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Single-walled Carbon Nanotube-Metalloporphyrin Chemiresistive Gas Sensor Arrays for Volatile Organic Compounds

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ABSTRACT: A chemiresistive sensor array was created from single-walled carbon nanotubes (SWCNTs) by non-covalent modification with late first-row transition metal complexes of *meso*-tetraphenylporphyrin. The responses to vapors of various volatile organic compounds (VOCs) were strong and were subjected to statistical analyses that enabled the successful classification of representative VOCs into five different categories (aliphatic hydrocarbons, alcohols, ketones, aromatic hydrocarbons, and amines) with 98% accuracy. With the exception of amines, which are capable of strong charge transfer interactions, the basis of classification appears to correlate with the differences in the solubility properties of the porphyrin compounds in the various VOCs as solvents. This feature suggests that an analyte with greater intermolecular affinity for the SWCNT-porphyrin composite will induce a greater response. These results further demonstrate the potential for porphyrin-functionalized SWCNT-based electronic noses for applications in inexpensive, portable chemical sensors for the identification of VOCs.

Single-walled carbon nanotubes (SWCNTs) have garnered considerable interest as materials suitable for use in electronically integrated chemical sensors.¹⁻³ SWCNTs are often functionalized—covalently or non-covalently—with other molecules in order to impart sensitivity or selectivity for a specific analyte.⁴ In particular, non-covalent functionalization, often through π - π interactions, allows for facile functionalization with minimal disruption of the electronic properties of the CNTs that generally accompanies covalent functionalization.⁵

Porphyrins are attractive choices for non-covalent functionalization of CNTs with highly polarizable aromatic porphyrinic cores that interact strongly with π -conjugated graphenic sidewalls. Indeed, they have been previously shown to both non-covalently⁶⁻⁹ and covalently functionalize CNTs,¹⁰⁻¹² typically for synthesizing hybrid materials intended for applications in energy conversion.

Porphyrins have shown promise for use in high-sensitivity chemical sensors,¹³⁻¹⁵ typically with mass- or optical-based transduction.¹⁶⁻¹⁹ However, despite their promise in sensing applications and their suitability for CNT functionalization, the application of metalloporphyrin-CNT hybrid materials in sensing remains relatively unexplored. Only a handful of previous studies have examined metalloporphyrin-CNT chemiresistive sensors.²⁰⁻²² These sensors have the advantage of being readily integrated into circuitry for mobile, low-power operation in inexpensive and compact electronic devices.²³

Previous studies on porphyrins in chemical sensing note that despite their promise for this application, a

drawback that limits their usage is that they are relatively unselective.²⁰ The aforementioned studies on sensors fabricated from porphyrin-CNT composites measured chemiresistive responses of only 2-3 metal centers to only 4-5 different analytes, but Penza et al. suggest that arrays using different metalloporphyrins could be used to ameliorate poor selectivity.³

Herein, we present a more comprehensive study on the chemiresistive responses of an array of non-covalent metalloporphyrin-SWCNT-based sensors to various classes of VOCs. This chemiresistive sensor array takes advantage of the suitability of porphyrins for CNT functionalization and their ability to increase sensitivity to various analytes. With the application of statistical analyses, the array device is capable of accurately distinguishing among five different classes of organic functional groups.

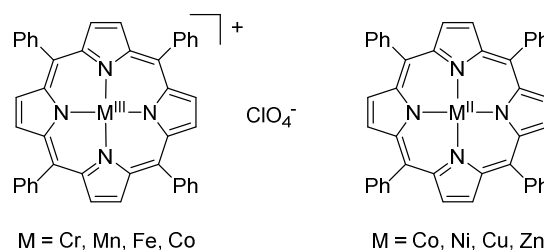


Figure 1. Chemical structures of metalloporphyrin complexes employed in the chemiresistive sensor array in this study. Axial H_2O ligands have been omitted for clarity.

We fabricated the device (Supporting Information Fig-

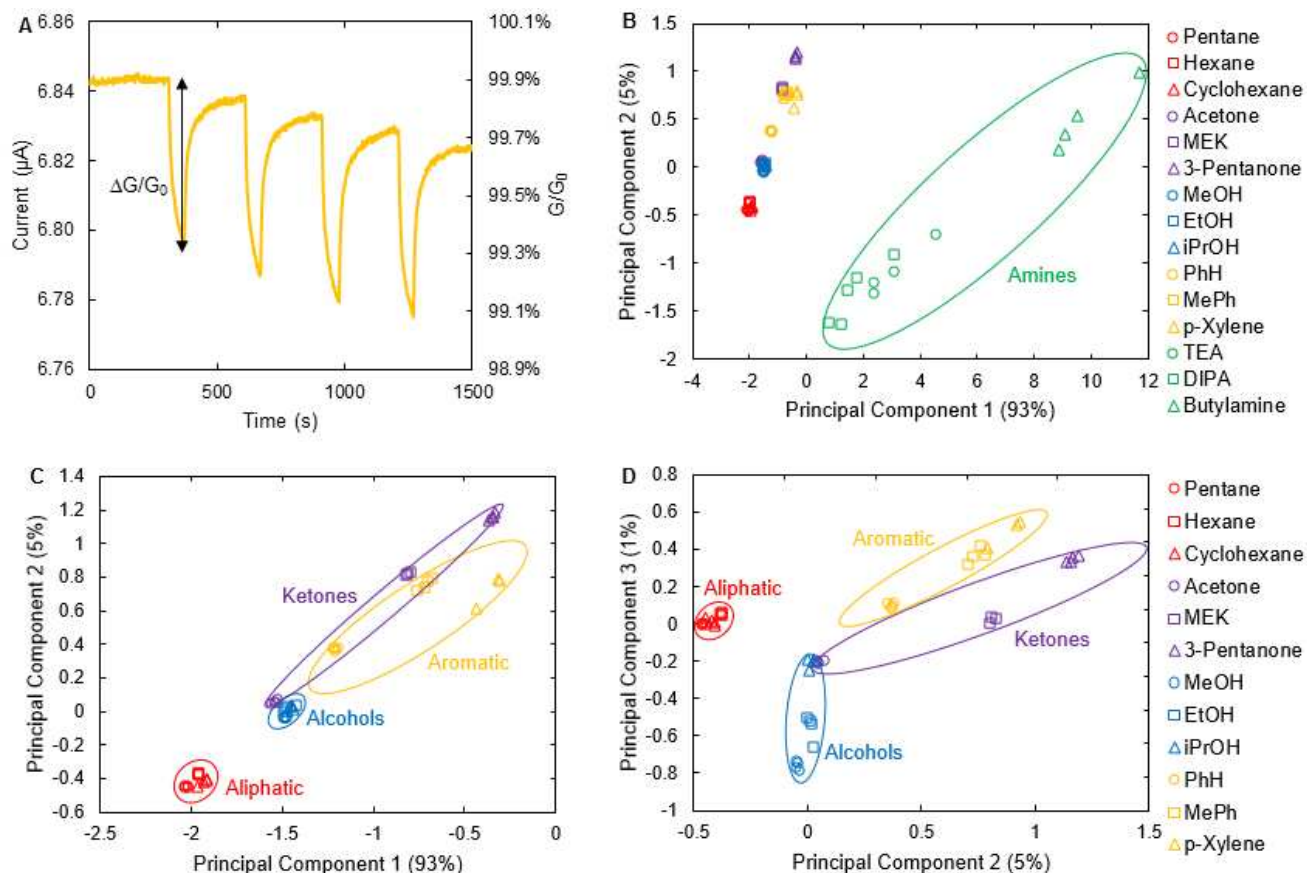


Figure 2. Principal component analysis of chemiresistive sensor array's responses to VOCs. (A) Current trace of SWCNT-[Fe(tpp)(H₂O)₂]ClO₄ with 0.100 V potential applied during four 60 s exposures of 1000 ppm toluene in N₂ gas. (B) PC 2 plotted against PC 1 for an array of 10 different SWCNT-based chemiresistors to 15 VOCs (3-4 trials each). (C) PC 2 plotted against PC 1 with amines excluded from the plot. (D) PC 3 plotted against PC 2 with amines excluded from the plot.

ure S₁) from complexes of *meso*-tetra-phenylporphyrin (tppH₂) in Figure 1. For sensing measurements, we delivered VOCs diluted in N₂ gas (2% relative humidity) into an enclosure holding the device. The VOC concentrations were 1000 ppm except for alkanes and for amines (2000 and 300 ppm, respectively, due to their relatively low and high signal inductions). A potentiostat applied 0.100 V across the electrodes and recorded current for at least three 60 s VOC exposures and 180 s of N₂ between exposures. After baseline correction, the change in current is converted to negative change in conductance ($-\Delta G/G_0$), which is taken as the device's response (Figure 2a).

Supporting Information Table S2 shows the average responses of the CNT-based array's channels to 3 representatives each of 5 classes of VOCs (alkanes, ketones, alcohols, aromatic hydrocarbons, and amines) normalized to the average responses of each composite to hexane in order to more readily compare the responses of each composite to different analytes. Measurements taken under air (10% relative humidity) show that O₂ and increase in humidity do not have a substantial effect on sensor response (see Supporting Information Figure S2).

We subjected the responses to principal component analysis (PCA),²⁴ a common unsupervised exploratory data analysis tool that transforms a data set to a new coordinate system such that the coordinates (the principal components) account for the greatest variance in the data. This approach results in grouping of analytes based on similarity of their data without prior knowledge of their classification. Supporting Information Figure S3 shows the scree plot with the variance accounted for by each PC. The amines are most readily distinguished as shown in the plot of PC 2 against PC 1 (Figure 2B) due to their strong response in functionalized and non-functionalized SWCNTs. In Figure 2C, the same plot without amines shows the remaining data more clearly, and they are distinguished further when PC 3 is considered (Figure 2D).

A more quantitative indication of the efficacy of the chemiresistive sensor array's efficacy toward distinguishing among these five groups of VOCs is afforded by linear discriminant analysis (LDA). This supervised method seeks to classify analytes in predetermined groups by using data from members of those groups to identify the group in which a new case would belong. We applied the

jackknife cross-validation method, which uses functions computed from all the data except the case being classified. The results are shown in the classification matrix in Table 1. The LDA demonstrated 98% accuracy in classifying 59 trials with only one aromatic hydrocarbon being mistaken for a ketone. This analysis shows that this chemiresistive sensor array can distinguish among these classes of VOCs with a high degree of confidence.

Table 1. Jackknifed classification matrix of chemiresistive sensor array's responses to five classes of VOCs.

	-ane	-one	ROH	Ar	Amine	Correct
-ane	12	0	0	0	0	100%
-one	0	11	0	0	0	100%
ROH	0	0	12	0	0	100%
Ar	0	1	0	10	0	91%
Amine	0	0	0	0	13	100%
Total	12	12	12	10	13	98%

Apart from the amines, whose large transductions are due to their charge transfer capabilities,^{1,25} distinguishing among the types of VOCs appears to rely on intermolecular interactions between the analytes and porphyrins as manifested by their solubilities (Supporting Information Figure S4). Pentane is a poor solvent for all of the porphyrins and elicits weak responses in all of the composites. Acetone is a good solvent for the cationic M^{3+} complexes and a mediocre solvent for the neutral M^{2+} complexes; methanol is a good solvent for the M^{3+} complexes and a poor solvent for the M^{2+} complexes; and toluene is a mediocre solvent for the M^{3+} complexes and a good solvent for M^{2+} complexes. These trends generally track with the data presented in Supporting Information Table S2. This observation is unsurprising as we would expect that analytes with a greater intermolecular affinity for a given SWCNT-porphyrin composite would give greater responses. This is clearly a simplified analysis of the factors contributing to the response but can be useful for directed sensor development as a predictive tool.

The observation that the responses track with solubility and intermolecular forces indicates that the analytes, in addition to modulating charge transfer effects between the metalloporphyrins and the SWCNTs as suggested by Penza et al.,²⁰ could also be inducing physical separations between the SWCNTs through solvation (swelling) that in turn cause the increase in resistance. Small expansion of the inter-SWCNT gaps is expected to dramatically reduce conductance of the material as a result of the exponential decrease in electron tunneling probability with distance. Swelling mechanisms have been posited previously for both polymer- and CNT-based sensors.^{2,3,23,24,26,27}

We used Raman spectroscopy to examine the changes in the sensing material caused by analytes and found that while relative effects observed in this experiment did not clearly correlate with the magnitude of different responses,

both ionic and neutral porphyrin-SWCNT composites exhibited changes in the relative intensities of the radial breathing mode (RBM) absorptions upon exposure to analytes, suggesting that analyte vapors induced changes in CNT-CNT interactions (see Supporting Information figures S9 and S10).^{28,29} We observe inverted behavior for the ionic metalloporphyrin composite upon exposure to analyte as compared to the neutral case, a relative increase in the peak at 265 cm^{-1} rather than a decrease.

To further probe the mechanism of the array's chemiresistive responses, we analyzed field-effect transistors (FETs) fabricated from non-functionalized SWCNTs as well as from composites with $[\text{Mn}(\text{tpp})]\text{ClO}_4$ and $[\text{Cu}(\text{tpp})]$ as representative ionic and neutral metalloporphyrins, respectively, and with neutral ligand tppH_2 (Supporting Information figures S11-S15). Prior to exposure to analytes, the threshold voltage of the FET with the ionic metalloporphyrin had a much higher threshold voltage than that of the other FETs, which suggests that the charged metalloporphyrin species is affecting the electronic structure of the SWCNTs. The higher D/G band ratio in the Raman spectrum of the ionic $[\text{Co}(\text{tpp})]\text{ClO}_4$ -SWCNT composite (Supporting Information Figure S5) compared to that of the neutral composites also suggests perturbation of the SWCNT electronic structure. We propose that the positive charge of the metalloporphyrin induces effective negative charges in the SWCNTs, thus making it harder to create the p-channel for hole transport and increasing the threshold voltage for the p-type semiconducting SWCNTs.

Upon exposure to analytes, the FETs with the ionic metalloporphyrin exhibited a reduction in the threshold voltage while the other devices exhibited an increase in threshold voltage (Supporting Information Figure S16). This inverted behavior is similar to what we observed with the Raman analysis. We hypothesize that solvation of the ionic metalloporphyrins screens the effect of their positive charge or increases the distance between the charged species and SWCNTs, resulting in a weaker electrostatic interaction on the CNT walls and thereby reducing the threshold voltage (positive shift) after exposure to the analyte. These results suggest that there is a possible electrostatic gating effect, but it can be attributed to the solvation of the metalloporphyrins rather than the doping mechanism suggested by Shirsat et al.²¹ Like with the Raman analysis, the relative effects observed in this experiment did not give a clear correlation with the magnitude of different chemiresistive responses; clearly, the origins of the conductance changes in this as well as other systems in the literature can have multiple possible origins not easily deconvoluted such as increases in capacitance between CNTs or in contact resistance.

To summarize, we have developed a chemiresistive sensor array fabricated from SWCNTs non-covalently functionalized with metalloporphyrins. With statistical analyses, its responses could accurately classify VOCs into five classes. With the exception of amines, the basis of differ-

entiation appears to correlate with the solubilities of the porphyrin complexes in the analytes, suggesting that swelling contributes to responses. This work shows that porphyrin-CNT composites have potential in identification of VOCs, which may lead to uses in environmental monitoring, security, and healthcare diagnostics.^{23,30}

ASSOCIATED CONTENT

Supporting Information. Synthetic procedures, device preparation and spectroscopic characterization, gas detection measurements, field-effect transistor measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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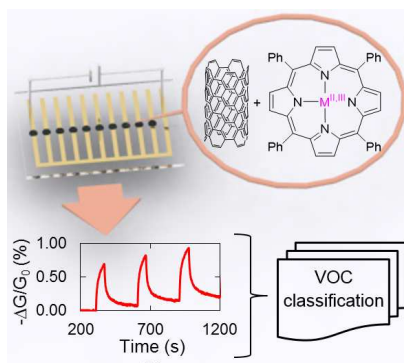
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