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Chiral tetrakis(4-carboxyphenyl)porphyrin aggregates induced by enantiomeric dibenzoyl tartaric acids at the air–water interface

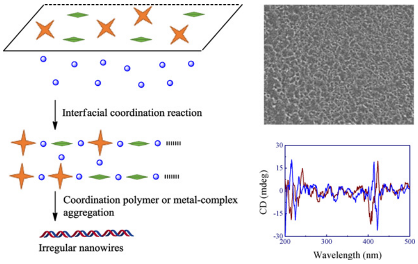
Hui-Ting Wang[a], Ying Tang[a], Meng Chen[a], Dong-Jin Qian[a,*], Li Zhang[b], Ming-Hua Liu[b]

[a] *Department of Chemistry, Fudan University, Shanghai 200433, China*
[b] *Beijing National Laboratory for Molecular Science, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, No. 2 Zhongguancun Beiyijie, Beijing 100190, China*

HIGHLIGHTS

- Chiral supramolecular porphyrin aggregates were induced by dibenzoyl tartaric acids.
- Chirality of the dibenzoyl tartaric acids remained in the LB films.
- Irregular nanowires formed for ternary aggregates composed of $CdCl_2$, tartaric acids and porphyrin.
- Coordination bonding effectively induced formation of chiral porphyrin aggregates.

GRAPHICAL ABSTRACT



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ABSTRACT

Enantiomeric dibenzoyl tartaric acid (DBTarA)-induced formation of chiral tetrakis(4-carboxyphenyl)porphyrin (TCPP) aggregates have been investigated in solutions and at the air–water interface. Surface pressure–area isotherms of the monolayers, UV–vis, and infrared spectra, as well as X-ray photoelectron spectra of the transferred Langmuir–Blodgett (LB) films, indicated that, though the small DBTarA molecules had difficulty forming insoluble monolayers at the interfaces, they could insert themselves in the matrix of porphyrins to form TCPP-DBTarA mixed monolayers and LB films. The inorganic salt of $CdCl_2$ in the subphase could stabilize the mixed monolayers due to formation of the coordination bond between Cd(II) ions and carboxylic acid substituents of TCPP and DBTarA. Mirror-imaged circular dichroism spectra were recorded with two signals centered at about 230–250 and 400–450 nm; the former indicated that chirality of the DBTarA remained in the LB films while the latter (corresponding to the Soret absorption band of porphyrins) indicated that the co-existing DBTarA could induce the formation of supramolecular chirality in the porphyrins. It was revealed that pure TCPP formed dot-like aggregates while its mixtures with DBTarA formed irregular nanowires on the $CdCl_2$ subphase surface, a phenomenon which may be attributed to the fact that the coordination bond of Cd—OOC connects TCPP and DBTarA molecules to form larger one-dimensional ternary molecular assemblies.

1. Introduction

Chirality has attracted much attention in various scientific disciplines, including studies of the origin of biomolecular chirality, enantiomerical drug purification, helical synthetic polymers, supramolecular systems, and the separation of racemic

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* Corresponding author. Tel.: +86 21 65643666.
E-mail address: djqian@fudan.edu.cn (D.-J. Qian).

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compounds [1–3]. Traditionally, asymmetric synthesis of novel organic and inorganic compounds has become a very successful area of chemistry and an important method for the preparation of novel chiral materials [4,5]. More recently, however, with the development of molecular self-assembling techniques, many effects have influenced the design and construction of chiral supramolecular complex structures with the use of achiral molecules induced by special chemical environments or by chiral compounds in solutions or at the interfaces. For instance, chiral porphyrin J-aggregates could be prepared in acid solutions and/or in the presence of cationic chiral templating reagents of octahedral metal complexes, simple amino acids or polylysines [6–8]. Similarly, chiral J-type aggregates of achiral perylene dianhydride dye have been created in acidic cetyltrimethylammonium bromide micelle solution, employing small molecules as the chiral auxiliary [9]. These J- or H-type aggregates can also be prepared by using molecular assembling techniques at the interfaces, such as Langmuir–Blodgett (LB) films, by which the control and storage of aggregate chirality from achiral molecules or building blocks becomes possible. In this research area, several research groups have published many articles on the design and assembly of chiral molecular aggregates [10–12]. Taking these investigations into account, we can expect to design and assemble more chiral aggregates with unique structures and functions if the assembling technique is combined with the chirality-inducer.

Recently, Schenning et al. reported that chiral dibenzoyl tartaric acid (DBTarA) can be used as a chiral supramolecular auxiliary to produce chiral one-dimensional helical self-assembled stacks of achiral oligo(*p*-phenylenevinylene) ureidotriazine monomers based on an orthogonal two-point ion-pair interaction [13]. They further found that the optical activity remained even when the chiral auxiliary was removed. Tartaric acid (TarA) has three isomers: L-, D- and *meso*-TarA [14]. It has been previously discovered that the TarA-silica composites have asymmetry-recognition abilities when they are used for packing in chromatography [15]. The TarA molecules can be further diastereoselectively encapsulated in a helically folded aromatic oligoamide with very high affinities and guest selectivities [16]. They can also act as a chiral templating agent to induce the formation of chiral J-aggregates of tetrakis(4-sulfonatophenyl)porphyrin in solutions [17,18]. Moreover, TarA can act as bidentate ligands to form chiral inorganic–organic frameworks with other ligands, which are of great interest for enantiomorphic separations and catalysis, and magnetic, optical, and dielectric properties [19].

We are currently interested in the design and assembly of two-dimensional molecular aggregates at interfaces, as well as in their optical, electrochemical and catalytic properties in organized ultrathin films [20,21]. Here, the monolayer behaviors of a pair of enantiomeric dibenzoyl tartaric acid (D- and L-DBTarA) molecules and their mixtures with tetrakis(4-carboxyphenyl)porphyrin (TCPP) were investigated at the air–water surfaces. Our results revealed that, because the DBTarA molecules are not typical amphiphilic ones, these small chiral organic acids could not form stable insoluble monomolecular layers on the pure water and $CdCl_2$ subphase surfaces. However, when they were mixed with TCPP, stable monolayers could be formed, especially on the $CdCl_2$ subphase surface. Multilayers for the mixtures of TCPP and D-/L-DBTarA were deposited on various substrate surfaces from either pure water or $CdCl_2$ subphase surfaces, which were characterized using UV–vis absorption, fluorescence spectroscopy, circular dichroism (CD), and X-ray photoelectron (XPS) spectroscopy, as well as by using a scanning electron microscope (SEM). It was revealed that the molecular chirality of DBTarA remained in the LB films; furthermore, chiral supramolecular TCPP aggregates were induced by the co-existing DBTarA due to a planar van der Waals interaction and the formation of a Cd—OOC coordination bond.

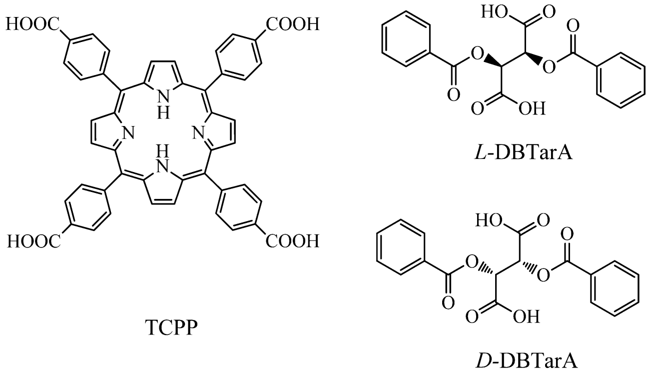

Fig. 1. Structure of porphyrin and dibenzoyl tartaric acids used in the present work.

2. Experimental

2.1. Materials

Tetrakis(4-carboxyphenyl)porphyrin and enantiomeric dibenzoyl tartaric acids were purchased from Aldrich Chemical Company; chloroform and methanol were purchased from Fisher Chemicals Company. All chemicals were used as received without further purification. Cadmium chloride was purchased from Shanghai Chemical Reagent Company. Ultrapure water (18.2 MΩ cm) was prepared with a RephiLe filtration unit (China).

2.2. Monolayers and Langmuir–Blodgett films of TCPP and its mixtures with D-/L-DBTarA

Monolayers of TCPP and its mixtures with D-/L-DBTarA were prepared by spreading a dilute ($\sim 1.25 \times 10^{-4}$ mol/l) chloroform–methanol (4:1, v/v) solution of TCPP or its mixtures with DBTarA (molar ratio, 1:1) onto the pure water or 0.1–100 mmol/l $CdCl_2$ subphase surface. The surface pressure–area (π-A) isotherm measurements and LB film transfer were done with the use of a KSV 5000 minitrough (KSV Instrument Co., Finland) using a continuous speed for two barriers of 10 cm^2/min at 25 °C. The accuracy of the surface pressure measurement was about 0.03 mN/m (Fig. 1).

The transfer of monolayers of TCPP and its mixtures with D-/L-DBTarA onto the hydrophilic quartz, CaF_2 and Si solid surfaces at various surface pressures was done using the vertical dipping method. For every transfer the dipping speed was 2 mm/min.

2.3. Spectroscopic measurements and characterization

UV-Vis spectra for TCPP (1.25×10^{-4} mol/l) and its mixtures with DBTarA (molar ratio of TCPP and DBTarA was 1:1) in the dilute methanol solutions and LB films were measured with the use of a Shimadzu UV-2550 UV-vis spectrophotometer. FTIR spectra were measured by using a Nicolet iS10 spectrometer, operating at a resolution of 0.5 cm^{-1} at 25 °C. For the spectral measurements, the quartz or CaF_2 substrate covered with 20 layers of the LB films was used.

XPS spectra were recorded using a VGESCALAB MKII multifunction spectrometer, with non-monochromatized Mg-Kα X-rays as the excitation source. The system was carefully calibrated with the Fermi-edge of nickel, Au $4f_{2/7}$, and Cu $2p_{2/3}$ binding energy; a pass energy of 70 eV and step size of 1 eV were chosen when taking spectra. In the analysis chamber, pressures of $1–2 \times 10^{-7}$ Pa were routinely maintained. The binding energies obtained in the XPS analysis were corrected by referencing the C1s peak to 284.60 eV.

SEM measurements were performed on a Philips XL30 electron microscope. The operating voltage was 20 kV. The LB films were deposited on the Si substrate surfaces.