Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thin Solid Films 496 (2006) 619 – 625
www.elsevier.com/locate/tsf

Spectroscopic and structural characteristics of Langmuir–Blodgett films of bis[2,3,9,10,16,17,24,25-octakis(octyloxy)phthalocyaninato] rare earth complexes

Xueying Wang [a], Yanli Chen [a,b], Hongguo Liu [a], Jianzhuang Jiang [a,*]

[a] *Contribution from the Key Lab for Colloid and Interface Chemistry of Education Ministry, Department of Chemistry, Shandong University, Jinan 250100, China*
[b] *School of Chemistry and Chemical Engineering, Jinan University, Jinan, 250022, China*

Received 23 December 2004; received in revised form 17 July 2005; accepted 16 September 2005

Abstract

The monolayer behavior of bis[2,3,9,10,16,17,24,25-octakis(octyloxy)phthalocyaninato] rare earth complexes $M[\mathrm{Pc}(\mathrm{OC}_8\mathrm{H}_{17})_8]_2$ (M=Eu, Dy, Er) at the air–water interface and their ordered molecular assemblies fabricated by Langmuir–Blodgett technique have been investigated by a series of techniques including surface pressure–area isotherms, electronic absorption spectra, polarized absorption spectra, low-angle X-ray diffraction patterns, and transmission electron microscope (TEM). The results indicated that bis(phthalocyaninato) rare earth molecules form well-ordered stable monolayers with a face-to-face configuration and edge-on arrangement to the water surface at the air–water interface and lamellar multilayers on solid substrates. The orientation angle of phthalocyanine rings with respect to the quartz plate surface in the Langmuir–Blodgett films has been determined to be 64.6°, 63.5°, and 63.3° for the Eu, Dy, and Er double-decker complexes, respectively, by the polarized absorption spectroscopy. High-resolution TEM reveals that a series of well-ordered rodlike aggregates of bis(phthalocyaninato) rare earth complexes, which can be considered as molecular cable arrays, were formed by self-organization in the monolayers.

PACS: 68.18.Fg; 68.37.Lp; 68.47.Pe
Keywords: Absorption spectroscopy; Lanthanides; Phthalocyanines; Molecular electronics

1. Introduction

The study of nano-sized supramolecular structures formed by self-organization is of great interest for the development of molecular electronics and ionic devices [1,2]. In this field, the construction of supramolecular wires and channels capable of transporting electrons is an attractive and challenging direction [3].

Phthalocyanines are an important class of pigments that have been found applications in various disciplines [4,5]. This series of tetrapyrrole derivatives can form complexes with almost the complete Periodic Table of elements. In particular, sandwich-type complexes of phthalocyanines with large metal ions such as rare earth, actinide, early transition, and main group metals have been obtained [6–10]. The rare earth sandwich complexes have attracted great attention due to their possible applications in molecular electronics, molecular optronics, and molecular iono-electronics [11]. Because of the conjugated π molecular structure and strong π–π interaction between the aromatic rings, phthalocyanine derivatives have been used as building blocks for ordered molecular systems. Among various approaches used to construct supramolecular structures for phthalocyaninato metal complexes, *Langmuir–Blodgett* technique has proved to be a versatile method [12–18]. A lot of work has been focused on the formation, structure, and gas-sensing properties of monomeric phthalocyanine derivatives. By contrast, the reports on the sandwich-type phthalocyaninato rare earth complexes have been rather scarce. Thus far, several research groups have studied and described, in scattered reports, the

---

* Corresponding author. Tel.: +8653188366188; fax: +8653188565211.
E-mail address: jzjiang@sdu.edu.cn (J. Jiang).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.09.131

formation characteristics, spectroscopic, electrochemical, electrical, and gas adsorption properties of pure LB films of unsubstituted bis(phthalocyaninato) compounds with a series of rare earth metals $M(\mathrm{Pc})_2$ for M = Ce, Pr, Eu, Gd, Tb, Yb, Lu, and Y [19–26]. The electrochromism and atomic force microscopy of mixed LB films of $\mathrm{Yb(Pc)_2}$ with stearic acid have also been reported [27,28]. It has been noted by the researchers in this field that in spite of the improved solubility of unsubstituted bis(phthalocyaninato) rare earth complexes in common organic solvents compared with monomeric counterparts, they are still not soluble enough to ensure the fabrication of high quality LB films [29]. Attempts have therefore been made to further improve the solubility by incorporating different substituents onto the peripheral positions of phthalocyanine ring. However, although the investigation over the LB films of substituted bis(phthalocyaninato) rare earth compounds has been started for quite a long time, still little is known, in particular about the relationship between the formation characteristics and the central rare earth ions as well as the substituents due to the lack of systematic work. In 1991, Liu et al. investigated the electrochemical and electrochromic characteristics of pure LB films of lutetium complexes of bis(phthalocyanine) substituted with four propyloxy and/or *tert*-butyl groups at the peripheral positions [29]. The latter *tert*-butyl-substituted bis(phthalocyaninato) rare earth complexes $M[\mathrm{Pc}(t\mathrm{Bu})_4]_2$ (M = Pr, Gd, Lu) were then studied by Souto et al., Rodriguez-Mendez et al., Vertsimakha, and Arrieta et al., for their spectroscopic and various kinds of gas adsorption properties [30–34]. The work on the LB films of alkoxy group substituted bis(phthalocyaninato) rare earth compounds has extended to those of $\mathrm{Sm[Pc(OC_3H_7)_8]_2}$, $\mathrm{Lu[Pc(OC_4H_9)_8]_2}$, and $\mathrm{Lu[Pc(15C5)_4]_2}$ [35–38]. With the provision of synthesized samples from this group, several investigators tried to make further extension of the work in this regard. Xie et al. tried to study the gas-sensing properties of mixed LB films of $\mathrm{Pr[Pc(OC_8H_{17})_8]_2}$ [39], $\mathrm{Sm[Pc(OC_8H_{17})_8]_2}$ [40], and $\mathrm{Er[Pc(OC_8H_{17})_8]_2}$ [41,42] with stearic acid or octadecanol. Liu et al. did preliminary work in order to know the influence of molecular structures on the supramolecular structures formed by LB technique using double-deckers $\mathrm{Eu(Pc)_2}$, $\mathrm{Eu(Pc)[Pc(OC_5H_{11})_8]}$, and $\mathrm{Eu[Pc(OC_5H_{11})_8]_2}$ [43]. Doling et al. reported the $\mathrm{NO_2}$ sensitivity of $\mathrm{Gd[Pc(C_7H_{15})_8]_2}$ LB film [44].

Recently, we have started to pay attention to the formation characteristics of sandwich bis(tetrapyrrole) rare earth complex LB films [45–47]. The aim of the present paper is not only to add more information on the LB film characteristics of bis(phthalocyaninato) rare earth compounds but also to give insight into the influence of the rare earth ionic size as well as the length of alkoxy side chains on the pure LB film formation of bis(phthalocyaninato) rare earth compounds. This also represents the effort of seeking the influence of rare earth metals in sandwich molecules on the interaction between the sandwich molecules. Herein we describe the spectroscopic characteristics and structures of self assemblies of bis[2,3,9,10,16,17,24,25-octakis(octyloxy)phthalocyaninato] complexes for a series of rare earth metals $M\mathrm{[Pc(OC_8H_{17})_8]_2}$ (M = Eu, Dy, Er), Fig. 1, formed by LB techniques.

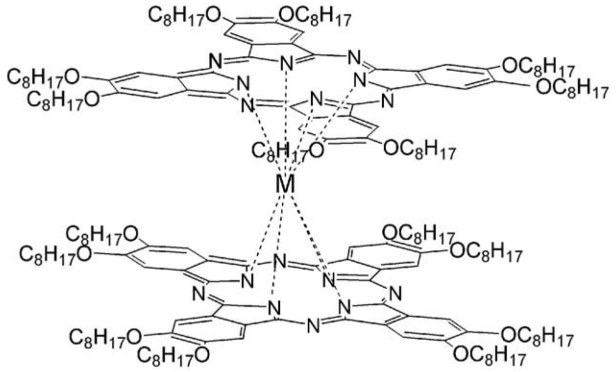

Fig. 1. The schematic molecular structure of $M\mathrm{[Pc(OC_8H_{17})_8]_2}$ (M = Eu, Dy, Er).

2. Experimental section

Homoleptic bis(phthalocyaninato) rare earth compounds $M\mathrm{[Pc(OC_8H_{17})_8]_2}$ (M = Eu, Dy, Er) were synthesized according to the published method [48]. Based on our recent work on the molecular structures of bis(tetrapyrrole) rare earth double-deckers [49–51], the rare earth ion in these homoleptic bis(phthalocyaninato) rare earth compound is believed to occupy a central position between two parallel but staggered (ca. 45°) phthalocyanine rings. Chloroform (chromatographic reagent) was used as received from Beijing Chemical Reagents without further purification.

All the monolayer measurements and LB film deposition were carried out with a NIMA 622 Langmuir–Blodgett trough (Great Britain) with Ehilhelmy Pt-plate kept in a clean room at 25 °C. Pure water (resistivity 18 MΩ $\mathrm{cm^{-1}}$) was used as subphase. $M\mathrm{[Pc(OC_8H_{17})_8]_2}$ (M = Eu, Dy, Er) solution in chloroform with concentration of 2×10^{-5}–3×10^{-5} mol $\mathrm{L^{-1}}$ was spread onto the subphase surface using a microsyringe. The floating *monolayer* was compressed, at a rate of 10 $\mathrm{cm^2\ min^{-1}}$, 15–20 min after spreading when $\mathrm{CHCl_3}$ solvent completely evaporated. LB films of $M\mathrm{[Pc(OC_8H_{17})_8]_2}$ were deposited by using vertical dipping method with a dipping speed of 5 mm $\mathrm{min^{-1}}$ while the surface pressure was kept at 23 mN $\mathrm{m^{-1}}$. The substrates for LB film deposition were hydrophobic quartz plates treated following the standard procedure of Hönig et al. [52]. The transfer ratio is often used as a measure of the quality of deposition. It is defined as the ratio of the area of monolayer removed from the subphase surface to the area of substrate coated by the monolayer. The monolayer of $M\mathrm{[Pc(OC_8H_{17})_8]_2}$ can be easily transferred onto hydrophobic substrates, layer by layer to form LB multilayers. It was found that the even layers had the transfer ratio ranging between 0.9 and 1.1, while the odd layers had a transfer ratio close to 0 except the first one. The monolayer transferred only in upstroke, the deposition mode is referred as Z-type [53]. To investigate the structure using TEM method, the monolayers were deposited onto Formvar-coated, 230 mesh copper grids by subphase-lowering method [54].

The electronic absorption spectra and the polarized absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. For the polarized absorption spectrum recording, a dichroic sheet polarizer was placed in front of the LB films with s- and p-polarized light, respectively. Low angle X-ray diffractions were carried out on a Rigaku D/max-γB X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm). The acceleration voltage is 40 kV, the tube current is 100 mA, and the scan rate is 1°/min. Transmission Electron Microscopy (TEM) images were obtained on a Philips Tecnai 20U-TWI transmission electron microscope with resolution of 0.194 nm.

3. Results and discussion

3.1. Monolayer behavior at the air–water interface

The surface pressure versus area ($\pi-A$) isotherms for the floating monolayers on water subphase at 25 °C are given in Fig. 2. As illustrated in this figure, the bis(phthalocyaninato) rare earth compounds $M[Pc(OC_8H_{17})_8]_2$ (M=Eu, Dy, Er) show similar mode of interface behavior. Stable monolayers of these compounds on the air–water interface can be formed in the pressure range of 15–28 mN m^{-1} and collapse at the pressure of ca. 30 mN m^{-1}. The limiting molecular area obtained by extrapolating the steeply rising part of the $\pi-A$ isotherm curve to zero surface pressure is about 2.3, 2.3, and 2.4 nm^2, respectively, for the bis(phthalocyaninato) complexes of Eu, Dy, and Er [55]. It is obvious that the radius of central rare earth ion gives almost no influence to the monolayer behavior at the air–water interface and the limiting molecular area. This is in line with the work on either the *unsubstituted* bis(phthalocyaninato) or the 2(3),9(10),16(17),24(25)-tetrakis(octyloxy) and 2(3),9(10),16(17),24(25)-tetra(*tert*-butyl) substituted bis(phthalocyaninato) rare earth complexes [29,33]. Similar monolayer behavior at the air–water interface has been observed for $M(Pc)_2$ (M=Pr, Gd, Lu) [33], $M[Pc(OC_3H_7)_4]_2$ (M=Er, Lu) [29], and $M[Pc(tBu)_4]_2$ (M=Er, Lu) [29] under the same experimental conditions, without showing any rare earth ionic size discrimination effect. Moreover, it is worth pointing out that the present result on the limiting molecular area for $M[Pc(OC_8H_{17})_8]_2$, ca. 2.3 nm^2, is rationalized by comparison with the previous data, 1.2 nm^2 for $Sm[Pc(OC_3H_7)_8]_2$ [37], and 2.0 nm^2 for either $Eu[Pc(OC_5H_{11})_8]_2$ [36] or $Gd[Pc(C_7H_{15})_8]_2$ [44], by taking the length of the side chains into consideration. However, it is in contradiction with the limiting molecular area, 2.4 nm^2 obtained for $Lu[Pc(OC_4H_9)_8]_2$, reported by Jones et al. [35]. Systematic investigation on the LB film formation properties over a series of bis(phthalocyaninato) rare earth complexes substituted with eight alkoxy side chains, OC_nH_{2n+1} (n=4, 5, 6, 7, 8, 12, 16), on the peripheral positions is therefore on the way to clarify this problem.

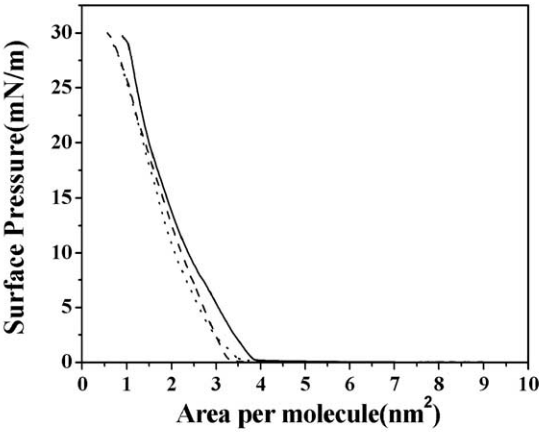

Fig. 2. $\pi-A$ isotherms of $Eu[Pc(OC_8H_{17})_8]_2$ (dotted line), $Dy[Pc(OC_8H_{17})_8]_2$ (dashed line), and $Er[Pc(OC_8H_{17})_8]_2$ (solid line).

For tetrapyrrole macrocycle derivatives, the face-on and edge-on configurations, which are determined according to their molecular orientation on interface, have usually been used to describe the molecular arrangement. The configuration for the phthalocyanine molecules at the air–water interface has been well determined by the limiting molecular area. The limiting area obtained for $M[Pc(OC_8H_{17})_8]_2$ in the present case suggests an edge-on orientation with the $M[Pc(OC_8H_{17})_8]_2$ molecules tilted and assembled with the *main molecular symmetry axis* parallel to the water subphase. Otherwise they should occupy an area much larger than 1.6 × 1.6 nm, 2.6 nm^2, if the phthalocyanine rings lie in the way completely parallel to the subphase surface, i.e. via the face-on arrangement. It is noteworthy that the diagonal distance across a phthalocyanine macrocyclic ring between the two oxygen atoms of the opposite octyloxy groups without considering the hydrocarbon side chains is approximately 1.6 nm according to our recent work on the bis(phthalocyaninato) rare earth molecular structures [56,57]. In other words, similar to other substituted bis(phthalocyaninato) rare earth analogues [29,35,37], $M[Pc(OC_8H_{17})_8]_2$ molecules on the air–water interface form film in a face-to-face configuration and edge-on arrangement on the water surface. This is also consistent with the stacking patterns observed for the substituted monomeric phthalocyanine derivatives [58,59].

3.2. The LB film forming properties

As indicated in the Experimental section, Z-type (upstrokes only) LB films of $M[Pc(OC_8H_{17})_8]_2$ were deposited on the hydrophobic quartz plates by using vertical dipping method with a dipping speed of 5 mm min^{-1} at 23 mN m^{-1}.

Fig. 3 compares the electronic absorption spectra of $Eu[Pc(OC_8H_{17})_8]_2$ in $CHCl_3$ solution and a 22 layers of LB film. In visible region, the absorption spectrum of this compound in $CHCl_3$ solution shows an intense band at 679 nm, corresponding to the Q band of bis(phthalocyaninato) rare earth double-deckers [48,49]. This absorption also appears in the LB film but shifts to the blue, 672 nm, in comparison with that in solution. Similar blue-shift in the Q band of multilayers of $M[Pc(OC_8H_{17})_8]_2$ (M=Dy, Er) LB films has also been observed with respect to their Q absorption in $CHCl_3$ solution. Along with the rare earth contraction, the charac-

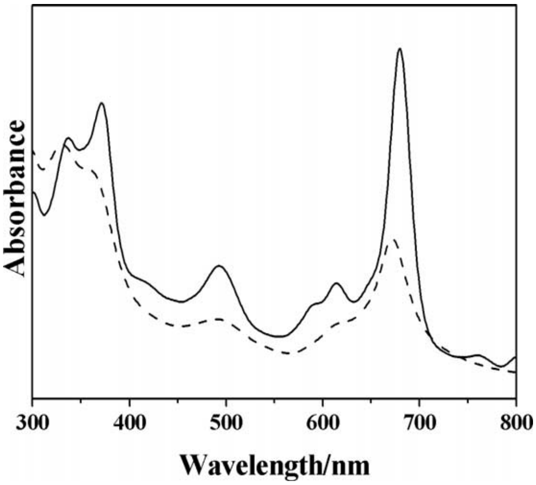

Fig. 3. Electronic absorption spectra of $Eu[Pc(OC_8H_{17})_8]_2]$ in $CHCl_3$ solution (solid line) and 22 layers of LB films (dashed line).

teristic Q band for the double-decker LB films takes a blue-shift, from 672 nm for $Eu[Pc(OC_8H_{17})_8]_2$, to 669 nm for $Dy[Pc(OC_8H_{17})_8]_2$, and 666 nm for $Er[Pc(OC_8H_{17})_8]_2$. This corresponds well with the findings that the Q band of the double-deckers in $CHCl_3$ solution also shifts to the blue, from 679 nm for $Eu[Pc(OC_8H_{17})_8]_2$, to 676 nm for $Dy[Pc(OC_8H_{17})_8]_2$, and 672 nm for $Er[Pc(OC_8H_{17})_8]_2$, along the same order of decreasing the rare earth ionic size [48]. It is worth pointing out that this appears to be the first report dealing with the blue shift of Q band in pure LB films of bis(phthalocyaninato) rare earth complexes using pure water as subphase, which is just in contrast to the results reported thus far. Under the similar experimental conditions, Q absorption of either unsubstituted or substituted bis(phthalocyaninato) rare earth complexes, for example $Lu(Pc)_2$ [25] and $Eu[Pc(OC_5H_{11})_8]_2$ [43], were found to shift to the red in their pure LB films compared with that in solution. These results seem to suggest that the wavelength of Q band in the LB films of bis(phthalocyaninato) rare earth complexes is related with the species and length of side chains incorporated onto the peripheral positions of phthalocyanine ligand. It is therefore interesting to systematically study the characteristics of LB films over a series of bis(phthalocyaninato) rare earth complexes substituted with different length of alkoxy side chains.

Polarized UV-vis absorption spectroscopy of LB films has been found an useful method to determine the orientation of phthalocyanine rings in LB films [35,47]. It is well known that the polarization direction of the $\pi-\pi^*$ transition band for phthalocyanine molecules is parallel to the molecular plane. When the polarized direction of light is parallel to the direction of the excitation dipole moment of the molecule, an intense absorbance can be observed. Otherwise, a weak absorbance will be recorded. The polarized UV-vis absorption spectra of multilayers of $M[Pc(OC_8H_{17})_8]_2$ (M=Eu, Dy, Er) LB films on quartz substrate were recorded with incidence angle of 0° and 45°, respectively. On the basis of method developed by Yoneyama et al. [60], the orientation angle of phthalocyanine rings of bis(phthalocyaninato) rare earth complexes to the quartz plate surface in the LB films can be determined by the following equation.

$$\cos^2\theta = \frac{D_0 - \left(1 + D_0\sin^2\beta\right)D_\beta}{\left(1 - 2\sin^2\beta\right)D_\beta - \left(1 + D_\beta\sin^2\beta\right)D_0}$$

Where θ is the orientation angle of Pc rings. The dichroic ratio D is defined as $A_{//}/A_\perp$, where $A_{//}$ and $A_\perp$ are the absorbances of the film obtained with s- and p-polarized light, respectively. D_0 and D_β are the dichroic ratios when the angles of incidence are 0° and 45°, respectively. $\beta=\sin^{-1}(\sin\beta'/n)$ when $\beta'=45°$, n is the refractive index of the LB films and a value of 1.148 is taken in the present calculation [54]. The results are organized in Table 1. As can be seen, the orientation angles of phthalocyanine rings of bis(phthalocyaninato) rare earth complexes to the quartz plate surface in the LB films have been determined to be 64.6°, 63.5°, and 63.3°, respectively, for the Eu, Dy, and Er compounds. They are bigger in comparison with those reported for the unsubstituted analogues $Eu(Pc)_2$ and $Lu(Pc)_2$, 51° and 53° [43,61]. Again, it is worth mentioning that the central rare earth ionic size seems to exert negligible effect on the LB films of bis(phthalocyaninato) rare earth complexes from the point of orientation of phthalocyanine rings with respect to the quartz plate surface.

Fig. 4 shows the beautiful low angle X-ray diffraction patterns of the 8 layers of LB films of $M[Pc(OC_8H_{17})_8]_2$ (M=Eu, Dy, Er), revealing the excellent molecular ordering of double-deckers in these LB films. According to the (001) Bragg peaks of these LB films, the periodic spacing distance (d) of $Eu[Pc(OC_8H_{17})_8]_2$, $Dy[Pc(OC_8H_{17})_8]_2$, and $Er[Pc(OC_8H_{17})_8]_2$ LB films were calculated to be 2.54, 2.60, and 2.47 nm, respectively. Due to the structures of the Z type LB films of bis(phthalocyaninato) rare earth complexes, the value of d calculated from the low-angle X-ray diffraction is actually the thickness of the monolayer.

Based on the structural investigation over the bis(phthalocyaninato) rare earth complexes [56,57], the thickness of $M[Pc(OC_8H_{17})_8]_2$ molecule is calculated to be ca. 0.55 nm while its macrocycle diameter (actually the distance between the two oxygen atoms of the opposite octyloxy groups) is approximately 1.6 nm without considering the hydrocarbon side chains. The length of a straightened octyloxy side chain is about 1.0 nm according to the CPK model. Provided that $M[Pc(OC_8H_{17})_8]_2$ molecules are densely stacked in a face-to-face configuration in the LB films and take the edge-on arrangement on the water surface, the

Table 1
The orientation angle of phthalocyanine ring to the quartz plate surface in the multilayers of LB films of $M[Pc(OC_8H_{17})_8]_2$ (M=Eu, 22 layers; Dy, 26 layers; Er, 28 layers) determined by polarized UV-vis absorption spectroscopy

Compound	0°			45°			θ (°)
	$A_{//}$	$A_\perp$	D_0	$A_{//}$	$A_\perp$	D_β	
$Eu[Pc(OC_8H_{17})_8]_2$	0.1227	0.0878	1.397	0.1067	0.0963	1.108	64.6
$Dy[Pc(OC_8H_{17})_8]_2$	0.1594	0.1047	1.522	0.1470	0.1221	1.204	63.5
$Er[Pc(OC_8H_{17})_8]_2$	0.2150	0.1279	1.681	0.1826	0.1413	1.292	63.3

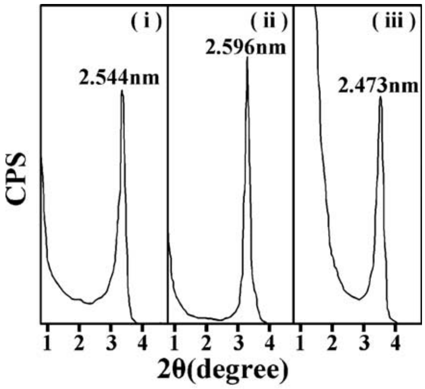

Fig. 4. Low angle X-ray diffraction patterns of the 8 layers of LB films of (i) $Eu[Pc(OC_8H_{17})_8]_2$, (ii) $Dy[Pc(OC_8H_{17})_8]_2$, and (iii) $Er[Pc(OC_8H_{17})_8]_2$.

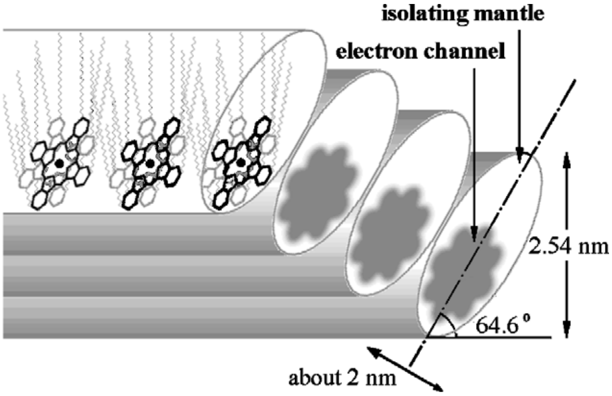

Fig. 6. Schematic representation of the molecular cables formed by aggregates of $Eu[Pc(OC_8H_{17})_8]_2$ molecules in LB films.

average molecular space would approximately be 1.9 nm^2 [$1.6 \times (1.6 \times \cos 64° + 0.55 \times \sin 64°)$] in the case that all the octyloxy side chains are straightened perpendicularly to the subphase surface. Actually, the octyloxy side chains bound to the middle phthalocyanine ring may have some contributions to the molecular areas. The actual molecular area thus should be larger than 1.9 nm^2. This is in line with the limiting molecular area of $M[Pc(OC_8H_{17})_8]_2$ obtained from the $\pi-A$ isotherms as discussed above, about 2.3 nm^2. With the orientation angle of phthalocyanine rings to the quartz plate surface in the LB films of $M[Pc(OC_8H_{17})_8]_2$, ca. 64° (Table 1), the thickness of the monolayer in the LB films should approximately be 2.7 nm ($0.55 \times \cos 64° + 1.6 \times \sin 64° + 1.0$). This is also in good accordance with that deduced from the low angle X-ray diffraction method, 2.47–2.60 nm, for these three double-decker complexes.

Fig. 5 displays the high-resolution TEM images of $Eu[Pc(OC_8H_{17})_8]_2$ monolayer on the Formvar-coated, 230 mesh copper grids. A series of parallel rodlike nanowires can be seen in this photograph. The widths of which are estimated to be ca. 2.0 nm. This is approximately the Pc macrocycle diameter [62]. It thus can be concluded that these rodlike nanowires observed are of monomolecular width. In these monomolecular wires, two types of non-covalent interactions between the sandwich molecules, i.e. $\pi-\pi$ interaction between the macrocycle rings and hydrophobic interaction between the octyloxy side chains, are considered to be responsible for the formation of the *supramolecular assemblies* on the air–water interface, which are maintained after transfer to the solid supports. The supramolecular $\pi-\pi$ interaction can be attested by the result of polarized UV-vis absorption spectroscopy. Separate monomolecular wires are collocated side by side by the interaction of Van der Waals attraction. The schematic parallel aggregates of $Eu[Pc(OC_8H_{17})_8]_2$ molecules in LB films are represented in Fig. 6. The isolated strands of molecules can be considered as molecular cables, which contain a central electron-transporting channel of stacked bis(phthalocyaninato) rare earth supramolecular structures surrounded by an insulating hydrocarbon mantle [3]. These arrays of parallel molecular cables in LB films should lead to anisotropic electron-conducting properties and may find application in molecular electronics. It must be pointed out that similar ordered rodlike aggregates of monomeric phthalocyanines substituted with

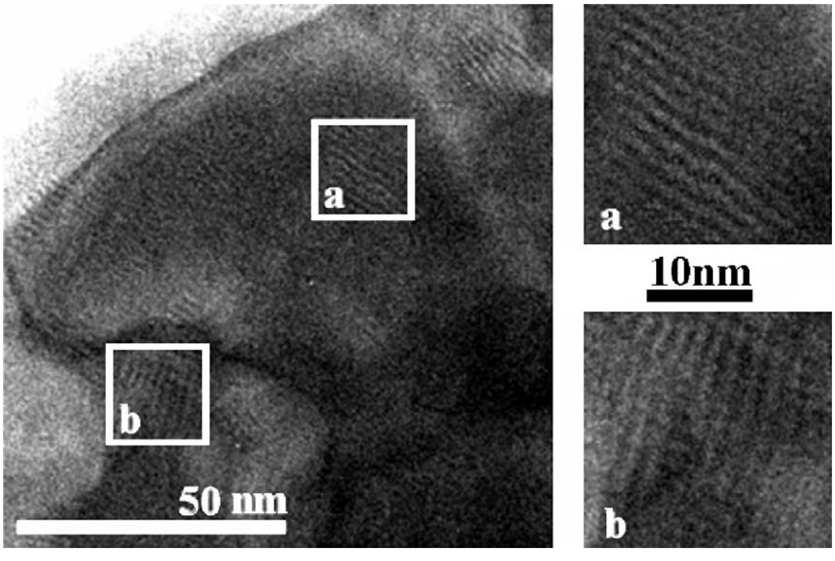

Fig. 5. The high-resolution TEM images of $Eu[Pc(OC_8H_{17})_8]_2$ monolayer.

eight 2-benzyloxyethoxy groups at the peripheral positions has also been found to be formed at the air–water interface [63–65].

4. Conclusion

A series of three bis(phthalocyaninato) rare earth complexes $M[Pc(OC_8H_{17})_8]_2$ (M=Eu, Dy, Er) have been found to form stable monolayer at the air–water interface and fabricated into multilayer films by LB technique. Comparative studies over the monolayer behavior and the spectroscopic and structural characteristics of their LB films for these three double-decker complexes containing different rare earth ions reveals that the difference in the rare earth ionic size is too small to exert obvious effect on the structure and inter-molecular interaction in the ordered assemblies of these bis(phthalocyaninato) rare earth complexes. The well-ordered rodlike aggregates of bis(phthalocyaninato) rare earth complexes formed in LB films may find application in molecular electronics.

Acknowledgements

Financial support from the National Science Foundation of China (Grant No. 20171028, 20325105, 20431010), National Ministry of Science and Technology of China (Grant No. 2001CB6105), Ministry of Education of China, and Shandong University is gratefully acknowledged.

References

[1] G.M. Whitesides, J.P. Mathias, C.T. Seto, Science 254 (1991) 1312.
[2] J.-M. Lehn, Angew, Chem. Int. Ed. Eng. 27 (1988) 89.
[3] C.F. van Nostrum, S.J. Picken, A.-J. Schouten, R.J.M. Nolte, J. Am. Chem. Soc. 117 (1995) 9957.
[4] A.B.P. Lever, C.C. Leznoff, Phthalocyanine: Properties and Applications, Vols. 1–4, VCH, New York, 1989–1996.
[5] N.B. McKeown, Phthalocyanines Materials: Synthesis, Structure and Function, Cambridge University Press, New York, 1998.
[6] K.W. Poon, W. Liu, P.-K. Chan, Q. Yang, T. Chan, J. Org. Chem. 66 (2001) 1553.
[7] J. Jiang, W. Liu, W.-F. Law, Inorg. Chim. Acta. 268 (1998) 49.
[8] J. Jiang, W. Liu, K.W. Poon, D. Du, D.P. Arnold, Eur. J. Inorg. Chem. (2000) 205.
[9] J. Jiang, W. Liu, K.-L. Cheng, K.W. Poon, Eur. J. Inorg. Chem. (2001) 413.
[10] J. Jiang, F. Furuya, T. Nyokong, D. Du, W. Liu, N. Kobayashi, Inorg. Chem. 39 (2000) 128.
[11] J. Jiang, K. Kasuga, D.P. Arnold, in: H.S. Nalwa (Ed.), Supramolecular Photosensitive and Electroactive Materials, Academic Press, New York, 2001, p. 113, chapter 2.
[12] G. Wegner, Mol. Cryst. Liq. Cryst. 235 (1993) 1.
[13] T. Sauer, T. Arndt, D.N. Batchelder, A.A. Kalachev, G. Wegner, Thin Solid Films 187 (1990) 357.
[14] J.-H. Wu, G. Lieser, G. Wegner, Adv. Mater. 8 (1996) 151.
[15] R. Silerová, L. Kalvoda, D. Neher, A. Ferencz, J. Wu, G. Wegner, Chem. Mater. 10 (1998) 2284.
[16] S. Englekamp, R. Meddelbeek, R.J.M. Nolte, Science 284 (1999) 785.
[17] S. Palacin, Adv. Colloid Interface Sci. 87 (2000) 165.
[18] D. Battisti, R. Aroca, J. Am. Chem. Soc. 114 (1992) 1201.
[19] R. Aroca, H. Bolourchi, D. Battisti, K. Najafi, Langmuir 9 (1993) 3138.
[20] M.L. Rodriguez-Mendez, R. Aroca, J.A. de Saja, Spectrochimica Acta. 49A (1993) 965.
[21] K.R. Rickwood, D.R. Lovett, B. Lukas, J. Silver, J. Mater. Chem. 5 (1995) 725.
[22] J. Souto, R. Aroca, J.A. de Saja, J. Phys. Chem. 98 (1994) 8998.
[23] J. Souto, M.L. Rodriguez-Mendez, J. de Saja-Gonzaler, J.A. de Saja, Thin Solid Films 284–285 (1996) 888.
[24] A. Dhanabalan, L. Gaffo, A.M. Barros, W.C. Moreira, O.N. Oliveira Jr., Langmuir 15 (1999) 3944.
[25] R.E. Clavijo, D. Battisti, R. Aroca, G.J. Kovacs, C.A. Jennings, Langmuir 8 (1992) 113.
[26] Y. Liu, K. Shigehara, A. Yamada, Thin Solid Films 179 (1989) 303.
[27] M. Petty, D.R. Lovett, J.M. O'Connor, J. Silver, Thin Solid Films 179 (1989) 387.
[28] L. Caffo, C.J.L. Constantino, W.C. Moreira, R.F. Aroca, O.N. Oliveira Jr., Langmuir 18 (2002) 3561.
[29] Y. Liu, K. Shigehara, M. Hara, A. Yamada, J. Am. Chem. Soc. 113 (1991) 440.
[30] J. Souto, L. Tomilova, R. Aroca, J.A. de Saja, Langmuir 8 (1992) 942.
[31] M.L. Rodriguez-Mendez, M.I. Gobernado-Mitre, J. Souto, J. de Saja-Gonzaler, J.A. de Saja, Sensors and Actuators B 24–25 (1995) 643.
[32] Y. Vertsimakha, Synthetic Metals 109 (2000) 287.
[33] M.L. Rodriguez-Méndez, Y. Gorbunova, J.A. de Saja, Langmuir 18 (2002) 9560.
[34] A. Arrieta, M.L. Rodriguez-Mendez, J.A. de Saja, Sensors and Actuators B 95 (2003) 357.
[35] R. Jones, R.A. Hunter, K. Davidson, Thin Solid Films 250 (1994) 249.
[36] R. Jones, A. Krier, K. Davidson, Thin Solid Films 298 (1997) 228.
[37] Y. Gorbunova, M.L. Rodriguez-Méndez, I.P. Kalashnikova, L.G. Tomilova, J.A. de Saja, Langmuir 17 (2001) 5004.
[38] M.L. Rodriguez-Mendez, J. Souto, J. de Saja-Gonzaler, J.A. de Saja, Sensors and Actuators B 31 (1996) 51.
[39] D. Xie, Y. Jiang, W. Pan, J. Jiang, Z. Wu, Y. Li, Thin Solid Films 406 (2002) 262.
[40] D. Xie, Y. Jiang, W. Pan, Y. Li, Thin Solid Films 424 (2003) 247.
[41] D. Xie, Y. Jiang, J. Jiang, Z. Wu, Y. Li, Sensors and Actuators B 77 (2001) 260.
[42] D. Xie, W. Pan, Y. Jiang, Y. Li, Mater. Lett. 1–4 (2002) 4171.
[43] H. Liu, X. Feng, J. Jiang, L. Zhang, W. Lan, Y.-L. Lee, K.-W. Jang, D. Qian, K. Yang, Mater. Sci. Eng. C 23 (2003) 501.
[44] C.M. Doling, T.H. Richardson, L. Vali, R. Rella, J. Jiang, Colloids and Surfaces A 198–200 (2002) 791.
[45] D. Qian, H. Liu, J. Jiang, Colloids and Surfaces A 163 (2000) 191.
[46] H. Liu, X. Feng, L. Zhang, J. Jiang, Y.-L. Lee, K.-W. Jang, D. Qian, K. Yang, Mater. Lett. 57 (2003) 2156.
[47] Y. Chen, H. Liu, N. Pan, J. Jiang, Thin Solid Films 460 (2004) 279.
[48] W. Liu, J. Jiang, D. Du, D.P. Arnold, Aust. J. Chem. 53 (2000) 131.
[49] Y. Bian, J. Jiang, Y. Tao, M.T.M. Choi, R. Li, C.H.Ng. Anthony, P. Zhu, N. Pan, X. Sun, D.P. Arnold, Z. Zhou, H.-W. Li, T.C.W. Mak, K.P.Ng. Dennis, J. Am. Chem. Soc. 125 (2003) 12257.
[50] J. Jiang, Y. Bian, F. Furuya, W. Liu, M.T.M. Choi, N. Kobayashi, H.-W. Li, Q. Yang, T.C.W. Mak, K.P.Ng. Dennis, Chem. Eur. J. 7 (2001) 5059.
[51] F. Lu, X. Sun, R. Li, D. Liang, P. Zhu, X. Zhang, C.-F. Choi, K.P.Ng. Dennis, T. Fukuda, N. Kobayashi, J. Jiang, New J. Chem. 28 (2004) 1116.
[52] E.P. Hönig, J.H.T. Hengst, D.D. Engelsen, J. Colloid Interface Sci. 45 (1973) 92.
[53] J.F. Liu, K.Z. Yang, Z.H. Lu, J. Am. Chem. Soc. 119 (1997) 11061.
[54] H.-Q. Xiang, K. Tanaka, A. Takahara, T. Kajiyama, Langmuir 18 (2002) 2223.
[55] R.D. Shannon, Acta Cryst. A 32 (1976) 751.
[56] Y. Bian, R. Wang, J. Jiang, C.-H. Lee, J. Wang, K.P.Ng. Dennis, Chem. Commun. (2003) 1194.
[57] Y. Bian, R. Wang, D. Wang, P. Zhu, R. Li, J. Dou, W. Liu, C.-F. Choi, H.-S. Chan, C. Ma, K.P.Ng. Dennis, J. Jiang, Helv. Chim. Acta. 87 (2004) 2581.
[58] C.F. van Nostrum, R.J.M. Nolte, J. Chem. Soc., Chem. Commun. (1996) 2385.
[59] P. Smolenyak, R. Peterson, K. Nebesny, M. Torker, D.F. O'Brien, N.R. Armstrong, J. Am. Chem. Soc. 121 (1999) 8628.

[60] M. Yoneyama, M. Sugi, M. Saito, Jpn. J. Appl. Phys. 25 (1986) 961.
[61] B. Lukas, R.E. Lovett, J. Silver, Thin Solid Films 210/211 (1992) 213.
[62] J.M. Robertson, J. Chem. Soc. (1936) 1195.
[63] S.A. Drager, R.A.P. Zangmeister, N.R. Armstrong, D.F. O'Brien, J. Am. Chem. Soc. 123 (2001) 3595.
[64] R.A.P. Zangmeister, P.E. Smolenyak, A.S. Drager, D.F. O'Brien, N.R. Armstrong, Langmuir 17 (2001) 7071.
[65] C.L. Donley, W. Xia, B.A. Minch, R.A.P. Zangmeister, A.S. Drager, K. Nebesny, D.F. O'Brien, N.R. Armstrong, Langmuir 19 (2003) 6512.