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Employing Halogen Bonding Interactions in Chemiresistive Gas Sensors

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Supporting Information Placeholder

ABSTRACT: This paper reports the use of halogen bonding interactions for gas-phase detection of pyridine in SWCNT-based chemiresistive sensors with sub-ppm theoretical detection limits. The chemiresistors are prepared by solvent-free ball-milling of single-walled carbon nanotubes (SWCNTs) and aryl halide-based selectors, compression into a pellet, and subsequent mechanical abrasion between gold electrodes on paper. The sensing responses reflect halogen bonding trends, with few exceptions. The predominant signal transduction mechanism is likely attributed to swelling of the insulating haloarene matrix.

KEYWORDS: halogen bonding, carbon nanotubes, gas sensors, chemiresistors, aryl halides

An ideal chemical sensor rapidly communicates small changes in chemical environment with selectivity and predictability. Currently, the most common methods for molecular detection and identification rely on high-performance liquid chromatography-mass spectrometry (HPLC-MS) or gas chromatography-mass spectrometry (GC-MS),^{1,2} both of which demand considerable resources — time, power, money, and physical space. Thus, the development of sensors that are rapid, low-power, inexpensive, robust, simple to use, and portable are highly desired. The resulting technology would have tremendous impact in environmental monitoring, diagnostic medicine, agriculture, food processing, and homeland security.

Carbon nanotubes (CNTs) are promising materials for chemical sensors as a result of an electronic structure that is sensitive to slight changes in local chemical environment.³ Additional advantages of CNTs for their application in chemical sensors are their nanoscale physical size, high electrical conductivity, remarkable strength, and extraordinary specific surface area.⁴ Furthermore, the chemistry for covalently and noncovalently functionalizing CNTs is well established,^{5,6} enabling the facile introduction of selectivity to the sensors.

A number of device architectures are available to exploit the high electronic sensitivity of CNTs, including resistors, field-effect transistors, and capacitors. The simple nature of a

direct current measurement with only two electrical contacts (source and drain) makes the chemiresistor an attractive architecture for sensors (Figure 1). The advantages of this simple design include portability, ease of use, low cost, and suitability for operation at room temperature. When located between two electrodes, individual CNTs or networks of CNTs can be considered a variable resistor whose resistance is modulated by changes in the chemical composition of their surrounding environment.

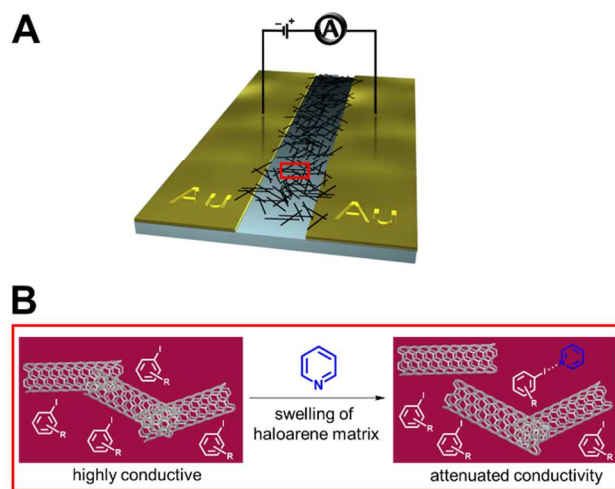


Figure 1. A) Schematic of a chemiresistor based on a randomly oriented network of CNTs deposited between two electrodes. B) Proposed sensing mechanism based on swelling of haloarene matrix upon exposure to pyridine.

The CNT networks can be deposited into a device using several approaches, including direct growth on substrates, deposition of dispersions, Langmuir-Blodgett, dip coating, and electrophoresis.⁷ However, there are a number of drawbacks to these methods, including the dependence on expensive, specialized equipment for growing CNTs directly on substrates. For solution-based methods, the main obstacles are the need for solution processing, the poor solubility of CNTs in most solvents, and the limited stability of dispersions of CNTs. Our group has reported the mechanical abrasion of compressed CNT composites on various substrates to overcome these difficulties.⁸⁻¹⁰

1 Although highly sensitive, SWCNT-based sensors often
2 suffer from a lack of selectivity. A strategy to address this
3 concern utilizes covalent or noncovalent functionalization of
4 SWCNTs with small molecules or polymers. Hydrogen bond-
5 ing motifs are often employed to introduce selective en-
6 hancement of signals towards targeted analytes.^{11,12} This ap-
7 proach, however, has limited selectivity, as many potential
8 interferents can compete with target analytes through hy-
9 drogen bonding. Thus, expansion of strategies for molecular
10 recognition of analytes with SWCNT-based sensors would
11 enable the improved design of selective and sensitive gas
12 sensors based on cross-reactive arrays.

13 We introduce halogen bonding moieties into our chemire-
14 sistive sensors to complement traditional hydrogen bonding
15 motifs. Halogen bonds (XBs) are generally described as elec-
16 trostatic interactions between an electrophilic halogen atom
17 (XB donor) and a Lewis base (XB acceptor). The nature of
18 halogen bonding is rooted in the σ -hole of the halogen, a
19 positive potential along the R-X bond axis. The σ -hole be-
20 comes more positive — and the halogen bonding interaction
21 becomes stronger — as i) X is less electronegative, ii) X is
22 more polarizable, and iii) R is more electron-withdrawing.¹³
23 It is important to note that the σ -hole forces halogen bond-
24 ing interactions to be highly directional: the R-X...Y bond
25 angle is approximately 180° . This restriction is in stark con-
26 trast to traditional hydrogen bonds and halogen...halogen
27 bonds.¹⁴

28 Halogen bonding offers an untapped new dimension of se-
29 lectivity in the creation of cross-reactive sensing arrays.
30 Many years after its discovery,¹⁵ the discovery of XB adducts
31 has led to modern advances in crystal engineering,^{16–18} liquid
32 crystals,¹⁹ and anion sensing.²⁰ Exploiting these strong N...X
33 halogen bonding interactions, we envisioned the detection of
34 nitrogen-containing heterocycles (e.g., pyridines) using ra-
35 tionally designed CNT-based chemiresistive sensors incorpo-
36 rating aryl iodides as “selectors.”

37 We fabricated the sensors employed in this study using
38 our previously reported fabrication techniques PENCIL (Pro-
39 cess Enhanced NanoCarbon for Integrated Logic) and
40 DRAFT (Deposition of Resistors with Abrasion Fabrication
41 Technique).^{8,9} Briefly, selectors and pristine SWCNTs were
42 combined in a 2:1 mass ratio, respectively, ball-milled for five
43 minutes at 30 Hz, and compressed into a pellet at 10 MPa for
44 one minute. The pellet was then mechanically abraded be-
45 tween thermally evaporated gold electrodes (120 nm thick
46 with a 1 mm gap between the electrodes) on weighing paper
47 (i.e., highly compressed cellulose) to attain resistances be-
48 tween 30 and 100 k Ω . It is important to note that the values
49 of the resistance did not affect the relative sensing response,
50 as long as the measured resistances were within the same
51 order of magnitude.

52 We chose the aryl halides in this preliminary study based
53 on their relative ambient stability, their commercial availa-
54 bility, and the following hypotheses: 1) the sensing response
55 of the selectors follows Cl < Br < I, consistent with solution-
56 phase studies and corresponding to the polarizability of the
57 XB donor; 2) electron-deficient aryl halides are stronger XB
58 donors than electron-rich aryl halides; and 3) longer alkyl
59 chains increase the interaction between the nanotubes and
60 the selector material, as a result of the geometrical fit be-
61 tween alternating methylene groups on the alkyl chain and
62 the centers of the CNTs' hexagonal rings.^{21,22}

We first investigated the *p*-dihalobenzene series, as shown
in Figure 2. *p*-Dichlorobenzene, *p*-dibromobenzene, and *p*-
diiodobenzene were chosen over the *ortho* and *meta* isomers
because the *para* isomers exist as solids at room temperature
and exhibit lower volatility compared to their *ortho*- and
meta- substituted counterparts. This property is necessary to
produce mechanically robust PENCILs for abrading a film on
paper. As predicted, the sensing response intensifies as the
polarizability of the halogen increases. This observation is
consistent with solution-phase studies.²³ For the *p*-
diiodobenzene composite, a maximum response is obtained
upon exposure to only 3 ppm pyridine ($-\Delta G/G_0 = 5.1 \pm 0.9\%$).
The response to pyridine for the chloro- and bromo-
derivatives rises as the concentration of pyridine is increased
to 25 ppm. In all cases, the response to pyridine is signifi-
cantly greater than the control sensors fabricated with pris-
tine CNTs in the absence of a selector (*p*-CNTs), where the
response was only $1.5 \pm 0.3\%$ at 25 ppm. We calculated the
theoretical limits of detection for pyridine of *p*-
diiodobenzene-, *p*-dibromobenzene-, and *p*-
dichlorobenzene-based composites to be 16, 37, and 92 ppb,
respectively. These values exceed previously reported detec-
tion limits for pyridine by at least 10-fold.²⁴

We attribute the significant enhancement of the response
with the composites as compared to the pristine CNT control
to the swelling of the haloarene matrix. Increased affinity for
the vapor leads to increased swelling. The resulting increased
intertube distance leads to the attenuation of conductivity
that is observed as the sensing response. Such swelling
mechanisms have been previously reported in the literature
with non-covalently functionalized CNTs.^{25,26} While it is pos-
sible that there is some covalent functionalization of the
CNTs induced by ball milling with “selectors,” the relatively
low resistances that we observe are inconsistent with a sub-
stantial degree of covalent functionalization, as we have pre-
viously demonstrated.⁹ Furthermore, experiments performed
by reacting CNTs with diazonium salts of haloarenes formed
in situ failed to result in the enhancements we observe with
the non-covalent mixture of aryl halide and CNTs, as de-
scribed in the Supporting Information.

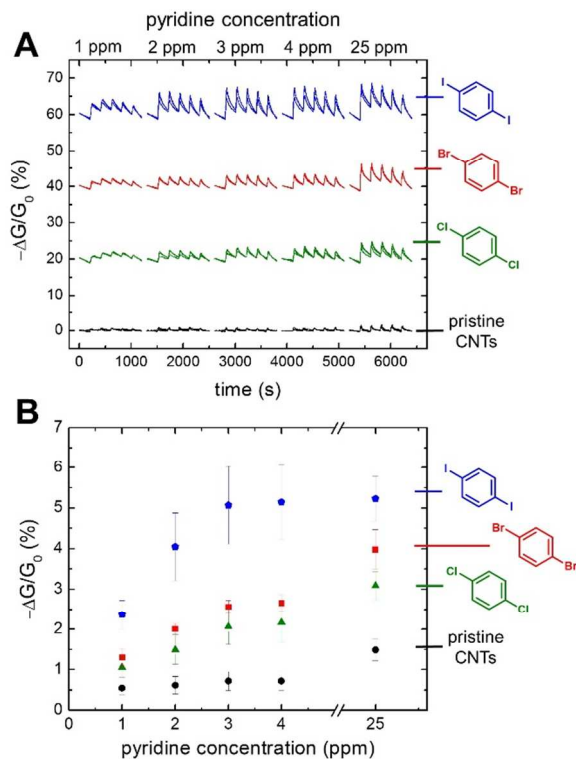


Figure 2. A) Sensing responses of *p*-dihalobenzene-SWCNT composites to varying concentrations of pyridine in N₂ carrier gas at room temperature. Each type of sensor was examined in triplicate. The three traces for each type of sensor are overlaid to display reproducibility. For clarity, each series is displayed with a 20% offset. B) Magnitudes of sensing responses shown in (A). The vertical error bars represent the standard deviation from the mean based on three devices.

To further investigate consistency with the effect of halogen bonding, sensing experiments were performed with bromodurene and iododurene, as shown in Figure 3 and Figure S2. In addition to their decreased volatility compared to the *p*-dihalobenzenes for higher device stability, we observed that the composites containing durene derivatives behaved more like waxes, enabling them to be drawn onto devices more easily, analogous to “Crayons.” A composite material with unsubstituted durene and the pristine CNT pellet were used as controls. These controls exhibited similar behavior with $-\Delta G/G_0 = 0.7 \pm 0.2$ % at 4 ppm whereas the bromodurene and iododurene composites produced responses of 2.2 ± 0.1 % and 3.2 ± 0.1 %, respectively.

Sensing measurements were also carried out using 4-picoline (4-methylpyridine) as an analyte, as shown in Figure 3 and Figure S2. As a result of the electron-rich character relative to pyridine, an enhanced sensing response is predicted by previous solution phase studies on halogen bonding.²³ Indeed, the sensing responses are significantly enhanced upon exposure to 25 ppm 4-picoline in comparison to 25 ppm pyridine; however, the pristine CNT and durene composite controls also exhibited an increase in the sensing response. Because the pristine carbon nanotube control lacks a swelling composite matrix, a greater propensity of 4-picoline to dedope the carbon nanotubes relative to pyridine is likely the operative mechanism that contributes most to the attenuated conductance. Signals for the iododurene composite

were 150 and 240% greater than the durene composite and pristine CNT controls in response to 25 ppm pyridine and 110% and 210% greater in response to 25 ppm picoline, respectively. Attempts for gas-phase sensing of other commercially available electron-rich or electron-poor pyridine derivatives were unsuccessful as a result of technical difficulties associated with the controlled generation of vapors from the selected compounds.

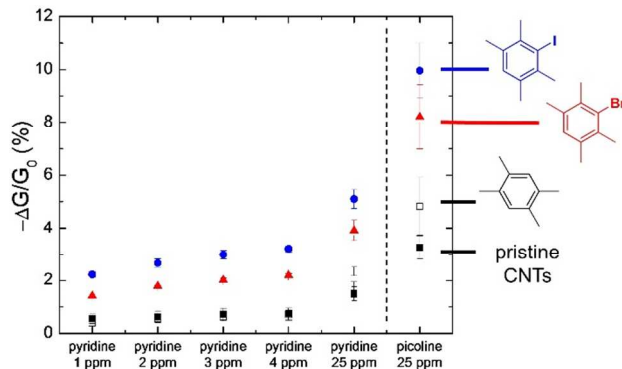


Figure 3. Sensing response of halodurene series to varying concentrations of pyridine (left) and picoline (right). A composite with unsubstituted durene and pristine CNTs were used as controls. Each type of sensor was examined in triplicate. The sensing traces for each data point can be found in Figure S2.

To supplement comparisons within the dihalobenzene and halodurene series, we investigated the effect of arenes’ electronics on the sensing response to pyridine, as shown in Figure S3. In addition to *p*-diiodobenzene, 1,4-diiodotetrafluorobenzene and 1,4-diiodo-2,5-dimethoxybenzene were investigated as electron-deficient and electron-rich analogues, respectively. As the group attached to the halogen atom becomes more electron-withdrawing, the σ -hole of the halogen atom becomes more positive, creating a better XB donor. Indeed, 1,4-diiodotetrafluorobenzene has been used as an ideal XB donor in solution phase assembly.²⁷ The N \cdots I interaction of 4,4’ dipyridyl and 1,4-diiodobenzene in an infinite chain is 13.2 kJ/mol but is strengthened to 24.3 kJ/mol when 1,4-diiodotetrafluorobenzene is used as the XB donor.^{28,29} Conversely, the introduction of electron-donating groups results in a worse XB donor.¹³ As expected, the methoxy-bearing selector resulted in an attenuated signal relative to *p*-diiodobenzene, although the response was significantly greater than that of pristine carbon nanotubes. Surprisingly, the electron-withdrawing tetrafluoro-containing selector behaved similarly to the selector possessing the electron-donating methoxy groups. This unexpected behavior could be ascribed to a number of factors. The perhalogenated XB-donor could produce a coating repulsive to most organic analytes of interest, similar to the interactive orthogonality of the fluororous effect.³⁰ The result would be diminished swelling effects and consequently weakened sensing response in the CNT composite. Alternatively, the introduction of four fluorine atoms changes the quadrupole moment of the benzene ring resulting in a different interaction with the carbon nanotubes. This interaction could alter the susceptibility of the CNTs to changes in local dipole moment or impose geometrical limitations on the halogen bonding interaction near

the nanotubes — i.e., the pyridine analyte is unable to comply with the strongly directional nature inherent to halogen bonding.

We also investigated the effect of alkyl chain length on the sensing response to pyridine, as shown in Figure S4. Longer alkyl chains could increase the interaction parameter between the carbon nanotubes and the selector, as a result of the geometrical fit between alternating methylene groups on the alkyl chain and the centers of the CNTs' hexagonal rings.^{21,22} Using 1,4-didodecyl-2,5-diiodobenzene as a selector produced a slightly greater response to pyridine than the xylene analogue. In addition to the greater interaction with the nanotubes, the dodecyl derivative is likely to exhibit greater swelling effects, which we expect to produce an increased sensing response. An additional benefit of the longer alkyl chain is the mechanical behavior of the composite pellet when depositing on paper. The pellet is robust enough to be easily manipulated by hand and abrades similar to a Crayon when abraded on the weighing paper. The ease with which uniform films are deposited likely explain the excellent reproducibility of this particular CNT composite sensor.

After assessing the trends associated with halogen bonding and carbon nanotube interactions, we investigated the response of our top selectors, 3-iododurene and 1,4-didodecyl-2,5-diiodobenzene, to elevated concentrations (> 1000 ppm) of hexanes, benzene, isopropanol, and acetonitrile in addition to varying low concentrations of pyridine (≤ 25 ppm). As displayed in Figure 4, both sensing composites responded more strongly to pyridine at a concentration of 1 ppm than to higher concentrations (> 1000 ppm) of the interferents. Interestingly, the composite with 3-iododurene produced a perceptible signal to hexanes and benzene. This result can almost certainly be attributed to swelling effects rather than local electronic changes near the carbon nanotubes. Exposure to acetonitrile resulted in no response, consistent with its significantly weaker interaction in halogen bonding in comparison to amines and pyridine as a result of the nitrogen's *sp* hybridization.

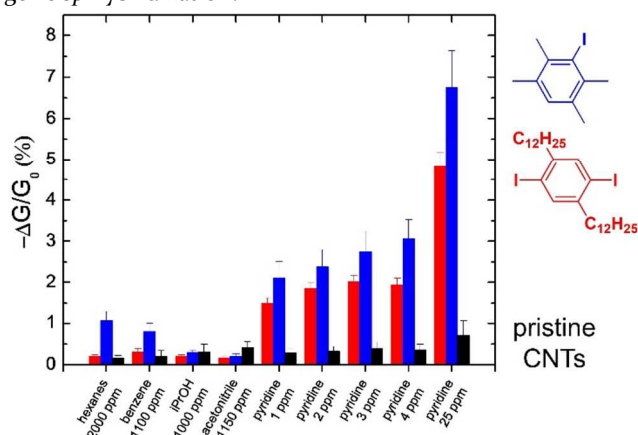


Figure 4. Screening for XB-specific signal enhancement. Pyridine was tested as an analyte in comparison to hexanes, benzene, isopropanol, and acetonitrile at significantly higher concentrations. The sensing traces for these bars can be found in Figure S5.

In conclusion, we utilized halogen bonding in carbon nanotube-based chemiresistive sensors to selectively enhance the response to the Lewis base pyridine. The chemire-

sensors were prepared by ball milling of SWCNTs and selectors, compression into a pellet, and mechanical abrasion between gold electrodes onto paper. *p*-Dihalobenzene and 3-halodurene derivatives were investigated and exhibited sensing responses consistent with halogen bonding. The fundamental transduction mechanism of these sensors is likely based on swelling of the CNT composite, which is dictated by the affinity of the insulating selector matrix for the analyte. We believe that these sensors can offer halogen bonding as an additional dimension in CNT-based cross-reactive sensing arrays. The development of more complex selectors — those with multiple halogen bonding sites at calculated spacings — could facilitate the specific detection of biologically relevant *N*-heterocyclic compounds in solution.

ASSOCIATED CONTENT

Supporting Information

Supporting Information Available: The following file is available free of charge: se-2015-001846_SI.pdf. Details fabrication of sensors, acquisition of sensing data, and additional sensing traces and plots.

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Notes

The authors declare no competing financial interests.

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