Organic Electronics 55 (2018) 50–62

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Electrical switching behaviour of a metalloporphyrin in Langmuir-Blodgett film

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ARTICLE INFO

Keywords:
Organic electronics
Bipolar switching
Threshold switching
MnTPPS
LB films

ABSTRACT

Here we report the resistive switching behaviour of an water soluble anionic metalloporphyrin 5,10,15,20-Tetrakis(4-sulfonatophenyl)-21H,23H-porphine manganese(III) chloride (MnTPPS) assembled onto spin coated as well as in Langmuir-Blodgett (LB) film. To prepare LB film, water soluble MnTPPS molecules were incorporated into monolayers of two cationic matrix molecules Octadecyltrimethylammonium bromide (OTAB) and N-Cetyl-N,N,N, trimethyl ammonium bromide (CTAB) through electrostatic interaction. Successful incorporation of MnTPPS molecules into the matrix (OTAB/CTAB) monolayers has been confirmed by measuring π – A isotherm, π – t curve and BAM investigations at air-water interface. From I – V characteristic it was found that by adjusting the measurement protocols (compliance current, sweeping direction) all the devices fabricated by using spin coated as well as LB films exhibit outstanding bipolar switching and threshold switching behaviour at room temperature. Presence of electron acceptor groups (SO_3H) and π – electron clouds on the MnTPPS molecules mainly play the crucial role for such observed switching behaviour onto ultrathin films. This type of bipolar memory switching and threshold switching in a single device is technologically very important to use as an active component for the non-volatile information storage and future optoelectronics devices.

1. Introduction

Electronic and optoelectronic devices are the leading tools for the modern society [1–7]. There is a growing interest for the development of nanoscale devices with new functionality and/or greatly enhanced performance. In recent years organic electronics deals with carbon-based conductive organic materials and are extensively studied due to their interesting optical, electrical, photoelectrical conducting, semiconducting, memory, storage and magnetic properties [8–12]. There are numerous potential applications of organic materials in the development of electronic devices such as sensors, solar cells, field-effect transistors (FET), switching devices, optical data storage, organic light emitting diode (OLED) etc [13–19].

Of late molecular electronics has emerged as an important technology which deals with the manipulation of organic materials at the nanoscale level to realize devices that will store and/or process information [20–22]. Here single molecule or an assembly of molecule will be used for the fabrication of electronic components. It has been observed that several organic molecules show rectification, switching, semiconducting and even metallic properties under certain conditions [23–26]. Therefore molecules that are probably suitable for the applications in molecular-electronic devices have recently been the subject of current interest.

On the other hand Langmuir – Blodgett (LB) technique is one of the few methods for preparing nanoscale organized molecular assemblies which are the pre-requisite for the realization of molecular electronic devices [27,28]. LB technique provides the opportunity to exercise molecular level control over the structure of organic thin layer of molecules [29–31].

Porphyrin derivatives have interesting characteristics such as rigid planar structure, high stability, intense absorption and small HOMO-LUMO energy gap. These characteristics make porphyrins a class of synthetic building blocks for functional nano materials suitable for molecular electronics [32]. Due to their interesting properties and extended π – conjugated structure, porphyrins have potential applications in nonlinear photonic devices [33–35] and for investigations of

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https://doi.org/10.1016/j.orgel.2017.12.038
Received 11 October 2017; Received in revised form 21 December 2017; Accepted 24 December 2017
Available online 30 December 2017
1566-1199/

artificial light harvesting systems [36]. Among the most commonly studied porphyrins the metalloporphyrins are the important class of compounds. The metalloporphyrin ring is found in variety of biological system and can be used to mimic many biological process [37]. They have wide applications in molecular electronic devices [38], as a catalysts in chemical reactions [39], photosensitizers [40], artificial photosynthesis [41] etc. Beletskaya and co-workers [42] suggested that these materials form organized multilayers which are used as models for biological processes and catalysts for many reactions due to axial coordination via central metal ion. Porphyrins form aggregates (J-or H-aggregates) under various conditions such as at specific pH, concentration, ionic strength etc [43–47].

In this manuscript we report the results of our investigations on the electrical switching behaviour of an anionic metallo porphyrin 5,10,15,20-Tetrakis(4-sulfonatophenyl)-21H,23H-porphine manganese (III) chloride (MnTPPS) assembled onto spin coated as well as in LB film. Presence of electron acceptor groups (SO_3H) and π – electron clouds on the MnTPPS molecules trigger us to study the electrical properties of this molecule onto thin films. Our investigations revealed that this porphyrin derivative show two types of resistive switching – non-volatile bipolar switching and threshold switching. This kind of observed bipolar memory switching and threshold switching in ultra thin films are the promising candidate for potential applications to the next generation non-volatile memory devices and/or logic circuits [48].

2. Experimental section

2.1. Materials

5,10,15,20-Tetrakis(4-sulfonatophenyl)-21H,23H-porphine manganese(III) chloride (MnTPPS), Octadecyltrimethylammonium bromide (OTAB) and N-Cetyl-N,N,N, trimethyl ammonium bromide (CTAB) has been purchased from Sigma Aldrich chemical Co., USA and were used as received. Chemical sctructures of MnTPPS, OTAB and CTAB are shown in Fig. 1. Spectroscopic grade chloroform (SRL, India) has been used as solvent. Ultra pure Milli-Q water (18.2 MΩ–cm) is used as subphase.

2.2. Isotherm measurement and film formation

A commercially available Langmuir-Blodgett (LB) film deposition instrument (Apex 2006C, Apex Instruments Co., India) was used for surface pressure vs area per molecule (π-A) isotherms measurement, surface pressure vs. time (π-t) characteristic study, and LB films preparation. The concentration of the stock solutions for OTAB, CTAB were 10^{-3} M and for MnTPPS aqueous solution concentration was 10^{-4} M. In order to measure the isotherm and film formation dilute chloroform solution of 80 μl OTAB or CTAB were spread by a micro syringe on water subphase of pure Milli-Q water (18.2 MΩ–cm) and subphase containing aqueous solution of MnTPPS at room temperature. After complete evaporation of volatile solvent, the barrier was compressed at a rate of 5 mm/min to record the surface pressure – area per molecule isotherms. The surface pressure (π) versus average area available for one molecule (A) was measured by a Wilhelmy plate arrangement [49]. Each isotherm was repeated a number of times and data for surface pressure – area per molecule isotherms were obtained by a computer interfaced with the LB instrument Before each isotherm measurement, the trough and barrier were cleaned with ethanol and then rinsed by Milli-Q water. Surface pressure vs. time (π-t) curve was recorded to monitor the progress of reaction. 80 μl chloroform solution of OTAB or CTAB were spread on the subphase containing aqueous solution of MnTPPS in different volume. The increase in surface pressure with time was recorded to have the π-t curve. After the completion of reaction kinetics the film was lifted vertically at that saturated pressure with the fixed position of the barrier. Smooth fluorescence grade quartz plates (for spectroscopy) and fresh cleaned ITO-coated glass (for electrical characteristic) were used as solid substrate. Y-type deposition at a particular surface pressure was followed to transfer Langmuir films at a deposition speed of 5 mm/min. The transfer ratio was estimated by calculating the ratio of decrease in subphase area to actual area on the substrate coated by the layer and was found to be 0.98 ± 0.02.

Spin coated film of MnTPPS has been prepared by using spin coater unit, Model: EZ spin-SD, Apex Instruments Co., India. For spin coating film the MnTPPS solution concentration was 10^{-4} M. Before film preparation the solution was stirred for almost 10 h. After that 500 μl aqueous solution of MnTPPS was spread onto ITO coated glass substrate drop wise. After each 1–2 drop the substrate was spun at a rotating speed of 1800 rpm for 30s. The resulted spin coating film was dried for more than 10 h in vacuum at room temperature followed by I-V characteristics measurement.

2.3. Brewster angle microscopy (BAM) imaging

The morphology of the film at the air-water interface was observed using a Brewster Angle Microscope (Accurion nanofilm_EP4-BAM, Serial No. 1601EP4030) equipped with a 30 mW laser emitting p-polarized light at 532 nm wavelength which was reflected off the air/

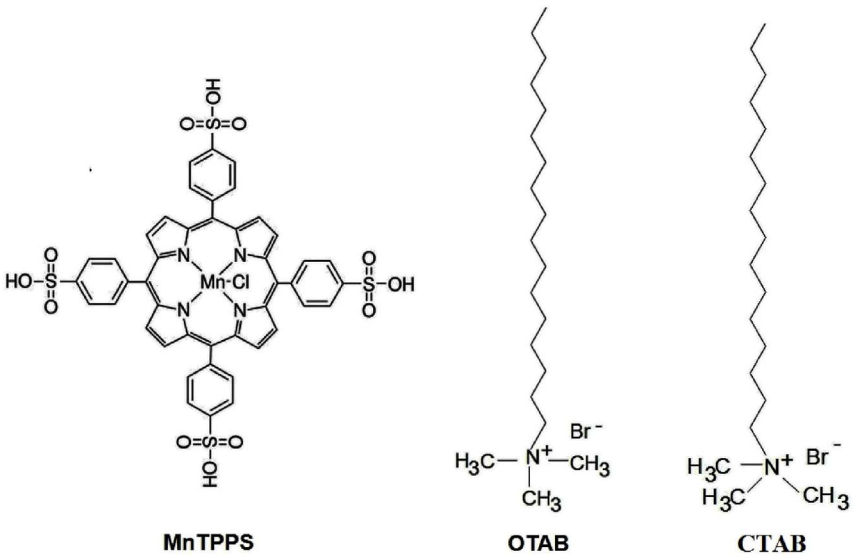

Fig. 1. Chemical structure of MnTPPS, OTAB & CTAB.