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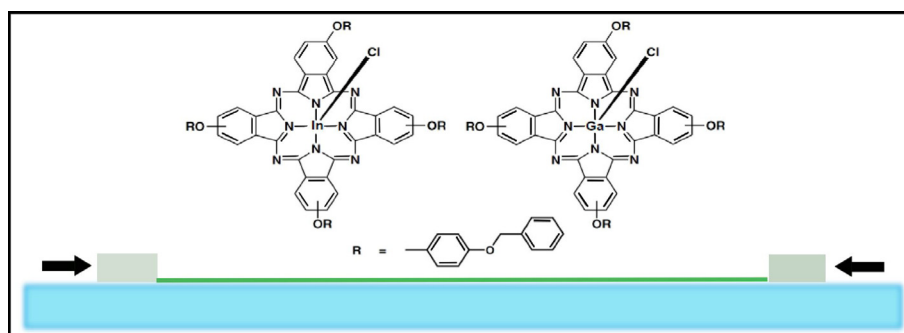
Indium–chlorine and gallium–chlorine tetrasubstituted phthalocyanines in a bulk system, Langmuir monolayers and Langmuir–Blodgett nanolayers – Spectroscopic investigations

B. Bursa^a, D. Wróbel^{a,*}, A. Biadasz^a, K. Kędzierski^a, K. Lewandowska^b, A. Graja^b, M. Szybowski^c, M. Durmuş^d^a Faculty of Technical Physics, Institute of Physics, Poznan University of Technology, 60-965 Poznań, Poland^b Institute of Molecular Physics, Polish Academy of Sciences, 60-179 Poznań, Poland^c Faculty of Technical Physics, Chair of Optical Spectroscopy, Poznan University of Technology, 60-965 Poznań, Poland^d Gebze Institute of Technology, Department of Chemistry, Gebze 41400, Turkey

HIGHLIGHTS

- Electronic, FTIR, Raman spectra of In-CITPC and Ga-CITPC in chloroform and *in situ* light absorption of Langmuir monolayers.
- In-CITPC forms the oblique coplanar aggregate while Ga-CITPC creates the H-type aggregate.
- The dyes in Langmuir–Blodgett layers are oriented nearly vertically in relation to the gold substrate.

GRAPHICAL ABSTRACT



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ABSTRACT

The paper deals with spectroscopic characterization of metallic phthalocyanines (Pc's) (indium and gallium) complexed with chlorine and substituted with four benzyloxyphenoxy peripheral groups in bulk systems, 2D Langmuir monolayers and Langmuir–Blodgett nanolayers. An influence of the molecular structure of dyes (the presence of metal and of substitutes attached to the phthalocyanine macrocyclic skeleton) on the *in situ* measurements of light absorption is reported. Molecular arrangement of the phthalocyanine molecular skeleton in the Langmuir monolayers on water substrate and in the Langmuir–Blodgett nanolayers is evaluated. A comparison of the light absorption spectra of the phthalocyanine monolayers with the spectra of the dyes in solution supports the existence of dye aggregates in the monolayer. It was shown that the type of dye aggregates (oblique and H types) depends markedly on the dye molecular structures. The NIR–IR, IR reflection–absorption and Raman spectra are also monitored for Langmuir–Blodgett nanolayers in non-polarized and polarized light. It was shown that the dye molecules in the Langmuir–Blodgett layers are oriented nearly vertically with respect to a gold substrate.

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Abbreviations: Pc, phthalocyanine; Ga-CITPC, gallium–chlorine benzyloxyphenoxy phthalocyanine; In-CITPC, indium–chlorine benzyloxyphenoxy phthalocyanine; L, Langmuir; LB, Langmuir–Blodgett; DMSO, dimethyl sulfoxide; HWMF, half width at full maximum; IR, infrared; IRRA, infrared reflection-absorption.

* Corresponding author. Tel.: +48 616653179; fax: +48 616653178.

E-mail address: danuta.wrobel@put.poznan.pl (D. Wróbel).

Introduction

Since the past decades phthalocyanines have been a subject of numerous papers because of their unique spectroscopic, photoelectric and magnetic properties [1]. Pc's are usually characterized

by large absorption coefficients and some of them are known as thermally stable molecular materials. They are still a subject of many studies due to their potential applications in science and technological fields due to their particular properties. Phthalocyanines are able to create coordination bonding, molecular aggregates, organic polymers and low-dimensional semiconductors and so on [1,2]. Moreover, because of their well known photoactivity more and more attention is put in investigations directed towards conversion of light energy to electric energy, photodynamic therapy, modeling of artificial photosynthesis, photocatalysis and tailoring sensors [1–7].

Characterization of nanolayers (mono- and multilayers) is extremely important when organic materials are supposed to be used as electronic elements in molecular electronic and optoelectronic devices in which they are in a close contact with metal or semiconductive electrodes. Therefore, it is interesting to follow their properties and processes occurring in ultra-thin films with densely packed dye molecules. In thin films their thickness can be controlled in the order of nanometers and their studies can give information on organic material-interface and organic molecule interactions. Moreover, the molecular arrangement in ultra-thin films can be also kept under observation. As a lot of phthalocyanine dyes are rather insoluble in organic solvents, substitution of dyes with peripheral groups allows to intensify their solubility. In this paper Pc derivatives – indium-chlorine phthalocyanine and gallium-chlorine phthalocyanine substituted with benzyloxyphenoxy peripheral groups are dissolved in chloroform because of their perfect solubility in this solvent. Besides fast evaporation of chloroform is also essential while forming dye Langmuir (L) layers. Moreover, some phthalocyanines show a trend towards aggregated structure creation when molecules are in highly concentrated solutions or densely packed in thin films [2,8].

Bulk systems and thin solid films can be characterized by the use of different spectroscopic and microscopic methods [9–16]. In this paper we take full advantage of Langmuir technique supported by the *in situ* measurements of light absorption. We also decided to benefit from IR transmission spectra of the samples in a bulk system and reflection-absorption spectroscopy of Langmuir-Blodgett (LB) layers in polarized light and also from Raman spectroscopy. With the use of these experimental methods we can get information on interaction of molecules with their vicinity (subphase and neighbor molecules). The L and L-B layer properties of In-CITPC and Ga-CITPC substituted with benzyloxyphenoxy peripheral group are presented. However, the *in situ* investigations were also done by us in [8] and also presented in [9] but for different porphyrin/phthalocyanine dyes.

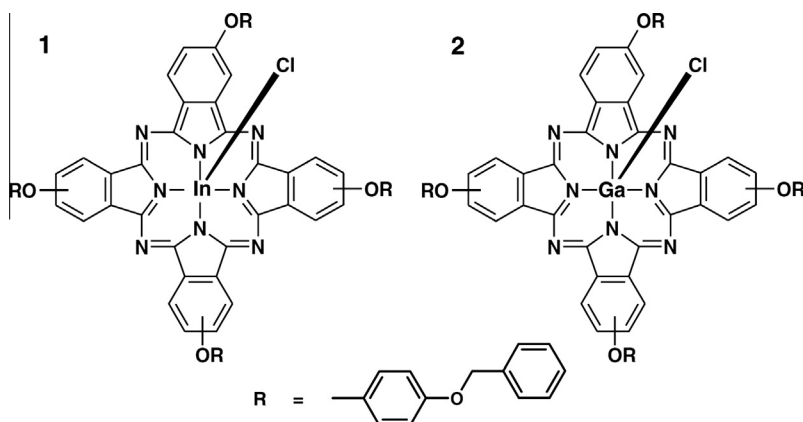
In our previous paper [8] we reported the results of the *in situ* measurements of light absorption of L monolayers of copper Pc's substituted with tetra-tert-butyl and octakis(octylxy) groups. In this paper we present the influence of metal ion (In or Ga) with covalently attached chlorine in the main π -electron macroring on some spectroscopic properties of the dyes in solution, monolayers and multilayers. Thus, firstly we extend our UV-Vis investigations done in organic solvents [10] with the use of the UV-Vis *in situ* measurements of light absorption for Langmuir monolayers. Secondly, we perform IR transmission spectra in KBr and polarized reflection-absorption spectra of LB layers on a gold plate as well as Raman spectra of the dye powder and LB systems. The molecular arrangement of the dyes in the L monolayers and L-B nanolayers is also evaluated.

Materials and methods

In these studies we present investigations of two metallic phthalocyanine dyes: 2,3-tetrakis(4-benzyloxyphenoxyphthalocyaninato)indium(III) (named herein **1**) and 2,3-tetrakis(4-benzyloxyphenoxyphthalocyaninato)gallium(III) (named herein **2**) in KBr, powder and in a form of Langmuir monolayers and Langmuir-Blodgett nanolayers. The detailed description of chemical synthesis of the dyes is presented in [10–17]. The molecular structures of the dyes under investigations are shown in Scheme 1.

A Varian spectrophotometer Cary 4000 is applied for recording of the electronic spectra in the range 300–800 nm. Absorption spectra of the dyes in chloroform are done for the 10^{-6} , 10^{-5} and 10^{-4} M samples.

We have also done the *in situ* measurements of light absorption of the dye L layer to get information about closely packed dyes in a compressed ultra-thin layer. The samples are dissolved in chloroform in view of their perfect solubility in this solvent and sufficiently fast evaporation to receive good L and LB layers. The L monolayers and the LB layers of the samples are created with a KSV 2000 minitrough (KSV Instruments Ltd.) equipped with a temperature control system. The Langmuir trough area is 364×75 mm². Temperature of subphase is achieved and kept constant (20 °C) with a cooling circulator. Deionized water (electrical resistivity 18.2 M Ω cm – Mili-Q Milipore Corp. water purification system) as the subphase is used. The sample dissolved in chloroform (10^{-4} M) is carefully spread on the subphase and chloroform evaporation takes 15 min. A floating film of the L layer is compressed symmetrically from both sides with motion barrier speed of 5 mm/min. The LB layers (5 layers on each side) are deposited on a gold plate (average transfer ratio = 0.92).



Scheme 1. Molecular structure of dyes **1** (2,3-tetrakis(4-benzyloxyphenoxyphthalocyaninato)indium(III)) and **2** (2,3-tetrakis(4-benzyloxyphenoxyphthalocyaninato)gallium(III)).

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