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

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Abstract

A series of five carefully designed tris(phthalocyaninato) gadolinium triple-decker complexes $[\mathrm{Pc(R)_8}]\mathrm{Gd}[\mathrm{Pc(R')_8}]\mathrm{Gd}[\mathrm{Pc(R'')_8}]$ ($\mathrm{R = R' = R'' = H}$; $\mathrm{R = R' = H, R'' = OC_8H_{17}}$; $\mathrm{R = R'' = H, R' = OC_8H_{17}}$; $\mathrm{R = H, R' = R'' = OC_8H_{17}}$; $\mathrm{R = R' = R'' = OC_8H_{17}}$) (**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.

Keywords: Sandwich compounds; Phthalocyanine; LB film; Arrangement

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-

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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].

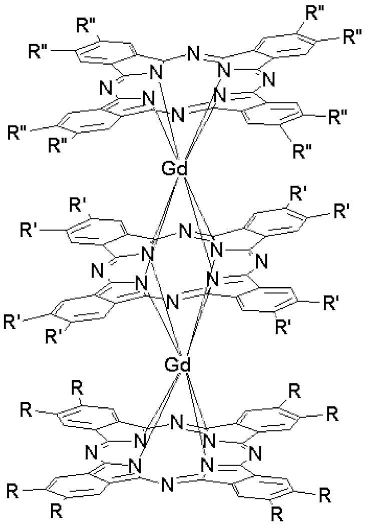
Oxygen atoms are usually introduced into typical amphiphilic molecules as the hydrophilic unit(s). As a result, introduction of alkoxy groups onto the phthalocyanine ring was generally considered to increase the hydrophilicity of phthalocyanine ring. This is also the reason that several research groups 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 $[Pc(R)_8]Gd[Pc(R')_8]Gd[Pc(R'')_8]$ ($R = R' = R'' = H$; $R = R' = H$, $R'' = OC_8H_{17}$; $R = R'' = H$, $R' = OC_8H_{17}$; $R = H$, $R' = R'' = OC_8H_{17}$; $R = R' = R'' = OC_8H_{17}$) (**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} mol L^{-1}. The monolayers of pure sample and their mixture with SA (1:4) were obtained by spreading chloroform solutions onto the pure water (resistivity: 18 MΩ 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 cm^2 min^{-1} at 20 °C.



1. R = R' = R" = H; **2**. R = R' = H, R" = OC_8H_{17}; **3**. R = R" = H, R' = OC_8H_{17}

4. R = H, R' = R" = OC_8H_{17}; **5**. R = R' = R" = OC_8H_{17}

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

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 Hönig 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-γB 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) gadolinum 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 ^{1}H NMR spectroscopy.

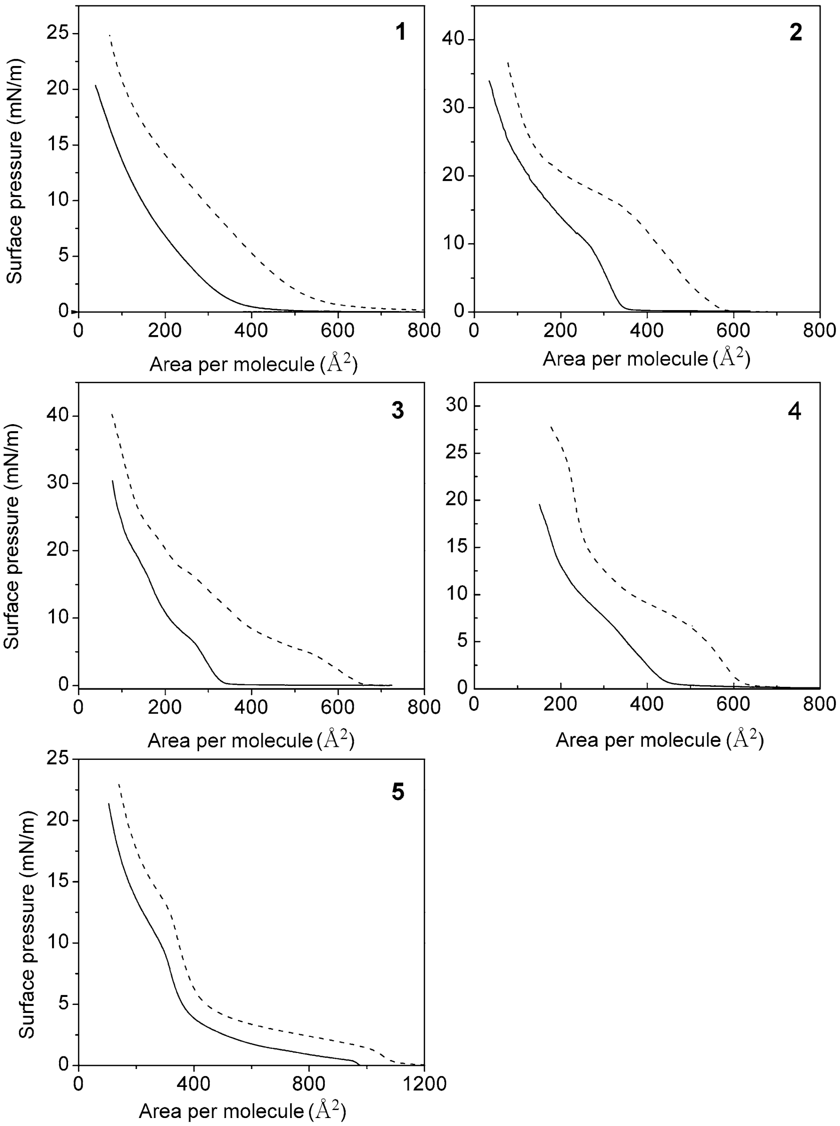


Fig. 2. (A) π–A isotherms of compound **1**–**5** on water surface, pure compound (solid line) and mixture with SA (1:4) (dash line).

3.2. Characteristics of pressure–area isotherms

Fig. 2 shows the pressure–area (π–A) isotherms of pure tris(phthalocyaninato) gadolinium compounds (**1**–**5**) and their mixtures with stearic acid (SA) in the molar ratio of 1:4 at the air/water interface. As can be seen from these figures, all these compounds can form stable monolayers at the air/water interface. According to the behavior of pure monolayers at the air/water interface revealed by the π–A isotherms, these triple-decker compounds can be divided into two groups. One is for compounds **1**, **2**, and **3**, the limiting molecular area (A_{limit}) of this group deduced by extra-plotting the most steeply rising part of the π–A isotherms to zero pressure is smaller than the area of one phthalocyanine plane (2.56 nm^2) [22] (Table 1) clearly suggesting an "edge-on" orientation of triple-decker molecules for these three compounds on water surface. However, the limiting molecular area of the other group compounds, 2.80 and 3.29 nm^2 respectively for **4** and **5** (Fig. 2) is bigger than the area of phthalocyanine plane. This suggests either a "face-on" orientation of the triple-decker molecules of **4** and **5** [9] or the additional contribution of side octyloxy chains to the A_{limit} of "edge-on" triple-decker compounds. However, the fact that the A_{limit} of **5** is obviously larger than that of **4** along with the increase of four additional octyloxy side chains seems to suggest that the larger A_{limit} for **4** and **5** is most likely contributed by the alkoxy side chains.

Table 1
The limiting molecular area of triple-deckers **1**–**5** in pure and mixed films obtained from the π–A isotherm studies

Compound	1		2		3		4		5	
	Pure	Mix	Pure	Mix	Pure	Mix	Pure	Mix	Pure	Mix
A_{limit} (nm^2)	1.97	2.75	1.85	2.63	1.89	2.69	2.80	3.50	3.29	4.10
A_{cal} (nm^2)[a]		2.77		2.65		2.69		3.60		4.09

[a] $A_{\text{cal}} = A_{\text{limit(pure)}} + 4A_{\text{SA}}$, A_{SA} is the mean molecular area of SA, 0.2 nm^2.

Plateaus are observed in the π–A isotherms of all the substituted phthalocyanine-containing triple-decker compounds **2**–**5**, indicating the existence of a phase transition. Nevertheless, the phase transition starts at an area of ca. 3.20 nm^2 for **2** and **3** and of ca. 4.30 nm^2 for **4** and **5**, respectively, suggesting the close relationship of the behavior of pure monolayers of these triple-decker complexes at the air/water interface with the number of substituents. We ascribe the phase transition to the orientation change of triple-decker molecules in which the phthalocyanine ring changes from the "face-on" to the "edge-on" form at the air/water interfaces. It is worth noting that the mean molecular area of a completely perpendicular standing tris(phthalocyaninato) gadolinum molecule at the air/water interface is only about 1.15 nm^2 [22], which is much smaller than the recorded mean molecular area of compounds **2–5** as well as **1** on water surface, indicating that the molecules of complexes **1–5** do not stand vertically on water surface but adopt a titled orientation with respect to the water surface.

The π–A isotherms of the mixture of tris(phthalocyaninato) gadolinum compounds with SA in a molar ratio of 1:4 resemble the feature of their pure films (Fig. 2). By employing the mean molecular area for closely packed SA, 0.20 nm^2 [41–43], and on the basis of the assumption that ideal mixing occurs in the mixed films of tris(phthalocyaninato) gadolinum with SA in the molar ratio of 1:4, the calculated limiting molecular area of compounds **1–5** is in good agreement with the experimental result (Table 1). This reveals that the SA molecules add no influence on the orientation of the phthalocyanine ring of triple-decker molecules in the mixed monolayers. This conclusion is in line with that deduced from the studying of mixed monolayers of SA with non-amphiphilic materials like polymethacrylate with dodecyloxy-substituted phthalocyanine in the side chains [44] or bis(phthalocyaninato) ytterbium compound [45].

3.3. UV–vis spectra and polarized UV–vis spectra

The pure monolayer of substituted phthalocyanine-containing triple-decker compounds **2–5** on water surface can be transferred to hydrophobic substrate by vertical dipping method to form LB films. However, similar to the unsubstituted monomeric phthalocyanine derivative [12], pure monolayer of the non-amphiphilic unsubstituted triple-decker $Gd_2(Pc)_3$ (**1**) cannot be transferred due to the very crisp nature of the monolayer.

Electronic absorption spectra of these compounds in solution and in film were recorded and the data are summarized in Table 2. Fig. 3 shows the typical UV–vis spectra of compound **3** in solution, pure film, and mixed film with SA. These compounds show intense Q band at about 640 nm and Soret band at ca. 350 nm in solution. It is worth noting that comparison of electronic absorption characteristics for monomeric-, bis-, and tris(phthalocyaninato) metal complexes with the same octa(alkoxy)-substituted ligand reveals that the Q absorption band shifts gradually to the higher energy side in the same order along with increasing the phthalocyanine rings in the molecule due to the increasing π–π interaction(s) [46–48].

Table 2
Electronic absorption and polarized electronic absorption data for the triple-deckers **1–5** in solution, pure, and mixed films

Compound	λ_1 (nm)[a]	λ_2 (nm)[b]		$\Delta\lambda$ (nm)[c]		θ (°)[d]	
		Pure	Mix	Pure	Mix	Pure	Mix
1	636 (THF)		667		31		15
2	640 ($CHCl_3$)	665	673	25	33	23.8	22.4
3	642 ($CHCl_3$)	666	672	24	30	35.5	35.8
4	643 ($CHCl_3$)	681	680	38	37	52.0	51.8
5	644 (toluene)	666	666	23	23	44.8	45.5

[a] Q band in solution.

[b] Q band in solid film.

[c] Red shift of the Q band with $\Delta\lambda = \lambda_2 - \lambda_1$.

[d] Calculated orientation angle (angle between the normal of the water surface and the normal of phthalocyanine plan) for the phthalocyanine ring of triple-deckers in solid film.

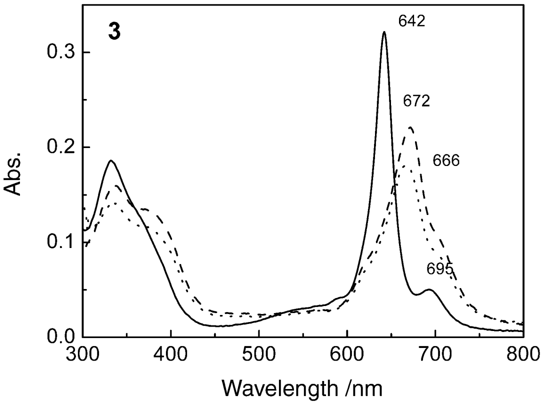


Fig. 3. Electronic absorption spectra of **3** in $CHCl_3$ (solid), pure film (dot), and mixed film with SA (dash).

As clearly shown in Fig. 3 and Table 2, significant red-shift was observed for the Q absorption band of triple-decker compounds **2–5** in solid film in comparison with that in solution, indicating the formation of *J* aggregates [46] and strong intermolecular interaction between triple-decker molecules in these *J* aggregates. It is worth noting that the formation of *J* aggregates revealed for these tris(phthalocyaninato) gadolinium complexes is in accord with those observed for other double- and triple-decker phthalocyaninato metal analogues but not for monomeric phthalocyanine derivatives [35,49,50].

As mentioned above, the transfer ratio for compound $Gd_2(Pc)_3$ (**1**) during the pure film deposition is very low (<0.5) and unstable due to the non-amphiphilic nature of this compound. Mixing of **1** with SA in the molar ratio of 1:4 has been found to significantly improve the film forming property of this complex [45,51–53]. For the purpose of comparative studies, mixed film of **2**, **3**, **4**, and **5** with SA have also been prepared.

As exemplified in Fig. 3, the absorption spectra of the mixed multilayer films are very much similar to those of pure films in feature. This indicates that *J* aggregates, similar to those in the pure film, is formed in the mixed film of triple-decker compounds with SA. This result is in line with that deduced from the π–A isotherm studies as addition of SA molecules does not affect the orientation of triple-decker molecules in solid film under ideal mixing.

Polarized absorption spectroscopy has been employed to determine the orientation of phthalocyanine ring in LB films. Following the Yoneyama equation [54–56], the orientation angles of phthalocyanine ring in triple-decker molecules with respect to the substrate in the films of **1**–**5** are calculated and organized in Table 2. It is worth noting that the orientation angle of phthalocyanine ring for **1** in pure film cannot be obtained due to the very poor transfer ratio of the monolayer and the bad quality of the deposited LB film. However, the orientation angle of phthalocyanine ring with respect to the substrate in the pure film of **1** can be derived from the result of its mixed film with SA, around 15°, on the basis of such a fact that the orientation angle of phthalocyanine ring in mixed film for all the four substituted phthalocyanine-containing compounds **2**–**5** corresponds well with that found in the pure film (Table 2). This further supports the point that the SA molecules mixed in an ideal manner with those of triple-decker compounds and therefore do not give any influence on the orientation of the molecule in the solid film. The results tabulated in Table 2 clearly indicate that the orientation angle of phthalocyanine ring in the triple-decker molecules changes depending on the number of octyloxy group in the triple-deckers. Along with the increase in the number of alkoxy side chains from **1**, **2** (or **3**) to **4**, the orientation angle also increases significantly in the same order, which probably is due to the increase in the hydrophobic characteristics of the whole triple-decker molecule associated with increasing the hydrophobic octyloxy groups. The increasing repulsion from water surface associated with the increasing number of hydrophobic alkoxy groups push the whole molecule away while the hydrophilic property of phthalocyanine ring try to keep the molecule close to the water surface, and these two contrary interactions force the molecules to adapt a more titled orientation. The exception in the orientation angle of phthalocyanine ring with respect to the substrate in the films for compound **5** is probably related to the fact that all the three phthalocyanine rings in the triple-decker molecule contain eight octyloxy groups which symmetrically distributed at the peripheral positions. The strong hydrophobic repulsion from water surface overpower the hydrophilic attraction and thus keep the whole molecules stay far away from the water surface and makes the triple-decker molecule of **5** adapt a more flat orientation than that for triple-decker molecule of **4**. Moreover, the difference in orientation angle of phthalocyanine ring between **2** and **3**, both of which contain the same number of octyloxy side chains in their molecules, suggests that substituted positions at phthalocyanine ring in the middle or the outer also play role in determining the hydrophobic property of the whole triple-decker molecule.

The quality of deposited LB films for compounds **1**–**5** has been further assessed using a low-angle X-ray diffraction (LAXRD) technique [57]. Fig. 4 shows the diffraction patterns of the all the pure and mixed LB films. The mixed film of **1** with SA shows one small peak at $2\theta = 6.6°$, corresponding to a periodic space of 1.34 nm, which is smaller than the diameter of phthalocyanine ring, 1.50 nm, obtained according to the minimized molecular structure, Fig. 5A [58]. This result therefore suggests that the phthalocyanine ring of the triple-decker molecules employs a titled orientation with respect to the substrate in the film. This conclusion is in line with that deduced from the π–A isotherm and polarized electronic absorption spectroscopic studies.

Both the pure and mixed films of **2** displayed one diffraction peak at about $2\theta = 3.72°$, Fig. 4, which corresponds to the periodic space of 2.37 nm. The fact that just the same periodic space is drawn from both the pure and mixed films suggests that SA molecules indeed give no effect on the molecular orientation of triple-decker **2** in monolayer, which was also revealed by the π–A isotherm studies. Similar conclusion can be drawn by comparing the diffraction patterns between the pure and mixed films for all the compounds **3**–**5** (Fig. 4). However, for compound **3**, a periodic space of 1.61 nm, drawn from the diffraction peak at about $2\theta = 5.45°$, is significant smaller than that for compound **2**. This fact clearly suggests the molecules of triple-decker **2** lying on the water surface with the unsubstituted phthalocyanine ligand close to the water surface and the substituted phthalocyanine ring bearing eight octyloxy groups far away from the water surface (Fig. 5B). Otherwise the periodic spacing distance drawn from the low angle X-ray diffraction pattern of films of **2** should smaller than that for **3** (Fig. 5C).

The pure and mixed films of **4** give one diffraction peak at $2\theta = 3.64°$, corresponding to a periodic space, $d = 2.40$ nm. This space distance is close to that of **2**, indicating again that the unsubstituted phthalocyanine ring in the triple-decker molecules keeps close to the water surface while the substituted phthalocyanine rings stay far away from the water surface.

The pure and mixed LB films of compound **5** give a diffraction peak at about $2\theta = 3.26°$, corresponding a periodic space, $d = 2.64$ nm. This value is a bit bigger than that of compounds **2** and **4**, suggesting that the triple-decker molecules of compound **5** have too many octyloxy side chains that they have to arrange in a more rigid manner compared with those in **2** and **4**.

It is worth pointing out that an additional primary Bragg peak occurs at ca. 1.80° for the mixed film of compound **3**, corresponding to a spacing of 4.90 nm. This value almost equals to twice the length of the hydrocarbon chains of SA molecules, indicating the formation of Y-type multilayer structure of SA molecules in the mixed film with compound **3** [59]. However, in the mixed SA films of compound **2, 4**, and **5,** only one diffraction peak, which is close to the one found in corresponding pure films, can be observed. The calculated space distance, accordingly, falls in the range of 2.34–2.64 nm. These values are not only consistent to the calculated layer thickness on the basis of the triple-decker molecular size and the orientation angle of the phthalocyanine ring, but also close to the length of the hydrocarbon chains of the SA molecule. Therefore it is reasonable to conclude that the diffraction peak observed in the mixed films of compounds **2**, **4**, and **5** should result from both the triple-decker and SA. This, in turn, suggests that the SA molecules in the mixed monolayers of **2**, **4**, or **5** must have overturned during the deposition process and lead to the formation of Z-type SA LB films [60].

4. Conclusion

In conclusion, systematic studies indicate that tris(phthalocyaninato) gadolinium complexes, in particular those con-

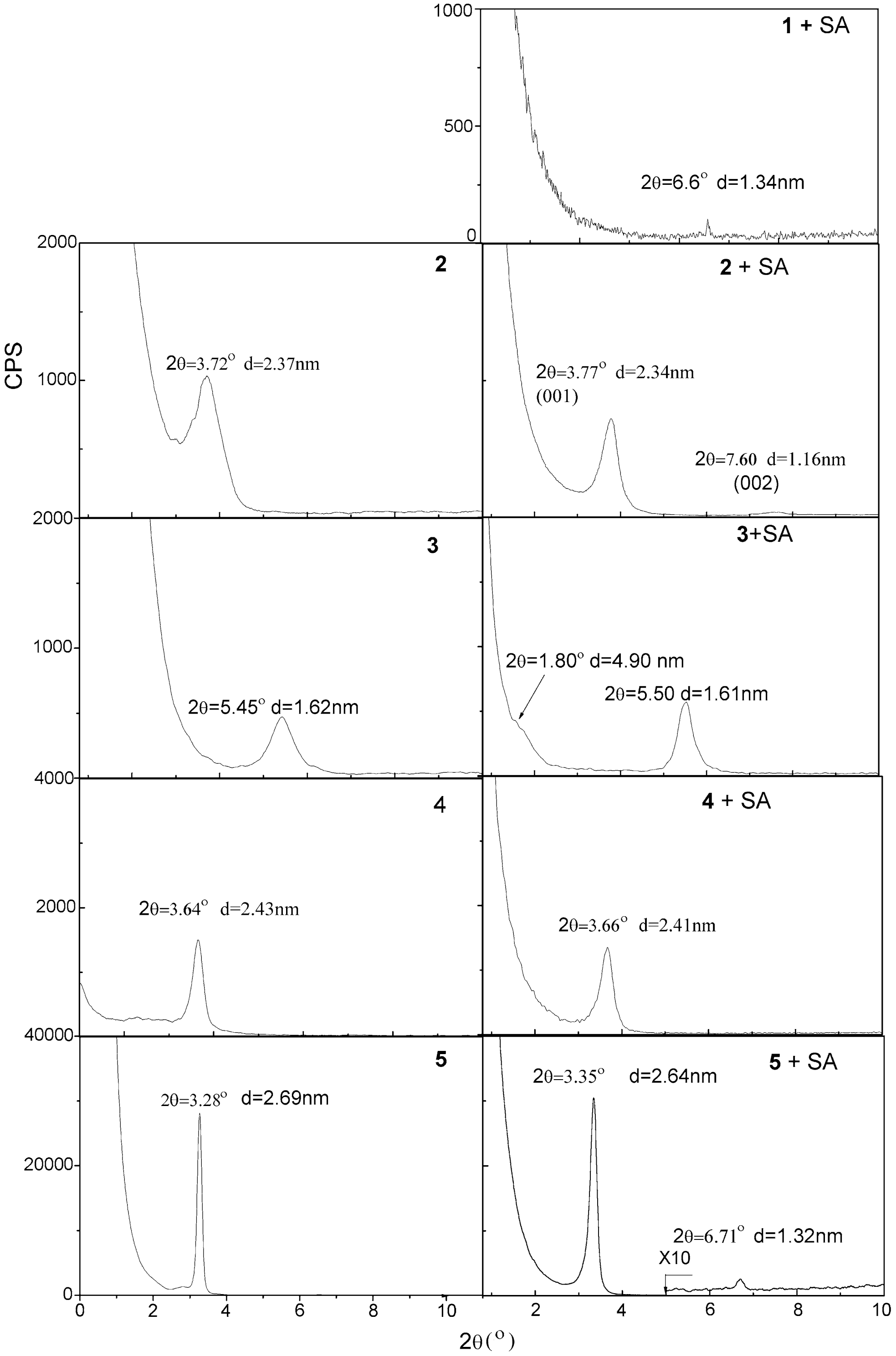


Fig. 4. Low angle X-ray diffraction patterns for the pure and mixed films of **1**–**5**.

taining octa(octyloxy)phthalocyanine ligand, can form stable monolayer on water surface. Significant red-shift observed for the phthalocyanine Q band in the films compared with that in solution reveals the formation of *J* aggregates in the LB films. Phthalocyanine rings of the triple-decker molecules take tilted orientation with respect to the normal of substrate or air/water interface. The number and position of octyloxy groups on phthalocyanine ring affect the orientation angle and film structure significantly. Compound **4** give the biggest orientation angle because of the balance between hydrophobic and hydrophilic interactions between molecule and water surface. Most importantly, comparative studies over the LB film forming properties of a series of well-designed tris(phthalocyaninato) gadolinium triple-decker complexes reveal that the triple-decker molecules pack on the water surface with the unsubstituted phthalocyanine ring close to the water surface and the sub-

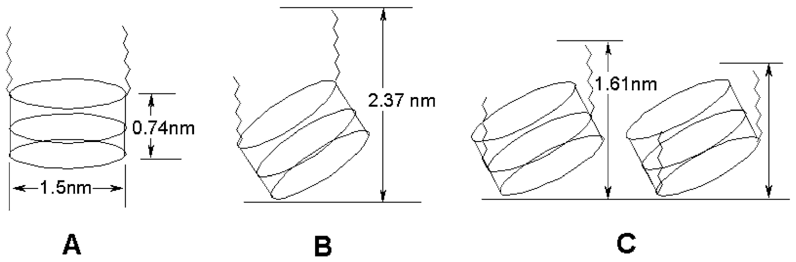


Fig. 5. (A) Dimensions of the triple-decker compounds, (B) the schematic indication of the orientation of **2** and **3** on water surface, and (C) schematic representation of **2** on water surface with octyloxy-substituted phthalocyanine ring close to the water surface.

stituted phthalocyanine ligand far away from the water surface.

Acknowledgments

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