



Materials science communication

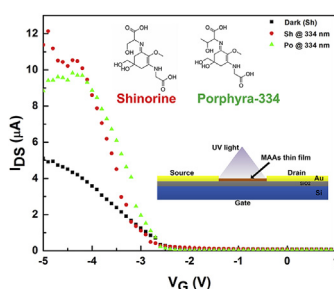
Photoinduced conductivity in mycosporine-like amino acids

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HIGHLIGHTS

- MAAs FET shows photoelectric effect upon UV illumination.
- Enhancement in photo conductivity is due to the hydroxyl ethyl group.
- Potential as bio-opto-electrical devices applications.

GRAPHICAL ABSTRACT



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ABSTRACT

Mycosporine-like amino acids (MAAs) are an important group of novel bioactive compounds having immense biotechnological potentials due to their UV screening properties and antioxidant activities. However, their photoelectric properties were not evaluated yet. In the present work two types of MAAs Shinorine and Porphyra-334, were extracted from algae; *Chlamydomonas hedleyi* and *Porphyra yezoensis* respectively and its electrical transport properties were investigated upon illumination of UV light. The combination of optical absorption and electron transport measurement of MAAs in a field effect transistor device reveals that these changes are mainly due to the carboxyl group present in MAAs. This study reports a platform technology for the development of novel biochemical–electrical devices.

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1. Introduction

There is growing interest in marine organisms to explore the bioactivity of various marine compounds associated with human life. In recent years, natural products from marine organisms have gained increasing research awareness, and a number of novel marine compounds of potential economic importance have been

reported from different marine organisms [1–3]. Mycosporine-like amino acids (MAAs) are natural compounds found in a wide variety of marine and freshwater organisms, including fungi, bacteria, cyanobacteria, phytoplankton, and macroalgae [4], have received much attention for their putative role in UV photo protection. They are water-soluble, molecular-weight less than 400 Da, colourless. Water soluble compounds composed of cyclohexenone or cyclohexenimine chromophore conjugated with the nitrogen substituent of an amino acids or its imino alcohol [5]. There are more than 20 different MAAs found in various organism. Generally, the ring

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system contains a glycine subunit at third carbon atom. Some MAAs also contains sulphate esters or glycosidic linkages through the imine substituents. Difference in the absorption spectra of MAAs is due to the variation in the attached side groups and nitrogen substituent's. The strong UV absorption maxima between 310 and 362 nm, high molar extinction coefficient and photostability in distilled and sea water in presence of photosensitizers [6], support the contention that MAAs has a photoprotective role [7,8]. MAAs has also been shown to be highly resistant against abiotic stressors such as temperature, UV radiation, various solvents and pH [9,10]. The increasing number of reports on the presence of MAAs in different marine species refers mostly to their potential photoprotective properties [11–14]. Besides the UV-protection, it has been suggested that mycosporines and MAAs may also have osmotic functions, particularly in cyanobacterial communities of hyper saline, environments [15], antioxidant activity [16] and regulatory role in reproduction [17]. In contrast with the abundant literature on the MAAs extraction from various species and its analysis, no works have been previously published on optoelectronic transport properties of MAAs. Herein, two MAAs (Shinorine and Porphyrin-334) were chosen to demonstrate their electrical conduction upon UV illumination with the help of field effect transistor (FET) device.

2. Experimental

For determination of MAAs content, cells were extracted from harvested *Chlamydomonas hedlyei* and *Porphyra yezoensis* biomass and washed twice with distilled water. Dried cells were suspended and homogenized in 20% (vol/vol) aqueous methanol at 45 °C in water bath for 2 h. After centrifugation, supernatant is filtered through whatman filters. Shinorine and Porphyrin-334 were isolated from *C. hedlyei* and *P. yezoensis* respectively.

High-performance liquid chromatography (HPLC) measurements were carried out for dried Porphyrin-334 and Shinorine, were dissolved 1 mg/ml in water and passing through 0.45 µm membrane filter. HPLC system consists of Waters1525 µ Binary HPLC Pump and Waters 996 Photo Diode Array detector. Analysis of MAAs were also performed on a ESI-MS/MS system consisting of a AB SCIEX 3200 QTRAP MS/MS (Applied Biosystems, Foster City, CA, USA) with an ESI source (Turbo Ionspray), Data acquisition and processing were achieved with AB SCIEX Analyst 1.5 software.

The transport properties of Shinorine and Porphyrin-334 were evaluated using FETs by loading the samples between the source and drain electrodes located 5.0 µm apart. The FET devices were fabricated from a silicon dioxide on a silicon wafer, which was used as a back gate electrode. Both the source drain electrodes were made of titanium capped with a 25 nm thick gold layer. MAAs thin film is formed between the Au electrodes by drop cast method. A 2.0 µL drop of both the MAAs (concentration of 1 mg/mL in DI water) is drop placed in the electrode gap and dried under vacuum conditions at room temperature. The FET device is then characterised using probe station and Semiconductor Parameter Analyser (SPA, Keithley, 4200, USA) under controlled source–drain and gate parameters.

A typical MAAs FET transport response was measured for dark and under UV light exposure (Monochromator, Newport, USA) typically $\lambda = 254$ nm, 334 nm and 365 nm in wavelength and at a fixed distance of approximately 2.0 cm away from the MAAs FET, which was kept under practical conditions, i.e. in air, at room temperature.

3. Results and discussion

Purified Shinorine and Porphyrin-334 were used for the evaluation. From the UV–Vis spectra (Fig. 1) it is observed that both the MAAs has absorption maxima at 334 nm, which is same as that of reported earlier [18–21]. Further the molar absorption coefficients observed (@ ϵ_{334}) are 24.18 M⁻¹ cm⁻¹ and 71.17 M⁻¹ cm⁻¹ for Shinorine and Porphyrin-334 respectively. This is mainly due to marine mycosporines which possess a common cyclohexenone ring system and a methoxy moiety at carbon 2 shows the same spectral characteristics, including the position of their absorption maximum. Typically MAAs are identified based on their retention time during HPLC and their characteristic UV absorption spectra obtained via diode array detection (DAD). The chromatograms of the aqueous extracts of Shinorine and Porphyrin-334, after the purification protocol shows the retention time of 4.395 min and 5.808 min respectively (data not shown here). Although DAD allows the fast acquisition of UV–VIS absorption spectra, the lack of fine spectral absorption and the influence of pH; for some specific MAAs, the wavelength absorption maxima found to be identical or only a few nm apart, makes it very difficult to distinguish MAA compounds based on absorption spectra only. To overcome this, mass spectrometry detection (HPLC/MS) using pure reference compounds, can make an invaluable contribution in the identification of MAAs because of its high sensitivity, and the availability of powerful tandem mass spectrometric techniques. The positive ESI mass spectral fragmentation patterns of Shinorine and Porphyrin-334, as obtained by *triplequadrupole* MS/MS (data not shown here), exhibited many characteristic features. The fragmentation patterns are as expected from Shinorine and Porphyrin-334 structures. From examination of the ion observed within each of the fragmentation spectra of the Shinorine and Porphyrin-334 analysed, a useful and potentially diagnostic pattern arises. The characteristic ion observed at m/z 137 and 186 were also the base peaks in the respective fragmentation spectra.

Fig. 2 demonstrates the typical $I_{DS} - V_G$ response for Shinorine FET (Sh-FET) and Porphyrin-334 FET (Po-FET) for $V_{DS} = 1$ V, which allows us to obtain more information about the MAAs FET device during the UV illumination process. As seen from the Fig. 2a, in case of Sh-FET the I_{DS} for $\lambda = 254$ nm and $\lambda = 365$ nm found to be similar as compared with the dark measurements. Similar is the case for

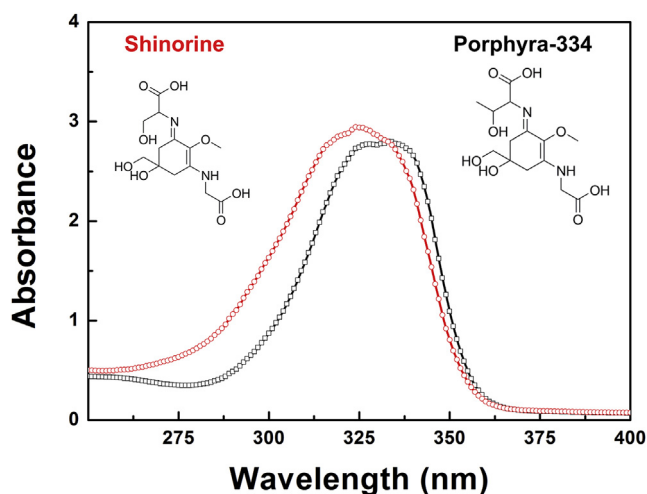


Fig. 1. Shinorine (red) and Porphyrin-334 (black) absorbance for 1 mg/ml concentration in aqueous phase (inset chemical structure of Shinorine and Porphyrin-334). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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