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Tuning the arrangement of mono-crown ether-substituted phthalocyanines in Langmuir–Blodgett films by the length of alkyl chains and the cation in subphase

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Abstract

Amphiphilic phthalocyanines with one crown ether and three alkyl chain substitutions can form stable monolayers on a water surface. This monolayer can be transferred to a substrate by a vertical dipping method. The arrangement of phthalocyanine molecules in LB films was affected by the length of alkyl chains and the coordination of alkali ions in crown ether. Davydov splitting was observed in the absorption spectra of the LB films of phthalocyanine with the shortest alkyl chain substitutions, and this splitting was affected by the alkali ions in the subphase.

Keywords: Phthalocyanine; Langmuir–Blodgett; Crown ether; Davydov splitting; Polarized UV–vis

1. Introduction

Because of the potential applications of phthalocyanine material in gas sensing, photovoltaic devices, solar cells, and other disciplines as a functional material [1–4], the fabrication and deposition of phthalocyanine thin film by the Langmuir–Blodgett (LB) method has attracted a lot of attention in the past several decades [5–7]. The first attempt to fabricate a phthalocyanine thin film from a nonsubstituted phthalocyanine, reported by Roberts and co-workers [8] in 1983, showed that it could form a stable but rigid monolayer on the water surface. This monolayer was very difficult to transfer to substrate. To fabricate a multilayer LB film, a “lubricant” material such as 1,3,5-trimethylbenzene is needed. Proper substitution of the phthalocyanine ring not only improves solubility in organic solvents and simplifies the procedures of LB film preparation, but also changes the electronic or optical properties of phthalocyanine [5,8]. Extensive research on the LB film-forming properties of tetra- or octasubstituted phthalocyanines has been published since then. Depending on the substitution, phthalocyanine rings in LB film show two kinds of aggregation behavior, J (head-to-tail) [9–12] and H (face-to-face) [13–16] aggregation. J aggregates show a red-shifted Q band while the H aggregates show a blue-shifted Q band [17]. These can be ascribed to exciton coupling between the neighboring molecules. In most of the cases, the LB film of phthalocyanine showed either red-shifted or blue-shifted absorption peaks, but Cook’s and other groups discovered another aggregation behavior, which gives splitting Q bands (Davydov splitting) for octasubstituted phthalocyanines with long alkyl chains [18,19]. Cook’s results tell us that in a nonperipheral unsymmetrically octasubstituted phthalocyanine, when the alkyl chains are longer than six carbons, the film shows a split Q band while a shorter substitution (such as n-C_6H_{13} or iso-C_5H_{11}) group presents normal red-shifted spectra. They ascribed this splitting to the “herringbone” arrangement of phthalocyanine rings in LB films. The detailed analysis of

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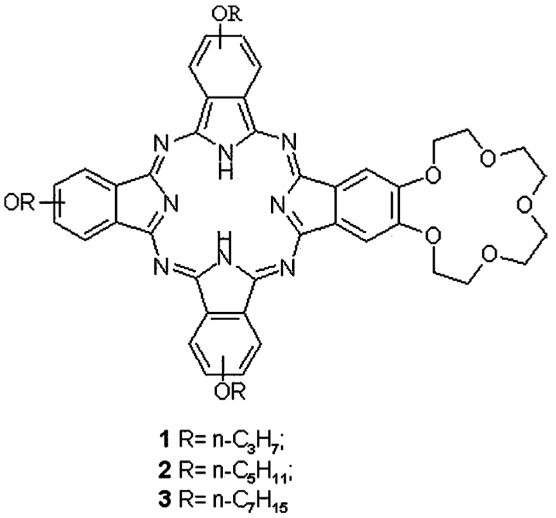

Fig. 1. The structure of the phthalocyanines.

the electronic spectra showed that the Davydov splitting for the longer chain compounds implied a herringbone structure with an angle between molecules of 75°. The decrease in length of the chains caused this angle to increase to 105.5°, resulting an increase in the distance between two molecules and a decrease in the interaction. The molecules with shorter chains did not form a herringbone structure and no Davydov splitting was observed. In research on gas-sensing properties of mono-crown ether-substituted phthalocyanines [20,21], we fabricated several asymmetrically substituted phthalocyanines into LB film and found that Davydov splitting can happen in tetrasubstituted phthalocyanine too. This splitting was affected by the chain length and the coordination of crown ether with alkali ions in the subphase. Here we report the results.

2. Experiment

2.1. Materials

Mono-crown ether-substituted phthalocyanines (Fig. 1) were prepared following the literature method [20,21] and the purity of the materials was proved by TLC, ^{1}H NMR, and the extinction coefficient in UV–vis absorption spectra. Water used as subphase was double-distilled water with resistance greater than 18 mΩ cm^{-1}. Other chemicals were all analytical grade and used as received without further purification.

2.2. Instruments and methods

The monolayers were prepared by spreading a solution of phthalocyanine in chloroform with a concentration of 10^{-3} mol L^{-1} on the surface of the subphase. In the case of using an alkali ion solution as subphase, the concentrations of potassium chloride or sodium chloride in the subphase are 10^{-3} mol L^{-1}. The π–A isotherms were recorded on a KSV-5000 twin-compartment LB instrument with a compression speed of 6 mm min^{-1}. The LB films were prepared by vertical dipping method with a dipping speed of 5 mm min^{-1} and a surface pressure of 30 mN m^{-1}. The LB films for the polarized UV–vis absorption spectra were deposited on a CaF$_2$ crystal, while those for the X-ray diffraction experiments were deposited on silicon crystal.

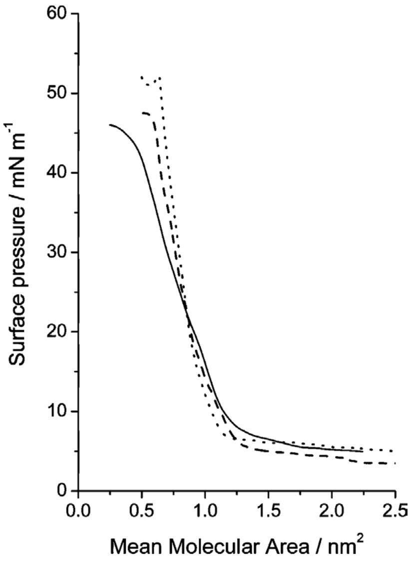

Fig. 2. π–A isotherms of compound 1 (solid), 2 (dash), and 3 (dot) on the water surface.

UV–vis and polarized UV–vis absorption spectra were recorded on a Hitachi 557 spectrometer. Low-angle X-ray diffraction experiments were carried out on a D/max-rA diffraction meter with Cu$K\alpha$ rays and Ni filter. The scan range is 1.3° to 15°.

3. Results and discussion

3.1. π–A isotherms

π–A isotherms of three mono-crown ether-substituted phthalocyanines on water surface (Fig. 2) show that all of them can form very stable monolayers. The collapse pressures are more than 40 mN m^{-1}. Extrapolating the π–A isotherms to surface pressure zero, we get the mean molecular area of these three compounds in monolayer (Table 1). The mean molecular area in the monolayer decreases steadily with the increase in length of the substituents. Previous research on other phthalocyanine molecules revealed that phthalocyanine rings in LB film can take two kinds of conformation, “face-on” or “edge-on.” The face-on conformation will give a bigger monomolecular area than that of the edge-on conformation. An ideal face-on conformation will show a monomolecular area that equals the area of the phthalocyanine plane. A molecule taking the edge-on conformation stands on the surface of the water with the

Table 1
Parameters of the film structure determined with different methods

Compound	Subphase	Orientation angles (°)[a]	Mean molecular area (nm^2)[b]	Layer thickness (nm)[c]
1	Water	39	1.15	1.9
	NaCl solution	45	1.02	–
	KCl solution	63	0.98	–
2	Water	56	1.00	2.2
	NaCl solution	62	0.97	2.26
	KCl solution	64	0.96	2.32
3	Water	57	0.98	2.9
	NaCl solution	61	0.96	2.9
	KCl solution	67	0.96	3.0

[a] Calculated from Yoneyama equation with the refraction index of the film $n = 1.148$ [28,30].
[b] Calculated from the π–A isotherms.
[c] Results of the XRD experiments.

molecular plan perpendicular to the surface of water. It always gives a monomolecular area close to the area of the molecular side (the thickness times the length of the molecule) [5]. For these three compounds, the monomolecular areas are smaller than the face-on conformation but larger than the edge-on conformation, indicating that the molecules take a titled edge-on conformation. This is easy to understand. The crown ether part of these amphiphilic molecules is hydrophilic, while the long alkyl chains on the other side are the hydrophobic part. On a water surface, the hydrophilic crown ether will stay close to the water surface, while the hydrophobic alkyl chains will try to stay away from the water surface and the molecules take an edge-on conformation. The driving force for a molecule to stand perpendicularly is the repulsion between alkyl chains and the water. The decrease in the mean molecular area when the alkyl chains changed from C3 to C7 indicates that the molecules stand more and more close to perpendicular. Big alkyl groups on one side of the molecule provide more hydrophobic properties and bigger driving force for the molecules to stand perpendicularly.

The addition of sodium or potassium chloride in the subphase changed the π–A isotherms of these three compounds too (Fig. 3 shows the π–A isotherms of compound 1 on the surface of aqueous NaCl or KCl). The mean molecular area of all these three compounds (Table 1) decreased compared with that on a pure water surface. A tetra-crown ether-substituted phthalocyanine on an aqueous sodium chloride solution gives a bigger mean molecular area than that on pure water. The coordination of crown ether with sodium increases the hydrophilicity of the whole molecule dramatically and a large part of the molecules is immersed into water. Because of the "face-on" conformation of these molecules on the surface of the subphase, this "sinking" of molecules into water increases the mean molecular area significantly [13,14]. The decrease in mean molecular area of our mono-crown ether-substituted phthalocyanine can be ascribed to a similar reason. The coordination of alkali ions with crown ether, which makes the crown ether more hydrophilic and a little bit bigger part of the molecule immersed into water and causes bigger repulsion from water surface, so a more perpendicular conformation was taken and a smaller mean molecular area was observed.

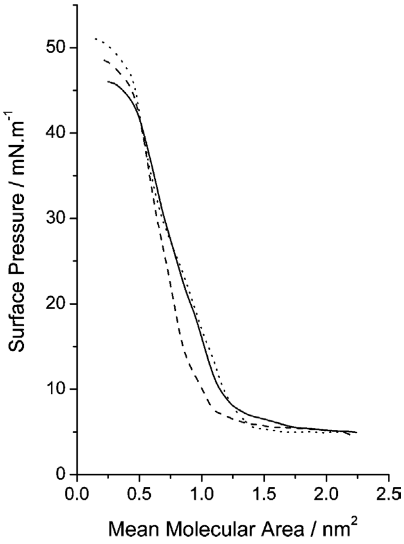

Fig. 3. π–A isotherms of compound 1 on the surface of water (solid), aqueous NaCl (dot), and KCl (dash) solution.

3.2. UV–vis absorption spectra

These stable monolayers can be transferred to substrates with a vertical dipping method. The transfer processes were monitored by the UV–vis absorption spectra. The results show that all the monolayers can be transferred with a reasonable transfer ratio and in most of the cases Y-type LB films were formed. One exception is compound 3 on water surface: when the layer number is bigger than 11, Z-type LB film was formed. Linear relationship between absorbance and layer number indicate a stable transfer.

Fig. 4 shows the absorption spectra of LB films of compound 3 with different layer numbers deposited from water surface. The LB films of compounds 2 and 3 show one similar peak at 630 nm, which indicates the formation of H aggregates in the film. This is similar to most of the asymmetrically substituted amphiphilic phthalocyanines

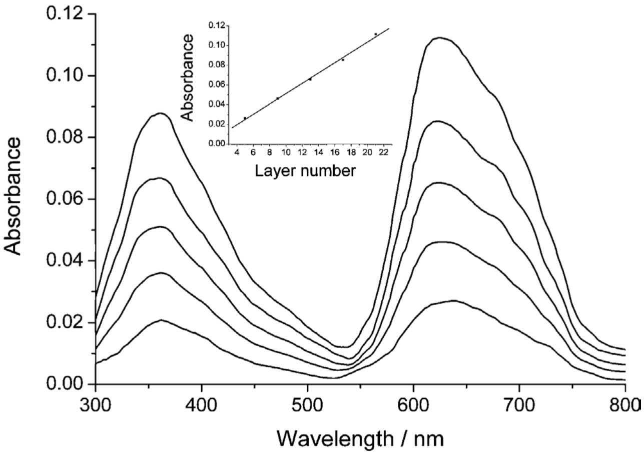

Fig. 4. UV–vis absorption spectra of the LB films of compound 3 deposited from the surface of water with different layer numbers (from bottom to top, layer number increased following the order 5, 9, 13, 17, and 21). The inset shows the plot of the absorbance of the LB films at 610 nm vs layer number.

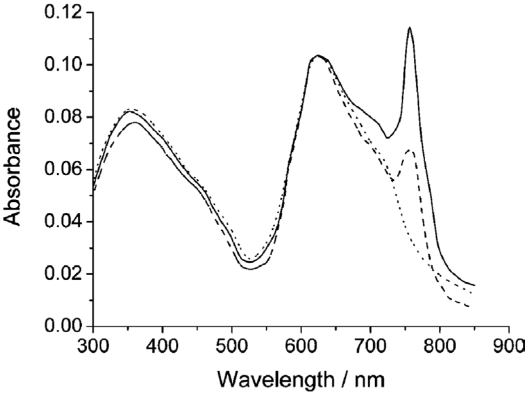

Fig. 5. UV–vis absorption spectra of the LB films of compound 1 deposited from the surface of water (solid), aqueous NaCl solution (dash), and KCl solution (dot).

(for example, [22,23]). But the LB films of compound 1 deposited from water surface give two peaks in the region of 600–800 nm (615 and 760 nm) (Fig. 5). These splitting Q bands have been observed by Cook and other groups in the LB film of asymmetrically octasubstituted phthalocyanines [18,19]. These splitting Q bands were also observed for the β form crystal of nonsubstituted phthalocyanine [24,25]. This Q-band splitting was ascribed to a special aggregation structure (herringbone structure, Fig. 6A) in the LB films by Cook. The splitting of the Q bands implied the presence of the "herringbone" structure with an angle between two molecules of ca. 75° [19]. For the octasubstituted phthalocyanines, only the molecule with chains with a length of six carbons or more shows the "herringbone" structure in LB films. Shorter substitutions will increase the angle between two phthalocyanine molecules and resulting in a bigger distance between two molecules. But for our tetrasubstituted phthalocyanines, only the shortest chain substitutions induced the formation of the "herringbone" structure. The longer substitution induced the formation of H aggregates. As shown in Figs. 6A and 6B, the splitting of Q bands of phthalocyanines in LB film was the results of the interactions between two herringbone-arranged closely packed phthalocyanine columns. The interaction between two columns depends on the distance (d1 and d2 in the figure) between them. The bigger the substituents on the peripheral position are, the bigger the distance between two columns is (d2 > d1). This is why we cannot observe the Q-band splitting for compounds 2 and 3 in LB films.

The alkali ions in the subphase did not affect the absorption spectra of the LB films of 2 and 3 much. No distinct shifting was observed in the absorption spectra. But a big difference was observed for the LB films of 1 deposited from different subphases. As shown in Fig. 5, the existence of sodium ions in water decrease the relative intensity of the Q bands at 763 nm and potassium ions can avoid this peak completely. This indicates that the coordination of alkali ions in crown ether drove the phthalocyanines to form H aggregates instead of a "herringbone" structure. As reported by several groups, the tetrasubstituted 15-C-5 phthalocyanine analogues formed sandwich-type complexes with potassium cations [26,27]. In our experiments, the cations hosted in crown ether increase the hydrophilicity and make the plane of phthalocyanine more perpendicular to the surface of water, and closer packing is possible for the phthalocyanine rings and thus increases the distance between the interaction columns. Further more the coordination of potassium with two crown ethers induced the formation of sandwich-type complex, and the neighboring two molecules were forced to form H aggregates (Fig. 6C).

Polarized absorption spectra (Fig. 7) of the LB films of compounds 2 and 3 deposited from water surface give big dichroisms, which indicative a highly ordered structure. The intensity of the Q band is bigger when the electric field vector of the polarized light was perpendicular to the dipping direction. It could be concluded that the planes of the phthalocyanine rings were preferentially aligned toward the normal to the dipping direction [18]. The LB film of 1 deposited from water surface gives dichroism in polarized absorption spectra too (Fig. 8). The band at 763 nm shows a higher intensity when the electric field vector of the polarized light is parallel to the dipping direction; at the same time the band at 610 nm gives a weaker absorption. These different properties of these two Q bands are more evidence that supports the formation of the "herringbone" structure in the LB film [18]. Following the Yoneyama equation [28], with the dichroisms measured in the polarized absorption spectra, we can calculate the orientation angles (dihedral between phthalocyanine plan and the substrate) of the phthalocyanine rings in the LB film. The results are listed in Table 1. For the LB films deposited from water surface, the orientation angles of the phthalocyanine rings increase with the increase in length of the alkyl chains. This is consistent with the results of π–A isotherms, which show the decrease in mean molecular area when the length of the alkyl chains increase from C3 to C7.

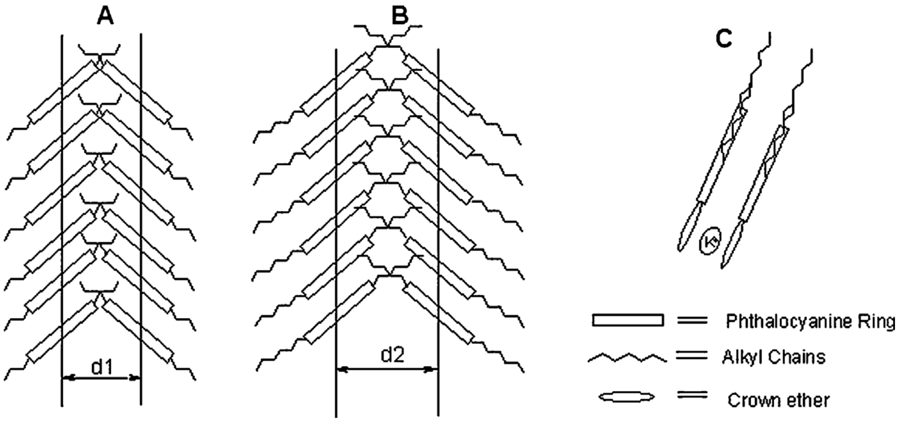

Fig. 6. Schematic drawing of the arrangement of phthalocyanines in LB film (A: herringbone structure formed by compound 1; B: arrangement of compounds 2 and 3 in the LB film, with a bigger distance between two columns; C: sandwich complex induced by the coordination of K^+).

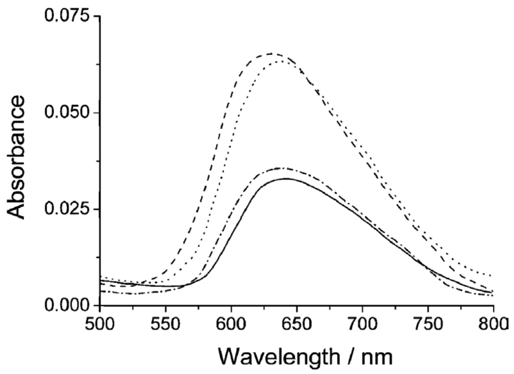

Fig. 7. Polarized absorption spectra of compound 2 deposited from the water surface (21 layers) with electric field vector of the polarized light perpendicular to the dipping direction (dashed line—incidental angle 0°; dotted line—incidental angle 45°) or parallel to the dipping direction (dash-dotted line—incidental angle 0°; solid line—incidental angle 45°).

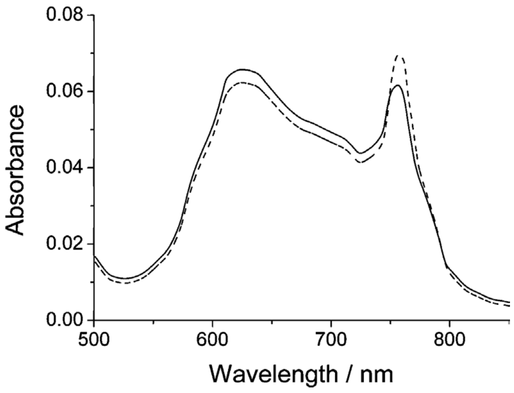

Fig. 8. Polarized absorption spectra of the LB films (21 layers) of compound 1 deposited from water surface (solid line: electric field vector of the polarized light perpendicular to the dipping direction; dashed line: electric field vector of light parallel to the dipping direction).

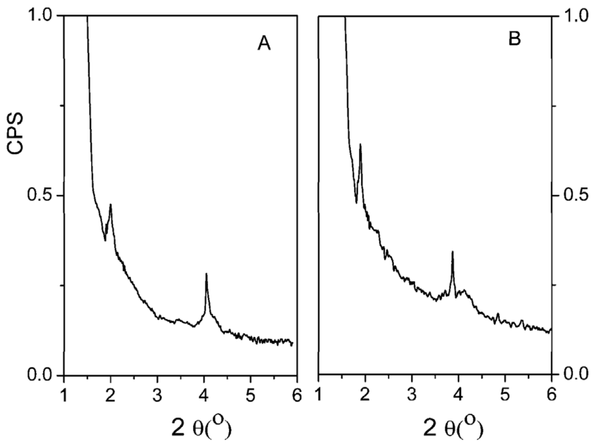

Fig. 9. XRD patterns of the LB films of compound 3 deposited from the surface of water (A) and aqueous KCl solution (B).

The LB films of compounds 2 and 3 deposited from the subphase containing alkali ions give good dichroism too. The orientation angles calculated from Yoneyama equation are also in accord with the results of π–A isotherms. Bonding with the alkali ions increases the orientation angle and decrease the mean molecular area. The LB films of 1 deposited from the alkali ion-containing subphase show very complicated results. They did not give big dichroisms and the X-ray diffraction experiments did not show any peaks in the small angle region. All these indicate an out-of-order layer structure.

3.3. X-ray diffraction experiments

The LB films of compounds 1, 2, and 3 deposited from water surface give one or two diffraction peaks (Fig. 9A shows the diffraction patterns of the LB films of 2 deposited from water or KCl solution), indicate ordered layer structures in the LB film. The LB films of 1 show two diffraction peaks in the pattern, corresponding to the first and the second diffraction peak with a periodic structure thickness of 3.8 nm while those of compound 2 and 3 are 4.4 and 2.9 nm, respectively. For the Y-type LB films of compounds 1 and 2, the thickness of one layer is half of the periodic structure thickness, 1.9 nm for 1 and 2.2 nm for 2. But for the Z-type LB films formed by 3, the thickness of the monolayer is the periodic structure thickness. The alkyl chains of compounds 1 and 2 in the LB film overlapped between neighboring layers while that of compound 3 did not with the reference of the dimensions of the molecules calculated from the molecular model [29].

The LB films of compounds 2 and 3 deposited from the surface of alkali ion-containing subphase give diffraction peaks too, indicating a layer thickness of 2.3 and 2.9 nm. Compared with the LB films deposited from water, a small increase was observed. This is in accordance with the UV–vis, polarized UV–vis, and π–A isotherms. The coordination of alkali ions in the crown ether increase the hydrophilicity and increase the orientation angle and also increase the layer thickness. As mentioned above, for compound 1, the LB films deposited from the surface of ion-containing subphase did not give diffraction peaks in XRD experiments and indicates an orderless structure. This promotes an idea that the balance between hydrophilicity and hydrophobicity is very important for an amphiphilic compounds to form a highly ordered LB film.

4. Conclusion

In conclusion, mono-crown ether-substituted phthalocyanines with different alkyl chains can form well-ordered monolayer on both pure water and alkali ion-containing subphase. The multilayer LB films can be fabricated by vertical dipping method. The structures of the monolayer and the multilayer LB films were affected by the length of the alkyl chains and the coordination of the alkali ions in the crown ether. “Herringbone” structure was observed for the first time for the tetrasubstituted phthalocyanine with short alkyl chains. The herringbone arrangement was changed to a normal H aggregates by the coordination of K^+ in crown ether. The balance between hydrophobic and hydrophilic properties is very important for an amphiphilic compound to form ordered LB films.

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