

### Electronic Supplementary Information

## **A patterned colorimetric sensor array for rapid detection of TNT at ppt level**

Anders Berliner,<sup>a</sup> Myung-Goo Lee,<sup>a, b</sup> Yagang Zhang,<sup>c, d</sup> Seong H. Park,<sup>b</sup> Raymond Martino,<sup>a</sup>  
Paul A. Rhodes,<sup>a</sup> Gi-Ra Yi<sup>\*b</sup>, Sung H. Lim<sup>\*a</sup>

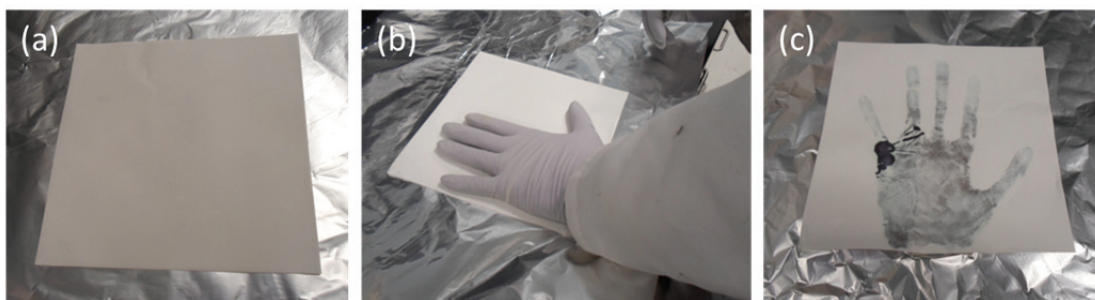
<sup>a</sup> iSense, LLC Mountain View, CA 94043 U.S.A.

<sup>b</sup> School of Chemical Engineering, Sungkyunkwan University, Suwon 440746, South Korea.

<sup>c</sup> Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, U.S.A.

<sup>d</sup> Current address: Xinjiang Technique Institute of Physics & Chemistry Chinese Academy of Sciences, Xinjiang 830011, China.

E-mail: [slim@isensesystems.com](mailto:slim@isensesystems.com) or [yigira@skku.edu](mailto:yigira@skku.edu)

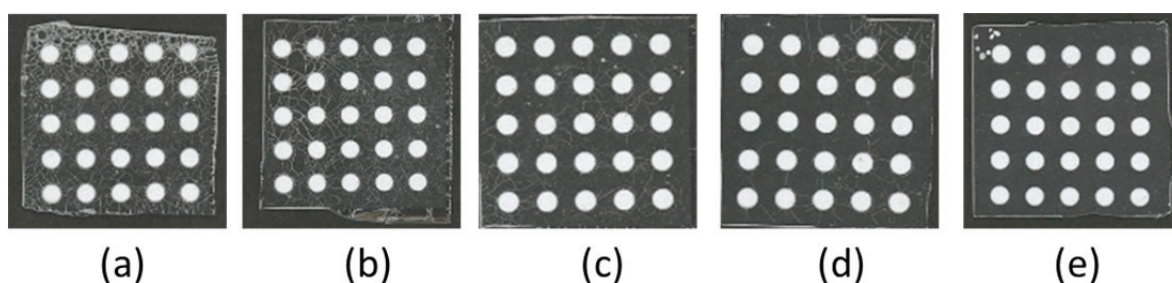


**Fig. S1.** Colorimetric response of Isamine T-101 to 2,4-DNT. (a) Isamine T-101 treated paper, (b) Sensor contact with 2,4-DNT contaminated glove, and (c) 2,4-DNT exposed sensor.

### **General procedure for UV-patterning**

A glass fiber membrane (Whatman, GF/C) was patterned using a 9:1 mixture of tri(propylene glycol) diacrylate (TPGDA, BASF) and trimethylolpropane triacrylate (TMPTA, BASF), containing 0.25 wt.% of photoinitiator (2-hydroxy-2-methylpropiophenone, Darocure 1173, BASF). After the membrane was completely

soaked in the photoresist mixture, a photomask (e.g., inkjet printed transparency film) was placed to selectively expose the photoresists to UV light ( $35 \text{ mW/cm}^2$ ) for 12 seconds. The photo-cured substrate was sequentially washed with acetone, ethanol and deionized water to remove unreacted photoresist, then dried at approximately  $50^\circ\text{C}$ . The patterned substrate can be printed with various formulations using a previously reported method. The printed sensor array is also commercially available from iSense, LLC (Mountain View, CA).



**Fig. S2.** Photo-patterned glass fiber membranes with the (a) 1:9, (b) 3:7, (c) 5:5, (d) 7:3, and (e) 9:1 mixture of TPGDA and TMTPA. White lines indicate the cracks in (a-d). No cracks were observed for sample (e).

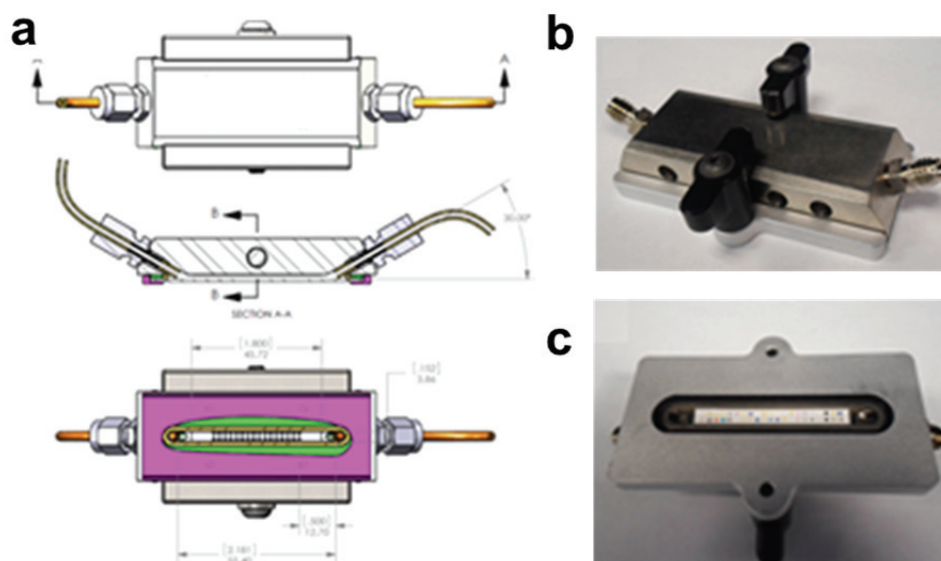
### Sensor Cartridge Design

Prior CSA designs have been rectangular and, the sensor response was fairly uniform at ppm levels. However, our recent flow experiments with low vapor pressure analytes, such as 2,4-dinitrotoluene (DNT, 180 ppb), revealed that the rectangular cartridge created a significant turbulence at the entry, causing non-uniform analyte deposition (Fig. S2). In order to characterize the vapor flow pattern, a DNT sensitive membrane big enough to cover the entire gas chamber was prepared, and the sensor response to 2,4-DNT was monitored over 10 minutes.

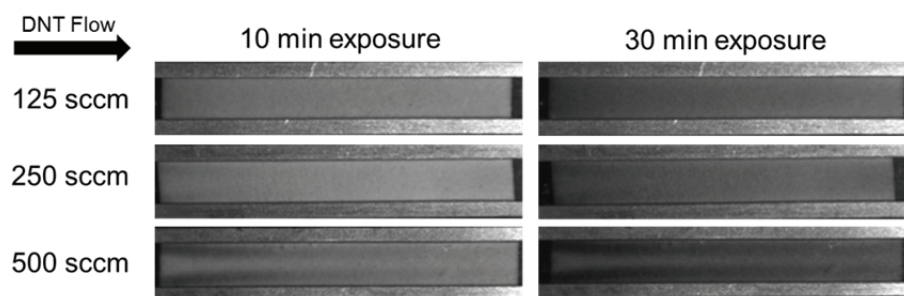


**Fig. S3.** Experiment with rectangular flow chamber shows non laminar entrance flow. Area near the inlet port changed the most, but very small color change is observed near the exhaust port. The membrane was exposed to saturated vapor of 2,4-DNT.

To address this non-uniform gas flow, a linear flow chamber with minimal dead space was designed as seen in Fig. S4. The dimensions of the flow path were 45 mm from inlet to outlet, 3 mm in width and 4 mm in depth. To determine the optimal flow rate, a Isamine treated membrane was placed inside the flow chamber. Saturated 2,4-DNT vapor was flowed through the flow chamber at different flow rates, ranging from 100 to 1000 sccm. Above 500 sccm, significant entrance effects and boundary layer formation were observed (Fig. S4). These effects were amplified in flowpaths with wider cross-sections. At 125 sccm, streamline analyte depletion, visible in the axial gradient of color change from inlet to outlet, was observed. Thus, 250 sccm, which showed the most uniform color change, was used as the total flow rate for all flow experiments in this study.



**Figure S4.** a) Schematic of a linear flow channel cartridge. b) top and c) bottom view photographs.

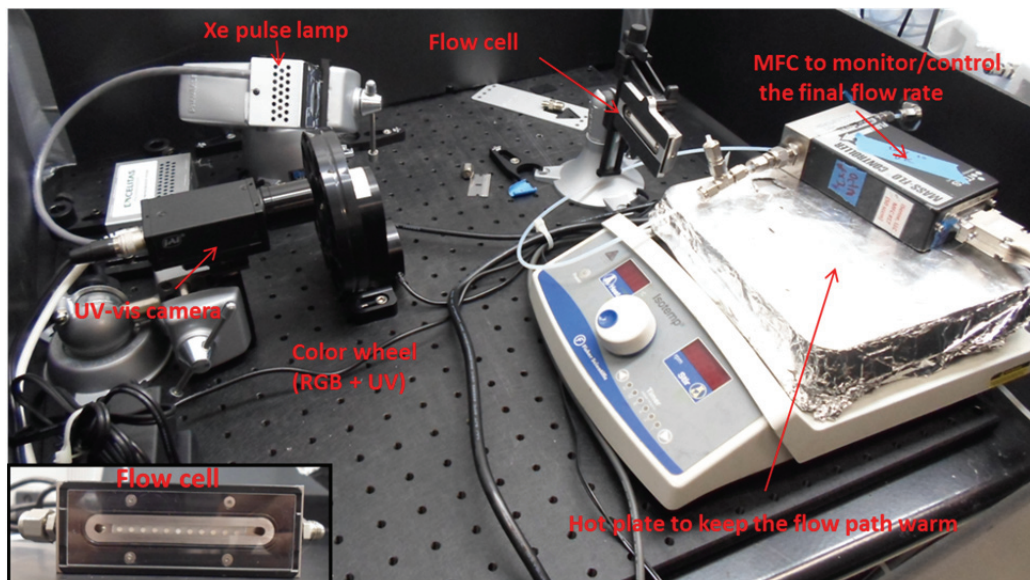


**Figure S5.** Blue channel images after 20 min of exposure to saturated 2,4-DNT vapor at varying flow rates. Flow rate of 250 sccm was optimal and provided most uniform sensor response.

### Optical Setup and Sensing Experiments

Sensor array imaging was done with a broad band camera with a colour wheel containing four colour filters (red, green, blue and UV) as shown in Fig. S5. The before image was collected before analyte exposure, and after exposure images were collected in one minute intervals for 30 minutes. For the discrimination of different nitroaromatics, all experiments were performed in minimum of quintuplicate runs. For interference experiments, experiments were performed in minimum of triplicate runs. Before each set

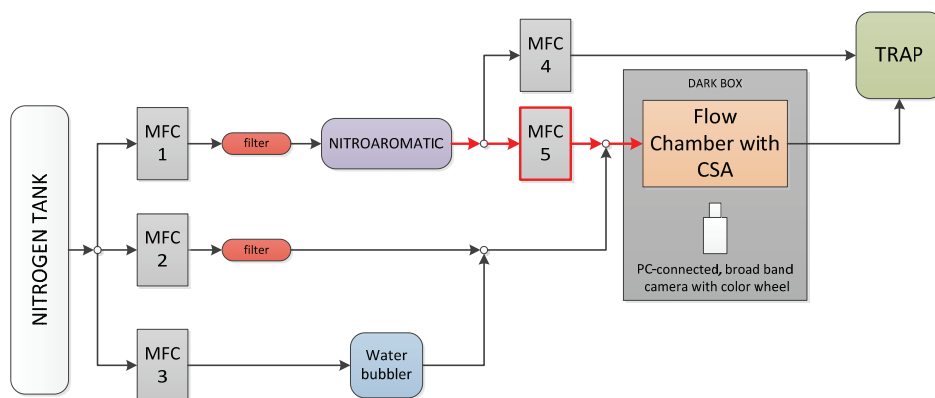
of experiments, control experiments were run to assure the flow system was clean and devoid of any residual vapour from previous runs.



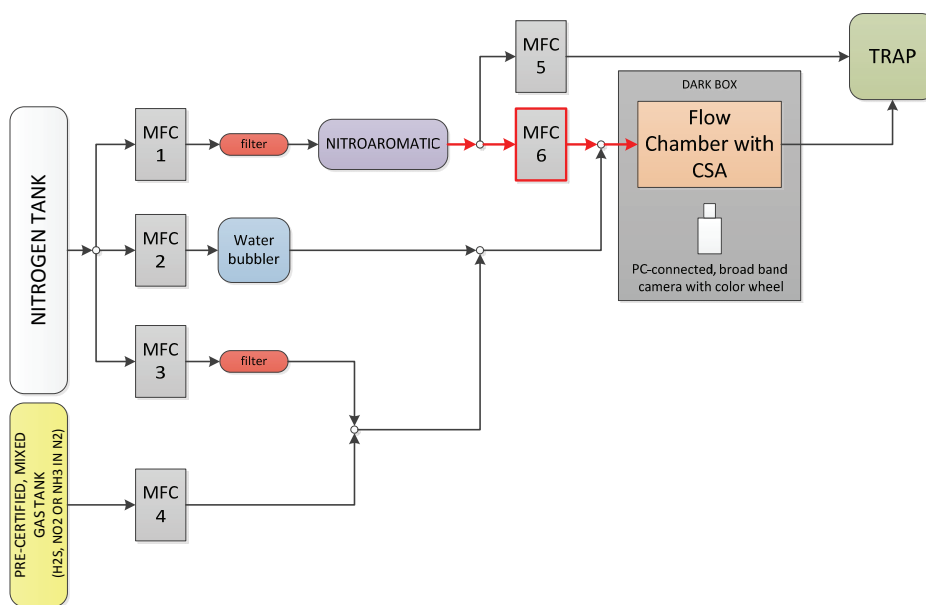
**Figure S6.** Experimental setup for colorimetric detection of nitroaromatics.

All tested analytes, except for TNT, were analytical-grades purchased from Sigma Aldrich, and used as received. TNT was purchased as 1 mg/mL solutions from Ultra Scientific, which was used after deposition of the TNT solution onto silica gel (Sigma Aldrich, Grade 40), and removing the solvent under vacuum. The experimental procedure for vapor generation depended on the analyte. When the analyte is in a liquid phase at room temperature, a gas dilution system was used to generate saturated vapor pressure by passing nitrogen through a fritted bubbler. When the analyte is a solid at room temperature, nitrogen was passed through a percolation tube packed with approximately 15g of the analyte. For TNT, the percolation tube was packed with 2 mg of TNT loaded silica for safety reasons. When the TNT percolation tube was heated to 100 °C, the resulting tube generates approximately 0.7 ppb of TNT, which was measured and compared to a calibration standard using a solid phase micro-extraction tube and gas

chromatography-mass spectroscopy. The resulting vapor stream is diluted with a series of mass flow controllers to obtain a desired concentration and relative humidity. To minimize the surface passivation, the gas flow path was heated to 60 °C using heating tape. An activated charcoal filter was used to trap exhaust gas streams. Gas dilution schematics for all experiments are shown in Fig. S6-8.

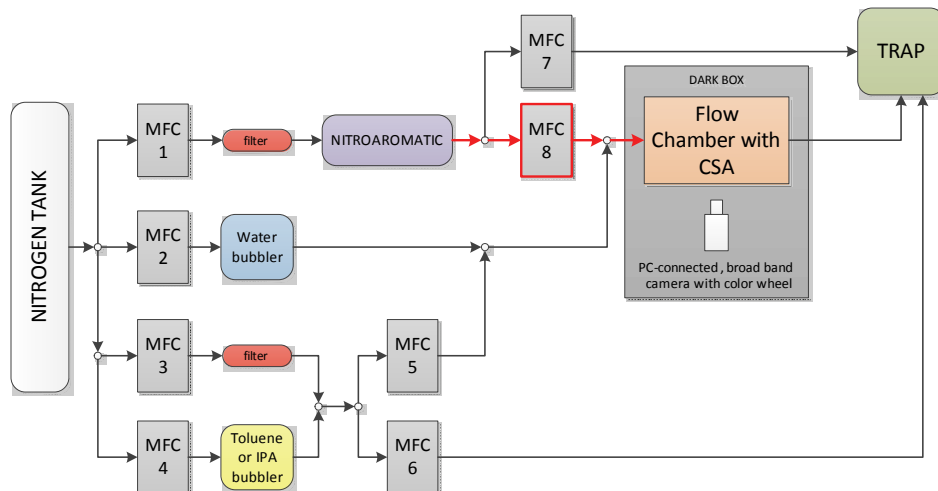


**Figure S7.** Gas dilution set-up for the discrimination of nitroaromatics and the impact of humidity.

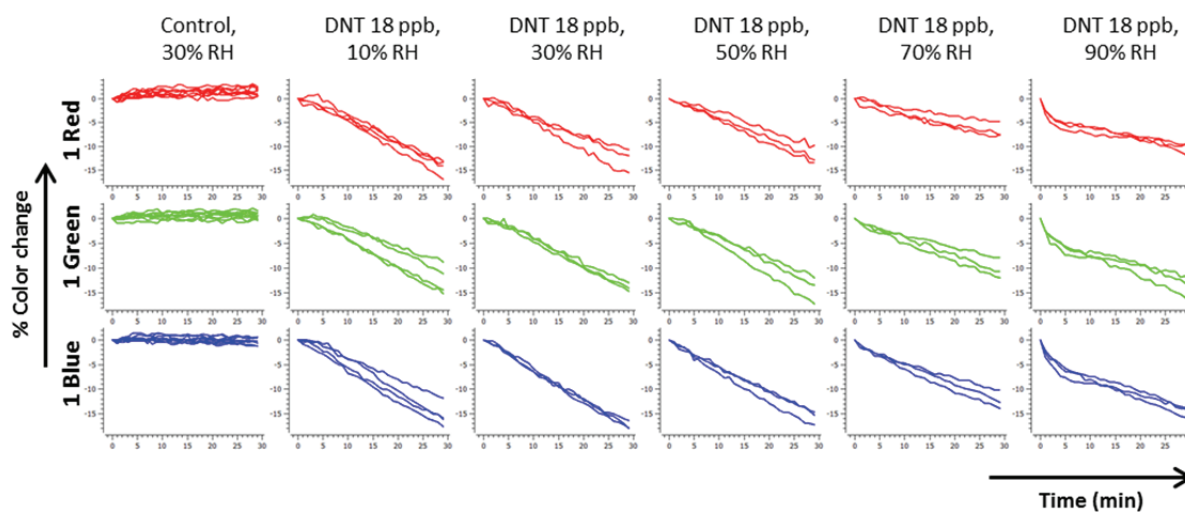


**Figure S8.** Gas dilution set-up for interferents for the following analytes: hydrogen sulfide, nitrogen dioxide and ammonia. Certified, pre-mixed gas tanks (Airgas) were diluted and combined with humidity and 2,4-DNT lines to achieve desired 2,4-DNT concentration, interferent concentrations and humidity levels.





**Figure S9.** Gas dilution set-up for interference experiments with toluene and isopropanol. Interferent vapor was generated by passing nitrogen through a fritted bubbler. Dilution and combination of interferent vapor lines with humidity and 2,4-DNT achieved desired 2,4-DNT concentrations, interferent concentrations and humidity levels.



**Figure S10.** Selected Sensor Response to 2,4-DNT at different relative humidity. Each subplot ranges from 0 to 30 minutes, -20 to +5 percent change.,

**Table S1.** List of chemically responsive indicators.

Spot #	Name
1	Isamine T-101 (alkylamines with polyethylene glycol)
2	Isamine J-101 (polyether amine mixture)
3	Isamine W-101 (alkylamine solution in water)
4	Nitrazine yellow + TBAOH
5	Bromophenol blue + TBAOH
6	7-amino-4-hydroxy-2-naphthalenesulfonic acid
7	Bromocresol purple + NaOH
8	<i>N,N</i> -diethyl- <i>p</i> -phenylenediamine
9	Pb(OAc) <sub>2</sub>
10	5,10,15,20-tetraphenylporphine zine
11	Octaethylporphine zinc
12	$\alpha$ -Naphthyl red
13	<i>N,N,N',N'</i> -Tetramethyl- <i>p</i> -phenylenediamine
14	2,3-Diaminonaphthalene
15	Bromocresol green
16	Nile red
17	Disperse orange #25
18	4-(4-Nitrobenzyl)pyridine + <i>N</i> -benzylaniline
19	Disperse red 1

TBAOH: 1.0 M Tetrabutylammonium hydroxide in 2-methoxyethanol

NaOH: 1.0 M Sodium hydroxide in water

### Calculation of Limit of Detection

The limit of detection (LOD) was calculated for each analyte by interpolating the response curve. First, the noise,  $N$ , in units of average pixel intensity change,  $\Delta I$ , was estimated as either 3 times the mean standard deviation of the control response – where the analyte and control responses were in different directions or, usually, where the control response was negligible – or as 3 times the mean control response at the time-point of interest – where the analyte and control responses were in the same direction. Then, a straight line was fit to the analyte response curve with an x-intercept of either 0 or an x-intercept of 5 (when the lag in response was considered). The slope of this line represents the signal,  $S$ , in average pixel intensity change per min ( $\Delta I/\text{min}$ ).



The LOD for an analyte exposed to the CSA at a given concentration, C (ppb), for a length of time, T (min), with noise, N ( $\Delta I$ ), and signal, S ( $\Delta I/\text{min}$ ), is then simply given by (Eqn S1):

$$\text{LOD (ppb)} = N/(S*C*T) \qquad \text{Equation S1}$$

Reported limit of detections represent those calculated from the best responding.