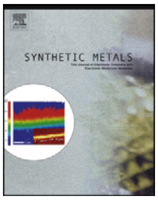
Synthetic Metals 167 (2013) 10–17

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Interfacial self-assembly of Zn(Fe)-bisterpyridine coordination polymers, their fluorescent and electrochemical properties in Langmuir–Blodgett films

Xue-Bing Ren[a], Hong-Xiang Huang[b], Meng Chen[a], Dong-Jin Qian[a,*]

[a] Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China
[b] State Key Laboratory of Molecular Engineering of Polymers, Fudan University, 220 Handan Road, Shanghai 200433, China

ARTICLE INFO

Article history:
Received 11 October 2012
Received in revised form 26 January 2013
Accepted 31 January 2013
Available online 6 March 2013

Keywords:
Self-assembly
Coordination polymer
Langmuir–Blodgett film
Fluorescence
Electrochemistry

ABSTRACT

Metal-bisterpyridine coordination polymers (CPs) have been synthesized at the air–water interface through an interfacial coordination reaction of metal ions (Zn^{2+}/Fe^{2+}) with bidentate ligand of 4,4′′′′-(1,4-phenylene)bis(2,2′:6′2′′-terpyridine) (PBTerpy). Surface pressure-area isotherms indicated that the average molecular area of PBTerpy was about 0.8 nm^2 on the pure water surface, which slightly increased to about 1 nm^2 on the inorganic salt subphase surfaces due to the formation of Zn(Fe)-PBTerpy CPs. Monolayers of the Zn(Fe)-PBTerpy CPs were deposited on the quartz, Si and indium tin oxide (ITO) substrate surfaces by the Langmuir–Blodgett (LB) method. The as-prepared LB films were characterized by using UV-vis absorption and fluorescence spectroscopy, X-ray photoelectron spectroscopy, as well as by using scanning electron microscope and atomic force microscope. The pure PBTerpy ligand and its LB films showed a broad fluorescent emission at about 350–370 nm. This emission red shifted to about 380–410 nm in the LB films of Zn(Fe)-PBTerpy CPs. Time-resolved fluorescent spectra revealed that the emission lifetime was about 1.2–2.4 ns for the pure PBTerpy ligand in the dilute methanol solution and its LB films, while it was about 5.0 ns in the LB film of Fe-PBTerpy CPs and 20.6 ns in the LB film of Zn-PBTerpy CPs. A couple of reversible redox wave was recorded and centered at about −0.53 V (vs Ag/AgCl) for the ITO electrode covered by the LB film of Fe-PBTerpy CPs, which was designated to one electron transfer process between the CPs of $Fe^{(II)}$-PBTerpy and $Fe^{(III)}$-PBTerpy. Since the PBTerpy can coordinate with lots of transition metal ions, we suggest that the present method may be used to prepare new optically and electrically active organic–inorganic composite materials.

1. Introduction

Metal-mediated synthesis of coordination polymers (CPs) or metal–organic frameworks (MOFs) have attracted growing attention because the target materials can be designed as the molecular building blocks with the desired architectural, chemical and physical properties [1,2]. They are generally of completely regular structure with high porosity and designable frameworks, the features of which can be designed and controlled with suitable choices of the metal ions (connectors) and multidentate ligands (linkers) [3]. The synthesis of CPs and MOFs can be performed under mild conditions in solutions [4–6], or at interfaces by the so-called bottom-up methods, such as the Langmuir–Blodgett (LB) films, self-assembled monolayers (SAMs) and layer-by-layer (LBL) assemblies [7–9]. Different from the solution synthesis, the bottom-up methods have the advantages of suitable design and facile step-by-step assembly of well-defined building blocks (usually directly on the solid surfaces) with interesting optoelectronic, magnetic, catalytic, and photosensitizing properties, thus leading quickly to practical applications [10].

Bisterpyridine (Bisterpy) derivatives are attractive linkers for the construction of CPs or MOFs because of their unique electrical, optical, magnetic and catalytical properties, as well as their strong coordination ability with many transition metal ions [11]. For instance, they can act as bidentate ligands to build up molecular wires at interfaces by stepwise coordination reactions with the metal ions of Fe(II) and Co(II) [12], or form two dimensional (2D) multicomponent metal–organic coordination networks together with tetrapyridylporphyrins [13], or form 2D redox-active adlayers on the substrate surfaces [14]. With a design of a spacer between two or three terpyridine substituents, many supramolecular building blocks with unique fluorescent emission behaviors have been prepared, which can be used as sensors for metal ions [15], novel luminophors or artificial light-harvesting units [16], as well as building blocks for constructing chiral nanostrutural aggregates [17]. More recently, terpyridine was covalently attached to the solid supports such as carbon nanotubes, gold nanoparticles, polyoxometalates and nanopores resulting in the formation

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* Corresponding author. Tel.: +86 13 918849977; fax: +86 21 65643666.
E-mail address: djqian@fudan.edu.cn (D.-J. Qian).

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http://dx.doi.org/10.1016/j.synthmet.2013.01.022

of multidentate-like hybrid materials [18–21], which were used as linkers to construct multifunctional nanoscale composites.

We have previously prepared multidentate Bisterpy derivatives by binding the terpyridine with 4,4′-bipyridine and poly(4-vinylpyridine) [22,23]. These Bisterpy derivatives could form viologen-like coordination polyelectrolyte multilayers or bimetallic 3D hybrid materials at interfaces through an intermolecular coordination reaction between the terpyridines and transition metal ions by the LB or LBL techniques. The as-prepared LB or LBL multilayers showed reversible or quasi-reversible redox behaviors of ligands or metal ions, luminescent emissions at 390–430 nm, as well as electrochromic response upon the applied potentials.

Here, we investigated monolayer behaviors of a bidentate ligand of 4,4′′′′-(1,4-phenylene)-bis(2,2′:6′2′′-terpyridine) (PBTerpy) on the water and inorganic salt subphase surfaces for the synthesis of metal-PBTerpy CPs at interfaces. With the use of the LB technique, 3D metal-PBTerpy (M-PBTerpy) CP LB films were constructed and characterized by using UV-vis absorption and fluorescence spectroscopy, X-ray photoelectron spectroscopy (XPS), as well as by using scanning electron microscope (SEM) and atomic force microscope (AFM). The as-prepared LB films of the M-PBTerpy CPs gave off fluorescent emissions at around 400 nm with the emission lifetime of about 5–21 ns. Additionally, the cyclic voltammograms of the Fe-PBTerpy LB films revealed a reversible one electron transfer process between the CPs of $Fe^{(II)}$-PBTerpy and $Fe^{(III)}$-PBTerpy.

2. Experimental

2.1. Materials

4,4′′′′-(1,4-Phenylene)bis(2,2′:6′2′′-terpyridine), chloroform, zinc trifluoromethanesulfonate, and iron tetrafluoroborate were purchased from Alfa Aesar®. All chemicals were used as received without further purification. Ultrapure water (18.2 ΩM cm) used for the preparation of the subphases was prepared with a Rephile filtration unit (China).

2.2. Preparation of metal-PBTerpy coordination polymers at interfaces

Monolayers of the ligand PBTerpy and its metal-mediated M-PBTerpy CPs were prepared by spreading a dilute ($\sim 1.6 \times 10^{-4}$ mol/l) PBTerpy chloroform solution onto the pure water or inorganic salt subphase surfaces. The surface pressure area (π–A) isotherm measurements and LB film deposition were carried out by using a KSV 5000 mini-trough LB instrument (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 about 0.03 mN/m. Both the π–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.

2.3. Characterization

UV-vis spectra for the dilute PBTerpy methanol solution and M-PBTerpy CP LB films were measured with the use of Shimadzu UV-2550 UV-vis spectrophotometer. Steady state fluorescence spectra were recorded by using Shimadzu RF-5300PC spectrophotometer.

Time-resolved single photon fluorescence measurements were performed using an Edinburgh Instruments LFS-920 spectrometer with a hydrogen-filled pulse lamp as the excitation source. Lifetimes were estimated by iterative convolution of the luminescence decay profile with the instrument response function using the software package provided by Edinburgh Instruments.

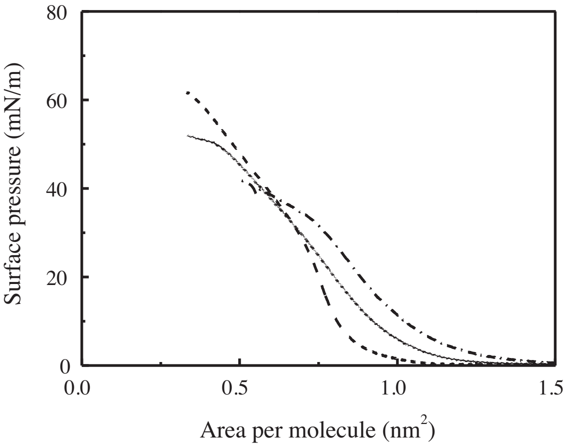

Fig. 1. Surface pressure-area isotherms for the monolayers of the bidentate ligand PBTerpy on the pure water (----), 0.1 mmol/l $Zn(CF_3SO_3)_2$ (-·-·-·) and $Fe(BF_4)_2$ (—) subphase surfaces at room temperature.

XPS spectra were recorded using a VGESCALAB MKII multifunction spectrometer, with nonmonochromatized Mg-Kα X-rays as the excitation source. The system was carefully calibrated by Fermi-edge of nickel, Au $4f_{2/7}$ and Cu $2p_{2/3}$ binding energy. 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 images were observed on a Philips XL30 electron microscope. The LB films were deposited on the Si substrate surface at different surface pressures. AFM measurements were performed by using a Shimadzu SPM-9500J3 scanning probe microscope. The LB films were also deposited on the Si substrate surface. Tapping mode was used with a NSG11 tip (NT-MDT, Russia) under ambient conditions. The spring constant of the Si cantilevers was kept between 2.5 and 10 N/m. These microscopic measurements were done at 25 °C.

2.4. Electrochemical measurements

The cyclic voltammograms (CVs) for the LB films of Fe-PBTerpy CPs were measured by using an electrochemical analyzer (CHI 601b, China). A Pt wire and Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively, and the indium–tin oxide (ITO) electrode, coated with the LB films, was used as the working electrode with 10 mmol/l KCl as the electrolyte. An initial potential of 0 V was applied for 2 s, and subsequently cyclic scans to a final potential of −1.2 V were done for 10 cycles. The CV curves and data reported in the present work were the 10th cycle. All electrochemical measurements were done under Ar atmosphere at room temperature.

3. Results and discussion

3.1. Monolayer behaviors of the ligand PBTerpy

Monolayers of pure PBTerpy and its metal-mediated CPs were investigated by spreading a dilute PBTerpy chloroform solution on the surfaces of pure water and the subphase containing 0.1 mmol/l $Zn(CF_3SO_3)_2$ or $Fe(BF_4)_2$ at room temperature. Based on our previous work [22,23], the monolayers were compressed 20 min after spreading. The π–A isotherms for the monolayers of PBTerpy were shown in Fig. 1, which revealed the following features.

Firstly, the surface pressures increased with compression of the monolayers in all cases, which indicated that PBTerpy could