Electrical switching behaviour of a metalloporphyrin in Langmuir-Blodgett film

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A B S T R A C T

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 $\pi$ – $\Delta$ isotherm, $\pi$ – $t$ 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$_3$H) and conjugated structure, porphyrins have potential applications in 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 $\pi$ – conjugated structure, porphyrins have potential applications in nonlinear photonic devices [33–35] and for investigations of 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].

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

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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 films. Presence of electron acceptor groups (SO3H) 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 structures 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/
water interface at the Brewster angle (53.1°). This reflected beam pass through a focal lens, into an analyzer at a known angle of incident polarization, and finally to a CCD camera, which measures gray level instead of relative intensity. The lateral resolution of the microscope was 2 μm, the shutter speed was 1/50 s and the images were digitalized.

2.4. UV-vis spectroscopy

UV–vis absorption of pure solutions, as well as those of mixed LB films, were recorded using absorption spectrophotometer (PerkinElmer, Lambda 25). The absorption spectra were recorded at 90° incidence using a clean quartz slide as reference.

2.5. I-V characteristic measurement

The current–voltage (I–V) characteristics were measured by using Keithley 2401 source meter. 60 layer LB films of mixed MnTPPS + OTAB and MnTPPS + CTAB were deposited onto ITO-coated glass substrates at 15 mN/m surface pressure. Pure MnTPPS thin films onto ITO coated glass slide was prepared using spin coating technique. Here ITO-coated glass substrate acts as bottom electrode and a gold tip, softly touching the surface of thin films was used as top electrode giving an active area of 1 mm² for measurement. The solutions were stirred for almost 10 h before the preparation of the films and the prepared thin films were dried in a vacuum desiccator for more than 10 h before characterization. During the experiment, the samples were not allowed to be irradiated by any light and always kept at room temperature. The I-V curves were recorded by applying different sweep voltage at a voltages scan rate of 2.5 mV/s.

3. Results and discussion

3.1. Monolayer characteristics at the air-water interface

The incorporation and packing of MnTPPS in ionic monolayers was investigated at the air–water interface by using LB technique. The tetra anionic MnTPPS is water-soluble and does not form a stable monolayer by itself. This has been confirmed by observing almost no surface pressure change upon compression of barrier in the Langmuir trough containing MnTPPS solution subphase.

Ideally, LB technique is suitable for preparation of mono- or multilayer thin film using water insoluble material [29,49]. However, there are several reports where water soluble ionic molecules were incorporated onto LB films through electrostatic interaction with a preformed ionic insoluble monolayer [50]. In the present case the molecule MnTPPS under investigation is anionic in nature with four SO₃⁻ groups. Therefore it is expected that MnTPPS can be incorporated onto ultrathin films through electrostatic interaction with a water insoluble monolayer of cationic matrix molecule. Accordingly, two cationic surfactants OTAB and CTAB were chosen as matrix molecule. Here, the matrix molecules (both OTAB and CTAB) were spread onto the LB trough containing MnTPPS solution (1.5 × 10⁻⁶ M) subphase. The incorporation of MnTPPS onto the floating matrix layer was investigated by recording the surface pressure – area per molecule (π – A) isotherm as well as the surface pressure – time (π – t) characteristics.

Fig. 2 shows the surface pressure –area (π-A) isotherms of OTAB and CTAB monolayer spread on to the aqueous subphase containing 1.5 × 10⁻⁶ M of MnTPPS for different waiting time after spreading. The isotherms of pure OTAB and CTAB measured on water subphase (Fig. 2) shows a very steep nature with mean molecular area 0.17 nm² and 0.15 nm². The shapes as well as nature of these isotherms are consistent with reported literature [51,52]. After spreading the matrix molecules onto the MnTPPS subphase, certain time was allowed for the interaction to occur followed by compression of the barrier to record the (π – A) isotherm. Interestingly, for all the cases in presence of MnTPPS subphase the isotherms were shifted to larger area for both the matrix molecules. The enlargement of molecular areas of isotherm on MnTPPS subphase indicates that there exists a strong interaction between the amphiphiles in monolayer and MnTPPS in the subphase and the consequent incorporation of MnTPPS molecule on the floating ionic films. Anionic MnTPPS molecules, being water soluble, remain in the aqueous subphase of the LB trough. When a Langmuir film of cationic matrix (OTAB or CTAB) was prepared at air – water interface, MnTPPS molecules from the aqueous subphase were adsorbed electrostatically on the floating matrix layer. With the passage of time matrix molecules (OTAB/CTAB) in the preformed Langmuir film was replaced by the MnTPPS – matrix complex i.e. either MnTPPS – OTAB or MnTPPS – CTAB complex at air – water interface. The size of these complex is larger compared to either OTAB or CTAB. Accordingly, the area per molecule in case of complex film shifted to the larger area.

It has been observed that with increase in waiting time, the isotherms were shifted to the larger area and for both the cases the isotherm attain maximum area per molecule with waiting time 2 h. Isotherm recorded with waiting time greater than 2 h did not show any further increase in area per molecule. The mean molecular area noted for all the complex isotherms are listed in Table 1. It has been observed that the mean molecular areas for both MnTPPS – OTAB and MnTPPS – CTAB complex isotherm reached its maximum value recorded with waiting time 2 h or more. Considering the MnTPPS molecule as square whose side length is ca. 1.3 nm according to CPK model, the area of MnTPPS molecule under flat surface conformation should be 1.69 nm² [53]. Again in the complex monolayer (MnTPPS – OTAB or MnTPPS – CTAB) long alkyl chain of OTAB or CTAB molecule was oriented outside the air – water interface and MnTPPS molecule occupied an area at the interface. Accordingly the mean molecular area in the complex isotherm should be 1.69 nm². However, in the present case the observed mean molecular area was less than this value for all the cases even when the complex isotherm attains maximum area per molecule. This indicates that the macrocyclic ring of the MnTPPS molecule do not remain flat at air-water interface rather become inclined to the plane of the complex monolayer [54].

Also it was observed that the mean molecular area changed with change in waiting time until stable configuration was attained. This indicates that change in orientation of the macrocyclic ring of the MnTPPS molecules occurred with time. Analysis of compressibility as well as BAM studies of the complex monolayer also suggested phase change in the complex monolayer upon change in waiting time. Corresponding results have been presented in the later section of this manuscript. However, with waiting time 2 h, orientation of macrocyclic ring become stabilized, showing no further change in mean molecular area with further increase in waiting time.

3.2. Studies of compressibility at the air-water interface

Compressibility of Langmuir film as a function of surface pressure can be calculated from the π – A isotherm using the following standard thermodynamic relation in two dimension [55] –

\[ C = - \frac{1}{A} \frac{dA}{d\pi} \]

Where “A” is the area per molecule at the surface pressure of π.

Idea about monolayer phases can be obtained from the compressibility versus surface pressure (C – π) curve [30]. The states of Langmuir film or the phase transition in the Langmuir film are reflected as the peaks in the C – π curve. Generally presence of peaks in the curve represents the inherent phase transitions involved in such systems [56].

From Fig. 3 it has been observed that compressibility curve for pure OTAB and pure CTAB show almost similar profile with two identical peaks in the range 0–5 mN/m and 15–22 mN/m regions. Here the two peaks correspond to the phase changes from gaseous to liquid and liquid to solid phase respectively. Similar nature of C – π curve for both pure OTAB and pure CTAB indicate that phase changes in pure matrix
monolayers are almost similar for both the cases. However, asymmetry of the peaks in the different C–π curves corresponding to complex monolayer for both the matrices clearly indicates that phase transitions of different complex monolayers are strongly dependent on the extent of interaction between the MnTPPS molecule and the matrix molecule (OTAB or CTAB). Also change in the curve for the complex monolayer with different waiting time clearly suggest that change of monolayer phases occurred in the complex film with time due to increase of MnTPPS molecules onto the complex film as well as their reorientation with time until final stable phase is reached after 2 h.

3.3. Surface pressure vs. time (π-t) characteristic studies at the air-water interface

In the present work we have incorporated the water soluble MnTPPS molecules onto ultrathin films using LB technique [50]. Here the water soluble MnTPPS molecules were adsorbed onto preformed floating ionic layer of OTAB or CTAB through electrostatic interaction. In order to monitor the reaction kinetics the change in surface pressure (π) with the passage of time (t) during the adsorption process was recorded.

Fig. 4 shows the corresponding surface pressure (π) vs. time (t) curves. Here in order to monitor the reaction kinetics, 80 μl chloroform solution of OTAB or CTAB (10^{-3} M) has been spread onto the LB trough containing MnTPPS solution (1.5 × 10^{-6} M) subphase. In all the cases, the starting point was the nominal surface pressure of 0.5 mN/m. From the figure it has been observed that as time passed, surface pressure gradually increased with the progress of adsorption. Despite of the barrier was kept fixed at a particular position (where the control...
pressure was arrived) the increase in surface pressure with time is an indication of the formation of MnTPPS + OTAB or MnTPPS + CTAB hybrid monolayer at the air-water interface. Initially the monolayer was occupied by only the OTAB or CTAB molecules and finally the monolayer was occupied by the complex molecules. Since the area per molecule of this complex is greater than the area per molecule of pure OTAB or CTAB molecules, hence the area per molecule of the complex monolayer tends to increase. But as the barrier was kept fixed at a particular position, the increase in the area per molecule was consequently manifested as the increase in surface pressure. From Fig. 4 it was also observed that as time progresses the rate of increase in surface pressure came down slowly. After 3 h the surface pressure reached its maximum value and became almost steady and parallel to the time axis, indicating the completion of reaction. At this stage the floating complex film was deposited onto solid substrate for further studies. It has also been observed that the increase in surface pressure as well as maximum surface pressure reached after the completion of adsorption process is higher in case of OTAB-MnTPPS film. This may be due to the fact that chain length of OTAB is longer than CTAB. Accordingly, size of the complex in case of OTAB is also bigger, affecting the adsorption process resulting attainment of higher surface pressure.

3.4. Brewster angle microscopy (BAM) imaging at air-water interface

In-situ Brewster Angle Microscopic (BAM) investigation is one of the most reliable tools to have visual idea about the microstructure of the complex monolayer at air-water interface. Domains of different sizes and shapes in the BAM images of Langmuir monolayer indicates the phase transition in the floating layer. In the present case, BAM images of MnTPPS + OTAB/CTAB complex Langmuir monolayer were taken at different interaction time during π-π measurement as well as at different surface pressure during π-π isotherm measurement at air-water interface.

BAM image of empty water surface showed completely dark image indicating no reflection of light (figure shown in supporting information, Fig. S1A). Again BAM image recorded for the MnTPPS aqueous subphase also showed almost black image (Fig. S1B). This is because, being water soluble, the MnTPPS molecules remain within the subphase of LB trough and hardly any MnTPPS molecule lie on the air-water interface. On the other hand BAM image recorded for the matrix monolayer (OTAB or CTAB) spread onto pure aqueous subphase showed almost similar continuous small circular domains having dimensions ranging from 5 μm–15 μm throughout the surface (Fig. S1C and D).

The images recorded just after spreading (waiting time 0 min) of the matrix molecules (OTAB or CTAB) onto MnTPPS subphase is also almost similar to that of pure matrix monolayer (Figs. 5A and 6A). However, with passage of time (Figs. 5B–D & 6B–D) marked changes in the BAM images occurred for both the matrix molecules. Here, upon passage of interaction time the number of domains, domain structures as well as background contrast in the BAM images changed gradually. BAM images recorded after waiting time 2 h showed maximum condensed domains with maximum surface coverage. Images recorded with waiting time higher than 2 h did not show any further marked change.

In the present case the water soluble anionic MnTPPS molecule adsorbed onto floating cationic matrix monolayer (OTAB/CTAB) through electrostatic interaction. Number of MnTPPS molecules adsorbed onto floating matrix layer increases with waiting time. Our isotherm study as well as compressibility analysis also suggested that with increase in waiting time the number of MnTPPS molecules adsorbed onto floating complex monolayer increased and reorientation of the MnTPPS molecules occurred. However, after passage of 2 h the complex monolayer gets stabilized and no further reorientation of molecules occurred. Consequently, BAM images recorded at different waiting time upto 2 h after spreading of matrix molecules showed gradual change and for the images recorded with waiting time more than 2 h remain almost unchanged.

BAM images recorded at different stages of compression during π – A isotherm measurement (Figs. S2 and S3) for the complex monolayers also showed that initially at lower surface pressure the BAM images were almost similar to the pure matrix monolayer (OTAB/CTAB). However, at higher surface pressure (> 10 mN/m) the BAM images showed marked change and became almost similar to that recorded during π – μ measurement with waiting time 2 h or more. This indicates the formation of condensed monolayer of MnTPPS-OTAB or MnTPPS-CTAB complex at air – water interface. As a whole BAM study gives compelling visual evidence of adsorption process as well as complex film formation at air-water interface.

3.5. UV–vis absorption spectroscopy

In order to check the possible aggregation nature of complex OTAB + MnTPPS and CTAB + MnTPPS in LB film we have recorded the UV–Vis absorption spectra of complex MnTPPS LB films along with pure MnTPPS and MnTPPS + OTAB/CTAB solution for comparison. Fig. 7 shows the corresponding UV–Vis absorption spectra. It is relevant to mention in this context that the absorption bands of porphyrins are ascribed to the in-plane π–π* transitions and can be explained by four orbital model of Gouterman [57]. Electronic transitions between these orbitals (two HOMO and two LUMO) results into two excited states which are split up resulting in two distinct transition bands one with higher energy called the Soret band or B band (S0→S1) and the other with lower energy called the Q band (S0→S2). There are some additional weak bands (N, L, M bands) in the UV range [58,59]. MnTPPS aqueous solution spectrum (curve 1, Fig. 7a and b) showed the intense Soret band at around 466 nm, the Q bands ranging from 525 to 670 nm and the additional N, L, M bands in the range 350–450 nm having peak positions 423, 400, 378 nm respectively. The Soret band position is sensitive to substituent groups and highly sensitive to microenvironments [59]. The absorption band of the MnTPPS + OTAB mixed solution (curve 2, Fig. 7a) shows the intense Soret band at around 470 nm which is nearly 4 nm red shifted with respect to pure MnTPPS solution. Also the bands in the lower wavelength (N, L, M) are broadened with respect to pure solution absorption spectrum. The observed 4 nm red shift of the soret band in the MnTPPS + OTAB mixed solution is owing to the closer association of the MnTPPS molecules while tagged onto the backbone of OTAB molecule and consequently formation of aggregates. It may be mentioned in this context that tetra anionic, MnTPPS molecule may not form aggregates in aqueous solution due to predominance of repulsive force among the MnTPPS molecules [59–61]. However, when MnTPPS molecules are adsorbed on the backbone of OTAB in the floating amphiphile layer, they may come close to each other due to electrostatic interaction and form traces of J-aggregates. Our isotherm studies also suggested that MnTPPS molecules obliquely stacked into the complex layer to form favourable condition of J-aggregate. It is well known that 5,10,15,20- Tetraphenylporphin tetra sulfonic acid is a water soluble porphyrin which formed J-aggregates in acidic water or in the presence of various organic and inorganic cations [62–64]. Although Takagi et al. [65] suggested that small red shift of 3–4 nm may also be due to the change in solvent polarity of the solution.

Here we have prepared the complex LB films following two procedure – (i) In the first case OTAB solution was spread onto the LB trough (expanded condition) containing MnTPPS aqueous solution subphase. After waiting 2 h the floating layer was compressed upto the surface pressure of 15 mN/m to deposite the LB monolayer film. (ii) In the second case OTAB solution was spread onto the LB trough containing MnTPPS aqueous solution subphase. The barrier was compressed to surface pressure of 0.5 mN/m and the reaction between MnTPPS and OTAB was monitored by observing the π-μ curve. After the completion of the reaction (pressure become parallel to the time axis) for waiting time five and half an hour the film was deposited onto solid substrate.
After that the absorption spectra for the LB films were recorded.

OTAB + MnTPPS complex LB film absorption spectrum showed interesting feature. The absorption spectra of the LB film prepared by procedure (i) (curve 3, Fig. 7a) showed prominent and intense band with peak position at 420 nm, which was almost a weak hump in case of solution absorption spectrum. Also the soret band decreased largely compared to its solution counter part with a shift of about 4 nm. The Q band intensity also decreased. On the other hand the absorption
spectrum of the LB film prepared following procedure (ii) (curve 4, Fig. 7a) showed almost similar spectral profile except the sort band was totally disappeared. It is relevant to mention in this context that isotherm studies revealed that when MnTPPS molecule comes onto air-water interface via electrostatic interaction with OTAB molecules, the macrocyclic ring of the MnTPPS molecule do not remain flat at air-water interface rather become inclined to the plane of the complex monolayer. Accordingly, when this floating complex monolayer is transferred onto solid support the staking of MnTPPS molecules are affected. This intern effects the in plane $\pi$ - $\pi^*$ transitions in case of LB film absorption spectra. Also the energy levels are deformed to a certain extent due to this change in organization of MnTPPS molecules in complex LB films resulting the observed change in the absorption spectra of LB films. However, the observed difference in the sort band for two LB film spectra may be due to the change in extent of deformation in energy level for the films prepared following two different procedure. As a whole the nature of LB film absorption spectra clearly indicate the formation of aggregates of MnTPPS molecule onto LB films. The absorption spectra of CTAB+MnTPPS LB films showed almost similar spectral profile to that of OTAB+MnTPPS LB films (Fig. 7b).

3.6. Resistive switching behaviour

Materials suitable for molecular scale switching devices, which can be used in both logic and memory circuits have recently been subject of much attention. A resistive switching device can be switched between two states, a high resistance (OFF) and a low resistance (ON) state by suitable applied voltage [66–70]. Based on volatility, there are two types of resistive switching (RS) - nonvolatile memory switching and threshold switching. In nonvolatile memory switching after the removal of external voltage both the low resistance state (LRS) and high resistance state (HRS) can be retained, whereas in threshold switching only the HRS is stable at low applied voltages [71]. This type of memory and threshold switching in a single device is technologically very important where the former is the key to realize the nonvolatile information storage and the later one plays a vital role to solve the sneak path problem in cross-point or multistack structures as a selector in series with a memory cell [72–75].

In the present case we expected the switching behaviour of MnTPPS due to the presence of electron-acceptor groups (SO$_3$H) and $\pi$-electron clouds over the surface of the MnTPPS molecule. Accordingly we have designed three devices – (i) Au/MnTPPS/ITO (ii) Au/MnTPPS + OTAB/ITO (iii) Au/MnTPPS + CTAB/ITO and investigated their bipolar resistive memory switching as well as the threshold switching behaviour by adjusting the measurement protocols [76]. The configurations of the devices are shown in supporting information (Fig. S4). It is possible to have different switching mode by adjusting the device configuration and measurement protocols (compliance current, Sweeping direction). These types of bistable organic switching devices are the promising candidates for next generation information storage and future optoelectronic devices [77,78].

3.6.1. I-V characteristic of MnTPPS onto spin coated film

In order to study the switching behaviour of pure MnTPPS a device having configuration Au/MnTPPS/ITO was prepared. For this purpose pure MnTPPS thin film was prepared onto ITO coated glass substrate using spin coating. Here ITO coated glass substrate served as the bottom electrode for the device. A gold tip softly touching the surface of the MnTPPS thin films acts as top electrode for the device.

The switching behaviour of this device has been studied by recording the $I – V$ characteristics in two sweep directions by applying scanning voltage from $+V_{\text{max}}$ to $-V_{\text{max}}$ followed by a separate reverse scan from $-V_{\text{max}}$ to $+V_{\text{max}}$. The typical I-V characteristics of Au/MnTPPS/ITO device for scan range $+4.5$ V to $-4.5$ V is shown in Fig. 8A.

Interestingly it has been observed that while scanning from $+V_{\text{max}}$ to $-V_{\text{max}}$ initially the device exhibits its low conducting state (OFF state), but when the voltage approaches to the so-called threshold voltage (about 4.1 V) the current increases rapidly, showing its high conducting ON state and again the device shows a transition from ON to OFF state after reaching the threshold voltage during scanning from $-V_{\text{max}}$ to $+V_{\text{max}}$ (Fig. 8A). We have changed the scanning range by increasing $V_{\text{max}}$ with increment of 0.1 V in each time and exactly similar bipolar switching behaviour was obtained up to $V_{\text{max}} = 5$ V. However, when $V_{\text{max}}$ exceeds certain value (beyond 5 V) driving the device to its ON state (scanning from $+V_{\text{max}}$ to $-V_{\text{max}}$), does not return back to its OFF state during scanning from $-V_{\text{max}}$ to $+V_{\text{max}}$ (Fig. 8B). Observed one way switching for higher $V_{\text{max}} = 5.1$ V may be explained as due to the short circuit of the organic layer between the electrodes in the ON state, when higher $V_{\text{max}}$ was applied [79]. Here in both the cases the current
in the OFF state are due to the low leakage current. The calculated values of OFF state and ON state resistances are listed in Table 2.

Apart from the bipolar resistive switching behaviour we have also investigated the threshold switching of the same device by adjusting the compliance current as well as sweeping direction. The threshold switching for both forward and reverse bias was observed when the compliance current was fixed at 10 mA. Fig. 8C represents the I-V characteristic for threshold switching of Au/MnTPPS/ITO device with scanning range 0–5 V. It has been observed that compliance current of 10 mA was the upper limiting value for having such threshold switching for this device. Also this type of threshold switching was observed by lowering the compliance current upto 5 mA. However, increasing the scan range (greater than 5.1 V) does not effect this threshold switching. This is because here increase in sweep voltage does not increase the current beyond compliance level. Accordingly the device does not get short circuited.

In the present manuscript for all devices the active junction area was 1 mm² for I-V measurement. However, we have also measured the I-V characteristic for different devices by varying the active junction area but no significant variation is observed (result not shown). There are

Table 2

<table>
<thead>
<tr>
<th>Device configuration</th>
<th>Bipolar switching</th>
<th>Threshold switching</th>
<th>Resistances at</th>
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<tbody>
<tr>
<td></td>
<td>Threshold voltage (V)</td>
<td>Maximum allowed Scanning Voltage (V)</td>
<td>Shorted Scanning Voltage (V)</td>
</tr>
<tr>
<td>Au/MnTPPS/ITO</td>
<td>4.1</td>
<td>5</td>
<td>5.1</td>
</tr>
<tr>
<td>Au/MnTPPS + OTAB/ITO (Procedure – i)</td>
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<td>3.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Au/MnTPPS + CTAB/ITO (Procedure – i)</td>
<td>2.05</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Au/MnTPPS + OTAB/ITO (Procedure – ii)</td>
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<td>3</td>
<td>3.1</td>
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<tr>
<td>Au/MnTPPS + CTAB/ITO (Procedure – ii)</td>
<td>1.5</td>
<td>2</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Fig. 8. I-V characteristic for bipolar resistive switching (A&B) and threshold switching (C) of the Au/MnTPPS/ITO device based on spin-cast films of MnTPPS for two sweep direction. Initial sweep voltages were (A) ± 4.5 V, (B) ± 5.1 V and (C) ± 5 V at 10 mA compliance current. Arrows show the sweep direction of applied voltage.
similar reports where it has been shown that variation in the active junction area did not affect the switching behaviour significantly [79].

3.6.2. I-V characteristic of MnTPPS on LB films

Keeping in mind the importance of LB technique towards molecular electronics [26,29] we have designed two devices, Au/MnTPPS + OTAB/ITO and Au/MnTPPS + CTAB/ITO devices. Here MnTPPS + OTAB as well as MnTPPS + CTAB thin films have been prepared using LB technique. These MnTPPS + OTAB and MnTPPS + CTAB LB films have been prepared following two procedures - (i) LB film deposited at 15 mN/m during compression. (ii) LB film deposited after completion of the reaction during \( \pi - \tau \) curve measurement. Details of these two procedures have been mentioned in the UV–Vis absorption spectroscopy section of this manuscript. I–V characteristics for the devices have been investigated to study the bipolar resistive switching as well as the threshold switching behaviour.

Figs. 9A and 10A show the typical representative I–V characteristics for two devices respectively where active layer (LB films) were prepared following procedure–(i). I–V characteristics for the devices where active layer (LB films) were prepared following procedure–(ii) are shown in supporting information (Figs. S5 and S6). The values of different parameters of I–V characteristics are listed in Table 2. Interestingly for both the devices switching occurred at lower threshold voltages compared to the device consisting of pure MnTPPS spin coated thin film.

Also for the device composed of mixed LB films the short circuit of the devices occurred at lower voltages compared to the pure MnTPPS device (Figs. 9B and 10B, Table 2). However, among the devices consisting of mixed LB films, in case of MnTPPS + CTAB thin film device the switching as well as short circuit occurred at lower values than that of MnTPPS + OTAB thin film device.

We have also observed the threshold switching for both forward and reverse bias for the devices consisting of mixed LB films, in case of MnTPPS + CTAB thin film device the switching was observed at lower compliance voltage compared to that of pure MnTPPS spin coated device. However, differences in threshold voltage as well as in measurement protocol were also observed for the devices where active layer (LB films) were prepared following two different procedure (Table 2).

We have also prepared the active layer (LB films) of the devices by changing the concentration of OTAB/CTAB and MnTPPS solution. However, no significant change in the switching behaviour was observed. It is relevant to mention in this context that in the present case water soluble MnTPPS molecules were incorporated onto LB film when they interacted electrostatically with the floating preformed film of either CTAB or OTAB. Thus complex monolayer of either OTAB-MnTPPS or CTAB-MnTPPS is formed. In this process one MnTPPS molecule interact with four OTAB or CTAB molecules. Progress of reaction
was monitored by observing the surface pressure vs time characteristics curve (Fig. 4). When plateau region (Fig. 4) was achieved then reaction was completed. Film was deposited onto ITO coated glass substrate when reaction was completed. After completion of reaction the area per molecule of OTAB-MnTPPS complex as well as CTAB-MnTPPS complex is fixed. During LB film preparation the deposition was done at a fixed area per molecule/fixed surface pressure. Therefore the concentration of OTAB or CTAB and MnTPPS did not affect the film structure as well as their properties. Accordingly no change in the switching behaviour was observed.

3.6.3. Discussion on switching behaviour

A number of mechanisms and strategies responsible for the two switching states in a variety of organic molecules have been proposed, such as conformational changing, rotation of functional group, charge transfer, and reduction–oxidation process, filamentary conduction, space charge and traps, ionic conduction etc [70–73].

In the present case, observed bipolar switching behaviour may be explained by reduction-oxidation process. The electron acceptor group ($SO_3H$) in MnTPPS molecule attracts $\pi$ electron clouds towards them and largely affects conjugation in the molecules. As a result the molecule shows very low OFF state leakage current. When the device is reverse biased to a certain value during scanning from $+V_{\text{max}}$ to $-V_{\text{max}}$ the molecule gets electron from external source, which reduces the effects of electron withdrawing group. Accordingly, the electron density in the benzene rings rearranges so as to restore the electron conjugation in the molecule. As a result the $\pi$ electron cloud extends over the entire molecule and opens up a conduction pathway to result in high conducting ON state. Again the device returns to its OFF state during scanning from $-V_{\text{max}}$ to $+V_{\text{max}}$ when the voltage reached to a suitable forward bias voltage, which oxidizes the molecule by withdrawing extra electron previously added.

In case of threshold switching the difference of work functions between the metals used as electrodes and resulting built-in internal field determine the bias direction as well as the amplitude at which the electron injection to LUMO level of the organic layer is favourable. Therefore depending on the bias the conjugation in the backbone of the molecule is presumably extended and/or HOMO–LUMO gap reduced to result in the high-conducting state. The carrier conduction involves both injection and transport. In other words, electro-reduction of the molecules in the device involves: (i) electron injection overcoming the barrier potential and (ii) hopping transport, which requires suitable field. With ITO and Au electrodes, the slope of LUMO level of MnTPPS in after contact condition disfavours electron transport from the ITO side. Hence, in these devices, even if electron barrier height is low in the reverse bias direction, a combined effect of barrier height and electron transport favours electron injection from Au electrode in the forward bias as compared to that from ITO in the reverse bias. Hence, electro-reduction of MnTPPS molecules occurred and the device switches to its high state at a forward bias. In these devices, electrons

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Fig. 10. I-V characteristic for bipolar resistive switching (A & B) and threshold switching (C) for two sweep direction of the LB film based Au/MnTPPS + CTAB/ITO device prepared by using procedure (i). Initial sweep voltages were (A) $\pm$ 2.2 V, (B) $\pm$ 2.6 V and (C) $\pm$ 5 V at 5 mA compliance current. Arrows show the sweep direction of applied voltage.
from Au electrode hop to the organic layer of the device due to favourable LUMO slope. During the transport, the electrons electro-reduce MnTPPS molecules to its anionic state, which has much lower HOMO–LUMO gap. The lower LUMO level of the reduced species, in turn, further offers lower barrier height for electron injection from the Au electrode. Enhanced electron injection and conduction via hopping through the percolating redox centers continue to result higher conductivity in the forward bias. When bias was swept to negative direction, the molecules in the organic layer of the device still remain reduced until opposite bias is large enough to remove the extra electron and oxidize them to their neutral state. Considering the thinness of the film, electrons can be tunnelled directly to the LUMO level of any of the molecules. Irrespective of the slope of LUMO level in after contact condition, electron tunnelling becomes possible in both bias directions. When amplitude of bias exceeds a certain value (threshold voltage) during scanning, electrons are injected reducing MnTPPS molecules and hence the LUMO level decreases in energy and band-gap (HOMO–LUMO gap) lowers. As a result the enhancement in charge carrier density caused by this injection mechanism occurs, the current density increases rapidly to switch the device to the ON state. Thus threshold switching in both bias directions is therefore observed in single molecular layer of MnTPPS.

The threshold voltage decreases for the devices consists of MnTPPS + OTAB or MnTPPS + CTAB LB films compared to pure MnTPPS spin coated films. Here anionic MnTPPS molecules were incorporated onto cationic matrix (OTAB or CTAB) layer through electrostatic interaction. As a result during LB film formation a strong electrostatic interaction between the anionic MnTPPS and cationic matrix molecules (OTAB or CTAB) occurred and facilitates a structural modification i.e. conformational changes in MnTPPS-OTAB or MnTPPS-CTAB system, which reduces the effects of the electron accepting groups in the MnTPPS moiety. That is why after applying the bias in device consisting of LB films, the high conducting switching state (ON state) occurs earlier compared to that device consisting of pure MnTPPS spin coated film. In order to confirm the ionotropic interaction between MnTPPS and OTAB or CTAB we have also measured the pH value for both pure and mixed solution. For pure MnTPPS solution the pH value was 5.92 whereas for the mixed MnTPPS + OTAB and MnTPPS + CTAB solution it was 5 and 5.2 respectively. This lower pH value for the mixed solutions compared to that of pure MnTPPS solution clearly indicates the strong interaction between the anionic MnTPPS and cationic matrix molecules.

Again LB technique is one of the best technique to prepare organized molecular assembly of almost uniform thickness ideally having one molecule thick [29]. On the other hand spin coated films are quite thick and have less control over the organization of molecules onto the thin films. Therefore lower thickness as well as difference in organization due to film formation technique may also play crucial role in the observed change in threshold voltage as well as compliance current in the device consisting of LB films.

It was observed that the device get short circuited when the scanning voltage exceeds beyond certain maximum limiting values. During ON state when current passes through the devices, the organic layer in the device heated up. With increase in current due to increase in bias voltage extent of heating also increases. As a result depending on bias voltage, when current passing through the device crosses certain maximum value the organic layer in the device damages resulting in short circuit of the device. In case of LB film based devices short circuit occurred at lower voltages compared to the devices consisting of spin coated films. This is because due to lower thickness of LB film, the organic layer damages earlier i.e. at lower bias voltages. The heat tolerance due to passage of current is lower in case of LB films since its thickness is very low compared to spin coated films. Observed difference in the measurement protocol as well as threshold voltage for LB film based devices where LB films were prepared following two different procedure is due to the difference in packing as well as conformation of the MnTPPS molecule onto complex LB films during LB film formation.

4. Conclusion

In summary, we have designed different resistive switching devices by using active layer of an anionic metallo porphyrin MnTPPS, MnTPPS + OTAB and MnTPPS + CTAB thin films. The active layer was prepared using spin coating and LB technique. Water soluble anionic MnTPPS molecules were incorporated onto LB films through electrostatic interaction with preformed cationic surfactant (OTAB or CTAB) Langmuir monolayer. π – A isotherm, π – t curve and BAM measurement clearly revealed the formation of complex monolayer of MnTPPS + OTAB & MnTPPS + CTAB as well as the strong electrostatic interaction between the binary molecules in complex monolayer at air-water interface. Successful transformation of the floating monolayer onto solid substrate has been confirmed by absorption spectroscopic investigation.

All the devices showed bipolar switching as well as threshold switching under certain conditions. Here presence of electron-acceptor groups (SO3H) and π-electron clouds over the surface of the MnTPPS molecule play the vital role for the observed switching behaviour. The observed switching behaviour has been explained in terms of reduction–oxidation process and conformational changes. Based on active layer formation techniques as well as composition different threshold voltages of the devices have been observed at different measurement protocol. This type of resistive bipolar and threshold switching in thin films are very important due to their promising application as the active components for the memory device and/or logic circuits to realize molecular electronics.

Author contributions

B.D., and S.A.H. designed the work. B.D. and S.C. performed all experiments and data analysis. S.A.H. D.B. and B.D. wrote the manuscript with input from Inamuddin, A.K., S.C.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2017.12.038.

References


