CHAPTER-5

FORMULATION OF BODIPY-SI-BASED MOLECULAR ELECTRONICS DEVICES
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5.1. Preamble

Silicon microelectronics, playing a dominant role in almost every sphere of our life, viz. automobiles, home appliances, telecommunications, medical and scientific equipments etc, has undergone relentless miniaturization during the last few decades. This has increased the speed and memory of computational devices. Now it is being anticipated that due to several physical as well as economic factors, the Si technology will face the scaling limits in very near future. Factors such as (i) unacceptable power dissipation, (ii) change in the Si band structure, (iii) difficulty in uniform doping of Si, (iv) limitation of lithographic techniques, and (v) exponential increase in financial investment would restrict attaining the sizes of the transistors to \( \leq 20 \) nm.

This has given birth to the concept of information processing at the molecular-scale (molecular electronics) as a promising alternative for the nano-electronics of the future. It is viewed as a technology wherein integrated circuitry (IC) will be constructed from component molecules acting as capacitors, resistors, logic gateways, memory registers, etc., joined by molecular wires. In molecular electronic devices, organic molecules are sandwiched between conducting electrodes. Supramolecular assembly of organic molecules on solid substrates is a powerful 'bottom-up' approach for the fabrication of devices for molecular-scale electronics. This is generally achieved by forming Langmuir-Blodgett (LB) films, or self-assembly of monolayers of organic molecules on solid substrates (SAM) via metal/molecules/metal (MMM) junction. However, chemically-grafted organic molecules on semiconductors like Si is most promising for this purpose because the surface potential of Si can be easily tailored to develop improved hybrid molecular devices. The p-n junction threshold voltage for rectification can be adjusted by changing the electronic nature of the organic \( \pi \) group molecules, instead of the classical method of doping.
**Si-hybrid nanoelectronics.** In the third approach, termed as Si-hybrid nanoelectronics, organic molecules exhibiting various functionalities, such as, dielectric, diode, memory and transistor are deposited to Si, so that the nanoscale electronic functionality of molecules can be utilized in Si-based microelectronics. The advantage of the molecule-on-Si hybrid concept is that the inputs available from an already existing powerful Si-based IC industry can be effectively used for the development of integrated hybrid devices. Thus, nonlinear charge transport in functional molecules grafted to Si has become a fundamental area of research in the development of various components for hybrid nanoelectronics e. g. molecular diodes, resonant tunnel diodes, memory devices, transistors etc.\(^\text{120}\)

**Organic molecules in molecular electronics.** Organic molecules are made up of mainly covalent bonds which are formed either by linear (σ bonds) or lateral overlap (π bonds) of the atomic orbitals. Electrons in σ bonds lie between two nuclei and are highly localized, whereas the electron density in π bonds is delocalized. In terms of molecular orbital theory, when two atomic orbitals overlap they form one bonding orbital (lower in energy than that of atomic orbitals) and one antibonding orbital (higher in energy than that of atomic orbitals). These molecular orbitals (MO’s) are filled up by Pauli’s exclusion principle. The energy difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is related to the band gap of the molecule. The HOMO-LUMO gap for the σ bonds is ~8 eV, whereas for the conjugated molecules this gap is in reduced to 2-5 eV. Therefore, under applied electric field, σ bonded molecules are expected to exhibit no charge transport, and may act as dielectrics in hybrid nanoelectronics. On the other hand, presence of extended electronic wave functions in the conjugated (π bonded) molecules is suitable as semiconducting channels in the hybrid devices. In these devices, highly doped Si (resistivity < 0.001 Ωcm) is used as substrate for organic
monolayer deposition so that it also acts as an electrode. The counter electrodes can be formed using techniques such as liquid Hg-drop, thermally evaporated Au/Al pads, CP-AFM/STM tip or carbon nanotubes. Using this type of assemblies, various devices such as, a) molecular dielectrics using alkyl-chains,\textsuperscript{123a} b) molecular diodes using \(\sigma-\pi\) molecules,\textsuperscript{123b} c) resonant tunnel diode or RTD using \(\sigma-\pi-\sigma\) molecules\textsuperscript{123c} etc. have been constructed. Here, the alkyl-chains of different lengths, and conjugated molecules were used as \(\sigma\) and \(\pi\) components respectively.

It is well-established that covalent attachment of the organic molecules onto Si-surfaces produces reproducible and robust hybrid nanoelectronics, suitable for device applications. Previously, \(\sigma-\pi\) systems grafted on Si through an alkyl spacer (\(\sigma\)) have shown current rectification behavior.\textsuperscript{124} The rectification property has been attributed to a resonant transport between the Si conduction band (CB) and the HOMO of the \(\pi\) group. The Fermi level pinning at the metal/\(\pi\)-group interface plays a key role in the electrical behavior of these molecular rectifying junctions. Molecules, showing rectification behaviour with high rectification ratio (RR) is very useful for making diodes.

The negative differential resistance (NDR) behaviour (\textit{i.e.}, an initial rise in current and its subsequent sharp drop even with progressively augmented voltage, as opposed to Ohm’s law) with high peak to valley ratio (PVR) has drawn significant attention because of its potential application in realization of logic devices and memory circuits,\textsuperscript{125a-c} and is found in a variety of molecular devices.\textsuperscript{125} The NDR behavior should be accompanied by hysteresis although in many cases it is observed without hysteresis.\textsuperscript{126} Several mechanisms such as charge transfer-induced change of the charge state, and chemical/conformational changes under finite bias have been proposed to explain NDR phenomenon.\textsuperscript{127} Recent theoretical studies showed that the origin of
NDR with hysteresis is associated with the polarization response, i.e., combined effects of charging and conformational change.

### 5.2. Concept of Si-BODIPY Devices

In principle, organic molecules with suitable redox properties such as high band gaps and ionization energies, and matching HOMO/LUMOs with the Fermi level of the electrodes are suitable for molecular electronics applications. To this end, a large number of electron-rich organic molecules such as the polyaromatic hydrocarbons, porphyrinoids etc. have been extensively used to construct Si-hybrid nanoelectronics. Rectification effect of several organic n-type molecules deposited on Si has been demonstrated previously. Nevertheless, developing devices that are environmentally stable, and show high-mobility and easy processability remains a specific challenge in this area. In particular, the performance and stability of organic n-type materials have significantly lagged behind their p-type counterparts.

The Bodipy class of compounds has rich redox chemistry with excellent reversibility both during oxidation and reduction. As discussed in section 1.5.2., the redox chemistry of the Bodipy derivatives depends on the type of substitution in the dipyrromethene core. When the dyes are completely substituted with alkyl or other groups, the radical ions are highly stable. But in absence of any substitutions, especially at the 2-, 6-, and meso-positions, highly reactive radical ions are generated, which can undergo dimerization or other reactions. The properties can be tuned by varying different substituents on the dye chromophore. Till so far, the Bodipy compounds have been used extensively for various photo-voltaic applications such as OLEDs, solar cell etc. The reversible redox property of Bodipy dyes, their robustness under ambient conditions and chemical tenability is very attractive for their use in molecular electronics which still remains unprecedented. Presently, the rectification property of some tailor-made Si-grafted
Bodipy monolayers, and their tuning to elicit NDR response by forming bi-layers with another Bodipy molecule is presented, and the electronic behaviors explained by theoretical calculations. These are sequentially presented below.

5.2.1. Molecular design

Given the importance of molecular bridges in nano-devices, design of the organic molecule is crucial in attaining the present objectives. The molecular design was conceived keeping in mind that the energy gap ($\Delta E$) between the energy states (LUMO/HOMO) of the molecular bridges and the Fermi levels of the donor and acceptor units control the electron-transfer rate and current flow. For constructing devices for current rectification, the required $\sigma$–$\pi$ systems were synthesized using the $O$-alkenylated analogs of the Bodipy 70. It was envisaged that the $\pi$–moiety (Bodipy core) and the $\sigma$–moieties (alkyl chains) will acts as a quantum well and the tunnel barriers respectively. For the $\sigma$–moieties, a C$_5$- and a C$_{11}$-alkenyl chains were chosen, because that would assist in subsequent fabrication of their monolayers on the highly-doped Si (111)-surface due to enhanced solubility and increased spacer lengths. Further, the alkenyl group can be used for electro-grafting the monolayers on Si surface.

Previous theoretical studies predicted that the molecules having redox properties and bias-induced conformational changes are potential candidates for NDR effect with hysteresis. However, it is difficult to change the conformation of a molecule that is chemically bonded, using a bias. But it will be easier in case of a bi-layer formed by physical interaction. Hence, such a bi-layer strategy was explored for making NDR devices which is currently lacking in literature.

5.2.2. Synthesis
The commercially available aldehyde 68 was subjected to a base-catalyzed alkylation of with 1-bromohexane and 1-bromoundec-10-ene to furnish the aldehydes 82a and 82b respectively. The aldehydes were individually subjected to a TFA-catalyzed condensation with kryptopyrrole (58), and the resultant dipyrrromethanes were subjected to oxidation with DDQ, followed by complexation with BF₃ in the presence of Et₃N as the base (Scheme 5.2.2.1) to afford the compounds 83a and 83b respectively. These compounds are also designated as BODIPY-C5 and BODIPY-C11, and characterized by the ¹H and ¹³C NMR spectra (Figure 5.2.2.1 and Figure 5.2.2.2). The major differences in the spectra of these compounds were the additional ¹H NMR singlet at δ 1.32 (12H) and the up-field ¹³C NMR resonances for the longer chain alkyl moiety of 83b.

Scheme 5.2.2.1 Syntheses of the Bodipys 83a and 83b.
Figure 5.2.2.1 The NMR spectrum of 83a (a) $^1$H NMR, (b) $^{13}$C NMR.
Figure 5.2.2.2 The NMR spectrum of 83b (a) $^1$H NMR, (b) $^{13}$C NMR.
5.2.3. Preparation of the Si(n++)-Bodipys assemblies

Monolayers formation by electro-grafting. Physisorption of organic molecules as Pockels-Langmuir (PL) films or by vapor-phase deposition on electrodes is often used to fabricate hybrid organic electronic devices. However, ordering of PL films are usually achievable with amphiphilic molecules only, restricting the molecular design. On the other hand, the vapor-phase deposition method usually results in poor deposition yield, disordered packing and random orientations. Further, the physisorbed molecules often move to seek a lower energetic state on the surface, or in response to an applied electric field. Instead, covalent linking of organic molecules to metal/semiconductor surfaces provides a better alternative.\textsuperscript{132} Extensive work using Au electrodes revealed them to be thermally unstable.\textsuperscript{133a,b} On the other hand, grafting of alkyl silanes monolayers on SiO\textsubscript{2} surface involves multi-steps protocol requiring stringent reactions conditions (optimized temperature and anhydrous conditions), besides the need to synthesize many of the alkyl silanes separately.\textsuperscript{123b,133c} Instead, cathodic electrografting of organic molecules having a cleavable group that reacts with H-terminated Si offers the advantage assessing the deposition process by \textit{in situ} measuring the redox peak of the electrografting reaction. The known cleavable electroactive group includes vinyl (C=C), ethynyl (C≡C), halide (Cl, Br, I), tetraalkylammonium salt, diazonium salt and silane.\textsuperscript{133d} Hence, we followed electrografting for an easy attachment of the porphyrins on Si (111) surface through the strong Si-C bond (Si-C \textasciitilde76 kcal mol\textsuperscript{-1}).

Thus, the molecules \textbf{83a} and \textbf{83b} were separately electrografted to H-terminated Si(n++) surface through their respective terminal alkene groups.\textsuperscript{134} The electrografting mechanism (Figure 5.2.3.1) is based on formation of Si-radicals on application of negative potential, which reacts with C=C group of the molecules to form Si–C bond.\textsuperscript{133d} The electrochemical deposition
was carried by cyclic voltammetry (CV) using the Si-H wafers as the working electrode (WE), Pt as the counter electrode (CE) and Ag/AgCl as the reference electrode (RE).

![Diagram](image)

**Figure 5.2.3.1** Schematic of the electrografting process on Si via Si–C bond formation.

Typical CV scans recorded using 83a and 83b (Figure 5.2.3.2) revealed appearance of an irreversible oxidation peak at -0.25 V. As the number of scans increased, the peak diminished owing to the non-availability of nucleophilic Si atoms at the surface and, eventually vanishes for 50\textsuperscript{th} scan. This confirmed the completion of multilayers deposition (AFM image, *vide infra*). At higher scans, formation of multilayers was evident by AFM analysis (data not shown). The irreversible CV peak indicated an irreversible reaction (i.e. the cleavage of vinyl-group) is associated with the electron transfer. No peak at -0.25V appeared when the CV was run using the TBAP solution alone.
Figure 5.2.3.2 Cyclic voltammograms (CVs) indicating electrografting of Bodipy compounds on H-terminated Si(n++) substrates. (a) compound 83a; (b) compound 83b.

**Bilayers formation by self-assembly.** For the bi-layer formation, compound 21 was chosen with the presumption that the planar molecule may easily intercalate onto Si-grafted monolayers of 83a and 83b by the self-assembly. This 2nd layer was formed by dipping the mono-layered Si wafers into a CH$_2$Cl$_2$ solution of 21 for 24 h. The film thickness did not increase by dipping the monolayers in the solution of 21 for several days, as well as increasing the concentration of 21. The bilayers are represented as 21:83a/Si(n++) and 21:83b/Si(n++) respectively.

Figure 5.2.3.3 Schematics of the bilayer formation process. Step 1: Electrografting of monolayers of 83a or 83b on H-Si(n++); Step 2: Intercalation of 21 into the monolayers.
5.2.4. Characterization of modified surfaces

The mono and bilayers were characterized by several techniques, such as, electrochemical characterization, contact angle measurements, ellipsometry, secondary ion mass-spectrometry (SIMS), atomic force microscopy (AFM) and X-ray reflectivity (XRR). Amongst these, SIMS is used for chemical analysis as well as for identifying the alignment of the molecules on the Si substrate. The thickness of the organic layers can be determined using ellipsometry, XRR, and SIMS depth profile. Contact angle measurements provide information on the surface groups of the grafted organic layer. The ordering of the monolayer can be also be assessed by imaging the surface morphology using AFM.

Electrochemical characterization. The fast scan (100V/s) CVs were recorded for 83a/Si(n++) and bilayer 21:83a/Si(n++) as the WE (surface area = 0.25 cm²) and 0.1 M TBAP as electrolyte with a Pt counter-electrode and an Ag/AgCl reference electrode (Figure 5.2.4.1.a). For the monolayer, a single peak was observed at 0.77 V. The bilayer CV showed two closely spaced oxidation peaks at 0.73 V and 0.83 V, indicating that the bilayer undergoes a double oxidation. Similarly for the monolayer of 83b/Si(n++) a single peak at 0.89 V was observed in the CV. But, in this case, even the bilayer CV showed only a single flattened peak at 0.94V, which may be due of two closed and unresolvable peaks.

The molecular densities of the monolayers and bilayers, determined by fast scan (10 V/s) CVs are shown in Figure 5.2.4.1. The net charge transferred during the oxidation process, calculated from the area under the oxidation peak were 7.92 × 10⁻⁷ C and 1.83 × 10⁻⁶ C respectively for 83a and 83b. These amounted to surface coverages of 4.12 × 10¹¹ and 1.69 × 10¹² molecules /cm² respectively for 83a and 83b. The surface coverages increased to 8.43 × 10¹¹ and 3.16 × 10¹² molecules /cm² respectively for the bilayers 21:83a/Si(n++) and
21:83a/Si(n\textsuperscript{++}) respectively. Thus, the mono- and bilayers of 83b were more compact with more (~ 4 times) surface coverage, compared to that of 83a. So, the numbers of BODIPY molecules almost get doubled after self-assembly, implying the 1:1 interaction between compound 21 and compound 83a/83b.\textsuperscript{136}

![Figure 5.2.4.1](image)

**Figure 5.2.4.1** Typical fast scan CVs (scan rate 100V/s) of the mono- and bilayers. (a) 83a/Si(n\textsuperscript{++}) and 21:83a/Si(n\textsuperscript{++}); (b) 83b/Si(n\textsuperscript{++}) and 21:83b/Si(n\textsuperscript{++}); (c) CV of compounds 83a and 83b recorded in CH\textsubscript{2}Cl\textsubscript{2} at 25 °C using 0.1 M Bu\textsubscript{4}NClO\textsubscript{4} (TBAP) as the supporting electrolyte and ferrocene (Fc) as internal reference at +0.38V.

**Contact angle measurements.** The contact angle measurement is a valuable tool to investigate the surface polarity and orientation of the attached molecules at a surface.\textsuperscript{137a} The contact angles of deionized water in case of Si wafers, grafted with 83a and 83b were 52.7° and 53.7° respectively, and on bilayer formation these increased to 56.0° and 60.7° respectively, whereas for the cleaned, ungrafted Si wafer it was 84°. Thus, in both the cases, the bilayers were more hydrophobic compared to their respective monolayers. However, the observed contact angles were much less than the reported values (97-108) of the methyl terminated alkyl chains.\textsuperscript{124b,137b,c} This suggested interaction of the water molecule with the Bodipys, possibly through their pyrrole rings, which is possible only when the molecules are tilted.
To understand the orientation of molecule 21 in the bilayers, the Owens and Wendt method was used to determine the total surface energy and its resolution into polar and dispersive components, wherein the total solid surface tension $\gamma$ was assumed to be of the general form as shown in equation (1)

$$l + \cos\theta = 2\sqrt{\gamma_s^d} (\sqrt{\gamma_l^d / \gamma_l^p}) + 2\sqrt{\gamma_s^p} (\sqrt{\gamma_l^p / \gamma_l^d})$$

(1)

In this equation, the subscripts, $s$ and $l$ refer to the solid and liquid surface tension respectively; the superscripts, $d$ and $p$ coincide with dispersive and polar components of total surface tension, where sum of these two values are equal to the total surface tension. In order to resolve the $\sqrt{\gamma_s^d}$ and $\sqrt{\gamma_s^p}$, the contact angles were measured independently using two different liquids (water and diiodomethane) whose surface tension components are known (Table 5.2.4.1). All samples showed high surface energies with no significant difference in the dispersive components (Table 5.2.4.2). However, compared to the monolayers of compounds 83a and 83b, their respective bilayers showed a decrease in the polar components, indicating their hydrophobicity. These results clearly indicated that the fluorine atoms of the Bodipys are less exposed to the space.

Table 5.2.4.1: The surface tension components of H$_2$O and CH$_2$I$_2$ at 20 °C

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\gamma_l$</th>
<th>$\gamma_l^d$</th>
<th>$\gamma_l^p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>68.9</td>
<td>18.6</td>
<td>50.3</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>49.7</td>
<td>48.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Table 5.2.4.2: Surface energy of modified Si surfaces

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface energy (mJ/m²)</th>
<th>Total Energy</th>
<th>Polar component</th>
<th>Dispersive component</th>
</tr>
</thead>
<tbody>
<tr>
<td>BODIPY –C5 Monolayer</td>
<td>55.1</td>
<td>15.7</td>
<td>39.4</td>
<td></td>
</tr>
<tr>
<td>BODIPY –C5 Bilayer</td>
<td>53.9</td>
<td>14.7</td>
<td>39.2</td>
<td></td>
</tr>
<tr>
<td>BODIPY –C11 Monolayer</td>
<td>56.1</td>
<td>15.1</td>
<td>41.0</td>
<td></td>
</tr>
<tr>
<td>BODIPY –C11 Bilayer</td>
<td>52.7</td>
<td>13.3</td>
<td>39.4</td>
<td></td>
</tr>
</tbody>
</table>

**Atomic force microscopy (AFM) and ellipsometry.** The AFM images (Figure 5.2.4.2) revealed that each of the mono- and bi-layers had granular surface morphology with an average grain size of 8 and 14 nm, respectively. The AFM analyses revealed that the mono- and bilayers of 83b were more organized, compact and uniform with lesser number of voids and hillocks than those 83a. The numbers of voids were less in the bilayers compared to the respective monolayers.

Measurement of the layer thicknesses is essential to determine if it is a monolayer or a multilayer. For a monolayer, its orientation on the surface can also be determined by comparing the experimental results and the theoretical lengths of the molecules. Amongst the methods, used for measuring the thicknesses of Si-grafted layers, presently ellipsometry and XRR technique were used. The ellipsometry data revealed the average thicknesses of respective monolayers as ~ 1.3 ± 0.2 nm in case of 83a and 2.2 ± 0.2 nm with 83b, while the corresponding theoretically calculated (using Molkel software) values were 1.3 nm and 2.25 nm. The thicknesses of the bilayers from 83a and 83b were 2.1±0.2 nm (theoretical: 2.0 nm), and 3.1±0.2 nm (theoretical: 2.95 nm) respectively. The thickness values, determined by ellipsometry also revealed doubling of the BODIPY molecules in almost 1:1 ratio after self-assembly in the bilayers, which is in
accord with the fast scan CV results. These data are also consistent with the AFM analyses, both revealing more compact monolayers with \(83b\) than \(83a\).

**Figure 5.2.4.2** The non-contact atomic force microscope images recorded for (a) \(83a/\text{Si}(n^{++})\) monolayer; (b) \(21:83a/\text{Si}(n^{++})\) bilayer; (c) \(83b/\text{Si}(n^{++})\) monolayer; (d) \(21:83b/\text{Si}(n^{++})\) bilayer, respectively.

**XRR analyses.** XRR is a non-destructive and non-contact technique for determination of thickness between 2-200 nm with a precision of about 1-3 Å. In addition, this technique is also employed to determine the density and roughness of films and multilayers. X-rays have a refractive index in solids which is fractionally smaller than unity, so if one approaches a surface at a sufficient grazing angle, total external reflection can be achieved below some critical angle (few tenths of a degree). For an angle of incidence greater than critical angle, the beam penetrates the film and interference between X-ray amplitudes reflected from surface and interfaces of a layered sample gives rise to a complex reflectivity pattern. This principle is
effectively utilized in the sensitive XRR technique wherein detailed analysis of this XRR data yields information about electron density profile as a function of depth, layer thickness and surface/interface roughness, regardless of the amorphous or crystalline nature of the sample.

The experimental data are fitted with a theoretical model of depth-dependent scattering length density (SLD), \( \rho \) that gives information about the composition and density gradient in a layered structure. Thus, the depth profile of electron SLD from XRR data (\( \rho^x \)) can be obtained. Scattering length densities in XRR are related to the atomic number densities in a system. The SLD values of different layers are calculated from the following equation (2):

\[
\rho^x(z) = r_e \sum_i N_i(z)(Z_i + f_i')
\]

where \( \rho^x(z) \) is the depth \( (z) \) dependent scattering length density (in units of \( \text{Å}^{-2} \)) for x-rays. \( Z_i \) and \( f_i' \) are the charge number and real anomalous dispersion factor respectively of the \( i^{\text{th}} \) element, \( r_e = 2.818 \text{ fm} \) is the classical electron radius and \( N_i \) are the corresponding depth-dependent number densities per unit volume of the components. The accuracy with which these parameters can be determined is typically of the order of a few nm or better, making it very useful for the study of ultrathin organic layers.\(^{138}\)

Since compound 83a with a small alkyl chain of less electron density formed less compact organic layers, we focused only on the monolayer 83b/Si(n\(^{+\text{+}}\)) and the bilayer 21:83b/Si(n\(^{+\text{+}}\)), and confirmed the films thicknesses using X-ray reflectivity (XRR) technique in specular mode. A specular geometry reflectivity measurement as a function of the incident angle provided a number of information \( \text{viz.} \) refractive index depth profiles, electron/mass density profiles along the normal axis direction, total and/or individual layer thicknesses, and interface roughnesses. Suitable model fitting of the reflectivity profiles confirmed formation of BODIPY-C11 monolayers and bilayers at the Si substrate (Figure 5.2.4.3). For the bilayer 21:83b/Si(n\(^{+\text{+}}\)),
the XRR data were modeled as arising from two layers of organic material, deposited on Si base. From the plot of SLD vs interface distance, the thicknesses for monolayer and bilayer were calculated as 2.40 ± 0.02 nm and 3.1 ± 0.02 nm respectively. The roughness values for the monolayer were higher than that of the bilayer of (BODIPY-C11).

![XRR plots](image)

**Figure 5.2.4.3** XRR plots of the BODIPY-C11 systems (a) 83b/Si(n++) monolayer; (b) 21:83b/Si(n++) bilayer. (inset: SLD plots).

**Secondary ion mass-spectrometry (SIMS).**

SIMS is most sensitive of all the commonly-employed surface analytical techniques, as it can detect impurities on a surface layer at < 1 ppm concentration, and in bulk at ~1 ppb concentrations, in favorable cases. In SIMS the surface of the sample is subjected to bombardment by high energy ions, ejecting (or sputtering) of both neutral and charged (+/-) species including atoms, clusters of atoms and molecular fragments from the surface. The ions are extracted from the sample region, and subjected to energy-filtering before they are mass analyzed by a quadruple or more often by a time-of-flight (TOF) mass analyzer, the latter providing substantially higher sensitivity and mass resolution, and a much greater mass range (albeit at a higher cost). In general, TOF analyzers are preferred for static SIMS, whilst
quadruple and magnetic sector analyzers are preferred for dynamic SIMS. Presently, the SIMS data of the monolayer of \textit{83a} showed peaks at m/z 325, 281 and 191 amu due to the Bodipy fragments (Figure 5.2.4.4a). Similar results were obtained with the \textit{83b} monolayer (data not shown). The SIMS data of the bilayer \textit{21:83b}/Si(n\textsuperscript{++}) showed an additional mass peak at m/z 317 amu, accounting for the [M-1]\textsuperscript{+} peak for compound \textit{21} along with the peaks due to the Bodipy fragments (Figure 5.2.4.4b). The SIMS data of the \textit{21:83a}/Si(n\textsuperscript{++}) were also similar (data not shown). Nevertheless, the SIMS data confirmed deposition of their respective layers on the Si wafers.

\textbf{Figure 5.2.4.4} TOF-SIMS of positive secondary ions desorbed from monolayer and bilayer by mono-isotopic \textit{\textsuperscript{69}Ga} projectile. (a) \textit{83a}/Si(n\textsuperscript{++}) monolayer; (b) \textit{21:83b}/Si(n\textsuperscript{++}) bilayer. (insets: enlarged plots.)

Since the SIMS mass fragmentation pattern did not provide much information about the orientation of the bilayers, the SIMS depth profile of the bilayer \textit{21:83b}/Si(n\textsuperscript{++}) was studied. The SIMS depth profile (Figure 5.2.4.5.a) revealed the thickness for the bilayer \textit{21:83b}/Si(n\textsuperscript{++}) as \textasciitilde3 nm, which was in good agreement with the XRR data. Further, the magnified SIMS data (Figure 5.2.4.5.b) of the monolayer \textit{83b}/Si(n\textsuperscript{++}) and the bilayer \textit{21:83b}/Si(n\textsuperscript{++}) showed fragmented
boron species B$_{10}$ and B$_{11}$ of the Bodipys, and as expected, the number of boron atoms in the bilayer was nearly double that of the mono-layer.

![Figure 5.2.4.5](image)

**Figure 5.2.4.5** (a) SIMS depth profile of bilayer of 83b, (b) SIMS spectra: B$_{10}$ and B$_{11}$ peaks for compound 83b.

### 5.2.5. J-V characteristics

To measure the J–V characteristics, a metal/molecule/Si (n++) structure was completed by using a tiny drop of liquid mercury of diameter ~500 µm as the counter electrode as illustrated in **Figure 5.2.5.1a/b (insets)**. The area in contact with the grafted monolayer was 0.018 mm$^2$. Typical current voltage (J-V) curves of undeposited Si (111) wafers are shown in **Figure 5.2.5.2a**. Compared to that, the J-V curves (**Figure 5.2.5.1a** and **5.2.5.1b** respectively) of the mono-layers 83a/Si(n++) and 83b/Si(n++) exhibited current rectification behavior in the forward bias, as per the hypothesis, proposed earlier in this chapter. The rectification ratio (RR) – defined as a ratio of current densities at ±1.5 V (in absolute value) (RR = | J$_{+1.5V}$ | / | J$_{1.5V}$ |) was found to be 37 for 83a/Si(n++) and 500 in case of 83b/Si(n++) monolayer. The RR values,
measured for 42 samples for the former varied in the range of 30-70, while for the latter the variation was 100-500. With 83a/Si(n++) , a larger number (20) of devices showed RR between 60-70. However, with 83a/Si(n++) , 15 out of 28 devices showed RR > 300 and 9 devices had RR between 100-300. The detailed statistics of the devices are presented in Table 5.2.5.1.

Table 5.2.5.1: Statistics of the current rectification by the monolayers

<table>
<thead>
<tr>
<th>Compound</th>
<th>No. of samples</th>
<th>No. of devices in each sample</th>
<th>Total no. of devices</th>
<th>No. of devices showing Rectification Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0-30</td>
</tr>
<tr>
<td>83a</td>
<td>6</td>
<td>7</td>
<td>42</td>
<td>6</td>
</tr>
<tr>
<td>83b</td>
<td>4</td>
<td>7</td>
<td>28</td>
<td>--</td>
</tr>
</tbody>
</table>

The significantly increased RR value increased for the 83b/Si(n++) monolayers may be due to their compact packing. Further, comparison of the results in Figures 5.2.5.1a-c revealed that the current rectification behavior is exclusively due to the Bodipy molecules. The J–Vs of these diodes also exhibited hysteresis, which could be due to formation of electric dipole under high applied electric field, as reported previously by others.139
Figure 5.2.5.1 Room temperature $J$-$V$ characteristic recorded for monolayers by scanning the bias in the sequence $-1.5 \, \text{V} \rightarrow 0 \, \text{V} \rightarrow +1.5 \, \text{V} \rightarrow 0 \, \text{V} \rightarrow -1.5 \, \text{V}$ at a scan speed of 5 mV/s. (a) undeposited Si surface; (b) compound 83a; (c) compound 83b. Insets: schematic of the device structures.

On the other hand, for a positive bias applied to the Hg-electrode, the bi-layers exhibited strong NDR effects concomitant with pronounced hysteresis(Figure 5.2.5.2a/b). The devise structure is schematically shown in Figure 5.2.5.2c. The PVR value measured, for 80 samples varied between 10 and 1000. The percentages of devices attaining the maximum PVR (1000) were 3.1 and 8.3 by the bilayers 21:83a/Si(n++) and 21:83b/Si(n++)respectively. Expectedly the devices made from the more compact 21:83b/Si(n++) bilayers showed better attributes such as (i) less failure (no NDR behaviour): 25% vs 31%; and (ii) PVR 1-10: 20.8% vs 27.7%; PVR 100-500: 12.5% vs 4.6%. The comparative PVR values are represented in the form of π-charts in Figure 5.2.5.3. It may be noted that NDR is obtained only in the first bias scan and in the subsequent scans NDR disappeared and the current remained low. However, if the electrodes are short-circuited, the neutral state is regained and hence the NDR effect reappears. Among the previous reported hybrid nanoelectronics with NDR property, only in one case the PVR as high as ours but the NDR effect was observed at low temperature (60 K). [126a-c]
Figure 5.2.5.2 Room temperature $J$-$V$ characteristics for the bilayers, recorded by scanning the bias in the sequence $-1.8 \text{ V} \rightarrow 0 \text{ V} \rightarrow +1.8 \text{ V} \rightarrow 0 \text{ V} \rightarrow -1.8 \text{ V}$ at a scan speed was 5 mV/s. (a) 21:83a/Si(n$^+$); (b) 21:83b/Si(n$^+$); (c) schematic of the devices employed for the measurements.

Figure 5.2.5.3 Comparative PVR values of NDR in bilayers (a) 21:83a/Si(n$^+$); (b) 21:83b/Si(n$^+$)

5.2.6. *Theoretical explanation*

In order to gain an insight into the rectification and NDR behaviors of the respective mon- and bi-layers, the HOMO and LUMO energies of BODIPY-C5 (or 83a) and PM567:BODIPY-C5 (or 21:83a) molecules were calculated using MO theory, as implemented in GAMESS software.$^{140}$ The geometries and total energies of the molecules were optimized under the density functional theory using the linear combination of atomic orbital (LCAO) approach. A standard 6-31G+(d,p) basis set was employed for this purpose. The exchange correlation energy
was calculated using B3LYP functional, which consists of Hartree-Fock exchange, Becke’s exchange and Lee-Yang-Parr correlation functional.¹⁴¹ Consistent with experimental the CV data (Figure 5.2.4.1.a), the theoretical calculation also predicted a single oxidation state of 83a, and two oxidation states for the 21:83a bi-layer. The double oxidation by the bilayer is expected as it has two Bodipy layers. The theoretically calculated spatial orientation of HOMO’s of neutral 21:83a, and after its Iˢᵗ and IIⁿᵈ oxidations are shown in Figure 5.2.5.1.a).

The HOMO of the BODIPY-C5 (or 83a) lies on the Bodipy moiety in both neutral and oxidized state. Thus, the rectification behavior of the monolayer i.e., Hg/ 83a /Si(n⁺⁺) is due to the resonant tunneling through the HOMO of the Bodipy moiety (π group) of compound 83a.¹⁴¹ Due to the lack any major conformational Changes after its oxidation, no NDR was observed with the monolayer of 83a. In case of the bi-layer, the HOMO lies on both the Bodipy moieties in the neutral state. After the Iˢᵗ oxidation, it still remains on the Bodipy moieties, but with a slight conformational change. However, after IIⁿᵈ oxidation, there is a huge conformational change, because the HOMO largely shifts to the alkyl-chain. This could be attributed to slippage or rotation at Bodipy interface, which is likely as the bi-layer is formed by weak interaction.

The schematic energy level diagram of Hg/ 21:83a/Si(n⁺⁺), obtained using the theoretically estimated values of HOMO and LUMO energies is shown in Figure 5.2.6.1.b. For the neutral state, the theoretical calculations show doubly degenerate HOMO (-5.26, -5.27eV) and LUMO (-2.67, -2.01 eV) energy levels, indicating that the bi-layered Bodipys can undergo double oxidation. At zero bias i.e., V = 0, the degenerate HOMO and LUMO levels of 21:83a are off-resonance with the Fermi level of the Hg electrodes. For an applied positive bias (V>0), a rise in current in the J-V curve (see Figure 5.2.5.2.a and b) is attributed to non-resonant tunneling. However, for bias >0.7 V, there is a sharp current rise due to the alignment of the
Fermi level of Hg with the HOMO energy levels, inducing a resonant tunneling. Since the molecule undergoes a first oxidation, without any major changes in the configuration, the current keeps rising sharply with the bias. However, at still higher bias, the molecule undergoes second oxidation leading to a large conformational change. Consequently, the HOMO and LUMO levels are shifted and become off-resonance to the Fermi level of Hg. As a result, the current drops sharply as it now can pass only though the direct tunneling process, and therefore, results in the NDR effect. The current always remains low in the subsequent $J-V$ cycles, indicating that the conformational changes achieved after second oxidation are quite stable. However, if the electrodes are short-circuited, the neutral state of 21:83a is regained, and the NDR effect reappears. For the negative bias on Hg electrode i. e. $V < 0$, the current remains low as a very high bias is required to obtain a resonance between the Hg Fermi level and LUMO of the molecule. Moreover, the molecule does not undergo any reduction, and therefore, no additional features other than non-resonant tunneling current, appears in the negative bias.
Figure 5.2.5.1 (a) Theoretically calculated geometries of HOMO of 21:83a under different oxidation states. (b) Schematic representation of the energy level diagrams for Hg/21:83a/Si(n++) device at different applied bias.

5.3. Summary

In conclusion, we have measured the charge transport properties of some tailor-made Bodipy monolayers and bilayers, grafted on Si (111) surfaces. Room temperature current rectification in the monolayer and NDR effect in the bilayer with PVR values upto 1000 were have demonstrated. The studies showed that the NDR associated with hysteresis is due to resonant tunneling through molecular orbital, and bias-induced conformational changes in the
molecules. The results presented here will clearly pave the way for design and development of new molecular devices suitable for molecules-on-Si hybrid nanoelectronics.

5.4. Experimental

5.4.1. General methods

The general details of the synthetic methodologies and spectroscopic studies have already been discussed in Chapter-2. The monolayers were characterized in terms of thickness, using an ellipsometer (Sentech: model SE400adv); surface morphology by AFM imaging (Multiview 4000, Nanonics), de-ionized water contact angle (Data Physics System, model: OCA20), and molecular mass by SIMS (BARC make, Kore’s Technology software). The current voltage characteristics were recorded in a dark box using a potentiostat/galvanostat system (model: Autolab PGSTAT 30).

5.4.2. Synthesis of Bodipys

4-(4'-penentenyloxy)benzaldehyde (82a) and 4-(10'-undecenyloxy)benzaldehyde (82b).

A mixture of 68 (4.0 g, 32.7 mmol), 1-bromopentene (39.3 mmol) or 1-bromo-10-undecene (39.3 mmol), K$_2$CO$_3$ (5.52 g, 40 mmol) and Bu$_4$NI (10 mol%) in acetone (100 mL) was refluxed. After completion of the reaction (cf. TLC ~ 16 h) the mixture was filtered, concentrated in vacuum, the residue taken in Et$_2$O (40 mL) and washed with H$_2$O (2 × 10 mL) and brine (1 × 20 mL), dried and concentrated in vacuo. The residue was purified by column chromatography (silica gel, 5% EtOAc/hexane) to give pure 82a (5.7 g, 91%) and 82b (8.1 g, 91%).

**Compound 82a**: Viscous liquid; IR : 3019, 1687 cm$^{-1}$; $^1$H NMR: $\delta$ 1.28-1.42 (m, 2H), 2.32 (t, $J$ = 6.8 Hz, 2H), 4.01 (t, $J$ = 6.2 Hz, 2H), 6.97 (d, $J$ = 9.5 Hz, 2H), 7.80 (d, $J$ = 9.5 Hz, 2H), 9.85 (s, 1H); $^{13}$C NMR : $\delta$ 13.6, 22.2, 25.3, 28.7, 31.2, 68.1, 114.4, 129.6, 131.5, 163.9, 190.1; Anal.
Calcd. for C\textsubscript{12}H\textsubscript{14}O\textsubscript{2}: C, 75.76; H, 7.42%. Found: C, 75.44; H, 7.16%.

**Compound 82b**: viscous liquid; IR: 3019, 2856, 1687 cm\textsuperscript{-1}; \textsuperscript{1}H NMR: \(\delta\) 1.38 (m, 12H), 1.82 (m, 2H), 2.05 (m, 2H), 4.04 (t, \(J = 6.0\) Hz, 2H), 4.98 (t, \(J = 10.0\) Hz, 2H), 5.79 (m, 1H), 6.99 (d, \(J = 8.0\) Hz, 2H), 7.83 (d, \(J = 8.0\) Hz, 2H), 9.88 (s, 1H); \textsuperscript{13}C NMR: \(\delta\) 25.9, 28.9, 29.0, 29.3, 29.4, 33.7, 68.4, 114.8, 129.9, 131.9, 139.1, 164.3, 190.6; MSMS (m/z): 275.1 (100) [M+H]\(^{+}\) amu; Anal. Calcd. for C\textsubscript{18}H\textsubscript{26}O\textsubscript{2}: C, 75.44; H, 7.16%. Found: C, 75.44; H, 7.16%.

**BODIPY-C5 (83a) and BODIPY-C11 (83b).**

As described in Chapter-2, compound 83a was synthesized using 58 (1.00 g, 8.1 mmol), 82a (0.70 g, 3.7 mmol), TFA (1 drop), DDQ (0.84 g, 3.7 mmol), Et\(_3\)N (3.1 mL) and BF\(_3\)Et\(_2\)O (2.8 mL, 22.2 mmol) in CH\(_2\)Cl\(_2\) (10 mL). Usual work-up, followed by column chromatography (silica gel, hexane-EtOAc) furnished pure 83a.

For the synthesis of 83b, compounds 58 (1.00 g, 8.1 mmol), 82b (0.99 g, 3.7 mmol), TFA (1 drop), DDQ (0.84 g, 3.7 mmol), Et\(_3\)N (3.1 mL, 22.2 mmol), BF\(_3\)Et\(_2\)O (2.8 mL, 22.2 mmol) and CH\(_2\)Cl\(_2\) (30 mL) were used.

**83a**: Yield: 0.24 g (13.7%); red square shaped crystals (CH\(_2\)Cl\(_2\)/cyclohexane); mp: 177-178 °C; IR: 2964, 2880, 1608, 1643 cm\textsuperscript{-1}; \textsuperscript{1}H NMR: \(\delta\) 0.98 (t, \(J = 7.6\) Hz, 6H), 1.34 (s, 6H), 1.93 (t, \(J = 7.7\) Hz, 2H), 2.16–2.36 (m, 6H), 2.53 (s, 6H), 4.03 (t, \(J = 6.5\) Hz, 2H), 5.00–5.12 (m, 2H), 5.89-5.99 (m, 1H), 7.01 (d, \(J = 6.7\) Hz, 2H), 7.13 (d, \(J = 6.7\) Hz, 2H); \textsuperscript{13}C NMR: \(\delta\) 11.7, 12.4, 14.5, 17.0, 28.3, 30.0, 67.2, 114.9, 115.2, 127.6, 129.3, 131.1, 132.5, 137.5, 138.4, 140.3, 153.3, 159.4; EI-MS (m/z): 464.0 [M]\(^{+}\). Anal. Calcd. for C\textsubscript{28}H\textsubscript{35}BF\textsubscript{2}N\textsubscript{2}O: C, 72.42; H, 7.60; N, 6.03%. Found: C, 71.95; H, 7.91; N, 6.28%.

**83b**: Yield: 0.36 g (17.8%); mp: 160 °C; IR: 2964, 2880, 1608, 1643 cm\textsuperscript{-1}; \textsuperscript{1}H NMR: \(\delta\) 1.02 (t, \(J = 7.6\) Hz, 6H), 1.32 (s, 12H), 1.57 (s, 6H), 1.78 (p, \(J = 6.4\) Hz, 2H), 2.02 (q, \(J = 7.8\) Hz, 2H), 7.82 (d, \(J = 8.0\) Hz, 2H), 9.87 (s, 1H); \textsuperscript{13}C NMR: \(\delta\) 11.7, 12.4, 14.5, 17.0, 28.3, 30.0, 67.2, 114.9, 115.2, 127.6, 129.3, 131.1, 132.5, 137.5, 138.4, 140.3, 153.3, 159.4; EI-MS (m/z): 464.0 [M]\(^{+}\). Anal. Calcd. for C\textsubscript{28}H\textsubscript{35}BF\textsubscript{2}N\textsubscript{2}O: C, 72.42; H, 7.60; N, 6.03%. Found: C, 71.95; H, 7.91; N, 6.28%.
$2.30\ (q,\ J = 7.6\ Hz,\ 2H),\ 2.51\ (s,\ 6H),\ 4.00\ (t,\ J = 6.4\ Hz,\ 2H),\ 4.90-5.03\ (m,\ 2H),\ 5.75-5.88\ (m,\ 1H),\ 6.95\ (d,\ J = 8.7\ Hz,\ 2H),\ 7.11\ (d,\ J = 8.7\ Hz,\ 2H);\ ^{13}\text{C}\ NMR:\ \delta\ 11.8,\ 12.5,\ 14.6,\ 17.1,\ 26.0,\ 28.9,\ 29.1,\ 29.3,\ 29.4,\ 29.5,\ 29.7,\ 31.6,\ 31.9,\ 33.8,\ 68.2,\ 114.1,\ 115.0,127.7,\ 129.4,\ 129.6,131.2,\ 132.6,\ 138.5,\ 139.2,\ 140.4,\ 153.4,\ 159.6;\ \text{EI-MS\ (m/z):\ 548.3\ [M]^+}.\ \text{Anal.\ Calcd.\ for}\ C_{34}H_{47}BF_2N_2O:\ C,\ 74.44;\ H,\ 8.64;\ N,\ 5.11\%.\ \text{Found:}\ C,\ 74.48;\ H,\ 8.48;\ N,\ 5.12\%.$

5.4.3. Preparation of the Si($n^{++}$)-Bodipys hybrids

The Si (111, resistivity $<10^{-3}$ $\Omega$cm) wafers were cleaned by heating them in 4:1 (v/v) of conc. $\text{H}_2\text{SO}_4$: 30% $\text{H}_2\text{O}_2$ (piranha) for 10 min at 80 $^\circ$C. Piranha is exceedingly dangerous and should be kept away from organic materials and treated with care. The wafers were removed, washed with excess $\text{H}_2\text{O}$, and immersed successively in a de-aerated (purged with high pure $\text{Ar}$ for 30 min) 40% aqueous $\text{NH}_4\text{F}$ for 10 min, and in 2% aqueous HF for 2 min. The wafers were further washed with deionized $\text{H}_2\text{O}$ for 1 min, dried under a stream of $\text{N}_2$ and immediately taken into the electrochemical cell for electro-grafting.

The electro-grafting of organic molecules to Si surface was carried out using a three-electrode electrochemical setup, as shown schematically in Figure 5.2.3.3. The H-terminated Si on which the molecules are to be grafted was used as the WE, while a Pt wire served as the CE. A pseudo RE was prepared by depositing AgCl layer over Ag by the galvanostatic method. For this, a constant current (1mA) between Ag wire and Pt electrode in 1 M $\text{HCl}$ was maintained for 15 min. The AgCl-coated Ag wire was washed thoroughly with de-ionized water to remove the acid, and dried. This was standardized with respect to the redox potential of ferrocene, and used for the experiments. The electro-grafting was carried out using CV using a solution containing 1:1(v/v) of 0.1 M TBAP as the supporting electrolyte and compounds 83a or 83b (1 mM) in dry CH$_2$Cl$_2$. The potential was scanned from −0.8 V to 0 V at a scan rate of 0.05 V/s for number of
scans. Control experiments were also carried out using TBAP solution alone to ensure no deposition of TBAP on Si. After electrografting, the WEs were sonicated in CH$_2$Cl$_2$, acetone and methanol for 10 min each to remove the physisorbed molecules and obtain monolayered Si-hybrids.

For the deposition of the bilayers, the Si-hybrid monolayers were dipped into a 1 µM solution of 21 in dry CH$_2$Cl$_2$ for 24h under inert atmosphere. The resultant self-assembled materials were sonicated in dichloromethane, acetone and methanol for 10 min as above to obtain the required materials. Additional similar experiments were also carried out by dipping the WEs in the 1 µM solution of 21 for 7 days, and also using a 3 µM solution of 21 to ensure uniform bilayer deposition.

5.4.4. Characterization of Bodipy monolayers and bilayers

The thicknesses of the deposited layers were measured by ellipsometry. The AFM images, used for characterizing the surface morphology were analyzed by WXSM software.

**Contact angle measurements.** Millipore-Q water (conductivity 0.05 µS.cm$^{-1}$) was used for contact angle studies. Dynamic contact angle analysis by wetting angle measurements was carried out to investigate the change in surface energy of samples and to investigate the kinetics. The measurement of contact angles of the sample was carried out by sessile drop technique using an image analysis software. A liquid droplet (1.5- 2.5 µL) was allowed to fall on the samples to be studied from a software-controlled syringe.

**SIMS analyses.** The SIMS was recorded using a TOF-SIMS instrument, consisting of a 25 KeV fine focusing primary Liquid metal Ion gun (Mono-isotopic $^{69}$Ga) that can focus ion beams to a spot size as small as 250 nm with current density of ~ 0.03 mA/cm$^2$. The primary ion beam was pulsed at high potential (+ 2000 VDC) at a rate of 10 kHz with a pulse width of approximately
10 – 15 ns. A modified Wiley-McLaren type Reflectron produces a uniform electrostatic field over a length of 415 mm. The secondary ions, generated from the impact of primary ions were accelerated and extracted (with a small delay) from the sample surface using a unique ion optical lens that employs large acceptance and a small energetic distribution. After passing through a flight tube, the extracted secondary ions with slightly varying kinetic energies were reflected and time focused onto a microchannel plate detector, operated in the ion counting mode with the help of a specially designed gridless reflectron (Model : R500, Kore Technology, UK). A fast pre-amplifier with a rise-time of <500 ps was used to detect and amplify the ion signals before being counted by a P7887 (Fast ComTec, Germany) Multi-scaler with a timing resolution of about 300 ps. Three ion pumps were utilized to ensure an ultimate low background pressure of < 1 × 10⁻⁹ mbar in both the analysis chamber and the flight tube. The signals, detected by the microchannel plate detector were amplified and coupled to a high-speed time to digital converter to generate the time spectrum which was directly converted into a mass spectrum using the following relation:

\[ m = \left( \frac{t - t_0}{C_b} \right)^2 \]

where \( t \) is the arrival time of the ions, \( t_0 \) and \( C_b \) are constants with values 1.105 and 5.00 respectively, depending on the geometrical parameters of the flight tube and the extraction optics. By rastering the primary ion beam over the sample surface, and detecting the secondary ions corresponding to each raster point, a chemical image of the sample surface was generated. The TOF-SIMS had a mass resolving power > 10,000, with a mass range of about 1500 amu and a dynamic range > 4 (4 orders of magnitude between the smallest peak and the largest peak). A low energy electron flood gun was used to neutralize charging of the insulating samples. A load lock chamber connected to the analysis chamber was used for loading samples from atmosphere which ensured that the analysis chamber was never exposed to
atmospheric contaminations. For the depth profiling studies, an Ar ion etch gun at 500 eV was interlaced with the primary liquid metal ion gun to etch sample surfaces. The depth profiles were obtained by alternating between sputter cycles and data acquisition cycles.

**XRR analyses.** The XRR measurements for the structural depth profiles were carried out in specular mode with a laboratory X-ray source using Cu Kα. The calculation of optical reflectivity of the X-rays in this case was based on recursive formalism for stratified media.\(^{142}\) The SLD profiles were produced as a function of depth in the sample by independently fitting the experimental reflectivity data from the XRR measurements through a theoretical model as a series of layers. Detailed significant information for the layers and the interfaces were gathered in terms of three characteristic parameters: thickness of the layers, interface roughness and scattering length density as a function of depth. Errors of the parameters gained from the fits were found to be within the range of 5–10%.

**5.4.5. Measurement of current-voltage characteristics**

To measure current–voltage (J–V) characteristics, a metal/monolayer or bilayer/ Si(n++) structure was completed by using a very small drop of liquid mercury as a counter electrode. The J–V was recorded at room temperature by scanning the bias in the sequence -1.8 V → 0 V → +1.8 V → 0 V → -1.8 V at a scan speed was 5 mV/s in a dark box using HP4140 (pA meter–dc voltage source).

**5.4.6. Theoretical computation**

We have theoretically calculated the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies for neutral, and at different oxidation state of BODIPY-C5 and \(\text{BODIPY}:\text{BODIPY-C5}\) molecules respectively. The geometries and total energies of molecules were optimized using the density functional theory with linear
combination of atomic orbital (LCAO) approach using General Atomic and Molecular Electronic Structure System (GAMESS). A standard 6-31G+(d,p) basis set was employed for this purpose. The exchange correlation energy was calculated using B3LYP functional. This function uses part of Hartree-Fock exchange and Becke’s exchange functional, and the Lee-Yang-Parr correlation functional. For the computation, PC and two supercomputers, namely, Ameya and Ajeya were used. Ameya is 128-proceseor ANUPUM supercomputer built on 64 dual Xeon servers (2.4GHz) as compute node, interconnected by a high-speed (300 MBps) communication network. The 512-processors ANUPAM-ameya supercomputer is built using 256 dual Xeon servers as a compute node. Each server is based on dual Xeon, 3.6 GHz processors. The inter-communication network is a Gigabit Ethernet with a node-to-node communication speed of 1 Gbps. The performance of ANUPAM-ameya is 1.73 Teraflops. The open source Linux operating system was used on each parallel processing node in these two supercomputers.