

# Surface-enhanced Raman spectroscopy of indole ring-terminated self-assembled monolayer on silver electrode

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A new indole ring-terminated thiol,  $\omega$ -mercaptooctyltryptamide (MOTA), has been synthesized and the structure of self-assembled monolayer (SAM) on Ag electrode was characterized by surface-enhanced Raman spectroscopy (SERS). The frequency of conformational marker W3 band has been found to increase by 3  $\text{cm}^{-1}$  in surface spectrum as compared with the FT-Raman spectrum of solid MOTA compound, indicating an increase in the torsional angle about the C $\beta$ -C3 bond from 95 to 103°. Potential-dependent spectral changes have indicated a blue shift of W3 mode at more positive potentials. Analysis of W17 mode in SERS spectra has shown that the hydrogen bonding interaction strength at N1H indole site increases in slightly alkaline solutions as compared with acidic conditions.

**Key words:** indole, tryptophan, silver, SAM, surface enhanced Raman spectroscopy

## INTRODUCTION

The indole ring comprises the main part of tryptophan side chain in proteins and plays an important role in the interactions between amino acid residues which control the protein-folding processes. In order to get better insights into the complex interactions through the extended  $\pi$  electronic system of the indole ring and hydrogen bonding through the NH group, it is necessary to create molecular systems with the properties variable in a controllable manner. The self-assembled monolayers (SAMs) constructed by the adsorption of thiols on coinage metals are widely used to create chemically modified surfaces for the studies of charge transfer processes [1, 2], ion-pairing at interfaces [3–5], electrocatalytical reactions [4, 5], and interaction between the surface confined molecular groups and solution species [2]. The properties of such two-dimensional ordered systems can be controlled through the composition of the monolayer and electrochemical polarization. Thus, SAMs constructed from bifunctional thiols containing a terminal indole ring group are particularly attractive as the model systems for studies of interaction and conformation of tryptophan residues.

For structural studies of the surface confined functional groups, a technique able to characterize a monolayer at the molecular level must be applied. Surface-enhanced Raman spectroscopy (SERS) provides *in-situ* a molecular level information on bonding,

orientation and conformation of chemisorbed molecules and ions at electrode / electrolyte interfaces [6–9]. Previously we have applied the SERS technique for the analysis of immobilized tryptamine on a gold electrode surface [10].

In the present work, we report a SERS study on the structure of indole ring-terminated self-assembled monolayer on silver electrode.

## EXPERIMENTAL

### Materials

8-bromooctanoic acid (97%) and tryptamine (98%) were obtained from Aldrich and were used without additional purification. Deionized and subsequently double-distilled water was used throughout the experiments.

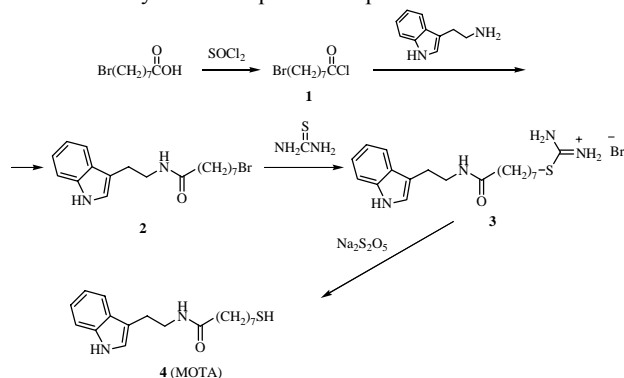
The synthesis steps of final MOTA compound are shown in Scheme 1.

**Synthesis of 8-bromooctanoylchloride (1).** 1.5 g (5 mmol) 8-bromooctanoic acid, 0.72 ml (10 mmol) thionyl chloride and 0.2 ml DMFA was kept for 15 h at room temperature. Thionyl chloride was removed under reduced pressure and **1** was used in the subsequent reaction without purification.

**Synthesis of 8-bromo-*N*-[2-(1*H*-indol-3-yl)ethyl]octanamide (2).** To a solution of 0.8 g (5 mmol) of tryptamine and 1 ml (8 mmol) of *N,N*-dimethylaniline (in 20 ml acetonitrile) a solution of **1** (obtained from 5 mmol 8-bromooctanoic acid, in 20 ml acetonitrile) was added and stirred at room temperature for 3 h. The reaction mixture was diluted with chlo-

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Scheme 1. Synthesis steps of compound MOTA



reform, washed with dilute HCl, dried over anhydrous  $\text{MgSO}_4$ , and concentrated in vacuum. The crude product was purified by silica gel column chromatography (acetone). The solvent was evaporated and the residue was crystallized from carbon tetrachloride. Obtained: 0.56 g (31%) of **2**, mp 59–62 °C. Found (%): C 59.47, H 7.11, Br 21.56.  $\text{C}_{18}\text{H}_{25}\text{BrN}_2\text{O}$ . Requires (%): C 59.18, H 6.90, Br 21.87. Data of  $^1\text{H}$  NMR spectrum ( $\delta$ , ppm): 1.28 (m, 4H,  $\text{CH}_2\text{CH}_2$ -18,19); 1.39 (m, 2H,  $\text{CH}_2$ -17); 1.58 (m, 2H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ ); 1.82 (m, 2H,  $\text{CH}_2\text{CH}_2\text{Br}$ ); 2.09 (t, 2H,  $\text{CH}_2\text{C}=\text{O}$ ); 2.98 (t, 2H,  $\text{CH}_2\text{CH}_2\text{NH}$ ); 3.39 (t, 2H,  $\text{CH}_2\text{Br}$ ); 3.60 (m, 2H,  $\text{CH}_2\text{NH}$ ); 7.03 (s, 1H, H-2); 7.12 (m, 1H, H-5); 7.21 (m, 1H, H-6); 7.38 (d, 1H, H-7); 7.60 (d, 1H, H-4).

**Synthesis of amino[(8-{[2-(1H-indol-3-yl)ethyl]amino}-8-oxooctyl)sulfanyl]methan iminiumbromide (3).** A solution of 0.52 g (1.5 mmol) **2** and 0.24 g (3 mmol) thiourea in 20 ml acetonitrile was boiled for 14 h. The solvent was evaporated and the residue was washed with and dissolved in hot water. The solution was cooled to room temperature and the precipitated oil **3** was used in the subsequent reaction without purification.

**Synthesis of N-[2-(1H-indol-3-yl)ethyl]-8-mercaptooctanamide (4).** To a solution of **3** (obtained from 1.5 mmol **2**) in 100 ml water a 50 ml of chloroform was poured, in the atmosphere of nitrogen 0.4 g (2 mmol)  $\text{Na}_2\text{S}_2\text{O}_5$  was added, and the mixture was boiled for 7 h. The organic layer was separated and dried ( $\text{MgSO}_4$ ). The solvent was evaporated and the residue was crystallized from hexane. Obtained: 0.12 g (25%) of **4**, mp 48–50 °C. Found (%): C 68.01, H 8.32, S 9.95.  $\text{C}_{18}\text{H}_{26}\text{N}_2\text{OS}$ . Requires (%): C 67.88, H 8.23, S 10.07. Data of  $^1\text{H}$  NMR spectrum ( $\delta$ , ppm): 1.26 (m, 6H,  $(\text{CH}_2)_3$ -17,18,19); 1.32 (t, 1H, SH); 1.58 (m, 4H,  $\text{CH}_2$ -16, 20); 2.09 (t, 2H,  $\text{CH}_2\text{C}=\text{O}$ ); 2.49 (2t, 2H,  $\text{CH}_2\text{SH}$ ); 2.97 (t, 2H,  $\text{CH}_2\text{CH}_2\text{NH}$ ); 3.61 (m, 2H,  $\text{CH}_2\text{NH}$ ); 7.03 (s, 1H, H-2); 7.12 (m, 1H, H-5); 7.21 (m, 1H, H-6); 7.38 (d, 1H, H-7); 7.60 (d, 1H, H-4).

### Raman measurements

Surface-enhanced Raman spectra were recorded using a 400 mm focal length,  $f/2.5$  spectrograph equip-

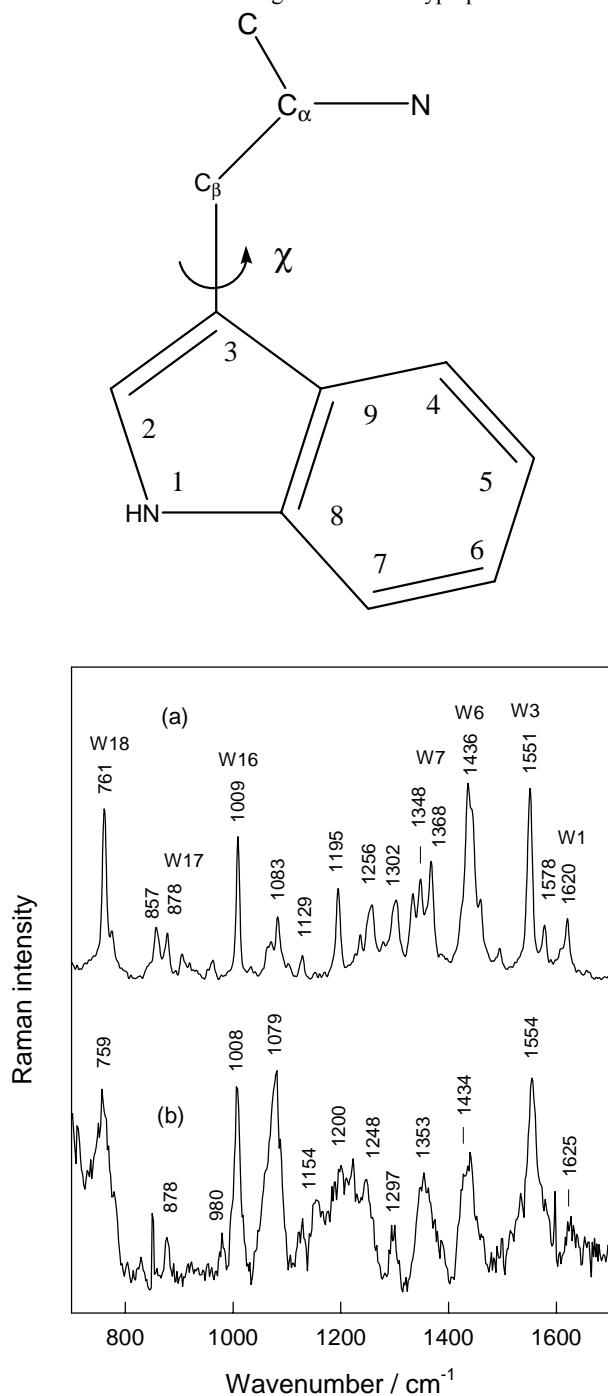
ped with 600 lines/mm grating and a thermoelectrically cooled (203 K) CCD camera (Princeton Instruments, Model: Spec-10:256E). An edge filter (Omega Optical, Inc., Model: 659AELP) was placed in front of the entrance slit of the spectrograph to eliminate Rayleigh scattering from the sample. Raman measurements were carried out in 90° geometry. The 647.1 nm beam of the Kr-ion laser (Coherent, Model: Innova 90-K) was used as the excitation source. The incidence angle of the laser beam was 60° and the laser power at the sample was typically 50–100 mW. The Raman frequencies were calibrated using the toluene spectrum. The integration time was 1 s. Each spectrum was recorded by accumulation of 100 scans. In order to reduce photo- and thermoeffects, the cell together with the electrodes was moved linearly with respect to the laser beam at the rate of about 20 mm/s [11].

SERS measurements were performed in a cylindrical closed three-electrode cell made from glass. A polycrystalline rod of Ag (99.99 % grade) pressed into a Teflon sleeve served as the working electrode. The counter electrode was a Pt wire. The potential of the working electrode was measured vs. the Ag / AgCl, 3M KCl reference electrode. All potentials are given vs. this electrode. The working electrode was electrochemically roughened in a separate cell containing 1M  $\text{NaClO}_4$  solution, by cycling three times from -0.5 to 0.6 V (sweep rate 100 mV/s), with holds of 30 s at the negative potential and 10 s at the positive potential [12]. After roughening, the electrode was immersed in ethanolic 1 mM MOTA solution for 24 hours. Subsequently, the electrode was rinsed with ethanol and water and transferred with a protective drop of water to the spectroelectrochemical cell containing the working solutions. A PI-50-1 potentiostat arranged with PR-8 model programmer was used throughout the experiments.

FT-Raman measurements of solid studied compound were carried out in 180° geometry with a FT-Raman spectrometer (Perkin-Elmer, Spectrum GX) equipped with an InGaAS detector operating at room temperature. The excitation was provided by an air-cooled diode-pumped Nd-YAG laser with an emission wavelength of 1064 nm. The laser beam was focused to a spot of area  $\sim 1 \text{ mm}^2$ , and the laser power at the sample was set to 50 mW. The experiments were carried out in 180° geometry. The spectral resolution was set at  $4 \text{ cm}^{-1}$  and the wavenumber increment per data point was  $1 \text{ cm}^{-1}$ . All of the spectra were acquired by 300 scans. None of the spectra presented have been smoothed.

### RESULTS AND DISCUSSION

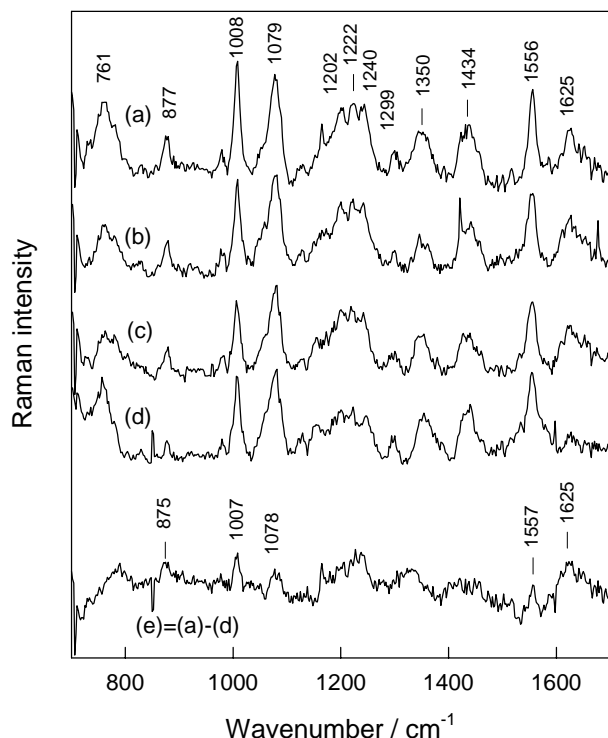
Vibrations of indole ring (Scheme 2) were extensively studied in the past and important conformation and hydrogen bonding interaction marker bands were de-

**Scheme 2.** Atom numbering scheme for tryptophan derivatives

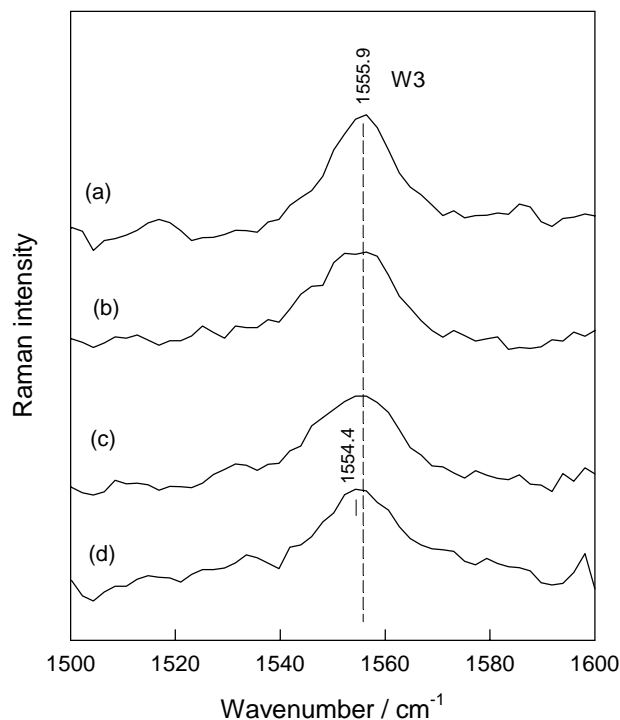
**Fig. 1.** Comparison of (a) the FT-Raman spectrum of solid compound MOTA and (b) SERS spectrum of SAM formed by MOTA on Ag electrode in 0.01 M phosphate buffer solution (pH 7.0) containing 0.1 M Na<sub>2</sub>SO<sub>4</sub> at -1.1 V vs. Ag / AgCl. The excitation wavelength is 1064 nm and 647.1 nm for FT-Raman and SERS measurements, respectively

terminated [13–19]. Figure 1 compares the FT-Raman spectrum of solid compound MOTA and SERS spectrum of MOTA SAM in 0.01 M phosphate buffer (pH 7.0) solution containing 0.1 M Na<sub>2</sub>SO<sub>4</sub>. Vibrational bands associated with the indole ring dominate in the spectrum of the solid MOTA compound. The well-

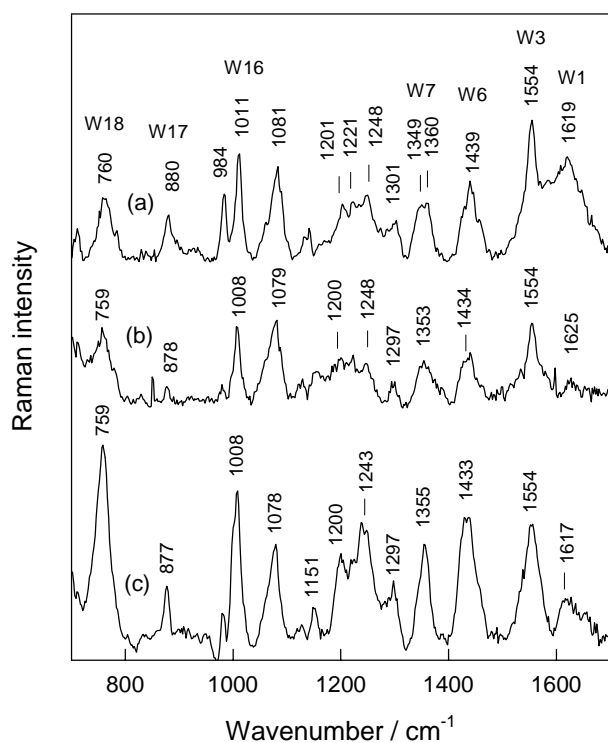
defined and intense 1551-cm<sup>-1</sup> band was assigned to pyrrole ring stretching vibration  $\nu(\text{C2} = \text{C3})$  localized primarily at the C2 = C3 bond (Scheme 2) and labeled as W3 [13–19]. It has been demonstrated that this mode is sensitive to conformation of tryptophan residues [17]. Because W3 mode involves vibration of C3 atom, its frequency depends on the torsion angle ( $\chi$ ) about the C2 = C3-C<sub>β</sub>-C<sub>α</sub> moiety (rotation around the C<sub>β</sub>-C3 bond) [17]. The relative intensity of this mode increases slightly in acidic solutions [15]. The high frequency and low intensity peak at 1620 cm<sup>-1</sup> (labeled as W1) belongs to a mixed vibrational mode best described as a superposition of in-plane benzene ring B8a-type mode and pyrrole ring N1-C8 bond stretching motion [19]. The frequency of this mode slightly decreases (~4 cm<sup>-1</sup>) upon deuteration at N1 site [19]. It should be noted that this mode is sensitive to the environment pH. The W1 frequency decreases (~9 cm<sup>-1</sup>) on going from alkaline to acidic solutions [15]. The broad 1436-cm<sup>-1</sup> band (labeled as W6) corresponds to a mixed mode of the N1C2C3 group symmetric stretching vibration coupled with N1H deformation and the benzene ring CH deformation vibrations [19]. Because of N1H bending contribution, this mode shifts considerably (~52 cm<sup>-1</sup>) upon deuteration at N1 site and can be used for the monitoring of isotopic exchange kinetics [19]. This mode may have a contribution from the alkyl chain methylene bending vibration [20]. The doublet at 1368 / 1348 cm<sup>-1</sup> (labeled as W7) arises from the Fermi resonance interaction of the indole ring N1C8 stretching vibration with the combination bands of out-of-plane bending vibrations [19]. The doublet is sensitive to the hydrophobicity of the environment. It has been demonstrated that the intensity ratio I1360 / I1340 increases in a more hydrophobic solvent [13, 19]. The intense and clearly resolved peak at 1009 cm<sup>-1</sup> (labeled as W16) belongs to benzene ring breathing vibration [19] and may serve as an intensity standard for indole-ring containing molecular systems [15]. The corresponding indole ring breathing vibration is seen at 761 cm<sup>-1</sup> (labeled as W18). The indole ring may participate in hydrogen bonding interaction through the N1H group as a proton donor. The peak at 878 cm<sup>-1</sup> (labeled as W17) sensitively probes this type of interaction, decreasing in frequency as the hydrogen bonding strength at N1H site increases [19]. The sensitivity of the W17 mode to hydrogen bonding interaction comes from the fact that this vibrational mode contains a contribution from the displacement of the N1H group along the direction of N1-H bond [13, 17]. Several bands in the FT-Raman spectrum of solid MOTA compound were attributed by us to vibrations of the alkyl chain spacer. It is well established that the frequency region between 1050 and 1150 cm<sup>-1</sup> contains C-C stretching modes sensitive to *gauche/trans* isomerization of alkyl chains [21–23]. In the solid state, the alkyl chains are expected to be in



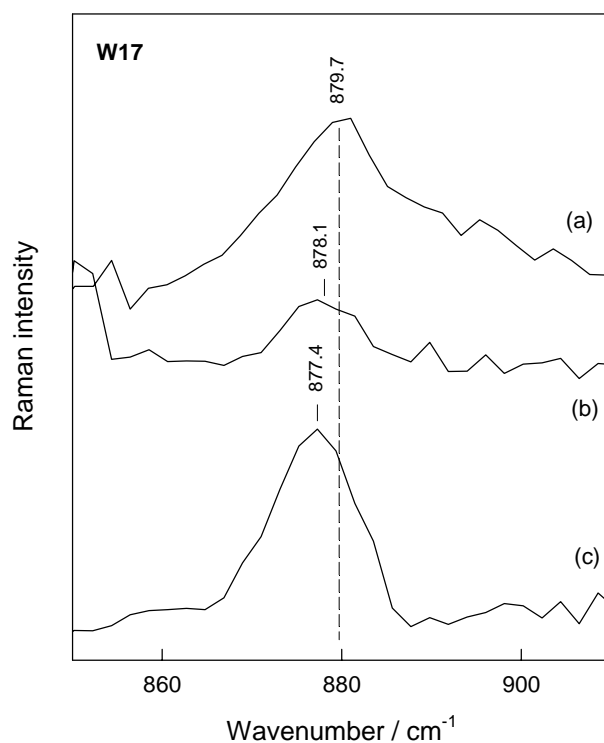
**Fig. 2.** Potential dependence of SERS spectra of MOTA SAM on Ag electrode in 0.01 M phosphate buffer solution (pH 7.0) containing 0.1 M  $\text{Na}_2\text{SO}_4$ . Potential (vs. Ag / AgCl): (a) 0.1 V, (b) -0.5 V, (c) -0.9 V, and (d) -1.1 V. The difference spectrum (e) is also shown. The excitation wavelength is 647.1 nm



**Fig. 3.** Potential dependence of SERS spectra in the W3 mode spectral region of MOTA SAM on Ag electrode in 0.01 M phosphate buffer solution (pH 7.0) containing 0.1 M  $\text{Na}_2\text{SO}_4$ . Potential (vs. Ag / AgCl): (a) 0.1 V, (b) -0.5 V, (c) -0.9 V, and (d) -1.1 V. The excitation wavelength is 647.1 nm.



**Fig. 4.** SERS spectra of MOTA SAM on Ag electrode in (a) 0.1 M  $\text{Na}_2\text{SO}_4$  + 0.01  $\text{H}_2\text{SO}_4$  solution at -0.4 V, (b) 0.1 M  $\text{Na}_2\text{SO}_4$  + 0.01 M phosphate buffer (pH 7.0) solution at -1.1 V, and (c) 0.1 M  $\text{Na}_2\text{SO}_4$  + 0.01 M NaOH solution at -1.1 V. Potentials are referred vs. Ag / AgCl. The excitation wavelength is 647.1 nm.



**Fig. 5.** Dependence of W17 mode in the SERS spectra of MOTA SAM on Ag electrode on the solution composition. Solutions: (a) 0.1 M  $\text{Na}_2\text{SO}_4$  + 0.01  $\text{H}_2\text{SO}_4$  at -0.4 V, (b) 0.1 M  $\text{Na}_2\text{SO}_4$  + 0.01 M phosphate buffer (pH 7.0) at -1.1 V, and (c) 0.1 M  $\text{Na}_2\text{SO}_4$  + 0.01 M NaOH at -1.1 V. Potentials are referred vs. Ag / AgCl. The excitation wavelength is 647.1 nm

the predominant trans-conformation. Therefore, two peaks at 1083 and 1129  $\text{cm}^{-1}$  we have assigned to C–C stretching vibrations of trans-conformers,  $\nu(\text{C-C})_{\text{T}}$  [22]. The well-defined 1302- $\text{cm}^{-1}$  peak falls in the frequency region of twisting vibrations of methylene groups [23]. Because no strong bands of the indole ring are expected in this frequency region [19] and the intensity of the methylene twisting mode is usually relatively strong in the Raman spectra, we have attributed the 1302- $\text{cm}^{-1}$  band to  $\text{CH}_2$  twisting motion,  $\text{t}(\text{CH}_2)$ . A comparison of the SERS spectrum (Fig. 1b) of MOTA in the monolayer with the FT-Raman spectrum of solid MOTA (Fig. 1a) revealed several interesting findings. First of all, the frequency of the conformational marker W3 increases by 3  $\text{cm}^{-1}$  in the surface spectrum, indicating that the torsional angle  $\chi$  increases from 95° to 103° [17]. The Fermi doublet W7 is broadened in the surface spectrum, most likely because of the environment heterogeneity near the indole ring. Absence of clearly established peak in the vicinity of 1360–1370  $\text{cm}^{-1}$  indicates a rather hydrophilic overall environment. Thus, indole rings in the monolayer are not buried, but are able to interact with the solution water molecules. This suggestion is corroborated by the frequency value of the W17 peak at 878  $\text{cm}^{-1}$ , which definitely indicates that N1H site of MOTA molecules in the monolayer is involved in a moderate hydrogen bonding interaction [17]. It should be noted that in the frequency region of C–C stretching vibrations of alkyl chains an intense feature is observed in the surface spectrum at 1079  $\text{cm}^{-1}$ . The broadening and shift to lower wavenumbers as compared with the solid state spectrum indicate the presence of a number of *gauche* defects in the monolayer [21–23]. Figure 2 displays the potential dependence of the SERS spectra in a neutral sulfate solution. The general tendency is a slight decrease in the intensity of most bands at more negative potentials, although the presented data clearly indicate stability of the monolayer in a wide potential region. Subtle spectral alterations might be a cache from the analysis of difference spectrum (Fig. 2e) constructed from the traces observed at 0.1 and -1.1 V potentials. The positive-going feature at 875  $\text{cm}^{-1}$  indicates that the relative intensity of W17 band increases and shifts slightly to lower wavenumbers at more positive potentials. The red frequency shift corresponds to an increase in hydrogen bonding interaction at N1H site at more positive potentials.

The second interesting potential-induced spectral perturbation is associated with W3 mode. Presence of 1557- $\text{cm}^{-1}$  feature in the difference spectrum is indicative of a shift to higher wavenumbers and an increase in the intensity of W3 band at positive electrode potentials. Such tendency is clearly observable in Fig. 3 where a narrow spectral region (1500–1600  $\text{cm}^{-1}$ ) is displayed. The position of the conformation-sensitive W3 peak shifts from 1554.4  $\text{cm}^{-1}$  at

-1.1 V to 1555.9  $\text{cm}^{-1}$  at 0.1 V. The observed frequency shift indicates an increase in the  $\chi$  angle at more positive potentials.

SERS revealed that MOTA SAM is stable in both slightly acidic and alkaline solutions (Fig. 4). The position of the conformational marker W3 band remains stable (1554  $\text{cm}^{-1}$ ) in the study solutions, indicating that solution pH does not affect the torsion angle  $\chi$ . However, we should note a broadening of the W3 mode in alkaline solution. This might be associated with an increased conformational disorder of the monolayer in slightly alkaline conditions. The changes in relative intensities of SERS bands point to the solution pH-induced orientation transformations of a terminated indole moiety. According to the SERS surface selection rules [24], the relative band intensities depend on the orientation of the molecular groups with respect to the surface. The most enhanced bands are related to the modes containing components of the polarizability tensor perpendicular to the surface. In the alkaline solution, the relative intensity of W18 band at 759  $\text{cm}^{-1}$  considerably increases (Fig. 4). Because W18 mode represents the breathing vibration of the indole ring [19], the observed spectral changes suggest the reorientation of MOTA in the monolayer in alkaline conditions so that the plane of the indole ring becomes more perpendicular with respect to the silver surface.

Finally, solution pH-induced changes in the position of W17 mode will be discussed (Fig. 5). It has been established that the frequency of this mode near linearly depends on the strength of hydrogen bonding interaction at N1H site of the indole ring [17]. A stronger interaction results in a lower frequency. The W17 frequency clearly decreased by 2.3  $\text{cm}^{-1}$  (from 879.7 to 877.4  $\text{cm}^{-1}$ ) when 0.01  $\text{H}_2\text{SO}_4$  in solution was replaced by 0.01 NaOH (Fig. 5). Thus, data presented in Fig. 5 provide an evidence for an increase in hydrogen bonding interaction strength at N1H site of MOTA SAM as the solution pH increases.

## CONCLUSIONS

Using *in situ* surface-enhanced Raman spectroscopy (SERS) with excitation at 647.1 nm, we have studied the structural properties of self-assembled monolayers of the newly synthesized  $\omega$ -mercaptooctyltryptamide (MOTA) on a silver electrode. The effects of the potential and solution composition on the structure of the monolayer were examined. The SERS spectra were found to be dominated by the bands of the terminal indole ring. A comparison with the FT-Raman spectrum of the solid MOTA compound revealed a blue shift of W3 band in the surface spectrum, indicating an increase in the torsional angle about the C $\beta$ -C3 bond from 95 to 103°. SERS data

have revealed that hydrogen bonding interaction strength at N1H indole ring site increases when 0.01 M H<sub>2</sub>SO<sub>4</sub> in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution is replaced by 0.01 M NaOH.

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#### INDOLO ŽIEDU TERMINUOTŲ SAVITVARKIŲ MONOSLUOKSNIŲ ANT SIDABRO ELEKTRODO TYRIMAS SUSTIPRINTOS PAVIRŠIUMI RAMANO SPEKTROSKOPIJOS METODU

##### Santrauka

Buvo susintetintas naujas junginys, indolo žiedu terminuotas tiolis – ω-merkaptooktiltriptamidas (MOTA). Savitvarkių monosluoksnių, suformuotų iš MOTA junginio, struktūra buvo tirama sustiprintos paviršiumi Ramano spektroskopijos (SPRS) metodu. Parodyta, kad paviršiaus spektre konformacijos žymeklio (W3) smailės dažnis padidėja 3 cm<sup>-1</sup>, palyginus su MOTA junginio miltelių FT-Ramano spektru. Tai rodo, kad kampas apie Cβ-C3 jungtį padidėja nuo 95 iki 103°. Tiriant spektrų priklausomybes nuo potencialo, buvo nustatyta, kad W3 smailės dažnis padidėja, esant teigiamiesiems elektrodo potencialams. Analizuojant W17 virpesio dažnį SPR spektruose, buvo parodyta, kad vandenilinės jungties, susijusios su N1H indolo grupe, stiprumas padidėja silpnai šarminiuose tirpaluose, palyginti su rūgštiniais tirpalais.