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Project Title: Development of New Generation Gas and Vapor Sensors
Using Organic Electronics

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List of Terms and Abbreviations

FET = Field Effect Transistor

OFET = Organic Field-effect transistor

OSCs = Organic Semiconductors

PET = polyethylene terephthalate

PQT-12 = poly (3,3''-didodecylquaterthiophene)

DPP-CN = 2,2'-[(2,5-dihexadecyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diylidene)dithiene-5,2-diylidene] dimalononitrile

Report Date: December 8, 2016

Abstract

The lack of simple, inexpensive and high throughput exposure assessment technologies has limited the ability of public health professionals to discover environmental and occupational causes of disease, and to conduct exposure assessments needed to control workplace risks. The need for the development and application of new technology to conduct exposure assessments is widely recognized by many groups including NIOSH and the National Institute for Environmental Health Sciences (NIEHS). Advances in nanotechnology and materials sciences offer unique opportunities for the development of new air sampling sensor technologies based on organic electronic circuits. Field-effect transistors are the basic building blocks for electronic circuits, and organic field-effect transistors (OFETs) are those made with organic semiconductors (OSCs). OSCs are susceptible to non-covalent interactions, trapping and doping, photoexcitation, dimensional deformation, and other mild transformations. These transformations alter the electronic input-output characteristics of the semiconductors and these changes in input-output characteristics can be used to detect and quantify the chemical and physical stimuli that cause these electronic modifications. Thus, we have designed a new platform, based on OSCs, for the construction of various types of sensors. **The long-term goal of this research was to develop inexpensive, compact, sensitive and reliable gas/vapor sensors using organic materials technology.** In this application, as a proof of concept, we developed a sensor that is able to detect low concentrations of ammonia for a variety of occupational and environmental applications. We used a novel OFET-based technology to develop these ammonia sensors as a proof of concept. These circuits can be made from a variety of materials with specific chemical interactions with environmental agents. To our knowledge, this is the first time this technology is applied to the development of air sampling sensors. For **Specific Aim 1** we investigated a range of organic materials that can be incorporated into OFET sensors for their response to ammonia. We selected the optimal materials and developed the printed circuit sensors for further testing. In **Specific Aim 2** we integrated multiple sensitive OFETs developed in Aim 1 into higher order circuits for synergistic responses, increasing sensitivity and specificity to ammonia, and ultimately other nitrogen containing compounds (e.g. aromatic amines, nicotine). In **Specific Aim 3** we conducted laboratory validation and characterization of the OFET samplers developed in Aims 1 and 2 using a small bench scale apparatus and **Specific Aim 4** consisted of a field validation of the samplers. The field tests revealed a fundamental flaw with the final prototype. The current change of a single device in response to interfering humidity is on the order of 5% for 40% humidity, but the interference from water vapor is comparable to the ammonia response at 70% humidity. We have secured funding to address this flaw and finalize a functioning prototype.

Section 1 (2-page limit)

Significant findings

For **Specific Aim 1** we investigated a range of organic materials that can be incorporated into OFET sensors for their response to ammonia, and we selected two optimal materials and developed the printed circuit sensors. A manuscript was published detailing the results.

In **Specific Aim 2** we integrated multiple sensitive OFETs developed in Aim 1 into higher order circuits for synergistic responses, increasing sensitivity and specificity to ammonia, and ultimately other nitrogen containing compounds (e.g. aromatic amines, nicotine). Two manuscripts describe the findings in detail.

In **Specific Aim 3** we conducted laboratory validation and characterization of the OFET samplers developed in Aims 1 and 2 using a small bench scale apparatus. Details are also reported in the manuscripts.

Specific Aim 4 consisted of a field validation of the samplers. Unfortunately, the field validation tests were not successful because of lack of time to build an adequate platform. We have obtained seed money from our university to finish this task.

Translation of findings

While the new sensor is able to detect ammonia concentrations for shorter periods of time and at lower concentrations than current technology allows, we were unable to have a prototype ready for production and mass field testing that can be deployed in new epidemiology studies.

Our sensor will be very useful for assessment of exposure to ammonia used in industrial processes, including primary ammonia production, as a feed chemical in the production the manufacture of fertilizers, cleaning agents, and pharmaceuticals. (Ammonia is one of the largest production volume chemicals with more than 130,000,000 metric tons produced worldwide in 2009 (DiFrancesco, et al.,2010)). However, where we foresee our sensor being most useful is for assessing worker exposures in industrial-scale animal handling facilities (such as feedlots and poultry-confinement buildings), who are at risk for ammonia exposure at lower, yet concerning levels of exposure due to decomposing animal waste (urine and feces). Farm workers can also be exposed to ammonia while handling or applying fertilizer. Studies of respiratory health with good exposure assessments in animal handling workers are currently lacking (Omland et al., 2002) Heederik et al., 2007). Our new ammonia sensor will therefore be a valuable addition to such future studies.

Outcomes/Impact

Currently, the exposure limit for ammonia is effectively dictated by the ammonia sensing capabilities of available technologies rather than any detailed study on the effects of lower ammonia concentrations on respiratory outcomes like asthma, severe respiratory inflammations, and other lung diseases.

We have developed a flexible and cost-efficient ammonia sensor platform with a sensitivity of 0.5 ppm and a limit of detection of 0.1 ppm that is well suited for large scale production. Devices based on two different semiconductor materials (PQT-12 and DPP-CN) give opposite responses to similar exposures to ammonia, which is essential to design a complementary logic-

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based ammonia sensor. The sensors are highly selective for ammonia over volatile organic compounds.

While developing a sensor to detect ammonia in the workplace is not novel, we have demonstrated a proof of concept for developing a whole new class of sensors that have the potential to revolutionize gas and vapor detection. With respect to ammonia, innovation comes from the fact that the new sensor is able to detect ammonia concentrations for shorter periods of time and at lower concentrations than current technology allows.

As soon as we have prototypes ready for field deployment, this technology can be deployed in new epidemiology studies designed to assess health effects of ammonia at exposure concentrations below current ammonia standards and guidelines. Potential policy changes may then be required depending on findings.

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Section 2

Scientific Report

Background: Current gas/vapor air sampling technology that draws air through a collection media where gas/vapor molecules are trapped for subsequent laboratory chemical analysis has changed little since the 1970s (1, 2). While the development of passive samplers in the 1970s made gas and vapor sampling easier and more acceptable to workers, laboratory analysis is still required for quantification in most cases. Direct reading instruments, using a range of detection techniques for quantification, including electrochemical cells, photoelectric effect, and spectrophotometry, suffer from interferences and have limits of detection that are too high for many exposure assessment applications. In addition, direct reading devices are often too large and/or expensive for mass deployment as personal samplers. The ideal personal sampler provides sensitive and specific measurements with temporal resolution. In addition, the sampler should be portable, easily deployed for area or personal sampling, and inexpensive to analyze.

In many cases the lack of simple, inexpensive and high throughput exposure assessment technologies has limited our ability to evaluate the environmental and occupational causes of disease (3).

The need for the development of new exposure assessment technology is widely recognized. One of the strategic goals of the exposure assessment cross-sector program element of the National Institute for Occupational Safety and Health (NIOSH) National Occupational Research Agenda (NORA) is to develop improved methods and tools to assess worker exposures (4). In addition, the National Institute for Environmental Health Sciences is currently funding an exposure biology research program to develop new exposure assessment technologies (5). While there have been tremendous investments and advances in medical diagnostic and biomonitoring technologies (e.g., glucose testing, genetic testing), comparable effort has not been invested in exposure assessment (1). A number of recent articles have indicated a “desperate” need to develop inexpensive and high throughput exposure assessment methods matching our ability to assess subclinical or susceptibility markers using “omics” techniques (e.g., genomics, metabolomics, etc), and that we need to invest in 21st-century exposure science to take advantage of the new generation of scientific tools developed to rapidly measure signals from cells, tissues, and organisms following exposure to chemicals (6,7).

Organic Electronics: Advances in nanotechnology and materials science offer unique opportunities for the development of new air sampling chemical sensor technologies. For the past 50 years, electronic circuits have been based on silicon and other inorganic semiconductors. Until recently, organic materials such as plastics were believed to be such poor conductors of electricity as to be considered insulators. In the late 1970’s, materials scientists first demonstrated that some plastics can be made to conduct electricity, thus opening the door to organic electronics (8). Field-effect transistors are the basic building blocks for electronic circuits, and organic field-effect transistors (OFETs) are those made with organic semiconductors (OSCs). The structure of an OFET is shown in Figure 1A. Semiconductors by design have multiple degrees of conductivity, depending on the amount of energy supplied to them. Accordingly, OFETs generally have two operating modes, OFF (Figure 1A) and ON (Figure 1B). In the OFF state, the semiconducting organic material ideally behaves electronically as an insulator, and no current will flow between source (S) and drain (D) electrode. In the ON state,

an electric field from the gate electrode induces a high charge density in the organic film, and current will flow between source and drain (9). For p-type semiconductors, these charges are positive; for n-type, they are negative. OSC films can be made fairly stable to reactive components of the atmosphere, including oxygen and water. Therefore, with proper packaging and attention to interface chemistry, OSCs are usable in various electronic components,

including organic light emitting diodes and display backplanes (10). They are also contemplated for use in more complex circuits such as radiofrequency identification tags and other complex electronic devices (9). OSCs have a number of important advantages over silicon-based semiconductors, including fabrication using solution-based processes, and compatibility with low-melting and flexible substrates. On the other hand, OSCs are susceptible to non-covalent interactions, trapping and doping, photoexcitation, dimensional deformation, and other mild and often reversible transformations. While not necessarily deactivating the devices, these transformations alter the electronic input-output characteristics of the semiconductors. Changes in input-output characteristics can be used to detect and quantify the chemical and physical stimuli that cause these electronic modifications. **Thus, OSCs are a promising platform for the construction of various types of sensors** (9). Such sensors could be endowed with highly specific functionality for well-resolved responses. One notable advantage is that OSCs can be produced using inkjet print technology, making them inexpensive to mass produce (*potentially as low as a few dollars per sensor if mass produced*).

As mentioned above, environmental contaminants (analytes) can have very specific effects on OFETs and other OSC devices. Non-covalent intermolecular associations such as hydrogen bonds and pi interactions cause attractions between analytes and OSCs that exceed simple van der Waals forces. The interactions can occur on the surfaces of OSC films, between crystallites that make up a polycrystalline OSC solid, in the free volume of OSCs that are either amorphous or intentionally supplied with flexible side chains, or at interfaces between OSCs and dielectrics or electrodes. Many analytes are dipolar, and thus induce local fields that are superimposed on the gate voltage, altering effective charge carrier mobilities. Even nonpolar analytes could conceivably alter mobility through induced dipoles and disruption of molecular packing in the OSC. Furthermore, depending on the relative positions of OSC and analyte carrier energy levels, analytes can cause the trapping of mobile carriers by localizing them on the analyte molecules, or doping by donating or extracting electrons from the OSC matrix. **The effects of doping and trapping on OSC conductivity and interfacial potential barriers can be profound, allowing for detection of analytes at low concentrations.** We (Dr. Katz' group) have explored the potential for OSCs to be used as environmental sensors in a recent publication (10).

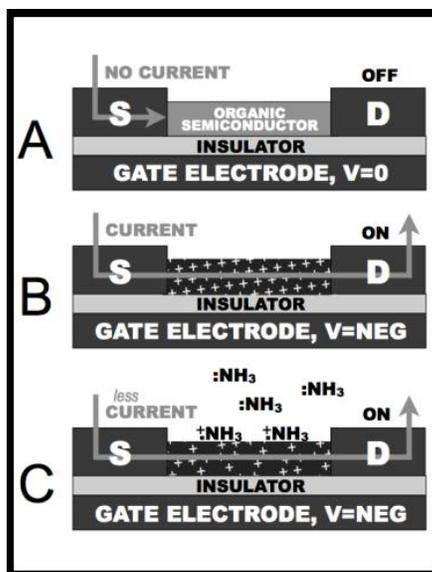


Figure1.
(A) OFET device structure in the OFF-state where no current flows between source (S) and drain (D) electrodes
(B) OFET in ON-state
(C) OFET sensing ammonia via depletion of charges resulting in less current flow

Choice of ammonia as model contaminant: Ammonia in the air is known to interact with many OSC films (11). The ionization potential of ammonia is in the range to enable it to give up electrons to positive charges in p-type materials. Higher concentrations of ammonia will quench more positive charges and lower the current. This mechanism is shown in Figure 1C. The concentration of ammonia found in the air is thus translated into a change in current that can be converted into an easily recorded and measured electrical signal. Another possible detection mechanism is *increasing* the number of *negative* charges in OSC films as discussed later in the preliminary results. Few molecules in the air have ionization potentials that could pose a threat of interference to ammonia detection in these p-type OSCs. Water or humidity is the most common interference for existing ammonia monitoring technologies. **An important benefit to our sensor materials is that the effect from humidity is negligible.** Future research will concentrate on expanding the range of analytes that can be detected.

While there are important practical reasons to start with ammonia (as mentioned above), there are numerous occupations with a demonstrated potential for ammonia exposures that could benefit from this sensor technology. Ammonia is used in many industrial processes, including primary ammonia production, and as a feed chemical in the production the manufacture of fertilizers, cleaning agents, and pharmaceuticals. Ammonia is one of the largest production volume chemicals with more than 130,000,000 metric tons produced worldwide in 2009 (12). As of 2004 there were 2,338 facilities that manufacture or process ammonia in the United States (13). According to the National Occupational Exposure Survey (NOES) of 1982–1984, it was estimated that almost 3 million workers are exposed to ammonia in the United States (14). In a 2004 literature review, the US Agency for Toxic Substances and Disease Registry (ATSDR) concluded that quantitative occupational monitoring data for ammonia is considered to be lacking (13). For example, ammonia exposures can occur among professional cleaners where concerns about exposure to cleaning agents (including ammonia) and occupational asthma are currently under (15-18) investigation. Rosenman et al. (2003) concluded that additional epidemiologic studies of exposed cohorts of cleaning workers are needed. A new ammonia sensor, developed as a part of this research, would be a valuable addition to such studies. Workers in industrial-scale animal handling facilities (such as feedlots and poultry-confinement buildings) are also at risk for ammonia exposure due to decomposing animal waste (urine and feces). Ammonia concentrations in the facilities are highly variable and can range from below one part per million to 40 ppm (19, 20). Farm workers can also be exposed to ammonia while handling or applying fertilizer. Studies of respiratory health with good exposure assessments in animal handling workers are lacking (21, 22).

Current portable sampling technology, either using integrated sampling methods or direct reading instruments, is adequate for detecting ammonia at concentrations approaching the current exposure guidelines. The current OSHA PEL for ammonia is 50 ppm expressed as an 8-hr TWA. The ACGIH TLV exposure guideline is 25 ppm as TWA and a 35 ppm STEL. These exposure guidelines were established over 40 years ago and are based on protecting workers from exposure to ammonia as an irritant (23). While existing methods are adequate for assessing ammonia at these concentrations, they are not adequate for conducting exposure assessments at sub-ppm concentrations or to assess temporal variability in exposure in a way that would support a longitudinal epidemiological study.

In conclusion, with this project we are proposing a new paradigm for air contaminant detection using organic electronics as chemical sensors. This technology holds tremendous

promise for developing small, sensitive samplers that will be inexpensive and easy to deploy and analyze. While we have initially developed an ammonia sensor, these sensors can be theoretically used to monitor any chemical that has the ability to react with the OSC films.

Exposure assessment is an integral component of occupational and environmental epidemiology, risk assessment and management, as well as regulatory compliance. For the most part, air sampling and analysis tools used in occupational and environmental exposure assessments are based on technologies that have changed little since the 1970s (1). In many cases the lack of simple, inexpensive, and high throughput exposure assessment technologies has limited epidemiologists' and risk assessors' ability to evaluate the environmental and occupational causes of disease. While there have been tremendous investments and advances in medical diagnostic and biomonitoring technologies (e.g., glucose testing, human genetics) there has been little effort invested in advancing the science of exposure assessment. In a 2005 article discussing gene–environment interactions, Wild (7) concluded that there is a **“desperate need” to develop inexpensive and high throughput exposure assessment methods** that match our ability to assess subclinical effects or susceptibility markers using “omics” techniques (e.g., genomics, metabolomics, proteomics). Cohen-Hubal (6) concluded that **investment in a 21st-century exposure science** is needed to take advantage of the new generation of scientific tools developed to rapidly measure signals from cells, tissues, and organisms following exposure to chemicals.

Advances in nano-technology and materials sciences offer unique opportunities for the development of new air sampling sensor technologies. **The long-term goal of this project is to develop a new generation of air sampling technology for a wide range of chemical substances based on organic field effect transistor (OFET) sensors.** Air samplers based on OFET sensor technology have the potential to provide small, sensitive, and inexpensive air samplers that can be easily mass produced to measure integrated or time-resolved exposures. Quantification of mass loading on OFET sensors is based on measuring changes in electrical properties associated with contaminant - OFET interaction, so traditional analytical methods (e.g., spectrophotometric or chromatographic analysis) are not needed. **We have designed an OFET-based air sampler that can detect airborne ammonia (NH₃) concentrations at less than 1 ppm in long- (8 hour) and short-term (15 minute) sampling periods.**

2.1. Methodology

The schematic of the PET OFET fabrication process and the device structure are shown in Figure 1. The modified OFET structure was developed on 12- μm thick PET sheets supplied by Mitsubishi

polyester films. poly (3,3''-didodecylquaterthiophene) PQT-12 and 2,2'-[(2,5-dihexadecyl-3,6-dioxo-2,3,5,6-

tetrahydropyrrolo[3,4-c]pyrrole-1,4-diylidene)dithiene-5,2-

diylidene] dimalononitrile (DPP-CN) were synthesized in our laboratory. DPP-CN [24] was prepared according to modified literature procedures. For (PQT-

12) synthesis, 5,5'-bis(trimethylstannyl)-2,2'-

bithiophene was purchased from Sigma-Aldrich and was further recrystallized for polymerization. 5,5'-Dibromo-4,4'-didodecyl-

2,2'-bithiophene [25] was synthesized.

5,5'-Dibromo-4,4'-didodecyl-2,2'-bithiophene [25] was synthesized.

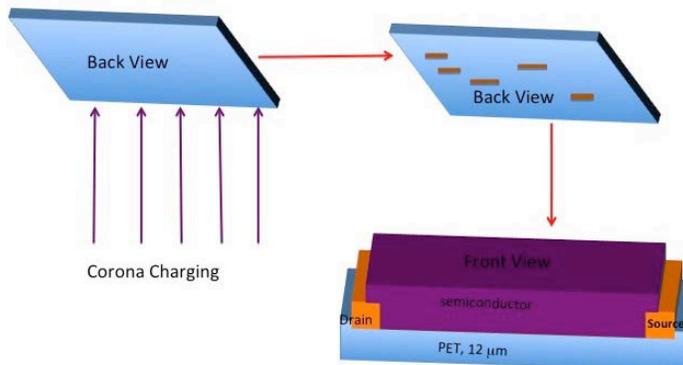
2.2 Synthesis of PQT-12 [26]

5,5'-Dibromo-4,4'-didodecyl-2,2'-bithiophene (0.5 mmol, 0.330 g), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.5mmol, 0.246g), tris (dibenzylideneacetone)dipalladium(0) (0.02 mmol, 18.3 mg), and tri(o-tolyl)phosphine (0.08 mmol, 24.4 mg) were added to a reaction vial, which was then purged with argon for 15 min. Anhydrous chlorobenzene (15 mL) was added through a septum and the reaction mixture was then stirred at 115 °C for 72 h. The reaction mixture was poured into methanol (150 mL) and HCl (10 mL). The polymer was filtered and subjected to Soxhlet extraction with acetone (24 h), hexane (24 h), dichloromethane (24 h) and chlorobenzene (24 h). The chlorobenzene fraction was concentrated and precipitated into methanol. Following filtration, the purified polymer (0.3 g, 90%) was obtained as a brown solid GPC: $M_n = 20.5 \text{ kg/mol}$; $M_w = 24.3 \text{ kg/mol}$; PDI = 1.2

2.3 Device preparation

The PET sheet was cut into 1 inch by 1-inch square samples that were cleaned in an ultrasonic isopropanol bath for 10 minutes and then rinsed with distilled water. Following the cleaning process, samples were dried at normal room temperature and pressure. Semiconductor mobilities were measured and printed electrodes were initially characterized on Si/SiO₂ substrates with 300 nm of oxide.

Source-drain electrodes were made either of vapor-deposited gold (for initial tests of responsive plastic device materials) or silver ink processed via a pneumatic printing technique. Gold electrodes (50 nm thickness) were deposited by thermal vapor deposition using an interdigitated mask (channel width/length ratio approximately 308 (77000 μm /250 μm)) at 0.3 $\text{\AA}/\text{s}$ under 5×10^{-6}



1. Schematic of the device fabrication process.

⁶ Pa. For printed silver electrodes on PET, the dispensing head is interfaced with a 3D stage, EFD dispensing system, and controlled by LabView for automated dispensing. The EFD system provides the back pressure before the dispensing step to allow suspension of the ink at the tip (Figure 2 – Note: Figures 2 to 14 at the end of the text). During dispensing, slight forward pressure is applied to allow the ink to contact the surface. The tip is then moved to draw the patterns while the ink continues to dispense by capillary action. The samples were baked at 110 °C for an hour after printing to allow the silver ink to cure. The printed silver source and drain with 100 μm and 300 μm channel length for the OFETs (W/L = 30) are shown in Figure 3.

PET substrates with source-drain electrodes already deposited were placed on the grounded metallic plate with the free surface (back side, opposite to the source-drain electrodes) facing up to the needle electrode. In the corona discharge setup the needle electrode connects to a high (usually negative) DC voltage to create corona discharge for charging. There is a grid electrode interposed between the grounded plate and the needle electrode. This grid electrode connects to another negative DC potential and helps to create an almost uniform field of desired strength. We applied a -10,000 volts DC voltage at the needle electrode, which was modulated using the grid electrode to give a local voltage of -1500 V. The non-metallized side of the sample was charged in the corona discharge apparatus for 5-10 minutes.

(PQT-12) and DPP-CN (Figure 4) were both used as 4 mg/ml solutions in chlorobenzene at 60°C , and were drop cast on the “front”, source-drain electrode side of PET substrates. Excess semiconductor solution was removed from the device with absorbent wipes to minimize semiconductor film thickness. For baseline devices on Si substrates, PQT-12 films were drop cast while DPP-CN films were spincoated . The solvent was then allowed to evaporate at room temperature; no annealing was done. Output curves for these devices are shown in Figure 4.

2.4. Film characterization and sensor test

All the OFET measurements were done using an Agilent 4155C semiconductor analyzer under ambient conditions. An NH₃ gas cylinder, concentration 5 ppm in nitrogen with blend tolerance +/- 10%, was purchased from Spec gas, Inc. An Enviromics gas dilution system (series 4040) was used to achieve an ammonia concentration of 0.5 ppm or lower by diluting 5-ppm ammonia with dry air. A sealed 1300 ml chamber with an outlet to allow continuous flow was used for ammonia exposure experiments; the flow rate of gas through the chamber was typically 1000 cm³/min for 0.5 ppm exposure. For 1.5 ppm and 0.1 ppm the flow rate was 600 cm³/min and 1500 cm³/min, respectively according to the volume of dry air required to achieve different concentrations.

Responsive devices were tested at intervals of 5, 20, and 30 minutes in air to make sure of the initial stability of the devices to ambient conditions. Once a device stabilized in stationary air, it was put into a testing chamber with a plain air flow of 1000 cm³/min to evaluate any effect of the increased air flow rate itself on device properties. For ammonia sensing experiments, devices were exposed to concentrations in the range of 0.1 to 1.5 ppm ammonia for 5 minutes or longer.

3. Results and discussion

3.1 PET device charging

PET has been well studied for its charge storage applications and electret properties [14–22][27]. Electret effects and stability of surface potential in polymeric films have been largely attributed to hetero and homo charge formation due to polarization at low field and charge injection at higher fields during corona charging [28][18][19]. Although the most important factors for these effects are the field strength and time of exposure to the corona field, other factors like defects and sample geometry can also be important [28]. Temporal decay of the surface potential is a crucial parameter for electret application and it has been related to processes such as surface conduction [29], atmospheric neutralization [30][28], sample polarization [31] and charge injection [14][32][28].

Inspired by the electret literature, plasma treatment using oxygen, UV and corona charging has been used to modulate threshold voltage of OFET's in several studies by modifying the density of states at the semiconductor-dielectric junctions. Chemical reaction between the charged plasma species and the dielectric surface can lead to trap states at the junction. Plasma treatment can introduce two types of charges, fixed and mobile. These charges are responsible for threshold voltage shift of the OFET due to the contribution to the field by the fixed charges and increase in conductivity due to mobile charges. The gate voltage does not modulate the mobile charges and hence this increase in conductivity is called parasitic conductivity [23].

We used corona-induced charge states in 12-micron thick sheets as the sole source of electric field instead of using interface trap states for threshold modulation. The implanted charges provide the field necessary to shift the threshold voltage so as to keep the device in accumulation mode. We found 12 microns to be the maximum thickness across which these charges were effective for our purposes. To optimize stability, grid voltage of -1500 V was chosen as charge decay has been reported to be slowest at -1500 V on PET surfaces [16].

Figure 5 shows I-V curves on PET substrates with static gate and gold electrodes, demonstrating the effect of corona charging in turning on the semiconductor by comparing charged and uncharged devices. For these experiments, electrodes were vapor-deposited through a TEM grid with $W/L=10$). It can be clearly seen that corona induced trap states are the sole source of field effect in the PET based devices as the device without the corona treatment remains in the off state. It should be noted that conductivity of PQT-12 is low; hence high source-drain voltages are applied.

The magnitude of the drain current is notably high compared to typical silicon-based devices, because of the huge applied voltage (-1500 V) used to implant the charges (as compared to gate voltages and drain voltages applied in typical silicon devices (maximum +/-100 Volts)), the accumulation of the charges is enhanced leading to higher drain currents and little apparent "saturation" regime. Note that the implanting voltage level does not need to be applied during the operation of the device.

Surface charge densities for corona-induced charges were calculated using the linear regime FET equations

$$I_D = \mu C_{ox} \frac{W}{L} (V_{GS} - V_T) V_{DS}$$

And

$$C_{ox} \times \Delta V = \frac{Q}{A}$$

The calculation was done assuming that all the charges are on the interfaces of the device. Mobility was calculated using OFET structure with 200 nm PET as dielectric.

The surface charge density calculated for different devices ranges between 2.4×10^{12} to $9 \times 10^{12} \frac{\text{charges}}{\text{cm}^2}$. This is a typical range for OFET gate-induced charge densities.

Wang et al. and Dawidczyk et al. made similar observations by oxygen plasma and corona charging of the dielectric layer in order to manipulate the threshold voltage. In those cases, external gate voltage was used to turn on the device and the semiconductor-dielectric interface was exposed to the treatments that led to introduction of unwanted parasitic mobile charges, which could not be modulated, by gate field. In the present device, as the treatment is done on the bare side of PET, the mobile charges would need to travel through a 12 micron thickness of PET, which is less likely to happen. Our results agree with the theories presented in the preceding literature [23].

We anticipate the future need to stabilize the corona charged state. Major decay of the charges might be due desorption or migration with time, leading to instability of the device performance. To trap the charges or at least slow down the processes of desorption, we spin-coated a very thin layer of polystyrene at 1000 rpm on the backside of the device after charging. Reports have shown that the charges can be stored better at the interface of two insulators [19]. Interaction of the semiconductor film with moisture and oxygen from air leads to decrease in drain current as does any decrease in the density of corona-embedded charges. The devices with additional polystyrene protection coating on the backside displayed better device performance than the devices without polystyrene. The stability increase given by the polystyrene layer is illustrated in Figure 6(a), where the polystyrene decreases the rate of loss of beneficial effects from the charging. After 24 hour aging in the open air, the devices become more stable. The stability of these charges and hence the resulting modified OFETs is comparable to that of silicon-based OFETs over a week's time (Figure 6 (b)), while our sensing experiments are performed over minutes time scales.

This experiment is just an initial demonstration of potential possible way to trap the electrostatic charges for longer periods of time in plastic substrate in order to obtain stable, always-on devices, and can clearly be further optimized, for example, by using a denser or even more hydrophobic polymer coating. Also, the effectiveness of this layer supports the hypothesis that the charged implanted from the back side are indeed active in controlling the conductance of the front-face semiconductor. There are several other polymers like Teflon and PEN etc., which can store charge better than PET but most of them have inferior mechanical, properties as compared to PET. According previous literature [27], charge storage lifetime for PET can be up to 300 days while for PEN it can be up to 90 years. As the cost and flexibility of the device are major considerations here, PET seems to be the best compromise for developing the low cost flexible devices being discussed here.

3.2 Ammonia response

The ammonia sensitivity was investigated by monitoring the percentage change in the drain current of PET-gold devices on exposure to 0.5 and 1.5 ppm of ammonia. The devices were exposed for 5, 20 and 30 minutes and the corresponding percentage decreases in current were 17.8%, 36.7% and 40.8% for 0.5 ppm exposure and 31.4%, 46% and 53.7% for 1.5ppm ammonia exposure respectively, as shown in Figure 7. Devices were also exposed to pure dry air at 1000 cm³/min to account for any sensitivity of the device to dry air alone. As can be seen in Figure 8, an average drain current decrease of only 2.9% was observed in 30 minutes, far less than the exposure-induced changes. These responses to ammonia are conservative as devices were measured outside the exposure chamber and there is a time lapse (>1minute) between ammonia exposure and recording of responses.

To enable more uniform flow and to demonstrate an ultimately applicable format, we incorporated a sensing device inside a modified wearable Ogawa badge, as exhibited in Figure 9. This badge includes a porous front end that collimates and moderates airflow in front of the device. Devices in the Ogawa badge, which used the printed electrodes, showed full recovery, in half the time, as compared to open-air devices. It is possible that for PQT-12, ammonia molecules delivered directly from atmospheric air have enough kinetic energy to reach less accessible but stronger binding sites, where they formed deeper and more stable traps, while the sampler limited the kinetic energy of the arriving ammonia and the vapor molecules only adsorbed on more exposed and more weakly binding sites. The limit of detection for these sensors is at least as little as 0.1 ppm, (Figure 10), which is below the current EPA regulation of 0.14-ppm ammonia exposure [33]. The response is also consistent with what was observed for higher concentrations in Figure 7.

Selectivity studies were conducted for common solvent vapors like acetone, methanol, ethyl acetate and dichlorobenzene, as these vapors can be present in agricultural or industrial environments. Methanol was especially chosen, as it is a very good analogue of water due to similar polarity, size, electronegativity and binding properties. The devices were exposed to saturated vapor concentration of the listed solvent for 5 minutes. The logarithms of percent current decreases per ppm of the analyte vapors are shown in Figure 11, where it can be seen that the response for ammonia is much greater than for all the other vapors. The sensor reacts with other amines but the response magnitude is smaller, probably due to the steric hindrance of those amines as compared to ammonia.

Along with selectivity, retention of the response is also a very important consideration for dosimetric sensors. As has been mentioned earlier, the reported devices recover when kept in open air and recording the response might not always be the most feasible option. This device if stored in a sealed Fluorware container after exposure, at -30°C, retains the response. Some further decrease in current is observed in the exposed devices as well as control samples (Figure 12) because of the sub-ambient temperature at which they are tested after cold storage, but the current difference due to ammonia exposure remains apparent, and would allow retention of any differential response measurement between an exposed and a reference device. The storage

temperature is apparently low enough to prevent debinding or diffusion of ammonia out of the device.

Besides using low temperature to slow desorption of ammonia, we could conceivably retain the response using a bistable circuit comprising a pair of complementary inverters fed back to each other, with the ammonia acting as the stimulus to switch the output voltages. Once the status of the circuit is changed due to this external stimulus, it would not be easily reversible. One necessary condition for such a device is two complementary semiconductors that give opposite responses to ammonia, but where the magnitude of the response is similar. We have matched PQT-12 with the n-channel solution-deposited small molecule DPP-CN which gives almost the same response (15% increase in drain current), (Figure 13) but in the opposite direction, to 0.5 ppm of ammonia in five minutes using the same configuration as the PQT-12 devices. Future work will utilize this or a similar pair of solution-deposited semiconductors with the goal of producing a responsive and all-printed bistable circuit.

PQT-12 is obviously sensitive to ammonia, but due to its moderate mobility, high voltage has been required for operation. Using a blend of high mobility material Lisicon® “SP210” from EMD Millipore Corporation (dba EMD Chemicals, catalog number 1.39695.0200 SP210.0001) and PQT-12 in a 3:1 ratio provided a good compromise between sensitivity and conductance. The sensitivity of the blend is lower than for pure PQT-12, but the device could operate well below 5 volts supply Figure (14). Another alternative for lowering operating voltage is to simply use higher W/L ratios.

Plans for the development of a working prototype. Additional money has been obtained to scale up the production of badge prototypes, using model printing methods, and test the prototypes for stability and reproducibility in real-world environments of greatest interest to public health and industrial environmental engineering customers.

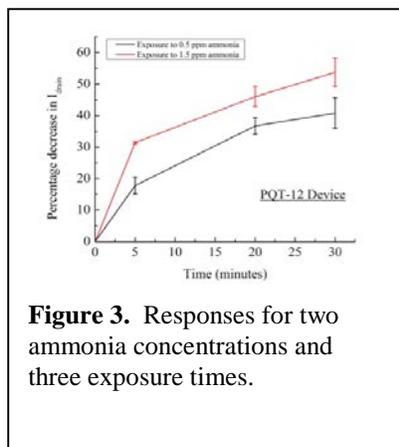


Figure 3. Responses for two ammonia concentrations and three exposure times.

Additional money has been obtained to scale up the production of badge prototypes, using model printing methods, and test the prototypes for stability and reproducibility in real-world environments of greatest interest to public health and industrial environmental engineering customers. The badge production consists of fabricating plastic-based semiconductor devices, mounting them with leads inside the sampling and reference compartments of the badges, sealing the reference compartments of the badges, and collecting electronic response data to different ammonia exposures over varied times and at different temperatures and humidities. Preliminary response ranges to different concentrations and exposure times are shown in Figure 3; uncertainties so far are on the order of 25%. This would not hinder the determination of orders-of-magnitude of exposure, but stronger statistics would be desired by customers. Also, the current change of a single device in response to interfering humidity is on the order of 5% for 40% humidity, much less than the responses to ammonia. On the other hand, the interference from water vapor is comparable to the ammonia response at 70% humidity. Water can be distinguished from ammonia because it generally decreases OSC conductivity regardless of whether the OSC is a hole- or electron-transporter (p or n types, respectively), so the use of the opposing responses by p and n semiconductors will further distinguish the presence of a strongly basic (electron donating) vapor, rather than water. Also, a further aspect of the prototyping will

be to incorporate a humidity filter in front of the responding and reference devices. Such a filter can be made from basic alumina, on which water would adsorb but through which ammonia, also a base, would pass through. The prototypes will be tested using a bench-scale ammonia exposure system that is currently in use by the PI team. The system can expose samples to a controlled concentration and dose of ammonia and water vapor, which can then be correlated with the response and performance of the ammonia sensing system. The product of this prototyping and testing work would be a fully qualified, wearable demonstration badge that could be demonstrated to customers with the assurance that such badges can be scaled up and used in customer-relevant environments. ***Reaching this development milestone is the key hurdle in commercializing these badges.*** The funds requested are being devoted to postdoctoral and graduate student investigator salaries for carrying out the fabrication and testing, and for the purchase of supplies to fabricate prototypes and conduct the environmental tests. Limited funds will be devoted to visits with potential customers and partners as described below at the end of the project period. In parallel with these visits, further integration of the prototype, for example, with power supplies and communications/data management channels, will be carried out.

Discussions with commercial partners. The research work was funded in part by a consortium of industrial partners known as Flextech. Among these partners, Cambridge Display Technologies (CTD, contacts Dr. Ilaria Grizzi and Dr. Graham Anderson), a subsidiary of Sumitomo, continues to express interest in the ammonia sensor as a commercial vehicle for their line of polymer semiconductors. They have agreed to supply a particularly promising ammonia-responsive semiconductor for continued prototyping aimed at opening up commercial markets. A visit to the CDT site is planned for June, 2015 to further this collaboration. A second partner, ThinFilm Electronics Inc., has expressed interest in integrating the output of our sensors into memory circuits for archiving purposes. More broadly, the Flextech Alliance includes about fifty large and small companies (see <http://flextech.org/member-benefits/member-directory/>), all of whom are aware of our previously funded work and several of whom participated in progress report presentations during the course of that work. Finally, once the sensors reach the stage of being applicable to a health care data network, Verizon has offered to donate hardware for implementing the network connections. A key aspect of our technology, the use of both p- and n-type semiconductors to digitize signals and increase selectivity, is protected by a full patent application being managed by Johns Hopkins Technology Transfer, Circuit Architectures for Organic Electronic Sensors, D11169.

Timeline. It is expected that a one-year effort devoted to the focused goals described in the work plan will produce the necessary reproducibility of the fabrication protocol and ammonia response statistics. At the conclusion of this period, discussions will be held with customer organizations and technology partners mentioned above to create a comprehensive supply chain and marketing plan.

Conclusion

We have developed a flexible and cost-efficient ammonia sensor platform with a sensitivity of 0.5 ppm and a limit of detection of 0.1 ppm that is well suited for large area (or roll-to-roll) processing. Devices based on PQT-12 and DPP-CN give opposite responses to similar exposures

to ammonia, which is essential to design a complementary logic-based ammonia sensor. The sensors are highly selective for ammonia over volatile organic compounds. Prototype development to have sensors ready for field deployment is currently under way.

Figures 2 to 14

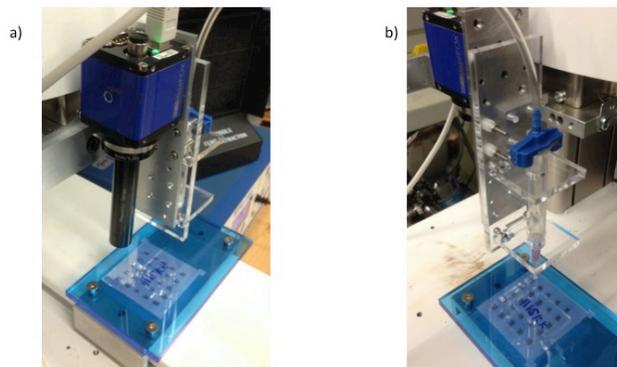


Figure 2. a) Bluefox camera interfaced with LabView for printing alignment, b) Pneumatic printing head interfaced with EDF

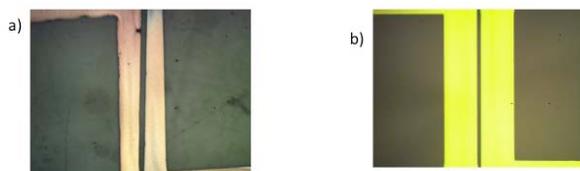


Figure 3. (a) Printed source and drain on Si/SiO₂ with channel length 300 μm (b) Printed source and drain on PET with channel length 100 μm.

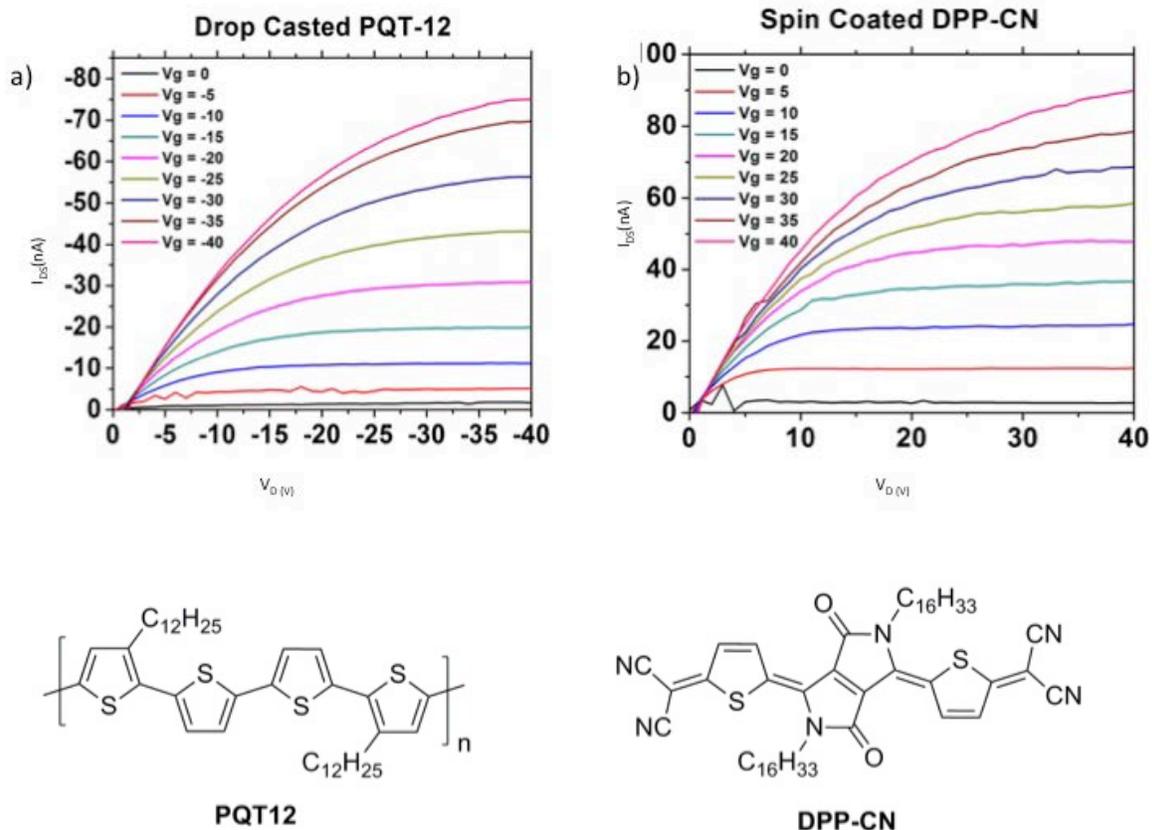


Figure 4. a) Output curve for silicon based PQT-12 OFET, b) Output curve for silicon based DPP-CN OFET. Chemical structures of the two semiconductors are also shown.

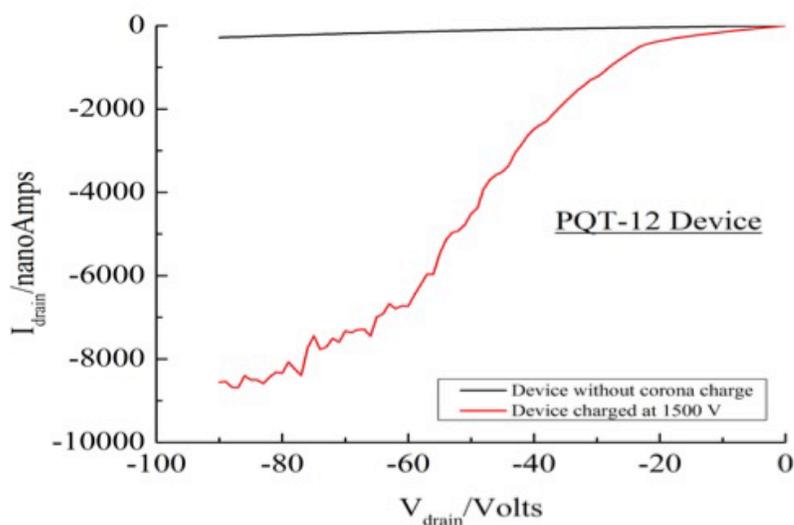
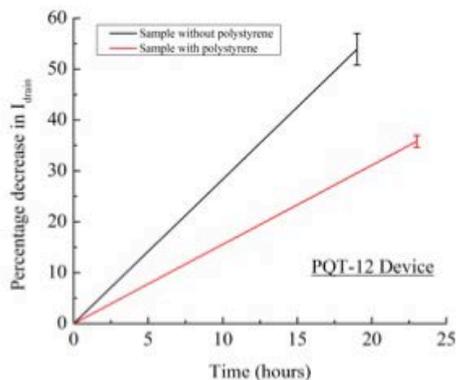


Figure 5. Output curve for a PQT-12 based device with static charges as gate

a)



b)

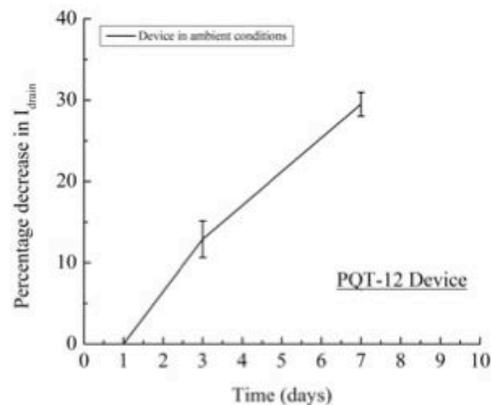


Figure 6. Demonstration of effect of additional polystyrene layer on the rate of charge desorption, average of 3 devices. a) Stability increase due to polystyrene layer (24 hour aging), time scale of hours; b) with the polystyrene layer, timescale of days

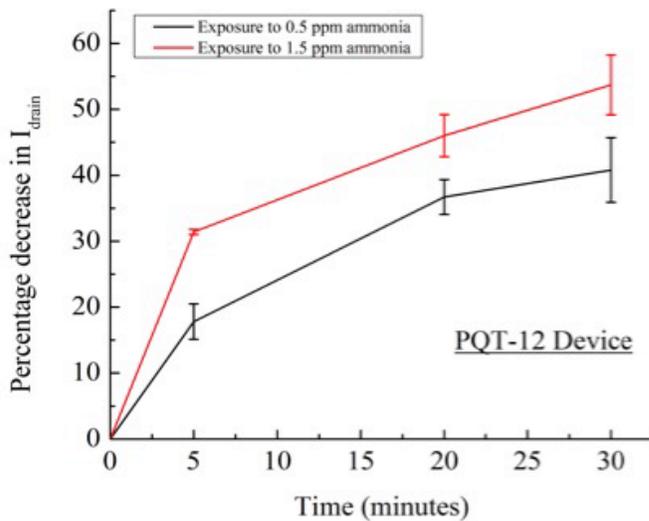


Figure 7. Percentage decrease in drain current on 5, 20, 30 minutes exposure to 0.5 ppm and 1.5 ppm ammonia, average of 3 devices

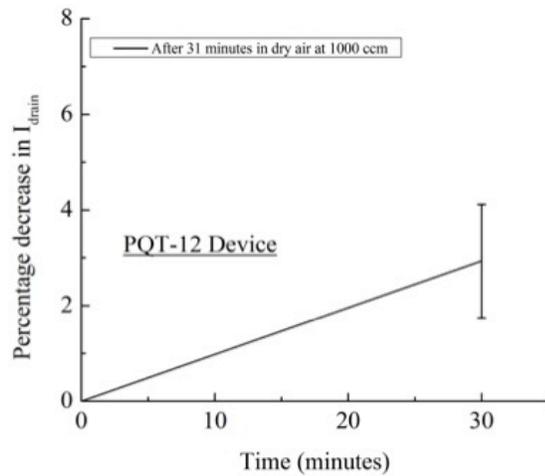


Figure 8. Effect of dry air exposure for 31 minutes at 1000 cc/min



Figure 9 Ogawa badge sampler with responsive device made with printed electrodes mounted inside

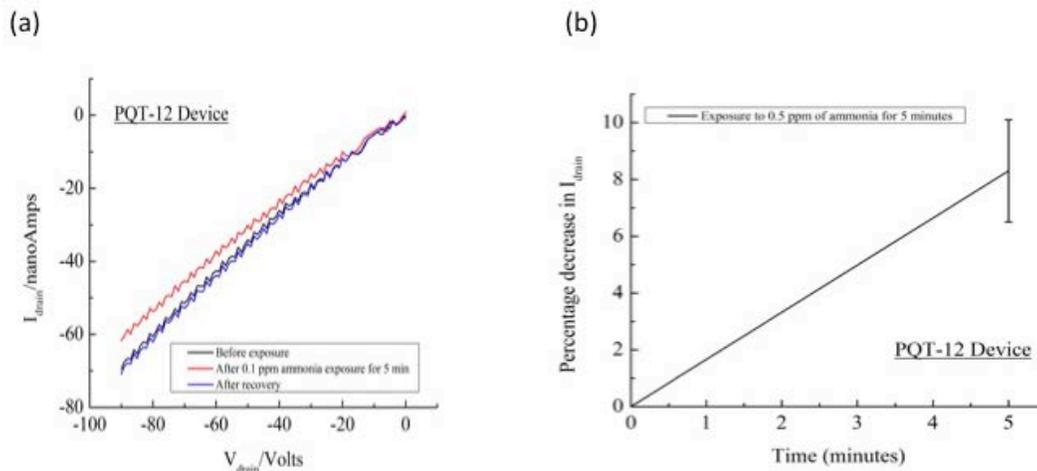


Figure 10. Response to 0.1 ppm of ammonia, printed device in Ogawa badge, flow rate 1500 cc/min, (a) I-V plot and (b) reproducibility of three devices

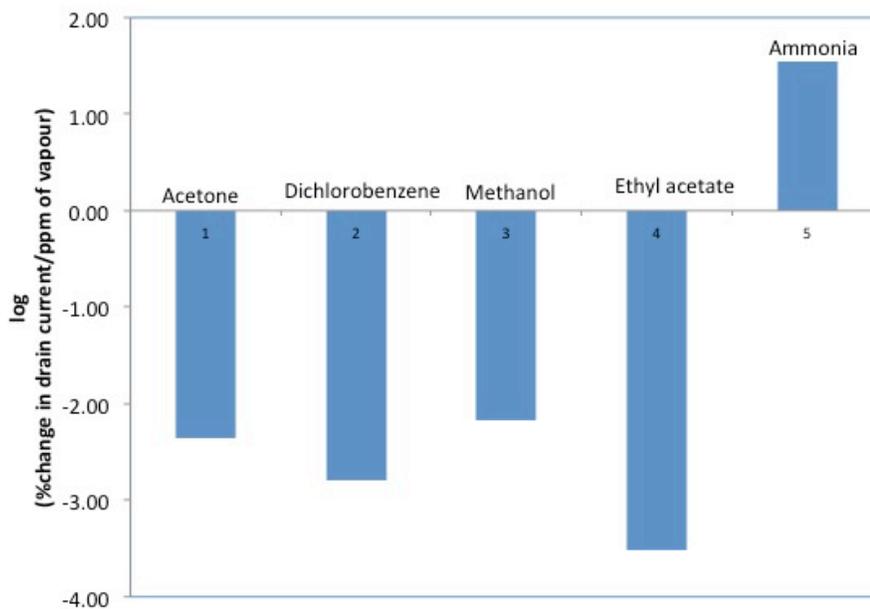


Figure 11. PQT-12 responses expressed as log percent change of current per ppm of analyte vapor

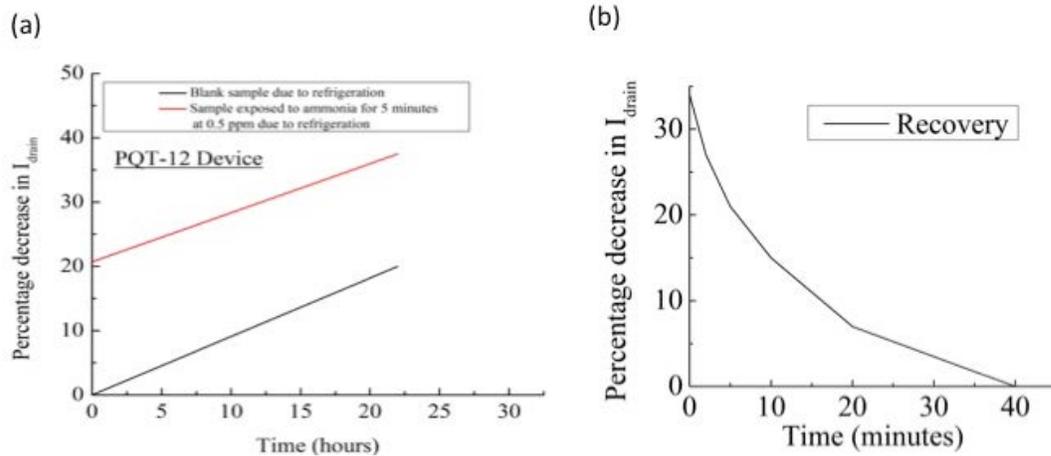


Figure 12. Current change of different exposed PQT-12 devices, (a) stored in refrigerator, (b) stored in air at room temperature after ammonia exposure

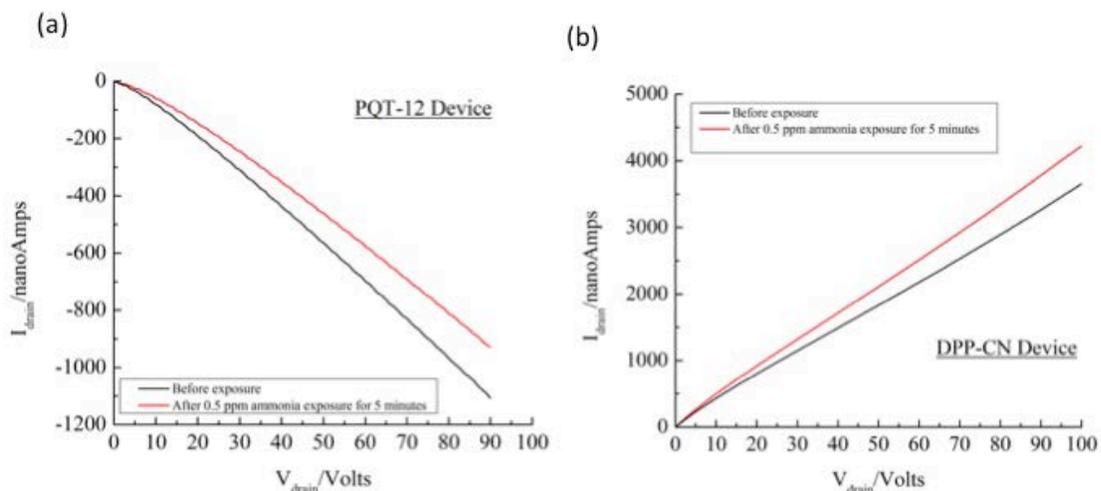


Figure 13. (a) PQT-12 device, 16.2% decrease in drain current, (b) 2,2'-[(2,5-dihexadecyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diylidene)dithiene-5,2-diylidene] dimalononitrile (DPP-CN) device, 15.3% increase in drain current, on 0.5 ppm ammonia exposure for 5 minutes

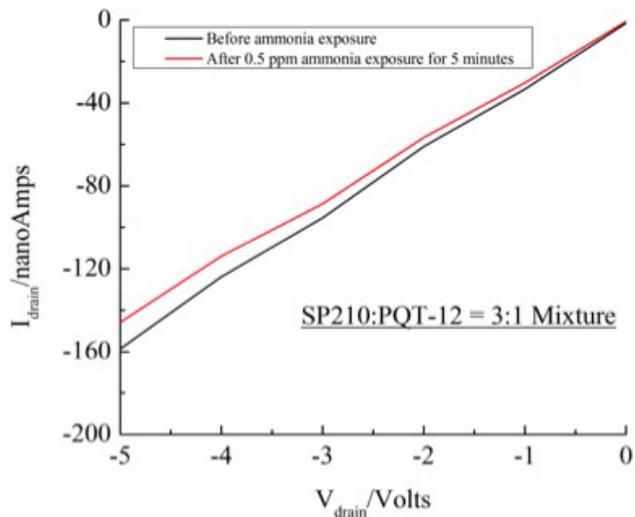


Figure 14. Low voltage operated device based on a blend of PQT-12 and another commercially available conductive polymer as the sensitive material

Publications

Besar, K; Yang, S.; Guo, X.; Huang, W.; Rule, A.M.; Breyse, P.N.; Kymissis, I.J.; Katz, H.E.

“Printable Ammonia Sensor Based on Field-effect Transistor”

Organic Electronics 15 3221-3230

2014

Huang, W.; Sinha, J.; Yeh, M.-L.; Martinez Hardigree, J.F.; LeCover, R.; Besar, K.; Rule, A.M.; Breyse, P.M.; Katz, H.E.

“Diverse Organic Field Effect Transistor Sensor Responses from Two Functionalized Naphthalenetetracarboxylic Diimides and Copper Phthalocyanine Semiconductors Distinguishable over a Wide Analyte Range”

Adv. Funct. Mat. 23, 4094-4104

2013

Huang, W.; Besar, K.; LeCover, R.; Rule, A.M.; Breyse, P.N.; Katz, H.E.

“Highly Sensitive NH₃ Detection Based on Organic Field-Effect Transistors with Tris(pentafluorophenyl)borane as Receptor”

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