Resistive Switching of the Tetraindolyl Derivative in Ultrathin Films: A Potential Candidate for Nonvolatile Memory Applications

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ABSTRACT: Bipolar resistive switching using organic molecule is very promising for memory applications owing to their advantages, such as simple device structure, low manufacturing cost, stability, and flexibility. Herein we report Langmuir—Blodgett (LB) and spin-coated-film-based bipolar resistive switching devices using organic material 1,4-bis(di(1H-indol-3-yl)methyl)benzene (Indole1). The pressure—area per molecule isotherm (π–A), Brewster angle microscopy (BAM), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were used to formulate an idea about the organization and morphology of the organic material onto thin films. On the basis of the device structure and measurement protocol, it is observed that the device made up of Indole1 shows nonvolatile resistive random access memory (RRAM) behavior with a very high memory window (∼10⁶), data sustainability (5400 s), device yield (86.7%), and repeatability. The oxidation—reduction process and electric-field-driven conduction are the keys behind such switching behavior. Because of very good data retention, repeatability, stability, and a high device yield, the switching device designed using compound Indole1 may be a potential candidate for memory applications.

INTRODUCTION

Resistive switching devices using organic molecules are gaining interest in the area of memory application due to the added advantage of using organic molecules.¹⁻⁶ At present, a majority of the memory devices available are based on silicon.⁷,⁸ However, silicon-based devices have some limitations, such as low write—erase speed, limited reusability of flash memory, the volatility of dynamic random access memory (DRAMs), and the slow response of hard disk drives (HDDs), that trigger the need for alternative memory materials. In this regard, memory devices using organic materials can substantially overcome the said limitations; therefore, memory applications using suitable organic materials are very attractive.¹⁰ Organic materials exhibiting nonvolatile bipolar resistive switching (RRAM) behavior may be a potential replacement for silicon in the memory industry. There are several advantages of these organic materials as memory elements such as very good read—write speed, scalability, easy device fabrication, excellent data endurance, retention, repeatability, very low power requirements, and good compatibility with existing CMOS technology.¹¹⁻¹⁶

Apart from memory applications, RRAM can be used in future artificial intelligence and neuromorphic computing.¹⁷⁻²⁰ Metal—insulator—ITO-based RRAM has organic material sandwiched between two electrodes. It can be switched between the low resistance state (LRS) and the high resistance state (HRS) on the basis of bias voltage. Depending upon the data retention characteristics, bipolar (nonvolatile) switching and threshold switching (volatile) are promising candidates for future memory technology.²¹ In bipolar switching after the removal of external voltage, both the HRS and LRS are retained, whereas in threshold switching only HRS is retained at a low applied voltage.²²⁻²⁴

Of late, much effort has been expended in the development and investigations of various new organic materials suitable for optoelectronic applications. Materials, preferably polar molecules, which can be easily polarized are suitable for optoelectronic device fabrication. Molecules having a π-conjugated system as well as an electron donor and/or acceptor group form a push—pull system (D−π−A). These types of molecules possess intermolecular charge transfer as well as very low energy barriers. Also, five or six different heterocycles may act as auxiliary acceptors or donors and can be used as π-conjugated backbones. This may include the overall performance of the device employing such molecules.²⁵⁻²⁷ In this context, indole derivatives are very...
important heterocyclic systems because of their π-conjugation and the presence of the −NH group on their pyrrole ring. Accordingly, indole derivatives are expected to have interesting electronic properties.

Recently, we synthesized several indole derivatives and studied their optical behavior.28 Interestingly, it has been observed that self-standing films of indole derivative mixed with clay particles exhibited optical switching under suitable conditions.28 Because of the oxidation−reduction capability as well as the presence of a high π-electron cloud in the molecular backbone of the indole derivative, we thought that this molecule may have interesting electrical behavior as well. Accordingly, we have studied the resistive switching behavior of the 1,4-bis(di(1H-indol-3-yl)methyl)benzene (Indole1) molecule assembled onto LB and spin-coated films. Interestingly, our results suggest that a switching device based on the Indole1 molecule exhibited bipolar resistive switching behavior with a very high memory window (∼106). This study suggests that the indole-based resistive switching device is very promising for use in next-generation high-performance non-volatile memory applications using organic molecules.

EXPERIMENTAL SECTION

Materials. We have synthesized organic materials indole derivatives, namely, 1,4-bis(di(1H-indol-3-yl)methyl)benzene (Indole1) and p-di(3,3′-bis(2-methylindolyl)methane)benzene (Indole2), which are reported in our previous work.28 Terephthaldehyde and DDQ were procured from Spectrochem Pvt. Ltd. and used as received. A working solution was prepared using methanol (spectroscopic grade, SRL, India) and chloroform (spectroscopic grade, SRL, India) as the solvent. Ultrapure (18.2 MΩ cm, Milli-Q) water was used as the subphase.

Isotherm Measurement and LB Film Formation. Measurements of the π−A isotherm and LB film deposition were made by means of an LB film deposition instrument (Apex 2000C, Apex Instruments Co., India). A chloroform solution (0.5 mg/mL, 90 μL) of Indole1 was spread using a microsyringe onto the subphase of pure Milli-Q water in order to measure the π−A isotherm and prepare films. The π−A isotherm was recorded at a 5 mm/min barrier compression rate after the evaporation of chloroform. The π−A isotherm was measured with the help of a Wilhelmy plate arrangement system. For film deposition, a silicon wafer was used for the AFM study, a quartz slide was used for the spectroscopic study, and an ITO-coated glass slide was used for the I−V measurement. Details of the LB technique have been reported elsewhere.29

Fabrication of a Spin-Coating Film. A spin-coating film deposition instrument (SCU 2005A, Apex Instruments Co., India) available in our laboratory was used to deposit the film of Indole1 and Indole2 onto an ITO-coated glass slide and a quartz slide. A 500 μL chloroform solution of Indole1 and Indole2 (0.5 mg/mL) was spread onto a cleaned quartz glass slide and an ITO slide dropwise, followed by spinning such that the sample solution spread almost uniformly over the whole surface of the slide. The substrate was allowed to spin (1500 rpm rotational speed for 120 s) for every 1 to 2 drop of the sample solution. Details of the spin-coating technique have been reported elsewhere.28

BAM Imaging. The morphological structure of the floating film at air−water interface was characterized by BAM (Accurion nano−film_EP4-BAM, serial no. 1601EP4030). The incident light used was p-polarized (30 mW, 532 nm). Details of the BAM imaging have been reported elsewhere.28

AFM Imaging. A commercially available AFM (Innova model, Bruker AXS Pte Ltd.) was used to take the AFM images of LB films. Intermittent-contact (tapping) mode was used during imaging. Details of the AFM imaging have been reported elsewhere.31

RESULTS AND DISCUSSION

Floating Monolayer at the Air−Water Interface. Pressure−Area (π−A) Isotherm. The preparation of a floating film (Langmuir film) at the air−water interface is the first step in depositing the LB film onto a solid substrate.29 Accordingly, we studied the thermodynamic behavior of the Indole1 molecule at the air−water interface by measuring and analyzing the pressure−area isotherm.29 The corresponding isotherm curve is shown in Figure 1.

**Figure 1.** π−A isotherm of the Indole1 molecule on a water subphase. The inset represents the chemical structure of the 1,4-bis(di(1H-indol-3-yl)methyl)benzene (Indole1) molecule.

The isotherm curve shows a continuous rise in surface pressure with a decrease in area per molecule with an initial lift-off area of 0.745 nm².31 The mean molecular area (area per molecule of the solid phase) obtained is 0.446 nm² (Figure S2 in the Supporting Information). To have an idea of the orientation of Indole1 molecule in the Langmuir film in the solid phase, we have analyzed the cross-sectional area of the...
molecule and compared the same with the mean molecular area. Assuming the Indole1 molecule to be a cuboid box having three sides with lengths of 1.412, 0.904, and 0.5 nm, we calculate the three cross-sectional areas to be 0.452, 0.706, and 1.276 nm² (Figure S3 in the Supporting Information). A close look at these values suggests that the mean molecular area (area per molecule for the solid phase) is very close to 0.452 nm² (i.e., the cross-sectional area corresponds to the vertical orientation of the molecule). This indicates that Indole1 molecules lie vertically oriented within the Langmuir film when the solid phase is reached. This also suggests that the Indole1 molecule forms a one-molecule-thick packed monolayer film at the air−water interface.22

Also, we have calculated the compressibility of the floating film within the 5−15 and 25−35 mN/m surface pressure regions following the procedure described elsewhere. It has been observed that the compressibility value in the higher surface pressure region (29.85 mN m⁻¹) is lower than that in the lower surface pressure region (40.42 mN m⁻¹). This also supports the fact that in the higher surface pressure (25−35 mN/m) region Indole1 molecule form a more compact film. An almost negligible variation in surface pressure was observed when the barrier was fixed for a certain time period at different surface pressures, viz., 25 and 30 mN/m during isotherm measurement. This also suggests that Indole1 molecules form a stable Langmuir film at higher surface pressure. Accordingly, we have chosen the 30 mN/m surface pressure for LB film deposition onto a solid support, which is the prerequisite for electronic device applications.33

**BAM Imaging of Langmuir Films.** To have a visual idea of the Langmuir film formation of the Indole1 molecule at the air−water interface, traditional imaging technique such as in situ BAM have been employed. The BAM image of the empty water surface before spreading of the molecules was completely dark, which indicates that no reflection of light occurred from the empty surface (Figure S4 in the Supporting Information). BAM images of the Langmuir film of Indole1 molecules measured at different surface pressures are shown in Figure 2. The image measured before the compression of the barrier showed large circular empty areas with molecules surrounding these areas (Figure 2a). There was much less surface coverage. However, with increasing surface pressure by compression, the surface coverage in the film increases, resulting in a lowering of the empty circular areas in the film (Figure 2b). Interestingly, at around 30 mN/m surface pressure, Indole1 molecules form a continuous smooth film with almost no empty space (Figure 2c). Isotherm studies of the Langmuir film also showed that at around 30 mN/m surface pressure a maximum compact uniform film was formed at the air−water interface. To check the stability of the film at 30 mN/m surface pressure, the barrier was kept fixed and successive BAM images were recorded for up to 5 h. Also, BAM images were recorded through successive compression−expansion cycles. No significant changes in the corresponding BAM images measured with time and compression−expansion cycle were observed (figure not shown). These observations indicate that Indole1 molecules form a stable Langmuir film at the air−water interface.

![BAM images of the Indole1 monolayer recorded during the π−A measurement at the air−water interface.](image-url)
interface at around 30 mN/m surface pressure. This justifies the selection of 30 mN/m surface pressure to deposit the floating film onto the ITO-coated glass substrate for switching device fabrication. However, the BAM images recorded beyond 35 mN/m showed significant changes in the film structure. The corresponding BAM image is shown in Figure 2d. Here, the continuous film breaks partially; this indicates that beyond 35 mN/m surface pressure a partial collapse of the Langmuir film may occur at the air–water interface.

AFM and SEM Imaging of LB Films. In the LB technique, the transfer of a floating Langmuir film onto a solid substrate is very crucial. The film structure largely depends on the deposition process. In some cases, changes in film structure with respect to Langmuir films have been observed. Therefore, to have an idea of the film structure, we investigated LB films of Indole1 deposited at 30 mN/m surface pressure using AFM and SEM. Representative images are shown in Figure 3. We have also designed resistive switching devices using such films. The physical picture of the corresponding device is also shown in Figure 3a.

AFM images of the LB monolayer film showed that the Indole1 Langmuir film has been successfully transferred onto a silicon substrate with very good surface coverage (>80%) (Figure 3b). Height profile analysis showed that the film thickness lies within the 1.5 to 2 nm range (Figure 3c). We have also analyzed the 60-layer LB film surface as well as the cross-sectional view of the Au/Indole1/ITO switching device using FESEM. The SEM image of the 60-layer LB film (Figure 3d) confirmed the formation of a very smooth and continuous film. From the cross-sectional view of the device, the Indole1 film and the ITO and Au electrode are clearly distinguishable. The corresponding image is shown in Figure 3e. It has been observed that the thickness of the 60-layer Indole1 film in the switching device is on the order of 82.16 nm. This value is reasonable considering that the height of the Indole1 molecule is ~1.412 nm in the vertical orientation. As a whole, both AFM and SEM studies give compelling visual evidence of the successful deposition of a uniform LB film onto silicon wafers as well as switching device formation.

Resistive Switching Phenomenon. The LB technique was used to prepare switching device as this technique allows the organization of molecules onto uniform thin films with molecular-level control. An LB-film-based resistive switching device using Indole1 molecules might be suitable for memory applications and future organic electronics. We have already observed interesting optical behavior of Indole1 molecules assembled onto self-standing films. Other indole derivatives with interesting optoelectronic behavior have also been reported. To study the $I−V$ characteristics, a 60-layer LB film of Indole1 molecules has been deposited onto an ITO-coated glass substrate. The device configuration was Au/Indole1/ITO. Here, Au and ITO acted as the top and bottom electrodes, respectively. While studying the switching behavior, we recorded the $I−V$ characteristics by applying a scanning micrograph.
voltage in both forward (+$V_{\text{max}}$ to $-V_{\text{max}}$) and reverse ($-V_{\text{max}}$ to $+V_{\text{max}}$) sweep directions.

Typical $I$–$V$ characteristics for the designed device are shown in Figure 4, presented on both a linear scale (Figure 4a) and a semilog scale (Figure 4b) while measuring from $+V_{\text{max}}$ to $-V_{\text{max}}$. Arrows in the figure show the scanning direction. At the onset of scanning, the device showed very low current and remained in a high resistance state (HRS). When the scanning voltage approached the typical switching threshold of about $-2.45$ V, the current through the device increased abruptly and the device switched to its ON state (i.e., from HRS to a low resistance state (LRS)). This is called SET operation, and the corresponding threshold voltage is known as the SET voltage.

Again, when the scanning voltage is reversed (i.e., $-V_{\text{max}}$ to $+V_{\text{max}}$), the device switched back to its HRS state, when the scanning voltage was reached at about $+2.58$ V. At this point, the device was RESET from its ON state (i.e., from HRS to a low resistance state (LRS)). This is called SET operation, and the corresponding threshold voltage is known as the SET voltage.

In these bipolar switching devices, the SET (transition from HRS to LRS) operation represents a "writing" operation for memory applications. The ON state (LRS) can be retained in the device even after the removal of bias, and the device subsequently returned to its OFF state (HRS) (erasing process) under the opposite bias.

To determine the directional dependence on the observed switching, we have also studied the $I$–$V$ characteristics by reversing the initial sweep direction. Here, initial scanning was applied from $-V_{\text{max}}$ to $+V_{\text{max}}$. In this case, the SET operation (i.e., HRS to LRS transition) occurred at a positive voltage, whereas RESET (LRS to HRS) occurred at a negative voltage (figure not shown). However, the amplitudes of the SET and RESET voltages remained almost unchanged with respect to the previous scanning direction. This suggested that in the present case the observed bipolar switching was independent of the initial scan direction.

The scanning voltage range used was $+3$ to $-3$ V. It was observed that when $V_{\text{max}}$ exceeds $\pm 3.5$ V, once the device switched to its highly conductive ON state, it did not return to its OFF (HRS) state even when the scanning voltage was reversed (Figure 4c,d). This may be due to the short circuit of the device. When current passes through the organic layer, the layer may be heated up. Depending on the bias voltage, if the current crosses a certain limiting value then the organic layer within the device may be damaged due to heating, resulting in a short circuit in the device. Therefore, in the present device, the maximum allowed scanning range is $\pm 3.5$ V.

To check the importance of the LB technique, during device formation with respect to switching performance, we also used a spin-coated film in between electrodes with configuration Au/Indole1-spin-coated film/ITO and observed the $I$–$V$ characteristics. Corresponding $I$–$V$ curves are shown in Figure S5 of the Supporting Information. Here also similar bipolar switching behavior was observed with SET and RESET voltages of $-3.51$ and $+3.56$ V, respectively. In the case of LB films, the switching voltages were much lower. For practical
and commercial applications, a lower switching voltage is advantageous. Various switching parameters as extracted from $I$–$V$ curves showing bipolar switching for both of the above devices along with some other similar reports of switching using organic molecules are listed in Table 1. The ON/OFF current ratio is an important criterion for switching devices in the case of memory applications. A high ON/OFF ratio is always expected for reliable memory performance. Interestingly, in the present case both devices had very high ON/OFF ratios ($\sim 1.67 \times 10^6$ for the LB film and $\sim 3.8 \times 10^5$ for the spin-coated film. A comparison with other reported results also suggested that the observed value of the ON/OFF ratio for the LB film device ($\sim 10^6$) is quite high (Table 1). Therefore, an LB-film-based switching device using the Indole1 derivative may have a very high potential for reliable memory applications. However, in the present case, the difference in performance for the two devices as observed is mainly due to the film preparation technique used. It is well known that the LB technique is very effective for the preparation of smooth, continuous, and uniform ultrathin films compared to the spin-coating technique. Thus, the morphology of the organic layer during switching device formation may be mainly responsible for the better performance in LB-film-based devices.

Data reproducibility and sustainability are essential for reliable, practical, and commercial applications of memory devices. To check the data sustainability, we have checked the data retention test for both devices. This gives us an idea of the ability of a memory device to retain the stored data (i.e., a particular state (HRS or LRS) for a prolonged time). Here we have investigated the data retention characteristics for both devices by studying the LRS and HRS with time. The LRS and HRS of the designed devices were recorded every 150 s over a time period of 5400 s with a very high memory window.

To check the repeatability of the designed memory device, we have investigated LB-film-based devices under several consecutive SET and RESET processes. The results suggested that the designed switching device switches between LRS and HRS and vice versa over at least 50 cycles with two stable and well-resolved resistance states having a memory window of $\sim 10^6$. Representative switching curves are shown in Figure 6. The inset shows the cumulative distribution of $V_{\text{SET}}$ and $V_{\text{RESET}}$ voltages. The results showed that the device exhibits a very good uniform and almost reproducible switching behavior. The average values of $V_{\text{SET}}$ and $V_{\text{RESET}}$ are $\sim 2.418$ and $\sim 2.658$ V, respectively, with standard deviations of 5.35 and 11.89%, respectively.

To check the stability of the designed device, the $I$–$V$ curve of the device has been measured with the passage of time. Interestingly, almost reproducible switching behavior has been observed even after 60 days of device fabrication. Cumulative standard deviations of $V_{\text{SET}}$ and $V_{\text{RESET}}$ measured with the passage of time have been found to be 9.59 and 20.60%, respectively (Figure S6 in the Supporting Information). To check the device yield, we have prepared 30 (5 × 6 array) switchable-independent cells (devices) using two different 60-layer LB films deposited onto an ITO-coated glass substrate. Thus, we get 60 cells with Au/Indole1/ITO device structure, and we measured the $I$–$V$ behavior under the same bias condition. The physical picture of the device is shown in Figure 3a. Interestingly, out of a total of 60 independent measurements in the case of 52 cells almost reproducible

![Figure 5. Retention characteristics of the Au/Indole1/ITO device with an LB film (blue) and a spin-coated film (green).](image)

| Device Configuration | $V_{\text{SET}}$ (V) | $V_{\text{RESET}}$ (V) | OFF State Resistance ($\Omega$) | ON State Resistance ($\Omega$) | Current ON/OFF Ratio | Retention Time (s) | Refs |
|----------------------|---------------------|-----------------------|-------------------------------|-------------------------------|----------------------|-------------------|------|
| Au/phenazine/Au       | $\sim 1.3$          | $\sim 1.4$            | $\sim 5 \times 10^7$         | $\sim 4 \times 10^2$         | $10^6$               | 21                |
| Au/imidazole/ITO      | $\sim 1.95$         | $\sim 1.95$           | $3.45 \times 10^6$           | $46 \times 10^1$            | 794                  | 22                |
| Au/MnTPPS/ITO         | $\sim 4.1$          | $\sim 4.1$            | $10.9 \times 10^3$           | $38 \times 10^1$            | $10^6$               | 23                |
| Ag/melanin/SS         | $\sim 0.6$          | $\sim 0.6$            | $\sim 6 \times 10^5$         | $\sim 5 \times 10^4$        | $10^6$               | 42                |
| Ag/CGMPs/FTO          | $\sim 1.33$         | $\sim 1.42$           | $\sim 9 \times 10^9$         | $\sim 210$                  | 4.37                 | 45                |
| Au/silk fibron/ITO    | $\sim 14$           | $\sim 14$             | $\sim 3 \times 10^3$         | $\sim 2.7 \times 10^5$      | 11                   | 46                |
| Ag/pectin/FTO         | $\sim 3.3$          | $\sim 4.5$            | $\sim 4.5 \times 10^5$       | $\sim 1 \times 10^4$        | 450                  | 47                |
| Al/parylene/W         | $\sim 2.2$          | $\sim 0.6$            | $\sim 5 \times 10^6$         | $\sim 4.5 \times 10^5$      | 10                   | 48                |
| Ag/sericin/Au         | $\sim 2.5$          | $\sim 1$              | $\sim 2.2 \times 10^6$       | $\sim 4.9 \times 10^3$      | $10^6$               | 49                |
| Pt/proton-doped polyazomethine/Pt | $\sim 3$        | $\sim 7$              | $\sim 8.2 \times 10^6$       | $\sim 4.6 \times 10^5$      | 10                   | 50                |
| Au/Indole1-spin coated film/ITO | $\sim 3.51$     | $\sim 3.56$           | $2.041 \times 10^7$          | $5.37 \times 10^3$          | $3.8 \times 10^3$    | 5400 present work |

![Image](image)

Table 1. Performance Comparison of Indole1-Based Memory Devices and Other Organic-Material-Based Memory Devices

![Figure 3a.](image)
switching behavior was observed with mean values of $V_{\text{SET}} = 2.423$ V and $V_{\text{RESET}} = 2.62$ V and standard deviations of $\sigma_{\text{SET}} = 17.3\%$ and $\sigma_{\text{RESET}} = 12.66\%$. The corresponding plot is shown in Figure S7 in the Supporting Information. These results indicate a device yield on the order of 86.7%. As whole data retention, repeatability and stability studies and a high device yield suggested that switching devices using the Indole1 molecule may be potential candidates for memory applications and the realization of organic electronics.

Several mechanisms and strategies such as reduction—oxidation, electron tunnelling and hopping, ionic conduction, conformational change, space—charge limited conduction, and traps have been proposed to explain the observed switching behavior. The device having the Au/Indole1/ITO configuration involves carrier conduction through injection and transport. A built-in internal field due to differences in work functions of the metal electrodes used along with the amplitude and the direction of bias voltage and electron injection from the metal electrode to the LUMO level of the Indole1 molecules was used. This intern switches the device to its ON state via electroreduction. Thus, conjugation within the molecules is extended, resulting in a lowering of the HOMO—LUMO energy gap. This leads the device to its highly conducting (low resistance) ON state. The observed electroreduction of Indole1 molecules may involve two possibilities: (i) injection of the electron when it overcomes the difference in energy between the LUMO level of the molecule and the work function of the ITO electrode and (ii) transport of the electron via applied-bias-dependent hopping.

Again, depending on the bias condition when the molecule gets oxidized, the device will return to its low conducting OFF state. Possible oxidation—reduction steps of the Indole1 molecule are shown in Figure 7.

To confirm the role of the reduction—oxidation process in the observed bipolar switching, we have synthesized the Indole2 molecule, where $-H$ of Indole1 has been replaced by a methyl group, and checked the $I$—$V$ curves of the device using Indole2. Because of the presence of the methyl group, oxidation—reduction of the Indole2 molecule was hardly possible. Interestingly, here no bipolar switching was observed. The molecular structure of Indole2 is shown in Figure S8 of the Supporting Information. This observation supports the role of the reduction—oxidation process in the observed bipolar switching for the devices using Indole1 molecules.

Cyclic voltammetry (CV) measurement also clearly supports the role of the reduction—oxidation process in observed bipolar switching. We have studied the CV curve for both Indole1 and Indole2 (Figure S9 in the Supporting Information). The CV curve of Indole1 molecules showed prominent oxidation and reduction peaks. On the other hand, the CV curve corresponding to Indole2 molecules did not show any prominent oxidation—reduction peaks.

To elucidate the conduction mechanism, further dependences of the SET and RESET threshold voltages on the active-layer thickness of the switching devices have been investigated. To do that, switching devices have been constructed from LB films with various thicknesses such as 10, 60, 70, 80, and 90 layers, and their $I$—$V$ characteristics were measured. Corresponding results are shown in Figure S10 of the Supporting Information. The results suggested that switching voltages gradually increase from $V_{\text{SET}} = 1.06$ to $3.51$ V and $V_{\text{RESET}} = -0.879$ to $-3.56$ V. Increases in switching voltages with the active-layer thickness indicate the possibility of electric-field-driven conduction in addition to the oxidation—reduction mechanism.

To understand the observed switching mechanism, a schematic of the energy-level diagram under various conditions has been shown in Figure 8. The slope of the LUMO energy level in “after contact” condition determines the direction of electron transport from the ITO side under the reverse bias condition while scanning from $+V_{\text{max}}$ to $-V_{\text{max}}$ (Figure 8i).

Hence, in this device, a combined effect of barrier potential and electron injection due to bias-induced reduction favors electron transport from the ITO electrode to the LUMO level compared to that from the Au electrode under the reverse bias condition. While scanning from $-V_{\text{max}}$ to $+V_{\text{max}}$ at the threshold ($V_{\text{RESET}}$), oxidation of the Indole1 molecules occurred, resulting in the device switching to its OFF state. On the other hand, under the forward bias condition while scanning from $-V_{\text{max}}$ to $+V_{\text{max}}$ at the threshold voltage Au electrode donates an electron to Indole1 molecule within the device (Figure 8ii). As a result, molecules near the Au electrode get reduced and the device gets switched to its ON state. Here, due to a higher barrier height the electron reached the LUMO level via hopping transport. Again while scanning from $+V_{\text{max}}$ to $-V_{\text{max}}$ at a particular threshold ($V_{\text{RESET}}$),

Figure 6. $I$—$V$ measurements of the Au/Indole1/ITO device over consecutive cycles. The inset represents the mean value ($\mu$) and standard deviation ($\sigma$) of $V_{\text{SET}}$ and $V_{\text{RESET}}$ voltages. A video showing 20 cycles of consecutive $I$—$V$ measurement has been given in the Supporting Information.

Figure 7. Oxidation—reduction steps of Indole1.
oxidation of the molecules occurred and the device switched back to its OFF state.

To have better understanding of the observed bipolar switching mechanism, $I$–$V$ characteristics of the Au/Indole1/ITO device have been investigated by varying the temperature from 293 to 343 K. At all temperatures, the device showed stable and almost reproducible switching behavior with mean values of $V_{\text{SET}} = 1.77$ V and $V_{\text{RESET}} = 2.32$ V and standard deviations of $\sigma_{\text{SET}} = 18.38\%$ and $\sigma_{\text{RESET}} = 16.83\%$. The corresponding plot is shown in Figure S11 of the Supporting Information. Interestingly, it has been observed that the resistance of the device in the LRS state increased with the increase in temperature (Figure 9). On the other hand, the resistance of the HRS state remained almost unchanged. The analysis showed that the relation between temperature and the LRS resistance of the device can be fitted with equation $R(T) = [R_0 + \alpha(T - T_0)]$, where $R_0$ is the resistance of the ITO/Indole1/Au device at temperature $T_0$, $\alpha$ is the thermal expansion coefficient of resistance, and $R(T)$ is the resistance at temperature $T$ (inset of Figure 9). $\alpha$ was estimated from the fitting of the experimental results and was found to be $\sim 4.26 \times 10^{-3}$ K$^{-1}$. This value is close to the temperature coefficient of gold. This indicates that there is a possibility of the formation of the Au filament in the Au/Indole1/ITO device in between two electrodes. Under positive bias, a few Au atoms may be oxidized, resulting in Au$^+$ cations in the indole layer within the device. On the other hand, negative bias on the bottom ITO electrode attracts these Au$^+$ cations and reduction occurs (Au$^+$ + e$^-$ → Au) near the bottom electrode. In this way, Au$^+$ cations are reduced to Au atoms and accumulated in between the two electrodes of the device until a conducting bridge of the Au atom is formed. This has been shown in Figure S12 in the Supporting Information. Thus, the device switched ON to its SET state. Under the application of reverse bias, when the top electrode was negatively biased with respect to the bottom electrode, a few Au atoms (near the Au electrode) within the filament were oxidized (Au → Au$^+$ + e$^-$) and at a particular bias ($V_{\text{RESET}}$) the conducting filament is almost completely broken up (Figure S12d in the Supporting Information). This in turn leads the device to its HRS (OFF state). Thus, the formation and disruption of the Au filament across the film in between two electrodes could be one of the key mechanisms involved in the observed bipolar switching.

To gain further insight into the conduction mechanism of the Au/Indole1/ITO device, we analyzed the $I$–$V$ curves on the double logarithmic scale as shown in Figure 10. For both positive (Figure 10a) and negative bias (Figure 10b), the $I$–$V$ curves exhibited linear behavior in the low-voltage region. However, in higher-voltage regions it follows quadratic behavior. Such charge transport behavior can be explained in terms of electron-injected trap-controlled space-charge limited conduction (SCLC) theory. At low voltage, the linear behavior follows Ohm’s law due to a thermally generated free electron within the film. The quadratic behavior in the higher-voltage region follows Child’s law, where $I \propto V^2$. To analyze the higher-voltage quadratic region of the curve further, we have plotted $I$ vs $V^2$ as shown in Figure 10c,d. The almost linear nature of the curves under both bias conditions suggested our assumption that here the current–voltage relation obeys Child’s law. A close look into Figure 10a showed that current decreased as the voltage increased within the range of 1.129–1.183 V. It seems that an anomalous negative differential resistance (NDR) effect was observed during the RESET process. However, after 1.183 V typical current behavior was observed. Interestingly, a similar NDR effect has been reported in many switching devices and explained by the charge trapping and detrapping near the electrode–active layer interface. In the present case, also we think that charge trapping followed by detrapping near the Au electrode–Indole1 film interface may be responsible for such observed behavior.

## CONCLUSIONS

We have designed and investigated resistive switching devices based on organic molecule Indole1. LB and spin-coating techniques were used to prepare the active layer of the switching device. Devices fabricated using both techniques showed bipolar resistive switching behavior suitable for organic memory application under an optimized measurement.
protocol. Bias-dependent oxidation and reduction and an electric-field-driven conduction mechanism was the key behind the observed switching. An analysis of the $I-V$ characteristics revealed that LB-film-based switching devices had a higher memory window ($\sim 10^6$) than that of the spin-coated-film-based devices ($\sim 10^4$). The data retention capability of the device was tested for up to 5400 s with very good and satisfactory performance. The performance of the device was also found to be very good in terms of data reproducibility (more than 50 cycles), stability (more than 60 days and up to 343 K), and device yield ($\sim 86.7\%$). As a whole, our investigation revealed that a switching device based on the Indole1 molecule may be a potential candidate for application in the RRAM device using organic molecules.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c03629. Schematic diagram for device Au/organic material/ITO configuration, $x-A$ isotherm of Indole1 showing the value of the limiting molecular area, dimensions of Indole1, BAM image of the air–water interface, bipolar resistive switching of the Au/Indole1-spin coated/ITO device, $I-V$ characteristics study for the stability of the device, variation of SET and RESET voltages with the number of individual cells in the devices, chemical structure of Indole2 and CV of Indole1 and Indole2, variation of SET and RESET voltage with thickness of the LB film-based switching devices, variation of SET and RESET voltages of the $I-V$ curve with temperature, and schematic illustration of the filamentary conduction (PDF).

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S.A.H. designed the work. S.S. performed all experiments. S.S. and H.B. analyzed the data. S.M. and B.D. synthesized the material. S.A.H. and S.S. wrote the manuscript with input from S.M., D.B., and P.K.P.

Notes
The authors declare no competing financial interest.

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