SYNTHESIS AND CHARACTERIZATION OF \(\sigma-\pi\) MOLECULES FOR HYBRID NANOELECTRONICS

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Abstract
For futuristic hybrid nanoelectronics, it is essential that functional organic molecules should be grafted to silicon. For this purpose, we have synthesized a specifically designed \(\sigma-\pi\) organic molecules, that is, 5-(4-allyloxyphenyl)-10,15,20-triphenylporphyrin (TPP-C3), and 5-(4-octenyloxyphenyl)-10,15,20-triphenylporphyrin (TPPC8) and electrografted these molecules on highly doped n-Si substrates. These molecules exhibited a hysteresis in the current–voltage (J–V) characteristics. The observed electrical bistability in these molecules can be utilized for the molecular memory devices.

Keywords: porphyrin, bystersis,electrografhting

Introduction
Hybrid nanoelectronics, in which molecules exhibiting different electronic functionalities are grafted on Si, is expected to extend the scaling limits of existing microelectronics down to nanoscale\(^1\). For the purpose, during last few years, we have electrografted several newly designed and synthesized molecules that exhibited various electronic functionalities viz. rectification, memory, negative differentials resistance (NDR) etc.\(^2,3\). Porphyrin molecule and its derivatives have been found to be potential candidates for charge storage devices\(^4\) and, therefore, grafting these molecules on Si substrates is essential for the development of memory elements for hybrid nanoelectronics. Here, we demonstrate that specifically designed vinyl-terminated derivative of porphyrin molecule can be easily grafted on doped n-Si substrates by an electrochemical process via formation of Si–C bonds. The current–voltage characteristics of these electrografted molecules exhibit a pronounced electrical bistability.

Experimental
Specifically designed \(\sigma-\pi\) organic molecules, that is, 5-(4-allyloxyphenyl)-10,15,20-triphenylporphyrin (TPP-C3), and 5-(4-octenyloxyphenyl)-10,15,20-triphenylporphyrin (TPPC8) were synthesized and their structures is shown in Fig. 1.(a). Synthesis of these molecules involved two steps. In the first step, 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (TPPOH) was synthesized. A solution of pyrrole in propionic acid was added to a solution of benzaldehyde and 4-hydroxybenzaldehyde (3:1 molar ratio) in propionic acid and refluxed for 1h. After that it was cooled to room temperature. A black precipitate thus obtained was collected and washed with methanol. The solid was...
purified by silica gel column chromatography (3.2% yield).

$^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 8.85 (s, 8H, pyrrole $\beta$-H), 8.2 (m, 6H, Ar-H), 8.04 (d, 2H, Ar-H), 7.76 (m, 9H, Ar-H), 7.12 (d, 2H, Ar-H), -2.70 (brs, 2H, NH).

In the second step, TPPC3 and TPPC8 were synthesized from alkenylation of TPPOH. TPPOH, alkenyl bromide (allyl bromide/8-bromo-1-octene) and anhydrous potassium carbonate were dissolved in N,N-dimethylformamide (DMF) and the mixture was stirred at 70°C for 16h. After the completion of the reaction, DMF was removed under vacuum. The gummy mass was quenched with water and TPPC3 (or TPPC8) extracted with chloroform. Removal of solvent yielded a purple mass, which was further purified by preparative thin layer chromatography (73% yield).

TPPC3: $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 8.90 (m, 8H, pyrrole $\beta$-H), 8.24 (m, 6H, Ar-H), 8.10 (d, 2H, Ar-H), 7.76 (m, 9H, Ar-H), 7.30 (d, 2H, Ar-H), 6.25 (m, 1H), 5.47 (m, 2H), 4.82 (m, 2H), -2.76 (brs, 2H, NH);

TPPC8: $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 9.06 (m, 8H, pyrrole $\beta$-H), 8.4 (m, 6H, Ar-H), 8.19 (d, 2H, Ar-H), 7.76 (m, 9H, Ar-H), 7.24 (d, 2H, Ar-H), 5.90 (m, 1H), 5.02 (m, 2H), 4.23 (m, 2H), 2.13 (m, 2H), 1.94 (m, 2H), 1.59 (brs, 8H), -2.75 (brs, 2H, NH).

The electrochemical grafting of above synthesized molecules on n-type Si (111) substrate (resistivity $<10^{-3}$ $\Omega$ cm) was carried out on H-terminated Si (H-Si).

The H-Si surface was prepared by dipping piranha solution (4:1 H$_2$SO$_4$ and H$_2$O$_2$ (v/v)) treated Si substrates into 40% ammonium fluoride solution, which was purged with argon gas for 15 min prior to dipping. The monolayer of TPPC3 and TPPC8 were deposited on H-Si using cyclic voltammetry (CV) 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 tetrabutylammonium perchlorate (TBAP) supporting electrolyte and 1 mM TPPC3 (or TPPC8) in dry dichloromethane. Control experiments were carried out using 1 mM 1-octene without porphyrin moiety as well as TBAP solution alone. In all the experiments, the CV were run under inert ambient in the potential range between 0 and -1 V at a scan rate of 0.05 V/s using a three-electrodes system, H-terminated Si: working electrode; Pt: counter electrode; and Ag/AgCl: reference electrode. Fourier Transform infrared (FTIR) spectra were recorded using Vertex 80v (Bruker) under vacuum in diffuse reflection mode using liquid nitrogen cooled MCT detector at a resolution of 2 cm$^{-1}$. In order to measure current–voltage (J–V) characteristics, a metal/monolayer/ Si(n++) structure was completed by using a very small drop of liquid mercury as counter electrode. The J–V’s were recorded at room temperature by scanning the potential in the sequence -1 V (r) 0 V (r) +1 V (r) 0 V (r) -1 V at a scan speed was 5 mV/s in a dark box using HP4140 (pA meter–dc voltage source).

**Results and discussion**

Typical CV scans recorded using TPP-C8 + TBAP, TPP-C3 + TBAP (not shown here) and 1-octene (C8) + TBAP solutions are nearly identical as shown in Fig. 1 (b). It is seen that the presence of an irreversible
oxidation peak at -0.3 V, observed for the first scan, disappears rapidly as the number of scans are increased and eventually vanishes for 50th scan. However, no peak at -0.3 V appeared when the CV was run using TBAP solution alone. This indicates that an irreversible oxidation peak at -0.3 V is associated with the bonding of TPP-C3/ C8 and C8 molecules to form Si–C bond and a new carbon radical is formed. The carbon radical then reacts with hydrogen of the surface leading to the formation of Si radical.

The FTIR spectra recorded for the TPP-C3/C8 and C8 monolayers are shown in Fig. 1.(c). It is seen that TPP-C3/ C8 monolayer exhibits a clear N–H stretching frequency at 3305 cm⁻¹, which confirms the presence of porphyrin group in the monolayer. For both monolayers, symmetric (n_s) and asymmetric (n_a) stretching modes of CH₂ group at −2881 and −2935 cm⁻¹, respectively, have been observed. AFM studies [Fig1.(d)] showed that surface coverage of TPP-C3 is less than TPP-C8. This difference in morphology is mainly due to the reduced van der Waals interactions among short chains. Roughness of the TPP- C8 (3.3nm) and TPP-C3 (2.2nm) monolayer resembles well with the theoretical thickness of single layer. The thickness was confirmed independently by ellipsometric measurement.

Typical J–V plots recorded for TPP-C8 and C8 monolayers are shown in Fig. 2. J–V’s are slightly asymmetric, which is attributed to the different work functions of the electrodes, i.e. Si (4.1 eV) and Hg (4.5 eV). It may be noted that the J–V’s of C8 monolayer does not exhibit any hysteresis; whereas for TPP-C8 monolayer a pronounced hysteresis is observed, indicating a predominant role of porphyrin ring. In the positive bias scan, i.e. from 0 to +1 V, current jumps by an order of magnitude at +0.6 ±0.1V. However, during reverse scan (1 to 0 V), current does not retrace the curve back, and remains at higher values. Thus, the J–V exhibits two conduction states: one with low current (OFF) and other with higher current state (ON). This electrical bistable behavior can be utilized for the molecular memory device.

The memory phenomenon in electrically bistable devices is best demonstrated under “write-read-erase-read” operations. In such a sequence of cycles, the low-conducting (“write”) and high-conducting (“erase”) states are induced repeatedly and the states are monitored (“read”) in between. In the present case, 0 V and +0.8 V pulses for 10 s were applied, respectively, to “write” the low-conducting state and “erase” to a high-conducting one. These states were continuously monitored (“read”) by measuring the device current (at 0.5 V), for more than 50 reading operations, and a section of “write-read-erase-read” operation recorded for our device is shown in Fig. 3. The magnitude of the device current under the “read” voltage pulse is 30 times higher for high-conducting state (“erase”) as compared to that for low-conducting state (“write”).

The J-V characteristics for the device structures using TPP-C3 were found to be nearly same as that observed for
TPP-C8, indicating that the memory effect is independent of the alkyl chain length.

Conclusions

We have demonstrated electrografting of 5-(4-allyloxyphenyl)-10,15,20-triphenylporphyrin (TPP-C3), and 5-(4-octenyloxoyphenyl)-10,15,20-triphenylporphyrin (TPPC8) monolayer on doped n-Si via formation of Si–C bonds. The current–voltage characteristics of these molecules exhibit a pronounced hysteresis and demonstrate that such electrical bistability can be utilized for the resistive molecular memory devices.

References