Metal-mediated Supramolecular Coordination Polyelectrolyte Films of Bisterpyridine Ligand at the Air–Water Interface

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Metal-mediated poly(viologen)-like coordination polyelectrolytes were prepared at the air–water interface via an interfacial coordination reaction of a multitopic bisterpyridine ligand with inorganic salts. By using anionic polymer as alternative support layer, organized organic–inorganic hybrid films were assembled and characterized.

Coordination polymers containing multitopic ligands and metal ions have been recently received great interest toward the design and fabrication of molecular materials and devices.[1] We are currently interested in the interfacial self-assembly of organized thin films of coordination polymers, their nanocrystals and building blocks by using the Langmuir–Blodgett (LB) and self-assembly methods.[2] Based on the coordinative features of the metal ions and multitopic ligands, large amount of coordination polymers with unique structural features and properties can be constructed.[3]

The multitopic ligand, 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine (pyterpy, Figure 1), contains one 2,2′:6′,2″-terpyridine (terpy) coordinative site and another pyridyl site at the 4′-position, these two sites are able to bind with different metal ions, thus leading to the coordination polymers produced with various frameworks.[4,5] It can further react with lots of transition-metal ions including Fe^{2+}, Cd^{2+}, Zn^{2+}, or Co^{2+} to form 4,4′-bipyridyl-like complexes and viologen-like hybrids.[6] Kurth et al. very recently found that, when pyterpy reacted with α,α'-dibromo-*p*-xylene, a new “bidentate-like” multitopic ligand **I** {1″,1‴″-[1,4-phenylenebis(methylene)]bis[6′-(2-pyridinyl)2,2′:4′,4″-terpyridinium] bis[hexafluoroborate(1−)]}, Figure 1} could be obtained.[7] This ligand **I** could coordinate with Co^{2+} ion to produce viologen-like polyelectrolytes with interesting electronic, optical, and magnetic properties.

We reported here several metal–ligand **I** coordination polyelectrolytes (M–**I**) assembled at the air–water interface, based on an interfacial coordination reaction of metal ions and **I**. Monolayers of the polyelectrolytes were stabilized on the surfaces of the subphases containing small amount of anionic poly(styerenesulfonate) (PSS). By using the LB method, organic–inorganic hybrid multilayers of M–**I**/PSS were prepared and characterized by absorption, fluorescence, and X-ray photoelectron spectra. It is suggested that this simple methodology allows a facile fabrication of various condensed and organized thin films of M–**I** coordination polymers.

The pyterpy and ligand **I** were synthesized according to literature methods and characterized by using ^{1}H NMR and elemental analysis.[5,8] Monolayers of the ligand **I** and metal-mediated coordination polymers of M–**I** were prepared by spreading a dilute ($\approx 5 \times 10^{-5}$ mol/L) chloroform/acetonitrile solution of **I** onto the inorganic salt (MX_n) subphase surfaces. The surface pressure–area (π–A) isotherm measurements and LB film transfer were performed using a KSV 5000 minitrough (KSV Instrument Co., Finland) operated at a continuous speed for two barriers of 10 cm^2/min at room temperature. Transfer of the monolayers of ligand **I** and M–**I** coordination polymers onto solid plates was done by a vertical dipping method at 20 mN/m. For every transfer, the dipping speed was 2 mm/min.

Figure 2 shows the π–A isotherms for the monolayers of **I** on the pure water, PSS and M–PSS subphase surfaces. Almost no increase of surface pressure was recorded for the ligand **I** on the surfaces of pure water and aqueous solutions of inorganic salts, indicating that **I** was unable to form stable monomolecular layer in these cases. These may be ascribed to the fact that the ligand **I** and M–**I** complexes could dissolve into water, resulting in the insoluble monomolecular layer difficult to form. However, when the ligand **I** was spread on the surface of subphase containing 0.01 mg/mL anionic polymer PSS, the surface pressure was largely increased up to over 30 mN/m after compression. The limiting molecular area of **I** could reach to about 0.8 nm^2. These enlarged surface pressure and molecular area indicated that PSS could prevent the ligand **I** from dissolving into the water and support the formation of stable monolayers of **I** due to strong electrostatic interaction between **I** and PSS.

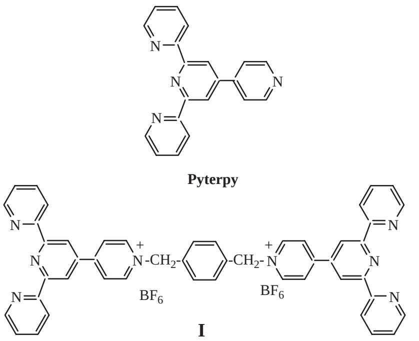


Figure 1. Multitopic ligands used in the present work.

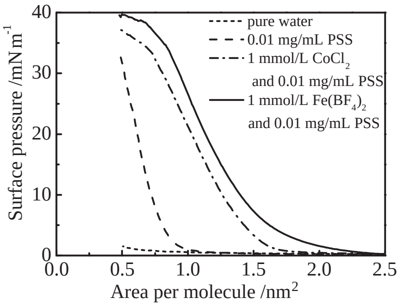


Figure 2. π–A isotherms for the monolayers of multitopic ligand **I** on different subphase surfaces at room temperature.

Table 1. Deconvolution of XPS peaks

LB films	S(2p)	C(1s)	N(1s)	O(1s)	F(1s)	M(2p/3d)
Co–**I**/PSS	167.8	284.8	400.2	532.7	684.8	781.4[Co(2p)]
Zn–**I**/PSS	168.2	284.8	399.8	532.5	685.2	1022.3[Zn(2p)]
Eu–**I**/PSS	168.1	284.8	400.0	532.5	684.6	1135.4[Eu(3d)]
Fe–**I**/PSS	167.6	284.8	400.1	532.6	685.6	705.8[Fe(2p)]
I/PSS	167.3	284.8	396.2	532.4	685.8	

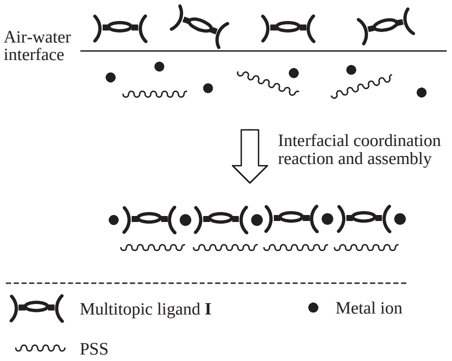
When the ligand **I** was spread on the PSS–MX$_n$ subphase surfaces,[9] the limiting molecular area of **I** increased to about 1.3–1.6 nm^2; larger than that on the PSS subphase surface. Previously studies have reported that some metal ions could react with pyterpy to form their complexes M(pyterpy)$_2$ via the coordination of M^{n+} with the terpy site of the ligand. Based on the model structure,[6] the molecular area of M–**I** was about 1.8 nm^2; close to that obtained at the aqueous solutions of the mixtures of inorganic salts and PSS. Thus, the increased limiting molecular area for **I** on the PSS–MX$_n$ surfaces may be attributed to the formation of M–**I** coordination polymers, which were positively charged polyelectrolytes. The anionic PSS stabilized M–**I** monolayers by the formation of M–**I**/PSS hybrid at the air–water interface.

By traditional vertical dipping method, monolayers of **I**/PSS and M–**I**/PSS coordination polymers were transferred onto substrate surfaces at 20 mN/m. The transfer ratios indicated that X-type of LB films was deposited. The compositions of the LB films were analyzed by using the XPS spectra, which showed several peaks in the binding energy from 190 to 1100 eV. Table 1 summarized the binding energy for each peak of the five LB films. These data confirmed that the LB films were composed of ligand **I**, metal ions (that is, M–**I** coordination polyelectrolytes) and PSS polymer.

The absorption spectra of five LB films composed of several peaks in the range of 240 and 350 nm, which were attributed to the ligand-based π–π^* and n–π^* transitions.[8,10] For the Fe–**I**/PSS and Co–**I**/PSS coordination polyelectrolytes, besides the peaks at about 241, 277, and 320 nm, these two polyelectrolytes showed another peak at around 602 or 500 nm, due to metal-to-ligand charge-transfer (MLCT) band. Furthermore, the absorption intensity was found to be linearly increased with the layer numbers of the LB films, indicating that similar amount of M–**I** coordination polyelectrolytes were transferred for each LB film deposition.

We have previously found that the ligand pyterpy could give off rather strong yellow light at 454 nm under UV radiation.[10] After it reacted with α,α'-dibromo-p-xylene, the ligand **I** gave off blue luminescent emission at around 412 nm. However, very weak fluorescent emission was recorded for the LB films of **I**/PSS or M–**I**/PSS. Based on control experiments in solutions, it was found that the anionic polymer PSS could quench the ligand emission. We are now trying to use other anionic polymers to replace PSS as the alternative supporting layer to prepare luminescent films of M–**I** coordination polyelectrolytes.

Based on the π–A isotherms, XPS, and spectral features, the crystal structure of the M(pyterpy)$_2$[BF$_4$]$_2$ complexes in the literatures,[11] we proposed a schematic model of the present M–**I**/PSS hybrid coordination polyelectrolytes. As shown in Scheme 1, each metal ion coordinated with two 2,2′:6′,2″-terpyridine units from two ligands to form six-coordinate metal ion center. Monolayers of the coordination polyelectrolytes were stabilized on the PSS subphase surfaces. During the LB film transfer, alternative organic–inorganic hybrid films composed of M–**I**/PSS could be prepared.



Scheme 1. Formation process of the M–**I**/PSS hybrid films.

In summary, we have demonstrated a simple route to construct organized coordination polyelectrolyte hybrid films. These films are of interesting electronic and optical properties, which are now under investigation in our group. Furthermore, since the geometric features of the metal ions can dominate the nanostructures of the coordination polymers,[2] it is expected that unique nanopatterns can be designed and assembled at the interfaces.

This work was supported by the National Science Foundation of China (No. 20421303) and Shanghai Leading Academic Discipline Project (B108).

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