



Research Paper

Exercising substituents in porphyrins for real time selective sensing of volatile organic compounds



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ABSTRACT

Herein, field effect transistors have been demonstrated for selective detection of organic vapours through strategic design of porphyrin wrapped single walled carbon nanotubes (SWNTs) as sensor channels. The high performance sensors exhibited significant selectivity among aliphatic and aromatic vapours at concentration down to 1 ppm with rapid response/recovery signature under real-time measurements.

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1. Introduction

Extensive industrial applications [1] and anthropogenic/natural emissions have lead to ubiquitous presence of volatile organic compounds (VOCs) in environment [2]. An extensive inventory of this class of materials has put forward safety challenges that range from low temperature flammability to pernicious effects on human and natural habitat [3]. Therefore, rapid, sensitive, reversible and room temperature detection of this class of toxins have garnered critical attention in recent years. Several of VOCs, emitted from livelihood commodities, are reported to have slow yet long term effect on human health [3(a)]. Hence, efficient quantification of such toxins warrants sincere attention, and challenge lies in terms of selective identification owing to characteristic similarity among different classes of VOCs [4].

Classic detection of VOCs using porphyrins/metalloporphyrins (MPs) is generally related to weak interactions [5] that results in adsorption of VOCs onto sensor surface; rendering quartz microbalance (QMB) architecture for VOCs sensing [6]. The selectivity that could be achieved with such sensors is wide, and reported to be primarily due to the variants of central metal ion that binds different

analytes at the axial positions [7]. However, the selective behaviour could be reflected through statistical analysis in most of the reports [5] and no encouraging outcome has been observed with real time measurements. Further, a comprehensive library of reports with QMB architecture reflects fundamental drawbacks like low resolution [8], complex design [9], and tendency of porphyrins to self aggregate in the thin layer configuration resulting in slow sensor response [10].

In order to address the issues of real time measurement, selective quantification, and simple device architecture, recently porphyrins/MPs have been reported to be employed for wrapping up single walled carbon nanotubes (SWNTs) for exploiting electrical transduction [11]. π electron conjugated porphyrins/MPs have a strong affinity with SWNTs through π - π interactions to obtain wrapped structure [12]. Selective property of such sensors, again, has been achieved only through aid of statistical tools, as reported literature suggests. Shirsat et al. [13] has reported a distinct response pattern to diversified group of organic vapours through principal component analysis. Recent report by Berrios et al. [14] suggests that discrimination is possible between the polarity of validated vapours, however, through chemometric analysis. Liu et al. [15] have been able to differentiate VOCs into distinct classes on the basis of solubilities of the porphyrin complexes employing principal component analysis. Such reports clearly indicate that significant work has been carried out towards selective

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determination of VOCs with porphyrins/MPs/functionalized structures with SWNTs, yet, none of them could tackle the issue of real time selective determination of VOCs.

To alleviate the requirement(s) of software based analysis, and to get proper insight into the plausible roles of the central metal ion and/or peripheral substituents in macrocyclic structures, strategic planning and dedicated course of investigation is required. Side substituents in porphyrins/MPs and functional groups present in different classes of VOCs can have profound impact on defining sensor signature; however, efforts in this direction are at infancy. Recently, Mori et al. [15b] have elaborated influence of VOCs structures on sensing behaviour of SmFeO₃ based sensor. Authors have studied the influence of side reaction of VOCs with the adsorbed oxygen on the sensor surface to probe the effect of VOC molecular structures.

Here, we report that judicious selection of porphyrin(s), through consideration of side substituent and structure of target analytes, can lead towards 'statistical tool' or 'software aid' free real time pathway for selective detection of organic vapours. As it has been demonstrated in this communication, octaethyl porphyrin (OEP) and tetraphenyl porphyrin (TPP) functionalized aligned SWNTs network(s), as channels in back-gated FETs, could well discriminate between aromatic and aliphatic class of VOCs at a concentration down to 1 ppm at room temperature. Metalloporphyrins have been deliberately kept out of the periphery of this course of investigation to have the sole review on possible role of side substituent(s) in porphyrins to shape the sensing mechanism.

2. Experimental methods

Field effect transistors using Si- back gated geometry was obtained by dielectrophoretically aligning SWNTs network on Au micropatterned substrates [16]. Aligned SWNTs were annealed and functionalized by OEP and TPP by non-covalent route of functionalization. This route is supramolecular in nature and ensures non covalent attachment of porphyrin(s) to SWNTs sidewalls via physisorption due to π - π interaction between respective porphyrin and SWNTs sidewalls [17]. To realize high-performance selective sensors, chemical structure of the target analyte(s) and peripheral substituent(s) of the porphyrin ring were considered. TPP was the particular choice for benzene (representative of aromatic compounds) considering the high degree of symmetry between aromatic, planer structured benzene and phenyl group of TPP, where a π - π transition could be apprehended. In similar line of consideration, OEP was preferred, in purview of the methyl group present in both OEP and acetic acid.

Prefabricated Au micro-patterned Si/SiO₂ substrate was chosen for the fabrication of sensor(s). The substrate consisted of highly p-doped silicon (Si; 525 μ m) as the base layer on which oxide layer (SiO₂; 100 nm) was grown by low-pressure chemical vapour deposition. Chromium (Cr; 20 nm) and gold (Au; 180 nm) were then subsequently deposited by e-beam and thermal evaporation, respectively. Finally, micro patterns were defined by standard lift-off and photolithography techniques. Electrodes were designed to be 200 μ m wide with a gap \sim 3 μ m in between adjacent Au fingertips. Substrates were ultrasonically cleaned in acetone prior to use. For deposition of SWNTs (Nanoshel LLC) onto the micro-electrodes, dielectrophoretic alignment technique was adapted. First, fine suspension of SWNTs was prepared in N,N-dimethyl formamide (N, N-DMF, GC grade; Rankem) (\sim 41 mg in 20 mL N, N-DMF) by sonication (90 min) in VWR 100C ultrasonic bath, followed by centrifugation (15000 rpm for 90 min) in Remi R-24 centrifuge at general laboratory conditions. After centrifugation, decanted suspension was stocked in ambient conditions for further use. Prior to use, a requisite amount of the stock suspension was used to be

sonicated for 30 min. A small drop (\sim 0.2 μ L) of the suspension was dispensed on the microgap present between two gold electrodes on the sensing chip. Dielectrophoretic alignment was carried out by 1.5 V_{p-p} (sinusoidal) AC signal at 4 MHz frequency. Resistance (measured after a stabilization duration of 10 min) of the devices were optimized by controlling the duration of applied signal. The aligned devices were washed by nanopure water followed by nitrogen blow to remove unbound SWNTs. Aligned structures were annealed at 300 °C under reducing (5% H₂ + 95% N₂) atmosphere.

To functionalize aligned SWNTs, separate 0.1 mM solutions of TPP and OEP (Sigma-Aldrich, 99.99%) were prepared in N, N-DMF by stirring (30 min) at room temperature. Functionalization of SWNTs by porphyrins was carried out by solvent casting technique. A 0.4 μ L drop of the respective porphyrin solution was placed on the pristine SWNTs device for 30 min followed by wash under nanopure water and annealing at 90 °C in N₂ atmosphere for 60 min. All measurements were carried out under standard laboratory conditions (25 \pm 1 °C, 35–40% R_H) unless stated otherwise.

3. Characterization

Structural characterizations such as field emission scanning electron microscopy (FESEM), and atomic force microscopy (AFM) were carried out for the confirmation of alignment of the SWNTs between the electrodes as well as for the confirmation of visual and structural functionalization of the SWNTs. FESEM images were recorded by Hitachi S4800 and Tescan MIRA3 microscope and AFM studies were carried out by Perk system XE-7 microscope in non-contact mode. Raman spectroscopy was carried out for the confirmation of functionalization of the SWNTs by Seki Technology STR 150 Raman spectrometer. Fabricated sensors were subjected to electrical characterization (I-V; Keithley 2400 SMU) to probe the effect of functionalization on the electrical characteristics of pristine SWNTs based sensor. To study current-voltage (I-V) characteristics of pristine as well as functionalized devices, voltage was swept from -1 to +1 V at 0.01 V s⁻¹ scan rate, and data was recorded at five different temperatures.

To have an insight on suggested sensing mechanism, SWNTs-porphyrin samples were subjected to UV-vis spectroscopic study under benzene and acetic acid environment. For this purpose, SWNTs were deposited and functionalized on a glass slide. Few drops of SWNTs suspension (in N, N-DMF) were deposited on flat glass slide through spin coating. After solvent evaporation, freshly prepared solutions of TPP and OEP (0.1 mM in N, N-DMF, separately) were dropped onto SWNTs deposited region for casting and subsequent functionalization. UV-vis spectra were recorded for functionalized SWNTs backbone(s), in ambient condition and after exposure to saturated vapours of benzene and acetic acid. Shimadzu 2400 UV-vis spectrophotometer was employed for this purpose.

To validate sensing performances, the sensor(s) were bonded to custom chip carrier (DIP) with necessary electrical throughputs and was placed in atmospheric isolation inside a quartz flow cell of volume \sim 8 cc as part of an indigenously designed dynamic gas sensing setup. Details of the sensing set-up has been provided as supplementary information (Text S1; ESI)

Prior to measurement, respective sensor(s) were exposed to base gas (N₂) for required duration (maximum 12 min) to achieve a stable baseline resistance of the sensors. To study the sensing characteristics in ChemFET modality, back gate configuration was used. FET transfer characteristics of pristine and porphyrin functionalized SWNT devices were studied by Keithley 2400 SMU and CHI 660C electrochemical workstation. The channel current (I_{DS}; in FET configuration) was recorded while sweeping gate to source voltage (V_{GS}) from -20 V to +20 V at a scan rate of 0.1 V s⁻¹

(using Keithley 2400 SMU) at a constant drain to source potential equal to -1 V (by electrochemical workstation; CHI660C). Measurements were recorded in benzene and acetic acid environment(s) at 5 ppm concentration of each analyte, once stable baseline was reached. For real-time analysis, sensors were subjected to various concentrations of benzene and acetic acid separately (1–25 ppm of analyte concentration in each case). Under a constant drain to source voltage (V_{DS}) equal to -1 V , the changes in channel current (I_{DS}), as a function of various concentrations of analyte, were recorded by SMU (Keithley 2400). During real time measurements, the gate to source voltage(s) (V_{GS}) was maintained at -16 V for both devices. Instantaneous device resistance was determined by

Ohm's law. Sensor responses were calculated by the formula $(R_{\text{analyte}} - R_{\text{basegas}}) / R_{\text{basegas}}$. Finally, in order to confirm whether the sensors have similar affinity to other members of aliphatic and aromatic family, they were further exposed to naphthalene, anthracene (aromatic compounds) and formic acid, propanoic acid (aliphatic compounds) under 5 ppm concentration of each analyte. At least 5 devices were validated in each case for studying device-to-device variation.

As the sensors were validated under base gas at isolation from ambient atmosphere; it was necessary to assess the characteristics of the sensors under pure humid atmosphere. For the same, sensors were introduced to pure humid condition at RH values

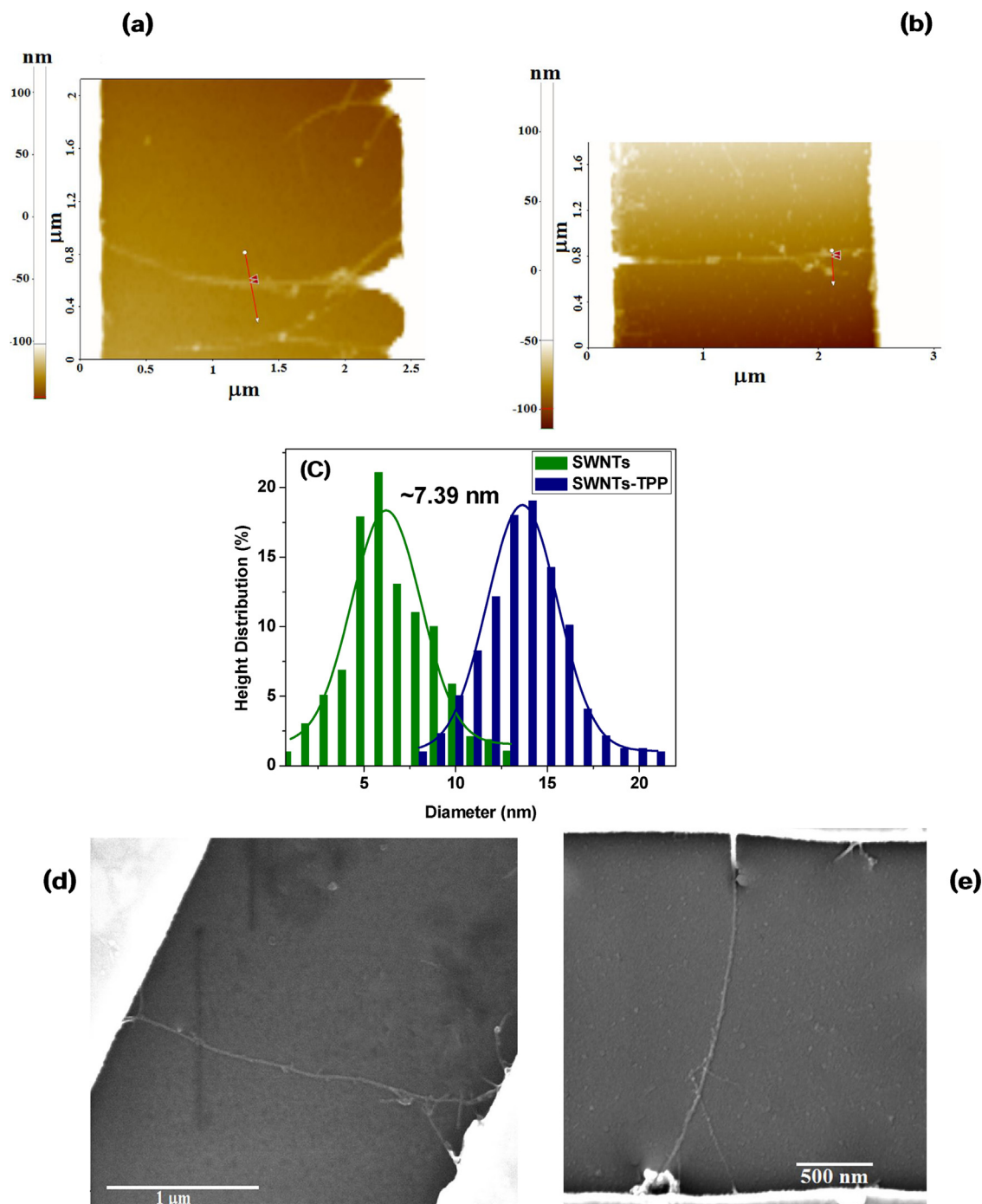


Fig. 1. AFM images of (a) SWNTs (b) SWNTs-TPP device; (c) height distribution histogram from AFM observations (d) FESEM images of SWNTs and (e) FESEM images of TPP functionalized SWNTs device.

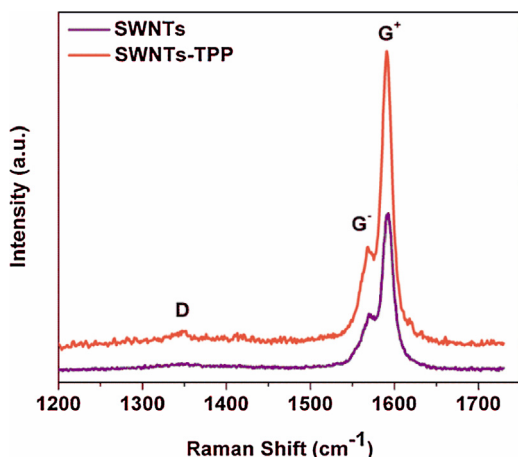


Fig. 2. Raman spectra of SWNTs and SWNTs-TPP.

of 30%, 60%, 90% and 100%. In order to accomplish the above, the gas sensor setup (as described in Text S1; ESI) was used and base gas was metered through a water bubbler (immersed in a temperature controlled bath; room temperature to 100 °C; ± 1 °C). Requisite concentration of the water vapour was achieved by controlled metering of base gas and flow through water bubbler while obtaining the final mixture.

All characterizations reported for confirmation of functionalization (AFM, Raman, IV) hereafter, reflect the observations with TPP functionalized device as the OEP functionalized devices had shown almost similar behaviour. However, sensing responses of both the devices have been presented.

4. Results and discussions

4.1. Morphological characteristics

Non-contact mode AFM image of bare aligned SWNTs network is shown in Fig. 1 (a) and a typical TPP functionalized device are shown in Fig. 1 (b). The alignment was found to be efficient as interlacing and/or intertwines were almost absent. Post functionalization increase in diameter for aligned structures was evident with uniform coating. Estimation of height distribution over entire electrode (Fig. 1 (c)) shows that average diameter has been shifted from 6.21 nm to 13.60 nm indicating an average increase of ~ 7.39 nm. Corresponding FESEM image of SWNTs and TPP functionalized SWNTs devices are shown in Fig. 1(d) and (e).

Fig. 1(d) shows the FESEM image of the aligned pristine SWNTs bridging ~ 3 μm apart Au microelectrodes by dielectrophoretic alignment. As the figure suggests, dielectrophoretic alignment technique was efficient in obtaining aligned structures. Fig. 1(e) shows a typical image of aligned SWNTs after functionalization by TPP. An increase of 11 nm (in diameter) could be estimated after functionalization (for this particular specimen) from the images. Similar observation could also be affirmed for OEP functionalization (data not shown).

4.2. Raman spectroscopy

The functionalization was further confirmed through Raman spectroscopy of SWNTs before and after functionalization (Fig. 2). The characteristics G^- and G^+ peaks could be observed at 1568 cm^{-1} and 1592 cm^{-1} respectively that bear SWNTs fingerprints. Such peaks originate due to symmetry breaking of the tangential vibration when the graphene sheet is rolled to form a cylindrical tube [18]. Observed nature of G^- and G^+ peak confirms the semicon-

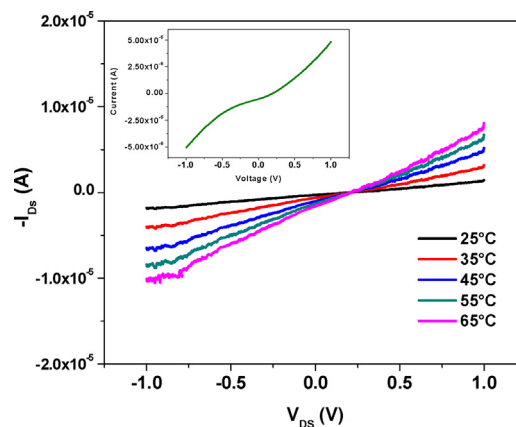


Fig. 3. (a) I-V profiles of SWNTs-TPP at different temperatures (inset I-V for pristine SWNTs).

ducting nature of SWNTs. Also, the weak D-peak around 1352 cm^{-1} signifies the defects created due to covalent attachment of $-\text{COOH}$ [18] moieties on SWNTs sidewalls. After functionalization, increase in I_D/I_G ratio could be observed but changes were not significant; that is well attributable to the non-covalent attachment of respective porphyrins to SWNTs [19].

4.3. Current-voltage (I-V) characteristics

To elucidate the electrical characteristics and subsequent VOCs detection, the sensors were wire bonded to a DIP chip carrier. The electrical characteristics were investigated by I-V measurements at different temperatures. Typical 'S' nature recorded for SWNTs based device (inset Fig. 3) exhibits schottky barrier contacts [20], indicating the majority of semiconducting SWNTs [18]. Post functionalization decrease in device current suggests potential electron donation by porphyrin to the p-type SWNTs [21]. Transfer of charge carriers are affected through extended π - π delocalization at SWNTs/porphyrin interfacial sites, which further indicates that any modulation occurring at porphyrin surface, under subject to analyte atmosphere will be transferred to the electronically active SWNTs surface efficiently [21]. As shown in Fig. 3, the device resistance (for TPP device) were decreasing with increase in temperature confirming retention of semiconducting characteristics in functionalized SWNTs.

4.4. ChemFET sensing characteristics

The sensors, in chemical sensitive field effect transistor (chem-FET) modality, were subjected to 5 ppm concentrations of benzene and acetic acid, while the gate supply was swept from -20 V to $+20\text{ V}$ (scan rate 0.1 V s^{-1}), and drain to source voltage was kept constant at -1 V to monitor the channel current. A generic p-type nature and decrease in device on-current was evident under analyte atmosphere (Fig. 4 (a) & (b)). Further, negative shift in threshold voltage (after functionalization) confirms the phenomenon of electron donation by the analytes [13].

The electrons donated by analytes combine with majority charge carriers of the functionalized nanostructures, resulting observed negative shift in threshold voltage (in comparison to dry air validation). At the same time, absence of any significant 'tilt' in transfer curves after analyte exposure suggests that the junction properties were not significantly modulated and electrostatic gating is the dominating phenomenon in shaping the sensor behaviour [22]. Estimation of decrease in majority carrier concentration (Text S2, ESI) in the sensors after analyte interaction, is reflected in Fig. 4 (c) that clearly offers a visual representation of the analyte discrimi-

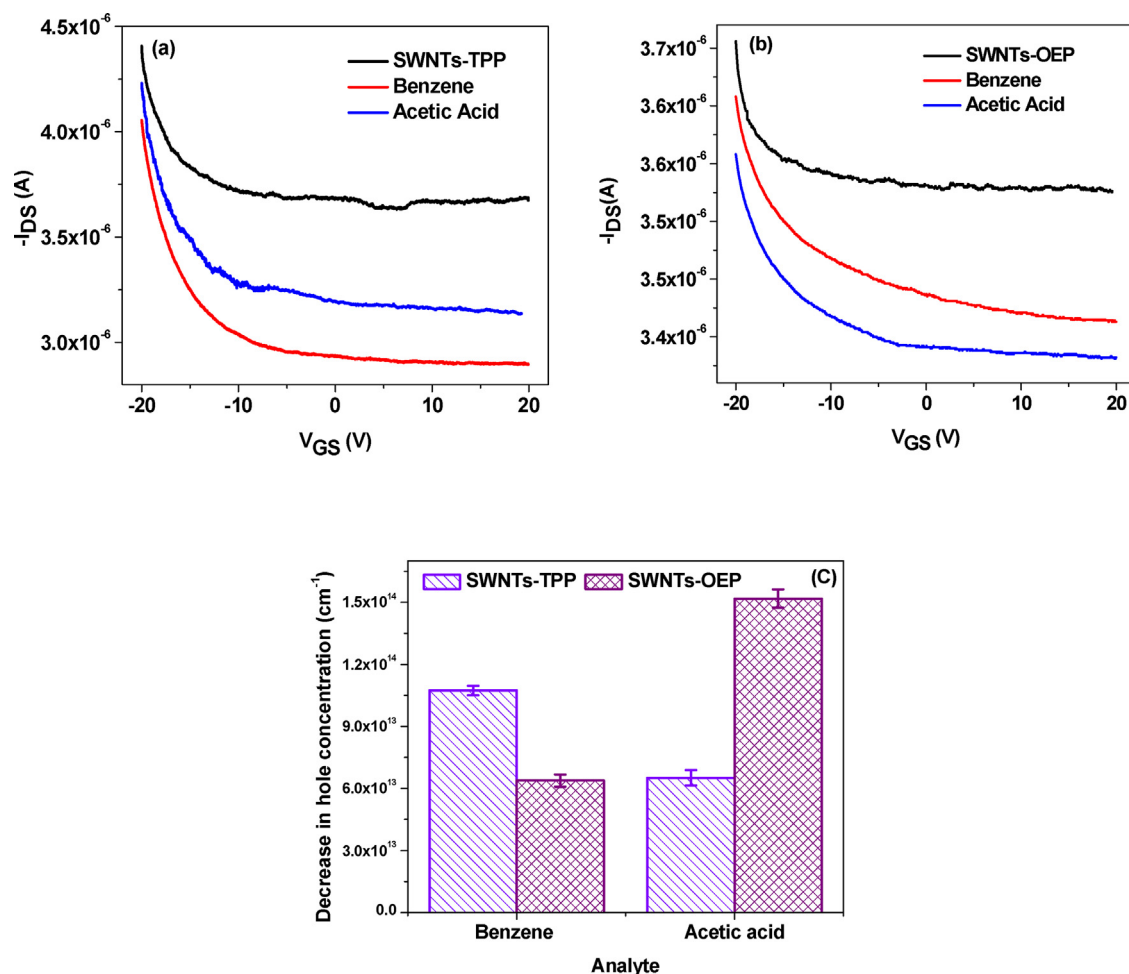


Fig. 4. (a) Transfer characteristics of SWNTs-TPP sensor at 5 ppm concentration of analytes, and (b) Transfer characteristics of SWNTs-OEP sensor(s) in 5 ppm concentration of analytes (c) Decrease in carrier concentration (with respect to base gas) of SWNTs-TPP and SWNTs-OEP sensor(s) after exposure to 5 ppm concentration of respective analytes.

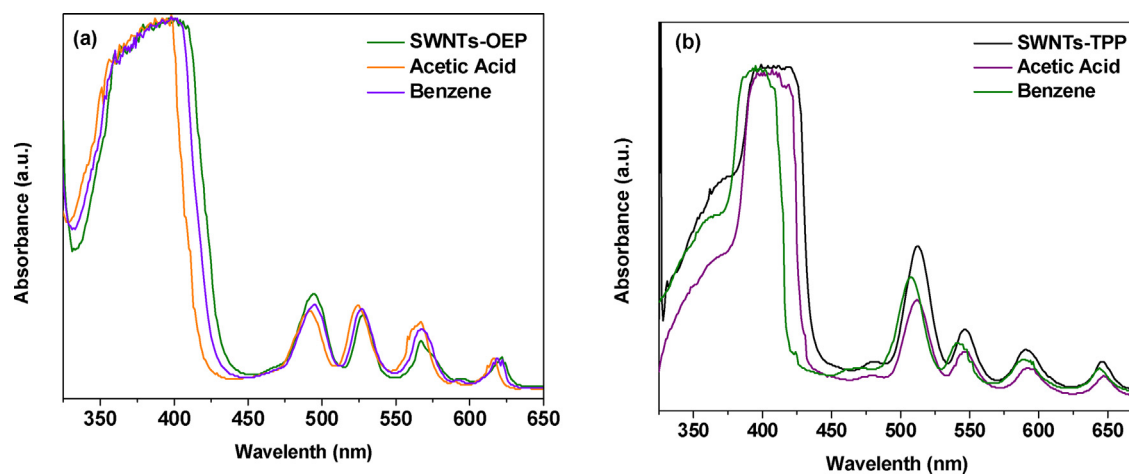


Fig. 5. UV-vis spectra of (a) SWNTs-OEP and (b) SWNTs-TPP under and without analyte environment.

nation capability of the fabricated sensors. As it is evident, benzene exhibits a higher degree of donation of electrons for SWNTs-TPP sensor whereas, effect of acetic acid is more profound for SWNTs-OEP sensor.

4.5. UV-vis spectroscopy under analyte atmosphere

To further validate our suggested model, we subjected the SWNT-porphyrin samples to UV-vis spectroscopic study under benzene and acetic acid environment. UV-vis spectra were

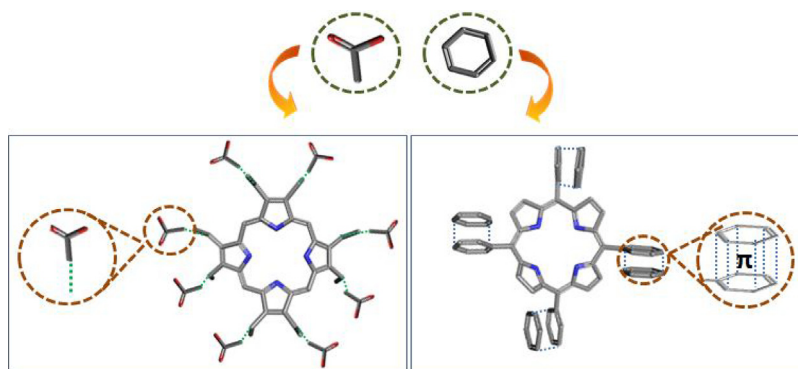


Fig. 6. Schematic of suggested sensing mechanism.

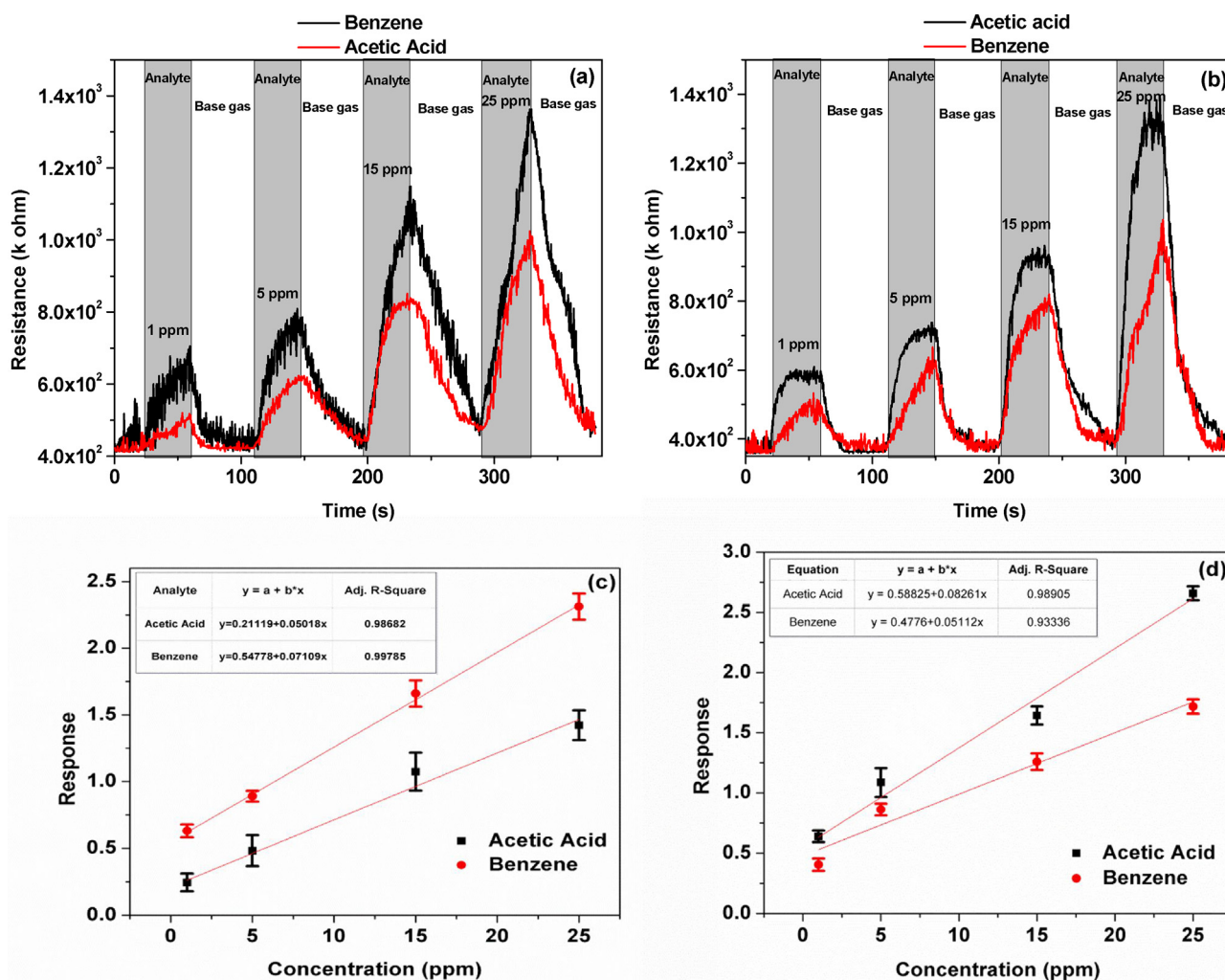


Fig. 7. Real time sensing characteristics of (a) SWNTs-TPP and (b) SWNTs-OEP in acetic acid and benzene environment (c) Calibration plot SWNTs-TPP and (d) calibration plot of SWNTs-OEP sensor.

recorded (Fig. 5 (a and b)) for functionalized SWNTs backbone(s), in ambient condition and after exposure to 5 ppm concentration of benzene and acetic acid.

Both TPP and OEP functionalized SWNTs samples exhibited broad Soret band around 391 nm and 375 nm respectively. In comparison to sharp Soret peak that is generally observed for free porphyrins [23], the broad band carries the signature of successful functionalization [24]. For TPP functionalized structure, peaks around 511, 587, 544 and 644 nm signifies Q-band peaks

[24]. Whereas, for OEP functionalized structure, the Q-peaks were recorded around 494, 524, 567, 618 nm respectively. After exposure, no significant change in the generic nature of the spectra could be observed. However, clear blue shifts after analyte exposure, was recorded for both porphyrins under all analyte atmosphere(s). Such blue shift corroborates to donation of electrons to the valance band of the p-type functionalized structure [25]. It could be clearly observed that for TPP functionalized structure, the shift was more severe under benzene atmosphere, whereas OEP functionalized

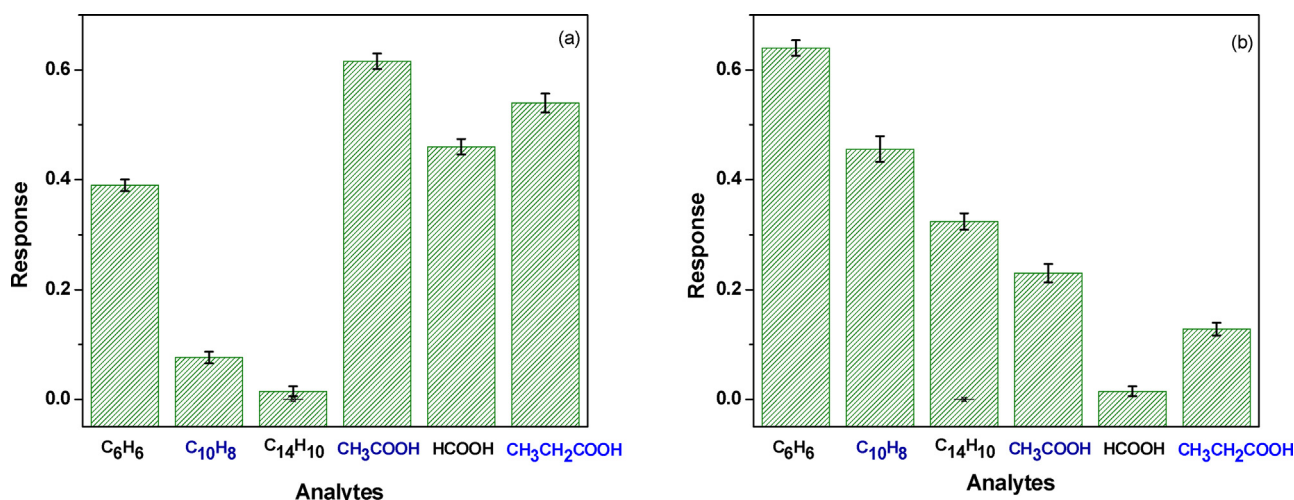


Fig. 8. Comparative performance of – (a) SWNTs-OEP sensor towards aliphatic and aromatic group of compounds, and (b) SWNTs-TPP sensor towards aliphatic and aromatic group of compounds.

structure exhibited a higher deviation for acetic acid exposure. Corroborating our observations for FET and UV measurements, it could be well envisaged that the side substituent in porphyrin had strong effect on deciding the sensors' behaviour towards particular analyte. The better affinity of TPP device towards benzene could be well attributed to the high degree of symmetry between aromatic structured benzene and phenyl group of TPP that facilitates in a transfer of electrons from benzene [26]. Such symmetry was not favoured with acetic acid structure. At the same point of consideration, it is certain to apprehend that π - π transition for benzene and OEP peripheral site(s) is not feasible and therefore, response of SWNTs-OEP sensor for benzene is perceptibly less than SWNTs-TPP based sensor. In the OEP structure, ethyl groups, being electron releasing in nature, might release electrons to adjacent carbon atom(s); thereby eight electron deficit sites are being created in outer porphyrin ring. Structural alignment is therefore favourable at 'ethyl' sites of OEP with 'methyl' sites of acetic acid, facilitating electron donation from methyl to electron deficit sites in OEP ring. Such differences in electron accepting ability of porphyrin(s), based on the peripheral substituent(s) present, have certainly drafted the affirmative behaviour towards the analytes. Schematic representation of the hypothesized mechanism is depicted in Fig. 6.

4.6. Chemiresistive sensing characteristics

For real-time analysis, sensors were subjected to various concentrations of benzene and acetic acid separately. Requisite concentrations of analytes were prepared by diluting them in base gas (N_2), while the cumulative flow rate was kept constant at 200 sccm. Channel current (I_D) was monitored, as a function of increasing concentration of analyte, at constant gate to source voltage (V_{GS} ; -16 V) and drain to source voltage (V_{DS} ; -1 V). Instantaneous device resistance(s) were finally calculated by Ohm's law [27]. At least 5 devices were validated in each case for studying device-to-device variation. Real-time response transients are furnished in Fig. 7 (a) and (b).

The response (~ 9 s to 35 s for OEP-SWNTs sensor and ~ 16 s to 36 s for TPP-SWNTs sensor through entire concentration range; IUPAC standard) and recovery (~ 13 s to 38 s for OEP-SWNTs sensor and ~ 7 s to 42.5 s for TPP-SWNTs sensor through entire concentration range; IUPAC standard) signature was clear and rapid for the sensors. The most significant part of real time sensing study lies with the fact that – i) TPP based sensor exhibited distinctly higher values of changes in normalized resistance for benzene in

comparison to acetic acid atmosphere and ii) the reverse condition was affirmed for OEP based sensor; that well distinguished the difference between behaviour of the sensors for the analytes. Linear regression fits (Fig. 7; c and d) to estimate the linear relationship between analyte concentration and sensor response show a sensitivity of $\sim 7.1\%$ for benzene (in contrast to 5.0% for acetic acid) for SWNTs-TPP sensor whereas; SWNTs-OEP sensor could be characterized with $\sim 8.2\%$ sensitivity for acetic acid (in contrast to 5.1% for benzene). Measure of goodness-of-fit of the linear regression, R^2 , was calculated to be 0.99 for SWNTs-TPP sensor in benzene atmosphere and 0.98 for SWNTs-OEP sensor in acetic acid environment. The regression plots and the overall comparative performance of the fabricated devices (Fig. 7; c and d) reflected highly trivial device to device variation. Fig. 8 shows response of the sensor(s) under 5 ppm concentration of benzene, naphthalene, anthracene, acetic acid, formic acid, and propionic acid where the sensors were observed to maintain the characteristic trend.

Effect of humidity on the fabricated sensor has been studied and given in Fig. S1 and Fig. S2 of ESI. It has been observed that SWNTs-OEP sensor were able to retain the characteristics up to $\geq 90\%$ RH value for OEP based sensor (Fig. S2; ESI), while complete deterioration could be observed at around 100% RH value. The TPP based sensor lost its stability for 90% RH value (Fig. S1, ESI). This clearly implies that porphyrin based SWNTs sensors have stable response in moderate humid atmosphere. It can be well concluded that the fabricated sensors show stable performance and exhibit good sensing characteristics for aliphatic and aromatic group of compounds.

5. Conclusion

To summarize, we have fabricated porphyrin functionalized SWNTs sensors with predictive control on their selective behaviour where porphyrin side rings have been successfully exercised to achieve said selectivity, after consideration of the structural signature of the validated analytes. The findings suggest a potential direction towards real time selective sensor arrays; however, a better inventory of data is warranted. The chemFETs developed in course of the study demonstrated selective, reproducible and reversible sensing behaviour with good sensitivity for benzene and acetic acid at room temperature and at concentration down to 1 ppm.

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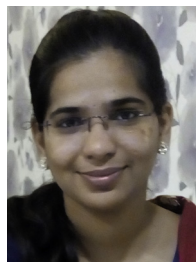
Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.snb.2017.10.147>.

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