

## Interfacial assembly and characterization of hybrid ultrathin films of manganese 5,10,15,20-tetra (4-pyridyl) porphine chloride tetrakis (methochloride) and its polymeric derivative with poly (4-vinylpyridine)

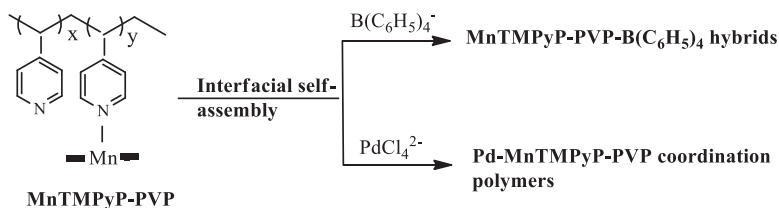
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### HIGHLIGHTS

- Polymeric manganese porphyrin PVP-MnTMPyP was synthesized.
- PVP-MnTMPyP-B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> hybrids were assembled.
- Pd-MnTMPyP-PVP coordination polymer multilayers were prepared.
- The hybrid and coordination polymer multilayer modified electrode showed reversible redox reaction.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Monolayers of a water-soluble metalloporphyrin, manganese tetra-(4-pyridyl) porphine chloride tetrakis (methochloride) (MnTMPyP), and its polymeric derivative with poly (4-vinylpyridine) (MnTMPyP-PVP) have been investigated at the air–water interface. These monolayers were transferred on the substrate surfaces to form hybrid ultrathin films by the Langmuir-Blodgett (LB) method. It was revealed that, although the water-soluble MnTMPyP could not form insoluble monomolecular layer on the pure water surface, it could be stabilized on the NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> subphase surface due to an electrostatic interaction between MnTMPyP and B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>−</sup>, resulting in the formation of MnTMPyP-B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> hybrids. On the other hand, its polymeric derivative of MnTMPyP-PVP could form stable insoluble monolayers on the pure water, NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and Na<sub>2</sub>PdCl<sub>4</sub> subphase surfaces. Composition, structure and microscopic morphology of the as-prepared LB films were characterized by using UV–vis absorption, infrared and X-ray photoelectron spectroscopy, as well as scanning electron microscope. The results suggested formation of the hybrid MnTMPyP-B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and MnTMPyP-(PVP)-B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and Pd-MnTMPyP-PVP coordination polymer ultrathin films at the interfaces. Cyclic voltammograms of the LB films revealed two couples of reversible redox waves centered at 0.2–0.3 and −0.1 to −0.2 V (vs Ag/AgCl), corresponding to the Mn<sup>(II)</sup>/Mn<sup>(III)</sup>TMPyP-(PVP)-B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and Mn<sup>(III)</sup>/Mn<sup>(IV)</sup>TMPyP-(PVP)-B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> electron transfer processes of the manganese porphyrins in the LB films.

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## 1. Introduction

Manganese porphyrins have attracted much attention because they are suitable model materials for the researches related to many biological phenomena, particularly for mimicking the role of the Mn complexes in photosystem II, in which the Mn complexes catalyze the reaction between hydroquinone and molecular

oxygen [1]. They are of high quantum efficiency in their photochemistry and relatively long lifetimes of their excited states [2]. High valent manganese-oxo porphyrins were also proposed as the catalytically active species in efficient biomimetic and artificial systems for the oxidation of organic compounds [3–5]. Moreover, Mn porphyrins exhibit attractive coordination, redox and catalytic properties which can serve as functional criteria in the design and construction of supramolecular systems [6,7].

Compared to the art of organic or inorganic synthesis to prepare multiporphyrin arrays or coordination polymers [8], the use of weak intermolecular forces (hydrogen bond, van der Waal force

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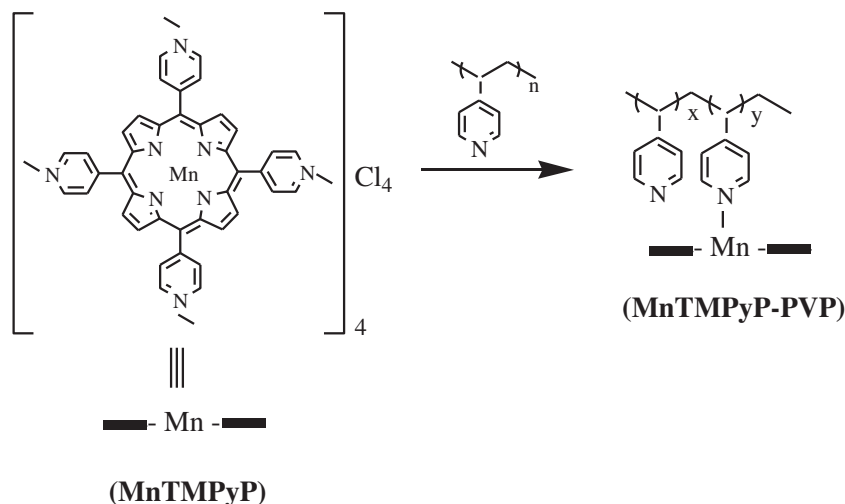


Fig. 1. Structure of porphyrin derivatives synthesized in the present work.

and coordination bond) to construct large, multicomponents or multifunctional multilayers or films of porphyrins has been well developed in the past several decades by the molecular assembling techniques, which include the Langmuir-Blodgett (LB) films, self-assembled monolayers (SAMs) and layer-by-layer (LBL) assemblies [9–11]. These techniques provide a bottom-up design and construction of organized ultrathin films or supramolecular systems with various manganese porphyrins as linkers. For instance, Ohtsuka and coworkers prepared SAMs of a series of disulfide-linked manganese porphyrins and revealed an effective electron transfer between electrode surface and manganese porphyrin, the redox potentials of which closely related to the length of the methylene-chains in the porphyrins [12]. Amphiphilic porphyrins could form two-dimensional (2D) rigid LB films at the air–water interface, which could be acted as sensors for the detection of gases, or as light-harvesting units for the energy conversion and heterogeneous catalysts [13,14].

We have prepared a water-soluble manganese porphyrin polyelectrolyte and constructed its multilayers together with an anionic polyelectrolyte (poly (styrenesulfonic acid-*o*-maleic acid): PSS) by the LBL method. The as-prepared LBL multilayers showed strong stability in solutions and could be used as a heterogeneous catalyst for the degradation of azo dye [15]. Here, we investigated monolayer behaviors and LB films of a water-soluble metalloporphyrin, manganese tetra-(4-pyridyl) porphine chloride tetrakis (methochloride) (MnTMPyP) and its polymeric derivative on the pure water and inorganic salt subphase surfaces. This polymeric porphyrin was prepared by an axial coordination reaction of MnTMPyP with poly (4-vinylpyridine) (PVP), thus it was an amphiphilic and positively charged polyelectrolyte with a lot of “free” pyridyl substituents capable of coordinative with other transition metal ions [16]. We prepared their hybrid ultrathin films on the inorganic salt subphase surfaces. Compositions and structural features of the as-prepared hybrid LB films were characterized by using the UV–vis absorption and infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscope (SEM). Moreover, electrochemical properties of the porphyrins in the solutions and LB films were investigated by cyclic voltammetry.

## 2. Experiments

### 2.1. Materials

Mn(III) 5,10,15,20-tetra-(4-pyridyl)-21,23H-porphine chloride tetrakis (methochloride), poly (4-vinylpyridine) and sodium

tetrachloropalladate(II) were purchased from Aldrich Chemical Co. Chloroform and methanol used as spreading solvents were from Fisher Chemicals Co. Sodium tetraphenylborate were obtained from Shanghai Chemical Reagent Co. All reagents were used as received without further purification. Ultrapure water (18.2 M $\Omega$  cm) used to prepare the subphases was purified with a Reophile filtration unit (China).

### 2.2. Synthesis of polymeric manganese porphyrin

Polymeric manganese porphyrin (MnTMPyP-PVP, Fig. 1) was obtained through the axial coordination of central Mn(III) ion of the metalloporphyrin (MnTMPyP) with the pyridyl substituent of the polymer PVP according to Campestrini and Meunier’s method [16,17]. Briefly, a mixture of MnTMPyP and PVP (molar ratio, 1:30) was refluxed in methanol for 24 h, which was then evaporated on a rotary evaporator, well washed by water to remove unreacted MnTMPyP (during experiments, we found that the aqueous phase became colorless, indicating that almost all porphyrins were coordinated with PVP), and finally dried under vacuum at room temperature. Molar fraction of MnTMPyP in the polymer of MnTMPyP-PVP was estimated by absorption spectra.

### 2.3. Monolayer and Langmuir-Blodgett films

Monolayer behaviors of the porphyrin MnTMPyP and its polymeric derivative of MnTMPyP-PVP were investigated by spreading a dilute chloroform–methanol (4: 1, v/v) solution of the porphyrins (concentration: 0.17 mmol/l for MnTMPyP-PVP, 0.22 mmol/l for MnTMPyP) onto the pure water, 0.1 mmol/l NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and 0.05–0.2 mmol/l Na<sub>2</sub>PdCl<sub>4</sub> subphase surfaces. The surface pressure area ( $\pi$ -A) isotherm measurements and LB film deposition were carried out with a KSV 5000 minitrough (KSV Instrument Co., Finland) or a JML04C2 trough (Powereach, Shanghai, China), with the two barriers compressed at a speed of 10 mm/min at room temperature. The accuracy of the surface pressure measurement was 0.03 mN/m. Both the  $\pi$ -A isotherm measurements and LB film deposition were performed 20 min after the spreading. The LB films were deposited at a certain constant surface pressure with a dipping speed of 2 mm/min.

### 2.4. Characterization

UV–vis spectra for the porphyrins in the dilute methanol solutions and LB films were measured with the use of Shimadzu

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