Interfacial self-assembly, characterization, electrochemical, and photo-catalytic properties of porphyrin-ruthenium complex/polyoxomelate triad hybrid multilayers

Wen-Li He, Jia-Lu Chen, Meng Chen, Dong-Jin Qian*

Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China

Abstract

Triad hybrid multilayers composed of tetrapyrroldiporphyrin (TPyP), bis(2,2'-bipyridyl)ruthenium chloride [Ru(bpy)₂Cl₂], and phosphomolybdic acid (PMA) have been prepared at the gas-liquid interface. The tetra-ruthenated porphyrin of TPyP-Rubpy complex was synthesized by the coordination interaction of TPyP with Ru(bpy)₂Cl₂. Surface pressure–area isotherms indicated that the average molecular area of the TPyP-Rubpy complex was in the range of 3.1–3.3 nm² when the PMA concentration was 0.1–0.3 mg/mL in the subphases. Monolayers of the TPyP-Rubpy/PMA triad hybrids were transferred onto the substrate surfaces by using the Langmuir-Blodgett (LB) method. The absorption spectra of the hybrid LB films revealed several strong peaks between 300 and 440 nm, attributed to the π – π^* electron transfer of the Rubpy substituent and the Soret band of TPyP. Under radiation, the TPyP-Rubpy complex gave off strong luminescence in the wavelength between 600 and 700 nm, attributed to the emissions from the Rubpy and TPyP substituents. These emissions largely weakened in the LB films of TPyP-Rubpy/PMA triad hybrids. Cyclic voltammograms showed six couples of redox waves in the potential range from –1.2 to 0.6 V (vs Hg/HgCl₂), which could be designated for the electron transfer processes of TPyP, Rubpy and PMA, respectively. Finally, it was revealed that the present triad hybrid LB films can be used as efficient light-harvesting units for the photo-catalytic oxidation of organic dyes and for light-induced photocurrent generation.

Keywords: Porphyrin; Ru complexes; Langmuir-Blodgett film; Electrochemistry; Photocatalyst; Photocurrent generation

* Corresponding author

E-mail: djqian@fudan.edu.cn

Tel/Fax: 86-21-65643666

1. Introduction

Porphyrin derivatives and Ru complexes have been widely used as light-harvesting units (light sensitizers) for the construction of artificial photosynthetic systems [1,2], dye-sensitized solar cells, and photoelectrochemical devices [3,4]. Synthetic porphyrins are considered to have excellent light-harvesting properties in the visible region as well as the facile tuning of their excited states and redox properties via the suitable attachment of organic substituents to macrocycles. They react with metal ions to form metalloporphyrins [5-8]. On the other hand, Ru complexes are also widely used as excellent light-harvesting units with the advantages of sufficient first-oxidation potential for water oxidation and the long lifetimes of their excited states for electron injection [9,10]. For instance, with the use of Ru-polypyridyl complexes as a light sensitizer, the power conversion efficiency of dye-sensitized solar cells could reach 11% [6]. When the Ru-complex sensitizer was combined with Pt and TiO₂ particles to form Ru-complex/Pt/TiO₂ nanocomposites, the photo-induced hydrogen evolution could reach 9500 $\mu\text{mol}(\text{g-catalyst})^{-1}$ [11]. However, both of them have some disadvantages; porphyrins have poor performance in photo-induced electron transfer, while Ru-complexes have rather poor absorbance in the visible region. Fortunately, it has been revealed that a combination of porphyrins and Ru-complexes can partly overcome their disadvantages while at the same time improving their opto-electrochemical performance. Thus, the supramolecular molecules in both metalloporphyrins and Ru-complexes are expected to be attractive materials for exploiting a highly efficient molecular artificial photosynthetic system [12-14].

Toma and coworkers completed earlier work on the supramolecular systems of porphyrin-Ru complexes in 1993 [15]. Since then, they have prepared a series of tetraruthenated porphyrins based on the coordination reaction of tetrapyrrolylporphyrin (TPyP) or its metalated derivatives with four Ru(bpy)₂Cl₂ (bpy = 2,2'-bipyridine) complexes [15-18], which have shown not only interesting optical properties but also many redox processes corresponding to the electron transfer processes in porphyrins and Ru-complexes. Further research found that the substrates or electrodes modified with tetraruthenated porphyrins (TPyP-Rubpy) were not so stable in the electrolyte solution because they were of high solubility in water. To improve the film stability, a negatively charged polyelectrolyte, such as Nafion, was often used as a supporting layer to co-assemble with the TPyP-Rubpy complex on the electrode surfaces based on an electrostatic interaction [19-21]. This method recently has

been widely used at the interfaces for the construction of organic-inorganic hybrid materials via molecular assembling techniques, such as Langmuir-Blodgett (LB) films and layer-by-layer (LBL) multilayers [22-24].

Polyoxometalates (POMs) are a well-known class of structurally defined negatively charged clusters with interesting electrochemical and catalytic properties, thus leading to potential applications in many fields of science, such as medicine, biology, catalysis, and advanced materials [25,26]. Recently, POMs have often been used as the counter ions for constructing well-defined two- or three-dimensional multi-functional molecular aggregates and organized ultrathin films at the interfaces through electrostatic interaction [27-29]. The larger anionic POM clusters can not only improve monolayer stability but also form multi-functional hybrid multilayers with charged amphiphiles or polymers. For instance, earlier research confirmed that POMs could support the formation of organized thin films of dimethyldioctadecylammonium and 1,2-dipalmitoyl-Sn-glycero-3-phosphorylcholine [30]. Later, many multi-functional hybrid films were designed and constructed, such as amphiphilic viologen-POM hybrids [27], polyplatinayne-POM composites [28], polyhedral oligosilsesquioxane-POMs [29], and others [31,32].

Here, phosphomolybdic acid (PMA), one kind of POM, was used as the counter ions to co-assemble with the TPyP-Rubpy complex at the gas-liquid interfaces to form triad hybrid TPyP-Rubpy/PMA monolayers, which were transferred on the substrate surfaces by using the LB method. Surface pressure-area isotherms indicated that, although the TPyP-Rubpy complex easily dissolves into water, it can form stable monolayers on the PMA subphase surface due to the formation of insoluble TPyP-Rubpy/PMA triad hybrids. The as-prepared hybrid LB films were characterized by using UV-vis absorption and X-ray photoelectron spectroscopy along with a scanning electron microscope (SEM) and an atomic force microscope (AFM). It was revealed that the TPyP-Rubpy complex gave off strong emissions corresponding to the TPyP and Rubpy substituents in the wavelength between 600 and 700 nm, which was strongly weakened in the LB films due to luminescent quenching by the co-deposited PMA. Cyclic voltammograms showed six couples of redox waves in the potential range from -1.2 to 0.6 V (vs Hg/HgCl₂), corresponding to the electron transfer processes of TPyP, Rubpy, and PMA. These triad hybrid LB films were finally used as light-harvesting materials for the photo-catalytic oxidation of organic dyes and for light-induced photocurrent generation.

2. Experimental

2.1. Materials

TPyP was purchased from Sigma-Aldrich Co. 5,10,15,20-Tetrakis(N-methyl-4-pyridyl)porphine tetratosylate (TMPyP) came from J&K Scientific Ltd. Ru(bpy)₂Cl₂ and tris(2,2'-bipyridyl)ruthenium(II) chloride [Ru(bpy)₃Cl₂] hexahydrate came from Stern Chemicals. PMA and methyl orange (MO) came from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received without further purification. The ultrapure water (18.2 ΩM cm) used for the preparation of the subphases was prepared with a Rephile filtration unit (China).

The TPyP-Rubpy (Figure 1) complex was synthesized according to Araki and Toma's method [15]. Anal. Calc. for TPyP-Rubpy, Ru₄C₁₂₀H₈₈N₂₄Cl₈·18H₂O: C, 50.03; H, 4.38; N, 11.67%. Found: C, 49.69; H, 4.22; N, 11.74%. Infrared spectrum (cm⁻¹): 3411, 3070, 1630, 1600, 1559, 1461~1444, 1417, 1263, 1158~1019, 970, 766, 726.

Figure 1

2.2. Monolayers and Langmuir-Blodgett films

Monolayers of the TPyP-Rubpy complex and its triad hybrids with PMA were prepared by spreading a dilute (6.03×10^{-5} mol/L) TPyP-Rubpy chloroform solution onto the pure water and 0.03–0.3 mg/mL PMA 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 on the substrate surfaces at a certain constant surface pressure with a dipping speed of 2 mm/min.

2.3. Characterization

Elemental analysis was performed on a VARIO EL3 elemental analyzer. Fourier transform infrared spectra (FTIR) were measured by using a Nicolet NEXUS 470 spectrometer operating at a

resolution of 0.5 cm^{-1} at 25°C . Thermogravimetric (TG) analysis was performed on a Perkin-Elmer TGA7, under a constant-flow air atmosphere, from room temperature to 800°C at a heating rate of $10^{\circ}\text{C}/\text{min}$. UV-vis spectra were measured by using the Shimadzu UV-2550 UV-vis spectrophotometer. Fluorescence spectra were recorded by using the Shimadzu RF-5300PC spectrophotometer.

XPS spectra were recorded using a VGESCALAB MKII multifunction spectrometer, with nonmonochromatized Mg-K α X-rays as the excitation source. The system was carefully calibrated by the Fermi edge of nickel, Au 4f $_{2/7}$, and Cu 2p $_{2/3}$ binding energy. The pass energy of 70 eV and a step size of 1 eV were chosen when taking the spectra. In the analysis chamber, pressures of $1\sim 2 \times 10^{-7}$ 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. Atomic force microscopic images were recorded using a Nanofirst 3600A AFM (Suzhou HZS-Nanosurf Nanotechnology Co., Ltd, China) by means of a tapping mode with a silicon cantilever having a force constant of 40 N/m and a resonance frequency of 300 kHz in air. The LB films were deposited on the mica substrate surfaces.

2.4. Electrochemistry

The cyclic voltammogram (CV) and photocurrent generation measurements for the TPyP-Rubpy/PMA LB films were performed by using an electrochemical analyzer (CHI 660E, China). A Pt wire and Hg/HgCl $_2$ 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 50 mmol/L KCl as the electrolyte. An initial potential of 1.0 V was applied for 2 s, and subsequently, cyclic scans to a final potential of -1.3 V were done for 10 cycles. The CV curves and data reported in the present work were the 10th cycle. To get the high-resolution redox properties of each electroactive species (TPyP, Ru-complex and PMA) in the LB films, the potential scans were completed in the range of $-1.3 \sim (-0.6)$, $-0.6 \sim 0.5$, and $0.5 \sim 1.0\text{ V}$, respectively. All electrochemical measurements were performed under Ar atmosphere at room temperature.

2.5. Photocatalytic properties

The photocatalytic activity of TPyP-Rubpy/PMA triad hybrid LB film modified quartz substrate was evaluated by the photocatalytic degradation of MO under irradiation with a 300 W Xe arc lamp (Bilon, China) at room temperature. The photocatalytic reaction was initiated when the quartz substrate covered with the LB films was immersed in an aqueous solution of MO (1.53×10^{-5} mol/L, 10 mL). After a certain period of irradiation, the substrate was withdrawn from the MO solution for the measurement of the absorption spectra to monitor the photo-oxidation of the MO (the photocatalytic reaction was stopped at the same time). The degradation rate was estimated based on the absorption intensity at 464 nm (the maximum absorption of MO).

For the photocurrent generation measurements, the irradiation was performed by using the 300 W Xe arc lamp with or without a 400 nm cutoff filter. The LB film was deposited on the ITO electrode surface at 20 mN/m with 50 mmol/L KCl as the electrolyte.

3. Results and discussion

3.1. Monolayer behaviors

Fig. 2A shows π -A isotherms for the monolayers of the TPyP-Rubpy complex on the 0.03–0.3 mg/mL PMA subphase surfaces at room temperature. All curves indicated an increase of the surface pressure after the monolayer was compressed, with the highest surface pressure reaching nearly 50 mN/m. The average TPyP-Rubpy molecular area calculated from the isotherms increased with increasing the PMA concentrations in the subphase. When the PMA concentration was about 0.1–0.3 mg/mL, the molecular area was in the range of 3.1–3.3 nm². During experiments, it was found that the TPyP-Rubpy complex hardly formed a stable monolayer on the pure water surface because of its high solubility in water [17]. Thus, the addition of the larger anionic PMA clusters in the subphase can reduce the solubility of TPyP-Rubpy and produce TPyP-Rubpy/PMA hybrid materials based on the interfacial electrostatic interaction [27-29].

As control experiments, we investigated the monolayer behaviors of TMPyP and Ru(bpy)₂Cl₂ on the PMA subphase surfaces. Instead of TPyP, which is a water-insoluble porphyrin, here, TMPyP was used as a reference. The chemical structure of TMPyP is much similar to that of TPyP, but it is a positively charged porphyrin and easily dissolves in water; both features are the same as those of the TPyP-Rubpy complex. Because of their water solubility, neither TMPyP nor Ru(bpy)₂Cl₂ can form

stable monolayers on the pure water surface.

Figure 2

Fig. 2B shows the π -A isotherms for the monolayers of TPyP and Ru(bpy)₂Cl₂ complexes on the 0.1 mg/mL PMA subphase surfaces. Both curves indicated an increase of the surface pressure after compression, suggesting that they could form insoluble monolayers on the PMA subphase surfaces. The average molecular area of TPyP and Ru(bpy)₂Cl₂ was approximately 0.53 and 0.32 nm², respectively. From the structural point of view, one TPyP-Rubpy molecule is composed of one TPyP and four Ru(bpy)₂Cl₂ substituents, so if the TPyP macrocycle and Rubpy substituents assume similar orientations and distributions in the monolayers, the molecular area of TPyP-Rubpy is expected to be approximately 1.89 nm². Here, we can find, from Fig. 2A, that a rather larger molecular area (3.1–3.3 nm²) of the TPyP-Rubpy complex exists, which may be attributed to the different arrangements or distributions of the porphyrin macrocycles and Rubpy substituents on the PMA subphase surfaces.

Figure 3

Previous work has revealed that the mean molecular area of tetraarylporphyrins, such as TPyP, is about 0.9 nm² if the porphyrin rings lie vertical to the water surface, and it is about 2.25 nm² if the porphyrin rings lie parallel to the aqueous surface [33,34]. However, in many cases, the average molecular area measured from the gas-liquid interface was smaller than 0.9 nm² [35], which has been attributed to the fact that the porphyrin macrocycles formed J-aggregates, with each macrocycle overlapped and tilted toward the water surface [36], as shown in Fig. 3A in the schematic model. Here, the TPyP molecular area was 0.53 nm² on the PMA surface, the data of which were similar to that of TPyP on the pure water surface as we observed previously [37], so it is suggested that the TPyP molecules are tilt oriented and form J-aggregates (Fig. 3A).

For the TPyP-Rubpy complex spread on the PMA subphase surface, the porphyrin macrocycles are hardly closely packed due to the steric interaction from four Rubpy substituents; these positively charged inorganic ones may strongly interact with the negatively charged PMA clusters at interfaces. As a result, porphyrin-porphyrin interaction is largely weakened, just like that involving porphyrin amphiphiles with four long alkyl chains are [36,38]. As shown in Fig. 3B, although the porphyrin macrocycles might have taken on a tilt orientation at the interface, they were hardly formed overlapped J-aggregates, so the average molecular area of TPyP-Rubpy was largely increased. The

assumption of such an arrangement of the porphyrin macrocycles on the water surfaces will be further confirmed and discussed together with their absorption features and morphologies in the transferred LB films below.

3.2. Langmuir-Blodgett films

Monolayers of the TPyP-Rubpy, TMPyP, and Ru(bpy)₂Cl₂ complexes on the 0.1 mg/mL PMA subphase surfaces were transferred onto the quartz, mica, and ITO substrate surfaces at 20 mN/m by the vertical dipping or horizontal lifting technique for the spectral, XPS, morphological, electrochemical, and photocurrent generation characterization.

3.2.1. Absorbance

Fig. 4A shows absorption spectra for the TPyP-Rubpy, TPyP, and Ru(bpy)₂Cl₂ complexes in the dilute methanol solutions, which revealed the following features. First, the spectrum of TPyP in the solutions showed a strong Soret absorption band at approximately 411.5 nm together with several Q-bands in the wavelength between 500 and 650 nm, in agreement with those reported in the literature [35]. Secondly, the spectrum of Ru(bpy)₂Cl₂ showed three absorption peaks at approximately 242, 286, and 450 nm, designated for the π - π^* electron transfer of the bpy ligand and metal-ligand charged transfer (MLCT) band of the Ru-complex [10,15]. Finally, for the TPyP-Rubpy complex in the solution, the absorption bands appeared at approximately 244, 293, and 414.5 nm, and there were several small bands from 500 to 650 nm. Apparently, these peaks corresponded to the π - π^* electron transfer of the bpy ligand and MLCT band of the Rubpy substituent, as well as to the Soret and Q-bands of the TPyP. Thus, the absorption spectral features confirmed that the TPyP-Rubpy complex was composed of TPyP and Rubpy substituents. Moreover, no significant peak shift was recorded, suggesting that the coordination reaction of TPyP and Ru(bpy)₂Cl₂ had almost no effect on the ground states of both light-harvesting units.

Figure 4

Fig. 4B shows the absorption spectra for the LB films of TPyP-Rubpy/PMA, TMPyP/PMA, and Ru(bpy)₂/PMA on the quartz substrate surfaces. For the LB film of the TMPyP/PMA binary hybrid, a broad band was recorded at about 444 nm, corresponding to the Soret absorption band of TMPyP. For the LB film of the Ru(bpy)₂/PMA binary hybrid, a broad absorption band was found at about 304

nm, corresponding to the $\pi-\pi^*$ electron transfer of the $\text{Ru}(\text{bpy})_2\text{Cl}_2$ complex. Compared with the absorption spectra of TMPyP (curves not shown) and $\text{Ru}(\text{bpy})_2\text{Cl}_2$ in the solutions, both peaks red shifted: approximately 32 nm for TMPyP and 18 nm for the $\text{Ru}(\text{bpy})_2\text{Cl}_2$ complex. This red shift has been attributed to the formation of J-aggregates in the LB films due to a planar molecular interaction among the light-harvesting units, the feature of which is well in agreement with those often observed in the organized thin films of macrocyclic compounds and inorganic complexes [39].

For the LB film of TPyP-Rubpy/PMA triad hybrids, two main absorption bands were recorded at approximately 299 and 438 nm, corresponding to the $\pi-\pi^*$ electron transfer of the Rubpy substituent and the Soret band of TPyP, respectively. Again, compared with the absorption features of the complex in the dilute solutions, we can find a 6-nm red shift for the Rubpy absorption band and a 23-nm red shift for the TPyP Soret band in the LB films. Such a red shift can also be attributed to the formation of TPyP-Rubpy aggregates in the LB films [36,39,]. However, a comparison of the content of the red shift in the LB film of the TPyP-Rubpy/PMA triad hybrids with that of the TMPyP/PMA and $\text{Ru}(\text{bpy})_2/\text{PMA}$ ones, we can find that such a red shift was smaller in the triad hybrid TPyP-Rubpy/PMA LB films. This difference suggested that the planar molecular interaction was weaker in the LB film of the TPyP-Rubpy/PMA triad hybrids than that in the TMPyP/PMA and $\text{Ru}(\text{bpy})_2/\text{PMA}$ ones, that is, the porphyrin macrocycles and Rubpy substituents are not as closely packed in the LB films (monolayers) of TPyP-Rubpy/PMA as in the LB films of TMPyP/PMA and $\text{Ru}(\text{bpy})_2\text{Cl}_2/\text{PMA}$. This conclusion confirmed the possible porphyrin arrangement in the monolayers as suggested in Fig. 3.

Finally, upon a close inspection of the absorption spectra of the LB films in Fig. 4B, one can find an increase of the absorption intensity in the wavelength between 200 and 300 nm. Compared with the absorption spectrum of the PMA in solution (Figure not shown), we can conclude that this absorption increase is due to the $\pi-\pi^*$ electron transfer of the PMA co-deposited in the LB films.

3.2.2. Morphology characterization

The morphology of the present triad hybrid LB films was characterized on the mica substrate surfaces by using the SEM and AFM techniques. As shown in Fig. 5A, a smooth SEM image was recorded for the monolayers of the TPyP-Rubpy/PMA hybrids deposited at (or below) 20 mN/m, suggesting that an almost uniform monolayer could be formed. When the monolayer was compressed

up to 30 mN/m, some sharp lines and irregular domains could be observed from the SEM images (Fig. 5B), which was due to the collapse of the monolayers, resulting in the formation of three-dimensional multilayers and/or aggregation of the TPyP-Rubpy and PMA.

Figure 5

To get more information on the morphology and height profile of the TPyP-Rubpy/PMA hybrid films, we measured their AFM images. As an example, Fig. 5C shows the AFM photo of one layer of the TPyP-Rubpy/PMA hybrids on the mica substrate surface prepared at a surface pressure of 20 mN/m. Again, a smooth two-dimensional image was recorded with an average layer thickness of about 2–3 nm. Taking into account the molecular structure of the porphyrins and PMA, the AFM images further confirmed that the monolayer was composed of the TPyP-Rubpy complex and PMA, as suggested in Fig. 3.

3.2.2. X-ray photoelectron spectroscopy

To confirm the formation of the TPyP-Rubpy/PMA triad hybrids, we used the XPS technique to detect the composition of the LB films. Fig. 6 shows the high-resolution XPS spectra for the LB films of the TPyP-Rubpy/PMA hybrids, which revealed seven peaks in the binding energy from 100 to 600 eV except for Si from the substrate. The binding energy for these peaks was at about 133.7, 197.3, 232.3/235.5, 284.7, 398.9, 461.7, and 532.1 eV, corresponding to the elements of P(2p), Cl(1s), Mo(3d), C(1s), N(1s), Ru(3p), and O(1s), respectively. Based on the chemical structure of TPyP-Rubpy and PMA, these peaks could be assigned as follows. The elements of C and N were from TPyP, while Ru, Cl and part of C and N were from the Rubpy substituents. P, Mo, and O were from the counter ion of PMA clusters adsorbed by the TPyP-Rubpy monolayer. Thus, the XPS results confirmed the formation of the TPyP-Rubpy/PMA triad hybrids at the gas-liquid interface.

Figure 6

3.2.3. Luminescence

It is well known that both porphyrin derivatives and Ru-complexes are not only efficient light-harvesting units but also strong luminescent materials, with the emissions in the wavelength ranging from 600 to 700 nm after radiation [39,40]. Here, we investigated the fluorescent emissions of TPyP and Rubpy substituents in the dilute solutions as well as those in the LB films of the TPyP-Rubpy/PMA triad hybrids as well as the TPyP/PMA and Ru(bpy)₂/PMA binary ones.

Fig. 7A shows fluorescence emission spectra for the TPyP-Rubpy, TPyP, and Ru(bpy)₂Cl₂ complexes in the dilute methanol solutions, which were excited at 420 nm. In detail, for the TPyP solution, two broad-emission bands were recorded at approximately 655 and 711 nm, designated for the Q(0,0) and Q(0,1) bands of the porphyrins [41]. For the Ru(bpy)₂Cl₂ complex, the fluorescent emission appeared at approximately 609 and 650 nm, attributed to the characteristic emissions from the MLCT excited state [42,43]. The relative intensity of two peaks was to some degree dependent on the excited wavelength and solvents. Finally, for the TPyP-Rubpy complex, three emission bands were recorded at approximately 607, 648, and 711 nm. Compared with the emissions from the TPyP and Ru(bpy)₂Cl₂ complexes, the peak at 607 nm and part of that at 648 nm could be assigned to the emissions from the MLCT excited state of the Rubpy substituent, while the peak at 711 nm and part of that at 648 nm could be assigned to the Q(0,1) and Q(0,0) emissions of the TPyP macrocycles. That is, the emission peak at approximately 648 nm was overlapped. Thus, the emission spectra further confirmed that the TPyP-Rubpy complex was composed of TPyP and Rubpy substituents and that the coordination reaction had almost no effect on the excited levels of each component.

Figure 7

Fig. 7B shows a fluorescence emission spectrum for the LB film of TPyP-Rubpy/PMA triad hybrids, excited at 445 nm. Different from that in the solution, here, a very weak fluorescent emission was recorded with the peaks at approximately 610 and 715 nm, designated for emissions from the TPyP and Rubpy substituents. To clarify why the fluorescent emission was largely weakened, we measured the fluorescence spectra of the mixtures of TPyP-Rubpy and TPyP with PMA at various molar fractions in the solutions. The results indicated a strong fluorescent quenching after the addition of the PMA (figure not shown), so we suggest that the fluorescence of TPyP-Rubpy/PMA triad hybrid LB films was quenched by the co-existing PMA.

3.2.4. Electrochemistry

Besides interesting light-harvesting and emission behaviors, both porphyrin and Ru-complexes are electroactive materials and have found various applications for the development of redox-based sensors, electroluminescent devices, and so on [44,45]. Further, PMA is a negatively charged electroactive material and is widely used as a counter ion to produce hybrid materials with organic or inorganic species, such as the carbon nanotubes and various metalloporphyrins [46,47]. Here, we

investigated the CV behaviors of these compounds in the hybrid LB films.

Fig. 8A shows the CV curve for the ITO electrode modified with three-layer LB films of the TPyP-Rubpy/PMA triad hybrids in the 50 mmol/L KCl electrolyte solution in the potential range of 1.0 to -1.3 V (vs Hg/HgCl₂) at a scan rate of 0.1 V/s. This curve revealed six couples of redox waves corresponding to the electro transfer processes of TPyP, Rubpy-complex, and PMA. However, the peaks were not as clear to distinguish because the relative intensity of the redox current intensity was much different for three kinds of electroactive species. To clarify, we measured the CV curves for each species in the different potential ranges as described in figures 8B-8D.

Fig. 8B shows the CV curve for the LB film of the TPyP-Rubpy/PMA hybrid modified electrode in the potential scan range from -1.3 to -0.6 V, which revealed two couples of redox waves with cathodic potentials (E_{pc}) at about -1.03 and -1.21 V, and anionic ones (E_{pa}) at about -0.86 and -1.04 V, respectively. The potential difference ΔE_p ($\Delta E_p = E_{pc} - E_{pa}$) was 0.17 V. Based on the existing literature [44,48], these two couples of waves corresponded to the formation of porphyrin anion and dianion radicals of TPyP^{•-}-Rubpy/PMA and TPyP²⁻-Rubpy/PMA, respectively.

One reversible couple was recorded with E_{pc} and E_{pa} at about 0.75 and 0.82 V from the CV curve measured in the potential range of 0.5 to 1.0 V (Fig. 8C). These redox potentials were similar to those of the (Co)TPyP-Rubpy complex directly immobilized on the glass carbon (GC) electrode surfaces [20] and could be attributed to one electron transfer process of TPyP-Ru^(II)bpy/PMA $\leftrightarrow$ TPyP-Ru^(III)bpy/PMA redox couple of the hybrids [23,49]. Because the GC electrodes immobilized by the pure (Co)TPyP-Rubpy complexes were not so stable in the electrolyte solutions, Nafion or nanoparticles were often co-assembled with the Ru-complexes, which resulted in the redox potential shifted to more positive potential ranges, for instance, both redox potentials reached to over 1.0 V when the complexes were mixed with SiO₂ nanoparticles and TiO₂-Nafion mixtures [50,51]. Further, our recent work found that the E_{pa} and E_{pc} were approximately 0.45 and 0.65 V for the Nafion-Ru(bpy)₂Cl₂-modified electrode, respectively [52]. When Ru(bpy)₂Cl₂ was immobilized on the nano-SiO₂ surface, the E_{pc} and E_{pa} shifted to 0.28 and 0.73 V, respectively. The potential difference ΔE_p was 0.07, 0.2, and 0.45 V for the present LB films, Nafion-Ru(bpy)₂Cl₂, and nano-SiO₂ surface, respectively [50]. It has been considered that the value of ΔE_p is closely related to the film resistance of the modified electrodes [23,52]; thus, we may suggest that, compared with the casting film of Nafion-Ru(bpy)₂Cl₂ and modified nano-SiO₂ particles, the present triad hybrid LB

films have low film resistance, which benefits the electrons transferring between the electroactive Rubpy species and the electrode surface.

Figure 8

Fig. 8D shows the CV curve for the TPyP-Rubpy/PMA hybrid LB film modified electrode measured in the potential scan range of -0.6 to 0.4 V, which revealed three couples of redox waves. The E_{pc} was about 0.31 , 0.10 , and -0.10 V, and the E_{pa} was 0.39 , 0.16 , and -0.02 V, respectively. Based on the literature [53,54], these redox waves corresponded to three successive electron processes of PMA. During experiments, we found that the CV measurements were well reproducible, further confirming the formation of stable TPyP-Rubpy/PMA hybrid LB films.

3.3. Catalytic oxidation of organic dyes and photo-induced current generation

As it has been pointed out, both porphyrin and the Ru-complex are good light-harvesting units that can adsorb light and then transfer the energy to acceptors for various applications, such as the degradation of organic dyes, light-induced photocurrent generation, photo-catalytic hydrogen production, and photo-sensitized solar cells [2,3,5-7,55]. Here, the photocatalytic activity of the TPyP-Rubpy/PMA triad LB films was evaluated by the photocatalytic degradation of MO and light-induced generation under irradiation at room temperature.

Figure 9

Fig. 9A shows the UV-vis absorption spectra of the MO solutions when the quartz substrate covered with 10 layers of the LB films of TPyP-Rubpy/PMA triads was immersed and irradiated for 0 to 5.5 hours to monitor the photo-oxidation of the MO. The reaction was started when the quartz substrate was immersed in the aqueous solution of MO (10 mL). These curves indicate that the concentrations of MO in the solutions decreased gradually with the radiation time [56]. Based on the maximum absorption of MO at 464 nm, a plot of the absorption intensity to the irradiation time is shown in Fig. 9B, which indicates that the initial degradation rate (k_i) was a little faster than that after one to two hours. Furthermore, it was found that about 50% of MO molecules could be degraded after 5.5 hours.

During experiments, it was found that, although the TPyP/PMA and Ru(bpy)₂Cl₂/PMA binary LB films also showed photocatalytic degradation of MO, these LB films were not so stable in the aqueous MO solution. That is, the LB films deposited were easily de-adsorbed from the substrate

surfaces. This may be attributed to the fact that the electrostatic interaction between layers of TMPyP (or Ru(Bpy)₂Cl₂) and PMA was not as strong as that between TPYP-Ru(bpy) and PMA. The light sensitizers of TMPyP or Ru(bpy)₂Cl₂ were easily dissolved into the aqueous solution.

Figure 10

Fig. 10 shows the photocurrent responses for the ITO electrode modified with the 10-layer LB film of TPYP-Rubpy/PMA triad hybrids under radiation with and without a 400 nm cutoff filter. The photocurrents were fast and uniform with high reproducibility under light irradiation, indicating that the LB film modified electrode was stable and that the photo-sensitizers were reversibly responsive to the radiation. The photogenerated excited species of TPYP-Rubpy^(*), TPYP^(*)-Rubpy, or TPYP^(*)-Rubpy^(*) can be quenched rapidly via electron transfer to the electrode surface or PMA (since PMA can quench the fluorescent emissions from the sensitizers). A stronger photocurrent was recorded for the measurement without the use of a cutoff filter than that with it, which can be attributed to the fact that the Rubpy substituent in the triad hybrid LB films has no absorption in the visible region. Further, based on the photo-induced electron transfer diagram that Yamamoto and coworkers proposed [12], the absorbed light energy of the Rubpy substituent may be possibly transferred to the electrode surface via the TPYP one.

4. Conclusions

We have demonstrated the preparation of tetrapyrrolylporphyrin-Rubpy complex/polyoxometalate triad hybrid materials at gas-liquid interfaces. Stable porphyrin-Rubpy/PMA LB films could be formed owing to the strong interfacial electrostatic interaction between the positively charged porphyrin-Ru complex and negatively charged PMA clusters. The LB film modified electrodes effectively showed reversible redox waves corresponding to the electron transfer processes of porphyrins, Ru-complex, and PMA substituents. The triad hybrid LB films can be used as a photosensitizer for organic dye degradation and photocurrent generation.

Acknowledgement. The authors are grateful for the National Science Foundation of China (21373058), the Program for Changjiang Scholars and Innovative Research Team in University (IRT_15R12), and Fudan's Undergraduate Research Opportunities Program (14008).

References

- [1] C.M. Drain, A. Varotto, I. Radivojevic, Self-organized porphyrinic materials, *Chem. Rev.* 109 (2009) 1630-1658.
- [2] X.H. Zhang, T.Y. Peng, S.S. Song, Recent advance in dye-sensitized semiconductor systems for photocatalytic hydrogen production, *J. Mater. Chem. A* 4 (2016) 2365-2402.
- [3] L.-L. Li, E.W.-G. Diau, Porphyrin-sensitized solar cells, *Chem. Soc. Rev.* 42 (2013) 291-304.
- [4] I. Beletskaya, V.S. Tyurin, A.Y. Tsivadze, R. Guillard, C. Stern, *Chem. Rev.* 109 (2009) 1659-1713.
- [5] Y.Z. Wu, W.-H. Zhu, S.M. Zakeeruddin, M. Gratzel, Insight into D-A- π -A structured sensitizers: a promising route to highly efficient and stable dye- sensitized solar cells, *ACS Appl. Mater. Interfaces* 7 (2015) 9307-9318.
- [6] P.A. Angaridis, E. Ferentinos, G. Charalambidis, K. Ladomenou, V. Nikolaou, S. Biswas, G.D. Sharma, A.G. Coutsolelos, Pyridyl vs. bipyridyl anchoring groups of porphyrin sensitizers for dye sensitized solar cells, *RSC Adv.* 6 (2016) 22187-22203.
- [7] J.F. Lu, H. Li, S.S. Liu, Y.-C. Chang, H.-P. Wu, Y.B. Cheng, E.W.-G. Diau, M.K. Wang, Novel porphyrin-preparation, characterization, and applications in solar energy conversion, *Phys. Chem. Chem. Phys.* 18 (2016) 6885-6892.
- [8] S. Singh, A. Aggarwal, N.V.S.D.K. Bhupathiraju, G. Arianna, K. Tiwari, C.M. Drain, Glycosylated porphyrins, phthalocyanines, and other porphyrinoids for diagnostics and therapeutics, *Chem. Rev.* 115 (2015) 10261-10306.
- [9] I. Gillaizeau-Gauthier, F. Odobel, M. Alebbi, R. Argazzi, E. Costa, C.A. Bignozzi, P. Qu, G.J. Meyer, Phosphonate- based bipyridine dyes for stable photovoltaic devices. *Inorg. Chem.* 40 (2001) 6073-6079.
- [10] K. Kalyanasundaram, Photophysics, photochemistry and solar energy conversion with tris(bipyridyl) ruthenium(II) and its analogues, *Coord. Chem. Rev.* 46 (1982) 159-244.
- [11] H.-Q. Zheng, Y.-P. Guo, M.-C. Yin, Y.-T. Fan, Synthesis, Characterization of a new photosensitive compound [Ru(bpy)₂(TPAD)](PF₆)₂ and its application for photocatalytic hydrogen producrion, *Chem. Phys. Lett.* 653 (2016) 17-23.
- [12] M. Yamamoto, L. Wang, F.S. Li, T. Fukushima, K. Tanaka, L.C. Sun, Visible light-driven water oxidation using a covalently-linked molecular catalyst-sensitizer dyad assembled on a TiO₂ electrode,

Chem. Sci. 7 (2016) 1430-1439.

- [13] R.N. Sampaio, M.M. Silva, A.A. Batista, N.M.B. Neto, Investigation of the photophysical and electrochemical properties of a free base tetrapyrrolyl porphyrin with meso carbon linked ruthenium(II) groups, *J. Photochem. Photobio. A: Chem.* 315 (2016) 98-106.
- [14] H.Z. Ke, W.P. Ma, H.D. Wang, G.E. Cheng, H. Yuan, W.-K. Wong, D.W.J. Kwong, H.-L. Tam, K.-W. Cheah, C.-F. Chan, K.-L. Wong, Synthesis, singlet-oxygen photogeneration, two-photon absorption, photo-induced DNA cleavage and cytotoxic properties of an amphiphilic β -schiff-base linked Ru(II) polypyridyl-porphyrin conjugate, *J. Lumin.* 154 (2014) 356-361.
- [15] K. Araki, H.E. Toma, Synthesis and characterization of a multibridged porphyrin complex containing peripheral bis(bipyridine)-ruthenium(II) groups, *J. Coord. Chem.* 30 (1993) 9-17.
- [16] B.K. Araki, L. Angnes, H.E. Toma, Rectifying properties and photoconductivity of tetraruthenated nickel porphyrin films, *Adv. Mater.* 7 (1995) 554-559.
- [17] C.M.N. Azevedo, K. Araki, H.E. Toma, L. Angnes, Determination of sulfur dioxide in wines by gas-diffusion flow injection analysis utilizing modified electrodes with electrostatically assembled films of tetraruthenated porphyrin, *Anal. Chim. Acta* 387 (1999) 175-180.
- [18] K. Araki, L. Angnes, C.M.N. Azevedo, H.E. Toma, Electrochemistry of a tetraruthenated cobalt porphyrin and its use in modified electrodes as sensors of reducing analytes, *J. Electroanal. Chem.* 397 (1995) 205-210.
- [19] M.S.M. Quintino, K. Araki, H.E. Toma, L. Angnes, New hydrazine sensors based on electropolymerized meso-tetra(4-sulphonatephenyl) porphyrinate manganese(III)/silver nanomaterial, *Talanta* 74 (2008) 730-735.
- [20] K. Calfumán, M.J. Aguirre, D. Villagra, C. Yañez, C. Arévalo, B. Matsuhira, L. Mendoza, M. Isaacs, Nafion/tetraruthenated porphyrin glassy carbon-modified electrode: characterization and voltammetric studies of sulfite oxidation in water-ethanol solutions, *J. Solid State Electrochem.* 14 (2010) 1065-1072.
- [21] R.A. Timm, M.P.H. Falla, M.F.G. Huila, H.E.M. Peres, F.J. Ramirez-Fernandez, K. Araki, H.E. Toma, Vanadium oxide-porphyrin nanocomposites as gas sensor interfaces for probing low water content in ethanol, *Sensors Actuators B* 146 (2010) 61-68.
- [22] H.H. Ma, Y.Y. Geng, Y.-I. Lee, J.C. Hao, H.-G. Liu, interfacial assembly of Pt nanoparticle-doped free-standing polymer foam films and their catalytic performance, *Colloids Surf.*

A: Physicochem. Eng. Aspects 419 (2013) 201-208.

[23] P. Bertoncello, L. Dennany, R.J. Forster, P.R. Unwin, Nafion-tris(2,2'-bipyridyl) ruthenium(II) ultrathin Langmuir-schaefer films: redox catalysis and electrochemiluminescent properties, *Anal. Chem.* 79 (2007) 7549-7553.

[24] C.L. Wirth, M.D. Volder, J. Vermant, Fabrication of planar colloidal clusters with template-assisted interfacial assembly, *Langmuir* 31 (2015) 1632-1640.

[25] W. Yang, L.H. Gao, K.Z. Wang, Photoelectric properties of polyoxometalate-based thin films-recent advances and future perspective, *Polyhedron* 82 (2014) 80-87.

[26] Y. Yang, B. Zhang, Y. Wang, L. Yue, W. Li, L.X. Wu, A photo-driven polyoxometalate complex shuttle and its homogeneous catalysis and heterogeneous separation, *J. Am. Chem. Soc.* 135 (2013) 14500-14503.

[27] D.J. Qian, H.X. Huang, W. Huang, T. Wakayama, C. Nakamura, J. Miyake, Preparation and electrochemical properties of organic-inorganic hybrids with the use of alkylammonium or alkylviologen cations and polyoxometalate anions, *Colloids Surf. A: Physicochem. Eng. Aspects* 248 (2004) 85-91.

[28] X.L. Wang, Y.L. Wang, W.K. Miao, M.B. Hu, J. Tang, W. Yu, Z.Y. Hou, P. Zheng, W. Wang, Langmuir and Langmuir-Blodgett films of hybrid amphiphiles with a polyoxometalate headgroup, *Langmuir* 29 (2013) 6537-6545.

[29] B.B. Zhang, C. Ma, X.G. Wang, M.B. Hu, X.L. Wang, W. Wang, Langmuir and of Langmuir-Blodgett films of two dumbbell-shaped hybrids composed of a polyoxometallate and two polyhedral oligosilsesquioxanes, *Acta Chim. Sin.* 73 (2015) 441-449.

[30] M. Clemente-Leon, B. Agricole, C. Mingotaud, C.J. Gomez-Garcia, E. Coronado, P. Delhaes, Toward new organic/inorganic superlattices: keggins polyoxometalates in Langmuir and Langmuir-Blodgett films, *Langmuir* 13 (1997) 2340-2348.

[31] L. Liu, L.X. Qiao, S.Z. Liu, D.M. Cui, C.M. Zhang, Z.J. Zhou, Z.L. Du, W.Y. Wong, Polyplatinayne/polyoxometalate composite Langmuir-Blodgett films: preparation, structural characterization, and potential optoelectronic application, *J. Polymer Sci.: Part A: Polymer Chem.* 46 (2008) 3193-3206.

[32] H.L. Zhang, J.M. Qi, L.H. Gao, K.Z. Wang, An electrostatically self-assembled hybrid film based on dinuclear ruthenium(II) polypyridyl complex and europium-substituted tungstoborate,

Colloid Surf. A: Physicochem. Eng. Aspects 492 (2016) 119-126.

[33] A. Ruauudel-Teixier, A. Barraud, B. Belbeoch, M. Roulliay, Langmuir-Blodgett films of pure porphyrins, *Thin Solid Films* 99 (1983) 33-40.

[34] J.Z. Jiang, D.K.P. NG, A decade journey in the chemistry of sandwich-type tetrapyrrolo-rare earth complexes, *Acc. Chem. Res.* 42 (2009) 79-88.

[35] H.G. Liu, X.S. Feng, L.J. Zhang, G.L. Ji, D.J. Qian, Y.I. Lee, K.Z. Yang, Influences of hydrophilic and hydrophobic substituents on the organization of supramolecular assemblies of porphyrin derivatives formed at the air/water interface, *Mater. Sci. Eng. C* 23 (2003) 585-592.

[36] H. Chou, C.-T. Chen, K.F. Storck, P.W. Bohn, K.S. Suslick, Langmuir-Blodgett films of amphiphilic push-pull porphyrins, *J. Phys. Chem.* 98 (1994) 383-385.

[37] D.J. Qian, C. Nakamura, J. Miyake, Multiporphyrin array from interfacial metal-mediated assembly and its Langmuir-Blodgett films, *Langmuir* 16 (2000) 9615-9619.

[38] H.G. Liu, X.S. Feng, K.Z. Yang, W.A. Liang, Studies on the structure of LB films of porphyrin derivatives containing different substituted alkyl chains, *Acta Chim. Sin.* 55 (1997) 117-122.

[39] Y.F. Qiu, P.L. Chen, M.H. Liu, Interfacial assembly of an achiral zinc phthalocyanine at the air/water, interface: a surface pressure dependent aggregation and supramolecular chirality, *Langmuir* 24 (2008) 7200-7207.

[40] M.D. Witt, S. Roughton, T.J. Isakson, M.M. Richter, Enhanced electrogenerated chemiluminescence of $\text{Ru}(\text{bpy})_3^{2+}$ /TPrA (bpy = 2,2'-bipyridine; TPrA = tri-n-propylamine) via oxygen quenching using melatonin, *J. Lumin.* 171 (2016) 118-123.

[41] J. Mohanty, A.C. Bhasikuttan, S.D. Choudhury, H. Pal, Noncovalent interaction of 5,10,15,20-tetrakis(4-N-methylpyridyl) porphyrin with cucurbit[7]uril: a supramolecular architecture, *J. Phys. Chem. B* 112 (2008) 10782-10785.

[42] I.D. Aguiar, S.D. Inglez, R.M. Carlos, Synthesis, spectroscopic characterization, photochemical and photophysical properties of mono- and tetranuclear Ru(II) and Mn(I) complexes with 4,4'-bipyridine ligand, *Inorg. Chem. Commun.* 44 (2014) 70-78.

[43] X.P. Cai, J.Y. Luo, X. Xu, Z.S. Jiang, H. Li, Tunable photoluminescence properties of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ bound to a BSA-SWCNTs film upon incorporation of $[\text{Co}(\text{phen})_3]^{3+}$, *J. Photochem. Photobiol. A: Chem.* 291 (2014) 1-8.

[44] E.V. Caemelbecke, A. Derbin, P. Hambright, R. Carcia, A. Doukkali, A. Saoiabi, K. Ohkubo, S.

- Fukuzumi, K.M. Kadish, Electrochemistry of $[(\text{TMpyP})\text{M}^{\text{II}}]^{4+}(\text{X}^-)_4$ ($\text{X}^- = \text{Cl}^-$ or BPh_4^-) and $[(\text{TMpyP})\text{M}^{\text{III}}]^{4+}(\text{Cl}^-)_4$ in N, N- Dimethylformamide where M is one of 15 different metal ions, *Inorg. Chem.* 44 (2005) 3789-3798.
- [45] I. Prieo, M.T. Martin, D. Mobius, L. Camacho, Electrochemical properties of Langmuir-Blodgett mixed films consisting of a water-soluble porphyrin and a phospholipid, *J. Phys. Chem. B* 102 (1998) 2523-2529.
- [46] S.P. Liu, L. Xu, F.Y. Li, W.H. Guo, Y. Xing, Z.X. Sun, Carbon nanotubes-assisted polyoxometalate nanocomposite film with enhanced electrochromic performance, *Electrochim Acta* 56 (2011) 8156-8162.
- [47] Y. Shen, J.Y. Liu, J.G. Jiang, B.F. Liu, S.J. Dong, Fabrication of a metalloporphyrin-polyoxometalate hybrid film by a layer-by-layer method and its catalysis for hydrogen evolution and dioxygen reduction, *J. Phys. Chem. B* 107 (2003) 9744-9748.
- [48] C.-L. Lin, M.-Y. Fang, S.-H. Cheng, Substituent and axial ligand effects on the electrochemistry of zinc porphyrin, *J. Electroanal. Chem.* 531 (2002) 155-162.
- [49] K.M. Lancaster, J.B. Gerken, A.C. Durrell, J.H. Palmer, H.B. Gray, Electronic structures, photophysical properties, and electrochemistry of ruthenium(II)(bpy)₂ pyridylimidazole complexes, *Coord. Chem. Rev.* 254 (2010) 1803–1811.
- [50] Z. Guo, Y. Shen, M. Wang, F. Zhao, S. Dong, Electrochemistry and electrogenerated chemiluminescence of SiO₂ nanoparticles/tris(2,2'-bipyridyl)ruthenium(II) multilayer films on indium tin oxide electrodes. *Anal. Chem.* 76 (2004) 184-191.
- [51] H.N. Choi, S.H. Cho, W.Y. Lee, Electrogenerated chemiluminescence from tris(2,2'-bipyridyl)ruthenium(II) immobilized in titania-perfluorosulfonated ionomer composite films. *Anal. Chem.* 75 (2003) 4250-4256.
- [52] H.X. Huang, W.L. He, Y.Y. Ma, Preparation, characterization, luminescent and electrochemical properties of Ru(bpy)₂-functionalized silica nanoparticles, *Chem. Res. Chinese Universities* 32 (2016) 695-701.
- [53] L. Ding, Y. Liu, S.-X. Guo, J. Zhai, A.M. Bond, J. Zhang, Phosphomolybdate@poly(diallyl-dimethylammonium chloride)-reduced graphene oxide modified electrode for highly efficient electrocatalytic reduction of bromate. *J. Electroanal. Chem.* 727 (2014) 69-77.
- [54] D.W. Fan, G.B. Li, J.C. Hao, Fabrication and electrocatalytic activities of porphyrin and

- 12-molybdophosphoric acid hybrid films, *J. Colloid Interface Sci.* 351 (2010) 151–155.
- [55] D.W. Pan, J.H. Chen, W.Y. Tao, L.H. Nie, S.Z. Yao, Polyoxometalate-modified carbon nanotubes: New catalyst support for methanol electro-oxidation, *Langmuir* 22 (2006) 5872–5876.
- [56] X.B. Ren, M. Chen, D.-J. Qian, Pd(II)-mediated triad multilayers with zinc tetrapyridylporphyrin and pyridine-functionalized nano-TiO₂ as linkers: assembly, characterization, and photocatalytic properties, *Langmuir* 28 (2012) 7711–7719.

Figure legends:

Fig. 1. Structure of the tetraruthenated porphyrin TPyP-Rubpy used in the present work

Fig. 2. Surface pressure-area isotherms for the monolayers of: (A) the TPyP-Rubpy complex on the surfaces of the subphases containing (----) 0.03, (—) 0.1, and (— · —) 0.3 mg/mL PMA and (B) the (—) TMPyP and (----) Ru(bpy)₂Cl₂ on the 0.1 mg/mL PMA subphase surfaces.

Fig. 3. Schematic drawing for the (A) TMPyP and (B) TPyP-Rubpy macrocycles distributed in the monolayers

Fig. 4. (A) Absorption spectra for the TPyP (----), Ru(bpy)₂Cl₂ (-----), and TPyP-Rubpy (—) complexes in the dilute methanol solutions. (B) Absorption spectra for the LB films of TMPyP/PMA (----), Ru(bpy)₂/PMA (-----), and TPyP-Rubpy/PMA (—) on the quartz substrate surfaces.

Fig. 5. SEM images of the TPyP-Rubpy/PMA monolayer deposited at (A) 20 mN/m and (B) 30 mN/m. (C) AFM image of the TPyP-Rubpy/PMA monolayer deposited at 20 mN/m

Fig. 6. High-resolution XPS spectra for the TPyP-Rubpy/PMA triad hybrid LB films

Fig. 7. (A) Fluorescent emission spectra for the TPyP (----), Ru(bpy)₂Cl₂ (-----), and TPyP-Rubpy (—) complexes in the dilute methanol solutions. (B) Fluorescent emission spectrum for the LB film of TPyP-Rubpy/PMA triad hybrids on the quartz substrate surface.

Fig. 8. Cyclic voltammograms for the ITO electrode modified with the LB films of TPyP-Rubpy/PMA hybrids in the 50 mmol/L KCl electrolyte solution at a potential scan rate of 0.1 V/s with different potential scanning ranges: (A) –1.3 ~ 1.0 V, (B) –1.3 ~ (–0.6), (C) –0.6 ~ 0.5, and (D) 0.5 ~ 1.0 V (vs Hg/HgCl₂)

Fig. 9. (A) UV-vis absorption spectra for the degradation of MO (1.53×10^{-5} mol/L) in aqueous solution under radiation at room temperature. The catalyst was a quartz substrate covered with four layers of the TPyP-Rubpy/PMA triad hybrid LB films. (Reaction time, top-down: 0, 0.5, 1, 1.5, 2, 2.5, 3.5, 4.5, and 5.5 h). (B) A plot of the absorption intensity at 464 nm to the irradiation time.

Fig. 10. Photocurrent responses for the ITO electrode modified with three-layer LB film of TPyP-Rubpy/PMA triad hybrids under radiation with (-----) and without (—) a 400 nm cutoff filter, as well as (····) a naked ITO electrode.

Interfacial self-assembly, characterization, electrochemical and photo-catalytic properties of porphyrin-ruthenium complex/polyoxomelate triad hybrid multilayers

Wen-Li He, Jia-Lu Chen, Meng Chen, Dong-Jin Qian*

Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Interfacial self-assembly, characterization, electrochemical and photo-catalytic
properties of porphyrin-ruthenium complex/polyoxometalate triad hybrid multilayers

Wen-Li He, Jia-Lu Chen, Meng Chen, Dong-Jin Qian^{*}

Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China