

# Composites of ion-in-conjugation polysquaraine and SWCNTs for the detection of H<sub>2</sub>S and NH<sub>3</sub> at ppb concentrations

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## Abstract

Several different methods are established for the analysis of gases, including optical spectroscopy, photoacoustic spectroscopy as well as colorimetric and resistive sensing, the measurements systems are either too complex or have limited sensitivity. In particular, when the goal is to apply a large number of sensors in networks, it is highly desirable to have devices that are simple, have low cost and energy consumption, yet sensitive and selective to monitor analytes even in traces. Herein, we propose a new type of resistive sensor device based on a composite of single-wall carbon nanotubes and an ion-in-conjugation polymer, poly(1,5-diaminonaphthalene-squaraine), capable of detecting H<sub>2</sub>S and NH<sub>3</sub> in air even at room temperature with a theoretical concentration limit of ~1 ppb and ~7 ppb, respectively. Density functional theory calculations revealed that H atoms of the analytes and O atoms of the polymer chain interact and form hydrogen bonds, and the electron withdrawal from the gas molecules by the polymer chain results in the change of its electrical conductivity. To demonstrate the feasibility of the new nanocomposites in sensing, we show the devices for monitoring food safety with good sensor stability of operation for at least 3 months of period of time.

Keywords: H<sub>2</sub>S/NH<sub>3</sub> gas sensors, ion-in-conjugation polymers, polysquaraine, tunneling composites, food quality monitoring

## 1. Introduction

H<sub>2</sub>S and NH<sub>3</sub> are important reactants of chemical processes. For instance, H<sub>2</sub>S is applied in large quantities in oil refinery for catalyst regeneration in hydrodesulfurization, in Kraft paper pulping process, and in mining industry for precipitating

metal cations;[1] whereas NH<sub>3</sub> is an indispensable platform chemical used for the production of e.g. nitric acid, fertilizers and organic amines.[2] On the other hand, these gases are also unpleasant concomitants of microbial decomposition of proteins, and are present in sewage systems, biogas and waste management plants, farms, as well as in food processing and storage facilities.[3-5] Since both gases are corrosive, highly

flammable, can irritate the eyes and the respiratory system (at 2 ppm and 50 ppm), can be even lethal (at 600 ppm and 5000 ppm, respectively for 5 min inhalation),[6-12] and their presence in foods (together with organic sulfides and amines) can indicate spoilage, detecting and monitoring such analytes have great economic value and play important role in environmental and health safety.

Gas sensors are ubiquitous in health, environmental, transport, infrastructure and industrial safety with continuously growing number of devices due to the expansion of Internet-of-Things. The ultimate gas sensors are sensitive, selective; and preferably reversible, have long operation life, free of critical elements, and recyclable or at least pose no risk when disposed.[13-15] A large variety of gas sensors exist today including for instance resistive, pellistor, chemical and photogated field-effect transistor, gas ionization device, as well as infrared and photoacoustic spectroscopy based measurement systems among many others.[16-20] Each of these aforementioned technologies has its benefits and disadvantages, however, when it comes to low cost, simplicity, and feasibility to connecting several devices into networks, probably resistive sensors are the most promising candidates among all. Resistive chemical sensing of H<sub>2</sub>S and NH<sub>3</sub> has been studied for several materials such as metal oxides,[21-23] metal sulfides[24, 25], carbon nanotubes[26, 27] and graphene;[28-30] however, CNTs and graphene based sensors typically lack selectivity and good recovery, whereas metal oxides work at elevated temperatures. Although layered 2-dimensional metal sulfide-based sensors hold promise owing to their low temperature operation and high sensitivity, the used transitional metals require proper recovery after the end of life of the devices to maintain long term sustainability and environmental safety.

In the recent years, organic semiconductor materials started to attract research interest in resistive gas sensing due to their large molecular diversity, low cost, good mechanical flexibility, potentially high chemical selectivity and operation at room temperature. Although their versatile chemistry and adjustable microstructure offer great freedoms to tune their intrinsic electrical properties and selective interaction with particular analytes,[31-40] only very few materials families have been reported so far. Like for other resistive gas sensors, the sensing performance of organic materials depends largely on the charge transfer from the interaction between analytes and the polymer. The interactions may occur on the surfaces of organic thin films but also in their bulk in case the polymer is porous and/or easily permeable with the gas. The specificity and strength of such noncovalent interactions (hydrogen bonding,  $\pi - \pi$  stacking and van der Waals forces) determine the variation of carrier density (and indirectly, the type of carrier transport) in the polymer, and thus play critical role in gas sensing.[41, 42] On the one hand, too weak dispersion forces result in poor charge transfer and consequently poor

sensitivity and selectivity of the sensor. On the other hand, too strong interactions limit desorption of analytes and can irreversibly alter the chemical structure and electrical properties of the polymer.[40, 43, 44] Therefore, a moderately strong reversible bonding between the gas molecules and sensory materials is critical for good sensing performance. In this regard, squaraines that are resonance-stabilized zwitterionic (N<sup>+</sup> and O<sup>-</sup>) structures composed of a squaric ring and an arylamine can offer ideal chemical sensing platforms. Such an ion-in-conjugation structure can form hydrogen bonds but also ion-dipole interactions of medium strength when exposed to target gases.[45-47] Any charge transfer between the gas molecules and the conjugated ion group of squaraine can modulate both the electronic density and shape of the potential well populated by the delocalized electrons thus influencing the local electrical conductivity in nanoscopic volumes of the polymer. However, as the major conduction mechanism in organic semiconductors (and also in squaraine) is charge hopping, the conductivity of the polymers is typically low, and the gas stimulus induced change in the transport is quite limited.[38] To overcome limitations of hopping based carrier transport, a plausible approach is the application of conductive nanomaterial fillers (e.g. metal nanowires, carbon nanotubes, graphene, MXenes) in the polymer host to form composites. Furthermore, the addition of fillers can increase the number of interacting sites with the analytes, increase mobility of charge in organic semiconductor or even enhance the affinity of the composite for gas analytes.[44, 48, 49]

Therefore, in this work, we synthesize and explore a new polysquaraine (PDNS, poly(1,5-diaminonaphthalene-squaraine)) and its composites with single-wall carbon nanotubes (SWCNTs) to detect gas analytes at room temperature in chemiresistor-type sensing. The devices based on PDNS-SWCNT composites with optimized composition were able to detect H<sub>2</sub>S and NH<sub>3</sub> at a calculated theoretical limit of ~1 ppb and ~7 ppb, respectively, while showing no any response to H<sub>2</sub>, CO and CH<sub>4</sub>, and only very small to NO. Devices tested for over 3 months proved to have excellent gas response with good repeatability and stability, and were shown to be feasible for monitoring changes of food quality upon storage. Furthermore, we performed simulations to reveal the interaction and charge transfer between the polymer and analytes.

## 2. Materials and Methods

Materials and characterization: Single wall carbon nanotubes (SWCNTs), 1,5-diaminonaphthalene, squaric acid, n-butanol and acetone were ordered from Sigma Aldrich. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Fisher Scientific Escalab 250 XI system with an Al K $\alpha$  source. Raman spectra was performed by Horiba Jobin-Yvon Labram HR800 UV-vis  $\mu$ -Raman

instrument ( $\lambda=448$  nm excitation). The thermal gravimetric analysis (TGA, Setaram Labsys) was carried out with a 10 °C/min from room temperature to 800 °C. The microstructure of the synthesized material was studied by field-emission scanning electron microscopy (FESEM, Zeiss ULTRA plus). Infrared spectra were recorded on a Bruker Vertex 70 FT-IR unit in transmission mode. Samples were homogenized in KBr matrix and measured against a pure KBr background.

Synthesis of poly(1,5-diaminonaphthalene-squaraine) (PDNS): 1,5-diaminonaphthalene 790 mg (5 mmol) and squaric acid 570 mg (5 mmol) were dissolved in 35 mL n-butanol in a flask. The mixture was then refluxed and stirred at 120 °C for 16 h. After being cooled to room temperature, the mixture was filtered and washed using acetone and deionized water 10 times. The obtained PDNS was dried in an oven at 80 °C for 24 h. The product was obtained as a dark green powder.

Preparation of PDNS/SWCNT composites: SWCNT and PDNS with mass ratios of 2, 5, 10, 20, 50 and 70 wt% (noted as PDNS-1, PDNS-2, PDNS-3, PDNS-4, PDNS-5 and PDNS-6 respectively) were dispersed in 5 ml ethanol separately using ultrasonication for 1 h and then mixed and stirred for another 1 h at room temperature. Finally, the composite was collected by vacuum filtration.

Sensor preparation and measurements: 20 mg of composite was mixed with 0.5 mL of absolute ethanol to form a paste, which was then brush-coated onto an Al<sub>2</sub>O<sub>3</sub> substrate (14 mm × 7 mm) printed with five pairs of Ag-Pd interdigitated electrodes (both electrode distance and width were 200 μm) to form a film, and dried at 70 °C for 2 h. The change of sensor

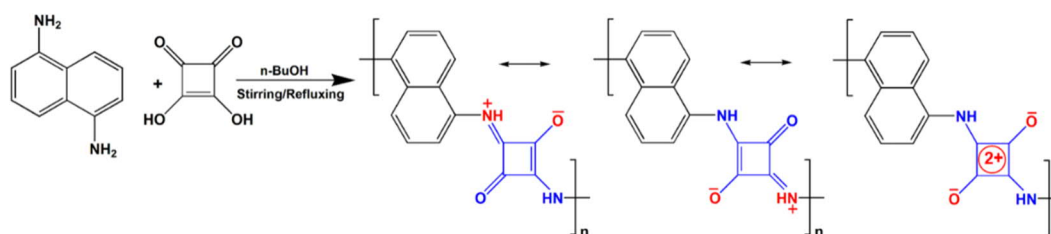
resistance was monitored in a Linkam THMS600 heating and freezing stage connected to an Agilent 3458A multimeter at 5 V of constant bias. Different concentrations of H<sub>2</sub>S, NH<sub>3</sub>, NO, CH<sub>4</sub>, CO and H<sub>2</sub> were set by LabView driven mass flow controllers. Dry synthetic air (AGA, 20.9% O<sub>2</sub> and 79.1% N<sub>2</sub> at a purity of 5.0) was used as a carrier to dilute these gasses to the desired concentrations and the operating temperature was maintained at near room temperature (30 °C). Exposure periods of 10 min gas pulses, and purging for 30 min between each pulse were applied. The total gas flow rate was set to 500 mL/min in each experiment. Sensor response is calculated as  $(R_g - R_0)/R_0 \times 100\%$ , where  $R_g$  and  $R_0$  are the resistance of the sensors with and without gas exposure.

Density functional theory calculations (DFT) were performed based on GGA-UBLYP/DNP implemented in DMol3 code. Intermolecular weak interactions were semi-empirically corrected by Tkatchenko-Scheffler scheme.[45] Different adsorption modes were optimized until converging within a criteria of  $1 \times 10^{-5}$  eV in energy and 0.02 eV/Å in residue force. The Hirshfeld partitioned scheme was applied to analyze charge populations.

### 3. Results and discussion

#### 3.1 Materials properties

PDNS was synthesized through the condensation between squaric acid (SA) and 1,5-diaminonaphthalene in equimolar ratio in n-butanol under reflux for 16 h.[51] The zwitterionic resonance structure is shown in **Figure 1**.



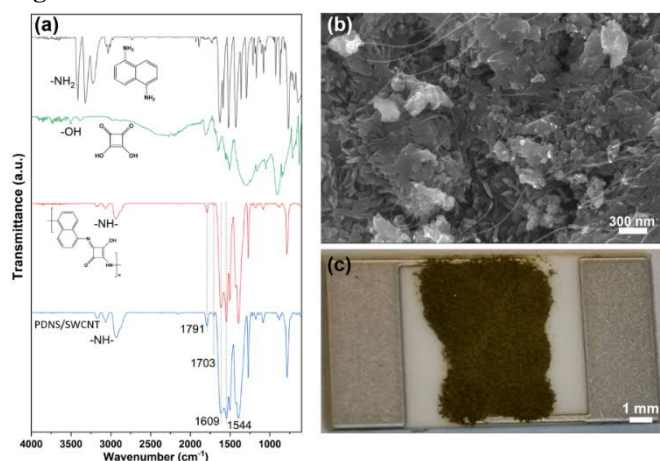
**Figure 1** Synthetic route of PDNS, and the scheme of its zwitterionic resonance structure.

Fourier-transform infrared spectroscopy (FTIR) of the product and the reactants in **Figure 2a** shows the -NH<sub>2</sub> and -OH stretches of reactants disappear and new peaks of -NH-stretching emerges in the product indicating the successful reaction of 1,5-diaminonaphthalene and squaric acid, i.e. the formation of PDNS. The characteristic strong absorption peak at 1609 cm<sup>-1</sup> in PDNS is a result of the zwitterionic resonance of the cyclobutene 1,3-diolate anion moiety. The peak at 1544 cm<sup>-1</sup> originates from the C=C stretching vibrations of four-membered ring. A small peak at 1791 cm<sup>-1</sup> is assigned to the ring breathing of the cyclobutene, and the peak at 1703 cm<sup>-1</sup> means the small amounts 1,2-squarate repeat unit in the polymer chain.[52, 53] Since the intrinsic electrical conductivity of PDNS was found rather small (out of the

measurement limit of our setup), we dispersed SWCNTs on the nanoplate shaped PDNS particles (**Figure 2b**) with different mass ratios from 2 to 70 wt% and then dispensed the powders onto ceramic chips having printed Ag-Pd interdigital electrodes to form resistive chemical sensor devices (**Figure 2c**). According to the FT-IR spectra, the addition of SWCNTs to PDNS does not change the chemical structure.

X-ray photoelectron spectra reveal the N 1s of 1,5-diaminonaphthalene at 398.6 eV, which shifts to ~400 eV and can be resolved with two peaks at 399.8 and 400.2 eV after the reaction with squaric acid indicating the presence of -NH- [54] and -N<sup>+</sup>H= [55] groups in the polymer chain, respectively (**Figure S1a**). The Raman spectrum of PDNS lacks any peaks i.e. the polymer is amorphous, whereas in the composite we

find the characteristic radial breathing mode (RBM) as well as in-plane (G) and out-of-plane (D) vibration modes of SWCNTs (**Figure S1b**). Thermogravimetric analysis (TGA) of the samples indicates high thermal stability of both PDNS and the PDNS/SWCNT composite with an onset of 5% weight loss at 272 °C and 262 °C, respectively (**Figure S1c**). The SWCNTs are well dispersed in the composite as illustrated by scanning and transmission electron micrographs shown in **Figure S2**.

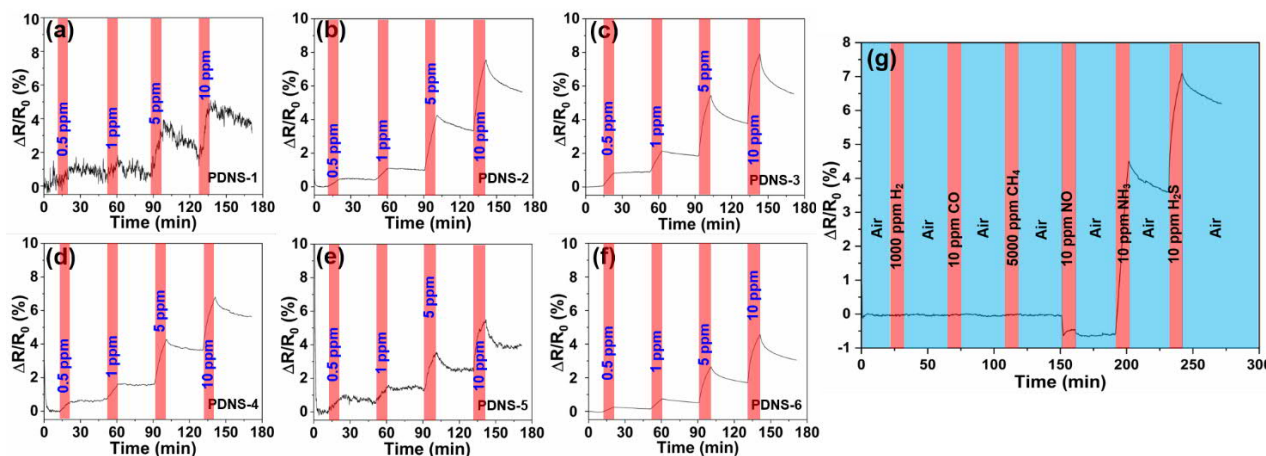


**Figure 2** (a) FT-IR spectra of reactants, PDNS and the composite of PDNS/SWCNT. (b) SEM image of the

composite and (c) optical picture of the sensor chip with brush coated composite.

### 3.2 Gas sensing properties

Based on results of preliminary gas exposure experiments,  $\text{NH}_3$  was found to induce the highest sensor response, thus we selected this analyte to optimize the composition of the sensing material. Composites of SWCNTs and PDNS with 6 different mass ratios (2, 5, 10, 20, 50 and 70 wt%, noted as PDNS-1, PDNS-2, PDNS-3, PDNS-4, PDNS-5 and PDNS-6) were prepared, and their sensing performance towards  $\text{NH}_3$  (from 500 ppb to 10 ppm) buffered in synthetic air were measured. The resistance of composites increases as exposed to  $\text{NH}_3$  suggesting p-type semiconducting behavior. The response of sensors shown in **Figure 3(a-f)**, were found to be the largest for PDNS-3 (1.2 to 2.1-fold compared to other composites with different SWCNT concentrations, as displayed in **Figure S3**) thus we continued our study using the PDNS-3 composite. Screening of sensors to various analytes showed high response for  $\text{H}_2\text{S}$  and  $\text{NH}_3$ , very moderate for  $\text{NO}$ , and practically no any for  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CH}_4$ . The increased resistance upon exposure to the reducing  $\text{H}_2\text{S}$  with a similar trend to the also reducing  $\text{NH}_3$ , and decreased resistance on the oxidizing  $\text{NO}$  gas confirming the p-type semiconducting behavior of the composite (**Figure 3g**).



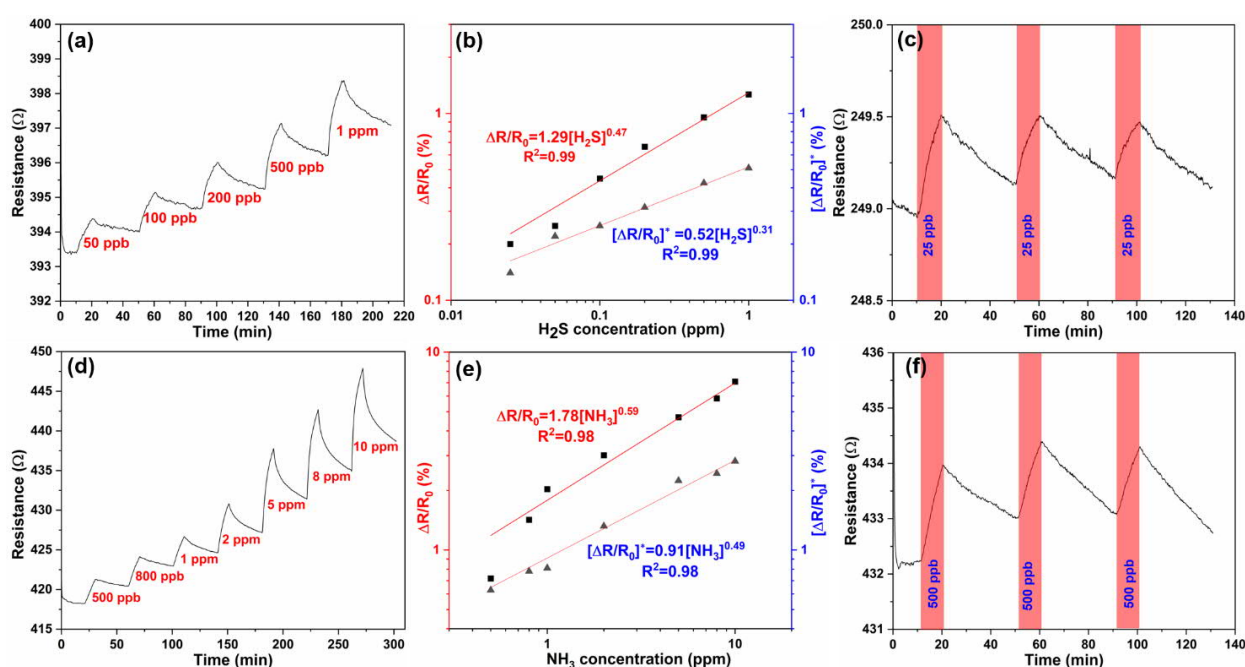
**Figure 3** Transient responses curve of sensors based on PDNS-SWCNT composites with SWCNT concentrations of (a) 2 wt.%, (b) 5 wt.%, (c) 10 wt.%, (d) 20 wt.%, (e) 50 wt.% and (f) 70 wt.% measured for  $\text{NH}_3$  at concentrations of 500 ppb, 1 ppm, 5 ppm, and 10 ppm. (g) Gas response of PDNS-3 composite (10 wt.% SWCNT) to various analytes in air buffer.

Because of the high response to  $\text{H}_2\text{S}$  and  $\text{NH}_3$ , we elaborated the measurements using these gases at concentration from 25 ppb to 1 ppm and from 500 ppb and 10 ppm, respectively. The change of sensor resistance upon the gas pulses in air buffer at the applied analyte concentrations (i.e. the  $R(c)$  curves) are well defined as shown in **Figure 4(a) and (d)**. Based on these  $R(c)$  curves, we calculate the responses of the sensors using two methods (**Figure S4**). In the first, we use the initial sensor resistance  $R_0$  to normalize

the change of resistance, i.e.  $(R_g - R_0)/R_0$ , whereas in the other, we consider also the background drift  $(R_g - R_0^*)/R_0^*$ . Now, by plotting both types of response data for both  $\text{H}_2\text{S}$  and  $\text{NH}_3$  as a function of analyte concentrations, we find the obtained calibration curves are nonlinear and follow power functions with fractional exponents similar to those for heterogeneous adsorption (Freundlich model) as displayed in **Figure 4(b) and (e)**. Accordingly, the highest sensitivity values appear at low analyte concentrations, and are  $1.3\% \text{ ppm}^{-1}$  for  $\text{NH}_3$  and

8.2% ppm<sup>-1</sup> for H<sub>2</sub>S. Experiments with gas mixtures show that analytes inducing small sensor response (H<sub>2</sub>, CO or CH<sub>4</sub>) are not influencing the response either when introduced in the gas chamber simultaneously with H<sub>2</sub>S or NH<sub>3</sub>. On the other hand, NO that causes small but opposite sensor response as compared to the other analytes in single analyte experiments, changes the sensor response considerably, when introduced together with H<sub>2</sub>S or NH<sub>3</sub>. We hypothesize that NO having oxidizing character, reacts with or helps in repelling the adsorbed H<sub>2</sub>S or NH<sub>3</sub> from the surface thus *resetting* the sensor. It is also interesting to note that adding a short pulse of 1 ppm NH<sub>3</sub> to a long pulse of 1 ppm H<sub>2</sub>S (or vice versa) the responses are superposed on each other (both gases increase resistance in a similar degree), which means that the composite cannot distinguish these two gases from each other (Figure S5).

Reproducibility is a critical key performance indicator of gas sensor operation. As shown in Figure 4 (c) and (f) (and in Figures S6 and S7), repeated gas pulses produce nearly identical responses. The slight baseline drift and not entirely complete recovery of the sensors within the time periods (30 min) between subsequent pulses can be relieved by increasing the operating temperature (Figure S8) or by applying higher flow rates of the flushing gas after the analyte pulses (Figure S9).[56] The noise of the  $R(t)$  curves is visibly low, which is due to the improved conductivity of the composite. Consequently, the theoretical limit of detection, which is calculated from the root-mean-square deviation of base line data and the sensitivity of the sensor (Figure S10), as low as 7.4 ppb for NH<sub>3</sub> and 0.8 ppb for H<sub>2</sub>S.[57] Such values are lower than those reported for most other sensing materials as listed in the Tables S1 and S2.

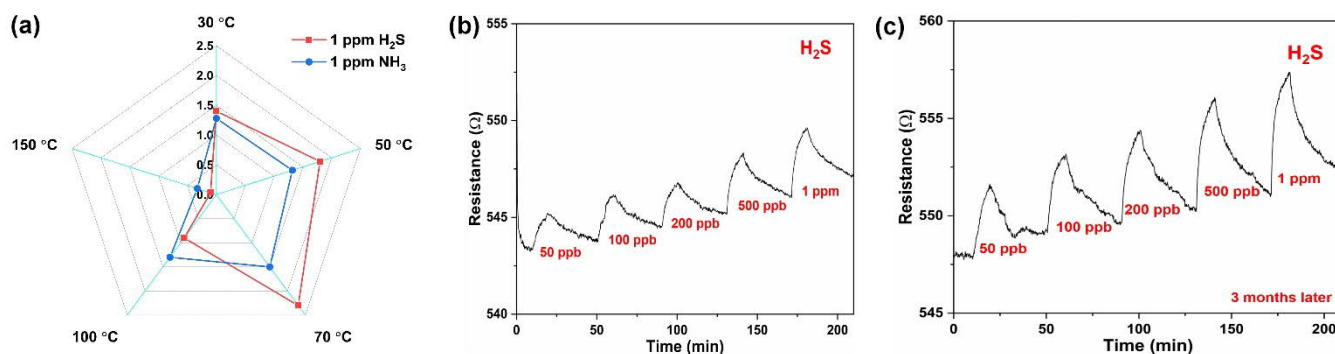


**Figure 4** Transient gas response curves of PDNS-3 for the detection of (a) H<sub>2</sub>S from 50 ppb to 1 ppm, and (d) NH<sub>3</sub> from 500 ppb to 10 ppm with their corresponding plots of the responses and calibration curves in panels (b) and (e). Repeatability of response curves measured for (c) 25 ppb H<sub>2</sub>S and (f) 500 ppb NH<sub>3</sub>.

To study the effect of operating temperature on the sensing performance, we analyze the response for 1 ppm H<sub>2</sub>S and NH<sub>3</sub> also up to 150 °C [Figure 5a]. The response of the sensors slightly improves with the increase of the working temperature and after an optimum at 70 °C it decreases. The presence of an optimum operation temperature indicates that several events compete with each other and influence the mechanism of sensing. Usually, increased temperatures cause higher charge transfer efficiency at interfaces, and also help gas molecules diffusing deeper into the bulk of the sensing material [58,59] thus influencing the sensor

response/operation. On the other hand, too high temperatures may compromise adsorption of analytes and interaction of the active sites with those thus reducing the sensitivity [60]. Besides, the recovery of the sensor at 70 °C is better than that at 30 and 50 °C, which is reasonable considering the favored analyte desorption process upon flushing with the carrier gas.[61] Furthermore, as shown in Figure 5b and c, the sensors have good long term stability measured for over 3 months periods indicating the feasibility of the devices for practical applications.



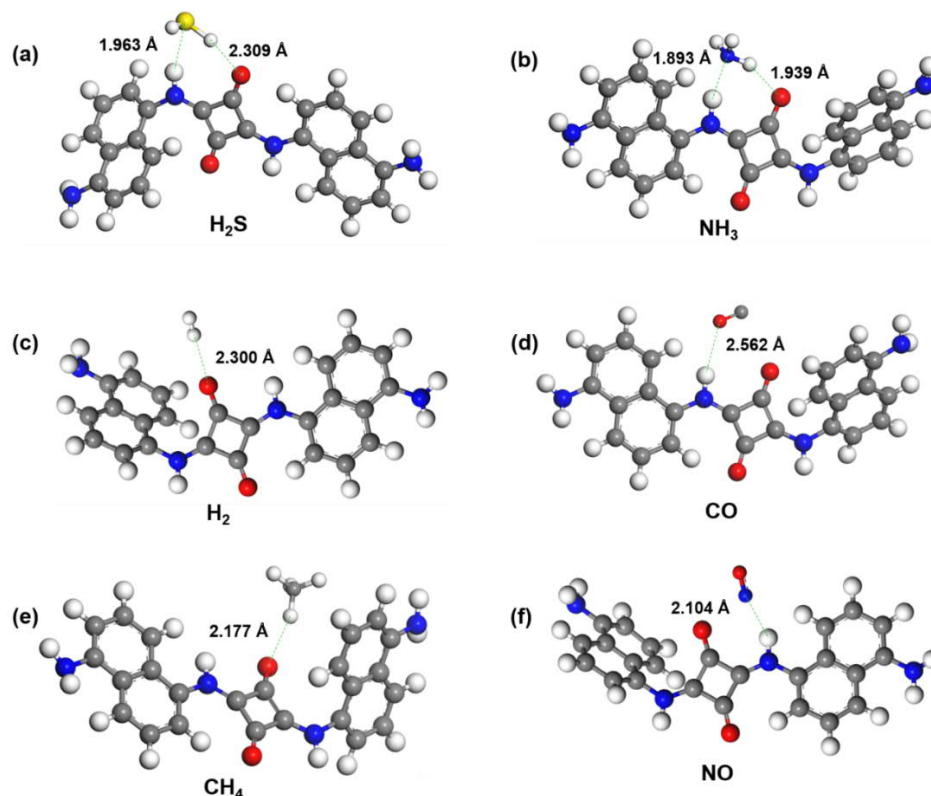


**Figure 5** (a) The temperature effect on the sensing response (%). (b) Sensor response for H<sub>2</sub>S, and (c) repeated measurement after 3 months of storage in air.

### 3.3 Mechanism of sensing

To study the mechanism of sensing with our composite, we assessed the adsorption sites, binding positions and energies of analytes on PDNS (employed by using one repeat unit in PDNS chain) using DFT calculations, and then estimated the degree of the eventual charge by applying the Hirshfeld scheme. Several different adsorption models of H<sub>2</sub>S and NH<sub>3</sub> on PDNS chain were surveyed and listed in **Figure 6a, b** and **Figure S11**. According to the various possible adsorption modes, the ones with hydrogen bonding were showing the largest binding energies with 0.53 eV for H<sub>2</sub>S and 0.71 eV for NH<sub>3</sub>. Therefore, we may assume that upon exposure of PDNS to H<sub>2</sub>S or NH<sub>3</sub>, the O and H atoms of the amide in the polymer

chain act as active sites, which form double hydrogen bonds with H and S atoms of H<sub>2</sub>S (or sulfide) or with N and H atoms of NH<sub>3</sub> (or amine). The moderate adsorption energy of NO (0.34 eV) and the very weak binding with H<sub>2</sub> (0.05 eV), CO (0.12 eV) and with CH<sub>4</sub> (0.07 eV) seem to correlate reasonably well with the observed experimental sensor response to these gases (**Table 1**). It is worth noting here that NO forms a single H-bond, which can also explain the moderate sensor response to this analyte. Furthermore, one may speculate that the Lewis acid/base character of the reactants plays a role in the sensing mechanism viz. both H<sub>2</sub>S or NH<sub>3</sub> can be considered as Lewis bases donating their dative electron pairs to the polymer, whereas NO as an acid acts oppositely in qualitative agreement with the sensor response data.



**Figure 6** Simulated adsorption of (a) H<sub>2</sub>S, (b) NH<sub>3</sub> (c) H<sub>2</sub>, (d) CO, (e) CH<sub>4</sub> and (f) NO on PDNS.

Apart from the intrinsic gas sensing behavior of the polymer, carbon nanotubes present in the composites can also contribute to sensing in several ways. Firstly, CNTs themselves can detect  $\text{NH}_3$  [62] and somewhat  $\text{H}_2\text{S}$  [63] and  $\text{NO}$ . [64] Secondly, in the PDNS-SWCNT composite, the nanotubes can extend the local electric field induced by the adsorbed analytes in the polymer. Thirdly, electrical transport across the tunneling junctions between adjacent SWCNTs in the percolating network may be influenced by the adsorbed moieties on the polymers. In a simplified picture, the tunneling barrier for electrons depends on the position of the LUMO (and for holes on the HOMO) level of the polymer, which shifts upon gas adsorption, consequently changes the tunneling probability. This effect can be significant, since the probability of tunneling [65] through the junction ( $P$ ) is an exponential function of the barrier height ( $\Phi$ ) as  $P = e^{-2d\sqrt{2m\Phi}/\hbar}$ , where  $d$  is the width of junction and  $m$  is the mass of electrons. [66-69]

**Table 1** The bonding length, binding energies and charge transfer of different analytes adsorbed on PDNS

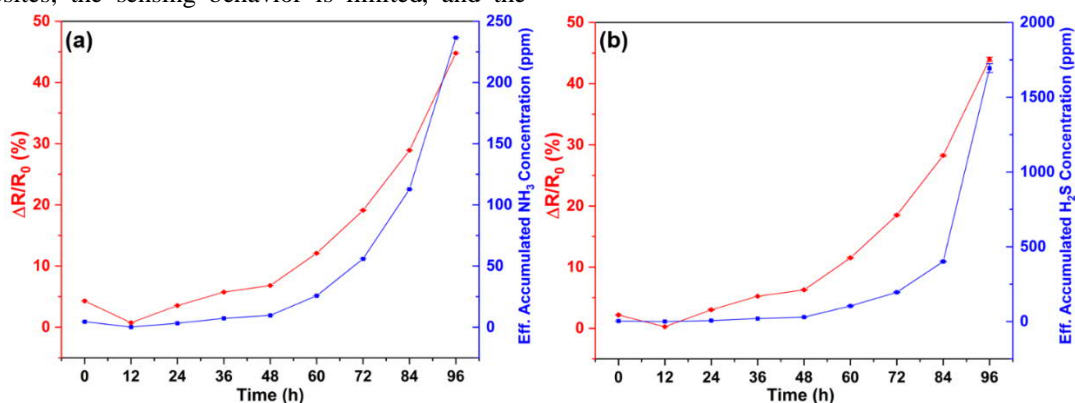
Analyte	Bonding length (Å)	Binding energy (eV)	Charge transfer ( $e^-$ )
$\text{H}_2\text{S}$	1.96/2.31	<b>0.53</b>	0.03
$\text{NH}_3$	1.89/1.94	<b>0.71</b>	0.08
$\text{H}_2$	2.30	0.05	0.05
$\text{CO}$	2.56	0.12	0.02
$\text{CH}_4$	2.18	0.07	0.07
$\text{NO}$	2.10	0.34	0.05

It is important to note here, that SWCNTs added in too high concentration in the composite reduce the gas sensitivity of the sensors (in our case, above 10 wt.%), since direct electronic transport is enabled through well-percolated 3-dimensional networks of highly conductive metallic nanotubes, which practically shunt the highly resistive tunneling junctions. In such composites, the sensing behavior is limited, and the

mechanism is expected to be close to those in pristine and polymer decorated or functionalized CNT networks. To demonstrate the extreme condition, we measure sensing with sensors based on purely SWCNT networks (**Figure S12**), whose gas response is clearly inferior compared to the PDNS-SWCNT composites.

### 3.4 Sensor application

The freshness of foods with protein content may be monitored by analyzing their decomposition products such as volatile amines and sulfides in the headspace of packaging. Since our sensors have proven to be suitable for detecting  $\text{NH}_3$  and  $\text{H}_2\text{S}$  in minute concentrations, we assess whether or not any sensor response would be visible upon measuring the headspace of containers having meat in those (**Figure S13**). Since our sensor material detects both  $\text{NH}_3$  and  $\text{H}_2\text{S}$ , which are expected to coexist upon meat degradation, the headspace of the container we apply desiccants to eliminate either of the decomposition products. Namely, to detect  $\text{NH}_3$  (and amines) pastilles of  $\text{NaOH}$  are applied to adsorb and react with  $\text{H}_2\text{S}$ , whereas for the detection of  $\text{H}_2\text{S}$  (and sulfides) powder of  $\text{P}_2\text{O}_5$  is used to eliminate  $\text{NH}_3$ . Sensor response data collected for 4 days are compared to the corresponding calibration curves shown in Figure 4 to estimate the concentrations of the decomposition products (**Figure 7**). The results suggest that after closing the container, a stabilization period of 12 hours is needed, after which the resistance is gradually increasing. After 48 hours, the increase of sensor response is pronounced for both types of setups, which indicates that the concentrations of both  $\text{NH}_3$  (and amines) and  $\text{H}_2\text{S}$  (and sulfides) have become significantly elevated from 0.8 to 2.2 ppm per gram meat for  $\text{NH}_3$ , and 2.1 to 8.3 ppm per gram meat for  $\text{H}_2\text{S}$ . After 4 days, the concentration of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  are 70 times and 163 times of that compared to the 0 day, respectively.



**Figure 7** (a) The effective  $\text{NH}_3$  and (b)  $\text{H}_2\text{S}$  produced in the storage process of pork at room temperature. The error bars are the standard error of three parallel measurements.

## 4. Conclusions

A new polysquaraine, poly(1,5-diaminonaphthalene-squaraine) was synthesized and compounded with single-wall carbon nanotubes to explore its resistive gas sensing properties. Sensors with optimized polymer to nanotube ratio were found to be highly sensitive H<sub>2</sub>S and NH<sub>3</sub> with a theoretical limit of detection of ~1 ppb and ~7 ppb, respectively, while showing practically no any response to H<sub>2</sub>, CO and CH<sub>4</sub>, and only very small to NO. The experimental results are supported well with DFT simulation data suggesting double hydrogen bonding formation between the polymer chain and NH<sub>3</sub> or H<sub>2</sub>S. The demonstrated devices showed good stability for at least 3 months of testing period, and proved to be suitable for monitoring the decomposition products of proteins in food packages upon storage.

Our results support previous findings [45-47, 70] on the highly sensitive nature of polysquaraines, and prompts the design of new polymers having ion-in-conjugation structure. Our work also indicates that the addition of conductive fillers (here SWCNTs) can sufficiently improve electrical transport thus making an even poorly conducting polymer a sensing material of practical relevance.

Furthermore, preliminary measurements in gas mixtures show that H<sub>2</sub>, CO or CH<sub>4</sub> are not affecting the sensor response to H<sub>2</sub>S or NH<sub>3</sub>. When NO is added to H<sub>2</sub>S or to NH<sub>3</sub> it resets the sensor. On the other hand, the response to NH<sub>3</sub> added to H<sub>2</sub>S (or other way around) superposes on the other response thus it is not possible to distinguish these two gases in their mixtures. Accordingly, to fully exploit the advantageous sensing properties of the reported composites, further exploration of sensing in analyte mixtures is needed, and should be combined with systematic data processing e.g. principal and multi-component analyses, pattern recognition and machine learning [71-74].

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