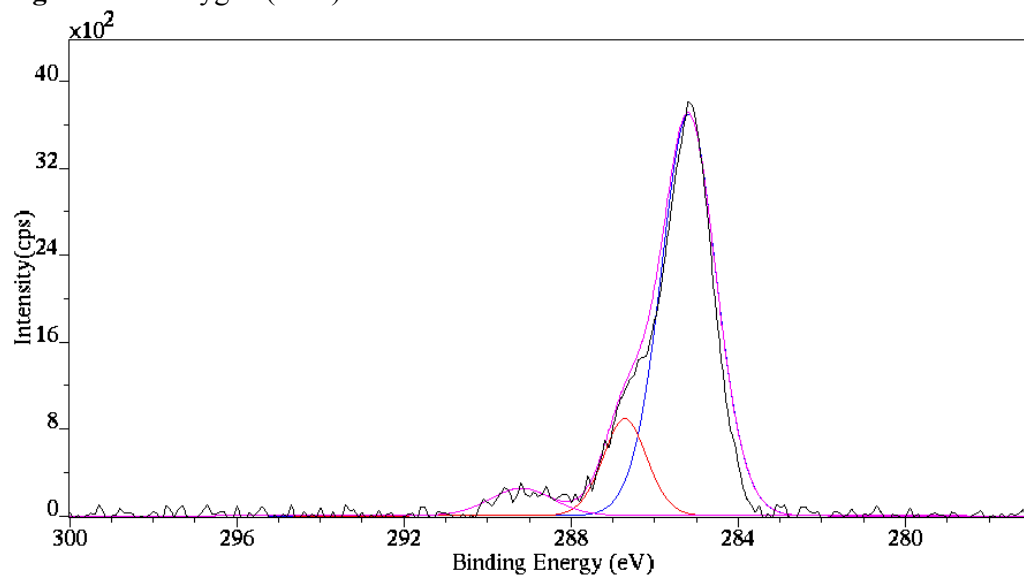
**Table S1: Quantitative Analysis**

Peak	Type	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
Au 4f	Reg	84.000	2.733	4834460.0	6.250	196.967	22.45	80.98
C 1s	Reg	285.000	3.037	527900.0	0.278	12.011	58.90	12.96
O 1s	Reg	532.000	3.111	285305.0	0.780	15.999	11.16	3.27
S 2p	Reg	162.000	4.260	60310.0	0.668	32.065	2.65	1.56
N 1s	Reg	402.000	5.034	79440.0	0.477	14.007	4.84	1.24

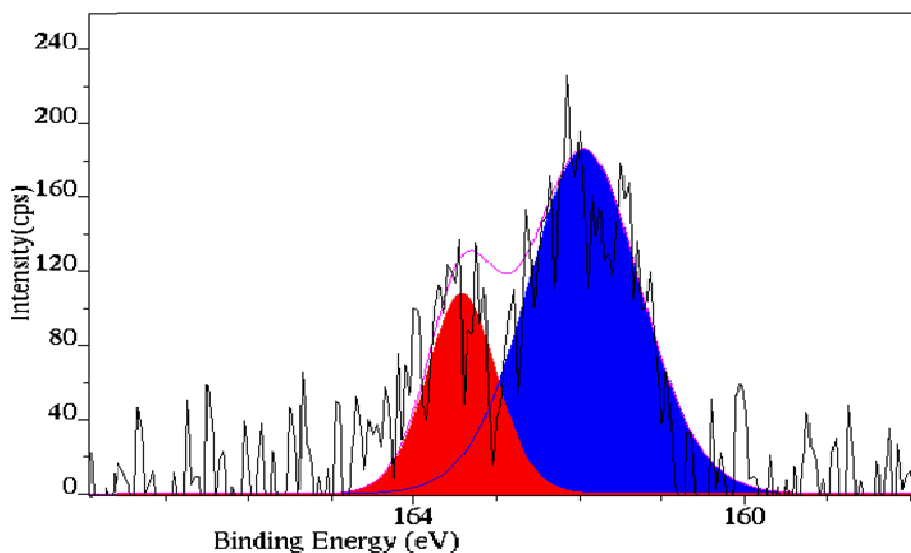
**Figure S10: Gold (Au 4f spectra)****Figure S11: Nitrogen (N1s)**



**Figure S12:** Oxygen (O 1s)



**Figure S13:** Carbon (C 1s)



**Figure S14:** Sulphur (S 2p)

The wide survey XPS spectrum demonstrates that the sample does not contain chemical elements other than anticipated. High resolution gold peak 4f spectra shifts binding of a thiol layer. Oxygen and nitrogen C1 peaks show single signals from carboxylate and quaternary ammonium group ion at 532 and 420 eV, respectively. In spectra for carbon 1s distinguished fitted values 285, 286 and 289 eV correspond to C-C, C-N and CO carbons signals, respectively. In S2p spectra there are observed typical double signals attributed to **1** with surface interaction.<sup>1</sup>

1. Ishida, T.; Choi, N.; Mizutani, W.; Tokumoto, H.; Kojima, I.; Azebara, H.; Hokari, H.; Akiba, U.; Fujihira, M. High-resolution X-ray photoelectron spectra of organosulfur monolayers on Au(111): S(2p) spectral dependence on molecular species. *Langmuir* **1999**, *15*, 6799-6806.