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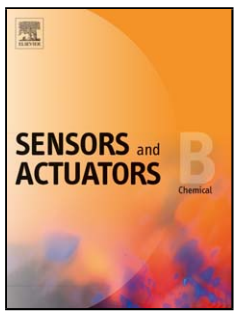

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Authors: R. Çapan, Z. Özbek, H. Göktaş, S. Şen, F.G. İnce, M.E. Özel, G.A. Stanciu, F. Davis

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Characterization of Langmuir-Blodgett films of a calix[8]arene and sensing properties towards volatile organic vapors

R. Çapan[1*], Z. Özbek[1], H. Göktaş[2], S. Şen[2], F. G. İnce[2], M. E. Özel[3], G. A. Stanciu[4], F. Davis[5]

[1]Balikesir University, Faculty of Arts and Science, Physics Department, 10145, Çağış, Balikesir TURKEY

[2] Onsekiz Mart University, Faculty of Arts and Science, Physics Department,17100 Çanakkale TURKEY

[3] Çağ University, Faculty of Arts and Science, Maths and Computing Science Department, 33800 Mersin TURKEY

[4] Department of Physics, Center for Microscopy- Microanalysis and Information Processing University "Politehnica" of Bucharest, Bucharest ROMANIA

[5]Institute of Bioscience and Technology, Cranfield University at Silsoe, Cranfield Centre for Analytical Science Silsoe, Cranfield MK45 4DT, UK

[*] Corresponding author e-mail: rcapan@baikesir.edu.tr
Tel: + 90 266 612 10 00 Fax: + 90 266 612 12 15

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Abstract

Within this article, we report the characterization and organic vapor sensing properties of Langmuir-Blodgett (LB) thin films of calix[8]arenes. Surface pressure-area isotherms show that very stable monolayers are formed at the air-water interface. The LB film could be deposited onto different substrates which allowed the films to be characterized by UV, quartz crystal microbalance (QCM), surface plasmon resonance (SPR) and atomic force microscopy (AFM). The results indicate that good quality, uniform LB films can be prepared with transfer ratios of over 0.95. QCM results showed that the deposited mass of calix[8]arene monolayer onto a quartz crystal decreased from 693 ng to 204 ng as the number of layers is increased. AFM studies showed a smooth, and void free surface morphology with a rms value of 1.202 nm. The sensing abilities of this LB film towards the development of room temperature organic vapor sensing devices is also studied. Responses of the LB films to various vapors are fast, large, and reversible. It was found that the obtained LB film is significantly more sensitive to chloroform than other vapors. It can be concluded that this molecule could have a potential application in the research area of room temperature vapor sensing devices.

Keywords: Langmuir-Blodgett thin film; organic vapor sensors; calixarene; surface plasmon resonance

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1. Introduction

Volatile organic compounds (VOC's) are organic chemical compounds which have a significant vapor pressure under ambient conditions. When released into the environment, they can contribute to global warming and also lead to soil, groundwater and air pollution within the environment [1]. VOC's are widely used in home or office environments for example within laser printers, cleaning solvents, paints, wood preservatives, carpet backing, plastics, and cosmetics. Other natural sources include trees and other plant and animal species as well as from synthetic sources such as petroleum derivatives. These vapors have been shown to contribute to several illnesses such as sick building syndrome [2], allergic sensitization [3], immune effects in infants or children or asthmatic symptoms [4], probably because concentrations of VOC's in indoor air are generally much greater than in outdoor air. Aromatic VOC's are suspected carcinogens and can potentially lead to leukemia and lymphoma upon prolonged exposure [5]. Therefore the detection of VOC's is an important issue to protect our health, wellbeing and environment. In recent years, a significant interest in chemical sensing applications of organic materials such as carbon nanotubes [6] porphyrins [7], phthalocyanines [8] and indane [9] have been studied in order to fabricate a highly sensitive, easy to use, cheap, selective and a long life VOC's sensor. When these types of organic materials interact with VOC's, their physical, chemical or structural properties were invariably found to change, either reversibly or irreversibly, i.e., color, mass, conductivity, film thickness, refractive index changes etc.

A large area of research in the sensor application area utilizes calixarenes and their derivatives due to their multiplicity of options for targeted structural design [10-15]. The general shape of calixarenes is that of a cup with a defined upper and lower rim and a central annulus, enabling calixarenes to act as host molecules as a consequence of their preformed cavities. It is easy to modify either the upper and/or lower rims to prepare various derivatives

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with differing selectivities for various guest ions and small molecules [16-19]. Cage compounds such as tert-butyl-calix[n]arenes often show highly pre-organized structures with highly symmetrical cavities suitable for host-guest interactions. The resultant chemical or physical changes can be detected using a very sensitive capacitive method for the detection of solvent vapors down to a concentration of a few ppm [20]. They are also capable of binding certain ions or small molecules within their cavities and for exhibiting high porosity to other species. Calix[n]arenes and their derivatives are an excellent material to organize as a monolayer on the water surface and to prepare Langmuir-Blodgett (LB) thin films [21,22]. These films have possible applications especially in the field of the environment protection such as detection of NO_2 [23], ozone [24], NH_3 or HCl gases [25], various ions [26] and various solvent vapors [20].

Calix[4]resorcinarenes have been previously incorporated into LB films and exposed to a wide range of vapors (e.g. amines, alcohols, thiols) to study the interaction mechanism between calix and vapors. It is observed that these type of LB films are capable of binding selectively to lysine, an important amino acid [27]. Other calixarenes were deposited as thin films onto Au-coated substrates by the spin coating method . SPR measurements on these systems were utilized for the detection of benzene, toluene, ethylbenzene and m-xylene. Selective, fast and reversible adsorption of the vapor molecules was detected via the resultant increase in film thickness and refractive index of the spun films. The adsorption behavior of calixarenes may be explained by the capture of guest molecules in the film matrix due to the cavitand nature of the film's molecules [28].

In the present article, a calixarene containing eight phenolic groups within the macrocycle substituted with $–O(CH_2)_3COOH$ side groups was selected to form LB films. Within this work we study the characterization of deposition via the LB method and utilize the resultant films as a sensing layer onto gold coated glass. The SPR method is used to

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investigate the sensing properties of calix[8]arene LB films towards organic vapors such as chloroform, toluene, benzene and ethyl alcohol.

2. Experimental Details

The chemical structure of the calix[8]arene-octa-acid is shown in Fig. 1. The calix[8]acid could be dissolved in chloroform to give a concentration of 0.25 mg ml^{-1}. Isotherm data was measured at room temperature using a NIMA 622 type alternate layer LB trough with a Lauda Ecoline RE 204 model temperature control unit. Monolayers at a surface pressure value of 22.5 mN m^{-1} were sequentially transferred by the vertical dipping method onto glass substrates for UV-visible and AFM measurement, onto 50 nm thick gold coated glass substrates for SPR measurement and onto quartz substrates for QCM measurement .

The UV-visible spectra of LB film were recorded in the ultraviolet and visible spectral region from 250 nm to 850 nm using an Ocean Optics UV-visible light source (DH-2000-BAL Deuterium Tungsten light source) and spectrometer (USB4000) in absorbance mode. Calix[8]acid solutions in chloroform were measured in quartz cuvettes. After the deposition of LB film multilayer onto glass substrates, UV-vis spectra were recorded as a function of number of layers.

For QCM studies, calix[8]acid layers were deposited onto a thinly cut wafer of raw quartz sandwiched between two gold electrodes in an overlapping keyhole design. After each deposition cycle, the LB film sample was dried and the mass change was monitored using a home-made computer controlled QCM measurement system. Dedicated software allows the on-line recording of the changes of the quartz resonance frequency. All measurements were taken at room temperature using an in-house designed oscillating circuit and standard quartz crystals with a nominal resonance frequency of 9 MHz. The quartz crystal was inserted into the electronic control unit and the frequency of oscillation was monitored as a function of time using a computer. Values of frequency changes, which indicate the degree of response, are measured with an accuracy of 1 Hz when the organic vapor is present.

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Atomic Force Microscopy analysis was performed by using a Quesant 350 Scanning Probe Microscope. The scale is set in such a way that light colors correspond to higher structures. The images were taken by using a standard silicon nitride tip (constant force 12 N/m) in the contact mode.

Surface Plasmon Resonance Spectrometer (BIOSUPLAR 6 Model) with a low power laser diode (630- 670 nm) light source was employed to perform SPR measurements with an angular resolution of 0.003 degrees. A glass prism (n=1.62) is mounted within a holder so as to be available for measurement in liquid or in air environments. Glass slides with the dimensions 20 x 20 x 1 mm are coated on top by a very thin homogeneous layer of gold. A transparent plastic flow cell was made in house to be allow vapor measurements. The cell has two channels, with inlets and outlets connected to silicone tubes. Biosuplar-Software is used to control the SPR system settings, measurements and data acquisition as well as data presentation. Several modes such as single measurements, tracking mode or slope mode can be utilized and the signal displayed as a function of time. Variations within both measurement channels can be displayed in real time using this software. The photodetector response was monitored as a function of time during periodic exposure of the sample to the organic vapor for at least 2 minutes, this was then allowed to recover after injection of dry air. WINSPALL software developed at the Max-Plank-Institute for Polymer Research, Germany was utilized for the fitting of SPR curves to determine thickness and refractive index values of the LB films.

3. Result and Discussion

3. 1 Isotherm graph

Isotherm graphs of the calix[8]acid monolayers (Fig.2) were obtained at the air-water interface by recording surface pressure as a function of surface area. These measurements were repeated several times using identical and differing volumes of the solution and the

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results demonstrated good stability and reproducibility of the monolayers at the air-water interface.

Isotherms of calixarene compounds have been extensively studied using different materials such as calix[8]arenes [29-31] and calix[4]resorcinarenes [32,27]. When compared to our results, similar isotherms has been observed for calix[8]arene monolayers at the air-water interface. The surface pressure increased with decreasing surface area without an obvious phase transition up to 40 mN m^{-1}. The floating monolayer was found to be stable at the surface pressure value of 22.5 mN m^{-1} which is selected for LB film deposition process.

3. 2 Deposition Properties

3.2.1 UV-visible Results

Fig. 3 shows typical UV-vis absorption spectra of calix[8]arene molecule as a solution in chloroform and absorption band observed at 280 nm. A similar spectrum of the same compound as an LB film with different layer numbers deposited onto the quartz substrate is shown in Fig. 4. UV-vis spectra of calix[8]acid LB films exhibit slightly red-shifted absorption bands compared to the spectrum of the chloroform solution. The shift in the absorption band of the LB film may be the result of some kind of molecular aggregation which takes place during film formation, such as dimerization [33, 34]. UV-vis spectra have been used to monitor the effect of the solvent on the complexation properties between chromogenic calix[4]arene derivatives and metallic cations with extensive studies being made in solvents such as tetrahydrofuran, chloroform, methanol, acetone, ethanol, acetonitrile, dimethylformamide) and dimethyl sulfoxide [35]. These results showed that the UV-vis spectra of the calixarenes are highly solvent dependent because the position, intensity and the shape of the absorbance bands of each compound in solution, have varied with changes in solvent and a red shift is commonly observed. Similar work has been found by Moreira using a calix[4]resorcinarene octafunctionalized with methyl α-acetate or methyl α-acetamide when deposited as LB films on several different substrates [32,36].

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The UV-vis absorption spectra of multilayered films consisting of polyvinylamine (PVA) and calix[4, 6 or 8]arenes have been studied to monitor transport properties using similar experimental conditions. The optical absorption spectra of these films were quite different depending on the size of calixarene rings, when the ring size increases in the ratio 4:6:8, the absorption increases in the ratio 1:2:3. It is proposed that the small rings tend to desorbs more easily because the number of sulfonate groups per molecule is smaller and small and large calixarene rings generally attain different conformations [37].

The inset in Fig. 4 shows a plot of the absorbance at 280 nm of the deposited calix[8]acid LB film versus the number of LB film layers and the linear relationship confirms a fairly constant transfer ratio during sequential dipping of the slide through the LB monolayer.

3.2.3 Quartz Crystal Microbalance Results

When the surface of a quartz crystal electrode is coated with a sensitive coating, it is possible to construct a mass sensitive sensor. Therefore, QCM measurements have been widely used for the confirmation of the reproducibility of LB film multilayers using the relationship between the QCM frequency changes against the deposited mass, which should depend on the number of layers in the LB film [9,38-40]. The resonant frequency, Δf, of the QCM crystal for an LB film described by:

$$\Delta f = \frac{-2 f_0^2 \Delta m}{K_q} N \qquad (1)$$

where f_0 is the resonant frequency of the fundamental mode of the crystal (Hz), Δm is the mass per unit area per layer (g), N is the number of deposition layers, $K_q = (\rho_q \mu_q)^{1/2} A$, A is the piezo-electrically active area (cm^{-2}), ρ_q is the density of quartz (2.648 g cm^{-3}), μ_q is the shear modulus of quartz (2.947X 10^{11} g cm^{-1} s^{-2}). It is clear that this equation has a linear relationship between the number of layers and the change in resonant frequency for an LB film that confirms the uniform transfer process of the LB film.

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Fig. 5 shows the transfer of calix[8]acid LB film onto a quartz crystal substrate. A systematic change in the frequency with the increase in the number of monolayers is clearly shown however, there are two regions observed for the change of resonant frequency. Initial changes up to seven deposited layers show a slope of 49.8 Hz and the deposited mass per monolayer is determined to be 693 ng. In the second region between 9 to 27 monolayers, the slope of graph and the deposited mass per layer decreased to 14.6 Hz and 204 ng, respectively. This decrease of deposition quality onto the quartz crystal substrate could be due to a change of the surface morphology of deposited layers. The change of frequency as a function of the number of monolayers is closely associated with the LB layer mass change, and the deposition process is strongly depend on the surface interaction between substrate and monolayer at the water-air interface.

3.2.4 Surface Plasmon Resonance Results

To get further insight into the deposition properties of the multilayer assemblies, surface plasmon reflectivity scans were taken from calix[8]acid LB films of different thicknesses. SPR measurements were made on the LB films deposited onto gold-coated glass substrates at a lateral pressure of 22.5 mN/m. The LB monolayers were transferred uniformly onto gold-coated glass substrate with Y-type deposition. Fig. 6 displays a set of typical SPR curves showing the variations in reflected intensity as a function of incidence angle for LB films. The SPR curve for the bare gold film is also included for reference. The SPR curves of the overlayer containing the LB films become broader and the minimum reflected intensity rises to a higher value as the number of LB layers is progressively increased. Similar SPR curve changes have been observed for novel octa-substituted metal-free phthalocyanine LB films [41]. The peak shifts ($\Delta\theta$) seen in the angular scans of the plasmon resonance curves of the LB film multilayer assemblies relative to bare gold, increased linearly with the number of layers. Furthermore, the observed results showed that in the case of calix[8]acid LB film, the width of the peaks broadens asymmetrically with increasing thicknesses, possibly due to an increasing surface inhomogeneity for the multilayers [42]. The multilayer thickness was

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[53] J. Li, V. Janout, S. L. Regen, Covalent Gluing and Post-Gluing of Langmuir-Blodgett Monolayers at Hydrocarbon Surfaces, Langmuir, 22 (2006) 11224-11229.

[54] S. Conoci, M. Palumbo, B. Pignataro, R. Rella, L. Valli, G. Vasapollo, Optical recognition of organic vapours through ultrathin calix[4]pyrrole films, Colloids and Surfaces A, 198-200 (2002) 869-873,

[55] B. Pignataro, S. Conoci, L. Valli, R. Rella, G. Marletta, Structural study of meso-octaethylcalix[4]pyrrole Langmuir-Blodgett films used as gas sensors, Materials Science and Engineering C, 19 (2002) 27-31.

[56] C. Dridi, R. Ben Chaabane, J. Davenas, I. Bonnamour-Dumazet, H. Ben Ouada, Nanostructural, optical and electrical properties of vacuum evaporated films of an azo-calix[4]arene derivative, Vacuum, 83 (2009) 883-888.

[57] T. Basova, E. Kol'tsov, A.K. Ray, A.K. Hassan, A.G. Gürek, V. Ahsen, Liquid crystalline phthalocyanine spun films for organic vapour sensing, Sens. Actuators B, 113 (2006) 127-134.

[58] A.K. Hassan, C. Goy, A.V. Nabok, Interaction of volatile organic vapours with azo-calix[4]-resorcinarene and poly(9-vinylcarbazole) thin films using SPR measurements, Thin Solid Films, 516 (2008) 9006-9011.

[59] Z. Cao, Y.L. Zheng, F.C. Gong, S. Long, P. Chen, X.C. He, Recognition of alkyl ketone molecules based on thickness-shear-mode acoustic sensors with calixarene derivatives, Microchemical Journal, 86 (2007) 71-79.

[60] RV. Khristosenko, Y.M. Shirshov, V.Y. Khoruzhenko, K.V. Kostyukevych, I.A. Samoylova, A.S. Pavluchenko, A.V. Samoylov, Y.V. Ushenin, Analysis of some alcohol molecules based on the change of RGB components of interferentially colored calixarene films, Sens. Actuators B,122 (2007) 2427-2436.

[61] D. Filenko, T. Gotszalk, Z. Kazantseva, O. Rabinovych, I. Koshets, Y. Shirshov, V. Kalchenko, I.W. Rangelow, Chemical gas sensors based on calixarene-coated discontinuous gold films, Sens. Actuators B, 111 (2005) 264-270.

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[62] A.R. Holloway, A. Nabok, M. Thompson, A.K. Ray, T. Wilkop, Impedance analysis of the thickness shear mode resonator for organic vapor sensing, Sens. Actuators B, 99 (2004) 355-360.

[63] I.A. Koshets, Z.I. Kazantseva, Y.M. Shirshov, S.A. Cherenok, V.I. Kalchenko, Calixarene films as sensitive coatings for QCM-based gas sensors, Sens. Actuators B, 106 (2005) 177-181.

[64] S. Munoz, T. Nakamoto, T. Moriizumi, Comparisons between calixarene Langmuir-Blodgett and cast films in odor sensing systems, Sensors & Materials, 11 (1999) 427-435.

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Biographies

Rifat Çapan received MSc degree at Hacettepe University Physics Engineering Department in 1991, Ankara-Turkey and his PhD at the University of Sheffield (UK) in 1998.He established first Langmuir–Blodgett Thin Film Research Group in Turkey. He had a PhD scholarship from Turkish High Education Council between 1993 and 1998 and had Oversea's Research Student Award (UK) from 1995 to 1998. His main interests are pyroelectric heat sensor, gas sensor for environment applications, the electrical and optical properties of organic thin film materials. Dr. Capan was appointed assistant professor between 1999 and 2002 and associate professor from 2002 to 2007 at University of Balikesir in Turkey. He became a deputy of head of physics department in 2001 andwas the head of physics department between 2003 and 2006. He has been working as a professor and the head of Department at the University of Balikesir since 2007. He is a member of American Chemical Society.

Zikriye Özbek received her MSc in physics from the University of Balikesir, Turkey in 2007. She is currently working toward the PhD degree at University of Balikesir, Turkey.

Hilal Goktas received the M. Sc., and Ph. D. degrees in physics from Middle East Technical University, Ankara, Turkey, in 1996, and 2001, respectively. He joined the Turkish Atomic Energy Authority in Ankara as a researcher in between 1995 and 2005. He was appointed as an assistant professor from 2005 to the middle of 2009 at the Physics Department of Canakkale Onsekiz Mart University in Turkey, and since then he was as an associated professor at the same department. His research interests include various aspects of gaseous discharge, pulsed power, organic thin film deposition via plasma method and the electrical and optical characterizations of organic thin film materials and their applications as anti-corrosive materials and as gas and bio-sensor.

Sibel Şen received MSc degree at Ankara University Physics Engineering Department in 1997, Ankara-Turkey and PhD at the University of Çanakkale Onsekiz Mart in 2008. Her research areas are the structural properties of organic thin films and gas sensor for environmental pollution determination application. She joined the staff of Çanakkale Onsekiz Mart University in 2002. She has been working as an assistant professor at Physics Department, University of Çanakkale Onsekiz Mart since 2009.

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Fatma Gül İnce received her MSc in physics from the University of Çanakkale Onsekiz Mart, Turkey in 2008. She is currently working toward the PhD degree at University of Çanakkale Onsekiz Mart, Turkey.

Mehmet E. Özel has received his MSc and PhD degrees at Middle East Technical University (Ankara-Turkey) in 1972 1nd 1978 respectively. His research area has been high energy astrophysics until he joined the staff of Çanakkale Onsekiz Mart University in 2002. He acted as the Director of Graduate School for Science and Engineering in the same university between 2002-2008. During this time, he has also participated in the re-definition of curriculum of Physics Majors in the Physics Dept. He participated in developing a health physics and material sciences options for physics graduates. He helped the development of these topics and related research through Turkish National Science Foundation (TUBITAK) projects jointly with Dr Rifat Çapan of Balıkesir University and Turkish Atomic Energy Comission (TAEK) programs. He is presently the Dean of Fac. of Arts and Sciences at Çağ University at Tarsus- Mersin.

George A. Stanciu, After finishing courses of Electronics Faculty from University "Politehnica" of Bucharest (1971) he worked as Engineer in R&D Institute for Electronic Components Bucharest. He joined University "Politehnica" of Bucharest in 1974, where he gained a PhD degree in Technical Physics in 1981. He became Professor of Physics in 1994. He has been working in the laser microscopy field (instrumentation and application) since 1974. In 1977 he developed the first laser scanning digital system, which was successfully used for various investigations on semiconductor materials and semiconductor devices. In 2001 he founded Center for Microscopy- Microanalysis and Information Processing in the frame of University "Politehnica" based on the research activities in Laser Scanning Microscopy and Atomic Force Microscopy fields. Professor George A. Stanciu published over 150 papers (including 56 papers in internationally refereed journals) in optoelectronics field (laser radiation detectors, investigation on semiconductor lasers and photodiodes), Faraday effect, laser scanning microscopy based on OBIC techniques, confocal laser microscopy, atomic force microscopy, thin films, semiconductor quantum dots and biomaterials.

Frank Davis graduated from Lancaster University (UK) in 1987 and obtained his PhD at the same institution in 1991. Following postdoctoral experiene at Manchester and Sheffield universities, he then spent four years within the battery research group at Gillette UKRDL, Reading. He joined Cranfield Health, Cranfield University (UK) in August 2002. He has a wide experience of the synthesis of calixarene type materials and novel amphiphilic and surfactant molecules. Much of his research is focussed towards the incorporation of novel sensing moieties within ultra-thin films and their use to detect a wide variety of species including organic solvents and carcinogens, as well as biological species such as ascorbate. Dr Davis is the author of in excess of 80 published papers and 6 patents. He is a member of the Royal Society of Chemistry and a Chartered Chemist.

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Figure Caption:

Figure 1: The chemical formula of Calix[8]acid molecule

Figure 2: Isotherm graph of Calix[8] acid material

Figure 3: The UV-visible spectra of calix[8]acid solution

Figure 4: UV-vis absorption of calix[8]arene LB film. (Inset) Linear relationship between absorbance and the number of bilayers, corresponding to the thickness of the films.

Figure 5: Frequency changes as a function of layer numbers

Figure 6: SPR curves of calix[8]acid LB films with increase in thickness. (Inset) Linear increase of thickness as a function of number of bilayers.

Fig. 7. (a): Complete measured (dots) and fitted (lines) SPR curves for clean gold surface,

(b): Complete measured (dots) and fitted (lines) SPR curves for 2 calix[8]acid LB film.

Figure 8: Modeled layer thickness as a function of layer number for calix[8]acid LB layers. The solid line is a linear regression fit to the data (R=0.9947).

Fig. 9 (a): AFM two dimensional imagine for a 15-layers LB film sample

Fig. 9 (b): AFM three dimensional imagine for a 15-layers LB film sample.

Figure 10: Kinetic response of Calix[8]acid LB film against VOCs (values for saturated vapours: chloroform 205000ppm, benzene 106000ppm, toluene 28700ppm, ethanol 57700ppm).

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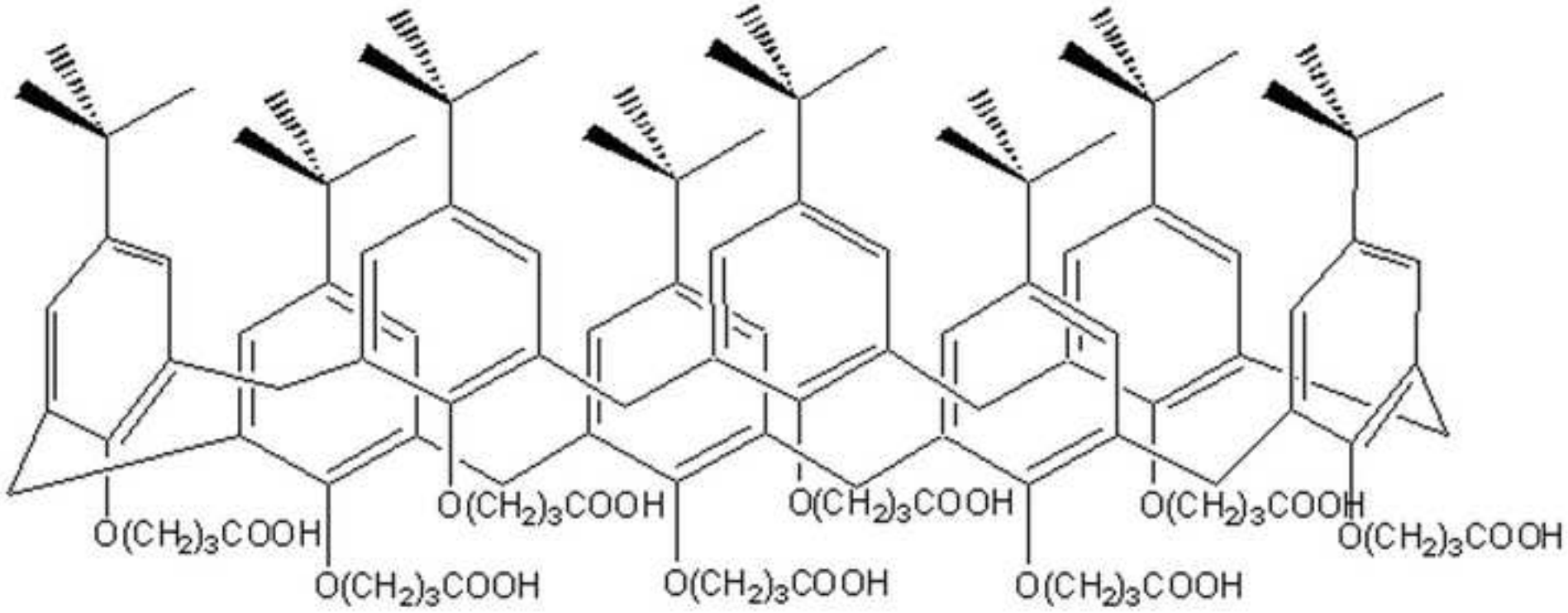
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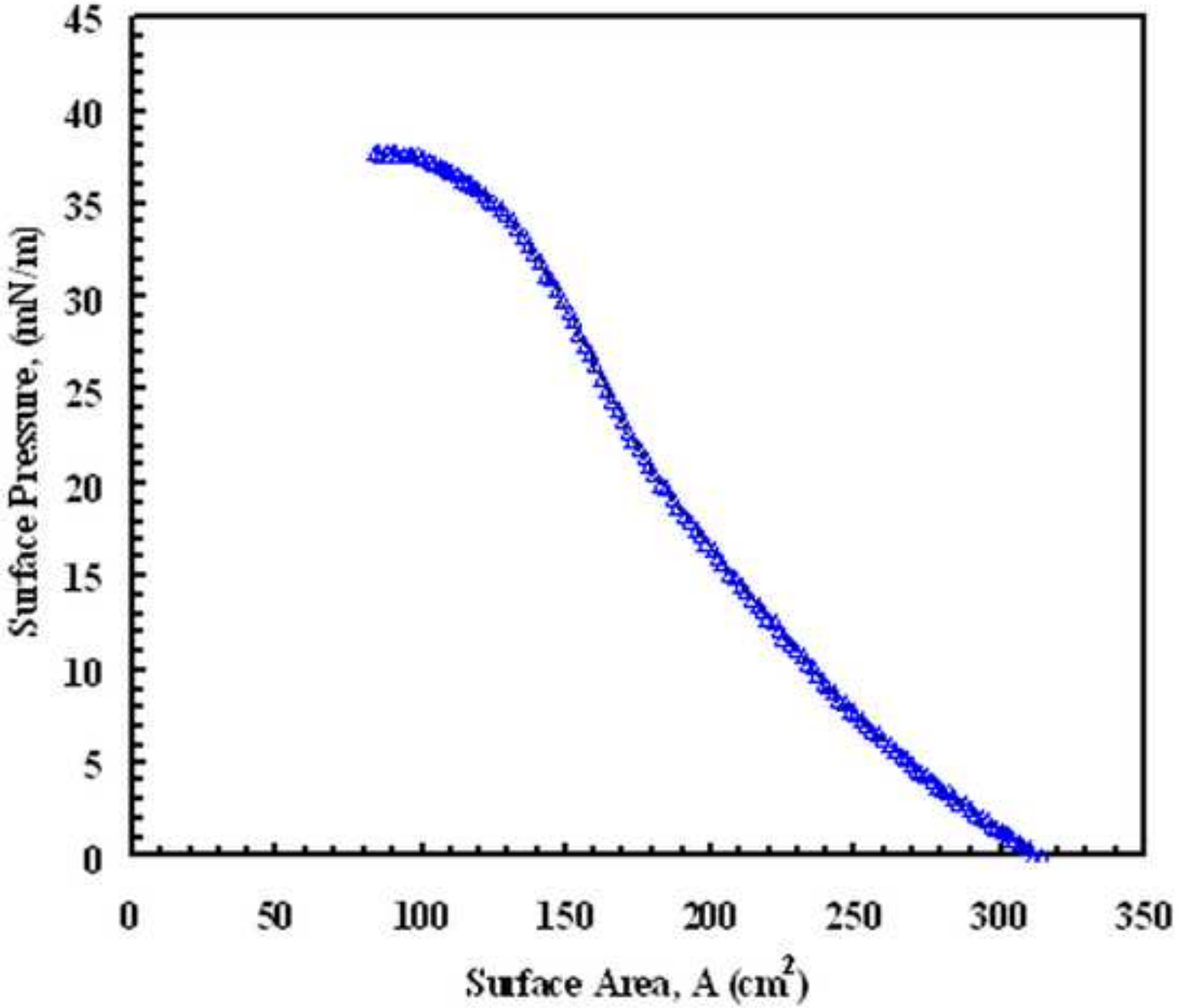
O(CH2)3COOH
O(CH2)3COOH

Fig. 1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40
35
30
25
20
15
10
5
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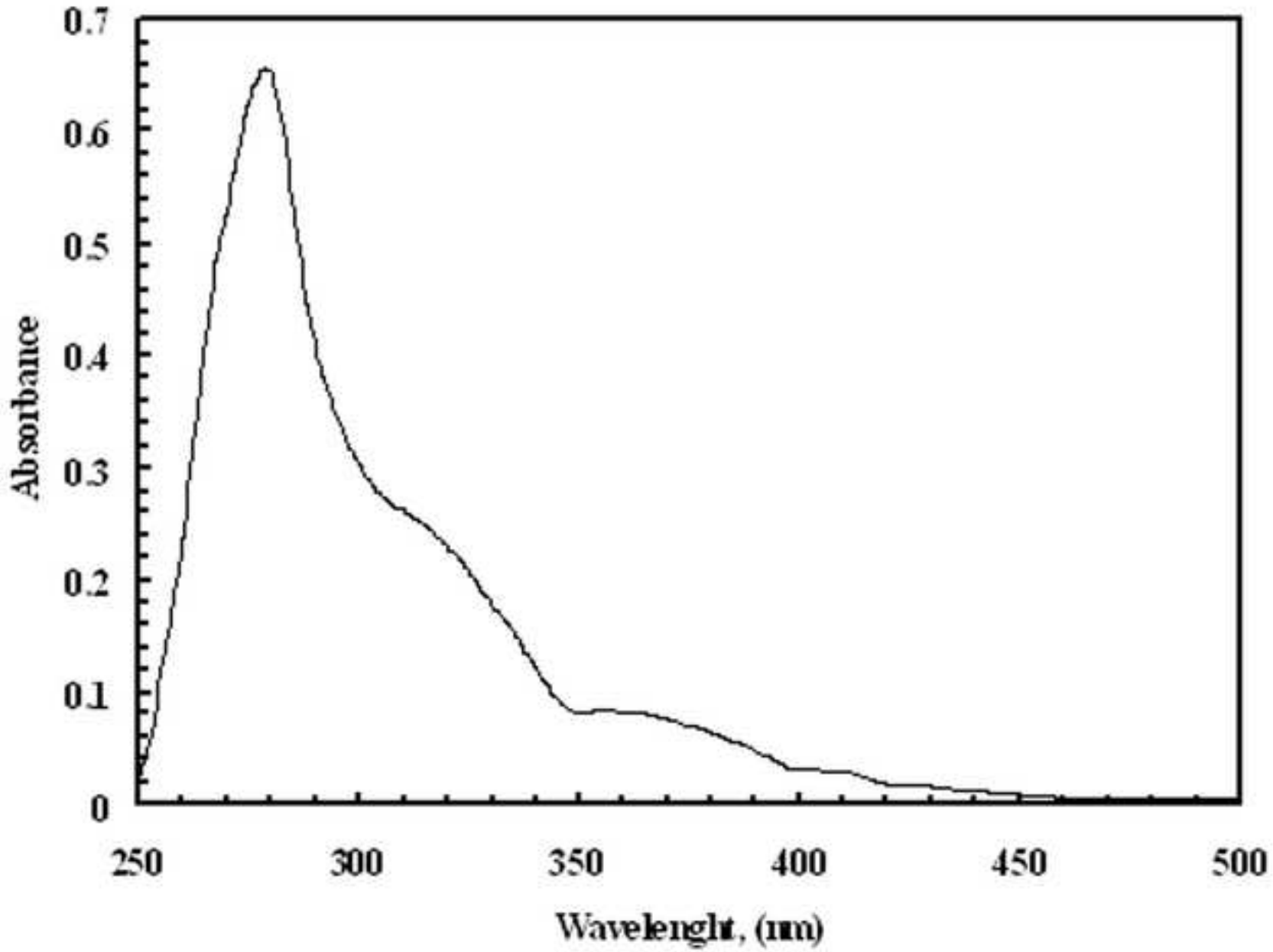
50
100
150
200
250
300
350
Suface Area, A (cm^2)

Fig. 2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0.6
0.5
0.4
0.3
0.2
0.1
0
Absorbance
250
300
350
400
450
500
Wavelenght, (nm)

Fig. 3

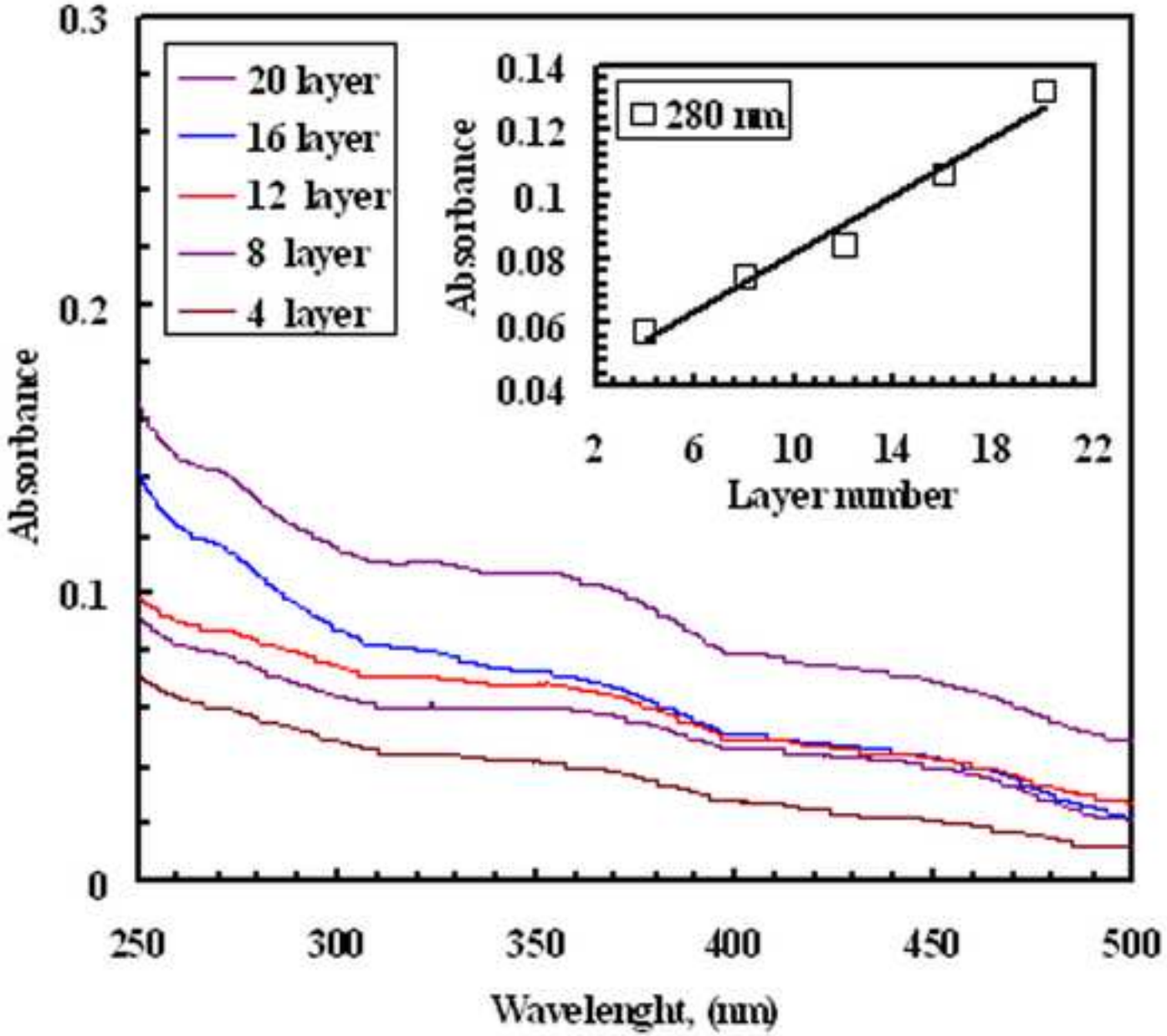
0.3
0.2
0.1
0
Absorbance
20 layer
16 layer
12 layer
8 layer
4 layer
250
300
350
400
450
500
Wavelenght, (nm)
0.14
0.12
0.1
0.08
0.06
0.04
Absorbance
280 nm
2
6
10
14
18
22
Layer number

Fig. 4

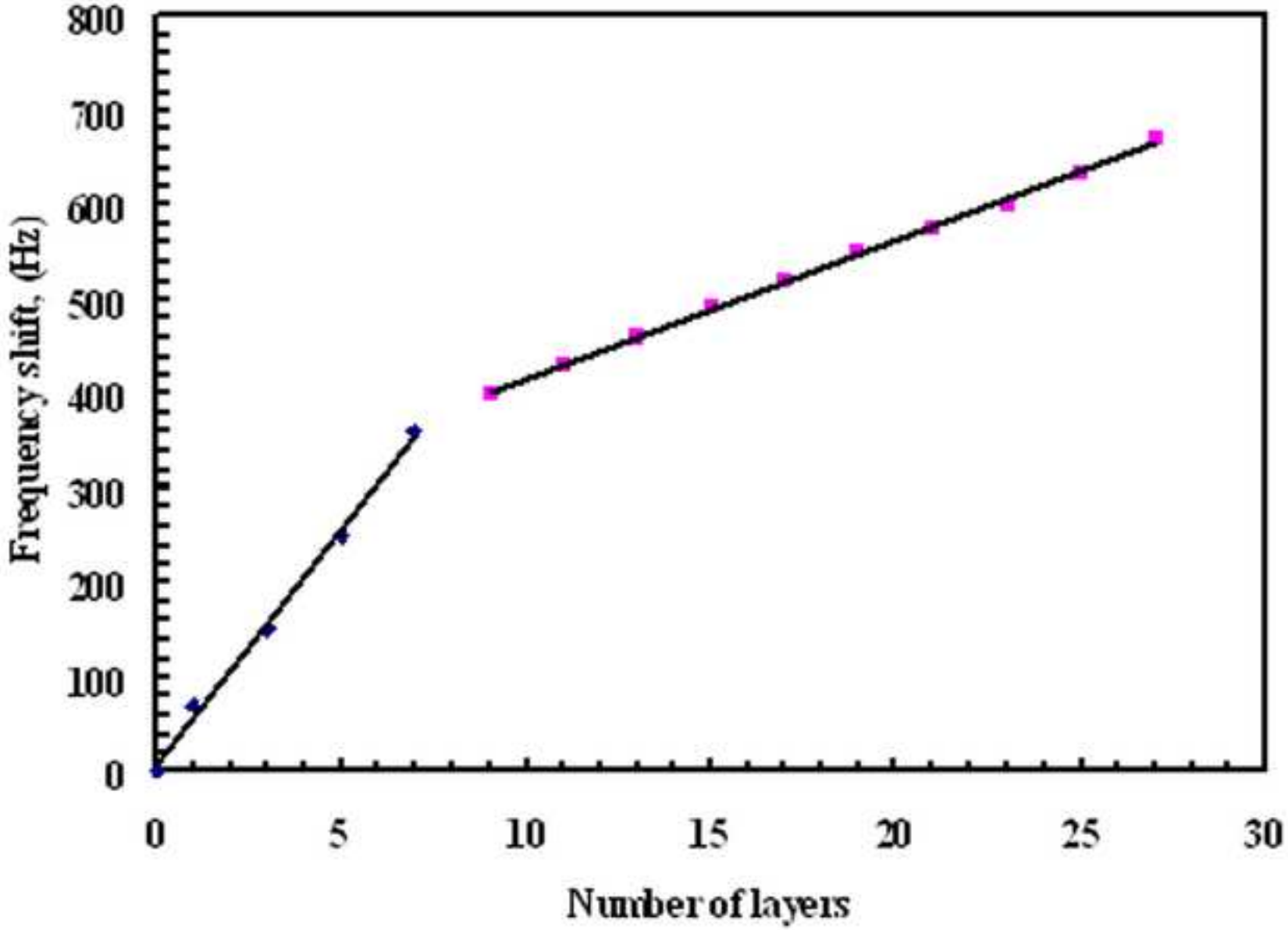
800
700
600
500
400
300
200
100
0
Frequency shift, (Hz)
0
5
10
15
20
25
30
Number of layers

Fig. 5

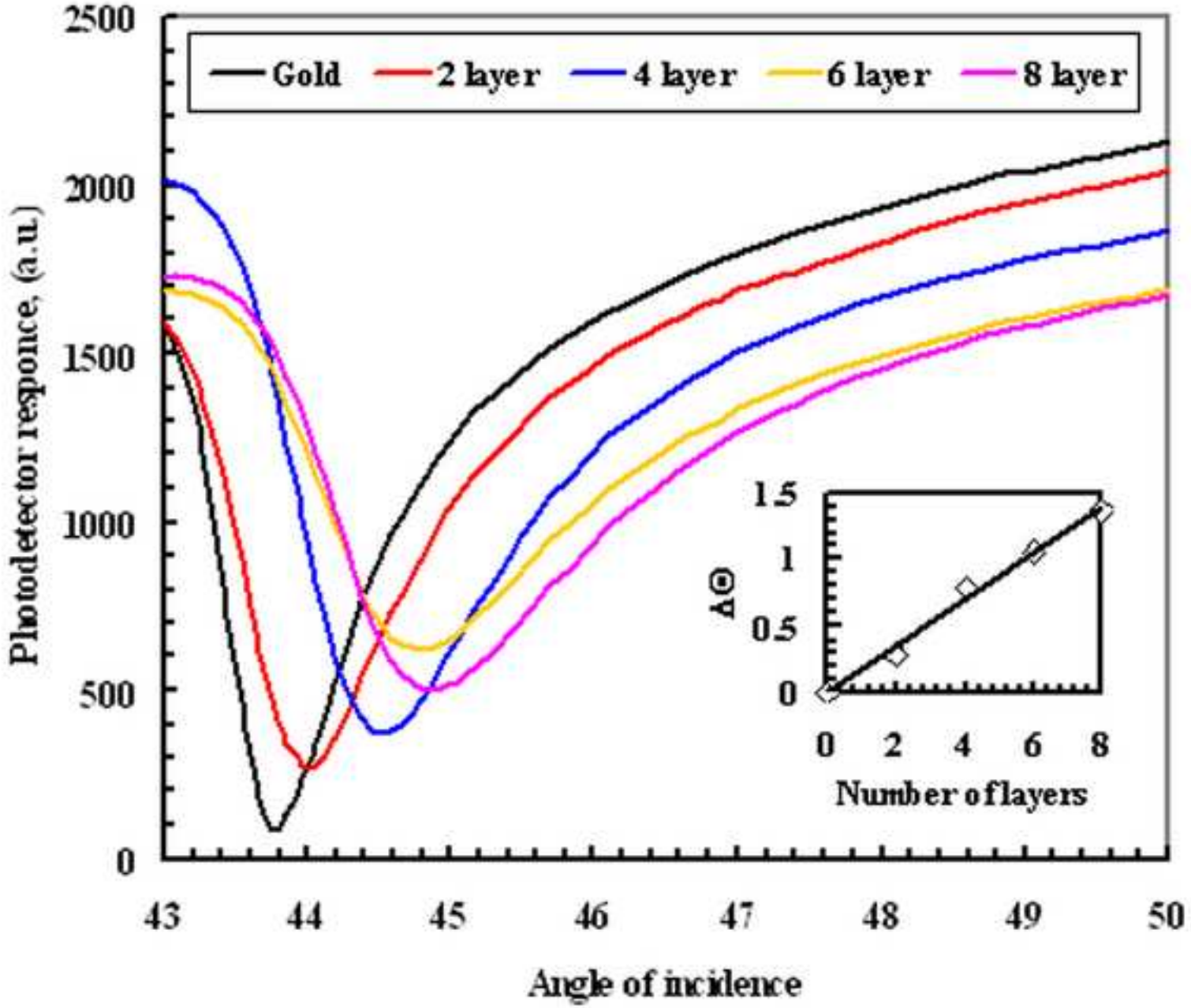
Gold
2 layer
4 layer
6 layer
8 layer
Photodetector responce, (a.u.)
2500
2000
1500
1000
500
0
43
44
45
46
47
48
49
50
Angle of incidence
Δθ
1.5
1
0.5
0
0
2
4
6
8
Number of layers

Fig. 6

Figure(s)

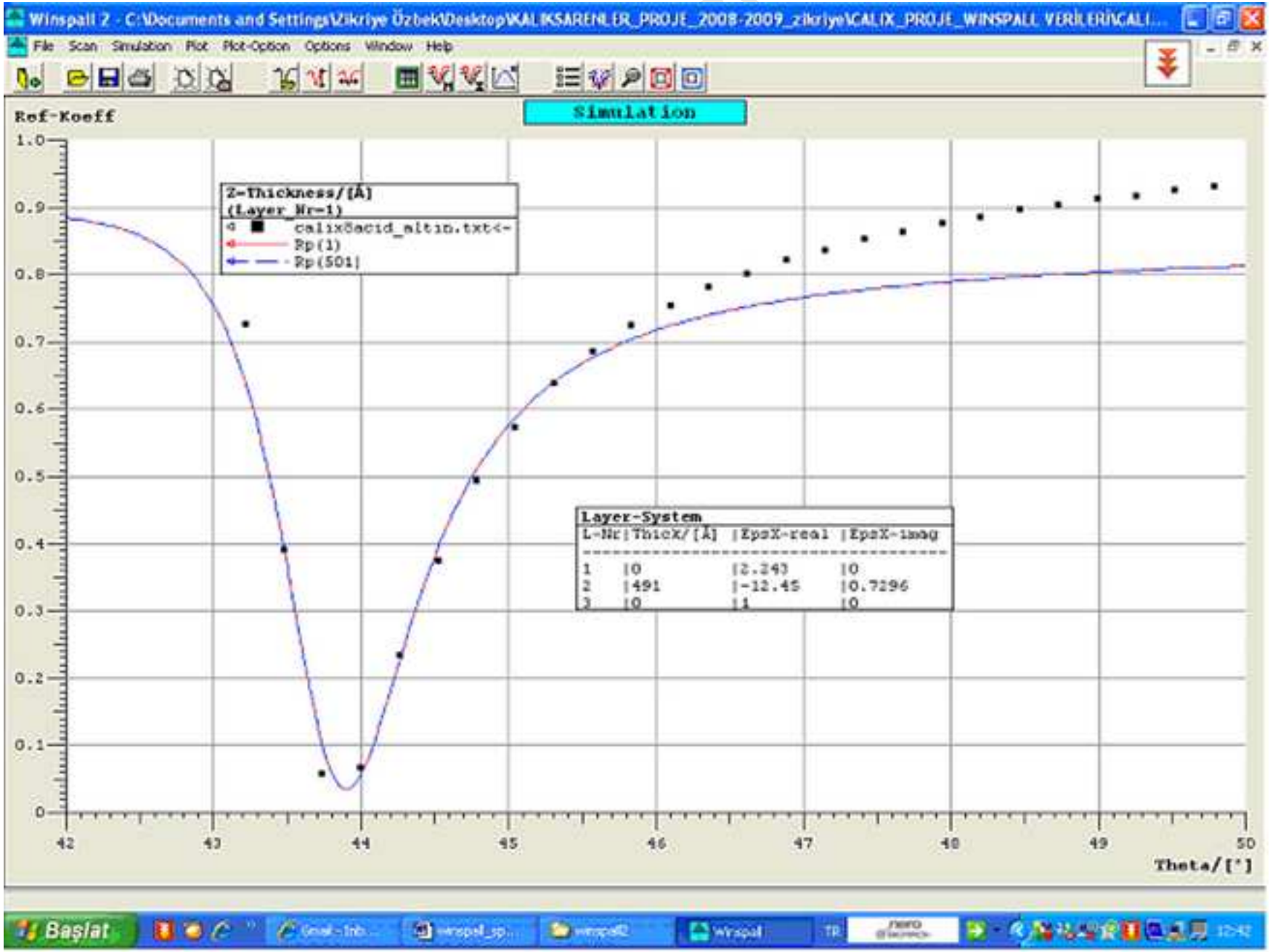

Fig. 7a

Figure(s)

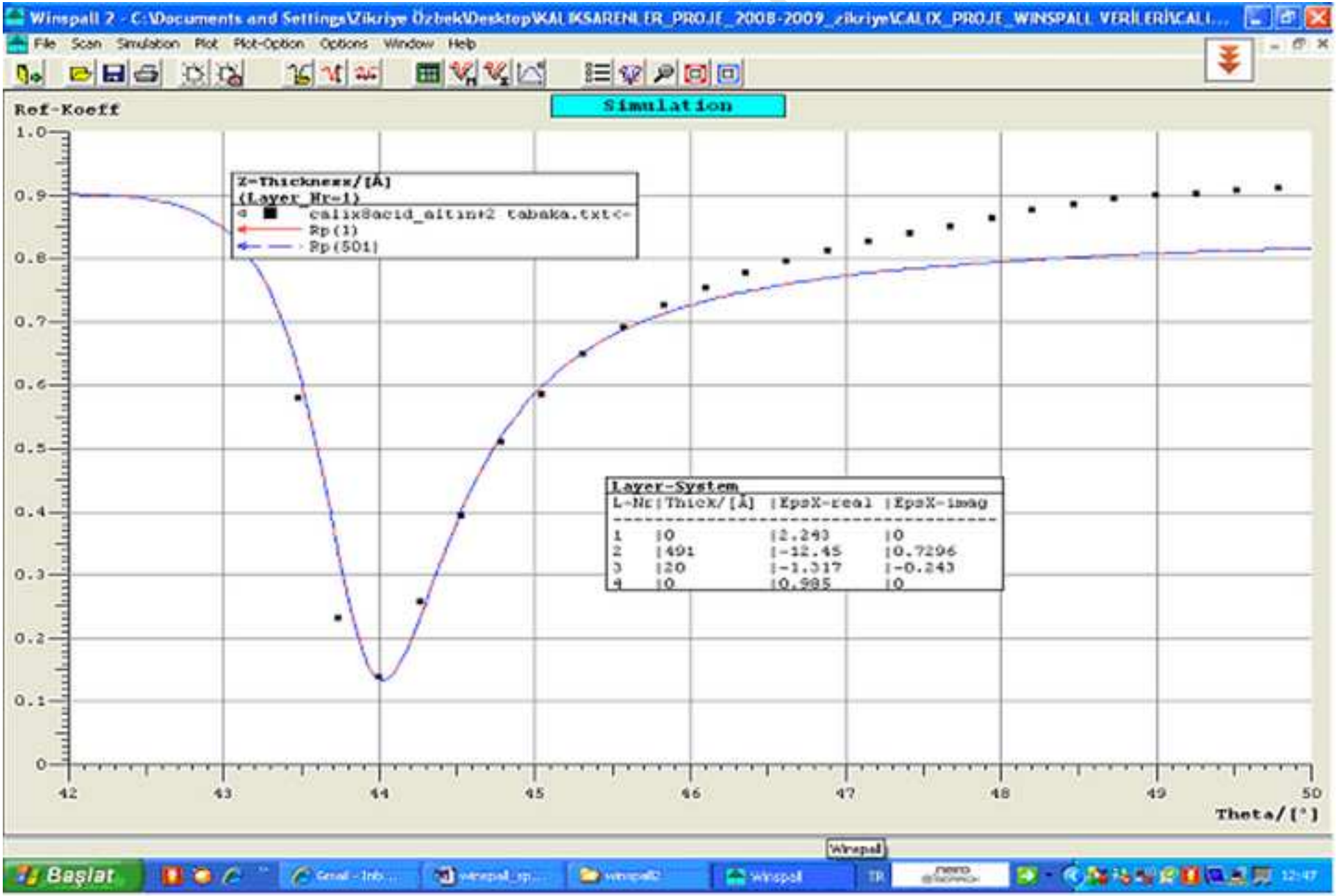

Fig. 7b

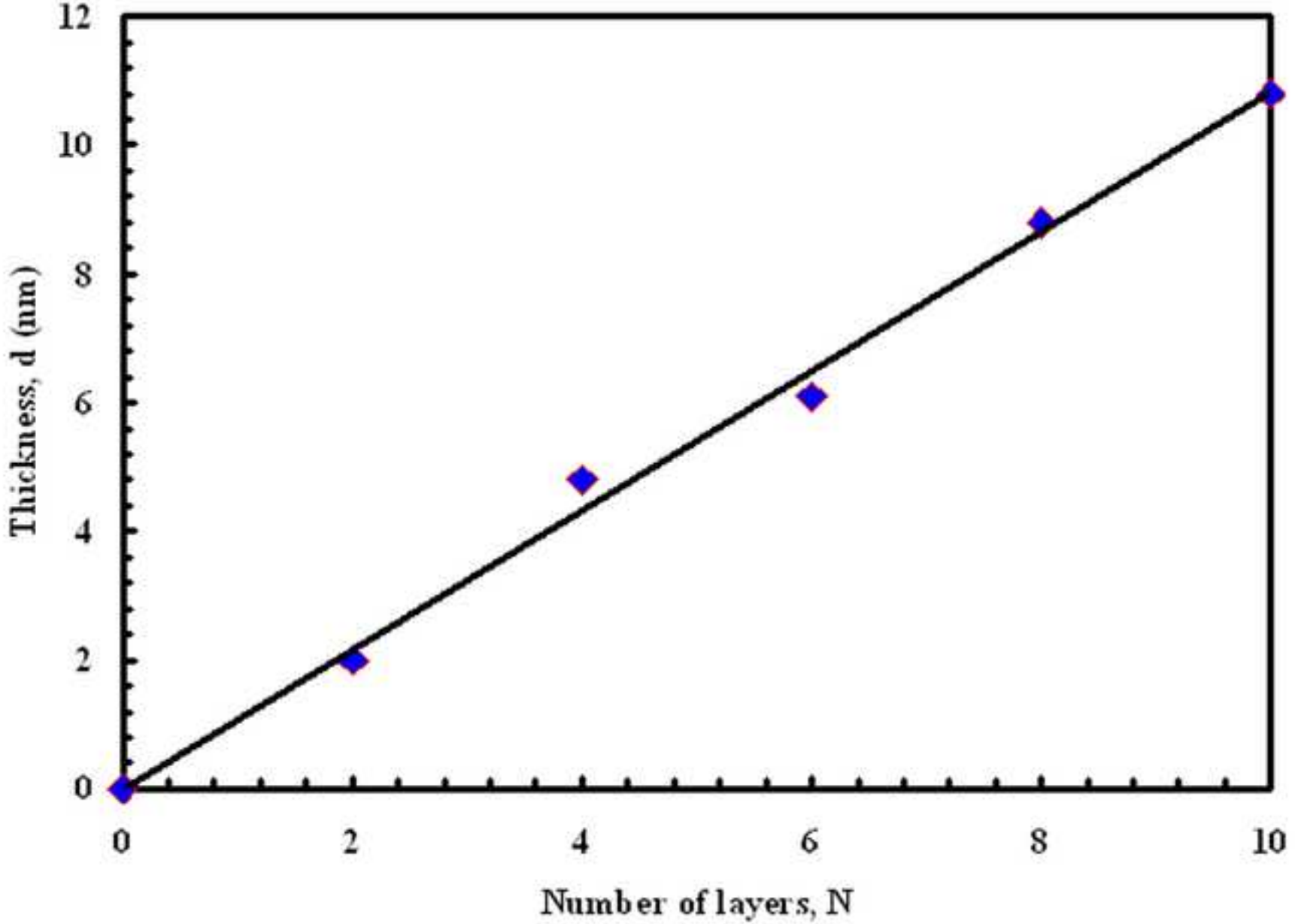

Fig. 8

Figure(s)

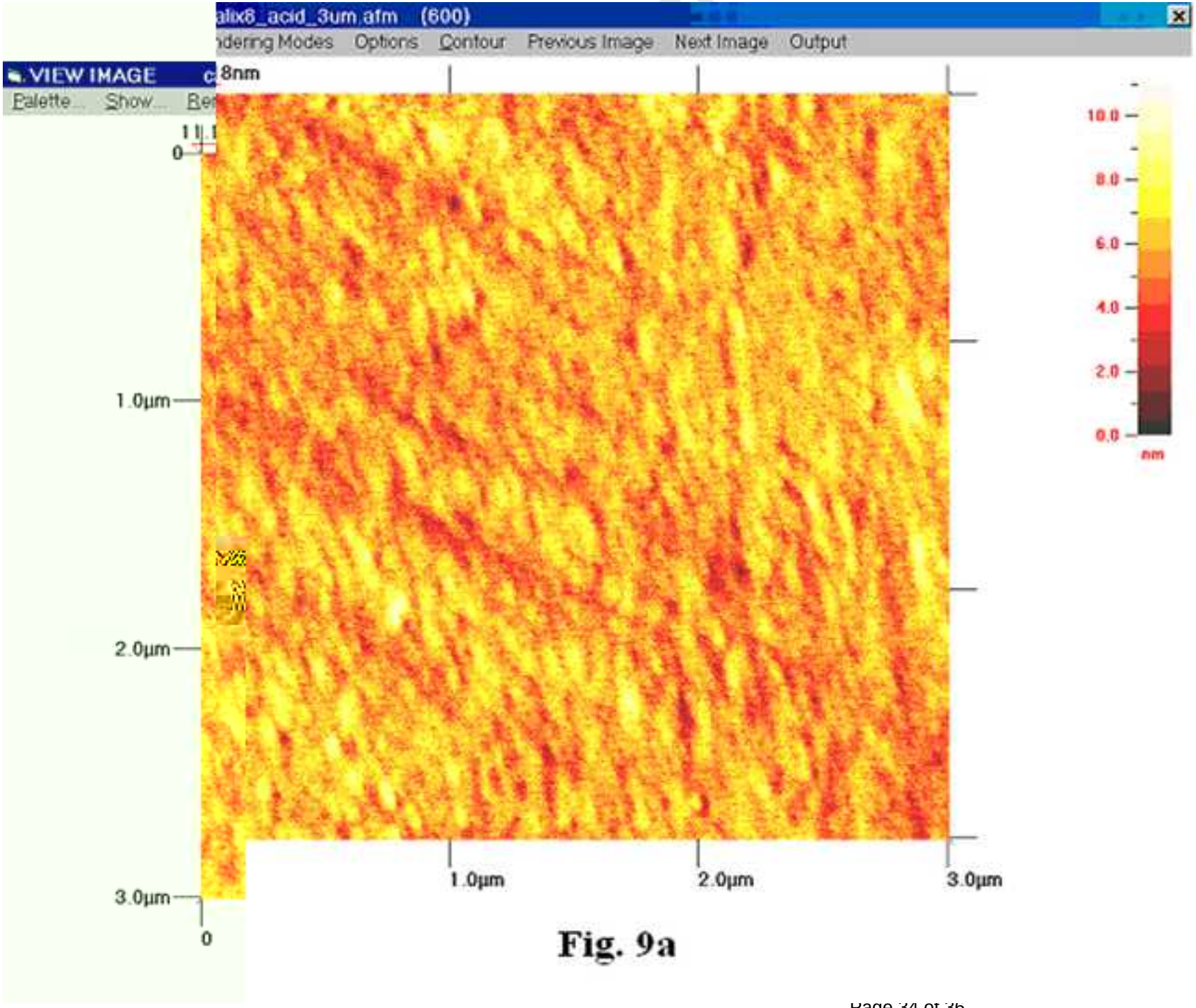

Fig. 9a

Figure(s)

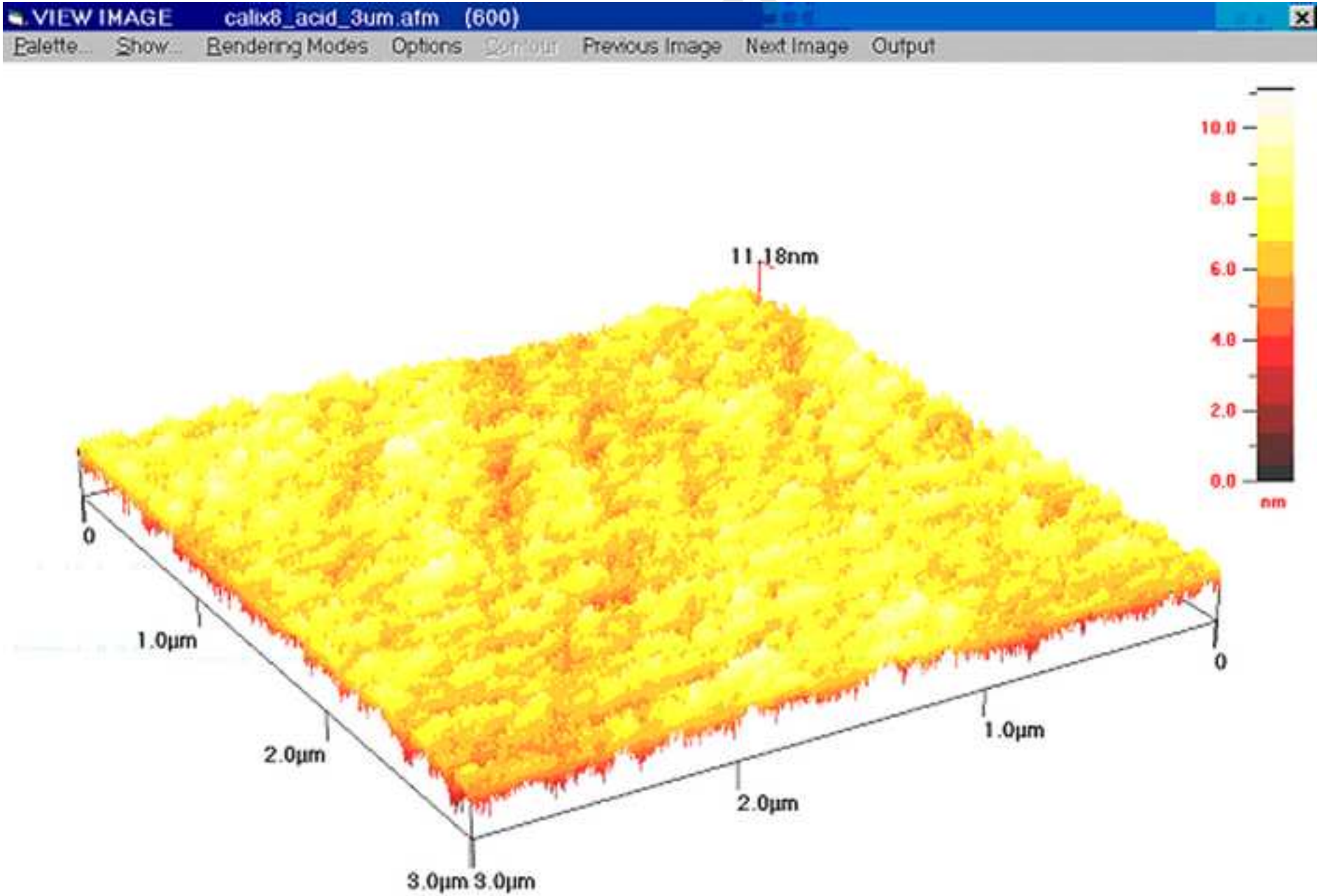

Fig. 9b

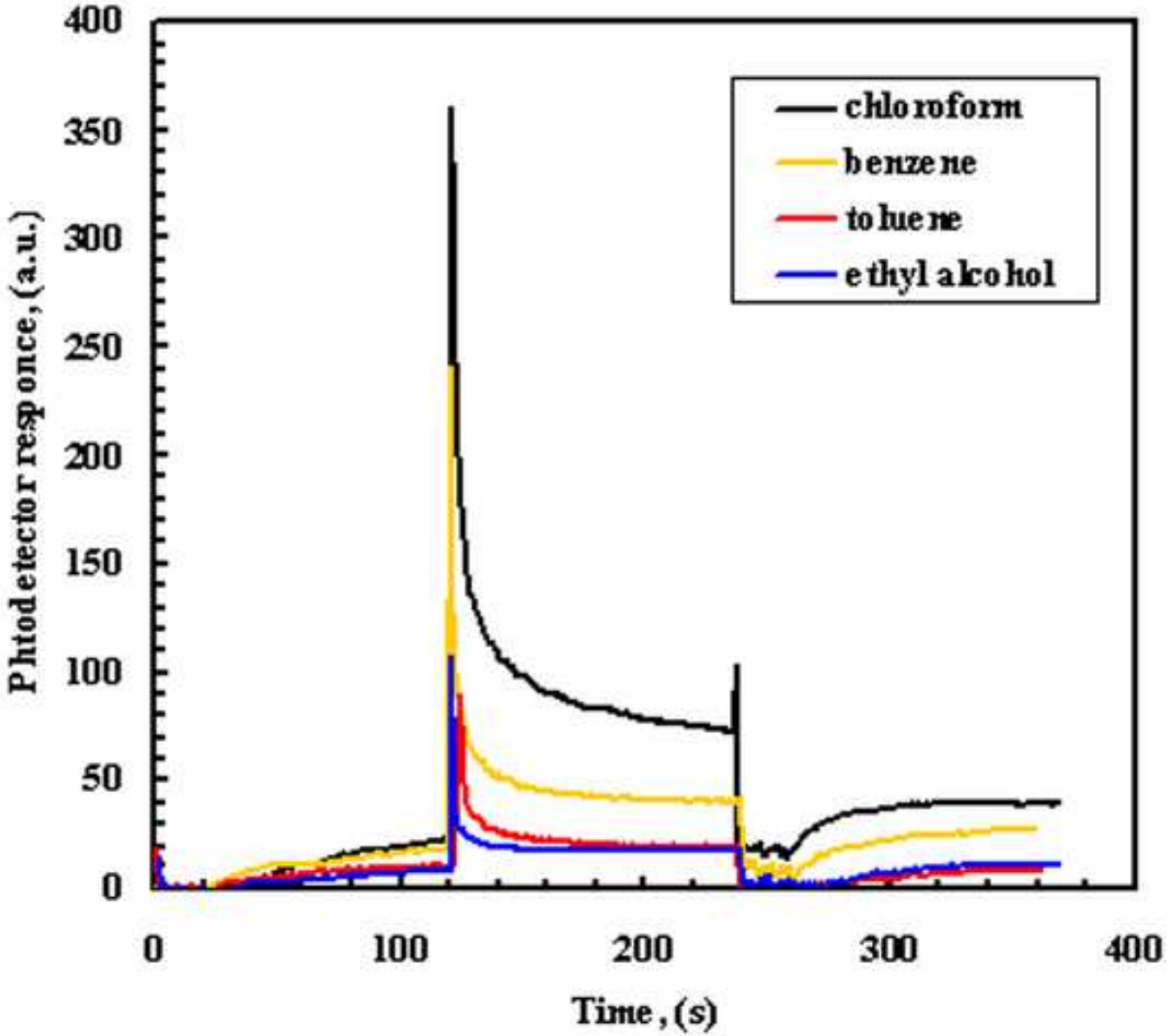
400
350
300
250
200
150
100
50
0
Photodetector responce, (a.u.)
0
100
200
300
400
Time, (s)
chloroform
benzene
toluene
ethyl alcohol

Fig. 10