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FULL PAPER

Sensory Arrays of Covalently Functionalized Single-Walled Carbon Nanotubes for Explosive Detection

*Jan M. Schnorr, Daan van der Zwaag, Joseph J. Walish, Yossi Weizmann, and Timothy M. Swager**

Chemiresistive sensor arrays for cyclohexanone and nitromethane are fabricated using single-walled carbon nanotubes (SWCNTs) that are covalently functionalized with urea, thiourea, and squaramide containing selector units. Based on initial sensing results and ^{1}H NMR binding studies, the most promising selectors are chosen and further optimized. These optimized selectors are attached to SWCNTs and simultaneously tested in a sensor array. The sensors show a very high level of reproducibility between measurements with the same sensor and across different sensors of the same type. Furthermore, the sensors show promising long-term stability, which renders them suitable for practical applications.

1. Introduction

The real-time detection of explosive compounds and markers for explosive compounds represents an ongoing challenge for gas sensor development. Explosive-based weapons remain the preferred tools of terrorism and it is likely that this threat will be a continuing concern to society for the foreseeable future.[1] It is therefore desirable to develop sensors capable of detecting the vapors emanating from explosives. The number of compounds that can serve as vapor signatures of explosives is considerable and goes beyond well-known highly energetic compounds such as 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), pentaerythritol tetranitrate (PETN), and 2,4,6-trinitrotoluene (TNT). For example, nitromethane is a common solvent but can be utilized in the formation of explosives mixtures.[2] Similarly a non-explosive vapor marker of some plastic explosives is cyclohexanone, which is used to recrystallize the explosive RDX.[3] As a result of its significantly higher vapor pressure, residual cyclohexanone is recognized as a marker for RDX-based explosives.[4] Several techniques have been used to detect these analytes including ion mobility spectrometry (IMS), mass spectrometry (MS), and gas chromatography (GC). Although these methods can provide sensitivity and selectivity, the instrumentation is bulky, costly, and can be complex to operate. It is therefore desirable to develop low-cost sensors compatible with portable platforms that are readily integrated into existing electronic systems. Carbon nanotube (CNT) based chemiresistors are an emerging class of sensors that fulfill these requirements and are displaying promising performance in a variety of sensing applications.[5,6] CNT chemiresistors can be deposited between electrodes by evaporation of dispersions, or can be effectively drawn from compressed CNT solids.[7] In order to improve the selectivity of CNT-based sensors for certain analytes, functionalization with selectors (groups designed to interact selectively with particular molecules) is usually required. This can be done by non-covalent functionalization with selector molecules with pendant pyrenes,[8] wrapping with functionalized polymers,[9] or by covalent functionalization of the sidewalls or the carboxylates found at the termini of oxidized CNTs.[10] A variety of selector types have been developed, ranging from chemically synthesized selectors that rely on polarity or acid-base interactions to enzymes for greater specificity.[5,11]

Dr. J. M. Schnorr, D. van der Zwaag, Dr. J. J. Walish,
Prof. Y. Weizmann, Prof. T. M. Swager
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139, USA
E-mail: tswager@mit.edu
D. van der Zwaag
Department of Chemical Engineering and Chemistry
Eindhoven University of Technology
5600 MB Eindhoven, The Netherlands
Prof. Y. Weizmann
Department of Chemistry
University of Chicago
Chicago, IL 60637, USA

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2. Results and Discussion

2.1. Functionalization of SWCNTs with Selectors and Initial Testing

To create SWCNTs capable of selective detection of nitromethane and cyclohexanone vapors, we have prepared a family of selectors that should provide specific interactions. Inspired by their capabilities for anion sensing in solution, we chose to investigate thiourea, urea, and squaramide groups which have been reported to interact strongly with nitrates, carboxylates and other compounds that resemble the structure of our target R–NO_2 and ketone- analytes.[12] We chose a two-step attachment strategy. First, amino groups were covalently attached to the sidewall of single-walled CNTs (SWCNTs) via thermal aziridination.[13] The resulting NH_2–SWCNTs were

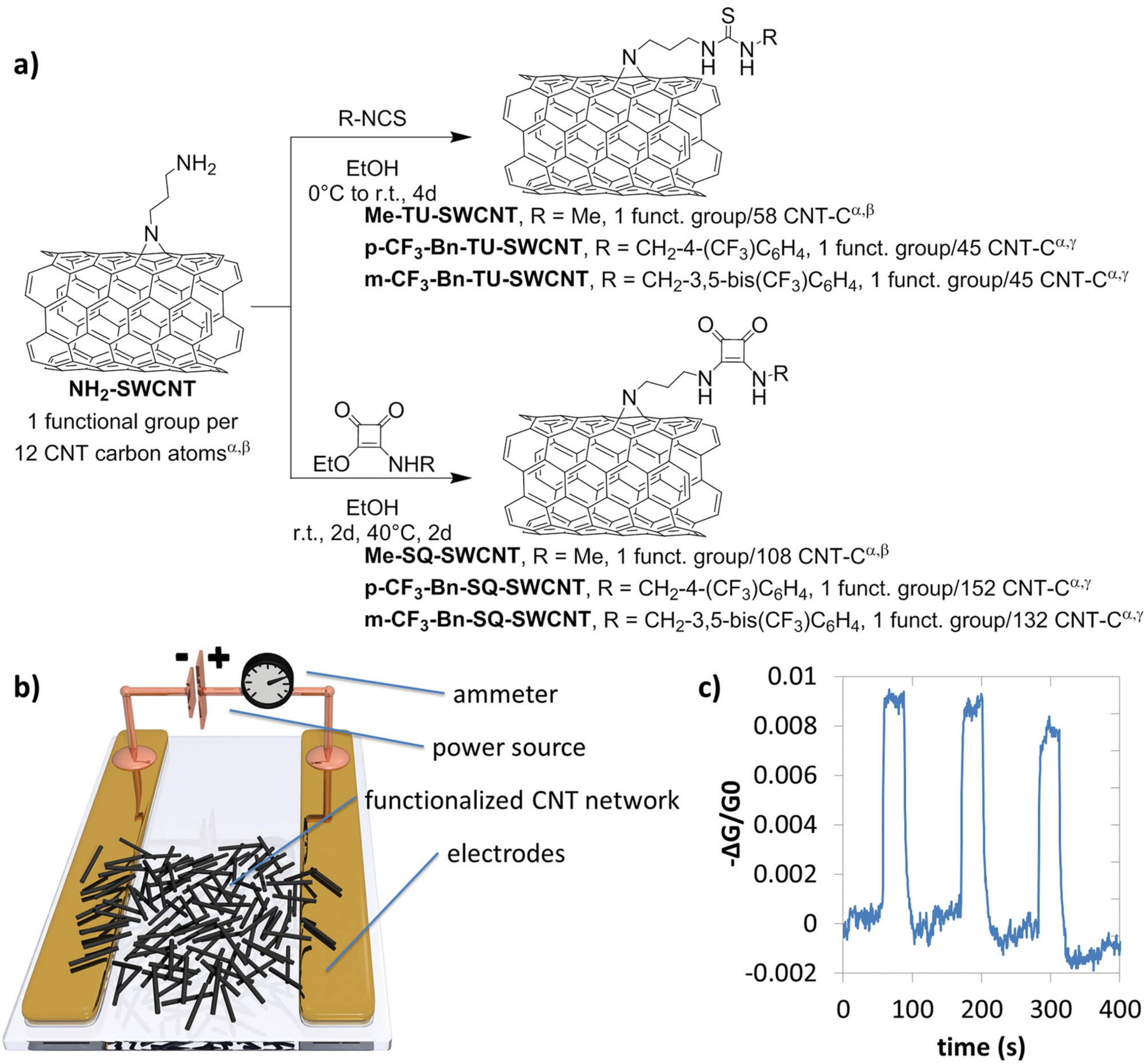

Figure 1. a) Functionalization of SWCNTs with selectors. α: Functional group density is determined by X-ray photoelectron spectroscopy. β: Based on O 1s and C 1s signals in the product compared to NH_2–SWCNT. γ: Based on F 1s and C 1s signals. b) Schematic representation of resistivity-based SWCNT gas sensor. c) Response of sensor based on m–CF_3–Bn–TU–SWCNT to 57 ppm cyclohexanone.

then allowed to react with a second reagent containing the desired selector. This two-step approach combines an established and reliable CNT functionalization method with the flexibility of using pendant amines to attach a variety of groups in the second step. It is important to note that covalent functionalization of the sidewalls disrupts the extended electronic states of SWCNTs and thereby increases the base resistance more than a non-covalent functionalization approach. An increased base resistance has the effect of lowering the sensitivity for the detection of analyte-induced resistance increases. Nevertheless, with modest degrees of functionalization, quality sensors have been obtained from covalently functionalized SWCNTs.[10b,14] An important advantage of covalent functionalization is that it produces a more durable sensor relative to non-covalent compositions that are prone to changes in structure, which can lead to CNT/selector phase separation and decreased sensor performance.

Using the two-step synthetic route, substituted thiourea and squaramide groups were attached to the surface of SWCNTs (**Figure 1**a). After confirming the successful introduction of the selector by X-ray photoelectron spectroscopy (XPS), sensors were fabricated from the functionalized SWCNTs by drop-casting the sensing material between two electrodes (Figure 1b). The sensor was loaded into an enclosure and a gas stream of either pure nitrogen or nitrogen containing an analyte vapor was passed over the device. A constant potential of 0.1 V was applied across the sensor and the relative current change when switching from pure nitrogen to the nitrogen-analyte mixture

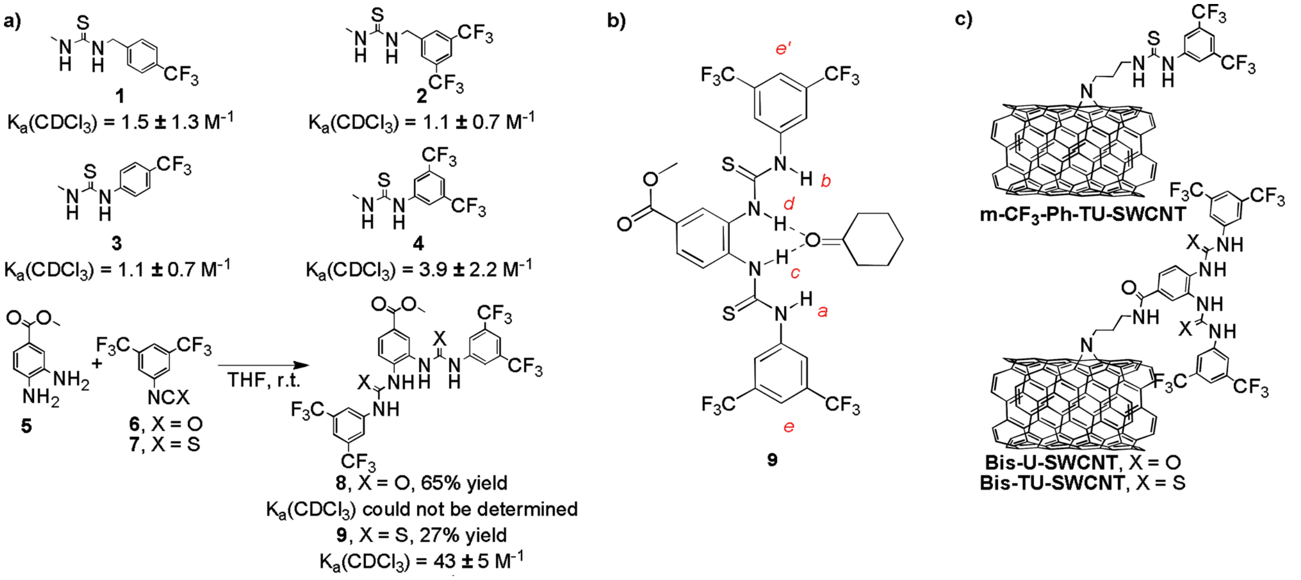

Figure 2. a) Model compounds for ^{1}H NMR binding study with cyclohexanone. Association constants and errors of 1–4 are based on shifts of two aromatic and two NH protons; association constant and error of 9 is based on proton e. b) Suggested interaction of cyclohexanone with 9 based on ^{1}H NMR binding study. c) Functionalized SWCNTs with selectors based on ^{1}H NMR binding study.

was recorded. Among the tested sensors, m–CF$_3$–Bn–TU–SWCNT led to the most pronounced sensing response of 0.9% when exposed to 57 ppm cyclohexanone (Figure 1c) and no clear response was observed for the squaramide-based sensors (see Supporting Information). We attribute the higher performance of m–CF$_3$–Bn–TU–SWCNT to the more acidic nature of NH protons in thiourea groups relative to those of the squaramide, and this increased acidity is further augmented by the electron poor benzyl substituent. Additionally, the highly reactive isothiocyanate reagent, which was used to introduce this selector, resulted in a higher functional group density of the thiourea groups as compared to their squaramide counterparts (see Figure 1a for functional group densities by XPS).

2.2. Optimization of Selector Moieties Based on NMR Binding Studies

Encouraged by these initial results, we investigated related receptors with the goal to further improve the sensing performance. Phenyl substituted selectors were included to probe both the effects of steric demand and electron affinity of the substituent. Additionally, we decided to investigate a selector containing two thiourea units in proximity, which could potentially lead to a higher binding affinity of the selector to its analyte by chelation.[15,16] Selector 9 is synthesized from diamine 5 and isothiocyanate 7 (**Figure 2**a). Although thiourea units have shown better interactions with analytes in previous studies,[12] it was not clear in this particular case if the steric bulk of the sulfur atoms would prevent a planar conformation in 9 and thereby compromise the binding of the selector to target analytes. As a result we also investigated 8, the urea counterpart of 9.

A challenge when investigating the performance of different selectors in CNT-based sensors is the complex dependence of the sensing response on a variety of contributing factors. Ideally the interaction of analyte and selector creates maximal resistance changes, but this performance is highly dependent on the selector attachment, their density on the CNT surface, and other functionality/structures present in the CNTs that are introduced in the synthesis or processing. To separate the effect of CNT attachment from the recognition performance of the selector, we performed a ^{1}H NMR binding study with model selectors and cyclohexanone in solution. The association constants for cyclohexanone and the model receptors in CDCl$_3$ obtained from these studies showed a clear advantage of the bidentate thiourea receptor over its analogues with only one binding site (see Figure 2a for the measured association constants). Interestingly, the ^{1}H NMR data from the titration experiment with 9 revealed no significant change in chemical shift for the NH protons further away from the central benzene ring upon addition of cyclohexanone (labeled a and b in Figure 2b, see Supporting Information for NMR data). The inner NH protons on the other hand (c and d in Figure 2b) experienced a significant downfield shift with increasing cyclohexanone concentrations. This suggests that the ketone participates in hydrogen bonding with one proton of each thiourea unit in 9 instead of binding to both NH protons of either thiourea group. Unfortunately, no association constant could be determined for 8, because the compound displayed very limited solubility in CDCl$_3$, presumably as a result of strong intermolecular hydrogen bonding.

2.2. Fabrication and Testing of Sensory Arrays

Guided by our initial sensing experiments as well as the ^{1}H NMR binding study, three additional selectors were attached to SWCNTs: the urea-based selector with two binding sites

(Bis–U–SWCNT), its thiourea counterpart (Bis–TU–SWCNT), and the phenyl analogue of m–CF_3–Bn–TU–SWCNT (m–CF_3–Ph–TU–SWCNT) (Figure 2c). Additionally, m–CF_3–Bn–TU–SWCNT, m–CF_3–Bn–SQ–SWCNT, and pristine (unfunctionalized) SWCNTs were included in further tests for comparison. To expose all sensors to exactly the same conditions, we developed a platform for the simultaneous measurement of several sensors. Glass slides having sensor arrays were connected to an array potentiostat through an edge connector and placed in a custom enclosure fabricated from polytetrafluoroethylene. The analyte gas could then be applied to all sensors, while the current was recorded at a constant potential (see Supporting Information for details).

These sensor arrays were exposed to 57 and 283 ppm cyclohexanone (1.3% and 6.3% of the equilibrium vapor concentration at 25 °C) as well as 57, 283 and 469 ppm nitromethane (0.1%, 0.6%, and 1% of the equilibrium vapor concentration at 25 °C) for evaluation of the chemiresistive properties (**Figure 3**a). To determine the reproducibility, two copies of each sensor were included on each glass slide and each exposure to the analyte was repeated five times. Using this data, the average response of each sensor type to the analytes at each concentration was determined (Figure 3b).[17] The results show that CF_3–Bn–SQ–SWCNT and Bis–TU–SWCNT are best suited for measurement of nitromethane while Bis–U–SWCNT performed best in the detection of cyclohexanone. The response to 283 ppm cyclohexanone was ca. 20% higher when using Bis–U–SWCNT compared to m–CF_3–Bn–TU–SWCNT, which displayed the best performance in the first round of testing. An increase in sensing response to 469 ppm nitromethane of 30% was observed when using Bis–TU–SWCNT compared to m–CF_3–Bn–TU–SWCNT. This improvement only required a simple additional synthetic step for the preparation of a new selector. One interesting aspect is that pristine SWCNTs show a significant response to cyclohexanone and a minimal response to nitromethane vapor.

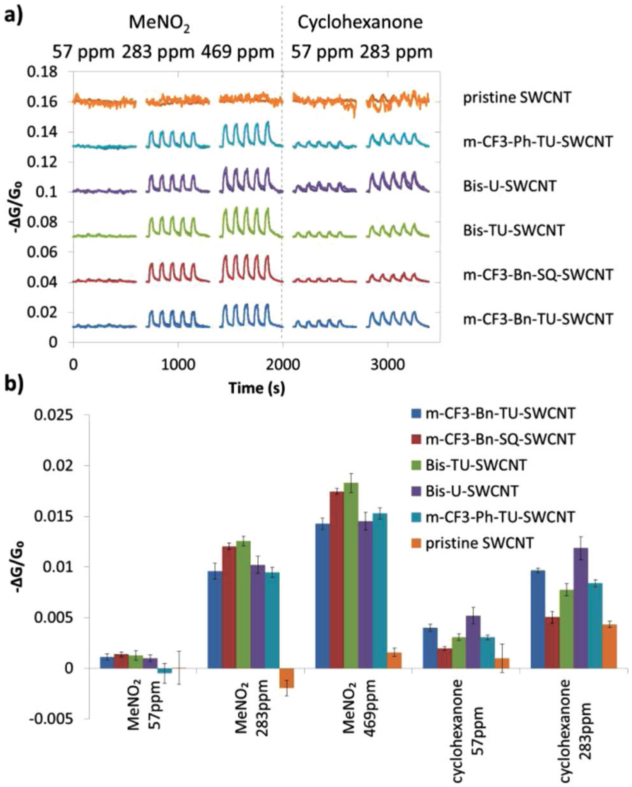

Figure 3. a) Sensing response of an array of SWCNT devices to nitromethane and cyclohexanone vapor at different concentrations. Data from two different sensors with the same type of functionalized SWCNTs are overlaid on each line. The traces appear in most cases as a single trace as a result of the excellent sensor to sensor reproducibility. b) Average sensing response and standard deviation over 4 peaks and two devices for each analyte and type of SWCNT. One pristine SWCNT device displayed an unusually high noise level and was therefore omitted to calculate the values for pristine SWCNT sensors.

Upon closer inspection of the sensing traces for each type of functionalized SWCNTs, it is evident that the responses of duplicate sensors using the same selector are virtually superimposable (see overlay of two sensing traces in each line of Figure 3a). To evaluate the level of reproducibility quantitatively, the difference between two sensors of the same type was calculated at each data point and averaged for each analyte and type of functionalized SWCNT (see Supporting Information for details and data). In units of $-\Delta G/G_0$, the average difference between the two sensing traces ranged from 0.02% ± 0.01% (m–CF_3–Bn–SQ–SWCNT measuring cyclohexanone 57 ppm) to 0.14% ± 0.01% (Bis–U–SWCNT measuring cyclohexanone 283 ppm), approximately one order of magnitude lower than the respective sensing responses. This high level of reproducibility is remarkable considering that no special precautions were taken when preparing the sensors other than ensuring the sensors have base resistances that are the same order of magnitude.

To better evaluate the effect of the optimized selectors on the sensing response to different molecules, sensors were exposed to a variety of analytes (**Figure 4**). Sensors based on pristine SWCNTs showed very low responses to all of the tested analytes. Sensors with optimized selectors on the other hand exhibited a significant enhancement in sensing response to analytes that are prone to hydrogen bonding interactions, for example, $MeNO_2$, acetone or cyclohexanone. Non-polar analytes such as hexanes or toluene did not induce a pronounce response. These findings are in accordance with the expected interaction of the respective analytes with the selector units on the functionalized SWCNTs.

The sensing responses were further analyzed using principal component analysis (PCA). PCA showed clustering of the responses for each analyte, which is remarkable considering the high similarity of the investigated receptors (**Figure 5**a). While the present sensor array contains similar selector functionalities and is thus not designed for high selectivity, adding different classes of selectors to an array is certain to improve sensor selectivity and will be investigated in future studies.

We also have performed initial studies that address sensor-to-sensor reproducibility as well as the long-term stability. These aspects are of critical importance if this platform is to ever be considered for commercial applications. The response of three separate sensors based on m–CF_3–Bn–TU–SWCNT to 57 and 283 ppm cyclohexanone was first evaluated shortly after their fabrication (Figure 5b). The sensor-to-sensor variance, although small, is much larger than we observe in our duplicate sensors

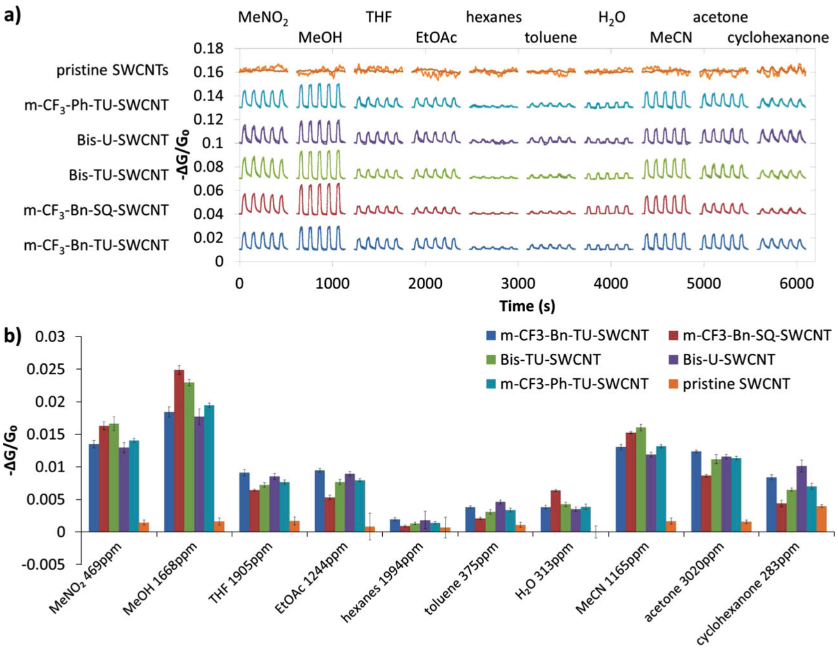

Figure 4. a) Sensing response of an array of SWCNT devices to different analytes. The concentration of each analyte represents 1% of its equilibrium vapour concentration at room temperature except cyclohexanone which was used at ca. 6% of its equilibrium vapour concentration at room temperature. b) Average sensing response and standard deviation over 4 peaks and two devices for each analyte and type of SWCNT. One pristine SWCNT device displayed an unusually high noise level (see sensing trace) and was therefore omitted to calculate the values for pristine SWCNT sensors.

on a given array. As a result, it is likely that these variations are mainly a result of the experimental setup, which includes the connectors, sample enclosure, and gas delivery. Subsequently, one of the devices was retested after 16 days as well as after 236 days of bench top storage under ambient conditions without special precautions (Figure 5c). The response was reduced after the nearly eight months period, but a clear signal upon exposure to 57 ppm of cyclohexanone could still be observed. We view these results as encouraging and suggest that with further development this sensor platform may be capable of producing sensors with small-enough drift to be viable for real-world applications.

3. Conclusions

In summary, we have developed SWCNT-based gas sensors with sensitivity to cyclohexanone and nitromethane, two compounds relevant for the detection of explosives. These resistivity-based sensing schemes have great potential as a result of simple fabrication, miniaturization, and facile integration into electronic circuits. Guided by initial sensing tests and ^{1}H NMR binding studies, improved selectors were synthesized and attached to SWCNTs to provide superior sensing performance. As a result, schemes involving the covalent attachment of selectors have promise for the systematic development of sensors for a wide range of analytes. The sensors showed a very high level of reproducibility between measurements with the same sensor and across different sensors of the same type. Furthermore, they exhibit promising long-term stability suitable for practical applications.

4. Experimental Section

Materials and Synthetic Manipulations: Synthetic manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Single-walled carbon nanotubes were purchased from Southwest Nanotechnologies (SWeNT CG100). All other chemicals were purchased from Sigma Aldrich and used as received. NMR spectra were recorded on Bruker Avance-400 spectrometers.

XPS Measurements: XPS spectra were recorded on a Kratos AXIS Ultra X-ray Photoelectron Spectrometer. The samples were drop-cast onto SiO$_2$/Si substrates for the measurements.

NH$_2$–SWCNT: SWCNTs (150 mg, 12.5 mmol C) were added to a flame dried Schlenk flask. 3-azidopropan-1-amine (6 g, 60 mmol) and 1,2-dichlorobenzene (30 mL) were added. The mixture was sonicated for 15 min and then equipped with a reflux condenser and stirred at 160 °C for 42 h. The solvent was distilled off and the residue was washed on a 0.2 μm fluoropore filter membrane with CH$_2$Cl$_2$, methanol, ethanol, water, methanol, and hexanes. The product was dried in vacuo. N/C ratio by XPS (based on N 1s vs. C 1s): 16.7% (functional group density: 8.3%).

m–CF$_3$–Bn–TU–SWCNT: NH$_2$–SWCNT (20 mg) were sonicated for 15 min in ethanol (15 mL). 1-(isothiocyanatomethyl)-3,5-bis(trifluoromethyl)benzene (256 mg, 1.0 mmol) in ethanol (5 mL) was added dropwise at 0 °C. The mixture was stirred for 48 h. The solid was collected by filtration and the product was washed on a filter with ethanol, CH$_2$Cl$_2$, methanol, water, methanol, and hexanes and subsequently dried in vacuo. Functional group density based on F 1s and C 1s signals by XPS: 45 CNT carbon atoms per functional group. Other thiourea derivatives were obtained following a similar procedure (see Supporting Information).

m–CF$_3$–Bn–SQ–SWCNT: NH$_2$–SWCNT (17.5 mg) were sonicated for 15 min in ethanol (15 mL). 3-(3,5-bis(trifluoromethyl)benzylamino)-4-ethoxycyclobut-3-ene-1,2-dione (319 mg, 0.87 mmol) in ethanol (15 mL) was added. The mixture was stirred for 48 h at room temperature and subsequently for 48 h at 40 °C. The solid was collected by filtration and the product was washed on a filter with ethanol, CH$_2$Cl$_2$, methanol, water, methanol, and hexanes and subsequently dried in vacuo. Functional group density based on F 1s and C 1s signals by XPS: 131 CNT carbon atoms per functional group. Other squaramide derivatives were obtained following a similar procedure (see Supporting Information).

m–CF$_3$–Ph–TU–SWCNT: NH$_2$–SWCNT (20 mg) were sonicated for 2 min in 15 mL THF. 1-isothiocyanato-3,5-bis(trifluoromethyl)benzene (271 mg, 1.0 mmol) was added and the mixture was stirred at room temperature for 3 days. The solid was collected by filtration and the product was washed on a filter with ethanol, CH$_2$Cl$_2$, methanol, water, methanol, and hexanes and subsequently dried in vacuo. Functional group density based on F 1s and C 1s signals by XPS: 180 CNT carbon atoms per functional group.

Methyl 3,4-bis(3-(3,5-bis(trifluoromethyl)phenyl)ureido)benzoate 8: 6 (2.81 g, 11.0 mmol) was added to 5 (831 mg, 5.0 mmol) in 30 mL THF. The mixture was stirred at room temperature for 24 h after which the solvent was removed in vacuo. The crude product was recrystallized from DCM (100 mL) and dried in vacuo. Yield: 2.17 g (3.2 mmol, 64%). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.95 (s, 1H), 9.78 (s, 1H), 8.55 (s, 1H), 8.39 (s, 1H), 8.09 (d, 4H, J = 18.4 Hz), 8.03 (d, 1H, J = 1.2 Hz), 7.93 (d, 1H, J = 8.8 Hz), 7.76 (dd, 1H, J = 8.4 Hz, 2.0 Hz), 7.61 (d, 2H,

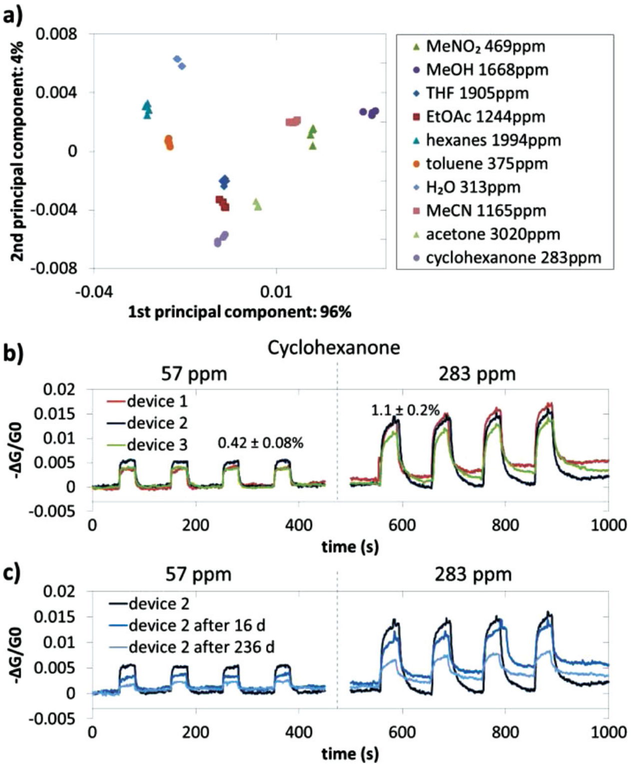

Figure 5. a) Principal component analysis of sensing response to different analytes using two sensors each based on Bis–U–SWCNT, Bis–TU–SWCNT, m–CF_3–Ph–TU–SWCNT, m–CF_3–Bn–TU–SWCNT, and m–CF_3–Bn–SQ–SWCNT. b) Sensing response of three different devices prepared with m–CF_3–Bn–TU–SWCNT to 57 ppm and 283 ppm cyclohexanone. Averages and errors are based on four measurements per analyte concentration and all three devices. c) Sensing response of one device prepared with m–CF_3–Bn–TU–SWCNT to 57 ppm and 283 ppm cyclohexanone, directly after device fabrication, after 16 days and after 236 days of storage under ambient conditions without additional precautions.

J = 8.4 Hz), 3.81 (s, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6, δ): 166.3 (s), 154.0 (s), 153.1 (s), 142.5 (s), 142.1 (s), 138.0 (s), 131.4 (q, J = 32.5 Hz), 131.3 (q, J = 32.5 Hz), 129.9 (s), 127.6 (s), 127.3 (s), 125.4 (s) 123.9 (q, J = 271.1 Hz), 123.9 (q, J = 270.9 Hz), 123.1 (s), 119.8 (s), 118.7 (s), 115.2 (s), 52.7 (s). HRMS *m/z:* $[M+H]^+$ calcd for $C_{26}H_{16}F_{12}N_4O_4$: 677.1053, found: 677.1073.

Methyl 3,4-bis(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)benzoate 9: 7 (2.98 g, 11.0 mmol) was added to 5 (831 mg, 5.0 mmol) in 30 mL THF. The mixture was stirred at room temperature for 22 h after which 7 (1 g, 3.7 mmol) was added. After stirring for two additional hours, the solvent was removed in vacuo. The crude product was washed with hexanes and DCM. Yield: 941 mg (27%). ^{1}H-NMR (400 MHz, DMSO-d_6, δ): 10.39 (s, 1H), 10.32 (s br, 1H), 10.02 (s, 1H), 9.91 (s br, 1H), 8.17 (d, 2H, J = 4.4 Hz), 8.06 (d, 1 H, J = 1.6 Hz), 7.91 (dd, 1 H, J = 8.4 Hz, 2.0 Hz), 7.76 (s br, 2H), 7.74 (d, 1H, J = 8.4 Hz), 3.88 (s, 3H). HRMS *m/z:* $[M+H]^+$ calcd for $C_{26}H_{16}F_{12}N_4O_2S_2$: 709.0596, found: 709.0611.

Bis–U–SWCNT: NH_2–SWCNT (20 mg) were sonicated for 5 min in ethanol (15 mL). 9 (709 mg, 1.0 mmol) was added and the mixture was refluxed for 4 days. The solid was collected by filtration and the product was washed on a filter with ethanol, water, ethanol, CH_2Cl_2, and hexanes and subsequently dried in vacuo. Functional group density based on F 1s and C 1s signals by XPS: 130 CNT carbon atoms per functional group.

Bis–TU–SWCNT: NH_2–SWCNT (20 mg) were sonicated for 5 min in ethanol (15 mL). 8 (676 mg, 1.0 mmol) was added and the mixture was refluxed for 4 days. The solid was collected by filtration and the product was washed on a filter with ethanol, water, ethanol, CH_2Cl_2, and hexanes and subsequently dried in vacuo. Functional group density based on F 1s and C 1s signals by XPS: 100 CNT carbon atoms per functional group.

Device Preparation: Glass slides (VWR Microscope Slides) were cleaned by ultrasonication in acetone for 10 min, and after drying they were subjected to UV radiation in a UVO cleaner (Jelight Company Inc.) for 3 min. Using an aluminum mask, layers of chromium (10 nm) and gold (75 nm) were deposited leaving a 1 mm gap using a metal evaporator purchased from Angstrom Engineering with home built aluminum shadow masks.

Pristine SWCNTs were added to CH_2Cl_2 at a concentration of 1 mg per 5 mL, NH_2–SWCNTs were added to ethanol and all other functionalized SWCNTs were added to 1:1 mixtures of CH_2Cl_2/iso-propanol at the same concentration. The samples were sonicated for 2 min (bath sonicator). Volumes of 1 µL of the respective SWCNT dispersion were drop-cast between the gold electrodes until a resistance of 5–20 kΩ was achieved.

Sensing Measurements: The devices were enclosed in a homemade polytetrafluoroethylene gas flow chamber for sensing measurement. The low concentration gas mixtures were produced using a KIN-TEK gas generator system.[18] A trace amount of analyte generated by heating the analyte is mixed with a nitrogen stream (oven flow), which can be further diluted with nitrogen (dilution flow). Calibration measurements were performed by placing the analyte in the oven flow for set amounts of time and determined its weight loss.

Electrochemical measurements were performed using a PalmSens handheld potentiostat (PalmSens Instruments) for single device measurements or an EmStat-MUX handheld potentiostat (PalmSens Instruments) for array measurements. A constant bias voltage of 0.1 V was applied across the device, while current versus time was measured. During the measurement the volume of gas flow over the device was held constant and switched between nitrogen and analyte/nitrogen.

NMR Binding Studies: The receptor was dissolved in $CDCl_3$ at a concentration of 0.01 M (for 1–4) or 2.5 mM (for 9) and a ^{1}H NMR spectrum was measured. Subsequently, cyclohexanone was added to achieve a ratio of cyclohexanone to the receptor of 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, 3.0, 5.0, 10.0, 15.0, 20.0, 25.0, and 50.0 (for 1–4) and 0.1, 0.3, 0.5, 0.7, 0.8, 1.0, 2.7, 4.4, 8.4, 12.5, 16.6, 20.7, 24.7, 40.4, and 144 (for 9). A ^{1}H NMR spectrum was recorded after every addition and the chemical shifts of the protons were recorded. Using the software package WinEQNMR2 with the chemical shifts of the NH and aromatic protons (for 1–4) or proton at the 4-position of the CF_3-substituted phenyl group in 9 (labeled e' in Figure 2a), association constants were determined.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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