

Arrangement of tris(phthalocyaninato) gadolinium triple-decker complexes with multi-octyloxy groups on water surface

Yanli Chen^{a,b}, Ying Zhang^a, Peihua Zhu^a, Yingju Fan^{a,b}, Yongzhong Bian^a, Xiyou Li^{a,*}, Jianzhuang Jiang^{a,*}

^a Key Lab for Colloid and Interface Chemistry of Education Ministry, Department of Chemistry, Shandong University, Jinan 250100, China

^b College of Chemistry and Chemical Engineering, Jinan University, Jinan 250022, China

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Abstract

A series of five carefully designed tris(phthalocyaninato) gadolinium triple-decker complexes $[\text{Pc}(\text{R})_8]\text{Gd}[\text{Pc}(\text{R}')_8]\text{Gd}[\text{Pc}(\text{R}'')_8]$ ($\text{R} = \text{R}' = \text{R}'' = \text{H}$; $\text{R} = \text{R}' = \text{H}$, $\text{R}'' = \text{OC}_8\text{H}_{17}$; $\text{R} = \text{R}'' = \text{H}$, $\text{R}' = \text{OC}_8\text{H}_{17}$; $\text{R} = \text{H}$, $\text{R}' = \text{R}'' = \text{OC}_8\text{H}_{17}$; $\text{R} = \text{R}' = \text{R}'' = \text{OC}_8\text{H}_{17}$) (1–5) were prepared and the film forming properties on water surface were systematically investigated. The limited mean molecular area obtained by π -A isotherms revealed an “edge-on” conformation for all these compounds. UV-vis absorption spectra showed red-shifted Q bands, indicating the formation of J aggregates and effective intermolecular interaction in solid film. Phthalocyanine rings were found to take tilted orientation with respect to the normal of substrate according to the polarized absorption spectroscopic measurements. Low angle X-ray diffraction results provide direct evidence and therefore clearly clarify the point, for the first time, that unsymmetrical triple-decker molecules pack on the water surface with the unsubstituted phthalocyanine ring set close to the water surface and the substituted phthalocyanine ligand with octyloxy groups lies on the top.

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1. Introduction

As one of the most useful functional materials, phthalocyanines have got a wide range of applications as photoconductor, organic semiconductor, data storage material, and gas sensor [1–8]. The performance of molecular materials has been revealed to depend dramatically on the quality of solid films, different deposition methods therefore were developed for phthalocyanine film fabrication [9]. Langmuir–Blodgett (LB) technique, which allows fine control of both the structure and the thickness of the film at molecular level [10,11], has been employed in building phthalocyanine films since 1983 [12]. However, because of the bad solubility in organic solvents as well as the non-amphiphilic nature of traditional unsubstituted phthalocyanine derivatives, their Langmuir film formed

at air/water interface is very rigid and orderless. Various substituents such as alkyl or alkoxy groups have been introduced onto the phthalocyanine ring not only to increase the solubility but also to improve the film forming ability [12]. Long alkoxy groups on the phthalocyanine ring have been found to add an ordering dimension to the LB film as these substituents are flexible and the alkyl chains are highly hydrophobic [13]. Nevertheless, plenty of examples revealed that the number and position of alkoxy groups at phthalocyanine ring give decisively influence on the conformation of phthalocyanine ring at the air/water interface [14,15].

Sandwich-type phthalocyaninato double- and triple-decker rare earth complexes have attracted increasing attention in the past several decades due to their special optical and electronic properties associated with the strong π - π interaction between the closely arranged phthalocyanine rings connected by rare earth metal(s) [16–26]. Compared with monomeric phthalocyanines, these double- and triple-decker complexes provide more choice for introducing substituents and there-

* Corresponding authors.

E-mail addresses: xiyouli@sdu.edu.cn (X. Li), jzjiang@sdu.edu.cn (J. Jiang).

fore tuning the LB film forming behavior of phthalocyanine derivatives to a large degree. Unfortunately, due perhaps to the difficulties in the synthesis of substituted double- and triple-decker compounds, restricted studies about the LB films of sandwich bis(phthalocyaninato) rare earth double-decker compounds with different substitutions have been conducted [27–33]. In particular, there is still no systematic study on the effect of side chains on the LB film forming behavior of tris(phthalocyaninato) rare earth complexes reported thus far [21,34].

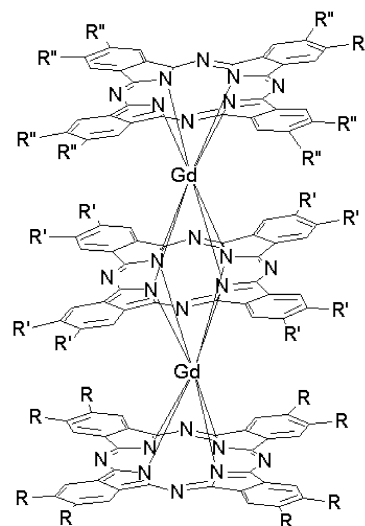
Oxygen atoms are usually introduced into typical amphiphilic molecules as the hydrophilic unit(s). As a result, introduction of alkoxy groups onto the phthalocyanine ring was generally considered to increase the hydrophilicity of phthalocyanine ring. This is also the reason that several research groups considered the substituted phthalocyanine (or even the substituted porphyrin) ring with alkoxy substituents in unsymmetrical bis(phthalocyaninato) [or bis(porphyrinato)] metal double-decker complex should stand closely to the water surface while the unsubstituted phthalocyanine (or porphyrin) ring would stay far away from the water surface [20,35]. However, studies on the Langmuir film characteristics of monomeric unsymmetrical phthalocyanines revealed that the long alkoxy groups act as hydrophobic groups, which push the phthalocyanine ring away from the water surface and thus make the unsymmetrically substituted monomeric phthalocyanine stand on water surface in an “edge-on” orientation with the unsubstituted part of phthalocyanine molecule close to the water surface [36–38]. These controversial points have co-existed for several years, but there is no clear answer yet due to the lack of direct evidence.

In the present paper, we report the design, synthesis, and their Langmuir film forming behavior of a series of tris(phthalocyaninato) gadolinium complexes of $[\text{Pc}(\text{R})_8]\text{Gd}[\text{Pc}(\text{R}')_8]\text{Gd}[\text{Pc}(\text{R}'')_8]$ ($\text{R} = \text{R}' = \text{R}'' = \text{H}$; $\text{R} = \text{R}' = \text{H}$, $\text{R}'' = \text{OC}_8\text{H}_{17}$; $\text{R} = \text{R}'' = \text{H}$, $\text{R}' = \text{OC}_8\text{H}_{17}$; $\text{R} = \text{H}$, $\text{R}' = \text{R}'' = \text{OC}_8\text{H}_{17}$; $\text{R} = \text{R}' = \text{R}'' = \text{OC}_8\text{H}_{17}$) (1–5) (Fig. 1). Systematic studies in a comparative manner reveal that one of the outer substituted phthalocyanine ring(s) with octyloxy groups in the triple-decker molecule is hydrophobic and stay far away from the water surface or hydrophilic substrate while the unsubstituted phthalocyanine ring stays close to the hydrophilic substrate or water surface.

2. Experiment section

Tris(phthalocyaninato) gadolinium compounds 1–5 were synthesized according to published procedure [22]. Elemental analysis and spectroscopic characteristic data are consistent with assigned triple-decker structure. Commercially available stearic acid (SA) with analytical purity was purified by recrystallization just before use.

The samples were dissolved in chloroform and the concentrations of 1–5 in both pure and mixed systems are in the range of 11.83×10^{-5} – 2.00×10^{-5} molL⁻¹. The monolayers of pure sample and their mixture with SA (1:4) were obtained by spreading chloroform solutions onto the pure wa-



1. $\text{R} = \text{R}' = \text{R}'' = \text{H}$; 2. $\text{R} = \text{R}' = \text{H}$, $\text{R}'' = \text{OC}_8\text{H}_{17}$; 3. $\text{R} = \text{R}'' = \text{H}$, $\text{R}' = \text{OC}_8\text{H}_{17}$
4. $\text{R} = \text{H}$, $\text{R}' = \text{R}'' = \text{OC}_8\text{H}_{17}$; 5. $\text{R} = \text{R}' = \text{R}'' = \text{OC}_8\text{H}_{17}$

Fig. 1. Schematic molecular structure of the tris(phthalocyaninato) gadolinium compounds.

ter (resistivity: $18 \text{ M}\Omega \text{ cm}^{-1}$, pH 6.4) subphase surface. The monolayer properties were studied by measuring pressure–area (π – A) isotherms on a NIMA 622 trough (Great Britain). The isotherms were recorded 15 min after spreading the chloroform solutions with a compression rate of $20 \text{ cm}^2 \text{ min}^{-1}$ at 20°C .

All LB films for low-angle X-ray diffraction, UV–vis, and polarized UV–vis spectroscopic measurements were deposited onto hydrophobic quartz plates by the vertical dipping method with a dipping speed of 7 mm min^{-1} . The time interval between two consecutive layers was 15 min. The fabricated LB films were air-dried for 15 min every other layer. The literature method described by Höning and co-workers was employed to treat the substrates [39].

UV–vis spectra and polarized UV–vis spectra were recorded on a Hitachi U-4100 spectrophotometer. For the polarized electronic absorption spectroscopic measurement, a dichroic sheet polarizer was placed in front of the LB films. Low angle X-ray diffraction (LAXRD) experiment was carried out on a Rigaku D/max- γ B X-ray diffractometer.

3. Results and discussion

3.1. Synthesis and characterization

The series of tris(phthalocyaninato) gadolinium compounds have been designed and synthesized according to published procedure [22,40]. These tris(phthalocyaninato) gadolinium compounds have been characterized by elemental analysis and a wide range of spectroscopic methods, in particular, their sandwich triple-decker nature was deduced undoubtedly by MALDI-TOF mass and ¹H NMR spectroscopy.

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