Array of Polycyclic Aromatic Hydrocarbons and Carbon Nanotubes for Accurate and Predictive Detection of Volatile Organic Compounds under Real-World Environmental Humidity Conditions

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Motivation

- *NMP.2013.1.2-1 Call: Nanotechnology-based sensors for environmental monitoring*

" Reliability is required within the foreseen operating environment, considering temperature, humidity, and other parameters affecting stability. "

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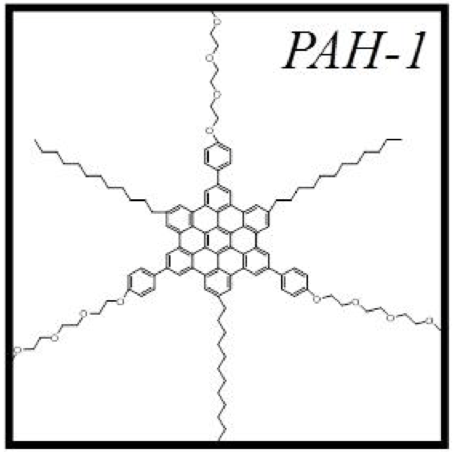
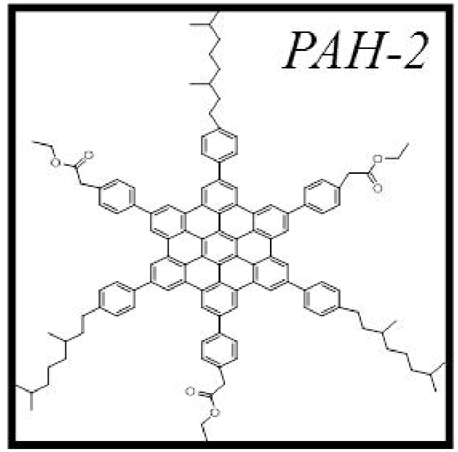
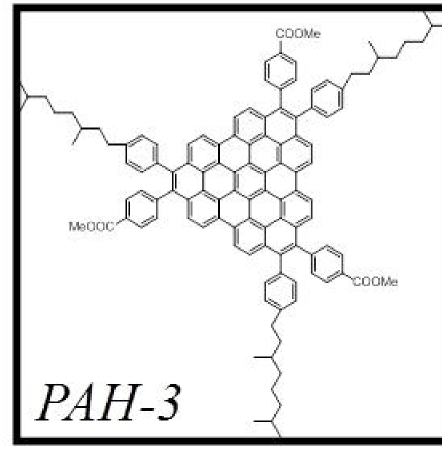
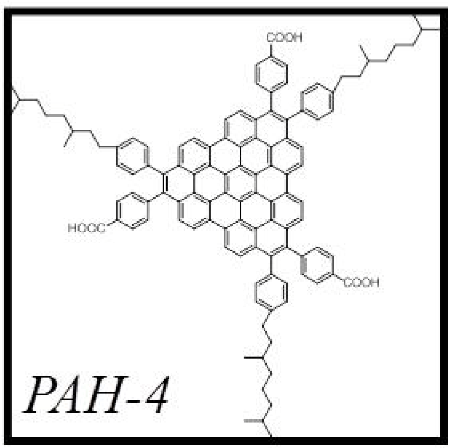
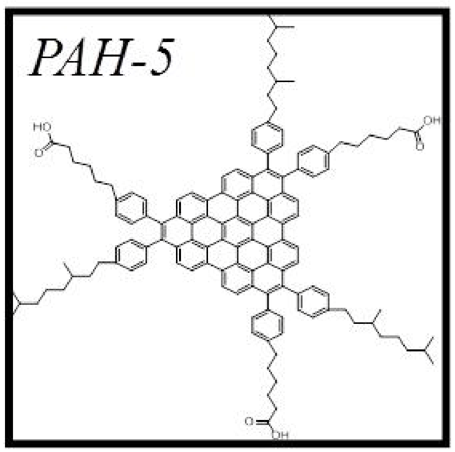
PAH Derivatives

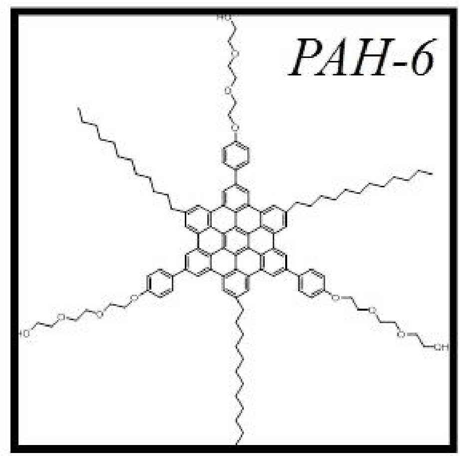


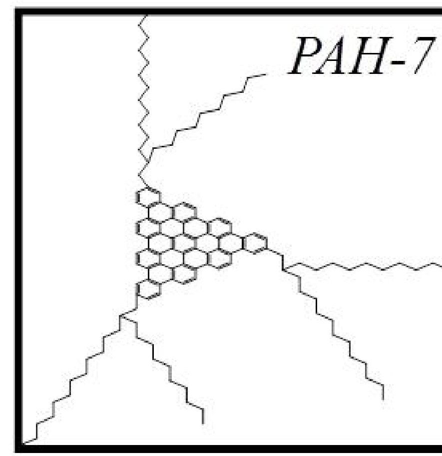












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PAH Derivatives

	Coronae	Carbon No.	Termination
PAH-1	Aromatic	42	Ether
PAH-2	Aromatic	42	Ester
PAH-3	Semi-Traingle-Shaped	48	Ester
PAH-4	Semi-Traingle-Shaped	48	Carboxylic Acid
PAH-5	Semi-Traingle-Shaped	48	Alkylic Side Chain + Carboxylic Acid
PAH-6	Aromatic	42	Alcohol
PAH-7	Triangle-Shaped	50	Carbon chains

- *Different coronae type and carbon number*
- *Side groups containing different hydrophobic mesogens terminated with different alkyl chains and functional substituents*

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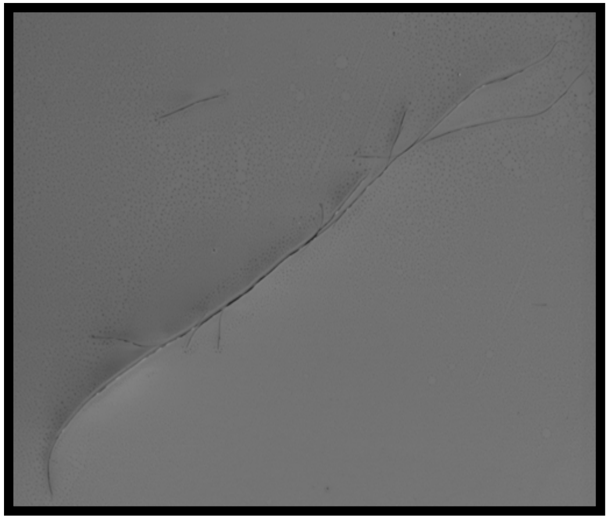
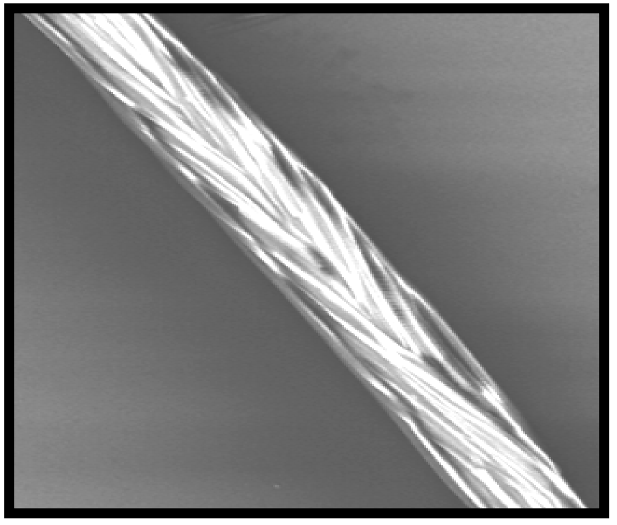
Properties of PAH Derivatives

- *The PAH molecules have high charge mobility due to their large corona (pi-pi interaction between one PAH corona to another one).*
- *PAH molecules may self-assembly into micro and/or nano columns:*
  - *Solvents*
  - *Concentration*
  - *Pre-aggregation*
  - *Functional side groups*
  - *Deposition method*
- *PAH self-assembly may produce a hydrophobic surface*





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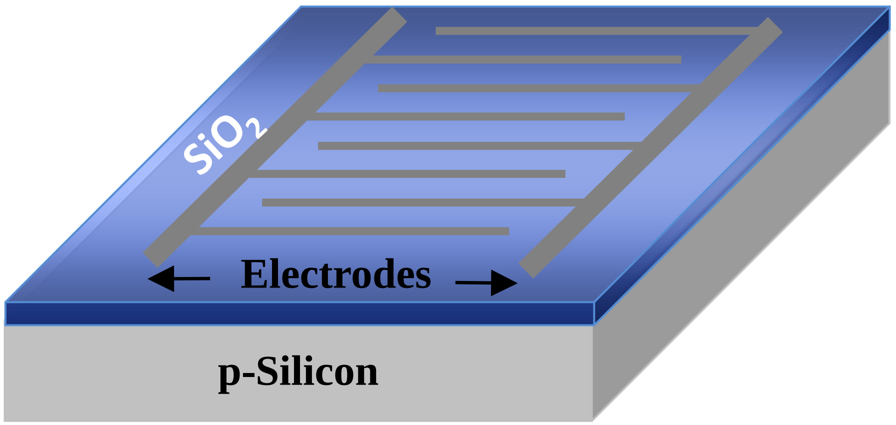
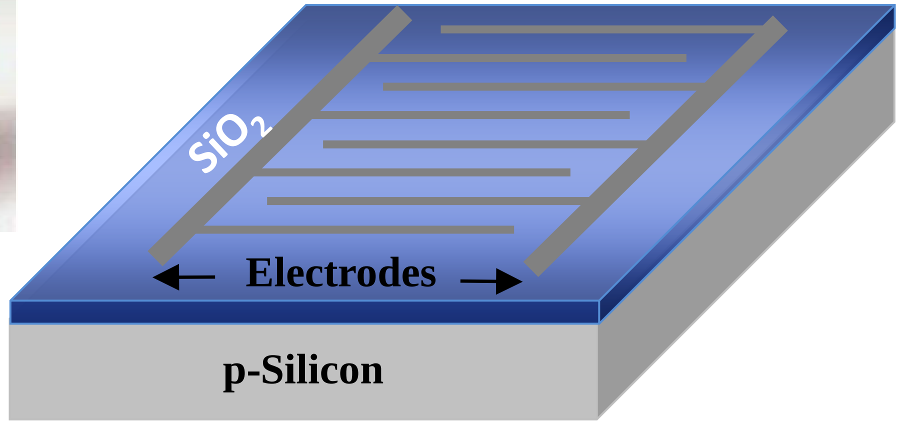
Sensors Fabrication



Sensing Device

- *p-type Si(100) wafers*
- *2 μm thick thermally grown SiO_2 insulating layer*
- *10 pairs of interdigitated electrodes, 4.5 mm wide, 100 μm spacing*
- *Evaporation of 5 nm/40 nm Ti/Pd layer through a shadow mask*

Sensors Fabrication



Bottom layer: SWCNTs

- *ARRY International LTD, Germany*
- *~30% metallic, ~70% semiconducting*
- *Average diameter = 1.5 nm; Length = 7 mm*
- *Dispersion in dimethylformamide using sonication for 15 min: 0.02 wt% dispersion*
- *Left for 0.5 h in a 50 mL vial for sedimentation of large aggregates*

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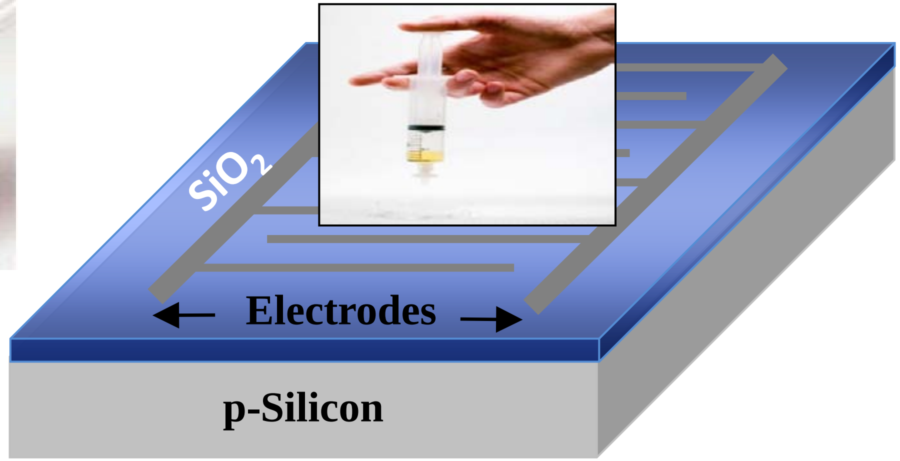
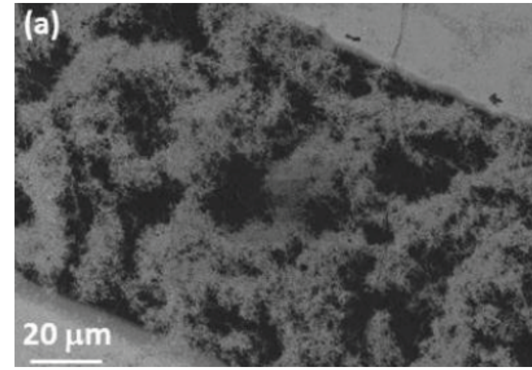
Sensors Fabrication





Bottom layer: SWCNTs

- *Dispersion above the precipitate: purified by ultracentrifugation for 25 min*
- *Drop-coating: Electrically continuous random network of SWCNTs*
- *Drying overnight under ambient conditions*
- *Resistance: 100 KΩ to 10 MΩ*

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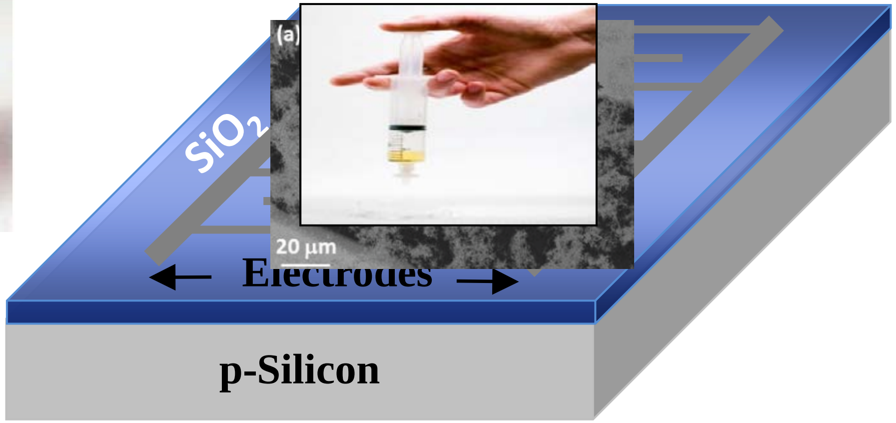
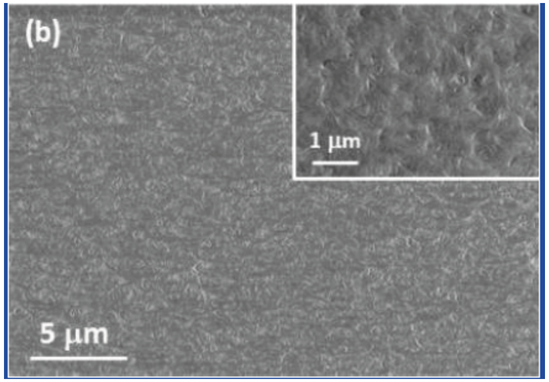
Sensors Fabrication

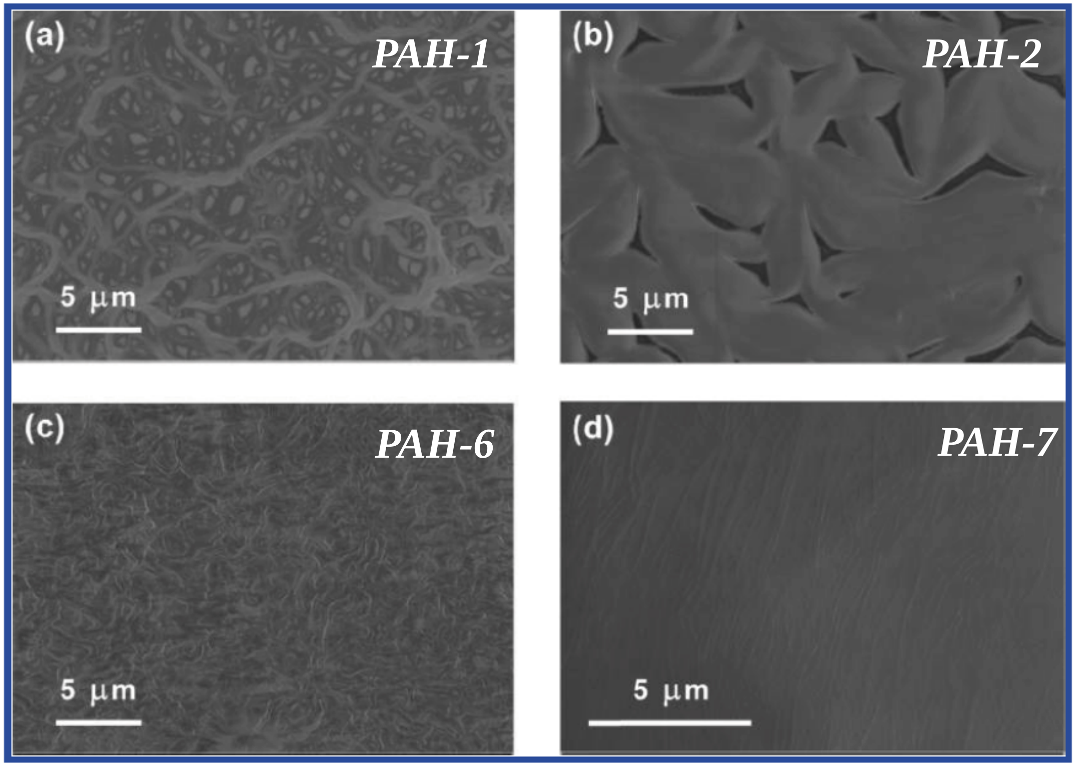




Upper layer: PAH

- *Solutions:*
  - *10^{-3} M solution of PAH-1, PAH-2, PAH-3, PAH-4 and PAH-7 in toluene*
  - *10^{-3} M solution of PAH-5 and PAH-6 in tetrahydrofuran*
- *Drop-coating 10 μl of solution over the SWCNTs layer*
- *Slowly dried under ambient conditions for 2-5 h*
- *Film thickness: 1-2 μm*

Sensing Films



FE-SEM images

The PAH derivatives assembled in different nano- or micro-structures:

- *PAH-1: Nanoropes*
- *PAH-2: Microflowers*
- *PAH-6: Nanocables with a winding pattern orientation*
- *PAH-7: Nanocables with quasi-uniform orientation*

Sensors Resistance:

- *SWCNTs: 100 KΩ to 10 MΩ*
- *Pristine PAH: 1-2 TΩ*
- *PAHs/SWCNTs bilayers:*
  - *PAH-4/SWCNTs: ~5 kΩ*
  - *Others: ~90 kΩ to few MΩ,*

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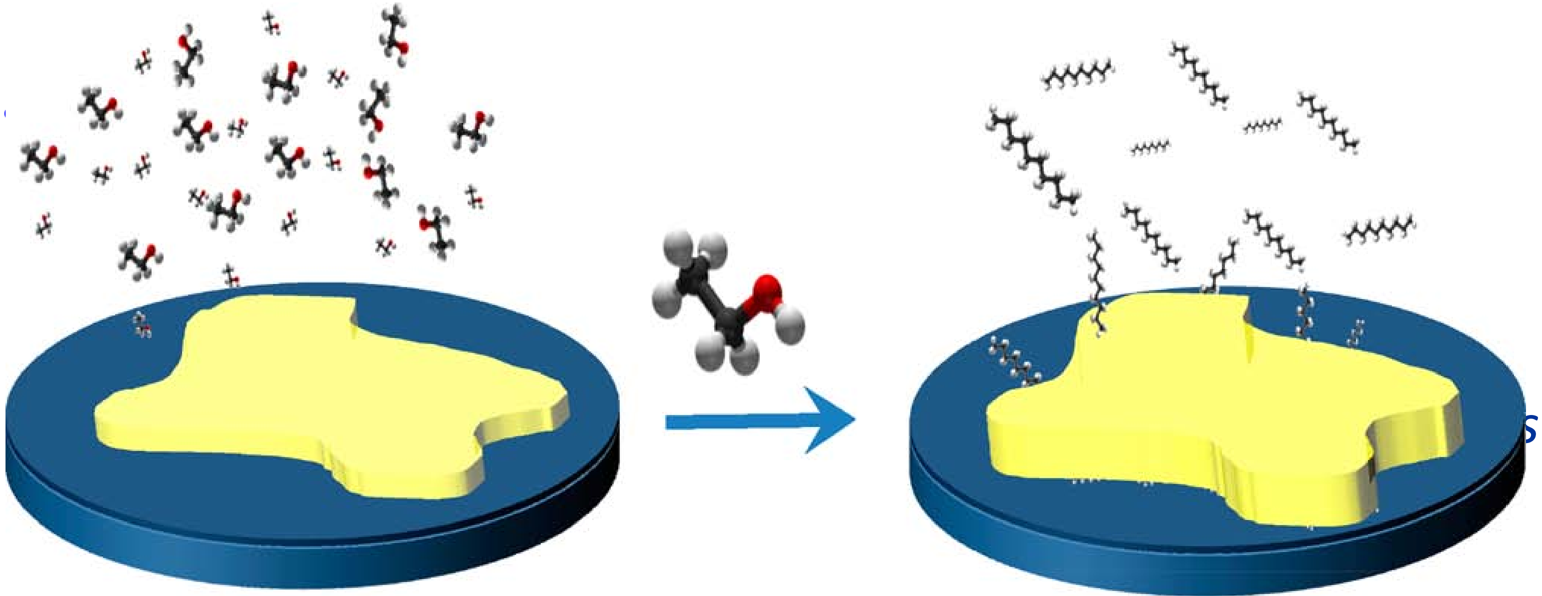
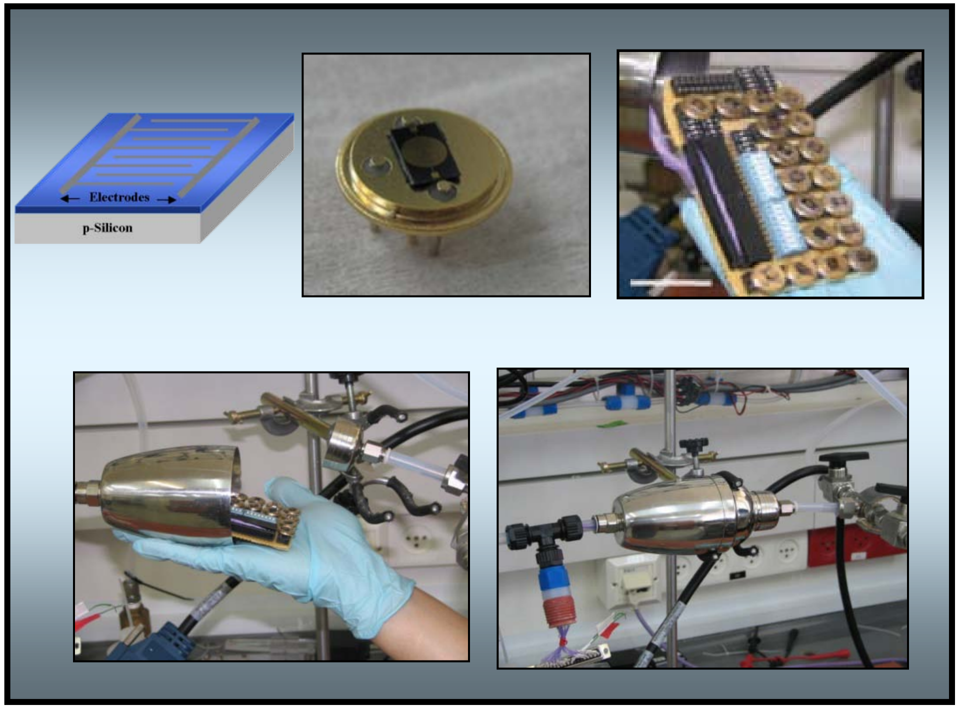
VOCs Classification

- *Nature of VOCs compounds:*



- *Detection of Non-Polar VOCs:*
  - *More difficult to achieve*
  - *Have to be detected indirectly via steric interaction between the sensing material and the VOC (e.g., film swelling)*

Sensing Measurements



VOCs Analysed

- ***Polar:***
  - *Hexanol*
  - *Octanol*
  - *Decanol*
  - *Ethanol*
- ***Non-Polar***
  - *Hexane*
  - *Octane*
  - *Decane*

- ***Aromatic*** *(Very Weak Polar)*
  - *Ethyl Benzene*
- ***Water Vapour*** *(Polar)*

Concentrations:

- *p_a/p_o = 0.04 to 1*
  - *p_a : Partial pressure of the VOC*
  - *p_o : Saturated vapor pressure at 21 ºC.*

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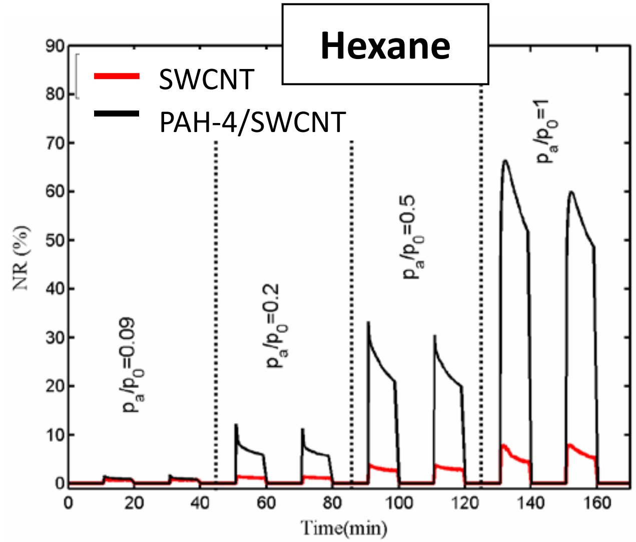
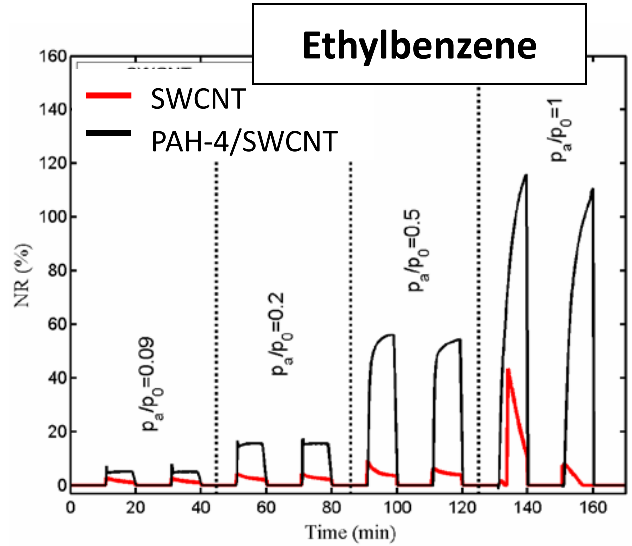
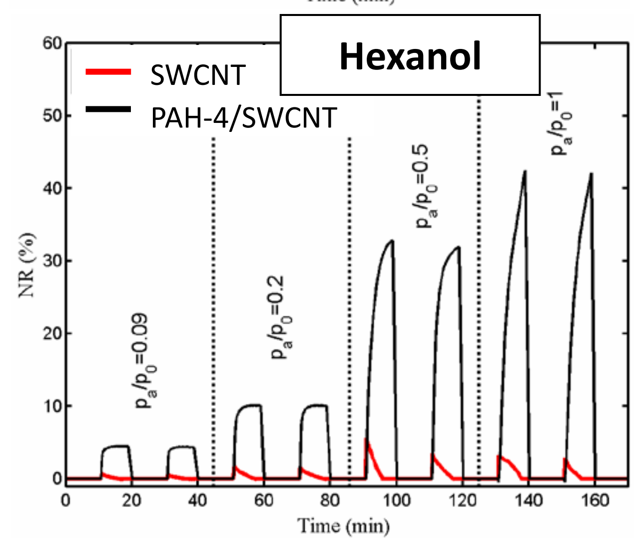
Results







- *Addition of PAH sensing layer dramatically improves the sensor sensitivity*
- *The sensitivities to non-polar and aromatic analytes are much higher than to polar analytes*

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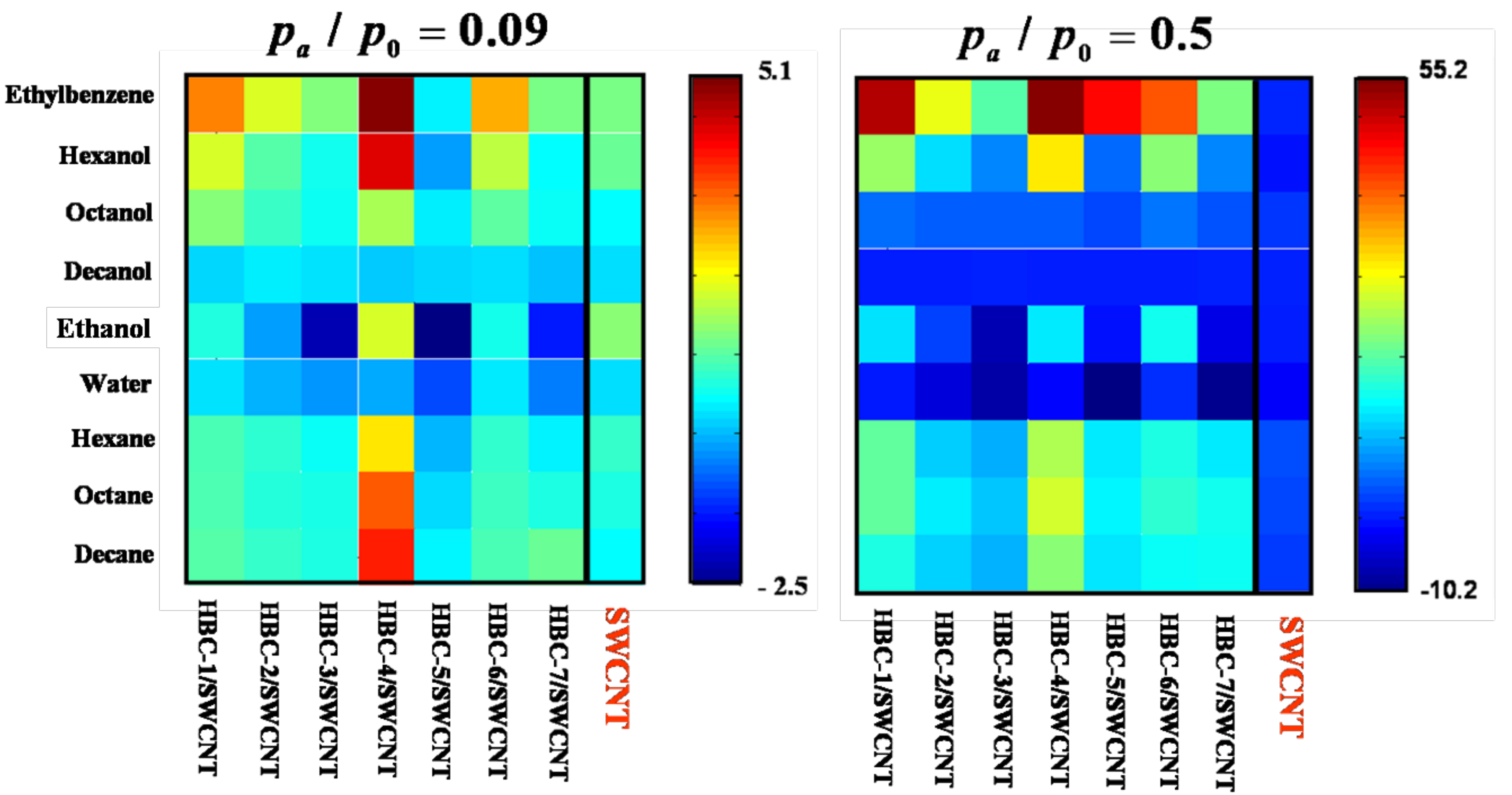
Hot Plot of Sensors Responses



The incorporation of the PAH derivatives improved the sensing signals toward part or all of the VOCs tested, compared to pristine SWCNTs

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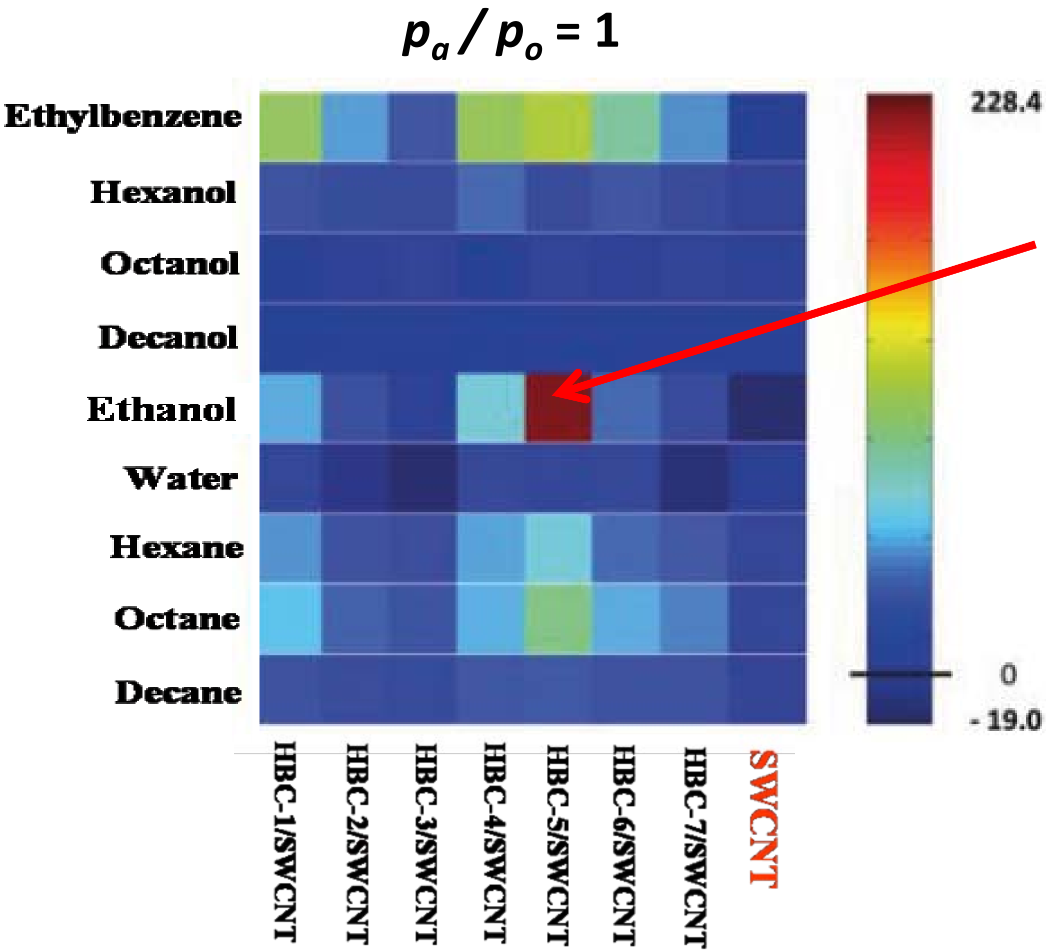
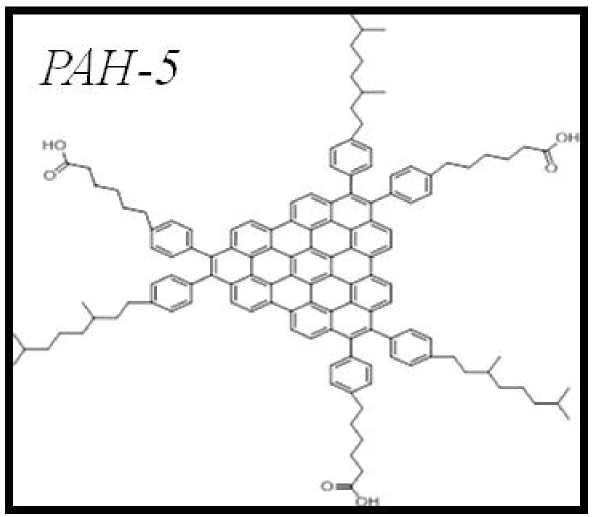
Analysis of Sensing Results



- *Highest response to* ***ETHANOL****:* ***PAH-5/SWCNT*** *sensor*
- *At p_a/p_o = 1: SR = 228.4% ; ~ 3 times higher PAH-4/SWCNT*
- *The high affinity of the PAH-5 to ethanol can readily be attributed to the carboxyl group of the substituent functionality.*



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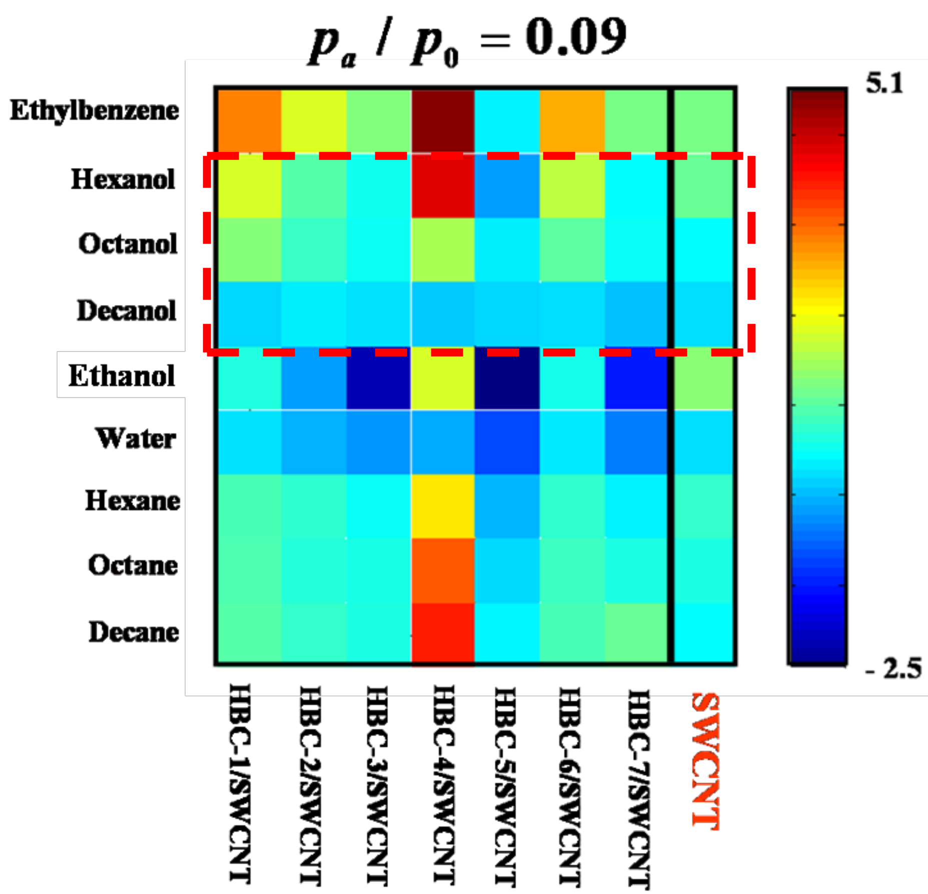
Analysis of Sensing Results



- *The detection of the* ***OH-terminated (polar) VOCs*** *was most likely promoted by the presence of oxygen in the substituent functionality* ***(PAH-1, PAH-2, PAH-4, and PAH-6).***
- *The longer the OH-terminated VOC, the lower the sensing signal.*
- *Most probably due to an increased steric effect.*

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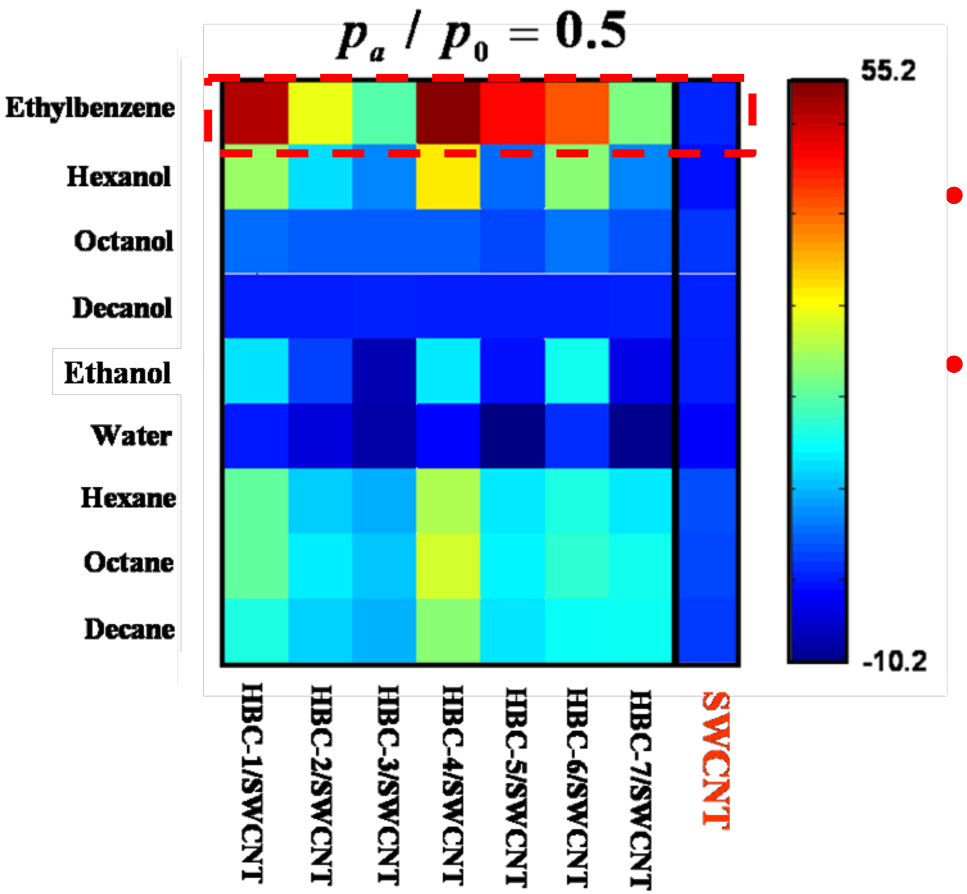
Analysis of Sensing Results



- *All PAH/SWCNTs exhibited high responses to* ***ETHYLBENZENE***
- *This can be explained by van der Waals interactions between the benzene rings of the ethyl benzene and PAH corona (which is made of fused benzene rings).*

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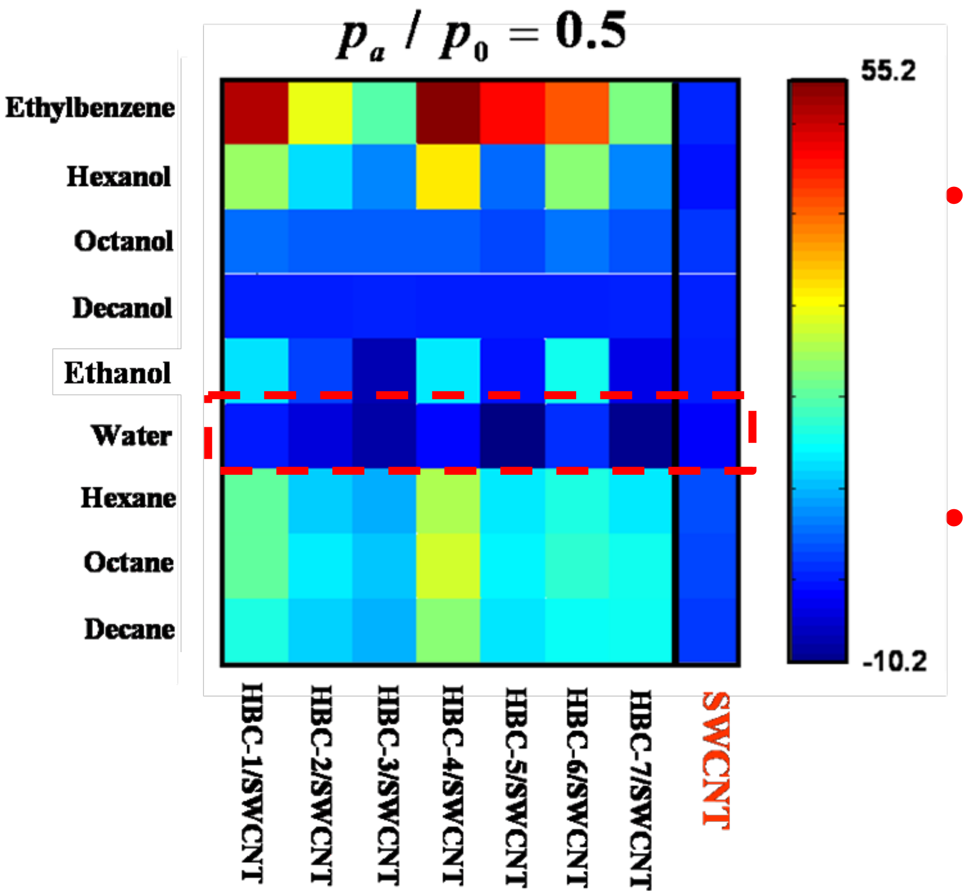
Analysis of Sensing Results



- *The response of the PAH/SWCNTs sensors to* ***WATER*** *vapor was* ***relatively low****, compared to the other VOCs*
- *Hydrophobic terminations of the VOCs*

VOCs Discrimination

Features extracted from each sensor response

- *F1 : Response at the middle of exposure*
- *F2 : Response at end of exposure*
- *F3 : Area under response curve*

Pattern recognition algorithm

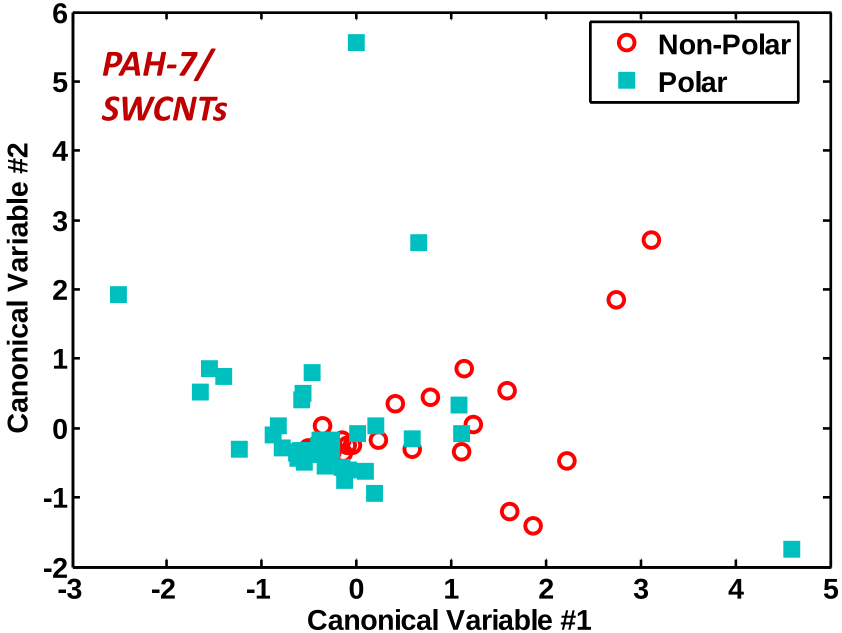
- *Discriminant Factor Analysis (DFA)*

Cross-validation method

- *Leave-one-out*

Polar vs Non-Polar VOCs

Employing single sensors



- ***Polar:***
  - *Hexanol*
  - *Octanol*
  - *Decanol*
  - *Ethanol*
  - *Ethyl Benzene*
- ***Non-Polar***
  - *Hexane*
  - *Decane*
  - *Octane*

	PAH1/ SWCNT	*PAH2/ SWCNT*	*PAH3/ SWCNT*	*PAH4/ SWCNT*	*PAH5/ SWCNT*	*PAH6/ SWCNT*	*PAH7/ SWCNT*	*SWCNT*
Non-Polar VOCs	37.5	45.8	50	50	37.5	41.7	50	58.3
Polar VOCs	79.2	77.1	81.3	79.2	77.1	72.9	83.3	62.5
Total	65.3	66.7	61.1	69.4	63.9	62.5	**72.2**	61.1

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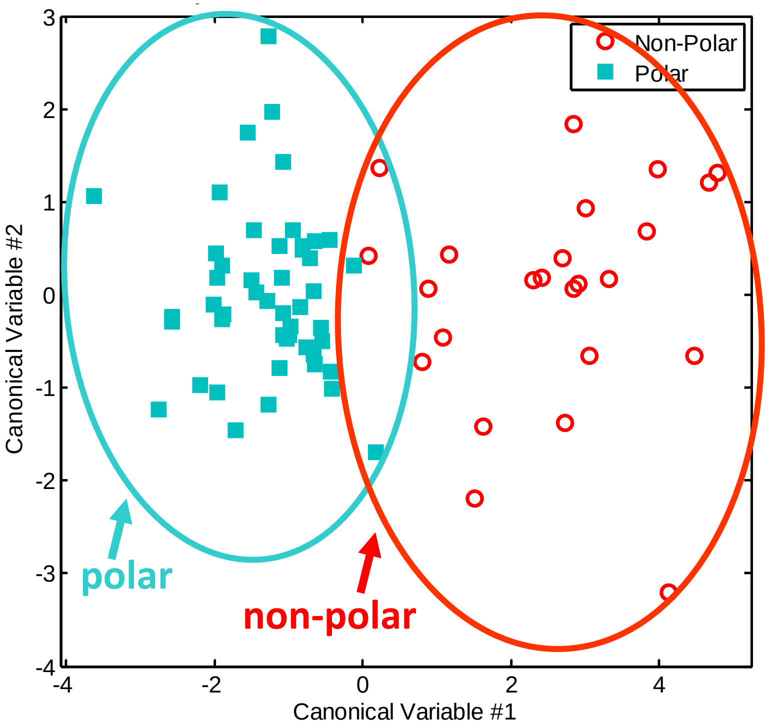
Polar vs Non-Polar VOCs

Employing combination of sensors

All PAH Sensors



- ***Polar:***
  - *Hexanol*
  - *Octanol*
  - *Decanol*
  - *Ethanol*
  - *Ethyl Benzene*
- ***Non-Polar***
  - *Hexane*
  - *Decane*
  - *Octane*

	7 PAHs/ SWCNT	*6 PAHs/ SWCNT*	*5PAHs/ SWCNT*	*4PAHs/ SWCNT*	*3PAHs/ SWCNT*	*2PAHs/ SWCNT*
Non-Polar VOCs	87.5	87.5	79.2	70.8	70.8	58.3
Polar VOCs	91.7	91.7	93.8	95.8	95.8	95.8
Total	**90.3**	**90.3**	88.9	87.5	87.5	83.3
PAH Molecules	All	1,2,3,4,6,7	1,2,4,6,7	1,3,4,7/ 1,4,6,7	1,4,7	6,7

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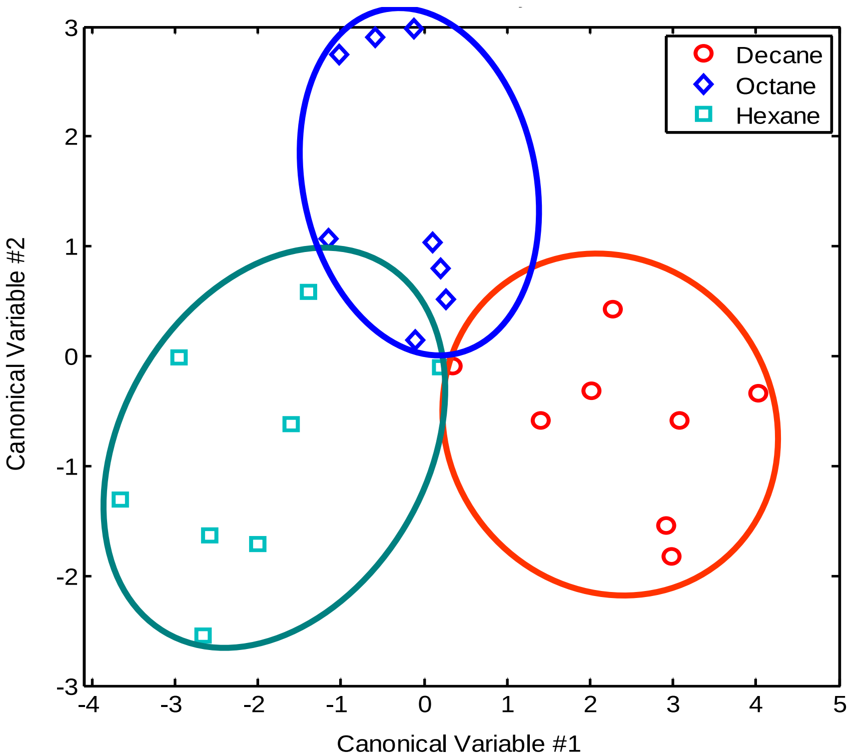
Discrimination of the Non-Polar VOCs

Employing combination of sensors

4 PAH/SWCNT Sensors

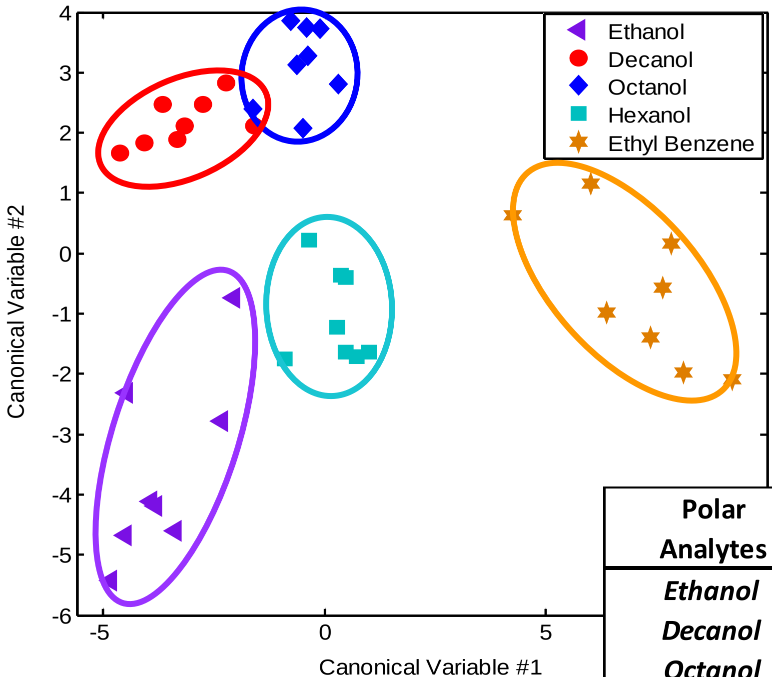


	4PAHs/ SWCNT	*3PAHs/ SWCNT*	*2PAHs/ SWCNT*
Decane	87.5	75	62.5 / 62.5
Octane	87.5	75	27.5 / 50
Hexane	62.5	62.5	87.5 / 75
Total	**79.2**	70.8	62.5
PAH Molecules	1,2,3,7	1,3,7	2,4 / 4,6

Discrimination of the Polar VOCs

Employing combination of sensors

5 PAH/SWCNT Sensors



Polar Analytes	*6 PAHs/ SWCNT*	*5PAHs/ SWCNT*	*4PAHs/ SWCNT*	*3PAHs/ SWCNT*	*2PAHs/ SWCNT*
Ethanol	50 ; 37.5	62.5	62.5	37.5	62.5
Decanol	87.5 ; 75	87.5	100	100	100
Octanol	75 ; 87.5	87.5	87.5	87.5	62.5
Hexanol	75 ; 75	87.5	75	75	75
Ethyl Benzene	50 ; 62.5	75	62.5	62.5	75
Total	67.5	**80**	77.5	72.5	75
PAH Molecules	1,2,3,4,6,7; 2,3,4,5,6,7	2,3,4,5,6	3,4,5,6	1,6,7	2,3

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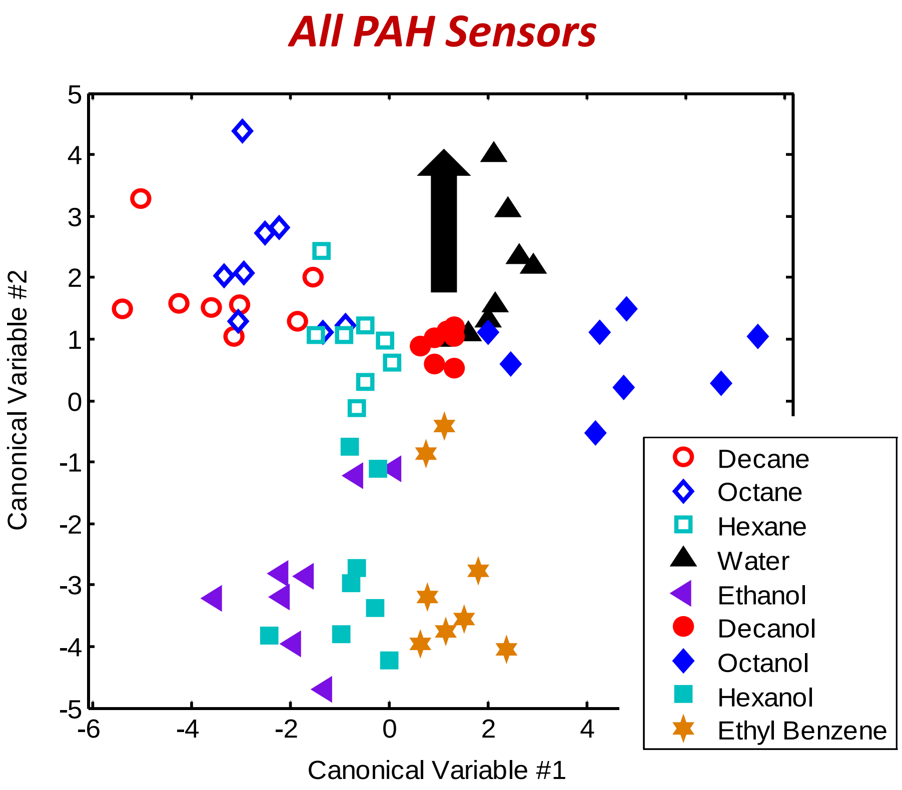
Simultaneous Discrimination of All VOCs



- *Plot center: lowest VOCs concentration ($p_a / p_o = 0.04$)*
- *Moving from center to periphery: increasing VOCs concentrations*

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VOCs Concentrations Prediction

Measurements available

- *4 concentrations / VOC*
- *2 repetitions / concentration*

Pattern recognition algorithm

- *Partial Least Squares (PLS)*

Cross-validation method

- *Leave-one-out*

Evaluation method

- *Correlation coefficient between real and predicted concentrations*

Concentration Estimation by PLS Models

VOC	PAH-1/ SWCNTs	PAH-2/ SWCNTs	PAH-3/ SWCNTs	PAH-4/ SWCNTs	PAH-5/ SWCNTs	PAH-6/ SWCNTs	PAH-7/ SWCNTs	SWCNTs
Decane	0.9755	0.9765	0.9814	0.9372	**0.9962**	0.9797	0.9815	0.9870
Octane	0.9896	0.9767	0.9797	**0.9990**	0.9336	0.9581	0.9730	0.9800
Hexane	0.9946	0.9810	0.9772	**0.9998**	0.9553	0.9835	0.9876	0.9877
Water	0.8563	0.6665	0.6187	0.7778	0.0998	**0.9564**	0.5682	0.9054
Ethanol	**0.9592**	0.9461	0.5619	0.9298	0.9027	0.9406	0.8416	0.9160
Decanol	0.7000	0.8450	**0.8678**	0.7421	0.6725	0.2943	-0.2290	0.4565
Octanol	0.5387	0.3742	0.3274	**0.8204**	0.3380	0.6277	0.3907	0.3021
Hexanol	0.8386	0.9036	0.9670	0.9020	0.9384	0.8680	**0.9841**	0.7120
Ethyl Benzene	0.9936	0.9605	0.9207	0.9937	0.9841	0.9770	**0.9962**	0.8223

- *Non-polar VOCs: Very good concentration estomation with all sensors*
  - *Octane and Hexane: Best sensor PAH-4/SWCNT*
  - *Decance: PAH-5/SWCNT*
- *Ethylbenzene and Hexanol: Excellent estimation using PAH-7*
- *Ethanol and Water: Correlation coefficients > 0.95*
- *Decanol: Slightly inferior results*
- *Octanol: PAH-4 was by far the only sensor which could acceptable estimate it*

VOCs Detection in High Humidity Environment

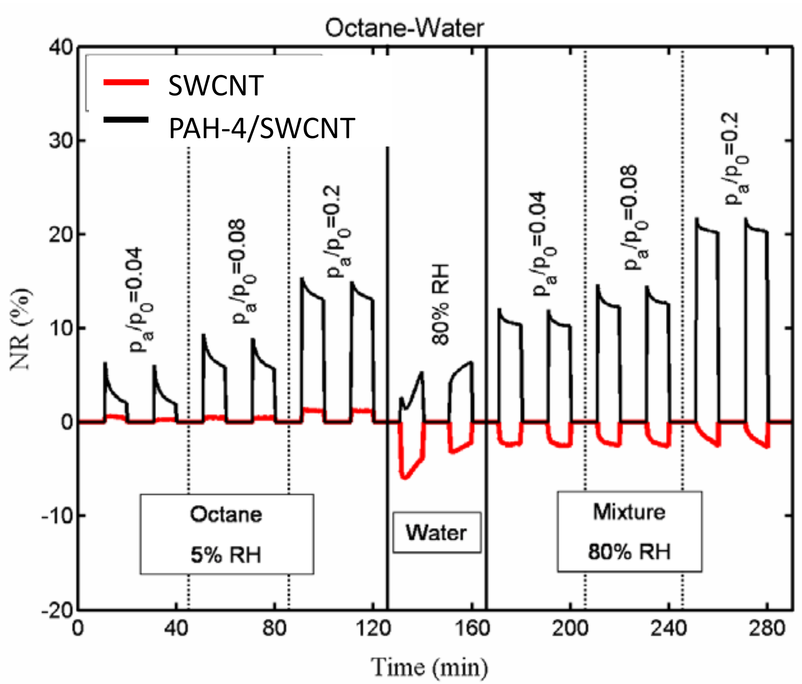
VOCs Measured

- *Octane (Non-Polar)*
- *Ethyl Benzene (Aromatic; Very Weak Polar)*
- *Ethanol (Polar)*

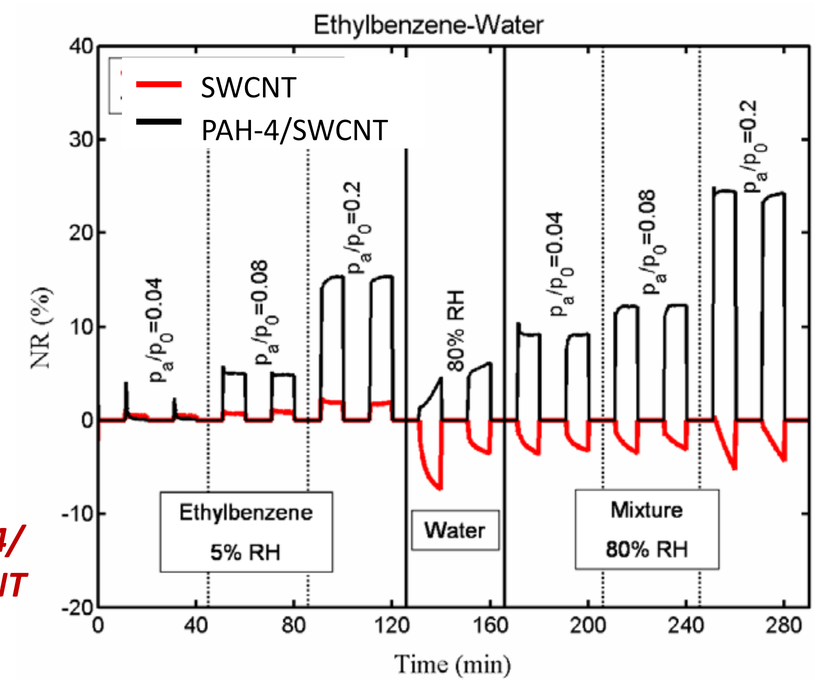
Humidity Levels

- *5 %*
- *80 %*

Sensors Responses



PAH-4/ SWCNT



- *SWCNT sensor: Positive response to VOCs, negative response to RH and VOCs in high RH background (dominant response to humidity)*
- *This turn over effect could be explained by the opening of electron channels at high humidity levels (>65%)*
- *Water molecules behave as electron donors to the SWCNTs*

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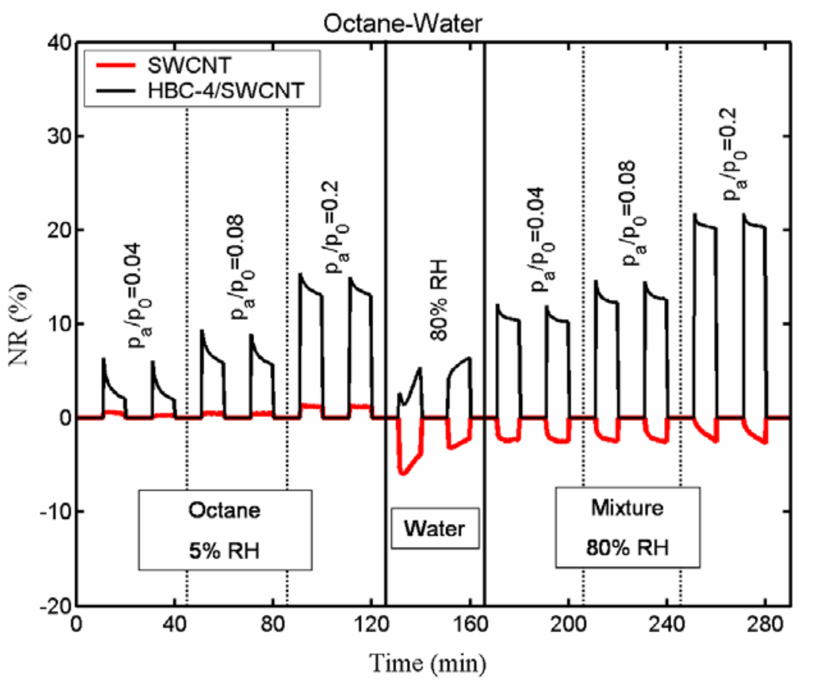
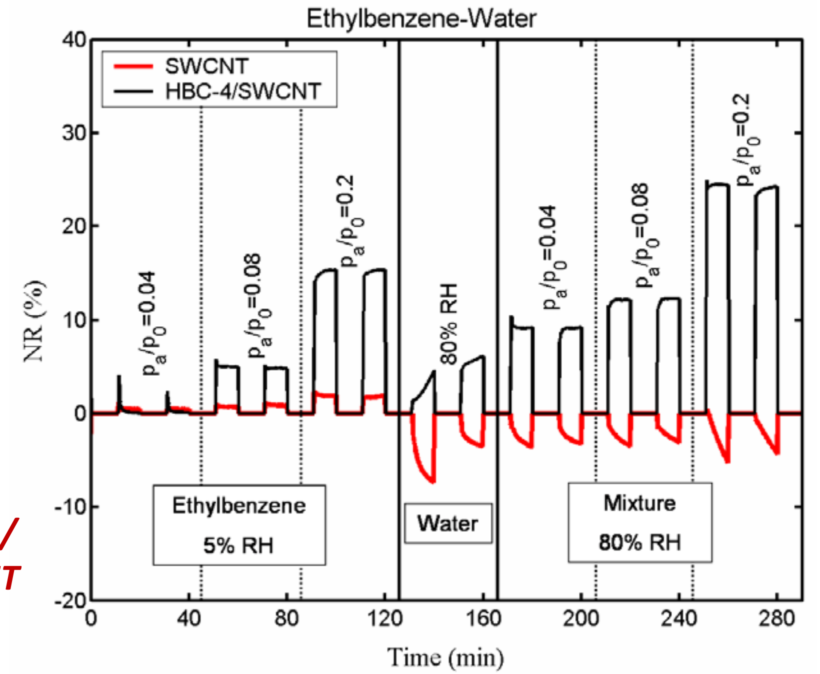
Sensors Responses



PAH-4/ SWCNT



- *Coating SWCNT with PAH: Dominant response to VOCs in presence of RH*
- *Possible mechanism:*
  1) *PAH film coating the SWCNTs acts as a water-selective filter that permits VOC diffusion and adsorption into the SWCNT network, but blocks the penetration of water molecules through the PAH-4 film*
  2) *The PAH film is the dominant sensing element for humidity in the PAH/SWCNT composites*

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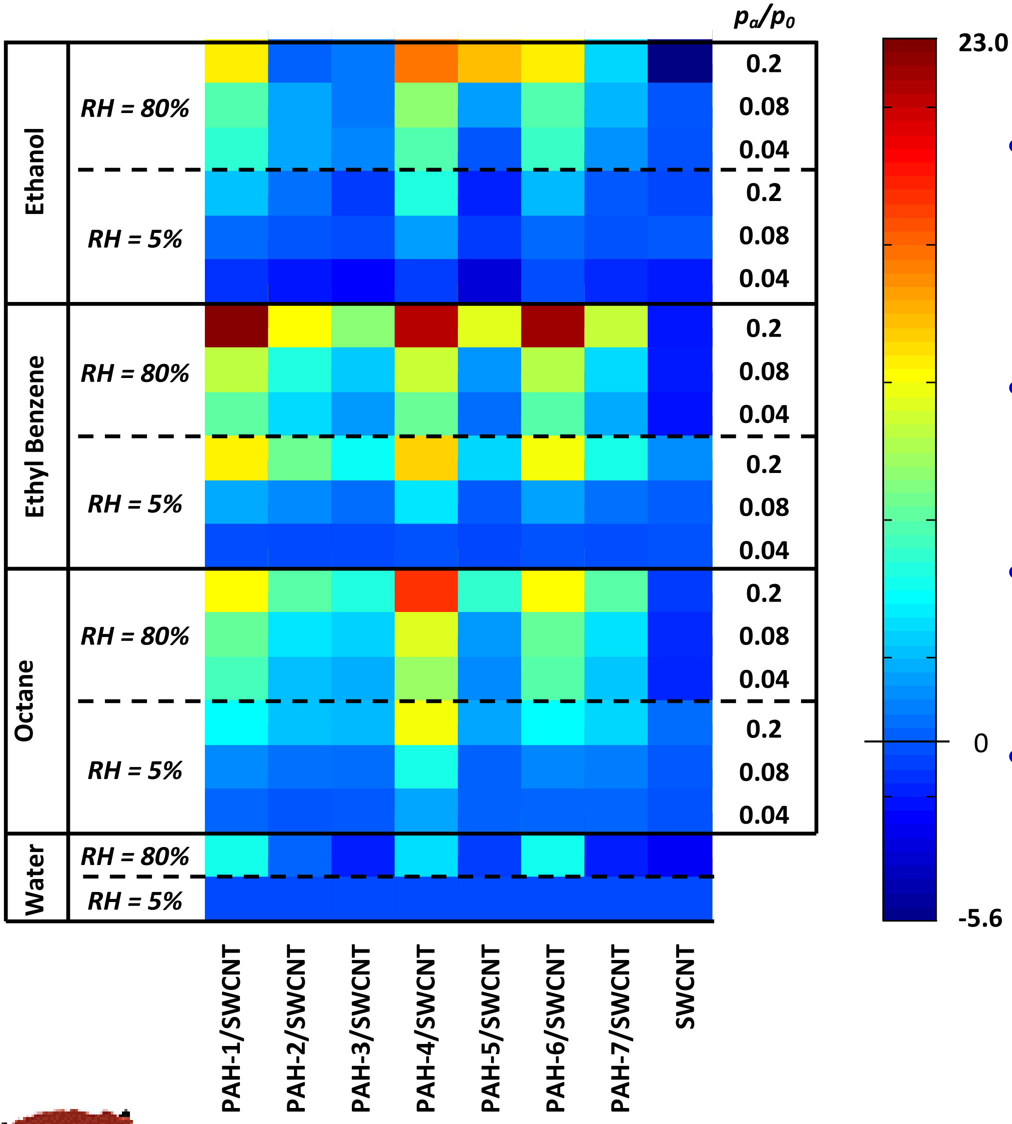
Hot Plot of Sensors Responses



- *Each point in these plots is an average of three independent exposures from three duplicated sensors*
- *PAHs incorporation slightly increased the sensitivity to humidity*
- *Response toward VOCs tested : Generally highly improved as compared to pristine SWCNTs*
- *Most cases, higher RH background, higher improvement compared to SWCNTs*

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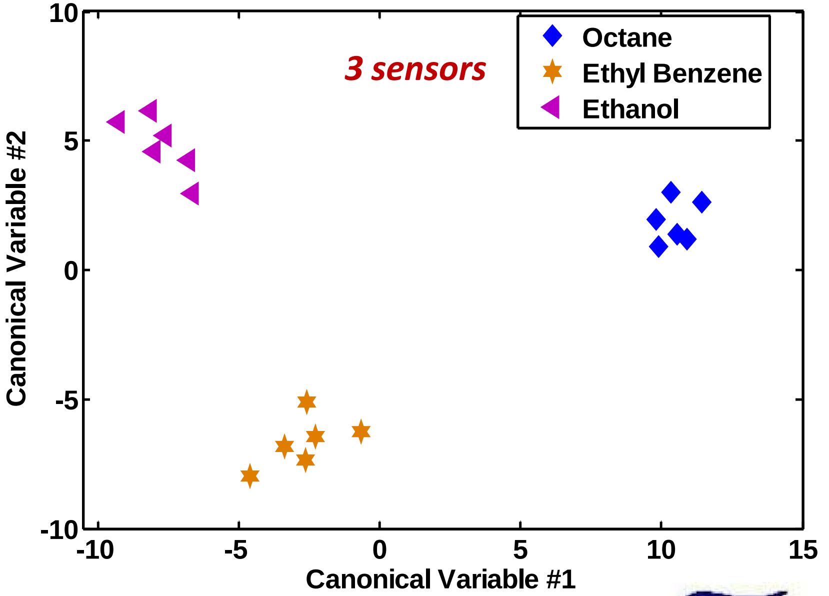
Discrimination of VOCs Measured in High RH

Employing Single Sensors

	PAH1/ SWCNT	*PAH2/ SWCNT*	*PAH3/ SWCNT*	*PAH4/ SWCNT*	*PAH5/ SWCNT*	*PAH6/ SWCNT*	*PAH7/ SWCNT*	*SWCNT*
Octane	33.3	16.7	0	33.3	16.7	50	0	16.7
Ethyl Benzene	83.3	83.3	33.3	100	83.3	83.3	66.7	50
Ethanol	100	100	100	83.3	100	83.3	100	100
Total	72.2	66.7	44.4	72.2	66.7	72.2	55.6	55.6

Employing Combination of Sensors

	3PAHs/ SWCNT	*2PAHs/ SWCNT*
Octane	100	100;100;100
Ethyl Benzene	100	100;83.3;83.3
Ethanol	100	83.3;100;100
Total	100	94.4
PAH Molecules	1,3,4	1,4;3,4;4,7



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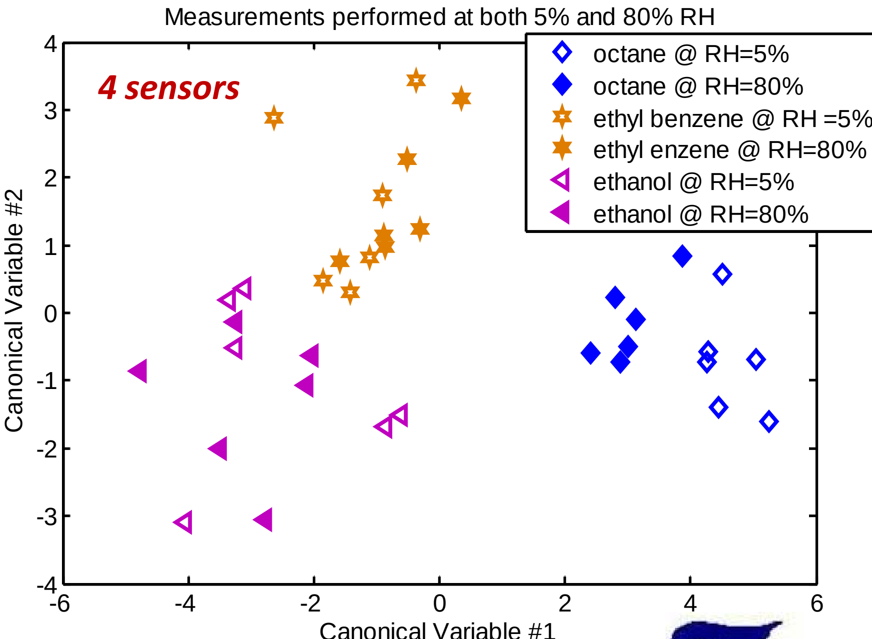
Discrimination of VOCs Under Various RH

Employing Single Sensors

	PAH1/ SWCNT	PAH2/ SWCNT	PAH3/ SWCNT	PAH4/ SWCNT	PAH5/ SWCNT	PAH6/ SWCNT	PAH7/ SWCNT	SWCNT
Octane	33.3	33.3	41.7	41.7	33.3	33.3	25	8.3
Ethyl Benzene	58.3	41.7	8.3	33.3	33.3	25	16.7	16.7
Ethanol	91.7	83.3	83.3	83.3	100	75	91.7	83.3
Total	61.1	52.8	44.4	52.8	55.6	44.4	44.4	36.1

Employing Combination of Sensors

	6 PAHs/ SWCNT	5PAHs/ SWCNT	4PAHs/ SWCNT	3PAHs/ SWCNT	2PAHs/ SWCNT
Octane	100	100	100	100	100
Ethyl Benzene	83.3	83.3	83.3	83.3	66.7
Ethanol	75	91.7	91.7	91.7	100
Total	86.1	91.7	91.7	91.7	88.9
PAH Molecules	1,2,4,5,6,7	1,2,4,5,7	2,4,5,6	2,4,6	2,4



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Concentration Estimation of VOCs Measured at 80% RH

VOCs at 80% RH	PAH-1/ SWCNTs	PAH-2/ SWCNTs	PAH-3/ SWCNTs	PAH-4/ SWCNTs	PAH-5/ SWCNTs	PAH-6/ SWCNTs	PAH-7/ SWCNTs	SWCNTs
Octane	0.9952	0.9913	0.9418	**0.9990**	0.9852	0.9729	0.9869	0.7849
Ethyl Benzene	0.9900	0.9675	0.9432	**0.9981**	0.9797	0.9246	0.9760	0.8885
Ethanol	0.9942	0.9432	0.7560	**0.9976**	0.9869	0.8281	0.4199	0.9415

VOCs at 5% RH	PAH-1/ SWCNTs	PAH-2/ SWCNTs	PAH-3/ SWCNTs	PAH-4/ SWCNTs	PAH-5/ SWCNTs	PAH-6/ SWCNTs	PAH-7/ SWCNTs	SWCNTs
Octane	0.9896	0.9767	0.9797	**0.9990**	0.9336	0.9581	0.9730	0.9800
Ethyl Benzene	0.9936	0.9605	0.9207	0.9937	0.9841	0.9770	**0.9962**	0.8223
Ethanol	**0.9592**	0.9461	0.5619	0.9298	0.9027	0.9406	0.8416	0.9160

- *Best correlation coefficient at 80% RH: PAH-4/SWCNTs sensor*
- *All PAH/SWCNTs sensors showed very similar performances at estimating octane and ethyl benzene concentrations at both 5% and 80% RH (correlation coefficient over 0.9 in all cases)*

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Summary and Conclusions

- *PAHs with various aromatic coronae and functional substituents allows reliable discrimination between polar and nonpolar compounds and, also, between the different components in each of these VOC groups.*
- *Using appropriate combinations of PAH/SWCNT sensors, the sensitivity and accuracy of the cross-reactive PAH/SWCNT array could be tailored according to the detection (or application) of interest.*
- *Combining the sensors with the PLS algorithm allowed prediction of VOC concentration in various constant humidity levels.*
- *This result is of great importance for the construction of smart, self-learning sensing systems that can work independently under real confounding factors.*
- *The results obtained could lead to the development of a cost-effective, light-weight, low-power, non-invasive tool for the widespread detection of VOCs in real-world applications, including environmental, security, food, health, etc.*

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Future Work

- *A study for understanding the structure-property relationship between the PAH corona, PAH substituent functionality, PAH/SWCNT binding interface, and the VOC chemical nature*

Acknowledgements

- *I acknowledge the "Ramon y Cajal" senior research grant from Ministry of Science and Innovation, Spain*

- *Xinliang Feng, Max-Planck-Institute for Polymer Research, Mainz, Germany: PAH synthesis*

- *Yael Zilberman, Technion – Israel Institute of Technology: Sensors fabrication and sensing measurements*

- *Hossam Haick, Technion – Israel Institute of Technology: Project coordination*

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