Preparation, characterization and photoelectric properties of dual-emissive Langmuir–Blodgett film of europium-substituted polyoxometalate and zinc(II) porphyrin platinum(II) complex

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Abstract

An organometallic/inorganic composite Langmuir–Blodgett (LB) film was prepared using a rigid-rod zinc(II) porphyrin platinum(II) complex coordinated with trans-bis(ethynylbenzene) (ZnPPT) as the π-conjugated organometallic molecule, and a europium-substituted polyoxometalate (POM), Na9EuW10O36 (EuW10) as the inorganic component. The structure and photophysical properties of the LB film were characterized by Π–A isotherms, UV–vis absorption and photoluminescence spectra, atomic force microscopy imaging and scanning tunneling microscopy. The results indicate that stable, well-defined Langmuir and LB films were formed using pure water and POM as subphases. Luminescence spectra of the hybrid LB film showed that the emission spectra were obtained due to the dual-emissive nature of the mixed ZnPPt/EuW10 blends, and EuW10 was able to enhance the emission of ZnPPT. The ZnPPT-based LB film displayed an interesting electrical conductivity behavior. The 3-layer film formed by ZnPPT/EuW10 complex had a strong electrical response, giving rise to a tunneling current up to ±100 nA when the voltage was monitored at −1.4–3.1 V. When it was excited by light, the LB composite film generated a photovoltage of 24 μV, indicating that the hybrid film had a strong photovoltage response as well.

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1. Introduction

Hybrid organic/inorganic materials are drawing great attention because they possess not only the stable and super optical, electrical, and magnetic properties of the inorganic components but also the structural flexibility of organic chromophores [1–3]. The construction of organic/inorganic hybrids is useful for obtaining multifunctional materials with desired electrical and/or optical properties [4].

The Langmuir–Blodgett (LB) method is one of the most useful techniques for the fabrication of functional ultrathin films with a controlled thickness and an ordered structure and the technique has been widely applied to the fabrication of various functional devices such as chemo- or biosensors, modified electrodes, optical logic gates, or molecular electronic devices [5,6].

Polyoxometalates (POMs) are typical inorganic metal oxide clusters with a wealth of topologies and optical, electrical, or magnetic properties, and are widely investigated in various fields such as catalysis, biology, medicine, and materials science [7,8]. Owing to their super structure and physiochemical properties, POMs are regarded as one of the best building blocks for the fabrication of functional hybrid materials [9–12]. For example, the lanthanide-POMs have been studied extensively for their luminescence and energy transfer processes [13–17].

Porphyrins are a type of chemical with a tremendous potential for the manifold applications because of their unique photophysical and electrochemical properties, remarkable stability, and predictable and rigid structures. These applications include nonlinear optics, catalysts, sensors, actuators, molecular sieves, and therapeutics [18–27].

Carbon-rich organometallic functional materials containing rigid, π-conjugated chains are also of various advanced applications [18–23] in lasers, photocells, organic light-emitting diodes and field-effect transistors. These materials possess particularly promising properties such as nonlinear optical effects [21,24–27], luminescence and photoconductivity [28–31], electronic communication as molecular wires [32], and liquid crystallinity [33–35].

Although the solution phase study of metal alkynyls in the form of bis(ethynyl) linkers by which
electronic delocalization within the LB film was achieved. The compound can be combined with an electron reservoir, i.e., a europium-substituted POM, to prepare organometallic/inorganic hybrid LB films [36–40]. Because of the highly ordered nature of the LB films, the intermolecular interactions in LB films could be remarkably different from those in solutions or in amorphous solids. A few studies have been reported on the LB films containing metallasenes [37–39] or rare-earth POMs [13]. However, the LB films combining the above two types of species together were not reported. In this paper, we report the preparation of a rigid-rod zinc(II) porphyrin platinum(II) complex coordinated with trans-bis(ethynylbenzene)/europium-substituted POM hybrid LB film and its structure and photovoltaic properties. The formula of the composites for the LB film is shown in Fig. 1.

2. Experimental section

2.1. Materials and their characterization

All reactions were carried out under nitrogen atmosphere with the use of standard Schlenk techniques, but no special precautions were taken to exclude oxygen during work-up. Solvents were predried and distilled from appropriate drying agents. All chemicals, unless otherwise specified, were obtained from commercial sources and used as received. Europium-substituted POM, viz. Na\textsubscript{6}EuW\textsubscript{10}O\textsubscript{36} (denoted as EuW\textsubscript{10}) and zinc(II) porphyrin platinyne complex coordinated with trans-bis(ethynylbenzene) (denoted as ZnPpt) were synthesized following a procedure reported previously [30,41]. Preparative thin layer chromatography separation was performed on 0.7 mm silica plates following a procedure reported previously [30,41]. Preparative thin layer chromatography separation was performed on 0.7 mm silica plates prepared in our laboratory. Infrared spectra were recorded on a PERKIN ELMER FTIR 550 spectrometer, using CaF\textsubscript{2} cells with a 0.5 cm path length. Nuclear Magnetic Resonance (NMR) spectra were measured in CDCl\textsubscript{3} on a Varian INOVA 400 MHz FT-NMR spectrometer, in which \textsuperscript{1}H and \textsuperscript{13}C NMR chemical shifts were quoted relative to tetramethylsilane and \textsuperscript{31}P chemical shifts were relative to an 85% H\textsubscript{3}PO\textsubscript{4} external standard. Fast atom bombardment mass spectra were recorded on a Finnigan MAT SSQ710 mass spectrometer.

2.2. Synthesis of ZnPpt

A mixture of trans-phenylethynylchlorobis(trin-butylphosphine)-platinum(II) (224 mg, 0.304 mmol) and 0.5 mol equivalent of 5,15-bis(1,4-ethynylbenzene)-10,20-di-n-pentylzinc(II)porphyrin (108 mg, 0.152 mmol) was dissolved in Pr\textsubscript{2}NH/CH\textsubscript{2}Cl\textsubscript{2} (50 mL, 1:1 v/v) and CuI (3 mg) was subsequently added. After stirring at room temperature for 12 h, all the volatile components were removed under reduced pressure. The residue was purified through column chromatography using silica and n-hexane/CH\textsubscript{3}Cl\textsubscript{2} (40:60, v/v) as eluent to give a red solution. After the removal of solvent by a rotary evaporator, a red powder of the title complex was obtained at a yield of 38.4% (122 mg). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 0.98–1.07 (m, 36 H), 1.53–1.65 (m, 28 H), 1.73–1.86 (m, 28 H), 2.28–2.36 (m, 24 H), 2.55–2.57 (m, 4 H), 5.00–5.05 (m, 4 H), 7.26–7.34 (m, 10 H), 7.68 (d, 4H, J = 10.3 Hz), 8.05 (d, 4H, J = 10.7 Hz), 9.02 (d, 4H, J = 6.4 Hz), 9.54 (d, 4H, J = 6.1 Hz). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 150.12, 149.27, 139.84, 134.19, 132.09, 130.82, 128.89, 128.49, 127.86, 124.82, 120.48, 119.96, 109.47, 109.11, 108.90, 108.06, 38.76, 35.73, 32.87, 26.47, 24.52, 24.00, 22.84, 14.18, 13.95. \textsuperscript{31}P NMR (CDCl\textsubscript{3}, 160 MHz): \(\delta\) 4.56 (\(\textsuperscript{3}J_{\text{P-P}} = 3102 \text{ Hz}\)). Elem anal. calcld (\%) for C\textsubscript{110}H\textsubscript{157}NaP\textsubscript{2}PtZn: C, 62.47; H, 7.48; N, 2.65. Found: C, 62.66; H, 7.70; N, 2.81.

2.3. Monolayer and LB film fabrication

The formula of the composites for the LB film is shown in Fig. 1. Europium-substituted POM can be organized as a monolayer using the LB technique. Monolayer formation and deposition were carried out on a French LB 105 slot under room temperature condition at 20 ± 1 °C under a continuous dry nitrogen flow. The surface pressure was measured by the Wilhelmy plate method. Triple-distilled water at pH = 6 with a resistivity higher than 1.8 × 10\textsuperscript{8} Ohm cm and surface tension of 70 mN/m was used as the subphase. The spreading solution of ZnPpt (5.0 × 10\textsuperscript{−3} mmol L\textsuperscript{−1}) in chloroform (HPLC grade) was spread onto the pure water subphase using a microsyringe. Compression was started at a compression rate of 0.3 cm\textsuperscript{2} min\textsuperscript{−1} after the solvent evaporated for 45 min and the isotherms were recorded. The procedure of LB film fabrication was essentially the same as that for the monolayer except that the subphase is POM aqueous solution (1.0 × 10\textsuperscript{−3} mol L\textsuperscript{−1}). All the experiments for monolayer deposition were performed under a surface pressure of 18 mN m\textsuperscript{−1}. In the case where a stable Langmuir monolayer of ZnPpt was formed on the subphase, the monolayer was subsequently deposited onto substrates [indium tin oxide (ITO) substrate for current–voltage (I–V) and surface photovoltage spectroscopy (SPS), quartz substrate for Ultraviolet–visible (UV–vis) and photoluminescence (PL)] by the vertical dipping method at a rate of 3 mm min\textsuperscript{−1}, resulting in a fairly good deposition of a typical Y-mode film. The number of layers of LB film prepared here is equal to the number of dipping or lifting processes, on each of which a dipping Langmuir monolayer was transferred onto the substrate with a good transfer ratio of ca. 1.

2.4. Characterization of the LB films

UV–vis spectra were measured on a UNICAM Helios \(\alpha\) spectrometer. SPS was measured on a D–300 surface photovoltage instrument. PL spectra were recorded on a SPEX F212 fluorescence spectrometer. Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) images of the LB films were measured on a SPA–400 conductive atomic force microscope.

3. Results and discussion

3.1. Synthesis of ZnPpt

Alkynylplatinum(II)–zinc(II) porphyrinate (ZnPpt) was prepared in 38.4% yield by the direct base-catalyzed dehydrohalogenation reaction of 5,15-bis(1,4-ethynylbenzene)-10,20-di-n-pentylzinc(II)porphyrin with 2 equivalents of trans-Pr\textsubscript{2}NH(n-Bu)\textsubscript{2}(C=CC\textsubscript{6}H\textsubscript{5})Cl in the presence of the ethynyl-activating reactant Cul and a base (i-Pr\textsubscript{2}NH) at room temperature. ZnPpt is readily soluble in chlorinated solvents such as CHCl\textsubscript{3} and CH\textsubscript{2}Cl\textsubscript{2} to give a red solution.
Spectroscopic characterization by NMR and mass spectrometry ascertained the identity of the ZnPPt. The platinum(II) complex displayed weak IR ν(C=C) absorption at ca. 2100 cm⁻¹. The C=C−H stretching mode in the starting diethynyl ligand was absent, indicating the formation of Pt−C bond. The symmetrical nature of ZnPPt was evident from the NMR spectral pattern. In ¹H NMR spectra, the proton signals arising from the aromatic and other organic groups were observed. The ³¹P NMR of the Pt(II)-containing complex exhibited a single resonance with a pair of Pt satellites. Moreover, two distinct ¹³C NMR signals for the individual sp carbons were observed, and they were shifted downfield with respect to the free ligand. The formula of ZnPPt was established by the presence of intense molecular ion peak in its positive FAB mass spectrum.

### 3.2. Surface pressure–area isotherms

Fig. 2 shows the surface pressure–area (π-A) isotherms of ZnPPt on the EuW₁₀ and pure water subphase solutions at 20 °C. The isotherm of ZnPPt on pure water was used as a reference. The isotherms were reproducible. The results showed that the complex was able to form stable monolayer Langmuir film at the air–liquid interface. The molecular area of ZnPPt on the EuW₁₀ aqueous solutions and pure water can be estimated by extrapolating the linear part of π-A isotherm to the abscissa. The relevant data were displayed in Table 1.

The isotherm was progressively modified by using EuW₁₀. For ZnPPt film spread on the pure water subphase, for instance, the limiting area per molecule was 3.00 nm², whereas that of ZnPPt in EuW₁₀ aqueous subphase was 8.10 nm². The collapse pressure of ZnPPt in of EuW₁₀ aqueous solutions was 28.0 mN m⁻¹, whereas that of ZnPPt in EuW₁₀ aqueous solutions was 28.0 mN m⁻¹, whereas that of ZnPPt in EuW₁₀ aqueous solutions was 28.0 mN m⁻¹.

### 3.3. UV–vis spectroscopy of LB films

ZnPPt/EuW₁₀ of multilayers (13 layers) as well as ZnPPt/H₂O of 13-layer LB films of high morphological stability were deposited onto quartz substrates by the vertical method. The transfer ratio was almost unity in both dipping and lifting processes, indicating the formation of Y-type LB films. As shown in Fig. 3, the absorption spectra are characterized by four regions. The m*'-type Q (500–600) and Soret (400–450 nm) bands are characteristic of the porphyrinate macrocycles [30]. The third region, 250–400 nm, exhibits lower-intensity bands, corresponding to porphyrin and [(p−C₆H₄−C≡C)Pt(PBu₃)₂(C=C−p−C₆H₄)] moieties. The assignment for the lowest-energy UV band for this latter Pt-containing unit is a mixture of ligand-to-metal charge transfer and metal-to-ligand charge transfer where M is the Pt atom and L represents the phenylethynyl unit, as demonstrated recently for analogous conjugated organometallic polymers [42]. As for the fourth region (200–250 nm), the hybrid LB films of ZnPPt/EuW₁₀ exhibit intense O₃=W peak (202 nm) of EuW₁₀ which is probably mixed with organic (π → π*) transitions (where O₃ represents the terminal oxygen atoms) [43]. The differences in intensity are possibly related to thickness differences of these films.

### 3.4. Photoluminescence properties of LB films

The photoluminescence spectra of the 13-layer LB films deposited on quartz were measured in the range of 350–525 nm and of 525–725 nm, with the corresponding excitation wavelengths being at 300 and 500 nm, respectively (Fig. 4). The two chromophores, zinc(porphyrin), known to be strongly fluorescent, and trans-bis(ethynylbenzene)platinum, which was strongly phosphorescent (especially at 77 K), were monitored. The emission spectra were dominated by the intense and long-lived phosphorescent band arising from the [(p−C₆H₄−C≡C)Pt(PBu₃)₂(C=C−p−C₆H₄)] spacer at 457 nm. Weaker fluorescence bands arising from the [(p−C₆H₄−C≡C)Pt(PBu₃)₂(C≡C−p−C₆H₄)] and zinc(porphyrin) unit at 406 and 635 nm were also apparent, respectively [30]. No phosphorescence due to the zinc(porphyrin) unit was seen at 293 K. Weak characteristic red emission peaks of Eu³⁺ were clearly seen at 595 and 703 nm corresponding to ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₄ electronic transitions, respectively [44,45]. Interestingly, inclusion of EuW₁₀ within the LB films induced a change in the PL intensity compared to the pure water. For hybrid LB films of ZnPPt/EuW₁₀, the PL intensities at 406 and 457 nm were lower than those of the ZnPPt/H₂O congener, whereas the PL intensity beyond 641 nm was slightly higher than that of the ZnPPt/H₂O system. The EuW₁₀ can partially facilitate the excited state luminescence of the porphyrinate chromophore in ZnPPt, possibly because of the triplet–triplet energy transfer from Pt moiety to ZnPPt moiety, increasing the ratio of fluorescence vs the phosphorescence. The appropriate energy level diagram entailing the photophysical processes involved was depicted in Fig. 5, which was similar to the case previously reported in solution [30].

### Table 1

<table>
<thead>
<tr>
<th>Langmuir film</th>
<th>Cross section (nm² molecule⁻¹)</th>
<th>Collapse pressure (mN m⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>ZnPPt/H₂O</td>
<td>3.00 ± 0.11</td>
<td>18.0 ± 0.1</td>
</tr>
<tr>
<td>ZnPPt/EuW₁₀</td>
<td>8.10 ± 0.19</td>
<td>28.0 ± 0.1</td>
</tr>
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</table>
3.5. Atomic force microscopy

Surface morphology structural characterization of the LB film by atomic force microscopy (AFM) has also been performed. The image and structure of the hybrid monolayer film deposited on mica was measured [Fig. 6]. The AFM images of ZnPPt/EuW10 show that the hybrid LB film consists of disperse particles with different domain sizes of 20.55 – 91.89 nm. The average root-mean-square (rms) surface roughness (Ra) is 1.2 nm and the largest roughness (Rz) is 25.6 nm. A dimensionally split phase structure can be observed in which the darker area is mostly filled with EuW10 domains and the higher and brighter area is mostly filled with ZnPPt. Since one molecule of ZnPPt is about 4 nm in length [30], the aggregates observed in the brighter domain may be formed by 5–23 ZnPPt molecules.

3.6. Electrical characterization of LB films by scanning tunneling microscopy

In our preliminary experiments, the electric conductivity behavior of ZnPPt/EuW10 3-layer LB films on ITO wafer was examined using scanning tunneling microscopy. Saliently, it was able to show good electrical conductivity and a representative I–V plot was shown in Fig. 7 for the device. I–V curve was reproducible and the tunneling current for the ZnPPt/EuW10 film amounted to ±100 nA when the voltage was monitored within −1.4–3.1 V. While pure platinum(II) polyyne is generally a very poor conductor in the intrinsic state, our hybrid LB composite in the device can be made to be semiconducting. While the zinc(II) porphyrin platinum(II) complex ZnPPt is generally a very poor conductor in the intrinsic state, whereas POM is easily reducible, we anticipate that when the two components are fabricated in an organic–inorganic hybrid, the good conductivity could have an origin of electron transfer.

3.7. Surface photovoltage spectroscopy

The photovoltaic effect of the 15-layer hybrid LB films deposited on the ITO was also studied after UV-irradiation using the surface photovoltage spectroscopy (SPS) technique. The results were shown in Fig. 8. The ZnPPt/EuW10 hybrid LB film displayed strong photovoltage effect at 358 nm. The photovoltage effect of ZnPPt/EuW10 was greater than that of ZnPPt/H2O. The photovoltage responses of ZnPPt/EuW10 was as high as 24.0 µV. EuW10 is a photosensitive substance and it acted as an electron acceptor, whereas the Zn-porphyrin containing π-conjugated electrons served as an electron donor. The ZnPPt/EuW10

![Fig. 4. PL spectra of LB films (13 layers) of (1) ZnPPt/H2O and (2) ZnPPt/EuW10 (a, λex = 300 nm; b, λex = 500 nm).](image)

![Fig. 5. Energy level diagram for ZnPPt/EuW10 hybrid. The relevant radiative (A = absorption, F = fluorescence, P = phosphorescence) and nonradiative (ISC = intersystem crossing, T1 ET = triplet energy transfer) are shown. 1 and 3 denote the singlet and triplet excited states, respectively. The phosphorescence from ZnP and EuW10 was not observed at 293 K.](image)

![Fig. 6. Tapping mode AFM image of the monolayer film of ZnPPt/EuW10.](image)

![Fig. 7. The I–V curve of a 3-layer film on the ITO wafer for ZnPPt/EuW10.](image)
the observed electrical conductivity of the fer between electron donor and acceptor are the key driving forces for alkyne bond of ZnPpt and the ligand aromatic system, and electron transport to the hybrid system would probably manifest donor–π–acceptor (D–π–A) structural motif and the π-conjugated system was used as an electron-transporting passage. The transfer process resulted in the observed conductivity. As the LB film was excited by light, a photovoltaic effect was readily observed.

4. Conclusions

A rigid-rod zinc (II) porphyrin platinum(II) complex functionalized with trans-bis(ethynylbenzene) can be used to build metallocomplex/europium-substituted POM layered structure. This structure can be applied in the construction of multilayered molecular devices in various photoelectric and optoelectronic applications. The material can form steady monolayer and multilayer films at the interface of air and POM aqueous solutions, which present attractive luminescent properties. In the hybrid ZnPpt-based LB films, strong π–π transition between the alkyne bond of ZnPpt and the ligand aromatic system, and electron transfer between electron donor and acceptor are the key driving forces for the observed electrical conductivity of the film. Such an organometallic/inorganic multifunctional assembly can afford ultrathin films, which enable creation of functional hybrid materials on realizing practical molecular devices with specific optoelectronic properties. By virtue of the D–π–A structure for the films, photococonductivity was easily observed upon photoexcitation. The photoluminescent activity of the LB films would provide a good potential for creating light-emitting multilayer films. Luminescence independently arising from both the Pt-containing complex and Eu entity is preserved in the LB films prepared, in which the dual emissions can constitute a red light band. Such work via a combination of simultaneous emission from both metal-containing complex and a rare-earth POM also represents a significant progress towards the realization of commercial red lighting sources and further work on fabricating suitable organic light-emitting devices is underway.

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