Supporting Information (SI)

Tuning of electron tunneling: A case study using BODIPY molecular layers

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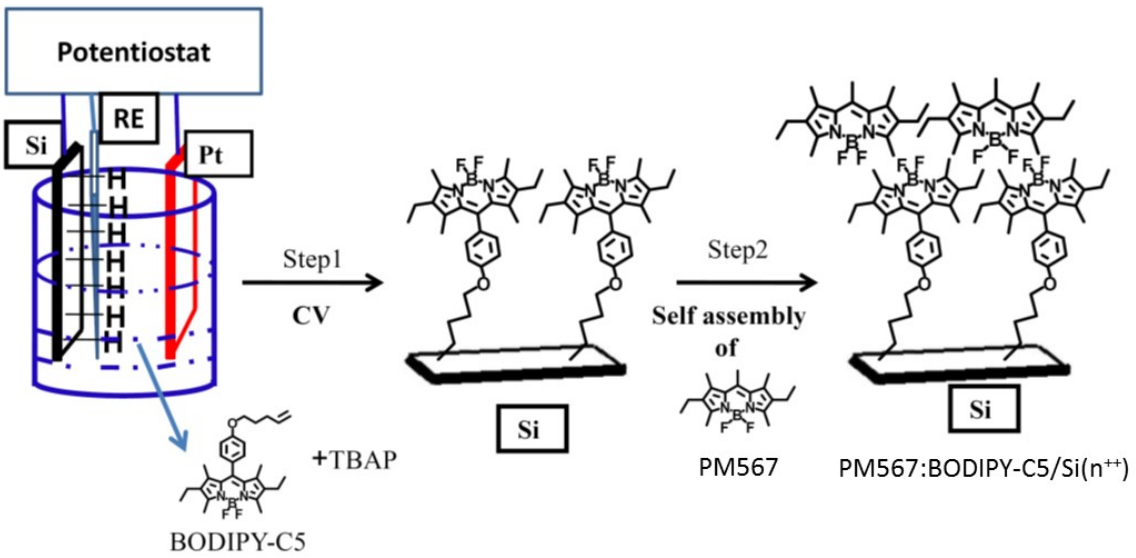
Content

1. BODIPY monolayer and bilayer formation on Si(n^{++})

BODIPY bilayer on H-terminated Si(n^{++}) substrates was deposited in two steps, see Scheme S1. The H-terminated Si substrates were prepared by dipping piranha solution [4:1 H_2SO_4 and H_2O_2 (v/v)] treated n-Si (111) substrates (resistivity <10^{-3} Ωcm) into 40% ammonium fluoride solution (purged with high pure argon gas) for 15 min. *Piranha is exceedingly dangerous and should be kept away from organic materials and treated with care*.



Scheme S1: Pictorial representation of two steps deposition process of BODIPY on Si(n^{++}). Step 1: Electrografting of BODIPY-C5 monolayer on H-Si(n^{++}); Step 2: formation of bilayer by self-assembly of PM567 onto BODIPY-C5/Si(n^{++}).

Monolayers formation by electro-grafting. We followed electro-grafting for an easy attachment of the BODIPY-C5 on Si (111) surface through the strong Si-C bond (Si-C ~76 kcal mol^{-1}).

Thus, BODIPY-C5 was electrografted to H-terminated Si(n^{++}) surface through its terminal alkene groups [1]. The electrografting mechanism (Figure S1) 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 [2].

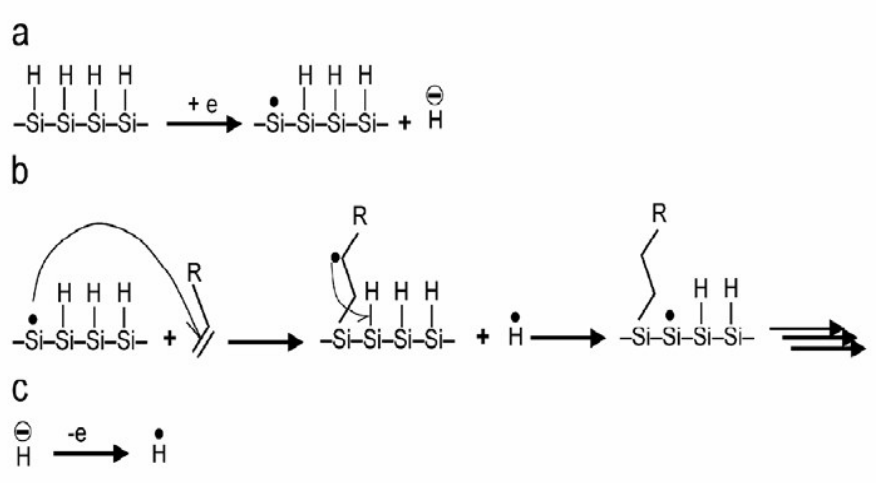


Figure S1. Schematic of the electrografting process on Si via Si–C bond formation.

In the Step 1, monolayer of BODIPY-C5 was electrografted to H-terminated Si(n^{++}) in the cyclic voltammetry mode (CV), which was carried out using a Potentiostat/Galvanostat system (model: Autolab PGSTAT 30). CV was carried out using a solution containing 1:1 (v/v) of 0.1 M tetra butylammonium perchlorate (TBAP) supporting electrolyte and 1 mM of BODIPY-C5. Control experiments were also carried out using TBAP solution alone, which revealed no deposition of TBAP on Si. In all the experiments, the CV's were run under inert ambient condition in the potential range 0 to –0.8 V at a scan rate of 0.05 V/s using three electrodes system: H-terminated Si as working electrode, Pt wire as counter electrode and Ag/AgCl as reference electrode. After electrografting of BODIPY-C5, it was sonicated in dichloromethane, acetone and methanol for 10 min each to remove the physisorbed BODIPY-C5.

Typical CV scans recorded using BODIPY-C5 (Figure S2) 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 50th scan. This confirmed the completion of multilayers deposition. The irreversible CV peak indicated an irreversible reaction (i. e. the cleavage of vinyl-group) is associated with the electron transfer. No peak at -0.25 V appeared when the CV was run using the TBAP solution alone.

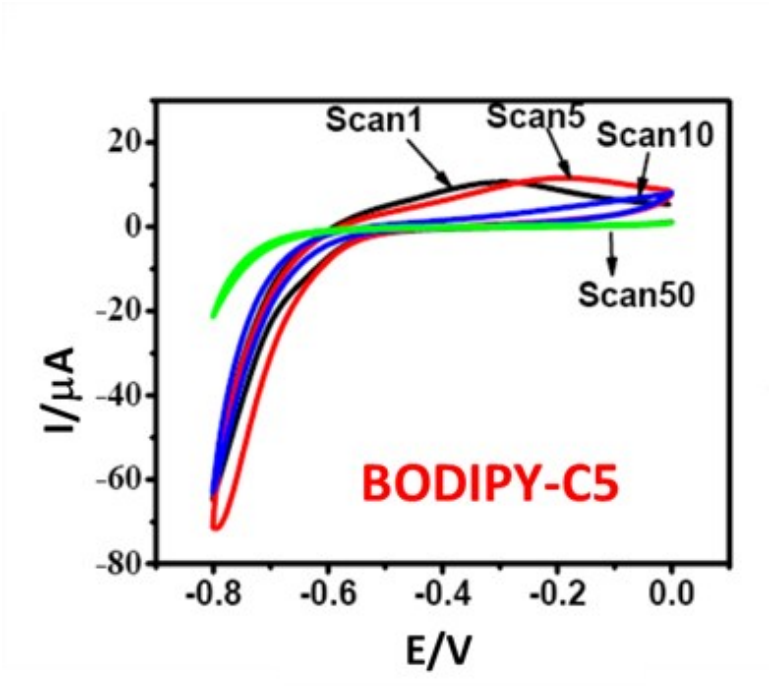


Figure S2. Cyclic voltammograms (CVs) indicating electrografting of BODIPY-C5 on H-terminated Si(n^{++}) substrate.

***Bilayers formation by self- assembly*.** In the Step 2, PM567 (Aldrich make) was deposited on BODIPY-C5/Si(n^{++}) monolayer by self-assembly process. For this purpose, BODIPY-C5/Si(n^{++}) monolayer was dipped into 1 μM PM567 solution (prepared in dichloromethane) for 24 h under inert atmosphere. PM567:BODIPY-C5/Si(n^{++}) was sonicated in dichloromethane, acetone and methanol for 10 min to remove any physisorbed molecules.

2. Characterization of BODIPY monolayer and bilayer

Thickness of the deposited layers was measured using ellipsometer (model Sentech SE400adv). The surface morphology was imaged using atomic force microscope, AFM, (Multiview 4000, Nanonics) and image was analyzed by WXSM software. Secondary ion mass spectra were recorded using TOF-SIMS instrument which consists 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 is pulsed at a rate of 10 kHz with a pulse width of approximately 10 – 15 ns. Secondary ions generated from the impact of primary ions are 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. The extracted secondary ions pass through a flight tube and are reflected and time focused onto a microchannel plate detector with the help of a specially designed gridless reflectron (Model : R500, Kore Technology, UK). Both the analysis chamber and the flight tube are always kept at a pressure of < 1 x 10^{-9} mbar. Signals detected by the microchannel plate detector are amplified and coupled to a high-speed Time to digital converter to generate the time spectrum which is 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 is generated. The TOF-SIMS has 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 is utilized to neutralize charging of insulating samples. A load lock chamber connected to the analysis chamber is used for loading samples from atmosphere which ensures that the analysis chamber is never exposed to atmospheric contaminations.

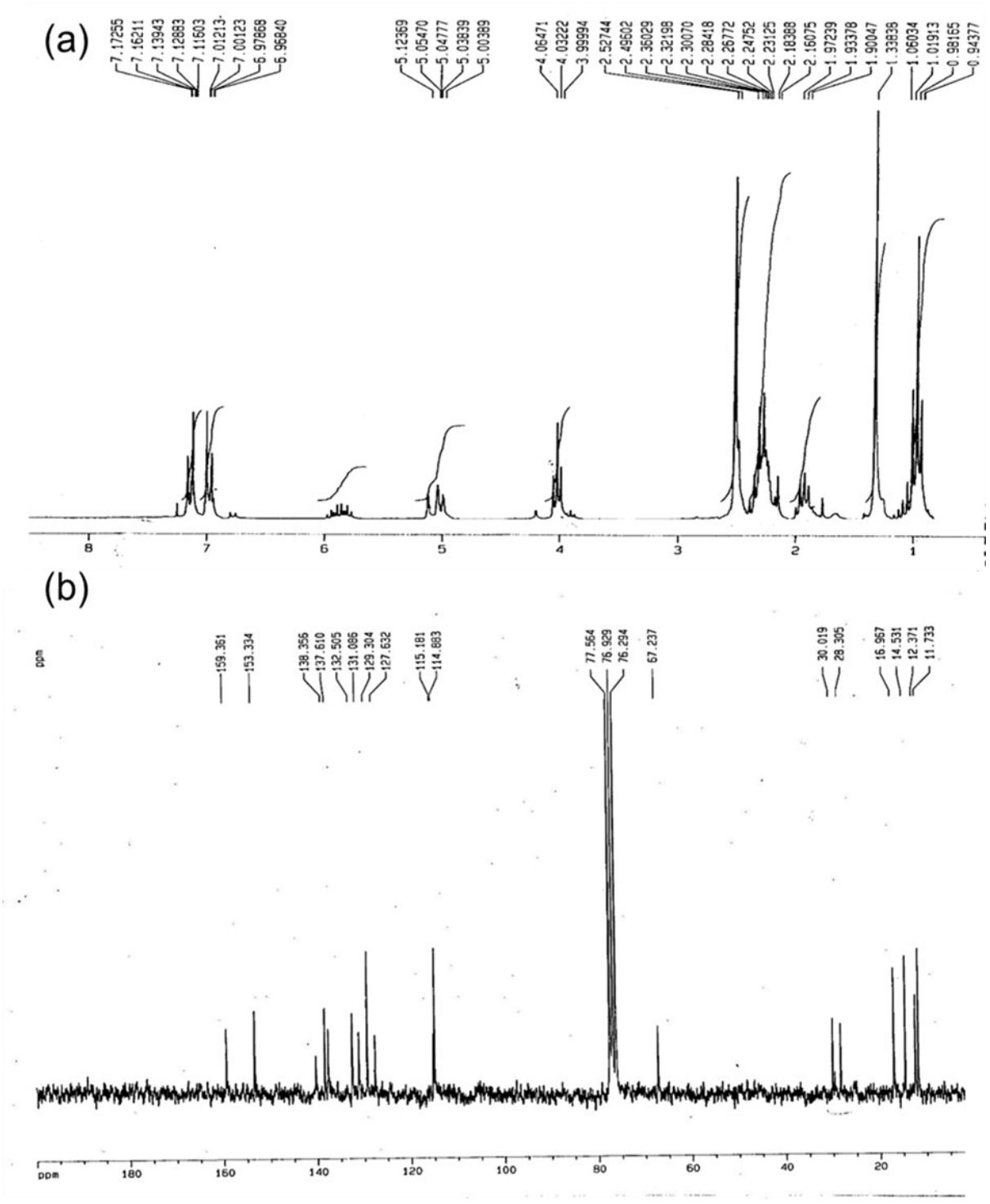


Figure S3. NMR spectrum of BODIPY-C5 (a) ^{1}H NMR and (b) ^{13}C NMR in $CDCl_3$.

References:

[1] (a) C. M. A. Brett and A. M. O. Brett, Electrochemistry: Principles, methods and applications, Oxford University Press, Oxford, Great Britain, 1994; (b) V. S. Bagolsky, Fundamentals of Electrochemistry, Wiley Interscience, New Jersey, 2006.

[2] D. K. Aswal, S. P. Koiry, B. Jousseleme, S. Palacin and J. V. Yakhmi, *Physica E,* 2009, **41**, 325–344.