

Alkali metal ions regulate the supramolecular chirality of interfacial assembly of achiral phthalocyanine

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ABSTRACT

Because of their unique optical, electrical, and magnetic properties, fabrication of novel phthalocyanines supramolecular assemblies is becoming extremely important. However, developing phthalocyanines assemblies with tunable supramolecular chirality is still difficult due to the good planarity of phthalocyanine molecules, which could induce strong π - π interaction and tight aggregation. Herein, the supramolecular chirality of interfacial assembly of achiral phthalocyanine was thoroughly regulated by simply using different alkali metal ions. Achiral phthalocyanine with crown ether substituents ($\text{H}_2\text{Pc}(15\text{C}5)_4$) could form chiral assemblies with helical nanostructures upon interaction with potassium ions at the air-water interface. It is found that the formation of phthalocyanine dimers plays very important role. However, smaller lithium ions cannot induce this achiral phthalocyanine form chiral assemblies. Although sodium ions can form good host-guest complex with crown ether substituents, only weak optical activity can be detected from $\text{H}_2\text{Pc}(15\text{C}5)_4/\text{Na}^+$ assemblies.

1. Introduction

Regulation of supramolecular chirality in the life system, such as changing of DNA helix, could be related with some important physiological processes [1,2]. Based on the idea of bionics for developing special applications, different supramolecular chiral assemblies with tunable helical nanostructures or optical activities have been studied [3–6]. In particular, the modulation of supramolecular chiral assemblies with different achiral components, including achiral molecules [7,8], light irradiation [9–12] or changing pH values [13–15], is gradually showing great value for further understanding many fundamental issues of supramolecular chemistry.

As one of the most important molecular building blocks, phthalocyanines with large π -conjugated ring have distinctive optical [16,17], magnetic [18,19] and electrical properties [20,21]. And the supramolecular assemblies of phthalocyanines have been developed as functional materials for many important applications, such as organic semiconductor [22–24] and nonlinear optical systems [25,26]. However, although the chiral supramolecular assemblies of phthalocyanines are attracting increased interests recently, tuning supramolecular chirality of phthalocyanines assemblies with achiral dopants were still rarely reported [27]. In this manuscript, we will show unexpected

results that alkali metal ions can regulate the supramolecular chirality of interfacial assembly of achiral phthalocyanines (Fig. 1).

The molecular building block for this study is the achiral phthalocyanine containing 15-crown-5 crown ether substituents ($\text{H}_2\text{Pc}(15\text{C}5)_4$, as shown in Fig. 2A) [28]. And the supramolecular assembly was performed at the air-water interface. In this regard, the different alkali metal ions dissolved in the aqueous subphase are expected to interact with crown ether substituents via the host-guest interactions, which could further affect the assembly of phthalocyanines. Air-water interfacial assembly is an efficient method for building different functional molecular devices. Due to the two dimensionally confined situation, some achiral molecules have been proven to form chiral supramolecular assemblies at the air-water interface [29–32]. Particularly, achiral phthalocyanines were found to form overcrowded molecular packing and supramolecular chirality on water surface, mainly because of the relatively large macrocyclic rings of phthalocyanines and strong π - π interactions upon aggregation [33,34]. In this context, the modulation of phthalocyanines interfacial assemblies is also difficult due to the tight aggregation of phthalocyanines. However, depending on the interactions between crown ether substituents and different alkali metal ions, regulating of interfacial assemblies of phthalocyanines can be achieved in this study (Fig. 1).

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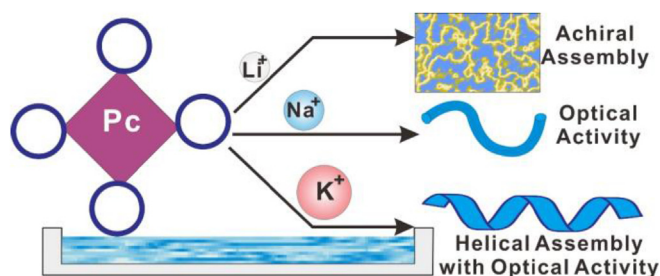


Fig. 1. Schematic illustration shows the air-water interfacial assembly of phthalocyanines ($\text{H}_2\text{Pc}(15\text{C}5)_4$) with different alkali metal ions. Although $\text{H}_2\text{Pc}(15\text{C}5)_4$ is achiral, the $\text{H}_2\text{Pc}(15\text{C}5)_4/\text{Na}^+$ co-assemblies formed at air-water interface have optical activity. And the $\text{H}_2\text{Pc}(15\text{C}5)_4/\text{K}^+$ co-assemblies further show clear helical nanostructures as well as stronger optical activity.

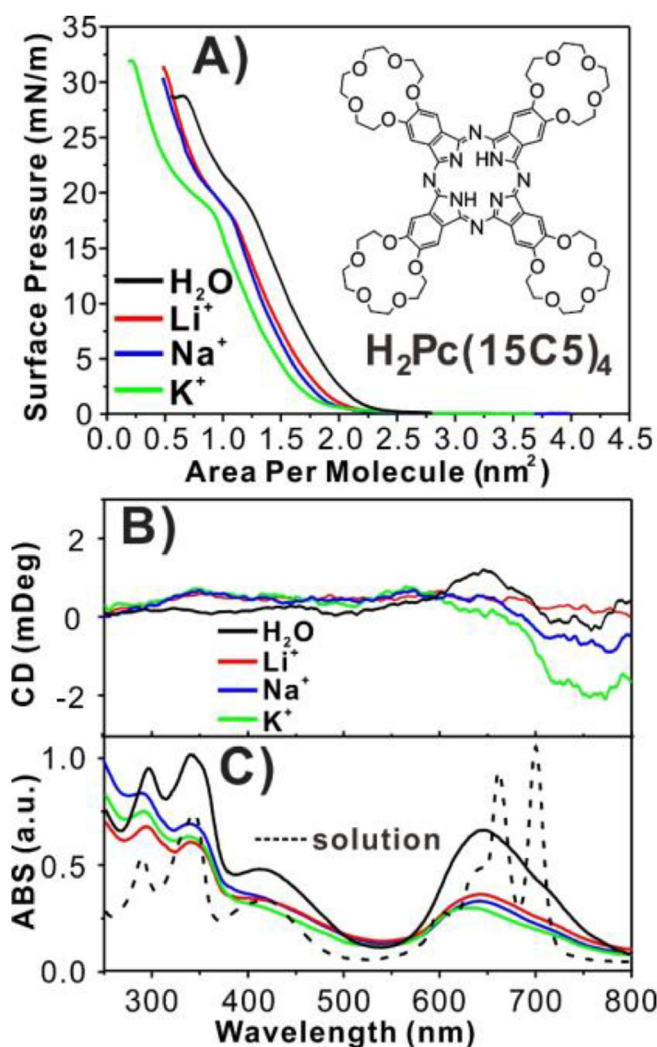


Fig. 2. A) π -A isotherms of $\text{H}_2\text{Pc}(15\text{C}5)_4$ flattening films on pure water, LiCl, NaCl and KCl aqueous solution (10^{-2} M), insert showing the molecular structure of achiral phthalocyanine ($\text{H}_2\text{Pc}(15\text{C}5)_4$); B, C) UV-Vis (C) and CD Spectra (B) of $\text{H}_2\text{Pc}(15\text{C}5)_4$ in chloroform (5×10^{-5} M, dotted line) as well as 20-layer $\text{H}_2\text{Pc}(15\text{C}5)_4$ LS films deposited from pure water, LiCl, NaCl and KCl aqueous solution.

Although the air-water interfacial assembly of crown ether phthalocyanine has been investigated previously [28,35], the formation of chiral assemblies from achiral phthalocyanine triggered by metal ions has not been reported to date. In the current study, when different alkali metal ions were added into the aqueous subphase, the

corresponding interfacial assemblies of $\text{H}_2\text{Pc}(15\text{C}5)_4$ could show very different properties and nanostructures. Thus, the LS films of $\text{H}_2\text{Pc}(15\text{C}5)_4$ can either become achiral or chiral, depending on the kinds of alkali metal ions in the subphase (Fig. 1). On the surface of lithium ion aqueous solution, $\text{H}_2\text{Pc}(15\text{C}5)_4$ cannot form the assemblies with supramolecular chirality. However, the CD spectra of the LS films based on $\text{H}_2\text{Pc}(15\text{C}5)_4/\text{Na}^+$ co-assemblies show clear cotton effects, suggesting the formation of supramolecular chirality. Most interestingly, the $\text{H}_2\text{Pc}(15\text{C}5)_4$ supramolecular assemblies obtained on the surface of potassium chloride aqueous solution show clear helical nanostructures with relatively strong optical activity.

2. Experimental section

2.1. Materials

2,3,9,10,16,17,23,24-tetrakis (15-crown-5) phthalocyanine ($\text{H}_2\text{Pc}(15\text{C}5)_4$) was prepared using the method previously reported [45]. Lithium chloride (LiCl, > 99.5%), sodium chloride (NaCl, > 99.5%) and potassium chloride (KCl, > 99.5%) were all purchased from *Sinopharm Chemical Reagent Co., Ltd.* and used without further purification. Chloroform was used as the solvent for phthalocyanines. Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}$) was used in the whole process.

2.2. Procedures

A chloroform solution of the $\text{H}_2\text{Pc}(15\text{C}5)_4$ (5×10^{-5} M) was spread onto the surface of subphase by a syringe. Single aqueous solution of LiCl (10^{-2} M), NaCl (10^{-2} M) and KCl (10^{-2} M) were used as subphase. After the evaporation of the chloroform solvent for 20 min, the spreading film was compressed with a rate of $20 \text{ cm}^2 \text{ min}^{-1}$, and the surface pressure-molecular area (π -A) isotherm was recorded. At the surface pressure of 10 mN/m, monolayer LB films were transferred onto mica plate using the vertical lifting method for AFM measurement. By horizontal lifting method, 20-layer LS films were fabricated onto quartz surface for UV-vis and circular dichroism (CD) spectral measurements, 30-layer LS films were fabricated onto silicon wafer plates for XPS measurements, and 50-layer LS films were respectively transferred onto silicon wafer plates and CaF_2 optical windows for XRD and FT-IR measurements.

2.3. Apparatus and measurements

The records of surface pressure-area (π -A) isotherms and film fabrication were carried out on a Nima 516 trough (Nima system, UK) at a room temperature of 25°C . The UV-vis and CD spectra were measured by using Lambda 750 UV-vis spectrophotometer and JASCO J-815 CD spectropolarimeter, respectively. In the process of CD spectral measurement, the sample was placed perpendicular to the light path and continuously rotated to minimize the linear dichroism (LD) effect [28,29]. XPS was measured using a PHI 5300 ESCA system (PerkinElmer, USA). FT-IR spectra were recorded on a Bruker Tensor 37 spectrometer. X-ray diffraction (XRD) was measured with a Rigaku TTRIII X-ray diffractometer (Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$), which was operated at 45 kV, 100 mA. AFM images were obtained from an atomic force microscope (Bruker Multimode 8 system) with a silicon cantilever using the tapping mode.

3. Results and discussion

The interfacial assembly of $\text{H}_2\text{Pc}(15\text{C}5)_4$ was performed on the surface of aqueous solution containing three kinds of alkali metal ions (Li^+ , Na^+ , K^+). And the surface pressure-area (π -A) isotherms of different systems were investigated, as shown in Fig. 2A. For $\text{H}_2\text{Pc}(15\text{C}5)_4$ on the surface of Li^+ , Na^+ , K^+ subphase, the onsets of the surface pressure were observed at 2.49, 2.47 and $2.41 \text{ nm}^2/\text{molecule}$,

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