### Declaration

I hereby declare that the work presented in this thesis titled 'Organotin Assemblies Containing Sn-S and Sn-O Units: Applications in Resistive Switching Device and Antibacterial Properties' submitted to the Indian Institute of Technology Jodhpur in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work carried out under the supervision of Dr. Ramesh K. Metre. The contents of this thesis in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma.

Ashistul Miscua.

Abhishek Mishra P17CY001

### Certificate

This is to certify that the thesis titled 'Organotin Assemblies Containing Sn-S and Sn-O Units: Applications in Resistive Switching Device and Antibacterial Properties', submitted by Abhishek Mishra (P17CY001) to the Indian Institute of Technology Jodhpur for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work done by him under my supervision. To the best of my knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Ramesh K. Metre Ph. D. Thesis Supervisor Date: 0////202/

### Acknowledgements

First and foremost, I would like to thank the almighty God for giving me the opportunity and granting uncountable blessings. As a result, I have been able to accomplish the thesis.

I would like to thank my Ph.D. thesis supervisor, Prof. Ramesh K. Metre, for his invaluable guidance and encouragement throughout my research journey. His research expertise and insightful feedback have always pushed me to learn and grow immensely. I have been constantly motivated and supported by him to acquire new skills. Besides his professional intellect, he has inspired me with his principles, discipline, and values. His positive aura has always cheered me up.

I am extremely grateful to Mr. Atanu Betal, Prof. Satyajit Sahu, Dr. Ravi Kumar, Prof. G. Rajaraman, Prof. Prem Lama, Dr. Amitap Khandelwal, and Prof. Meenu Chhabra for the successful collaboration and fruitful discussions.

I thank all my labmates Vivek, Nisha, Sunita, Dipanjana, Sahid, Mayank, Suman, Swathy, Aayush, Arpan, Simran, Pallavi, Praveen, Nitin, Arun, Neelam, Moorthi for their continuous support and encouragement. I owe my deep gratitude to Dr. Gaurav Bahuguna, Ms. Sheeba Malik, and Ms. Ayushi Awasthi for their constant and valuable support. It has been a pleasure to have them in tough times as both companions and torchbearers.

I thank all the professors, office staff, and technical staff of the Department of Chemistry for their kind support and cooperation.

Thanks to all the mess, security, housekeeping, medical and administrative staff for always being friendly and cooperative.

I thank MHRD for providing financial support through JRF and SRF fellowships.

I thank the CASE facility, IIT Jodhpur, for assisting me in my research by providing access to the instruments.

Thanks to all those friends who never gave up and supported me in every walk of life.

I thank all my friends, seniors, and juniors at IITJ who have always been there in my ups and downs. The memories created in the hostel, campus, and outside the campus will be missed.

Thanks to these five years of Ph.D. for preparing me to handle hardships, failures, disappointments, stress, and everything else that comes my way. I appreciate myself for not giving up and keeping my spirit up regardless of the circumstances.

I am thankful to Nidhi Sharma for always being there for me regardless of the circumstances.

Last but not least, I wish to acknowledge my beloved family, who has always backed me with their love, sacrifice, and trust. Their blessings have contributed immensely to my achievements. I wholeheartedly dedicate this thesis as a token of respect to my family.

Apristule Miscua.

Abhishek Mishra Ph.D. Student

## List of Figures

Figures Title

- 3.1 Schematic diagram of the device in which complex **1**: PS (60:40) is used as an active layer.
- 3.2 (a) <sup>1</sup>H NMR, (b) <sup>13</sup>C NMR, and (c) <sup>119</sup>Sn NMR of complex 1 recorded in CDCl<sub>3</sub>.
- 3.3 (a) FTIR spectrum, (b) UV-Vis spectrum (conc. 10<sup>-5</sup>M in CHCl<sub>3</sub>), (c) TGA (under N₂ 31 atmosphere), (d) ESI-MS spectrum and (e) CHN analysis for complex 1.
- 3.4 (a) Molecular structure of complex 1. Bond distance (Å) and bond angle (°) parameters: Sni-S1, 2.4177(1); Sn1-C12, 2.1316(3); Sn2'-S2, 2.4775(1); Sn1-S1-Sn2, 108.727(5)°; Sn1-S3'-Sn2', 86.825(5)°; (b) Sn₄S<sub>6</sub> core structure with a plane passing through two S atoms (S1 and S1'); (c) coordination environment of Sn in complex 1; Sn1-S3', 2.4816(1); Sn1-S2, 2.4001(1); Sn1-N1, 2.5657(2); C12-Sn1-S3', 103.142(9)°, N1-Sn1-S1, 84.243(6)°; N1-Sn1-C12, 70.144(1)°; N1-Sn1-S3', 169.838(8)°; S2-Sn1-S1, 124.835(5)°.
- 3.5 (a) One-dimensional supramolecular assembly of 1 formed by CH... $\pi$ , S...H interactions. 33 Metric parameters are as follows;  $\pi$ -H3, 3.6052(2) Å;  $\pi$ -H47, 2.7356(1) Å; S3-H46, 3.1859(2) Å; S2-H27, 3.5054(2) Å; (b) One-dimensional supramolecular assembly formed by  $\pi$ ... $\pi$ , S...H interactions. Metric parameters are as follows;  $\pi$ - $\pi$ , 3.7640(2) Å; S4-H35, 3.1715(1) Å.
- 3.6 Two-dimensional supramolecular architecture of 1 formed by CH... $\pi$ ,  $\pi$ ... $\pi$ , S...H 33 interactions. Metric parameters are as follows;  $\pi$ - $\pi$ , 3.7283(2)Å;  $\pi$ - $\pi$ , 3.7640(2)Å;  $\pi$ -H47, 2.7356(1)Å;  $\pi$ -H42, 2.8738(1)Å; S5-H3, 3.1036(2)Å; S2-H27, 3.5054(2)Å; S3-H46, 3.1859(2)Å.
- 3.7 Computed absorption spectra (in red) of complex 1 using TD-DFT calculations and its 34 corresponding orbitals involved in the transitions. The experimental spectrum of 1 is given in the black line for comparison.
- 3.8 The diagram shows the **(a)** HOMO and **(b)** LUMO orbital pictures of complex **1**. The orbital 34 with orange color represents the alpha orbital, and the violet color with a beta orbital. The contour value used to plot these is 0.03 a.u.
- 3.9 I-V characteristic curve of the devices in which an active layer as (a) Complex 1 (b) 35 Polystyrene mixed with complex 1 (40:60) as a matrix was used, the black and blue arrows show the current direction during voltage sweep. (c) Write-read-erase-read sequence to check the consistency of writing and erasing state. Writing pulse was given at -1.4V for 10 s, and erasing voltage was given at 1.4V for 10 s. All the states were read at -0.25V for 10 s, i.e., 40 s were taken to complete one cycle. More than 2500 such cycles were taken to check consistency, and the device was found to be consistent (d) After giving a write pulse and erase pulse at -1.4 V and 1.4 V, respectively, testing of stability at a particular state was done by giving a constant reading pulse at -0.25 V for 10000 S.
- 3.10 AFM image of the device (a) image of complex 1 on 1µm x 1µm area (b) image of the complex 36
   1 and PS material on 5µm x 5µm scan area. These devices are prepared in the same environment and concentration. (c) Fitting of current vs. voltage curve in logarithm scale with voltage sweep starts from oV to -1.4V again to oV. Fitting shows the different regions of current conduction.
- 3.11 Band diagram for current conducting mechanism (a) conduction current due to thermally excited charge carriers (red balls) which can tunnel the barrier are very less in number, and Ohm's law was followed. (b) Defect states are partially filled, and charge carriers follow Child's law (I  $\alpha$  V<sup>2</sup>). (c) The defect states are almost filled, so the SCLC mechanism (I  $\alpha$  V<sup>n</sup>) was followed. (d) All the defect states are partially filled, and the charge carrier makes the conduction path, and again, Ohm's law was followed.
- 4.1 (a) FTIR spectrum, (b) TGA plot (under N<sub>2</sub> atmosphere) and (c) CHN analysis of complex 2.
- (a) Molecular structure of complex 2; Bond distance (Å) and bond angle (°) parameters: Sn1-S1, 2.3879(1) Å; Sn1-S2, 2.4190(1) Å; Sn1'-S2, 2.5813(1) Å; Cu1-S1, 2.2165(1) Å; Sn1-S2-Sn1', 88.077(3)°; S1-Sn1-S2, 116.841(3)°, Sn1-S1-Cu1, 105.014(4)°; Sn1-S2-Cu1''', 99.687(3)°; (b) Core structure with a molecular plane; (c) Coordination environment of Sn in complex 2; Sn1-N2, 2.5131(3) Å; Sn1-S2', 2.5813(1) Å; Sn1-C1, 2.1329(3) Å; N2-Sn1-S2', 168.455(6)°; N2-Sn1-S2, 88.843(6)°; C1-Sn1-S2, 122.683(9)°; S2'-Sn1-S2, 91.889(3)°; (d) Coordination environment of Cu in complex 2; Cu1-S1, 2.2165(1) Å; Cu1-S2'', 2.4669(2) Å; Cu1-S1''', 2.3020(2) Å; S1-Cu1-S2'', 117.032(4)°; S1-Cu1-S1''', 142.828(4)°.
- 4,3 One-dimensional supramolecular assembly of **2** formed by CH... $\pi$ , CH...S interactions. H 44 atoms are omitted to show the interactions clearly. Metric parameters are as follows; H2- $\pi$ ,

xiii

page

30

31

42 43

3.6982(1) Å; H3-S1, 3.3634(2) Å; H4-S2, 3.8053(2) Å. (b) Two-dimensional supramolecular architecture of **2** formed by CH... $\pi$ , CH...S, CH...N interactions. H atoms are omitted to show the interactions clearly. Metric parameters are as follows; H10- $\pi$ , 3.7857(1) Å; H5- $\pi$ , 3.8321(2) Å; H3-S1, 3.3634(2) Å; H4-S2, 3.8053(2) Å; H8-N1, 3.6266(3) Å; H8-N2, 2.4296(3) Å.

- DFT-computed HOMO-LUMO energies, gap, and their corresponding molecular orbital 48 4.4 diagram of complex **2**. The contour value used to generate the plots are 0.03 a.u.
- Natural bonding orbital (NBO) diagram for the Sn<sup>IV</sup>-coordinated environment of complex 2. 4.5 49 The contour value used to generate the plots are 0.03 a.u.
- Natural bonding orbital (NBO) diagram for the Cu<sup>1</sup>-coordinated environment of complex 2. 4.6 50 The contour value used to generate the plots are 0.03 a.u.
- AIM topological analysis diagram showing bond critical points (BCPs) in gray dots and ring 4.7 51 critical points (RCBs) in light pink dots for complex 2.
- 4.8 Electrostatic Surface Potential (ESP) mapped on the 0.001 a.u. Electron density surface of 52 complex 2. Here, the blue color indicates the positive region with less electron density, while the red color indicates the negative region with high electron density.
- (a) <sup>1</sup>H NMR, (b) <sup>13</sup>C NMR, and (c) <sup>119</sup>Sn NMR of complex **3** recorded in CDCl<sub>3</sub>. 5.1
- (a) UV-Vis spectrum (conc. 10<sup>-5</sup>M in CHCl<sub>3</sub>), (b) FTIR spectrum, (c) TGA (under N<sub>2</sub> atmosphere) 5.2 57 (d) ESI-MS spectrum and (e) CHN analysis of complex 3.

56

68

- (a) Molecular structure of complex 3; Bond distance (Å) and bond angle (°) parameters: Sn1-58 5.3 S1', 2.4007(1) Å; Sn1'-S1, 2.4761(1) Å; Sn1-S1-Sn1', 85.907(3)°; Sn1-S1'-Sn1', 85.907(3)°, S1-Sn1-S1', 94.093(3)°; (b) Core structure with a molecular plane; (c) Coordination environment of Sn in complex 3; Sn1-S1, 2.4007(1) Å; Sn1-S1', 2.4761(1) Å; Sn1-N2, 2.6335(2) Å; Sn1-C1, 2.1365(2) Å; Sn1-C13, 2.1306(3) Å; N2-Sn1-S1', 167.175(5)°; N2-Sn1-S1, 82.547(5)°, C1-Sn1-C13, 126.094(1)°; C1-Sn1-S1, 115.586(7)°.
- (a) One-dimensional supramolecular assembly of 3 formed by CH... $\pi$ , CH...S, CH...N 5.4 59 interactions. Metric parameters are as follows; H22-π, 3.4881(1) Å; H3-S1, 3.0710(1) Å; H4-S1, 3.2938(1) Å; H14-N1, 3.4615(2) Å; H15-N1, 3.0605(2) Å. (b) Two-dimensional supramolecular architecture of **3** formed by CH... $\pi$ ,  $\pi$ ... $\pi$ , CH...N interactions. Metric parameters are as follows; H21-π, 3.6737(1) Å; π...π, 3.9903(1) Å; H10-N3, 3.0460(2) Å; H21-N4, 3.3569(2) Å; H9-N3, 3.4469(3) Å; H21-N1, 2.9805(3) Å; H21-N3, 3.1785(2) Å.
- DFT-computed absorption spectra (in red) of complex 3 using TD-DFT calculations and its 5.5 60 corresponding orbitals involved in the transitions. The experimental spectrum of 3 is given in the black line for comparison.
- Natural bonding orbital (NBO) diagram for the Sn<sup>IV</sup>-coordinated environment of complex **3**. 5.6 61 The contour value used to generate the plots are 0.03 a.u.
- DFT-computed HOMO-LUMO energies, gap, and their corresponding molecular orbital 62 5.7 diagram of complex **3**. The contour value used to generate the plots are 0.03 a.u. 63
- 5.8 Inhibition zones of Complex 3 against E. coli and M. Luteus.
- The schematic diagram of the crossbar architectured device in which ITO is the bottom 68 6.1 contact and Al is the upper contact for electrical characterization.
- 6.2 (a) <sup>1</sup>H NMR, (b) <sup>13</sup>C NMR, and (c) <sup>119</sup>Sn NMR of complex 4 recorded in CDCl<sub>3</sub>.
- (a) FTIR spectrum, (b) UV-Vis spectrum (conc. 10<sup>-5</sup>M in CHCl<sub>3</sub>), (c) TGA (under N<sub>2</sub> atmosphere) 6.3 69 (d) ESI-MS spectrum and (e) CHN analysis of complex 4.
- 6.4 (a) Molecular structure of complex 4. Bond distance (Å) and bond angle (°) parameters: Sn2-70 O1, 2.0251(3)Å; Sn2-O2, 2.2214(3)Å; Sn1-O2, 2.0503(3)Å; Sn1-O1, 2.1625(2)Å; Sn1-O1-Sn2, 110.907(1)°; Sn1-O2-Sn2, 107.669(1)°; (b) Core structure with a molecular plane. (c) Coordination environment of Sn in complex 4; Sn1-N1, 2.4015(7)Å; Sn1-C12, 2.1139(4)Å; Sn1-Cl1; 2.3935(1)Å; Sn1-Cl2, 2.4102(2)Å; O1-Sn1-O2, 71.078(1)<sup>0</sup>, N1-Sn1-Cl2, 173.935(1)<sup>0</sup>; N1-Sn1-Cl2, 73.468(1)°; Cl1-Sn1-Cl2, 95.699(5)°.
- (a) One-dimensional supramolecular assembly of 4 formed from C-H... $\pi$  and CH...Cl 6.5 70 interactions. Metric parameters are as follows;  $\pi$ -H11, 3.3861(2)Å; H21-Cl1, 3.5767(1)Å; H22-Cl1, 2.8670(1)Å; H9-Cl4, 3.5511(1)Å; H10-Cl4, 2.8765(1)Å (b) One-dimensional supramolecular assembly of **4** formed by C-H... $\pi$  and C-H...Cl interaction. Metric parameters are as follows;  $\pi$ -H25B, 3.7914(3)Å; H25A-Cl4, 2.7698(1)Å; H2-Cl4, 3.0026(1)Å.
- Two-dimensional supramolecular architecture of **4** formed from C-H... $\pi$ , C-H...N, and C-6.6 71 H...Cl interactions. Metric parameters are as follows:  $\pi$ -H11, 3.3861(2)Å; H17-Cl1, 3.5806(1)Å; H3-Cl2, 3.0179(1)Å; H15-Cl3, 2.9103(1)Å; H16-Cl1, 3.2513(1)Å; H16-N2, 2.8670(1)Å.
- A comparative absorption spectrum of complex 4 where experimental data is shown in black 6.7 72 and TD-DFT computed data in red along with the corresponding orbital transitions.
- Molecular orbital diagram of complex 4 (a) HOMO and (b) LUMO with its singly reduced 6.8 72

form (c) SOMO and (d) LUMO orbital pictures. The orbital with orange color represents the alpha orbital and the violet color with a beta orbital. The contour value used to plot these is 0.03 a.u.

- 6.9 Overlay diagram of complex **4** with its reduced species. Note, here; the grey carbon structure 73 is for complex **4** while the pink carbon structure is for singly reduced species.
- 6.10 Current-Voltage and NDR characteristics plot of the device. The red arrows showed the 74 current path during the full I-V cycle. The current starts increasing to reach peak maxima and valley minima at 1.5V and 2.5V, respectively. 1<sup>st</sup>, 10<sup>th</sup>, 20<sup>th</sup>, and 50<sup>th</sup> I-V cycles are plotted here. The current ratio between on and off state is given in the upper inset Fig. **6.10(a)**. The logarithmic plot of current and voltage is shown in lower inset Fig. **6.10(b)**.
- 6.11 (a) RAM behavior of the device with write, read, erase voltage of -3.2V, 1.5V, 3.2V respectively
   74 for 10 s each. Voltage vs. time (red color) and current vs. time (blue) plots were shown. (b)
   retention of the device checked up to 2000 s with the read voltage 1.5V and -3.2V, 3.2V as the write and erase voltages, respectively. The device retains its state the whole time.
- 6.12 AFM image of the device taken in the non-contacting mode with a scan speed of 0.3 nm<sup>2</sup>/Sec. 75 The circle and rectangle show the holes on the surface, which are responsible for leakage current.

83

83

84

- (a) <sup>1</sup>H NMR, (b) <sup>13</sup>C NMR, and (c) <sup>119</sup>Sn NMR of complex 5 recorded in CDCl<sub>3</sub>.
- (a) <sup>1</sup>H NMR, (b) <sup>13</sup>C NMR, and (c) <sup>119</sup>Sn NMR of complex 6 recorded in CDCl<sub>3</sub>.
- 7.3 (a) <sup>1</sup>H NMR, (b) <sup>13</sup>C NMR, and (c) <sup>119</sup>Sn NMR of complex 7 recorded in CDCl<sub>3</sub>.
- (a) UV-Vis spectrum (conc. 10<sup>-5</sup>M in DCM), (b) FTIR spectrum, (c) TGA (under N₂ atmosphere)
   84 (d) CHN analysis of complex 5.
- (a) UV-Vis spectrum (conc. 10<sup>-5</sup>M in DCM), (b) FTIR spectrum, (c) TGA (under N₂ atmosphere)
   (b) CHN analysis of complex 6.
- (a) UV-Vis spectrum (conc. 10<sup>-5</sup>M in DCM), (b) FTIR spectrum, (c) TGA (under N₂ atmosphere)
   (b) CHN analysis of complex 7.
- 7.7 (a) Molecular structure of complex 5. Bond distance (Å) and bond angle (°) parameters: Sn3-O6, 2.0970(2)Å; Sn3-O3', 2.1109(3)Å; Sn2-O6, 2.0694(3)Å; Sn1-O9-Sn3, 133.850(1)°; Sn1-O3-Sn2, 134.388(1)°, O6-Sn3-O9, 103.509(1)°; Sn2-O9'-Sn1', 99.9(1)°; H atoms are omitted for clarity. (b) Core structure with a molecular plane. (c) Coordination environment of Sn in complex 5; Sn1-O3, 2.0707(3)Å; Sn1-O5', 2.1884(3)Å; Sn1-C1; 2.1447(4)Å; Sn1-O1, 2.1427(3)Å; Sn1-O9, 2.0985(3)Å; C1-Sn1-O6', 175.415(1)°; O3-Sn1-O5', 162.269(1)°, O3-Sn1-C1, 106.304(1)°; O5'-Sn1-C1, 88.292(1)°; O1-Sn1-O6', 85.350(1)°.
- (a) Molecular structure of complex 6. Bond distance (Å) and bond angle (°) parameters: Sni-O5, 1.9455(9)Å; Sni-O1, 2.2794(1)Å; Sni-O2, 2.2837(1)Å; Sni-O3, 2.1429(1)Å; Sni'-O5, 1.9455(9)Å; Sni-O5-Sni', 123.008(1)°; H atoms are omitted for clarity. (b) Coordination environment of Sn in complex 6; Sni-O4, 2.2369(1)Å; Sni-C1, 2.1092(2)Å; Sni-N1; 2.4376(2)Å; C1-Sni-O5, 173.210(5)°, O3-Sni-N1, 146.398(6)°; O4-Sni-C1, 89.477(6)°; N1-Sni-O5, 85.350(1)°; O1-Sni-O3, 100.371(4)°; C1-Sni-N1, 72.93(7)°.
- (a) Molecular structure of complex 7. Bond distance (Å) and bond angle (°) parameters: Sn1-O1, 1.9406(3); Sn1-O1', 1.9867(3); Sn1-O1-Sn1''', 129.396(1)°; O1-Sn1-O1', 104.482(1)°; H atoms are omitted for clarity. (b) Sn4O4 core structure with a plane passing through no atom; (c) coordination environment of Sn in complex 7; Sn1-C1, 2.1328(5); Sn1-C13, 2.1321(5); Sn1-N4, 2.6678(4); N4-Sn1-O1', 162.673(1)°, N4-Sn1-O1, 87.571(1)°; N4-Sn1-C1, 86.794(1)°; N4-Sn1-C13, 66.952 (1)°; C1-Sn1-C13, 129.258(2)°.
- 7.10 (a) One-dimensional supramolecular assembly of **5** formed by CH... $\pi$  and CH...N 88 interactions. Metric parameters are as follows; H18- $\pi$ , 3.5806(1) Å; H23- $\pi$ , 3.6629(1) Å H46-N2, 3.7850(4) Å; H5-N6, 3.0071(4) Å. (b) Two-dimensional supramolecular architecture of **5** formed by CH... $\pi$ ,  $\pi$ ... $\pi$  and CH...N interactions. Metric parameters are as follows; H8- $\pi$ , 3.8126(1) Å;  $\pi$ ... $\pi$ , 3.8616(1) Å; H46-N2, 3.7850(4) Å; H18-N6, 3.5772(4) Å; H5-N6, 3.0071(4) Å.
- 7.11 **(a)** One-dimensional supramolecular assembly of **6** formed by CH... $\pi$ ,  $\pi$ ... $\pi$ , and CH...O 89 interactions. Metric parameters are as follows; H10- $\pi$ , 2.6680(4) Å;  $\pi$ ... $\pi$ , 3.7610(5) Å; H12-O1, 3.1452(1) Å; H12-O2, 3.4579(2) Å; H24-O2, 2.9568(2) Å. **(b)** Two-dimensional supramolecular architecture of **6** formed by CH... $\pi$ ,  $\pi$ ... $\pi$ , CH...O interactions. Metric parameters are as follows; H10- $\pi$ , 2.6680(4) Å;  $\pi$ ... $\pi$ , 3.7610(5) Å; H24-O2, 2.9568(2) Å.
- 7.12 (a) One-dimensional supramolecular assembly of 7 formed by CH... $\pi$ ,  $\pi$ ... $\pi$ , and CH...N 90 interactions. Metric parameters are as follows; H23- $\pi$ , 3.1509(5) Å H8-N3, 2.8275(4) Å; H8-N4, 3.5921(4) Å;  $\pi$ ... $\pi$ , 3.7587(6). (b) Two-dimensional supramolecular architecture of 7 formed by CH... $\pi$ ,  $\pi$ ... $\pi$ , and CH...N interactions. Metric parameters are as follows; H23- $\pi$ , 3.1509(5) Å H8-N3, 2.8275(4) Å; H8-N4, 3.5921(4) Å;  $\pi$ ... $\pi$ , 3.7587(6).

7.13 7.14	Inhibition zones of Complex <b>5</b> against E. coli and M. Luteus. Inhibition zones of Complex <b>6</b> against E. coli and M. Luteus.	91 92
7.15 7.16	Inhibition zones of Complex <b>7</b> against E. coli and M. Luteus. DFT-computed HOMO-LUMO energies, gap, and their corresponding molecular orbital diagram of ( <b>a</b> ) complex <b>5</b> , ( <b>b</b> ) complex <b>6</b> , and ( <b>c</b> ) complex <b>7</b> , respectively. The contour value used to generate the plots are 0.03 a.u.	92 93
8.1	Schematic diagram of metal-insulator-metal type sandwich device where the active material is sandwiched between Aluminium and ITO.	98
8.2	(a) <sup>1</sup> H NMR, (b) <sup>13</sup> C NMR, and (c) <sup>119</sup> Sn NMR of complex 8 recorded in CDCl <sub>3</sub> .	99
8.3	(a) FTIR spectrum, (b) TGA (under N <sub>2</sub> atmosphere) and (c) ESI-MS spectrum, and (d) CHN analysis of complex 8.	99
8.4	<ul> <li>(a) Molecular structure of complex 8. H atoms of 2-phenylazophenyl are omitted for clarity.</li> <li>(b) Skeletal core of 8. Four o-capped clusters are labeled as OCC1, OCC2, OCC3 and OCC4. Bond distance (Å) and bond angle (°) parameters; Sn1-O3, 2.0990(7) Å; Sn1-O22, 2.0719(8) Å; Sn12-O26, 2.0630(8) Å; Sn2-O4, 2.0545(8) Å; Sn3-O8, 2.0637(8) Å; Sn11-O23, 2.0488(9) Å; Sn7-O15-Sn8, 98.594(3)°; Sn2-O7-Sn4, 137.077(4)°; Sn12-O24-Sn10, 135.367(4)°; Sn2-O4-Sn3, 137.793(4)°. (c) Coordination environment of Sn center.</li> </ul>	101
8.5	Two-dimensional supramolecular architecture assembled from $\pi$ $\pi$ , CH $\pi$ and CHN interactions. H atoms are omitted for clarity. Metric parameters are as follows; $\pi$ $\pi$ , 3.732 (3) Å; H99 $\pi$ , 3.093 (2) Å; H100 $\pi$ , 3.850 (3) Å; H39 $\pi$ , 3.057 (2) Å; H40 $\pi$ , 3.671 (3) Å; H128N4, 3.270 (9) Å; H83N12, 3.546 (1) Å; H21N22, 3.769 (8) Å; H20N22, 3.071 (9) Å; H82N12, 3.060 (1) Å.	102
8.6	(a) I-V characteristics of the device, the red arrows show the current direction with applied voltage iteration. The 1 <sup>st</sup> , 50 <sup>th</sup> , 100 <sup>th</sup> , and 200 <sup>th</sup> voltage sweeps have been conducted and shown by different colored spheres. (b) The retention of the device at the write and erase state. (c) Set-read-reset-read cycle of the devices indicating two different states after write and erase.	103
8.7	(a) AFM image of the deposited thin film using spin coating. (b) line scanning data and (c) line histogram of the AFM image.	103
9.1	(a) <sup>1</sup> H NMR, (b) <sup>13</sup> C NMR, and (c) <sup>119</sup> Sn NMR of complex <b>9</b> recorded in CDCl <sub>3</sub> .	110
9.2	(a) <sup>1</sup> H NMR, (b) <sup>13</sup> C NMR, and (c) <sup>119</sup> Sn NMR of complex 10 recorded in CDCl <sub>3</sub> .	110
9.3	(a) <sup>1</sup> H NMR, (b) <sup>13</sup> C NMR, and (c) <sup>119</sup> Sn NMR of complex 11 recorded in CDCl <sub>3</sub> .	111
9.4	(a) UV-Vis spectrum (conc. 10 <sup>5</sup> M in DCM), (b) FTIR spectrum, (b) TGA (under N <sub>2</sub> atmosphere) and (c) ESI-MS spectrum of complex 9.	111
9.5	(a) UV-Vis spectrum (conc. 10 <sup>5</sup> M in DCM), (b) FTIR spectrum, (b) TGA (under N <sub>2</sub> atmosphere) and (c) ESI-MS spectrum of complex 10.	112
9.6	(a) UV-Vis spectrum (conc. 10 <sup>-5</sup> M in DCM), (b) FTIR spectrum, (b) TGA (under N₂ atmosphere) and (c) ESI-MS spectrum of complex 11.	112
9.7	(a) Molecular structure of complex 9. Bond distance (A) and bond angle (°) parameters: Sn1- O1, 1.9635(4); Sn2-O1, 1.9617(4); Sn2-Cl2, 2.4145(2); Sn1-O1-Sn2, 137.361(2)°; (b) coordination environment of Sn in 9; Sn1-N2, 2.5223(5); Sn1-N4, 2.7509(4); Sn1-C1, 2.1423(4); Sn1-C13, 2.1310(5); Sn1-Cl1, 2.4229(2); Cl1-Sn1-N2, 162.92(1)°, N2-Sn1-N4, 74.699(1)°; Cl1-Sn1-C1, 96.37(1)°; N2-Sn1-O1, 95.022(1)°.	113
9.8	(a) Molecular structure of complex <b>10</b> . Bond distance (Å) and bond angle (°) parameters: Sn1-O1, 2.1702(27); Sn1-O2, 2.3016(27); Sn1-Cl1, 2.4740(22); O1-Sn1-O2, 67.968(87)°; (b) Coordination environment of Sn in <b>10</b> ; Sn1-N4, 2.6316(31); Sn1-N6, 2.5734(30); Sn1-C13, 2.1310(5); Sn1-C19, 2.1149(35); Sn1-C7, 2.1194(29); C19-Sn1-O2, 89.587(104)°, Cl1-Sn-O1, 747.770(68)°; Cl1-Sn1-C7, 95.042(77)°; N6-Sn1-N4, 68.277(80)°; N6-Sn1-C19, 70.192(108)°.	114
9.9	(a) Molecular structure of complex 11. Bond distance (Å) and bond angle (°) parameters: Sn1-O1, 1.9406(3); Sn1-O1', 1.9867(3); Sn1-O1-Sn1''', 129.396(1)°; O1-Sn1-O1', 104.482(1)°; H atoms are omitted for clarity. (b) $Sn_4O_4$ core structure with a plane passing through all atoms; (c) coordination environment of Sn in 11; Sn1-C1, 2.1328(5); Sn1-C13, 2.1321(5); Sn1-N4, 2.6678(4); N4-Sn1-O1', 162.673(1)°, N4-Sn1-O1, 87.571(1)°; N4-Sn1-C1, 86.794(1)°; N4-Sn1-C13, 66.952 (1)°; C1-Sn1-C13, 129.258(2)°.	114
9.10	Hirshfeld surfaces generated using d <sub>norm</sub> over the color range of -0.200Å (red) to +1.000Å (blue) (a), (b) for complex 9; (c), (d) for complex 10; (e), (f) for complex 11.	115
9.11	2D fingerprint plots of de vs d ranging from 1.0 to 2.8 Å indicating different intermolecular	116

interactions for (a) complex 9, (b) complex 10, (c) complex 11.
9.12 Representation of some intermolecular interactions in the supramolecular assembly of (a) 117 complex 9, (b) complex 10, and (c) complex 11.

- 9.13 **(a)** One-dimensional supramolecular assembly of **9** formed by C-H... $\pi$ , N...H, and Cl...H 118 interactions. Metric parameters are as follows;  $\pi$ -H11, 3.4963(1) Å; N7-H21, 3.3316(4) Å; Cl2-H3, 2.9810(2) Å; **(b)** Two-dimensional supramolecular architecture of **9** formed by CH... $\pi$ , Cl...H interactions. H atoms are omitted to clarify the interactions. Metric parameters are as follows;  $\pi$ -H39, 3.0996(2) Å; Cl1-H10, 2.6799(2) Å; Cl2-H3, 2.9810(2) Å; Cl1-H34, 2.9021(2) Å; Cl2-H40, 3.5116(2) Å.
- 9.14 **(a)** One-dimensional supramolecular assembly of **10** formed by C-H... $\pi$ , N...H, and Cl...H 118 interactions. Metric parameters are as follows;  $\pi$ -H23, 3.3706(19) Å; N1-H22, 3.36368(35) Å; Cl1-H16, 3.6916(33) Å; N2-H22, 3.4101(38) Å; **(b)** Two-dimensional supramolecular architecture of **10** formed by CH... $\pi$ , O...H, N...H, Cl...H interactions. H atoms are omitted to clarify the interactions. Metric parameters are as follows;  $\pi$ -H21, 3.9157(27) Å;  $\pi$ -H27, 2.9692(19) Å;  $\pi$ -H28, 3.9028(33) Å; Cl1-H22, 3.7584(32) Å; Cl1-H21, 3.0405(19) Å; N1-H28A, 3.1813(32) Å; O1-H22, 3.2306(33) Å.
- 9.15 **(a)** One-dimensional supramolecular assembly of **11** formed by C-H... $\pi$ , N...H, and O...H 118 interactions. Metric parameters are as follows;  $\pi$ -H45, 3.6709(15) Å;  $\pi$ -H59, 3.7268(18) Å; N5-H59, 3.5298(61) Å; O5-H58, 2.6753(46) Å; **(b)** Two-dimensional supramolecular architecture of **11** formed by  $\pi$ -H, N...H, O...H, interactions. H atoms are omitted to clarify the interactions. Metric parameters are as follows;  $\pi$ -H59, 3.7268(18) Å; N7A-H65, 3.6292(131) Å; N7A-H46, 3.626 Å; O6-H58, 3.5987Å.
- 9.16 (a)-(c) Calculated Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied 120 Molecular Orbitals (LUMO) using density functional theory for complexes 9, 10, and 11, respectively.
- 9.17 Comparative study of UV-vis absorption spectra and corresponding orbital transition of 120 complex **9**. The black line shows theoretical analysis, and the red line shows experimental absorption spectra.
- 9.18 Comparative study of UV-vis absorption spectra and corresponding orbital transition of 121 complex **10**. The black line shows theoretical analysis, and the red line shows experimental absorption spectra.
- 9.19 Comparative study of UV-vis absorption spectra and corresponding orbital transition of 121 complex 11. The black line shows theoretical analysis, and the red line shows experimental absorption spectra.

# List of Tables

Table	Title	page
3.1	Crystal data and structure refinement parameters for complex 1.	29
4.1	Crystal data and structure refinement parameters for complex 2.	41
4.2	The comparative structural parameters of X-ray crystal structure and their DFT-computed structure of complex <b>2</b> .	45
4.3	Coordinates of the optimized structure.	45
4.4	The metal (Sn and Cu) coordinated bond lengths and their corresponding Wiberg bond index (WBI).	48
4.5	The Natural population analysis (NPA) charges on metals and coordinated atoms.	49
4.6	The second-order perturbation analysis of donor (i) and accepter (j) orbital with their stabilization energies (5.) (in least	50
. –	Stabilization energies (E <sub>2</sub> ) (in Kcai/mol).	
4.7	i ne important bond critical points (BCPS) for complex 2.	51
5.1	Crystal data and structure refinement parameters for complex 3.	54
5.2	B3LYP-computed bond lengths and their corresponding Wiberg bond index (WBI) around Sn1 center.	60
5.3	The Natural population analysis (NPA) charges on metals and coordinated atoms.	60
5.4	The second-order perturbation analysis of donor (i) and accepter (j) orbital with their stabilization energies $(E_2)$ (in kcal/mol).	61
5.5	Inhibition zone of the complex <b>3</b> and the antibiotic agents.	63
6.1	Crystal data and structure refinement parameters for complex 4.	66
7.1	Crystal data and structure refinement parameters for <b>5-7</b> .	79
7.2	Inhibition zone of the complexes 5-7 and the antibiotic agents.	91
8.1	Crystal data and structure refinement parameters for complex 8.	97
9.1	Crystal data and structure refinement parameters for complexes 9-11.	108

Symbol	Description
μ	Bridging
λ	Wavelength
К	Карра
δ	Chemical shift
V	Volume
0	Degree
%	Percentage
d	Interplanar distance
θ	Theta
η	Isobidentate bridging
ν	Frequency
A	Absorbance
lo	Intensity of incident light
I	Intensity of transmitted light
I	Path length
E	Molar extinction coefficient
c	Concentration
S	Second
h	Hour
τ	Addison's parameter
π	Pi
σ	Sigma
Å	Angstrom
I	Current
mV	Millivolt
mA	Miliampere
eV	Electron volt
1D	One-dimensional
2D	Two-dimensional

# List of Abbreviations

Abbreviation	Full form
PVC	Polyvinyl Chloride
DNA	Deoxyribonucleic Acid
Fc	Ferrocene
NHC	N Heterocyclic Carbene
DD	Double-Decker
AD	Adamantane
TMEDA	Tetramethylethylenediamine
DTC	Dithiocarbamate
NLO	Non-linear optics
EFISH	Electric Field-Induced Second-Harmonic
EUVL	Extreme ultraviolet lithography
ITO	Indium Tin Oxide
MIM	Metal-insulator-metal
CVD	Chemical Vapor Diffusion
AACVD	Aerosol-Assisted Chemical Vapor Diffusion
PMMA	Poly(methyl methacrylate)
SC-XRD	Single-Crystal X-ray Diffraction
FTIR	Fourier Transform Infra-red
NMR	Nuclear Magnetic Resonance
UV	Ultra Violet
ESI-MS	Electron Spray Ionization Mass Spectrometry
TGA	Thermogravimetric Analysis
AFM	Atomic Force Microscopy
DCM	Dichloromethane
THF	Tetrahydrofuran
OLED	Organic light emitting diode
OFET	Organic field emitting transistor
CIF	Crystallographic information file
TD-DFT	Time-dependent density functional theory
DFT	Density functional theory
НОМО	Highly occupied molecular orbital
LUMO	Lowest Unoccupied molecular orbital
SOMO	Singly occupied molecular orbital
HRS	High resistive state
LRS	Low resistive state
RAM	Random-access memory
NDR	Negative differential resistance
SCLC	Space charge limited conduction
СРСМ	Conductor-like Polarizable Calculation Model
NBO	Natural bonding orbital
AIM	Atom in molecules
NPA	Natural population analysis
ESP	Electrostatic Surface Potential
WBI	Wiberg bond index
ТВР	Tetragonal Bipyramidal
Td	Tetrahedral
Oh	Octahedral
ТР	Trigonal planer
PBP	Pentagonal Bipyramidal
LP	Lone pair
BCP	Bond critical points
ZOI	Zone of inhibition
DI	De-ionized
OCC	O-capped cluster