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

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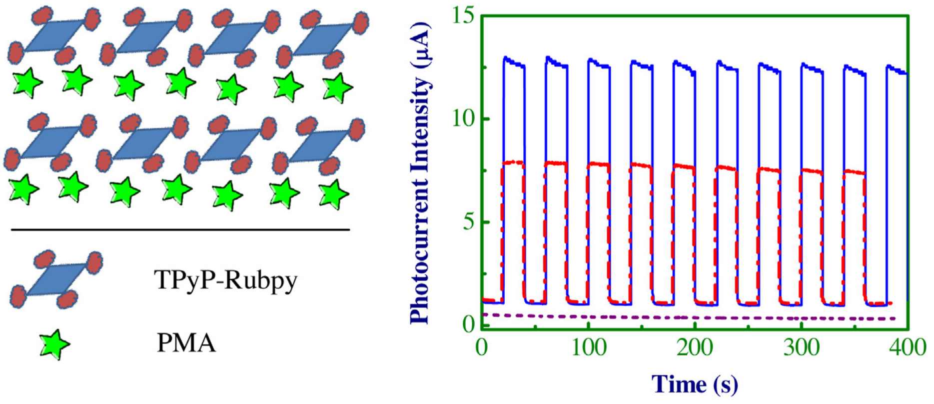
HIGHLIGHTS

- Tetraruthenated porphyrin/phosphomolybdic acid triad hybrids were prepared.
- Six reversible redox waves corresponded to TPyP, Rubpy complex and PMA.
- TPyP-Rubpy/PMA hybrids were used as photo-catalyst for degradation of organic dye.
- TPyP-Rubpy/PMA hybrids used as light-harvesting units for photocurrent generation.

GRAPHICAL ABSTRACT



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ABSTRACT

Triad hybrid multilayers composed of tetrapyridylporphyrin (TPyP), bis(2,2′-bipyridyl)ruthenium chloride [$Ru(bpy)_2Cl_2$], and phosphomolybdic acid (PMA) have been prepared at the gas-liquid interface. The tetraruthenated porphyrin of TPyP-Rubpy complex was synthesized by the coordination interaction of TPyP with $Ru(bpy)_2Cl_2$. Surface pressure–area isotherms indicated that the average molecular area of the TPyP-Rubpy complex was in the range of 3.1–3.3 nm^2 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 $Hg/HgCl_2$), which could be designated

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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.

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 TiO_2 particles to form Ru-complex/Pt/TiO_2 nanocomposites, the photo-induced hydrogen evolution could reach 9500 μmol(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 metalloprphyrins 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 tetrapyridylporphyrin (TPyP) or its metalated derivatives with four Ru(bpy)$_2$Cl$_2$ (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-pho-sphorylcholine [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/HgCl$_2$), 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)$_2$Cl$_2$ and tris(2,2′-bipyridyl)ruthenium(II) chloride [Ru(bpy)$_3$Cl$_2$] hexahydrate came from Sterm 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 (Fig. 1) complex was synthesized according to Araki and Toma's method [15]. Anal. Calc. for TPyP-Rubpy, $Ru_4C_{120}H_{88}N_{24}Cl_8 \cdot 18H_2O$: 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.

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