Aggregation Behavior of Heteroleptic Tris(phthalocyaninato) Dysprosium Complexes with Different Alkoxy Chains in Monolayer or Multilayer Solid Films

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Three heteroleptic tris(phathlocyaninato) dysprosium triple-decker complexes with different alkoxy groups at the peripheral positions of the medium phthalocyanine ligand (Pc)Dy[Pc(OC_nH_{2n+1})$_8$]Dy(Pc) (n = 4, 8, 16) (**I**−**III**) {Pc = unsubstituted phthalocyaninate; Pc(OC_4H_9)$_8$ = 2,3,9,10,16,17,23,24-octakis-(butyloxy)phthalocyaninate; Pc(OC_8H_{17})$_8$ = 2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyaninate; Pc-($OC_{16}H_{33}$)$_8$ = 2,3,9,10,16,17,23,24-octakis(hexadecyloxy)phthalocyaninate} have been synthesized, and their aggregate behaviors in monolayer and multilayer solid films have been comparatively studied. The pure compounds and their 1:4 mixtures with stearic acid (SA) have been found to form a stable monolayer at the air/water interface with a tilted edge-on orientation of (Pc)Dy[Pc(OC_nH_{2n+1})$_8$]Dy(Pc) molecules. In the pure monolayers of the three triple-decker compounds, wirelike molecular aggregates were observed by high-resolution transmission electron microscopy (HRTEM). Adding SA has been found to prevent triple-decker compounds (Pc)Dy[Pc(OC_4H_9)$_8$]Dy(Pc) (**I**) and (Pc)Dy[Pc(OC_8H_{17})$_8$]Dy(Pc) (**II**) from forming large aggregates, and small domains with a diameter of ca. 10 nm were observed in the mixed monolayers. HRTEM studies revealed that two crystalline phases with rectangular and hexagonal lattice structure are present in the small domains. However, both $\pi-A$ isotherms and HRTEM studies indicated that the mixed monolayer of compound (Pc)Dy[Pc($OC_{16}H_{33}$)$_8$]Dy(Pc) (**III**) with SA did not show a difference from the corresponding pure monolayer. The SA molecules were pressed into the cavity above the phthalocyanine ring formed by the eight long hexadecyloxy side chains of the medium macrocycle ligand in **III**. The multilayer LB films of all of these triple deckers fabricated by the vertical dipping method showed very good layered structure as revealed by the multiple-order diffraction peaks in low-angle X-ray diffraction (LAXRD) patterns.

Introduction

Sandwich phthalocyaninato and/or porphyrinato metal double-decker complexes have attracted increasing research interest in areas of molecular devices because of their unique optical and electronic properties associated with the intriguing interring $\pi-\pi$ interactions.[1,2] For most of the applications, the properties of the molecular devices are closely related to the structure of the solid films. The study of fabrication techniques for a highly ordered film is therefore of great interest for molecular electronics and photonics. Thin films of tetrapyrrole rare earth double-decker compounds have actually been fabricated by vapor-phase deposition, a self-assembly method, and Langmuir monolayer techniques.[3,4] The supramolecular assemblies formed have also been investigated by transmission electron microscopy (TEM) and scanning tunneling microscopy (STM).[5,6] It is worth mentioning that the fabrication of supramolecular structures with molecular control using techniques such as Langmuir−Blodgett (LB)[7,8] and self-assembly[8] usually has a twofold aim. First, structures may be envisaged in which control of molecular architecture is achieved. Second, it renders the possibility to exploit material properties in the ultrathin films that may be markedly different from those of the same material in other forms.

Very recently, tetrapyrrole rare earth triple-decker analogues have aroused increasing attention because of the extension of the π networks along the axis perpendicular to the macrocycle plane and the further decreased HOMO−LUMO gap compared with that of its double-decker counterparts.[9] The self-assembled monolayer of a mixed (phthalocyaninato)(porphyrinato) europium triple-decker compound formed on a Si(100) platform exhibits excellent redox behavior that is useful for information

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(1) (a) Jiang, J.; Kasuga, K.; Arnold, D. P. In *Supramolecular Photosensitive and Electroactive Materials*; Nalwa, H. S., Ed.; Academic Press: New York, 2001; Chapter 2, pp 113−210. (b) Ng, D. K. P.; Jiang, J. *Chem. Soc. Rev.* **1997**, *26*, 433. (c) Jiang, J.; Liu, W.; Arnold, D. P. *J. Porphyrins Phthalocyanines* **2003**, *7*, 459.

(2) Bian, Y.; Jiang, J.; Tao, Y.; Choi, M. T. M.; Li, R.; Ng, A. C. H.; Zhu, P.; Pan, N.; Sun, X.; Arnold, D. P.; Zhou, Z.; Li, H.-W.; Mak, T. C. W.; Ng, D. P. K. *J. Am. Chem. Soc.* **2003**, *125*, 12257.

(3) Chen, Y.; Liu, H.-G.; Pan, N.; Jiang, J. *Thin Solid Films* **2004**, *460*, 279.

(4) Kadish, K. M.; Smith, K. M.; Guilard, R. *The Porphyrin Handbook*; Academic Press: San Diego, CA, 2000−2003; Vols. 1−20.

(5) Zhang, W. P.; Kuo, K. H.; Hou, Y. F.; Ni, J. Z. *J. Solid State Chem.* **1988**, *75*, 373.

(6) Binnemans, K.; Sleven, J.; Feyter, S. D.; Schryver, F. C. D.; Donnio, B.; Guillon, D. *Chem. Mater.* **2003**, *15*, 3930.

(7) Petty, M. C. *Langmuir−Blodgett Films: An Introduction*; Cambridge University Press: New York, 1996; Chapter 3.

(8) Oliveira, Jr., O. N.; Raposo, M.; Dhanabalan, A. *Handbook of Surfaces and Interfaces of Materials*; Academic Press: New York, 2001; Vol. 4, Chapter 1.

(9) (a) Arnold, D. P.; Jiang, J. *J. Phys. Chem. A* **2001**, *105*, 7525. (b) Ishikawa, N.; Iino, T.; Kaizu, Y. *J. Am. Chem. Soc.* **2002**, *124*, 11440.

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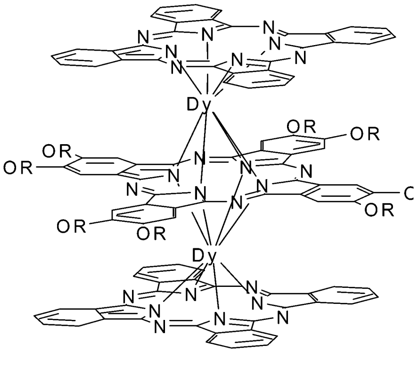
Scheme 1 Schematic Molecular Structure of $(Pc)Dy[Pc(OC_nH_{2n+1})_8]Dy(Pc)$ (n = 4, 8, 16)



(**I**) R = C_4H_9, (**II**) R = C_8H_{17}, (**III**) R = $C_{16}H_{33}$

storage.[10] These molecular media have been found to be stable under extremes of temperature (400 °C) and do not degrade under large numbers of read–write cycles (10^{12}). However, studies on the fabrication and aggregation behavior of triple-decker compounds are still rare.

As part of our continuous effort to construct sandwich double- and triple-decker tetrapyrrole metal complexes into ordered structures,[11] we investigated and described the aggregation behavior of three triple-decker dysprosium complexes $(Pc)Dy[Pc(OC_nH_{2n+1})_8]Dy(Pc)$ (n = 4, 8, 16) (**I**–**III**) containing alkoxy groups with different lengths of alkyloxy chains at the peripheral positions of the medium phthalocyanine ligand, Scheme 1, in Langmuir and LB films in either pure form or in a mixture with stearic acid (SA) (1:4 molecular ratios).

Results and Discussion

Characteristics of Pressure–Area Isotherms. Figure 1 shows the pressure–area (π–A) isotherms for pure triple-deckers $(Pc)Dy[Pc(OC_nH_{2n+1})_8]Dy(Pc)$ (n = 4, 8, 16) and their mixtures with SA in a molar ratio of 1:4 at the air/water interface. As can be seen, the 1:4 mixed floating monolayer isotherms of the three complexes follow closely those of corresponding pure monolayers. For example, a phase transition occurs at 10 mN/m for the pure film of **II** and at 16 mN/m for the mixed film of **II** with SA. A long plateau appears at 6–15 mN/m in the isotherm of the pure film of **III**, and a similar one was observed at 11–16mN/m for the mixed film of **III** with SA. Both of the plateaus might be attributed either to a phase transition from a liquid expanded phase to a liquid condensed phase or to the formation of double-layer structures. The limiting mean molecular occupied areas, which are estimated by extrapolating the steeply rising part of the π–A isotherm curves to zero pressure, are 1.91, 1.81, and 1.45 nm^2 for pure films of **I**, **II**, and **III**, respectively. These values are much smaller than the area of the phthalocyanine ring plane, ca. 2.56 nm^2, calculated on the basis of the crystal structure.[12] The values for the former two complexes are in good accord with the area reported for double-decker counterparts $M[Pc(OC_3H_7)_8]_2$ {M = Er, Lu; $Pc(OC_3H_7)_8$ = 2,3,9,10,16,17,23,24-octakis(propyloxy)phthalocyaninate}, 1.80 nm^2.[13] It can be found in the present case that the limiting mean molecular occupied area of triple-decker compounds in a pure film is dependent on the alkoxy side chains, decreasing along with the increase in the alkoxy chain length. These results indicate that the alkoxy side chains of the medium phthalocyanine ring of triple deckers **I**–**III** do not contribute to the mean molecular area in the monolayers and suggest that an edge-on orientation was employed by the triple-decker molecules with the phthalocyanine rings tilted and assembled with the main molecular axis parallel to the water surface. The alkoxy side chains bound to the middle phthalocyanine ring may extend to the air and are packed tightly themselves because of the hydrophobic interaction at the air/water interface. The fact that the mean molecular area for **III** in the monolayer, 1.45 nm^2, is much smaller compared with those of **I** and **II** can be ascribed to the formation of a partial double-layer film due to the strong hydrophobic interaction among the long hexadecyloxy chains of different triple-decker molecules in addition to the π–π interaction between the phthalocyanine rings.

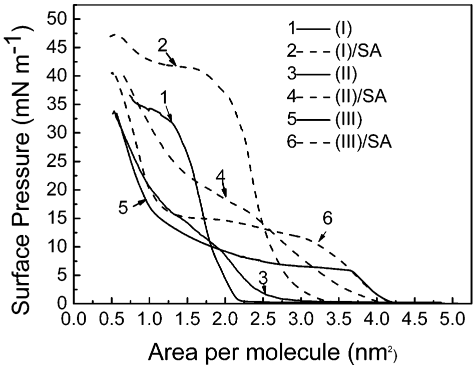


Figure 1. π–A isotherms of **I**, **I**, and **III** on a water surface at room temperature.

Table 1. Experimental Data for Tris(phthalocyaninato) Dysprosium Triple-Decker Complexes

	I		II		III	
	pure	mixed	pure	mixed	pure	mixed
A_{limit} (nm^2)	1.91	2.72	1.81	2.57	1.45	1.48
A_{calcd} (nm^2)[a]		2.71		2.61		2.25
$\Delta\lambda_{\max}$[b]	18	16	25	27	14	15
α(deg)[c]	42.6	44.4	39.3	40.5	40.4	42.8
calculated layer space (nm)[d]	1.65	1.68	2.11	2.20	3.13	3.16

[a] Limiting molecular areas calculated assuming an area of 0.20 nm^2 for one stearic acid;[13,14] $A_{\text{cal}} = A_{\text{limit(pure)}} + 4A_{\text{SA}}$. [b] $\Delta\lambda_{\max} = \lambda_{\max}$(film) − $\lambda_{\max}$(solution). [c] Orientation angles calculated from polarized absorption spectra. [d] (1.32 × sin α + 0.71/2 × cos α + the length of the alkoxy chain) assuming that the length of the alkane chain is 0.5, 1.0, and 2.0 nm for n = 4, 8, and 16, respectively.

As reported in Table 1, the limiting mean molecular occupied areas are 2.72, 2.57, and 1.48 nm^2, respectively, for mixed films of SA with **I**, **II**, and **III**. By means of the molecular area for closely packed SA, 0.20 nm,[2,14,15] and on the basis of the assumption that ideal mixing occurs in the mixed films of triple deckers with SA in the ratio of 1:4, the calculated limiting molecular areas ($A_{\text{calcd}} = A_{\text{limit(pure)}} + 4A_{\text{SA}}$) of compounds **I**, **II**, and **III** in the mixed monolayers with SA are 2.71, 2.61, and 2.25 nm^2,

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[10] Liu, Z.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. *Science* **2003**, *302*, 1543.

[11] (a) Xie, D.; Jiang, Y.; Jiang, J.; Wu, Z.; Li, Y. *Sens. Actuators B* **2001**, *77*, 260. (b) Liu, H. G.; Feng, X. S.; Zhang, L. J.; Jiang, J.; Lee, Y.; Jang, K.; Qiang, D. J.; Yang, K. Z. *Mater. Lett.* **2003**, *57*, 2156. (c) Chen Y. L.; Liu H. G.; Pan N.; Zhang X. X.; Liu W.; Cheng C. F.; Jiang J. *Sci. China, Ser. B* **2001**, *44*, 650.

[12] Zhu, P.; Pan, N.; Li, R.; Dou, J.; Zhang, Y.; Cheng, D. Y. Y., Wang, D.; Ng, D. K. P.; Jiang, J. *Chem.—Eur. J.* **2005**, *11*, 1425.

[13] Liu, Y.; Shigehara, K.; Hara, M.; Yamada, A. *J. Am. Chem. Soc.* **1991**, *113*, 440.

[14] Rapaport, H.; Kuzmenko, I.; Berfeld, M.; Kjaer, K.; Als-Nielsen, J.; Popovitz-Biro, R.; Weissbuch, I.; Lahav, M.; Leiserowitz, L. *J. Phys. Chem. B* **2000**, *104*, 13998.

[15] Zhang, R. J.; Krûger. P.; Kohlstrunk, B.; Lösche, M. *ChemPhysChem* **2001**, *7*, 452.

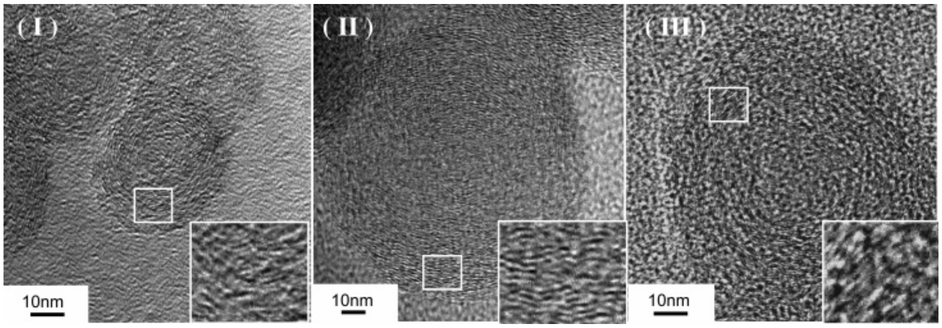

Figure 2. HRTEM images of the pure monolayer for **I**−**III**.

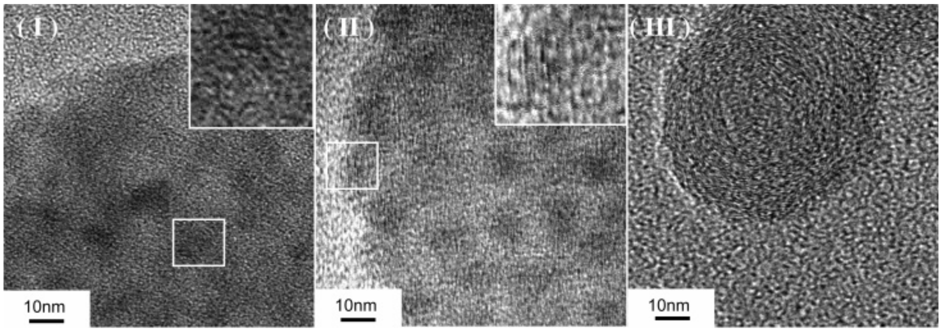

Figure 3. HRTEM images of the mixed monolayer of **I**−**III** with SA.

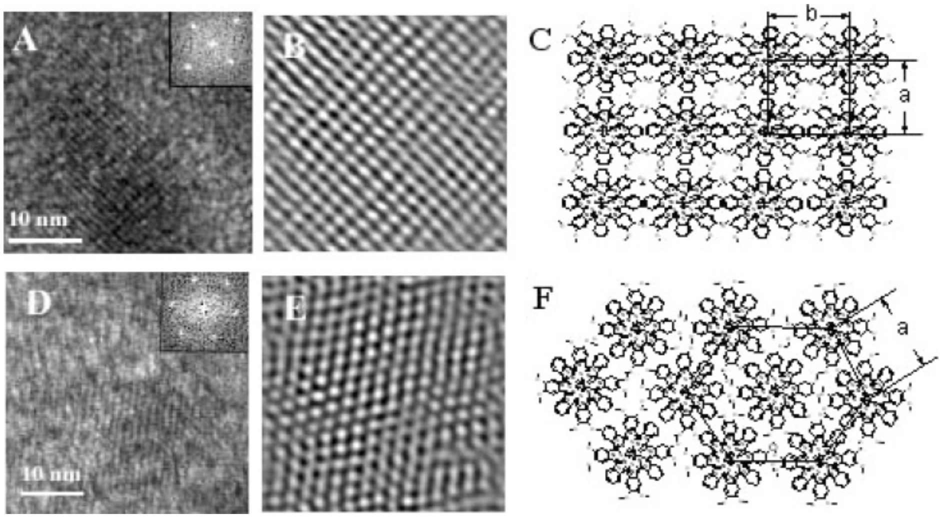

Figure 4. HRTEM images of the mixed monolayer of **II** with SA: lattice images (A, D) with their fast Fourier transformation (FFT) images (insets of A and D) and IFFT images (B, E) with schematic molecular arrangements (C, F).

respectively (Table 1).[16] It is clear that the data calculated for **I** and **II** are in good agreement with those obtained by experiments, indicating that the SA molecules have no influence on the orientation of the phthalocyanine units in the mixed monolayers. This is in line with the conclusion deduced from studying the mixed monolayers with SA of nonamphiphilic materials such as polymethacrylate with dodecyloxy-substituted phthalocyanine units in the side chains[17] and a bis(phthalocyaninato) ytterbium compound.[18] However, as expected from their behaviors in pure films, compound **III** behaves differently from **I** and **II**. In the mixed film of **III** with SA, the average area per molecule of **III** is only 1.48 nm^2, which is almost equal to the value found for **III** in a pure film, 1.45 nm^2, but much smaller than that expected from calculation, indicating that the area occupied by each SA molecule in the mixed film of **III** is close to zero. It is therefore concluded that the SA molecules make no contribution to the measured area in the mixed film of **III** with SA. These results suggest that the SA molecules in the mixed film of **III** with SA were pressed into the cavity formed by the phthalocyanine ring and the surrounding long upward-extending eight hexadecyloxy chains because of the strong hydrophobic interaction between SA and the hexadecyloxy chains (Figure 7). Further evidence comes from the low-angle X-ray diffraction (LAXRD) experimental result as also detailed below. It is worth noting that the butyloxy or octyloxy side chains in **I** and **II** are too short to form the cavity like that in the film of **III** and then to keep the SA molecules inside.

High-Resolution Transmission Electron Microscopy (HRTEM) Characterization. To investigate the

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[16] Liu, H.-G.; Qian, D.-J.; Feng, X.-S.; Xue, Q.-B.; Yang, K.-Z. *Langmuir* **2000**, *16*, 5079.

[17] van Nostrum, C. F.; Nolte, R. J. M.; Devillers, M. A. C.; Oostergetel, G. T.; Teerenstra, M. N.; Schouten, A. J. *Macromolecules* **1993**, *26*, 3306.

[18] Gaffo, L.; Constantino, C. J. L.; Moreira, W. C.; Aroca, R. F.; Oliveira, O. N. Jr. *Langmuir* **2002**, *18*, 3561.

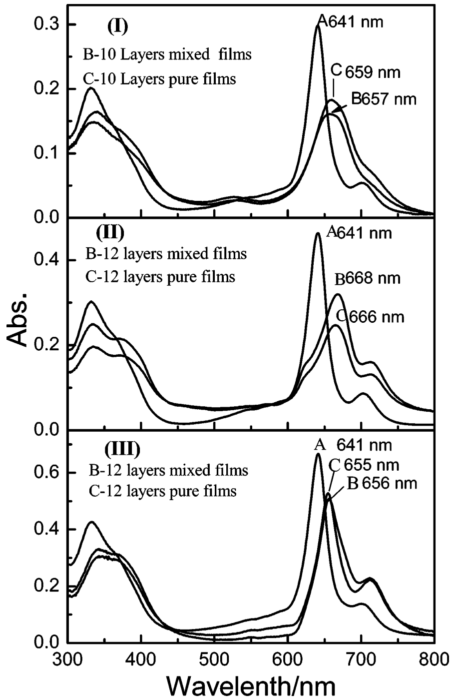

Figure 5. Electronic absorption spectra of (Pc)Dy[Pc-$(OC_nH_{2n+1})_8$]Dy(Pc) in $CHCl_3$ (A), mixed (B), and pure LB films (C).

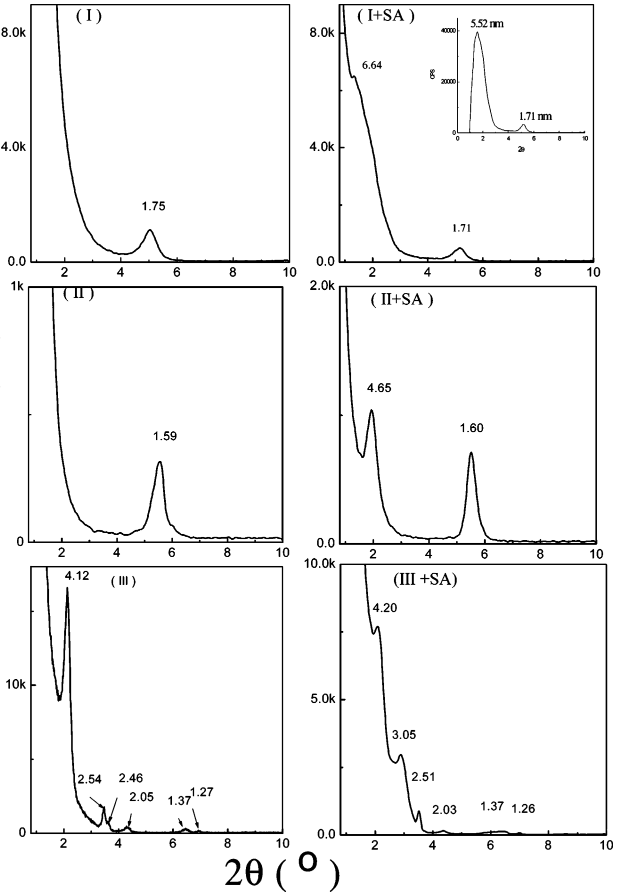

Figure 6. LAXRD patterns of the LB films of **I**–**III** and their mixtures with SA (1:4) soon after deposition.

structure of the monolayers using the HRTEM technique, the monolayers were deposited onto Formvar-coated 230 mesh copper grids by a subphase-lowering method. Figure 2 displays the HRTEM images of the pure monolayers for **I**, **II**, and **III**. It can be seen that a large number of nanocolumns construct nestlike structures with a diameter of 40–90 nm in the pure monolayer of these complexes. The phthalocyanine columns in pure films were found to show an average width of ca. 1.3 nm regardless the length of the alkoxy chains, which is consistent with the diagonal dimension of the core of the rigid phthalocyanine ring.[19] As clearly shown in Figure 2, among the three compounds the pure monolayer of **II** displays the best long-range order within the columns probably because of the proper balance between the phthalocyanine $\pi-\pi$ interaction and the interaction among the alkoxy side chains among triple-decker molecules because of the suitable length of the octyloxy groups in **II**.[20]

The structures of mixed films with SA for **I**–**III** were also similarly examined, and the HRTEM images are given in Figure 3. As shown in this Figure, significant change takes place in the supramolecular structures of the film of **I** and **II** when SA molecules are added, but not for **III**. Two different phases with irregular forms were observed in the HRTEM micrograph of the mixed monolayers of **I** and **II**. The dark, round domains with a dimension of ca. 10–20 nm are the aggregates of triple-decker molecules, and the bright ones are the domains of SA. Although irregular domains were present for the mixed monolayer of **I** with SA, well-ordered 1D columnar supramolecular structures can still be seen in some of the domains (inset of Figure 3I), and the width of the phthalocyanine column is estimated to be about 1.25 nm, which is only slightly smaller than that found in the pure monolayer of **I**, suggesting the slightly tighter molecular arrangements of (Pc)Dy[Pc$(OC_4H_9)_8$]Dy(Pc) molecules in the mixed monolayer than in the pure monolayer. This is also true for **II**. However, unlike **I** and **II** no phase separation is observed in the mixed film of compound **III** with SA. Just the same nestlike structures with similar dimensions constructed by nanosized phthalocyanine columns as in the pure monolayer of **III** were observed in the mixed film with SA of **III** (Figure 3). This supports the conclusion deduced from the $\pi-A$ isotherm experimental result that the SA molecules do not contribute to the mean molecular area in the mixed film of **III** with SA.

To know more about the internal structure and packing arrangement in the mixed monolayers with SA of triple-decker compounds, the inverse fast Fourier transform (IFFT) images of compound **II** in the small domains are given in Figure 4.[19] Similar to the monomeric phthalocyaninato copper counterpart,[21a] two crystalline phases with either hexagonal close-packed or slightly distorted rectangular lattice were observed. For the hexagonal lattice, $a = 1.4$ nm, and for the rectangular lattice, $a = 1.1$ nm and $b = 1.6$ nm. Both values of 1.1 and 1.4 nm are even smaller compared with the diagonal dimension of the rigid phthalocyanine core and the distance between the diagonal oxygen atoms in $Pc(OC_8H_{17})_8$, 1.3 and 1.6 nm,[19] indicating that the planes of phthalocyanine rings in the triple-decker molecules of **II** were tilted with respect to the column axis, which is further proved by the polarized UV–vis measurement result, vide infra. Such behavior is common in binary component systems according to previous studies.[21b]

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(19) Kobayashi, T.; Isoda, S. *J. Mater. Chem.* **1993**, *3*, 1.

(20) Eichhorn, H.; Bruce, D. W., Wöhrle, D. *Adv. Mater.* **1998**, *10*, 419.

(21) (a) Donley, C. L.; Xia, W.; Minch, M. A.; Zangmeister, R. A. P.; Drager, A. S.; Nebesny, K.; O'Brien, D. F.; Armstrong, N. R. *Langmuir* **2003**, *19*, 6512. (b) Velez, M.; Vieira, S.; Chambrier, I.; Cook, M. J. *Langmuir* **1998**, *14*, 4227.

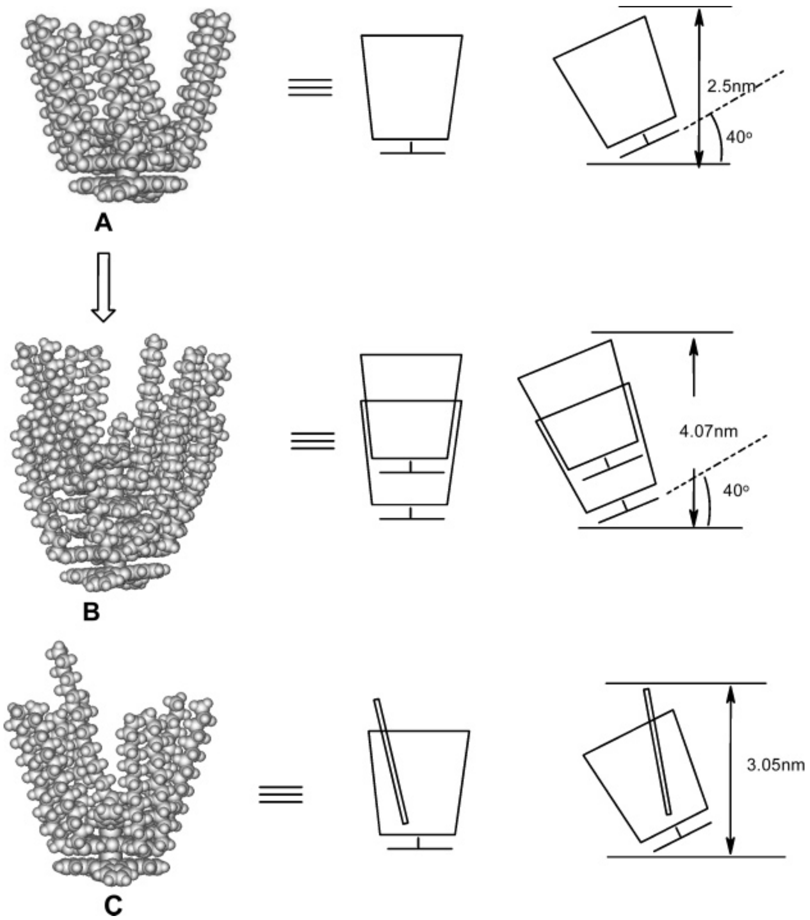

Figure 7. Arrangement of **III** in the pure film or mixed film with SA (CPK model): (A) cuplike conformation of **III** on the water surface; (B) dimerlike supramolecular structure formed from the strong hydrophobic interaction among hexadecyloxy chains and $\pi-\pi$ interaction between the phthalocyanine rings of the different triple-decker molecules; (C) cup hosting the SA molecule in its cavity (for clarity only one SA molecule is shown).

UV−Vis Spectra and Polarized UV−Vis Spectra. Multilayer films of three complexes and their mixtures with SA (1:4) have also been obtained by depositing monolayers at a constant surface pressure of 20 mN/m using the vertical dipping method. The absorption maxima obtained from the electronic spectra of the chloroform solution and pure and mixed LB films on quartz slides for **I**, **II**, and **III** are compared in Table 1, and the spectra are illustrated in Figure 5. It is worth pointing out that the increased absorbance of the 1:4 mixed film with SA of compound **II** compared with its pure film with the same number of layers can be attributed to the larger transfer ratio and better quality of the mixed film.

As shown in Figure 5, in $CHCl_3$, the intense Q band with a weak shoulder for all the three triple-decker complexes **I**−**III** appears at almost the same wavelengths, 641 and 703 nm, without showing a detectable shift along with the change in the length of the alkoxy groups at the peripheral positions of the medium phthalocyanine ring. In both the pure and mixed films, these absorptions are broadened and red shifted to 655−668 and 712−715 nm, respectively, indicating the formation of J aggeragates in the multilayers due to the strong exciton coupling.[18] These results are in line with the behavior found for bis(tetrapyrrole) rare earth counterparts, namely, $Lu[Pc(tBu)_4]_2$ with $[Pc(tBu)_4$ = 2(3),9(10),16(17),23(24)-tetrakis(*tert*-butyl)phthalocyaninate],[22] $Eu[Pc(OC_5H_{11})_8]_2$ with $[Pc(OC_5H_{11})_8$ = 2,3,9,10,16,17,23,24-octakis(pentyloxy)phthalocyaninate],[23] and Ce(TPyP)(Pc) with [TPyP = tetrakis(pyridyl)porphyrinate],[24] whose Q band assigned for the phthalocyanine ligand in the absorption spectra of LB films is also red shifted with respect to that in solution. However, the shift of Q bands in the absorption spectra in LB films of triple deckers **I**−**III** is different, showing a dependence on the length of the side chains incorporated onto the peripheral positions of the medium phthalocyanine ligand. For instance, in the pure and mixed films the main Q band with stronger intensity is red shifted by 16−18 nm for **I**, 25−27 nm for **II**, and 14−15 nm for **III** (Table 1 and Figure 5). These results reveal that the length of substituted alkoxy chains has a great influence on the intermolecular interaction in solid films. It is worth noting that for the same compound the Q band in the pure multilayer is almost in the same position as in the mixed multilayer, which indirectly suggests similar aggregation behavior of triple-decker molecules in the pure and mixed films.

The orientation angle of the phthalocyanine ring with respect to the substrate in the films of **I**−**III** has been determined by a polarized UV−vis technique according to a literature method.[25,26] As shown in Table 1, the

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(22) Rodriguez-Mendez, M. L.; Aroca, R.; DeSaja, J. A. *Chem. Mater*. **1993**, *5*, 933.

(23) Liu, H.-G.; Feng, X.-S.; Jiang, J.; Zhang, L.-J.; Lan, W.-Z.; Lee, Y.-I.; Jiang, K.; Qian, D.-J.; Yang, K.-Z.; *Mater. Sci. Eng., C* **2003**, *23*, 501.

(24) Qian, D.-J.; Liu, H.-G.; Jiang, J. *Colloids Surf., A* **2000**, *163*, 191.

(25) (a) Bourgoin, J.-P.; Doublet, F.; Palacin, S.; Vandevyver, M. *Langmuir* **1996**, *12*, 6473. (b) Xiang, H.-Q.; Tanaka, K.; Takahara, A.; Kajiyama, T. *Langmuir* **2002**, *18*, 2223.

difference in the orientation angle, α, of the phthalocyanine ring between the pure and mixed films of **I**−**III** is in the range of 1.2−2.4°, which is within the uncertainty of the measurement method, ±5°, indicating again that the SA molecules have no influence on the ring orientation, consistent with results reported elsewhere.[15,27,28] Nevertheless, the difference in the orientation angle, α, measured for the films of all three compounds **I**−**III** is also within the uncertainty of the measurement method, 3.3 and 3.9° for the pure and mixed films, respectively. Therefore, no obvious difference in the orientation angle exists among the multilayer films of these three compounds.

According to exciton theory,[29] the shift in the absorption spectra is related to the distance between two neighboring molecules (R), the transition dipole moment (μ), and the angle between two dipole moments (α). For compounds **I**, **II**, and **III**, μ and α are the same; therefore, the red shift is directly related to the distance between two neighboring molecules. We suggest that the distance between the neighboring molecules in the multilayer films of **II** is a bit of smaller than that of **I** because of the larger degree of red-shifted phthalocyanine Q bands in the films of **II** than in those of **I**. However, the smallest red shift in the phthalocyanine Q bands of pure and mixed films of **III** compared with those of **I** and **II** does not mean the largest distance between neighboring triple-decker molecules in its films because of the formation of partial double-layer supramolecular structures.

X-ray Diffraction Patterns. The quality of LB films can be further assessed using a low-angle X-ray diffraction (LAXRD) technique.[30] Figure 6 shows the LAXRD patterns of the films for compounds **I**−**III** soon after deposition. The first-order Bragg peak at ca. 5.05° for a pure LB film of **I** corresponds to a periodic distance of 1.75 nm, which is consistent with the calculated value based on the molecular size and the orientation angle of the phthalocyanine ring (Table 1). As displayed in Figure 6 (**I** + SA), the LAXRD pattern of the mixed LB film of **I** with SA displays two peaks, one of which is similar to the one shown in the pure LB film, suggesting that there is similar periodic structure of triple-decker complexes in the pure and mixed LB films for **I**. Another peak is shown at 2θ = 1.33°, which results from the overlap between a new weak diffraction peak of the mixed film and the intense background peak that is always present in small angle region of 0.8−3°. Normalization of the diffraction patterns of the pure film and the mixed film of **I** with SA at 2θ = 0.8° results in a curve showing a new peak at 2θ = 1.6°, inset of Figure 6 (**I** + SA), which suggests a periodic distance of 5.52 nm. This distance is equal to a layer thickness of the *Y* type (actually a bilayer) LB film of the stearic acid (SA).[31]

As shown in Figure 6, the LAXRD experimental data clearly indicate that the aggregation behavior of triple-decker **II** is similar to that of **I** in both the pure film and the mixed film with SA. The primary Bragg peak for pure and mixed films of **II** occurs at ca. 5.55 and 5.53°, respectively, resulting in layer spaces of 1.59 and 1.60 nm, respectively. These layer spaces are much smaller than those calculated, Table 1, implying that the octyloxy chains maybe tilted, folded, or interpenetrated. Comparison of the LAXRD patterns of pure and mixed film with SA of **II** also reveals that the width of the Bragg peak for the mixed film is smaller than that for the pure film, suggesting an increased order of triple-decker molecules in the *z* direction in the mixed film when SA is present.[21a] Different from that of **I**, an extra peak in the small-angle region is clearly observed at 2θ = 1.90° for the mixed film of **II** with SA, corresponding to a layer space of ca. 4.65 nm. We ascribe this peak to the *Y*-type LB film of stearic acids with a little bit interpenetration between their alkyl chains.

As for compound **III**, the LAXRD patterns for both pure and mixed films are quite different from their analogues **I** and **II**, Figure 6, clearly revealing different aggregation behavior of this compound from those of analogous **I** and **II** in the films. In the pure film, three diffraction peaks at 2θ = 2.13, 4.32, and 6.45° are the first-, second-, and third-order diffractions corresponding to a layer space of 4.12 nm, which is ascribed to a dimerlike supramolecular structure (Figure 7B). As revealed by the above-described $\pi-A$ isotherm study result, molecules of all three triple-decker compounds **I**−**III** stand on the water surface with a tilted conformation. However, when the long hexadecyloxy groups are attached at the peripheral positions of the medium phthalocyanine ring, each tilted triple-decker molecule of **III** forms a "cup" on the substrate with the eight long hexadecyloxy chains extending upward (Figure 7A). This cup is able to host another cup in the center because of the hydrophobic interaction among the hexadecyloxy chains of the different triple-decker molecules in addition to the $\pi-\pi$ interaction between the phthalocyanine rings, forming a dimerlike supramolecular structure. The dimension of this dimerlike supramolecular structure calculated from the minimized structure is 4.07 nm, Figure 7B, corresponding well with the X-ray diffraction result, 4.12 nm. Nevertheless, the formation of such a dimerlike supramolecular structure is also supported by the fact that compound **III** gives a very small mean molecular area from the $\pi-A$ isotherm as mentioned above. Diffraction peaks at 2θ = 3.47 and 6.94° are the first- and second-order diffractions corresponding to a layer space of 2.54 nm. Another diffraction peak at 2θ = 3.59° represents a layer space of 2.46 nm, both of which can be ascribed to a monolayer structure because they are very close to the dimension of the triple-decker molecular cup, 2.51 nm as calculated from minimized structure (Figure 7A). The slight difference in these two layer spaces is aroused from the liquid crystal characteristic of the film due to the introduction of long hexadecyloxy chains at the rigid phthalocyanine core of **III** (i.e., the fluidity of the side hexadecyloxy chains in the film inducing a slight difference in the bending or tilting of the alkoxy chains). Figure S1 (Supporting Information) compares the LAXRD patterns of the pure film for compound **III** soon after deposition and kept at ambient temperature for three months. As can be seen, the intensity of the diffraction peak at 2θ = 3.47° decreases, but that at 2θ = 3.59° increases when the pure film is kept at ambient temperature for three months. This gives direct evidence for the liquid crystal property of the film of triple-decker complex **III** and the fluidity of the side hexadecyloxy chains in the film.[32]

The appearance of the second-order diffractions at 1.21 and 1.27 nm for the peaks at 2.43 and 2.54 nm, respec-

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(26) Yoneyama, M.; Sugi, M.; Saito, M.; Ikegama, K.; Kuroda, S.; Iizima, S. *Jpn. J. Appl. Phys.* **1986**, *25*, 961.

(27) Chou, H.; Chen, C.-T.; Stock, K.-F.; Bohn, P. W.; Suskick, K. S. *J. Phys. Chem.* **1994**, *98*, 383.

(28) Kroon, J. M.; Sudholter, E. J. R.; Schenning, A. P. H. J.; Nolte, R. J. M. *Langmuir* **1995**, *11*, 214.

(29) (a) Kasha, M. *Radiat. Res.* **1963**, *20*, 55. (b) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371

(30) Swalen, J. D. *J. Mol. Electron.* **1986**, *2*, 155.

(31) Pretty, M.; Lovett, D. R.; O'Connor, J. M.; Silver, J. *Thin Solid Films* **1989**, *179*, 387.

(32) Xue, Q. B. Ph.D. Thesis, Shandong University, 1998.

tively, demonstrates the increased ordered structure of the pure film of **III** after being kept for three months. It is noteworthy that no further change can be found in the LAXRD pattern of the pure film for compound **III** after three months. As can be expected, the relative intensity attributed to the monolayer structures in the mixed film with SA of **III** also showed a similar change with time and stabilized after being kept at ambient temperature for three months. In good contrast, neither the peak intensity nor the position in both the pure and mixed films of **I** and **II** changes with time because of the lack of apparent liquid crystalline properties of these two compounds due to the incorporation of relatively short butyloxy and octyloxy chains attached at the phthalocyanine ligand.

The mixed film of **III** with SA gives a new peak at $2\theta = 2.89°$, corresponding to a layer space of 3.05 nm, in addition to those peaks assigned in pure films. As described above, the $\pi - A$ isotherm studies reveal that SA molecules make no contribution to the mean molecular area in the mixed film and most likely are pressed into the cavity formed by the phthalocyanine ring and the surrounding hexadecyloxy chains.[33] A model is thus built for this structure in the mixed films of **III** with SA (Figure 7C). It can be found that the dimension calculated from the minimized structure according to this model, 3.05 nm, is in agreement with the experimental layer space.

Conclusions

The aggregate behavior of heteroleptic tris(phthalocyaninato) dysprosium compounds in monloayers and multilayers has been revealed to be dependent on the length of the alkoxy side chains at the peripheral positions of the medium phthalocyanine ligand. Both (Pc)Dy[Pc(OC_4H_9)$_8$]Dy(Pc) (**I**) and (Pc)Dy[Pc(OC_8H_{17})$_8$]Dy(Pc) (**II**) with relatively short alkoxy groups attached at the peripheral positions of the medium phthalocyanine ring form wirelike molecular aggregates of monomer nature in either pure or mixed monolayer films with stearic acid (SA). However, the increase in the length of the alkoxy side chains to the hexadecyloxy groups at the same position of the triple-decker molecules induces the formation of partial dimerlike supramolecular structures in both the pure and mixed films with SA of (Pc)Dy[Pc($OC_{16}H_{33}$)$_8$]Dy(Pc) (**III**). Furthermore, in the mixed film of **III** with SA, strong interaction between the long hexadecyloxy side chains of triple-decker compounds and SA molecules relocate all of the SA molecules from the water surface to the cup above the phthalocyanine ring formed by the eight upward-extending hexadecyloxy side chains. The structure of monolayers and multilayers of tris(phthalocyaninato) rare earth complexes thus can be modulated by changing the species and length of the peripheral substituents.

Experimental Section

The synthesis and characterization of (Pc)Dy[Pc(OC_nH_{2n+2})$_8$]Dy(Pc) ($n = 4, 8, 16$) have been reported elsewhere.[12] Elemental analysis and spectroscopic characteristic data are consistent with assigned structure. Commercially available stearic acid (SA) with an analytical purity reagent was purified by recrystallization just before use.

The samples were dissolved in chloroform, and the concentrations of (Pc)Dy[Pc(OC_nH_{2n+1})$_8$]Dy(Pc) ($n = 4, 8, 16$) in both pure and mixed systems are in the range of l 6.23×10^{-5}−6.39×10^{-5} mol L^{-1}. The monolayers of pure (Pc)Dy[Pc(OC_nH_{2n+1})$_8$]Dy(Pc) 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 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. The monolayers for the high-resolution transmission electron microscopy (HRTEM GEOL-2010) were transferred to 230 mesh copper grids covered with Formvar by a subphase lowing method.

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} while the surface pressure was kept at 20 mN m^{-1}. The time interval between two consecutive layers was 15 min.

The transfer ratio was found to be close to unity for mixed (Pc)Dy[Pc(OC_nH_{2n+1})$_8$]Dy(Pc)/SA (1:4) and smaller than unity (ca 0.5−0.8) for pure (Pc)Dy[Pc(OC_nH_{2n+1})$_8$]Dy(Pc). The fabricated LB films were air dried for 15 min for every other layer. The literature method described by Hönig et al. was adopted to treat the substrates.[34]

UV−vis spectra and polarized UV−vis spectra were recorded on a Hitachi U-4100 spectrophotometer. For the polarized absorption spectra recording, a dichroic sheet polarizer was placed in front of the LB films with s- and p-polarized light, respectively. The low-angle X-ray diffraction (LAXD) experiment was carried out on a Rigaku D/max-γB X-ray diffractometer.

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Supporting Information Available: LAXRD patterns of the pure LB film of **III** (a) soon after deposition and (b) kept for three months. This material is available free of charge via the Internet at http://pubs.acs.org.

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[33] (a) O'Driscoll, B. M. D.; Ruggles, J. L.; Gentle, I. R. *Langmuir* **2004**, *20*, 6246. (b) Matsuzawa, Y.; Seki, T.; Ichimura, K. *Langmuir* **1998**, *14*, 683.

[34] Hönig, E. P.; Hengst, J. H. T.; Engelsen, D. D. *J. Colloid Interface Sci.* **1973**, *45*, 92.