



Substrate-induced self-assembly of donor–acceptor type compounds with terminal thiocarbonyl groups



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ABSTRACT

Two types of conjugated thiocarbonyl-terminated compounds have been synthesized and their ability to be adsorbed on surfaces of the different nature, namely, glass, polytetrafluoroethylene (PTFE), and gold has been studied. Different morphology of the films prepared by thermal vacuum evaporation and drop-casting from solutions has been observed depending on the surface used. It has been found that gold surface has a unique property to influence self-assembly of both monolayer and larger aggregates or crystals of the compounds, in contrast to glass and PTFE substrates. It was found that thiocarbonyl group is able to be chemisorbed to the gold surface. However, it was concluded that in spite of the fact that the thiocarbonyl groups are important for the chemical interaction with the gold surface, physical adsorption on the substrate surface, compound–compound and compound–solvent (when using solution) interactions are of great significance to drive self-assembly of the final film.

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1. Introduction

Adsorption of cyanine dyes to solid surfaces was a subject of the intense interest from both basic and technological points of view. Heterogeneous photocatalysis, dye fabrics, spectral sensitization of silver halides, colorants, nonlinear optical application, light energy conversion in photochemical cells, etc., are some of the interesting applications of these dyes adsorbed on a solid surface [1–4]. Morphology of the adsorbed films is strongly dependent on the structure of adsorbate and the nature of the adsorbent used. For example, some merocyanine dyes can exhibit, depending on their structure, H- or J-aggregation when adsorbed on metal oxide surfaces, such as TiO₂, Al₂O₃, ZrO₂, etc [5]. For the last decades, the research work has been concentrated on self-assembled monolayers (SAMs) of thiolates as a challenge for the controlled organic film deposition. The studies focused basically on the assemblies formed by the adsorption of organosulfur compounds from solutions or vapor phase onto planar metal substrates of gold and silver [6–18]. Particularly, these studies dealt with three types of organosulfur compounds: alkanethiols (HS(CH₂)_nX), dialkyl disulfides (X(CH₂)_mS–S(CH₂)_nX), and dialkyl sulfides (X(CH₂)_mS(CH₂)_nX), where *n* and *m* are the number of methylene units and X represents the end group of the alkyl chain (–CH₃, –OH, –COOH). The experiments established many of the

basic structural characteristics of these systems (surface structure, chain organization, orientation), practical protocols for preparing SAMs (concentrations, immersion time, nature of solvents, temperature), and some details of the thermodynamics and kinetics governing the process of assembly. Comprehensive reviews of the related work are described in refs. [19–21].

Except for thiolates, molecules with other sulfur groups, including the thiocarbonyl one, have also been studied in order to clarify their chemisorption on gold surfaces. It should be noted, however, that the thiocarbonyl group is often a part of more complex moieties which contain, as a rule, other sulfur groups, for example, a thiol group in dithiobenzoates [22], etc, where the latter is responsible for chemisorption of the molecule to the gold surface. There are few reports which describe such nontrivial interaction for compounds containing other sulfur groups, for example, isothiocyanate group [23]. On the other hand, direct interaction of the thiocarbonyl group and gold surfaces has not been studied well until now.

It is worthy to note that the thiocarbonyl group cannot be converted spontaneously to the thiol group which is known to be chemisorbed to the gold surface easily [21], because tautomerization reaction is hardly possible there without exterior agents. In a similar way, it was proved that sulfide moiety in dialkyl sulfides does not adsorb on gold as thiolates, but remains intact, despite the weaker binding of sulfides to gold [24]. Therefore, it is of great importance to clarify if the chemisorption of the thiocarbonyl group takes place on gold surfaces and controls formation of SAMs, respectively.

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This work is devoted to investigation of donor–acceptor compounds of two types, i.e., null-methine merocyanine derivative of pyridine and thiobarbituric acid (**1**, Scheme 1) and derivative of cyclohepta[c]pyrrole (**2**, Scheme 1), aiming to show their different ability to be adsorbed on substrates of the different nature, such as glass, polytetrafluoroethylene (PTFE) and gold, and different morphology of their assembled films. The above substrates were selected due to their different surface energy, different wettability by solvents used, as well as by different ability to keep local charge at their surface.

2. Experimental details

2.1. Synthesis of the materials

5-(2,6-Dimethyl-1-phenyl-1,4-dihydropyridinylidene-4)-1,3-diethylthiobarbituric acid (null-methine merocyanine, **1**) was synthesized by heating of 2,6-dimethyl-1-phenyl-4-pyridone [25] with 1,3-diethylthiobarbituric acid in acetic anhydride. Yield 76%, m.p. >250 °C, $\lambda_{\max} = 400$ nm, $\epsilon = 59150$ M⁻¹ cm⁻¹ in CH₂Cl₂; ¹H in nuclear magnetic resonance (NMR) (CDCl₃): δ , ppm 1.36 (t, J = 6.9 Hz, 6 H, CH₃), 2.21 (s, 6 H, CH₃), 4.66 (q, 4 H, NCH₂), 7.19–7.23 (m, 2 H, ArH), 7.63–7.68 (m, 3 H, ArH), 9.04 (s, 2 H, β -H). C₂₁H₂₃O₂N₃S (381.5); calcd. C 66.12, H 6.08, N 11.01, S 8.40; found C 66.14, H 6.05, N 10.87, S 8.12.

2-(4-Butoxyphenyl)-1,3-dimethylcyclohepta[c]pyrrole-6(2H)-thione (compound **2**) was synthesized by multi-step synthetic scheme (the general approach to this preparation was described in ref. [26]) starting from 1-(4-butoxyphenyl)-2,5-dimethyl-1H-pyrrole [27]. The last step, i.e., the reaction of 2-(4-butoxyphenyl)-1,3-dimethylcyclohepta[c]pyrrol-6(2H)-one with phosphorus pentasulfide in pyridine, was performed accordingly [28,29]. Yield 80%, m.p. 142–144 °C, $\lambda_{\max} = 420$, 312 nm in C₂H₅OH; ¹H NMR (DMSO-d₆): δ , ppm 0.96 (t, J = 6.9 Hz, 3 H, CH₂CH₃), 1.47 (m, 2 H, CH₂CH₃), 1.74 (m, 2 H, NCH₂CH₂), 2.20 (s, 6 H, CH₃), 4.06 (t, J = 6.6 Hz, 2 H, NCH₂), 7.11 (d, J = 9 Hz, 2 H, ArH), 7.24 (m, 4 H, ArH), 7.32 (d, J = 9 Hz, 2 H, ArH). C₂₁H₂₃NOS (337.48); calcd. C 74.74, H 6.87, S 9.50; found C 74.60, H 6.62, S 9.64.

2.2. Sample preparation

Three different methods of sample preparation have been used in order to distinguish influence of molecule–molecule and molecule–substrate interactions on the film morphology, i.e., adsorption from a solution, film-casting from a solution and thermal deposition in vacuum. The first two methods provide film formation under equilibrium conditions of which the first one can yield formation of a monolayer through prevailing molecule–substrate interactions. The vacuum deposition method leads to formation of a film under non-equilibrium conditions, since the molecules sharply reduce their mobility when dropping onto the surface.

Thermal deposition of films has been performed using VUP-5 vacuum equipment with computerized control system and optical spectrometer “Polytec” for transmission spectra measurements during the film growth *in situ*. Base pressure in the chamber was 10⁻³ Pa. The quartz crucible was used for the powder evaporation. The crucible temperature was monitored by a chromel–alumel thermocouple. Film

thickness and growth rate were measured using a quartz microbalance technique.

Glass plates, gold and PTFE films have been used as substrates for film deposition. PTFE films were deposited by decomposition of the bulk PTFE pellets and activation of the gaseous elements with accelerated electrons. Compounds were evaporated from thermally heated crucible. Glass and silicone plates were used as supports for deposition of PTFE. Further details of the deposition technique can be found elsewhere [30].

The substrate temperature was kept constant at room temperature during film deposition of **1** and **2**. For the correct comparison of the samples all three types of substrates, i.e., PTFE, Au and glass have been used in the same deposition process. The deposition rate was chosen in the range between 0.1 and 0.2 nm/s. The distance between evaporators and substrate was 10 cm. The deposition process was stopped at reaching the optical transmission of the film of about 50%.

Dimethylformamide (DMF), dioxane and toluene (spectrophotometric grade, Sigma-Aldrich) were used as solvents to prepare solutions of the compounds with concentration of 10⁻³ M. SAMs have been prepared by dipping of the gold substrate into the toluene solution of the compound for 40–50 min followed by washing with the pure toluene. To prepare a cast film, a small drop of the solution (ca. 20 μ l) was ejected from a syringe onto the substrate followed by evaporation of the solvent under ambient conditions.

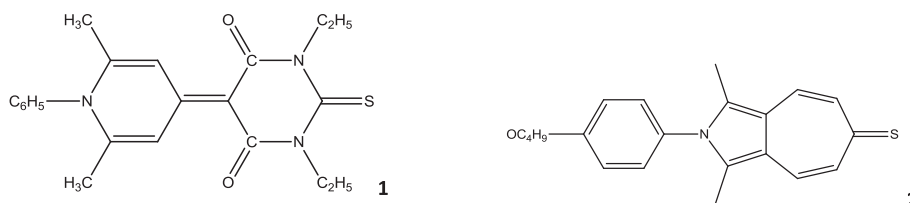
2.3. Morphological studies and contact angle measurements

Film morphology and thickness were studied by atomic force microscope (AFM) Nanoscope IIIa Dimension 3000™ at ambient conditions. Dark and bright field optical microscopy investigations were performed with Carl Zeiss NU-2E optical microscope. Surface morphology of investigated samples was mapped using ultra-sharp silicon AFM tips (MicroMasch Co.) with nominal tip apex radius less than 10 nm under the tapping mode AFM operation.

Contact angle measurements of the solution drop were carried out using a home-made automated macro-imaging and image analysis software module. Solvent evaporation and changes in the contact angle of the solution drop were monitored through a photcamera connected to the computer. Contact angle of the solution drop on the surface was measured using a small volume (~3 μ l) of the solution carefully deposited on the substrates under investigation. The liquid drop was under the quasi-closed space conditions during the experiment to provide a slow evaporation of the solvent. Sequences of micro-images of a sessile drop have been collected with the same time interval and treated by analytical software. Measurements were carried out using solution drops prepared in the same cycle on an Au film of 20 nm thickness which was deposited in vacuum on silicon substrate and on a PTFE film (60 nm) deposited over the Au film. The same solution drops prepared on the glass substrates have been studied in the analogous way. The same procedure was performed using a drop of the pure solvent.

2.4. Spectral studies

Electronic absorption spectra of solutions were measured using an AvaSpec-2048 spectrometer, with the pure solvent as a reference



Scheme 1. Chemical structure of the compounds used.

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