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SPECTROSCOPIC AND ATOMIC FORCE MICROSCOPY STUDY OF A NEW HEMICYANINE DYE

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ABSTRACT. The new hemicyanine dye, named 1,3,3-trimethyl-2-[2-(4-florophenylamino) ethenyl]-3-H-indolium chloride **1**, was synthesized and characterized by spectroscopic methods (UV-VIS, IR, ^{1}H-NMR) and by atomic force microscopy (AFM). The AFM data, obtained on thin films deposited on solid substrates, glass and mica plates, indicated that the hemicyanine **1** is aggregated as clusters containing thousands of molecules. These data are in substantial agreement with UV-VIS absorption spectra, obtained both in solution and on films adsorbed on glass or mica plates, suggesting that hemicyanine **1** is aggregated both in bulk solution and in adsorbed films on solid substrates.

Keywords: hemicyanine dye, 1,3,3-trimethyl-2-[2-(4-florophenylamino) ethenyl]-3-H-indolium chloride, synthesis, spectroscopic characterization, AFM

INTRODUCTION

The hemicyanine dyes are widely used for dyeing textile fibers [1-4], as laser dyes and fluorescence probe [5], as well as in sensitization of silver halides in photography [1, 2, 6-8]. For such applications, spectroscopic and aggregation properties are important [1, 4, 5, 9]. Generally, the aggregation properties of dyes have been studied especially by UV-VIS spectroscopy [1, 9-19] and recently by atomic force microscopy [20].

Taking into account the large application potential of hemicyanine dyes and the influence of molecular aggregation on their properties we synthesised a new hemicyanine dye (noted compound **1**, in Scheme 1) and investigated its aggregation capability. The rational name for the new hemicyanine dye **1** is 1,3,3-trimethyl-2-[2-(4-florophenylamino)ethenyl]-3-H-indolium chloride.

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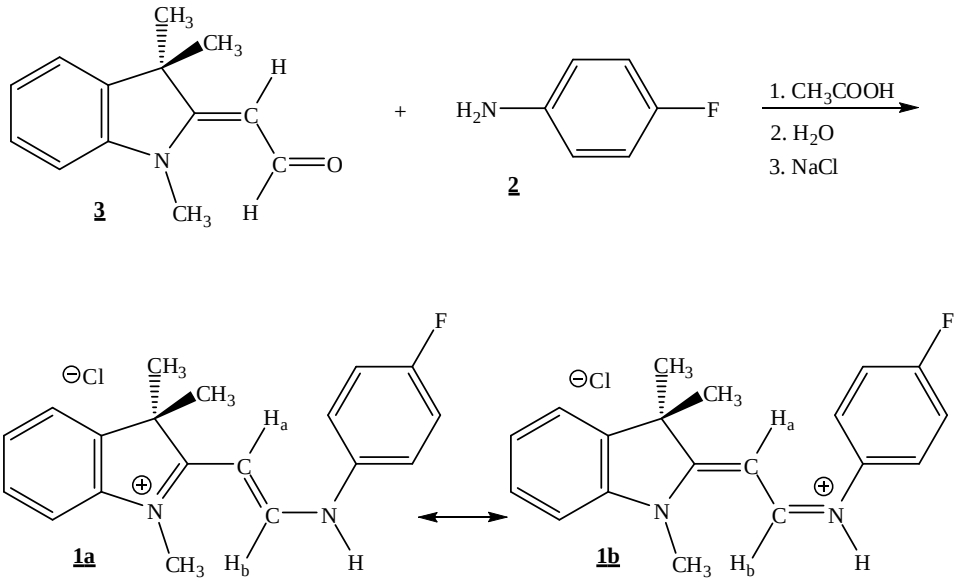


Scheme 1. Synthesis of 1,3,3-trimethyl-2-[2-(4-florophenylamino)ethenyl]-3-H-indolium chloride (1)

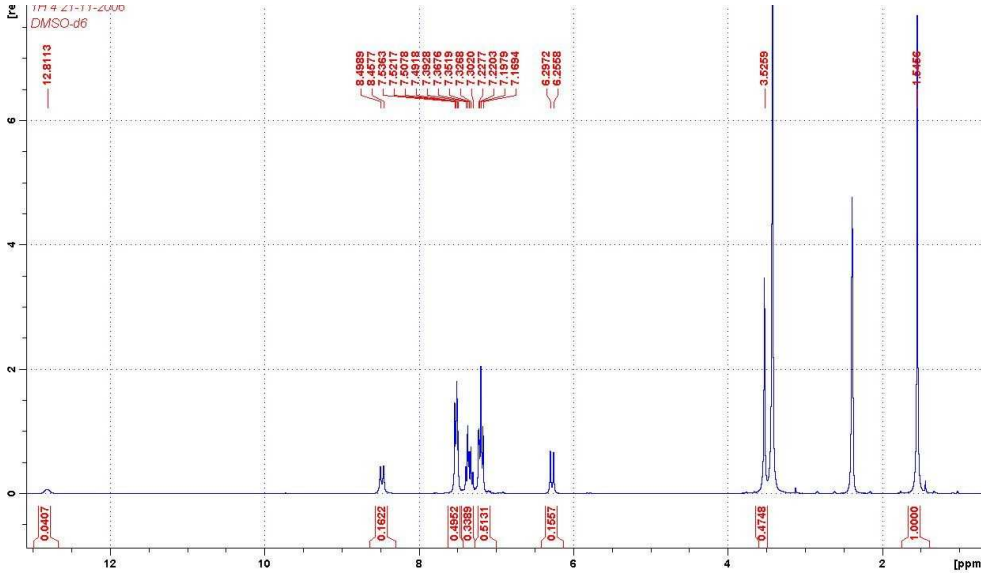


Fig. 1. The ^{1}H-NMR spectrum of hemicyanine dye, compound **1**.

EXPERIMENTAL PART

Materials

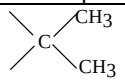
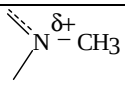
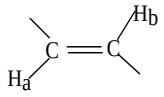
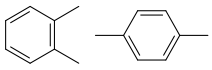
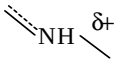
4-floroaniline (**2**) was purchased from Fluka (Buchs), glacial acetic acid, ethanol, methanol and diethylether from Chimopar (Bucharest) and hexadeuterated dimethylsulfoxid (CD_3SOCD_3) from INCDTIM (Cluj-Napoca). The aqueous solutions were prepared by using demineralized and twice distilled water. The 1,3,3-trimethylindolin-2-ylidene acetaldehyde (TIA), **3**, was synthesized as previously described [21].

Synthesis and characterization of hemicyanine **1**

The hemicyanine **1** was synthesized [2-4] by the condensation of TIA, **3** (0.01 mol) with 4-floroaniline (**2**) in glacial acetic acide (5 ml) (Scheme 1). The mixture was stirred at room temperature for 17 hours, then diluted with water (25 ml) and salted out with NaCl (5 g). The orange precipitate was filtered, washed with water, ethanol and finally with diethyl ether. After recrystallization from methanol: m.p. = 218 -221 ^oC, yield 40%, UV-VIS spectrum: λ_{max} (methanol) = 406 nm; ε_{max} = 43,000 L mol^{-1} cm^{-1}; IR spectrum (KBr pellet) ν_{NH} = 3,384 cm^{-1}; $\delta_{-CH=CH-\ (trans)}$ = 931 cm^{-1}. The ^{1}H-NMR spectrum (300 MHz, in hexadeuterated dimethylsulfoxid) is given in Fig. 1. For each type of protons (Scheme 1), the chemical shift expressed in δ [ppm], using tetramethylsilane as internal standard, the multiplicity (s = singlet, d = doublet, m = complex multiplet), the number of protons and the coupling constant J [Hz] are given in Table 1. The presented spectroscopic data confirm the ascribed structure **1**.

Table 1.

^{1}H-NMR spectrum of hemicyanine ***1***

Group	δ [ppm],	Multiplicity	Nr. of protons	J[Hz]
	1.55	s	6	
	3.53	s	3	
	H_a 6.28 H_b 8.48	d d	1 1	12.4 12.4
	7.1 – 7.6	m	8	
	12.81	s	1	

Instrumentation and measurements

The UV-VIS spectra were recorded on a Jasco spectrophotometer (V-530 and V-650 models) at 25 ^{o}C. The IR spectrum was registered as KBr pellet on a Nicolet Impact 410 FT-IR spectrometer. The ^{1}H-NMR spectrum was performed at room temperature using a FT-Bruker Avance 300 NMR spectrometer. The AFM measurements were carried out, as previously described [22-24], with an AFM-JEOL 4210 scanning microscope on samples of hemicyanine **1** as solid films deposited on glass and mica plates. The same samples were also used for the recording of UV-VIS spectra for **1** in solid state. The hemicyanine **1** solid films were obtained by application of drops of 10^{-4} M aqueous acidic (pH = 3.3) solution of **1** on glass or mica plates, followed by the complete evaporation of water at room temperature and atmospheric pressure. The size of the plates varied between 2.5 cm x 2.5 cm and 1 cm x 1 cm. The UV-VIS spectra in solution were measured on aqueous acidic (HCl) solution (pH = 3.3) in the range of about 10^{-5} M to 10^{-4} hemicyanine dye concentration.

RESULTS AND DISCUSSION

In the present paper the focus is on the examination of the capability of the hemicyanine **1** to aggregate, since aggregation properties of dyes are known [1, 5, 9, 19, 20] to be involved in many of their applications.

As the hemicyanine **1** in aqueous solution is implicated in an acid-base equilibrium [2, 3] it is very difficult to provide evidence on aggregation in solution [19, 25, 26]. Therefore we have tried to prove the capability of aggregation of **1** by comparing the UV-VIS absorption spectra of **1** in aqueous acidic solution (when the acid-base equilibrium is shifted towards form **1**) with that in solid films on mica (Fig. 2).

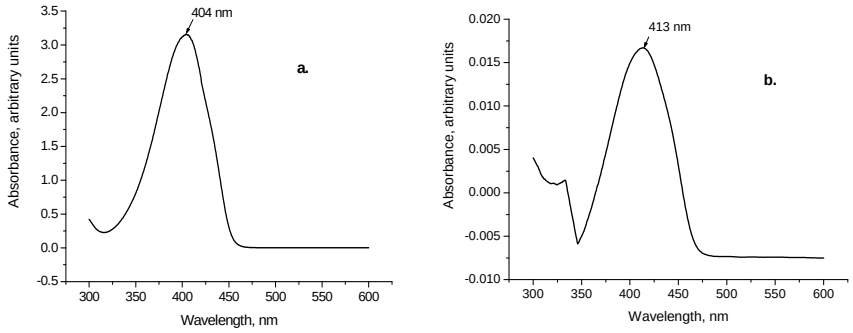


Fig. 2. UV-VIS absorption spectra of hemicyanine *1* in aqueous acidic solution (10^{-4} M, pH = 3.3) (a) and on solid film on mica (b).

As it can be seen (Fig. 2), the two spectra, both in solution (a) and in the solid state, adsorbed on mica (b), look very similar, although in the spectrum of the solid film (b) the absorption maximum is shifted bathochromically with 9 nm and the band width is slightly larger.

Since in solid state, both as crystals or adsorbed on solid substrates, as a rule dyes are considered to be aggregated [1, 9, 11, 13, 15, 16, 20, 27-30], the similar spectra obtained for hemicyanine **1** in solution (Fig. 2a) and in adsorbed solid state (Fig. 2b) could be an argument for the appearance of aggregation of **1** in bulk solution as well. The presence of hemicyanine **1** as aggregates in its solid films, adsorbed on glass or mica (having the UV-VIS absorption spectrum presented in Fig. 2b), has been also confirmed by AFM measurements (Figs. 3-6).

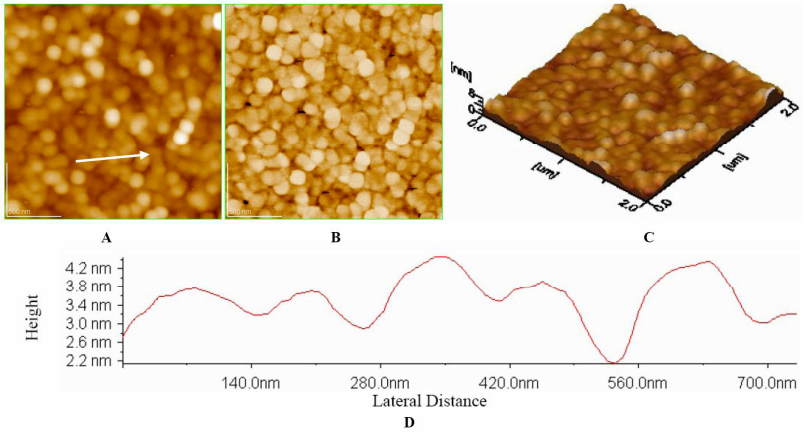


Fig. 3. AFM images of the hemicyanine **1** film deposited from aqueous solution (10^{-4} M, pH = 3.3) on optically polished glass. Scanned area: 2 x 2 μm^2. A) 2D- topographic image; B) phase image; C) 3D-topographic image; D) cross section profile along the arrow in Fig. 3A.

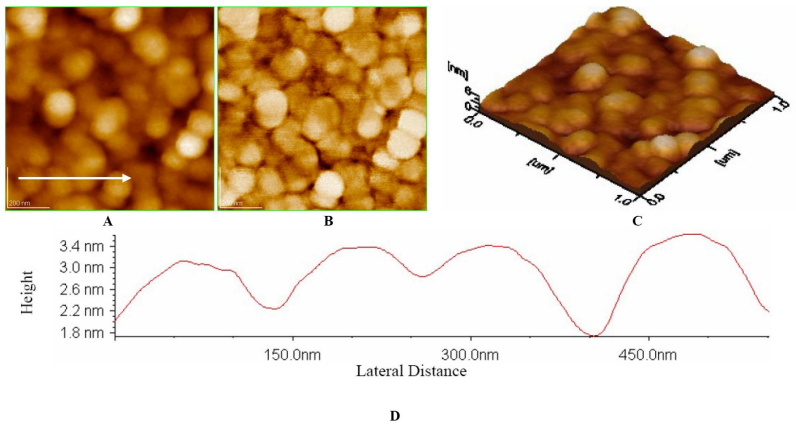


Fig. 4. AFM images of the hemicyanine **1** film on optically polished glass (see Fig. 3). Scanned area: 1 x 1 μm^2. A) 2D- topographic image; B) phase image; C) 3D-topographic image; D) cross section profile along the arrow in Fig. 4A.

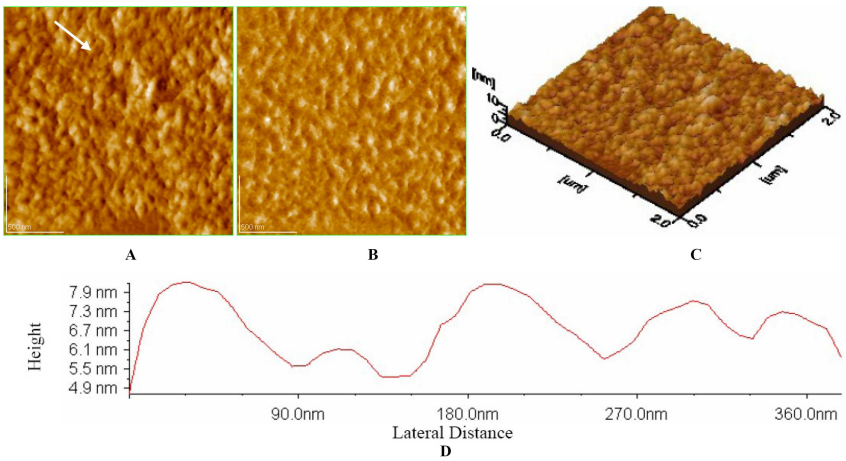


Fig. 5. AFM images of the hemicyanine **1** film deposited from aqueous solution (10^{-4} M, pH = 3.3) on mica. Scanned area: 2 x 2 μm^2. A) 2D- topographic image; B) phase image; C) 3D-topographic image; D) cross section profile along the arrow in Fig. 5A

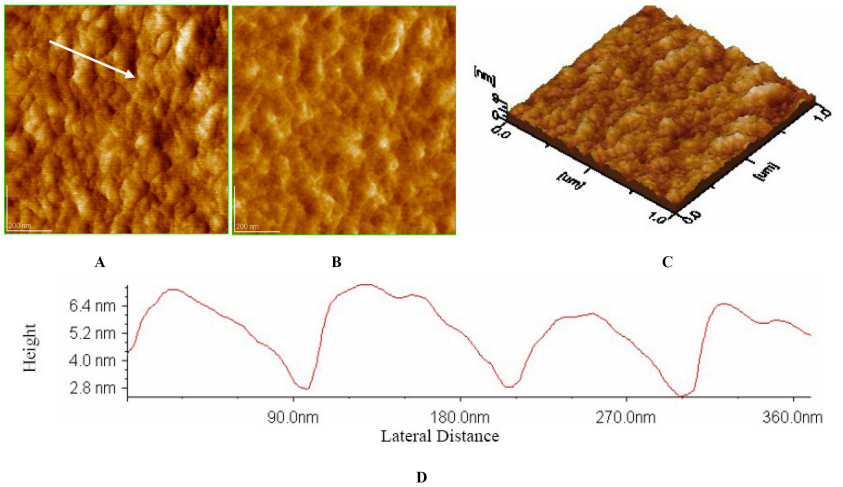
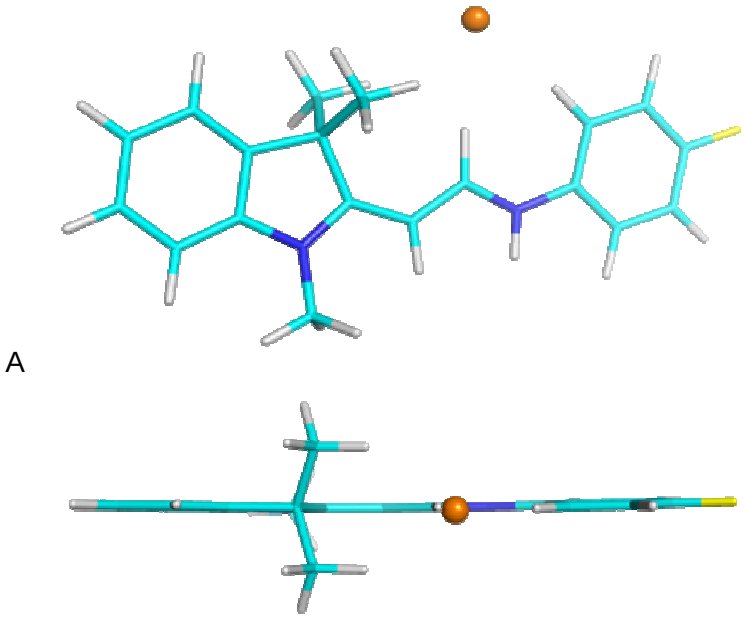


Fig. 6. AFM images of the hemicyanine **1** film on mica (see Fig. 5). Scanned area: 1 x 1 μm^2. A) 2D- topographic image; B) phase image; C) 3D-topographic image; D) cross section profile along the arrow in Fig. 6A

From Figs. 3-6, it is observed that the solid films of hemicyanine **1** adsorbed on glass (Figs. 3, 4) or on mica (Figs. 5, 6) appear as multilayers and have island structures. The clusters of hemicyanine **1** within these films correspond to supramolecular assemblies of approximately spherical shape, having a 70 ± 5 nm radius on glass (Figs. 3, 4) and about 45 ± 5 nm on mica.

A full geometry optimization was carried out using the *ab initio* Hartree-Fock 6-31G* level of theory implemented in the Gaussian 03. The

geometry of hemicyanine **1** molecule is given in Fig. 7. The van der Waals surface-bounded molecular volume is 946 Å^3, and the dimensions of the molecule are: length of about 14.2 Å; width of 4.3 Å and height of 5.8 Å.



A

B

Fig.7. The hemicyanine **1** molecule represented in the plane of the first two inertial axes (A) and of the first and third inertial axes (B). The red ball represents the chloride anion.

Taking into account the estimated volume of a hemicyanine **1** molecule (about 1 nm^3), it might be concluded that the clusters of hemicyanine **1** adsorbed on glass or mica plates contain at least thousands of molecules.

CONCLUSIONS

The new hemicyanine dye **1** was synthesized and characterized by spectroscopic methods (UV-VIS, IR, ^{1}H-NMR) and by atomic force microscopy. The obtained data show that in solid films deposited on glass or mica plates, the hemicyanine **1** appears as supramolecular clusters. These data suggest that the hemicyanine **1** might also build aggregates in bulk solutions.

ACKNOWLEDGEMENT

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