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Detection and Classification of Volatile Organic Amines and Carboxylic Acids Using Arrays of Carbon Black-Dendrimer Composite Vapor Detectors

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Carbon black-insulator composite chemiresistive vapor detectors have been prepared using dendrimers as the polymeric constituent of the composite. Amino-terminated dendrimer-carbon black composites exhibited an enhancement in detection sensitivity of $\sim 10^3$ for volatile carboxylic acids as compared to nondendrimeric insulating polymer-carbon black composites. Similarly, protonated carboxylato-terminated and protonated amino-terminated dendrimer-carbon black composites showed an $\sim 10^3 - 10^4$ increase in sensitivity for detection of volatile amines relative to the response of nondendrimeric insulating polymer-carbon black composites. The protonated amino-terminated dendrimer carbon black composite detectors exhibited a signal-to-noise ratio (S/N) of 22.4 ± 0.9 upon exposure to 2.7 ppb of butylamine in air, whereas poly(ethylene oxide)-carbon black composites exhibited a S/N of 3.5 ± 1.2 at 54 ppm of butylamine. The protonated amino-terminated dendrimer-carbon black detectors additionally exhibited relatively small responses to water vapor. Compositional diversity in an array of protonated amino-terminated dendrimeric vapor detectors was obtained by varying the type and generation of the dendrimer, and the type and concentration of the acid dopant. Fifteen analytes chosen from primary amines, branched amines, anilines, and non-amine organic analyte vapors were all robustly discriminated from each other by their different response patterns on the dendrimer-containing detector array. The signals produced by these 15 analytes additionally clustered into groups based on the chemical class of the analyte.

I. Introduction

Detection of volatile amines and volatile carboxylic acids is of interest because these vapors play a prominent role in such diverse fields as environmental and industrial monitoring,[1,2] quality control of food,[3−14] and medical diagnosis of certain types of disease.[15−17] For example, 5 ppm is the recommended threshold for human exposure to the primary irritants butylamine and isopropylamine. Biogenic amines and organic carboxylic acids are biomarkers for certain disease states, such as uremia (dimethylamine and trimethylamine),[17] lung cancer (aniline and *o*-toludine),[16] larynx cancer (C_2 to C_6 aliphatic acids), and cirrhosis (acetic acid, propionic acid).[15] Detection of organic amines and carboxylic acids has been achieved using tin oxide sensors,[18−20] electrochromic polymers,[21] pH indicators,[22] and dye-doped sol−gel glass films[23] in conjunction with potentiometric, conductometric, fluorometric, or gas or liquid chromatographic techniques.

Recent work in our laboratory has focused on detection, classification, and quantification of vapors using arrays of chemiresistive polymer-conductor composites.[24−33] In such an array, each detector is composed of a conductor (typically

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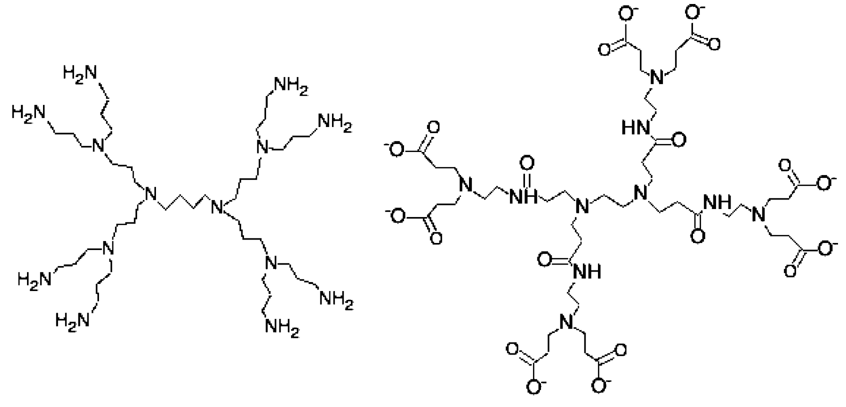
Scheme 1



Dendrimer DAB-AM
generation 2

Dendrimer PAMAM
generation 0.5

carbon black) dispersed into an insulating organic polymer. The pattern of resistance changes produced by exposure of the detector array to an analyte of interest is diagnostic of the vapor or vapor mixture, while the amplitude of the pattern indicates the concentration of the analyte. The basic properties of such arrays, including the mechanism of signal transduction,[31,34] limits of detection,[27,35,36] classification properties,[25,33] geometric aspects of signal-to-noise ratio (S/N) optimization,[37] detector response time,[38] and spatiotemporal-based detection of analyte mixtures[37] have been described in detail.

Through a combination of quartz crystal microbalance, ellipsometric, and dc electrical resistance measurements, studies of carbon black-polymer composite detectors formed from either poly(ethylene oxide) or polycaprolactone have indicated that sorption-induced polymer swelling dominates the dc resistance response of such composites.[31] Hence, improved sensitivities to a target class of analytes can be achieved in principle by increasing the polymer/vapor partition coefficient, increasing the swelling per mole of sorbed analyte, and/or increasing the conductivity change in response to a given level of film swelling. Improved sensitivity to volatile carboxylic acids, for example, has been obtained through the use of carbon black composite detectors formed using linear poly(ethyleneimine) and low carbon black loadings.[39]

In this work, we have explored the use of dendrimers as the insulating component of the conductor composite vapor detectors. Polyamidoamine dendrimers with carboxylato surface groups (PAMAM) and polypropylenimine dendrimers with primary amino surface groups (DAB-AM) (Scheme 1) have been used in this work. The surface groups and the internal tertiary amino groups in these two types of dendrimers can be protonated using acids of the appropriate pK_a. The question of interest is whether large polymer/vapor sorption coefficients, and thereby large relative differential resistance responses, can be induced for vapors that can undergo complimentary proton-transfer reactions with the Brønsted acidic and/or Brønsted basic sites in the two types of dendrimers. Accordingly, we have investigated the response properties of carbon black composites formed from the protonated PAMAM dendrimer to primary, secondary, and tertiary amines and from the unprotonated DAB-AM dendrimers to acetic acid. We additionally have compared the response of protonated PAMAM dendrimers and unprotonated DAB-AM dendrimer carbon black composites to the response of composites formed using nondendrimeric polymers such as poly(ethylene oxide). Compositional diversity in an array of protonated amino-terminated dendrimer-carbon black composite vapor detectors was achieved by varying the generation and type of dendrimer and the type and concentration of the acid dopant. The classification ability of such an array was investigated for a series of 15 test organic vapor analytes having a variety of hydrogen-acid bond strengths.

II. Experimental Section

A. Materials. The carbon black used to fabricate the composite detectors was Black Pearls 2000, a furnace black made by the Cabot Corp. Polypropylenimine dendrimers with primary amino surface groups (DAB-AM-16 generation 3.0, DAB-AM-32 generation 4.0, and DAB-AM-64 generation 5.0) and polyamidoamine dendrimers with carboxylato surface groups (PAMAM generation 3.5) were purchased from Aldrich and were used as received. Poly(ethylene oxide) (PEO), polymethyloctadecylsiloxane (PMODS), ethyl cellulose (Cellulose), poly(ethylene-*co*-vinyl acetate) (PEVA) (40% vinyl acetate), poly(styrene-*co*-isoprene) (14% styrene) (PSIP), poly-

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(styrene-*co*-butadiene) (PS−PBD) (30% styrene), *l*-polyethylenimine (PEI), and polycaprolactone (PCl) were used as received from Scientific Polymer Products, Inc. (SP^2). The acids used for dendrimer protonation were methanesulfonic acid (MSA), ethanesulfonic acid (ESA), *p*-toluenesulfonic acid (TSA), and dodecylbenzesulfonic acid (DBSA). The solvents methanol, ethanol, toluene, 40% methylamine(aq), 70% ethylamine(aq), propylamine, *n*-butylamine, iso-butylamine, octylamine, 40% dimethylamine(aq), 40% trimethylamine(aq), triethylamine, aniline, pyridine, *n*-methylaniline, acetic acid, butyric acid, valeric acid, and hexanoic acid were obtained from Aldrich and were used without further purification. Then 18 MΩ-cm resistivity deionized water was obtained from a Barnstead Nanopure purification system.

B. Detectors. Suspensions for fabricating detector films were formed by first dissolving the desired quantity of dendrimer in 20 mL of methanol at room temperature. For the amine vapor detectors, acid dopants (such as MSA and DBSA) were added to the dendrimer to obtain a desired protonation ratio while producing a total mass of dendrimer and acid dopant of 160 mg. For example, DAB-AM-64 was completely protonated (both at the terminal primary amino and internal tertiary amino groups) by MSA at a DAB-AM-64:MSA mole ratio of 1:122. Similarly, PAMAM 3.5 was completely protonated (both at the terminal carboxylato and internal tertiary amino groups) by MSA at a PAMAM:MSA mole ratio of 1:124. Forty milligrams of carbon black was then added, and the suspension was sonicated for >1 h at room temperature prior to fabrication of the detector films. Carboxylic acid vapor detectors were made by dissolving 120 mg of the DAB-AM-64 dendrimer in 20 mL of methanol at room temperature for several hours, and then 80 mg of carbon black was added. The suspension was then sonicated for >30 min. Nondendrimeric polymer-carbon black composites were made by dissolving 160 mg of each polymer in 20 mL of a compatible solvent for several hours either at room temperature or, if necessary, at 35−40 °C. Carbon black was then added to the solution and the resulting suspension was sonicated for at least 30 min at room temperature.

Detector substrates were fabricated by evaporating 300 nm of chromium and 700 nm of gold onto glass microscope slides using 0.8-mm-wide drafting tape as a mask. After evaporation, the mask was removed and the glass slides were cut into 10 mm × 25 mm pieces. The 0.8 mm gap region was then sprayed with the carbon black-polymer suspension until the initial resistance between the two leads was 30−100 kΩ.

C. Detector Array. The detector array consisted of three nominally identical copies of 13 distinct types of detectors. The insulating components of the 13 detector types were as follows: DAB-AM-16 (stoichiometrically protonated with DBSA), DAB-AM-16 (stoichiometrically protonated with MSA), DAB-AM-32 (stoichiometrically protonated with DBSA), DAB-AM-32 (stoichiometrically protonated with MSA), DAB-AM-64 (stoichiometrically protonated with DBSA), DAB-AM-64 (stoichiometrically protonated with MSA), PAMAM 3.5 (half protonated with DBSA), PAMAM 3.5 (half protonated with MSA), poly(ethylene oxide) (PEO), poly(styrene-*co*-isoprene) (PSIP), poly(ethylene-*co*-vinyl acetate) (PEVA), polymethyloctadecylsiloxane (PMODS), and ethyl cellulose (Cellulose).

D. Measurements. The instrumentation and apparatus for resistance measurements and for delivery of analyte vapors has been described previously.[29,31,36] To initiate an experiment, the detectors were placed into the flow chamber and a background flow of compressed air was introduced until the resistance of the detectors stabilized. An individual analyte exposure to the carbon black-insulator composite detectors consisted of a three-step process that was initiated with 1000 s of airflow to achieve a smooth baseline resistance. Analyte vapor at a controlled concentration in flowing laboratory air with 1.10 ± 0.15 parts per thousand, ppth, of water vapor was then introduced to the detectors for 2000 s, followed by 8000 s of airflow to restore the baseline resistance value for most amine vapors.

The fifteen analytes were divided into three randomly chosen groups, with each group comprising one experimental run. Within each run, every exposure was assigned a randomly generated index number using the Microsoft Excel random number generator. The exposures were then presented to the detector array in ascending order of the assigned index values. To obtain signatures for the different analytes of interest, each analyte in the three groups was exposed three times to the vapor detector array at a fixed value of $P/P°$, where $P°$ is the vapor pressure of the analyte at room temperature and P is the partial pressure of the analyte.

A homemade headspace injection system was used to investigate the detector response at low analyte concentrations (typically <54 parts per million (ppm)). First, a small amount (usually 25 μL, 100 μL, 250 μL, or 1 mL) of analyte-saturated air was injected into a 2000 mL sealed glass container that contained a magnetically controlled fan to mix the headspace air in the vessel. Serial dilution was performed to produce lower analyte concentrations. For example, a small amount of diluted vapor (usually 25 μL, 100 μL, 250 μL, or 1 mL) was withdrawn using a clean syringe, and this aliquot was injected into a second 2000 mL headspace apparatus. This second apparatus contained the mixer and detectors described above. Injection of 1 mL of air saturated with *n*-butylamine into the 2000 mL container yielded an analyte concentration of 54 ppm, whereas injection of 1 mL of diluted *n*-butylamine vapor yielded an analyte concentration of 27 parts per billion (ppb).

E. Data Processing. Although the resistance of each detector was sampled every 3−8 s during each exposure, only the maximum relative differential resistance change, $\Delta R_{\max}/R_b$, was used in analysis of the data, with $\Delta R_{\max}$ the maximum resistance change of the detector during the analyte exposure and R_b the baseline resistance of the detector prior to the exposure. The data were corrected for any baseline slope by fitting a line to the 80 data points that preceded an analyte exposure, with the average of these 80 slope-corrected points taken as R_b. The value of $\Delta R_{\max}$ was computed by subtracting R_b from the maximum baseline-corrected resistance value observed during an exposure. Data were converted to $\Delta R_{\max}/R_b$ form in Microsoft Excel, while principal components analysis (PCA) was performed using Matlab.

III. Results and Discussion

A. Response of Various Insulator-Carbon Black Composites Detectors to *n*-Butylamine. Figure 1a depicts the relative differential resistance behavior of various carbon black-insulator composite vapor detectors when exposed to *n*-butylamine at $P/P° = 0.020$. The unprotonated amino-terminated DAB-AM dendrimers showed very small responses to this concentration of butylamine, whereas the carbon-black nondendrimeric polymer composite detectors generally exhibited $\Delta R_{\max}/R_b = 0.2-0.6$ under such conditions. The DAB-AM-64 dendrimers with low protonation ratios generally showed similar responses to those of the nondendrimeric carbon black composite detectors. In contrast, the DAB-AM-64 dendrimers with protonation ratios >0.9 showed large responses to *n*-butylamine. In addition, detectors formed using the PAMAM generation 3.5 dendrimer protonated with DBSA produced $\Delta R_{\max}/R_b > 290$, i.e., approximately 5000 times larger than the response

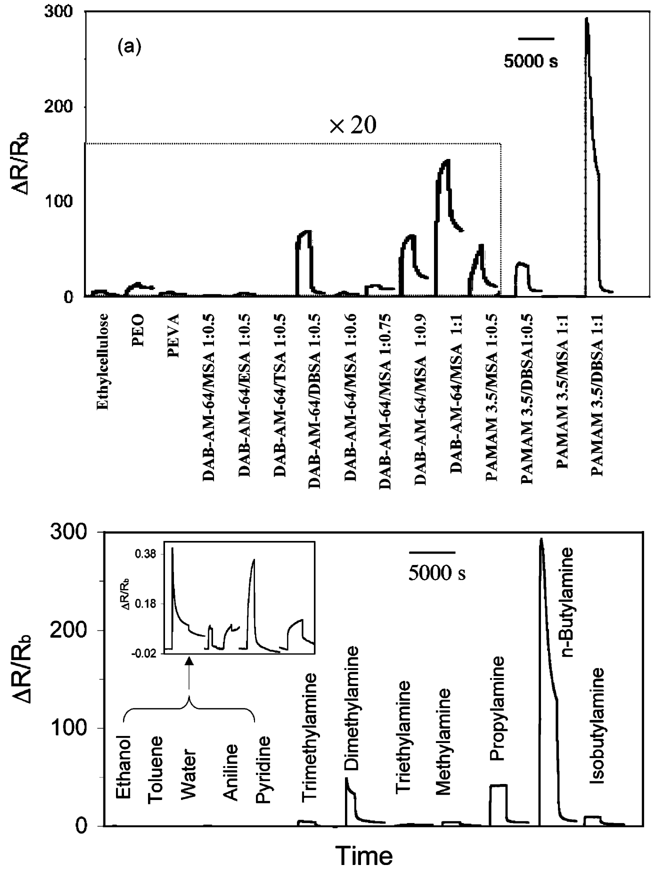

Figure 1. (a) $\Delta R/R_b$ response of 15 carbon black-insulator composite detectors exposed to *n*-butylamine vapor at $P/P° = 0.020$ in laboratory air. Each exposure involved 1000 s of air flow, followed by 2000 s of *n*-butylamine and then 2000 s of background air at a constant total flow velocity of 5 L min^{-1}. The data for all but the last three types of detectors are shown on an expanded ordinate. (b) $\Delta R/R_b$ response of a PAMAM 3.5/DBSA (protonation ratio 1:1)/carbon black (80:20 by mass) vapor detector exposed to ethanol, toluene, water, aniline, pyridine, 40% (aq) trimethylamine, 40% (aq) dimethylamine, triethylamine, 40% (aq) methylamine, propylamine, *n*-butylamine, and isobutylamine, at $P/P° = 0.020$. Each curve (except for toluene) was collected using 1000 s of air flow (at 5 L min^{-1}) followed by 2000 s of analyte at $P/P° = 0.020$, and then 2000 s exposure to background air. The toluene data were collected using a 500 s exposure to air, a 500 s exposure to toluene at $P/P° = 0.020$, and then 500 s of background air, at a flow velocity of 5 L min^{-1}. The inset shows the data for the first five analytes on an expanded ordinate.

to butylamine exhibited by the nondendrimeric carbon-black polymer composites (Figure 1).

Comparison of detectors fabricated using four different acid dopants indicated that, for both the DAM-AM-64 and PAMAM generation 3.5 dendrimer composites, protonation using DBSA yielded the largest $\Delta R_{max}/R_b$ response to *n*-butylamine at $P/P° = 0.020$. The DBSA-protonated dendrimer-carbon black composites also had a faster response time than composites formed from MSA-protonated dendrimers. Furthermore, as shown in Figure 1a, the responses of the dendrimers can be tuned by appropriate adjustment of the preparation conditions such as the types of dendrimer, the type of doping acid, and the protonation ratio. These differences in response indicate that compositional diversity in an array of amine-sensitive vapor detectors can be obtained by varying the concentrations of these components of the composite films.

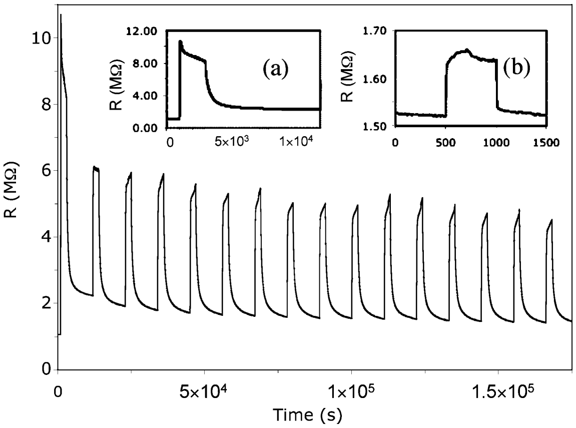

Figure 2. Resistance of a DAB-AM-64/DBSA (protonation ratio 1:1) dendrimer-carbon black (80:20) detector as a function of time upon repeated exposures to *n*-butylamine vapor at $P/P° = 0.020$ in laboratory air. Each exposure involved 3000 s of air, followed by a 2000 s exposure to *n*-butylamine, followed by 8000 s of flowing laboratory air. Inset (a) represents the resistance response of the detector in the first exposure. For comparison, the resistance response of the detector to toluene vapor at $P/P° = 0.020$ in laboratory air is shown in inset (b). The detector was exposed to toluene vapor at $t = 500$ s and was flushed with laboratory air at $t = 1000$ s.

B. Response of a PAMAM 3.5/DBSA-Carbon Black Composite Detector to Various Analytes. Figure 1b presents the $\Delta R/R_b$ responses to various organic vapors at $P/P° = 0.020$ of a carbon black-insulator composite detector formed using the PAMAM generation 3.5 dendrimer that had been stoichiometrically protonated using DBSA. The $\Delta R_{max}/R_b$ response decreased in the following order: primary amines > branched amines > anilines > non-amine vapors. Figure 1b also indicates that exposure to aliphatic amine vapors produced a $\Delta R_{max}/R_b$ response approximately 10^3 larger than the response produced to the same activity ($P/P° = 0.020$) of non-amine organic vapors or water vapor. Hence, the $\Delta R_{max}/R_b$ per unit of analyte concentration in the gas phase is higher by a factor of ~100 for primary amines relative to water vapor. Such detectors are therefore attractive for use in breath sampling, in which amine vapors are present in a background of nearly saturated water vapor.

Because the pK_a values of MSA, ESA, TSA, and DBSA are between ca. −2 and −3.5, the DAB-AM dendrimers, which have terminal primary amino groups and internal tertiary amino groups, and the PAMAM dendrimers, which have terminal carboxylato groups and internal tertiary amino groups, can be easily and fully protonated. This high degree of protonation makes the resulting dendrimeric clusters effectively a large charged sphere of weak acid functionality. Hence, such dendrimers should be very effective at binding analytes such as amine vapors that have complimentary hydrogen bond acid functionality, which is consistent with the data presented in Figures 1a and 1b.

C. Reversibility of the Response of Dendrimeric-Carbon Black Composite Detectors to Volatile Amine Vapors. Figure 2 depicts the time dependence of the resistance response of a typical stoichiometrically protonated DBSA-doped DAB-AM generation 5 dendrimer-carbon black detector upon repeated exposures to butylamine vapor at $P/P° = 0.020$ in air. The response in the first exposure reached its maximum value after 3 min and drifted during the whole exposure time (2000 s), and 50 min of purging with background air was required to return $\Delta R/R$ to within

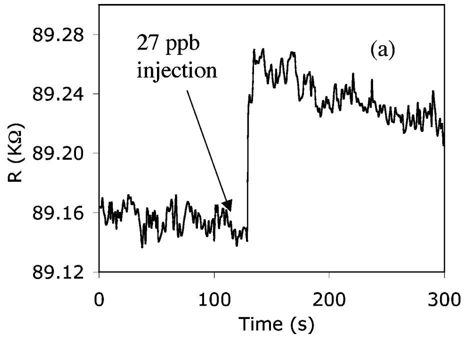

Figure 3. Resistance of two dendrimer(acid)/carbon black (80:20) composite detectors as a function of time during an injection of *n*-butylamine. The dendrimers are (a) DAB-AM-16 (generation 3) and (b) DAB-AM-64 (generation 5).

Table 1. Response Characteristics of Several Polymer-Carbon Black Detectors to *n*-Butylamine

	concentration	$\Delta R_{max}/R_b$	S/N
DAB-AM-16/MSA	27 ppb	1×10^{-3}	4.7
DAB-AM-16/DBSA	1 ppm	2×10^{-3}	8.5
DAB-AM-32/MSA	2.7 ppb	$(5.1 \pm 0.2) \times 10^{-3}$	$(3.6 \pm 0.2) \times 10$
DAB-AM-64/MSA	2.7 ppb	$(6.3 \pm 0.1) \times 10^{-3}$	$(2.2 \pm 0.1) \times 10$
PAMAM 3.5/MSA	27 ppb	$(2.4 \pm 1.7) \times 10^{-3}$	8.7 ± 11.3
PAMAM 3.5/DBSA	54 ppm	$(8.2 \pm 4.4) \times 10^{-1}$	$(4.0 \pm 3.7) \times 10^{3}$
poly(ethylene oxide)	54 ppm	$(4.5 \pm 1.3) \times 10^{-4}$	3.5 ± 1.2
ethyl cellulose	54 ppm	$(3.1 \pm 0.3) \times 10^{-2}$	2.0 ± 0.2
polymethyloctadecylsiloxane	54 ppm	$(3.0 \pm 1.0) \times 10^{-3}$	7.1 ± 4.0
poly(styrene-*co*-isoprene)	54 ppm	$(6.7 \pm 3.3) \times 10^{-3}$	$(2.8 \pm 1.4) \times 10$
poly(acylic acid)	5.4 ppm	no signal	N/A

120% of its original baseline resistance value (inset (a) of Figure 2). Subsequent exposures produced somewhat smaller $\Delta R_{max}/R_b$ values, but the responses were reasonably consistent (2.27 ± 0.17) over many exposures to butylamine. In contrast, such composite detectors exhibited much shorter (on the order of 60 s) sorption and desorption times to non-amine organic analyte vapors (inset (b) of Figure 2).

The increased sorption and desorption times for amine vapors indicate that the response to amines is not purely a physical absorption and desorption process and is consistent with the presence of significant chemical interactions between the proton-donating groups in the protonated dendrimeric-carbon black composite and the Brønsted basic groups in the amine analytes. This behavior suggests that the response to repeated exposures to amines is mainly associated with the reversible absorption of analyte into the composite film whereas the first exposure involves significant contributions from both chemical reactions and physical adsorption, with the chemical interaction being largely nonreversible.

D. Limits of Detection of Dendrimeric-Carbon Black Composite Detectors for *n*-Butylamine. Headspace injection methods were used to evaluate the limit of detection of the dendrimer-carbon black sensors to various amine vapors. Figure 3 shows the response of representative protonated dendrimer-carbon black composite detectors to 27 and 2.7 ppb, respectively, of *n*-butylamine in laboratory air. The MSA/DAB-AM-16 generation 3 composite produced $\Delta R_{max}/R_b = 0.001$ with a signal/noise ratio of 4.7 upon exposure to 27 ppb of *n*-butylamine (Figure 3a), whereas the MSA/DAB-AM-64 generation 5 composite exhibited a higher response ($\Delta R_{max}/R_b = 0.0051$), with S/N = 22.4, upon exposure to a lower (2.7 ppb) concentration of butylamine (Figure 3b).

Table 1 compares the signal/noise ratios at selected analyte concentrations of protonated dendrimer-carbon black composites to the performance of selected nondendrimeric polymer-carbon black composite detectors. To explore polymers that contained complimentary functionality as pendant groups along a polymer backbone, carbon black-poly(acylic acid) composites were also evaluated. The carbon black-poly(acylic acid) detector showed no detectable response to 5.4 ppm of *n*-butylamine vapor, while the PAMAM-carbon black composites exhibited large responses. The pendant group plays a minor role in determining the polymer size, and thus our studies indicate that the complimentary component must be on the dendrimer periphery or polymer backbone (PEI). In general, composites formed from the higher generation dendrimers yielded improved responses to the amine vapors. The best detection limit observed for *n*-butylamine, <2.7 ppb, was obtained with the MSA-doped DAB-AM generation 4 or generation 5 dendrimer-carbon black detectors (all at a 1:1 protonation ratio) (6 out of 8 samples tested). This detection limit is 10^3 lower than that exhibited by typical polymer-carbon black detectors, which generally displayed S/N = 2−27 upon exposure to 54 ppm of *n*-butylamine (Table 1). Similarly, the PAMAM generation 3.5/DBSA composite detectors displayed 10^2−10^3 larger S/N values than the nondendrimeric polymer−carbon black detectors toward butylamine. The protonated dendrimer−carbon black composite detectors can thus be tuned to have better sensitivity than typical carbon black-insulating polymer composites at both low (Table 1) and high (Figure 1a) concentrations of amine vapors.

In contrast to the behavior of nondendrimeric polymer-carbon black detectors, the dendrimer-carbon black detectors exhibited a nonlinear response to the concentration of amine vapor. For example, PAMAM generation 3.5/DBSA composite detectors (at a 1:0.5 protonation ratio) showed nonobservable signals to 27 ppb − 5.4 ppm of *n*-butylamine vapor but showed $\Delta R_{max}/R_b = 0.82$ with a S/N ratio of 4.0

Table 2. $\Delta R_{max}/R_b$ Response of Several Carbon Black-Composite Detectors to Acid Vapors at $P/P° = 0.010$

	acetic acid 160 ppm	butyric acid 9 ppm	valeric acid 2 ppm	hexanoic acid 274 ppb
DAB-AM-64/40% carbon black	8.75×10^2	1.5	1.1	6×10^{-2}
l-polyethylenimine	2.2×10	1.1	3×10^{-1}	3×10^{-2}
polysulfone	6×10^{-3}	4×10^{-4}	1×10^{-4}	1.3×10^{-5}
poly(ethylene-*co*-vinylacetate)	2×10^{-2}	9×10^{-3}	5×10^{-3}	1×10^{-3}
polycaprolactone	3×10^{-2}	1×10^{-2}	9×10^{-3}	2×10^{-3}
poly(styrene-*co*-butadiene)	2×10^{-2}	9×10^{-3}	5×10^{-3}	2×10^{-3}
poly(ethylene oxide)	8×10^{-2}	2×10^{-2}	1×10^{-2}	4×10^{-3}
polyvinylpyrrolidone	1.3×10^{-1}	2×10^{-3}	1×10^{-2}	8×10^{-3}
poly(4-vinylpyridine)	5×10^{-2}	5×10^{-4}	6×10^{-3}	3×10^{-3}

$\times 10^3$ to 54 ppm of *n*-butylamine. The MSA-protonated detectors exhibited limits of detection that were 10−100-fold lower than those exhibited by the DBSA-protonated detectors (Table 1). Interestingly, this behavior occurred even though at high concentrations of amine vapor the DBSA-protonated detectors showed a larger $\Delta R_{max}/R_b$ signal than the MSA-protonated detectors (Figure 1a). Additionally, DAB-AM dendrimer-carbon black composite detectors generally exhibited lower detection limits than the analogous PAMAM dendrimer-carbon black composites.

E. Detection of Carboxylic Acid Vapors Using Dendrimer-Carbon Black Composites. To evaluate whether dendrimers could be used in conjunction with other hydrogen-bond complimentary chemical interactions to obtain enhanced vapor detection sensitivities toward targeted classes of analytes, carbon black-insulator composites were also investigated using nonprotonated amino-containing dendrimers. Upon exposure to acetic acid at $P/P° = 0.010$ in air, a DAB-AM-64 40% carbon black detector produced $\Delta R_{max}/R_b = 875$, as compared to a value of <0.1 for the PCl or PEO-carbon black composite detectors. Although enhanced $\Delta R_{max}/R_b$ responses to volatile carboxylic acids have been demonstrated recently through the use of *l*-PEI-carbon black detectors,[39] the DAM-AM-64-carbon black composite yielded an even larger response to acetic acid than did the *l*-PEI-carbon black composite film (Figure 4).

Table 2 lists the $\Delta R_{max}/R_b$ values observed upon exposure to $P/P° = 0.010$ of acetic acid (160 ppm), butyric acid (9 ppm), valeric acid (2 ppm), and hexanoic acid (274 ppb), respectively, for carbon black composite detectors fabricated from DAB-AM-64, *l*-PEI, and other selected insulating polymers. The $\Delta R_{max}/R$ response to these carboxylic acid vapors of the dendrimer-carbon black detector was 10^1-10^3 larger than the response of the other carbon black-insulator composites. This behavior is consistently ascribed to the charge repulsion induced by protonation of the amino functionality on the dendrimer inducing a large swelling-related resistance change in the vapor detector film. Such behavior makes the dendrimer-carbon black composites a versatile sensing matrix because the same base material shows enhanced sensitivity to carboxylic acids, when in its nonprotonated form, and to organic amines in its protonated form.

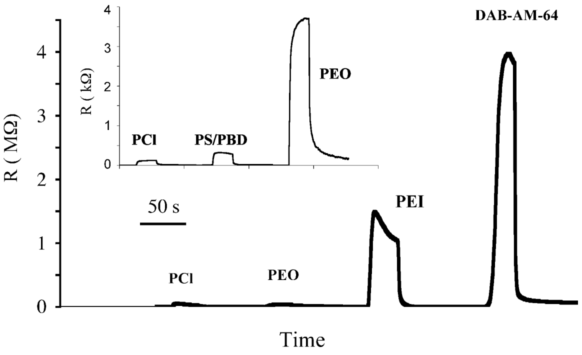

Figure 4. Resistance response of carbon black-insulator composite detectors formed from polycaprolactone (PCl), poly(styrene-*co*-polybutadiene) (PS/PBD), poly(ethylene oxide) (PEO), *l*-polyethyeleneimine (PEI), and DAB-AM-64, respectively. Each exposure was to acetic acid at $P/P° = 0.010$ in air. All detectors were 20 wt % carbon black except for the DAB-AM-64 composite, which was 40 wt % carbon black. The inset shows data with the ordinate on an expanded scale.

F. Classification of Amine Vapors Using Arrays of Dendrimer-Carbon Black Composite Detectors. As displayed in Figure 1, dendrimers with different type, different generation, different acid dopants, and different acid concentrations yield different responses to amine vapors. Deliberate manipulation of these variables thus offers the opportunity to construct a detector array that can classify the type of amine vapor while providing the high sensitivity associated with the protonated dendrimer-carbon black composites. Arrays of carbon black detectors, primarily from DAM-AM with either MSA or DBSA as the dopant, were

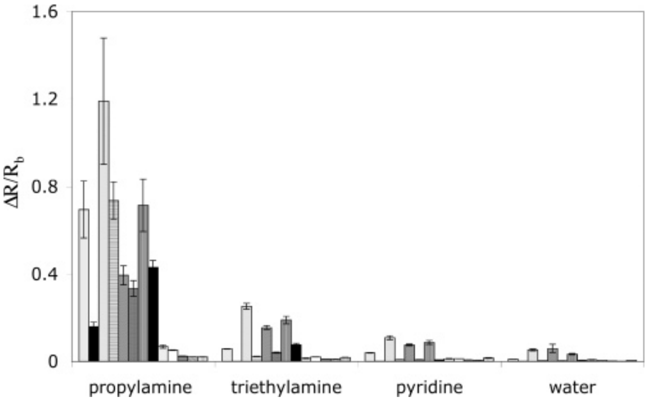

Figure 5. $\Delta R_{max}/R_b$ response of an array of carbon black-protonated dendrimer composite detectors and several nondendrimeric insulating polymer-carbon black vapor detectors exposed to propylamine, triethylamine, pyridine, and water, respectively, each at $P/P° = 0.0090$. The means and standard deviations are for 3 exposures of 3 detectors to each analyte, with exposures alternating between different analytes. The 13 detector types from left to right for each analyte are DAB-AM-16 (stoichiometrically protonated with DBSA), DAB-AM-16 (stoichiometrically protonated with MSA), DAB-AM-32 (stoichiometrically protonated with DBSA), DAB-AM-32 (stoichiometrically protonated with MSA), DAB-AM-64 (stoichiometrically protonated with DBSA), DAB-AM-64 (stoichiometrically protonated with MSA), PAMAM 3.5 (half protonated with DBSA), PAMAM 3.5 (half protonated with MSA), poly(ethylene oxide) (PEO), poly(styrene-*co*-isoprene) (PSIP), poly(ethylene-*co*-vinyl acetate) (PEVA), polymethyloctadecylsiloxane (PMODS), and ethyl cellulose (cellulose).

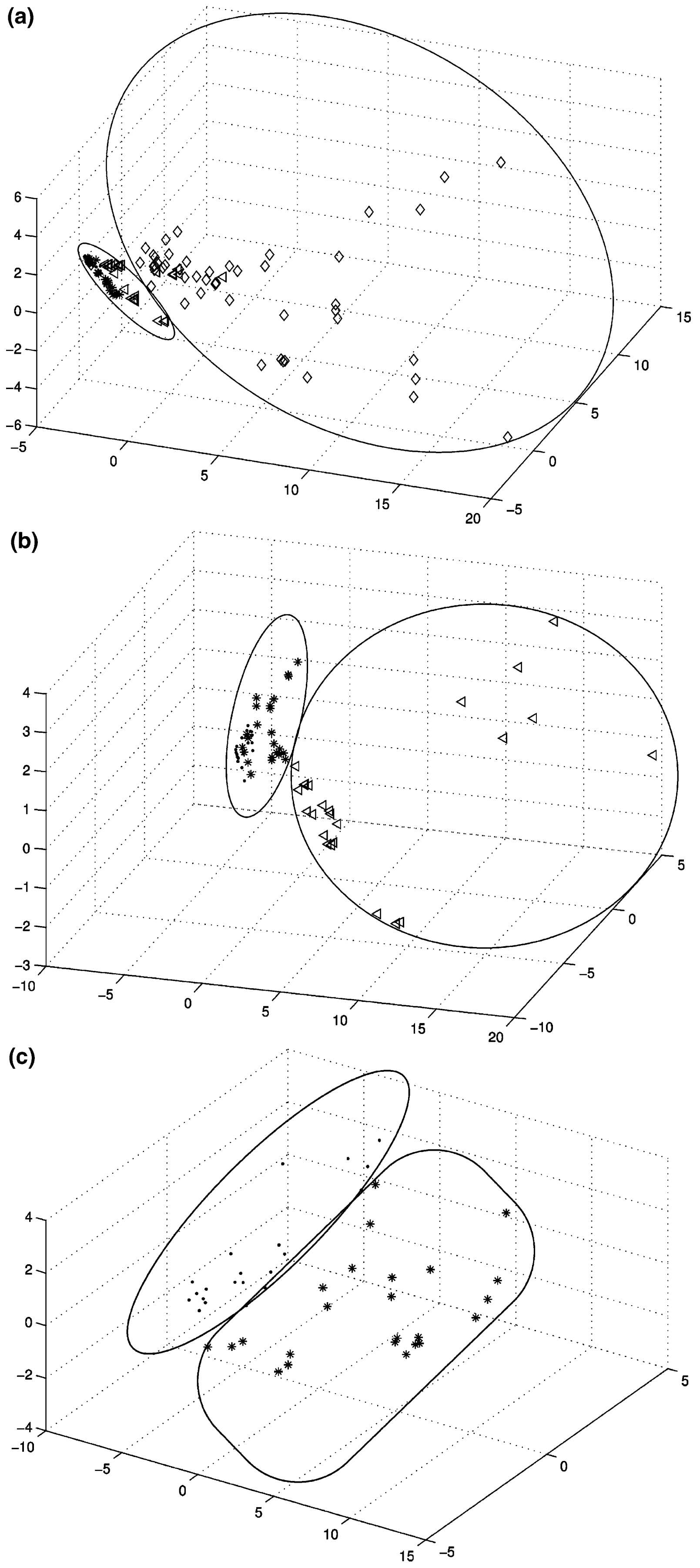

Figure 6. Principal components analysis plots of the $\Delta R_{\mathrm{max}}/R_{\mathrm{b}}$ response of the detector array of Figure 5. The symbols ◇, ▽, ∗, and ● represent primary amines, branched amines, anilines, and normal organic vapor, respectively. (b) Principal components analysis plot excluding exposures to primary amines. (c) Principal components analysis plot excluding the exposures to primary, secondary, and tertiary amines. The circles are guides to the eye that enclose the data points originating from a particular class of analytes.

therefore evaluated for their performance in a series of vapor classification tasks.

A 13-type detector dendrimer-carbon black composite detector array was investigated upon exposure to octylamine, butylamine, isobutylamine, proylamine, ethylamine, methylamine, triethylamine, dimethylamine, trimethylamine, pyridine, *n*-methylaniline, aniline, water, ethanol, and toluene, respectively. Figure 5 shows the response pattern of the 13-type detector dendrimer-carbon black composite detector array to $P/P° = 0.0090$ of propylamine, triethylamine, pyridine, and water, respectively. The entire array response data are contained in the Supporting Information. In accord with the behavior of Figure 1, the detectors showed a mean $\Delta R_{max}/R_b$ response decreasing in the order of primary amines > less branched amines> more branched amines > anilines > normal organic vapors.

Figures 6a−6c depict the $\Delta R_{max}/R_b$ responses of the detector array in principal components space. Each analyte produced a distinct response cluster that was differentiable from the response cluster of every other analyte investigated. The primary amines (◊ in Figure 6a) were readily distinguished as a class from other analytes because the primary amines clustered together in principal component space. The only overlap of the primary amines and branched amines was with dimethylamine. A more detailed analysis, depicted in Figures 6b and 6c, indicated that vapors could additionally be robustly classified as either branched amines, ▽, anilines, ∗, or non-amine organic vapors, ●.

IV. Conclusions

Chemiresistors formed from carbon black composites of protonated amino-terminated and carboxylato-terminated dendrimers displayed relatively large relative differential resistance responses to organic amine vapors, with sensitivities 10^1-10^3 larger than those of typical insulating polymer−carbon black composite detectors. Moreover, these dendrimer composite detectors showed much lower responses to nonbasic organic vapors such as ethanol or water vapor. Thus, these vapor detectors have potential for practical breath testing in a saturated water vapor environment. Variation in the type of dendrimer and/or the composition and concentration of the acid dopant produced arrays of detectors that classified amine vapors while preserving the enhanced sensitivity of the dendrimeric composites toward this class of analytes. In addition to differentiating between individual analytes, arrays of compositionally different dendrimer-carbon black detectors allowed classification of analytes into the categories of primary amines, branched amines, anilines, and non-amine-based organic vapors. Finally, unprotonated dendrimer-carbon black composites provided relatively sensitive detectors for volatile carboxylic acids, indicating that the dendrimer unit is a versatile and attractive material for use in chemiresistive carbon black composite vapor detectors.

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Supporting Information Available: Additional table (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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