Optically Active Phthalocyaninato−Polysiloxane Constructed from Achiral Monomers: From Noncovalent Assembly to Covalent Polymer

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ABSTRACT: In this paper, we reported that optically active supramolecular assemblies of an achiral phthalocyanine derivative, silicon 2,3,9,10,16,17,23,24-octakis(octyloxy)-29*H*,31*H*-phthalocyanine dihydroxide (*Pc* 1), could be easily achieved through the Langmuir and Langmuir−Schaefer (LS) technique. We have found that the LS film of Pc 1 showed weak Cotton effect (CE) when it was subjected to the circular dichroism (CD) measurements. The chirality of the LS film was suggested to be due to the spontaneous symmetry breaking occurred at the air/water interface. More interestingly, such assemblies connected through the noncovalent bond could be further converted into covalent bond under heating at 180 °C in a high vacuum for 10 h. UV−vis spectra and FT-IR have confirmed the polymerization of Pc 1 in the LS film during the heating, which resulted in the formation of the corresponding phthalocyaninato−polysiloxane (PcPs 2) polymer. Stronger Cotton effect was detected for the thin solid film of PcPs 2 compared with that of the Pc 1 LS film, suggesting that more efficient exciton coupling existed between the covalently linked phthalocyanine chromophore in the polymer PcPs 2. The investigation provided an easy way of constructing optically active polymeric PcPs films exclusively from achiral monomer unit by the preassembly of monomer through interfacial organization.

Introduction

Phthalocyanine derivatives (Pc) are one of the most important functional dyes that have unique properties related to advanced materials and devices.[1] Among various Pcs, phthalocyaninato−polysiloxane (PcPs) are particularly interesting because of their conductivity, one-dimensionality and high stability, and thus have received continuous attention during the past decades.[1a,2,3] Besides other properties, optically active assemblies of Pc and PcPs have also been intensively investigated, because they are inclined to cofacially stack and may arrange in one-dimensional helical superstructure, which is the most fascinating and beautiful structures found in nature. Additionally, much more intense Q-band of Pcs corresponding to the longest allowed transition is helpful for researchers to have a deep insight into the generation mechanism of the circular dichroism (CD).[4] So far, lots of systems on the chiral assemblies of Pcs and PcPs have been established. For examples, Nolte and co-workers have reported that Pcs monomers bearing peripherally chiral side groups on the molecular skeletons could be assembled and/or polymerized into optically active helical supramolecular assemblies and/or polymers.[5−7] More recently, Watarai et al. have reported the formation of helical J-aggregate of chiral thioether-derivatized phthalocyanine bound by palladium(II) at the toluene/water interface.[8a] They also have found that the optically activities of thioether-phthalocyanine aggregates could be well controlled by chiral Pd(II)−BINAP complexes in toluene and at the toluene/water interface.[8b] Kobayshi and co-workers have recently studied the synthesis and self-organization properties of adjacent-type metal phthalocyanines (MPc) substituted with long branched alkyl chains and an optically active bridging unit. They suggested that the low symmetry of the MPc building blocks provides new opportunities for the construction of well-defined supramolecular organizations.[9a] The group has also found that ZnPc functionalized with a chiral diol and chiral branched alkyl chains could form a stable optically active dimer in chloroform solution through the formation of an intermolecular hydrogen bond between two diol groups.[9b] Fujiki and co-workers have demonstrated that homochiral NiPc molecules, bearing four enantiomerically pure 1-(*p*-tolyl)ethylaminocarbonyl groups at their peripheral positions, could self-assembly into mesoscopic supramolecular helical fibers in a solution and on solid surfaces.[10] It however seems that the ever addressed chiral Pcs and/or PcPs assemblies to date are constructed by using Pcs and PcPs building blocks that have intrinsically chiral groups on the molecular or polymer skeleton, or induced by a chiral inducer.[4−12] Considering the difficulty in synthesizing the chiral molecules than achiral building blocks, it is also very important to establish a facile way to assemble the optically active Pcs and PcPs assemblies exclusively using the achiral building blocks.

Previously, we have found that achiral molecules could be assembled into chiral assemblies through the interfacial organization, owing to the symmetry breaking at the air/water interface.[13,14] In this paper, we present our interesting results on the fabrication of optically active Pcs assemblies by employing an achiral dihydroxy(phthalocyanine)silicon, silicon 2,3,9,10,16,17,23,24-octakis(octyloxy)-29*H*,31*H*-phthalocyanine dihydroxide (Pc 1, shown as an insert in Figure 1), through the interfacial assembly. The strategy involved two steps (Scheme 1). First, the achiral Pc 1 was faricated into optically active assemblies through the Langmuir−Schaefer (LS) method. Second, a subsequent polymerization in the LS film at 180 °C in vacuo resulted in the formation of optically active PcPs 2. So far as the optically active Pcs and PcPs have been studied, we presented the first example that optically active assemblies of Pc and PcPs could be derived from the wholly achiral

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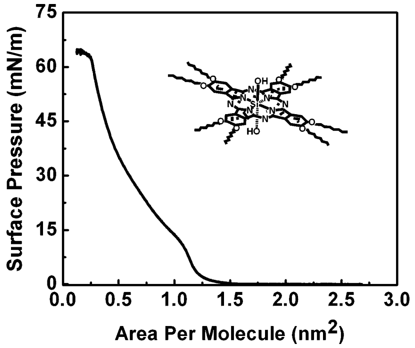
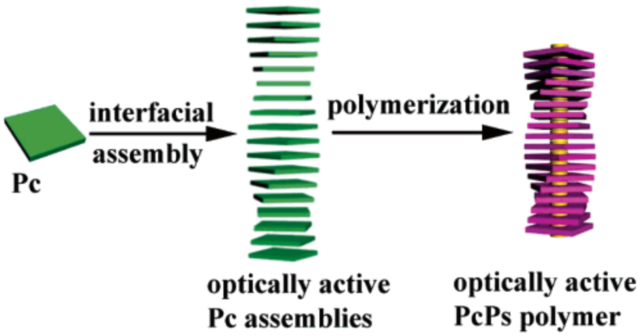


Figure 1. Surface pressure-molecular area (π−A) isotherm of Pc 1 on Milli-Q water at 20 °C. Inset: chemical structure of Pc 1.

Scheme 1. Illustration of the Fabrication of Optically Active Pcs Assemblies and PcPs Polymer through Interfacial Organization and the Subsequent Polymerization[a]



[a] The green bricks represent the achiral monomers Pc 1. When this achiral Pc was assembled at the air/water interface, it mainly formed H-aggregate (middle), where a helical stacking of the macrocyclic rings was formed due to the spontaneous symmetry breaking. The purple bricks represent the optically active polymer PcPs 2, which was formed due to the polycondensation of the Si−OH group to the Si−O−Si (yellow rods) connected polymer. The helical structure was kept after the polymerization. The alkyl chains, Si−OH were not shown for clarity.

monomer without introduction of any chiral units or seeds. The significances of the results are twofold. First, we have verified that achiral Pc could form chiral molecular assemblies through the interfacial organization. Second and more importantly, thus-formed supramolecular chirality could be further fixed through the conversion of the noncovalent bond to covalent bond.

Experimental Section

Materials and Producers. Silicon 2,3,9,10,16,17,23,24-octakis(octyloxy)-29*H*,31*H*-phthalocyanine dihydroxide (Pc 1) was purchased from Aldrich. The apparatus employed for measuring surface pressure−area (π−A) isotherms and depositing multilayer LS films is a computer-controlled KSV-1100 film balance (KSV instruments, Helsinki, Finland). The solution of Pc 1 in chloroform (1×10^{-4} M) was dropped by a syringe onto the pure Millipore water (18.2 MΩ cm, 20 °C) surface, after waiting 20 min for the evaporation of the solvent, the π-A isotherm was recorded by compressing the film with a rate of 2 mm min^{-1}. The floating film was transferred by the horizontal lifting method onto CaF_2 and/or quartz and single face polished silicon slice (for UV−vis, CD, SEM and FT-IR investigations) slides, at 20 and/or 62.5 mN/m, to obtain multilayer LS films of Pc 1. The polymerization was performed by heating the samples at 180 °C in vacuo for 10 h. After being cooled to room temperature, they were again subjected to the above measurements. The dehydration−polymerization reaction from monomer Pc 1 to polymer PcPs 2 had been confirmed by the FT-IR spectrum. The resulted LS film of the polymer was put into chloroform under ultrasound, and the degree of polymerization of thus synthesized polymer PcPs 2 was investigated in positive ion detection mode by matrix-assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectrometry. For parallel experiments, the cast films were fabricated by dropping the solution of Pc 1 in chloroform onto the substrate surface by using a syringe. After the evaporation of the solvent, the casting film was then subjected to the above-mentioned investigations.

In order to obtain UV−vis and CD spectra with good quality, 40-layer LS film was fabricated at 20 mN/m. In the case of the collapsed LS film deposited at 62.5 mN/m, we deposited film with 28-layer, since it had approximately the same UV−vis absorption intensity as that of the 40-layer LS film deposited at 20 mN/m.

Apparatus and Measurements. JASCO UV-530 spectrophotometer and JASCO J-810 CD spectropolarimeter were employed for the UV−vis and CD spectra measurements, respectively. In the measurement of the CD spectra, the samples were placed perpendicular to the light path and rotated within the film plane in order to avoid the polarization-dependent reflections and eliminate the possible angle dependence of the CD signal. The angle dependence behavior of all 36 CD spectra, which were measured in steps of 10° about the optical axis, was determined as described elsewhere.[13−15] The SEM measurement was performed by using a Hitachi S-4300 system. In order to obtain SEM figures of the samples, about 30 nm Pt was deposited on the sample surface by vacuum deposition. FT-IR spectra of the samples were measured using a JASCO 660. The MALDI−TOF mass spectrometry of the samples was investigated on BIFLEX III MALDI−TOF mass spectrometer (Bruker Inc.) equipped with a pulsed N_2 laser (337 nm). The laser intensity was 210 mJ. Operating conditions were set as follows: ion source 1 = 19.00 kV, ion source 2 = 14.50 kV, lens voltage = 7.00 kV, optimized pulsed in extraction time = 5000 ns, and positive liner mode. The matrix employed for the MALDI−TOF MS experiments is α-cyano-4-hydroxycinnamic acid (CCA).

Results and Discussions

Surface Pressure—Molecular Area Isotherms of Langmuir Film of Pc 1 at Air/Water Interface and the Polymerization of Pc 1 in the Transferred LS Films. Pc 1 was spread from chloroform solution onto Milli-Q water surface at 20 °C, and reproducible surface pressure-molecular area (π-A) isotherm was obtained. As shown in Figure 1, Pc 1 could form a stable floating Langmuir monolayer at the air/water interface, which was collapsed at 62.5 mN/m. The molecular area of 1.25 nm^2 deduced from the isotherm indicated the formation of monolayers on the subphase surface.[16]

Multilayer LS films of Pc 1 on solid supports deposited at selected surface pressures can be achieved by a horizontal transferring method. UV−vis spectra a, b, and c in Figure 2 give the absorbance spectra of Pc 1 in chloroform solution, in a 40-layer LS film deposited at 20 mN/m before and after polymerization reaction, respectively. A strong absorption band maximum at 680 (Q_{0-0}), two shoulders at 650 (Q_{1-0}), 613 (Q_{2-0}) nm, and 430, 358, 300 nm (B-bands), were observed from the UV−vis spectrum of the chloroform solution. Formulated as LS film, the B-bands almost kept unchanged, whereas Q_{0-0} became broadened and blue-shifted to a new band centered at 641 nm, suggesting that Pc 1 monomers took H-aggregation in the supramolecular assemblies. When the LS

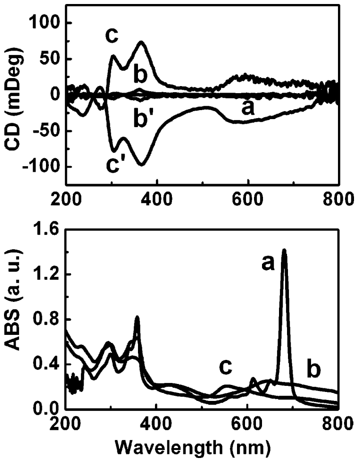


Figure 2. Bottom: UV−vis spectra of Pc 1 in chloroform solution (a), in a 40-layer LS film transferred at 20 mN/m before (b) and after (c) the polymerization. Top: CD spectra of 40-layer LS films of Pc 1 deposited at 20 mN/m in different batches before (b and b', respectively) and after (c and c′, respectively) the polymerization and CD spectra of Pc 1 in chloroform solution (a).

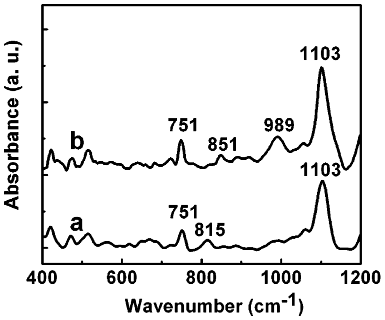


Figure 3. FT-IR of a 40-layer LS film of Pc 1 before (a) and after (b) polymerization. The LS film was deposited at 20 mN/m.

film was heated at 180 °C in vacuo for 10 h, the Q-band became more broadened and further blue-shifted to 550 nm. This confirmed the achievement of polymerization reaction from the noncovalent assembly of monomer Pc 1 to covalent polymer PcPs 2, where the macrocyclic rings were covalently and tightly connected in a cofacial geometry through a polysiloxane backone.[2,3] These dramatic spectral changes are due to the fact that covalently stacking of the Pc 1 units in the PcPs 2 polymer caused more close inter-ring distance (0.33 nm) which favor efficient intermacrocyclic $\pi-\pi$ interactions.[3] Comparatively, the Q-band of the LS film before and after the polymerization reaction both exhibit apparent blue-shifts compared with that in the chloroform solution, while a more dramatic blue-shift was observed for the latter case. This suggested that more efficient exciton coupling existed between the covalently and closely linked Pc chromophore units in the polymer PcPs 2.[3] Whereas the axially attached hydroxyl groups on the macrocyclic ring of the Pc 1 could arise a steric hindrance and thus weaken the $\pi-\pi$ interactions between the Pc 1 units before the polymerization. The degree of polymerization of thus synthesized polymer PcPs 2 was evaluated to be about 27 according to the semiempirical method proposed by Fujiki and co-workers (see Supporting Information).[6,17]

The dehydration−polymerization reaction from monomer 1 to polymer 2 has also been confirmed by the FT-IR spectrum, as shown in Figure 3. The vibrational bands at 751 and 1103 cm^{-1}, ascribing to the aromatic C−H out-of and in-plane bending mode of the Pc ring, respectively, kept their styles after the polymerization. Upon heating, the band at 815 cm^{-1}, assigned to the local O−Si−O antisymmetric stretch disappeared, accompanied by the appearance of a new band at 989 cm^{-1}, which can be assigned to the antisymmetric Si−O−Si stretch. The newly appeared peak at 851 cm^{-1} after the polymerization was one of the typical band of PcPs.[2a] This confirmed the realization of the dehydration−polymerization reaction from monomer 1 to polymer 2.[2b]

Optically Active Properties of the Thin Solid Films. As expected, Pc 1 gave no CD signal in chloroform solution, as indicated in Figure 2. However, when its 40-layer LS film deposited at 20 mN/m was subjected to the CD spectral measurements, it is interesting to observe a weak Cotton effect (CE) around 358 nm, corresponding to the B-band of the monomer. While the CD signals from the Q-band are too weak to be detected. As shown in Figure 2, it was found that the weak CD signals of Pc 1 in LS films could show both positive and negative values for the films deposited in the different batches in most of the cases. These facts indicated that the observed macroscopic chirality was indeed not from any chiral impurities but from the chiral supramolecular assemblies of Pc 1 units, where the achiral building blocks were cooperatively stacked in helical sense columns, as shown in Scheme 1. This phenomenon is essentially the same as those reported on the chirality of the films obtained from achiral building blocks.[13,14,18] Due to the interaction between the adjacent Pc rings and the OH groups, the monomer unit took a cooperative arrangement along a preferential direction (right- or left-handed), resulting in the optically active assembly.

Much more interestingly, when thus-formed Pc 1 assemblies were subjected to the polymerization, remarkable increment of the CD signals was observed. As shown in Figure 2, after the as-deposited LS film was heated at 180 °C in vacuo for 10 h for polymerization, distinct CD signals at 560 nm corresponding to the Q-band of PcPs 2 was observed. Simultaneously, CD signals corresponding to the B-bands of PcPs 2 at 362, 300, 275, and 240 nm increased significantly. Two crossovers were observed at 287 and 258 nm in the CD curves of PcPs 2. These results confirmed that strong efficient exciton coupling existed between the neighboring Pc chromophore units in polymer PcPs 2.

In the CD measurement, we further found that once a certain CD signal was obtained for the LS film before the polymerization, the CD signal that detected after the polymerization would have the same signs. Therefore, we can suggest that the macroscopic chirality of the film was formed in the assembly stage. The polymerization has two effects on the CD signals. First, polymerization fixed the helical staking of the Pc 1 assembly from noncovalent bond to the covalent bond. Second, owing to the polymerization, the CD intensity is remarkably amplified due to the covalently and tightly packing of the macrocyclic ring. It should be noted that during the polymerization, the preformed Pc 1 assemblies played an important role in the subsequent covalent polymer, which followed the chirality of the initially formed chirality of the noncovalent assemblies. This is somewhat similar to the case of the Sergeants and Soliders rule in the amplification of the chirality.[19]

In order to solidly confirm that PcPs 2 really has genuine intrinsic macroscopic chirality, we have measured the angle dependence of the CD spectra, which were operated by measuring the CD spectra in a step of 10°around the optical axis.[13−15] The angle dependence of the CD amplitude was determined by the difference between the maximum value at 367 nm and minimum value at 277 nm, and the corresponding angle dependence of the background was determined by the

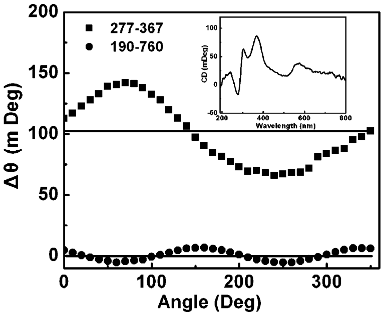


Figure 4. Angle dependence of the CD amplitude (■) and the background (●) of the CD spectra of the thin solid film of PcPs 2, which was fabricated by polymerization of the LS film of Pc 1 deposited at 20 mN/m. The film was turned about the optical axis in a step of 10° within the sample plane. The CD spectrum employed for the extraction measured by rotating the sample within its plane is presented as an insert.

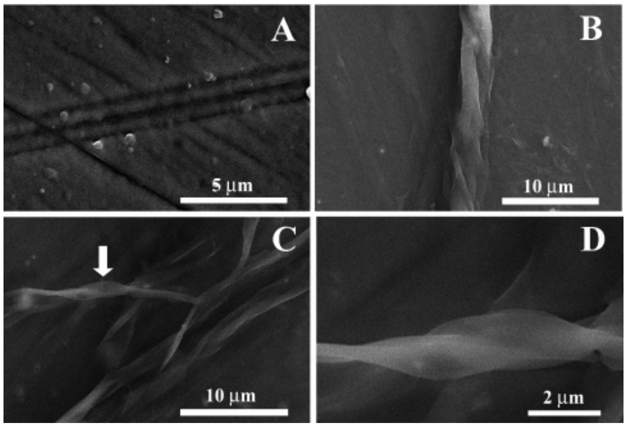


Figure 5. SEM images of LS of Pc 1 deposited at 20 (A) and 62.5 (B, C and D) mN/m. Key: (A, B) before polymerization; (C) after polymerization; (D) enlarged image corresponding to the marked section in part C. 40- and 28-layer LS films were used for image A, and the last three images, respectively.

difference between the values at the lower edge at 190 nm and upper wavelength edge at 760 nm, which were shown as filled squares and circles, respectively, in Figure 4. In the case of angle dependence of the background, the observed differences between the values at the upper wavelength and lower edges fluctuated around zero millidegree. Whereas, that of amplitude, exhibiting as a single cosine function, fluctuated around 103 millidegree, which was positively shifted about 103 millidgrees compared with that of the background. This apparently indicated that the sample indeed had genuine intrinsic charilty.[13−15]

Comparatively, we have cast the Pc 1 solution onto the quartz plates and done parallel experiment as in the case of LS films described above. Although polycondensation occurred in the cast film also, they did not show any CD signals. This strongly suggested that interfacial preorganization of Pc 1 was of great importance for obtaining the optically active thin solid film of polymer PcPs 2.

SEM Image of the LS Films. A further support for the macroscopic chirality as well as the helical structures of the films was stemmed from the SEM observation. Figure 5 shows the SEM pictures before and after the polymerization. Before the polymerization, a homogeneous film without any notable feature was observed from the SEM image of the LS film deposited at 20 mN/m (figure not shown). Nanofibers (width: ca. 550 nm) with indistinct helical structure could be constrainedly observed from the SEM image of the film after the polymerization, as shown in Figure 5A. This limply suggested the polymer PcPs 2 really has a helical structured conformation, which is in agreement with the CD spectra investigations. Because the LS film is too flat to be observed clearly by SEM, we have transferred collapsed film (at 62.5 mN/m) onto solid substrate for further SEM confirmation. In the UV−vis and CD spectral measurement, they showed the same absorption bands and CD signals as those deposited at 20 mN/m. In addition, the same spectral changes occurred for the collapsed films after polymerization (see Supporting Information). As shown in Figure 5, parts B, C, and D, apparent helical fibers (width: ca. 1.5 μm) were detected both before and after the polymerization. The widths of the observed helical fibers, however, are evidently larger than the dimension of the investigated molecules, indicating the observed helical fibers are actually the supercoils formed by the twisting of the supramolecular assemblies of Pc 1 and/or PcPs 2.[5] This result undoubtedly proved that the noncovalent $\pi-\pi$ stacking induced columnar supramolecular stacks of Pc 1 and the covalently connected polymer PcPs 2 surely have helical sense conformations, which strongly support the deduction form the CD spectra.

Conclusions

In summary, we have shown that an achiral dihydroxy(phthalocyanine)silicon could be interfacially assembled to form macroscopically optically active LS films, where the achiral building blocks were arranged in a helical sense stacking. Such helical sense supramolecular assemblies exhibited faint Cotton effect. Upon subsequent polymerization, the helical stacking was fixed through the conversion of noncovalent interactions to covalent bond, resulting in the remarkable increasing of the Cotton effect of convalent polymer phthalocyaninato−polysiloxane. The results described here provided a strategy for constructing optically active thin solid polymeric films exclusively from achiral monomer unit by the pre-assembly of monomer through interfacial organization.

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Supporting Information Available: Figures showing MALDI−TOF MS of the PcPs polymer and related data about the LS film deposited at 62.5 mN/m and cast film. This material is available free of charge via the Internet at http://pubs.acs.org.

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