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Inkjet-Printed Paper-Based Colorimetric Sensor Array for the Discrimination of Volatile Primary Amines

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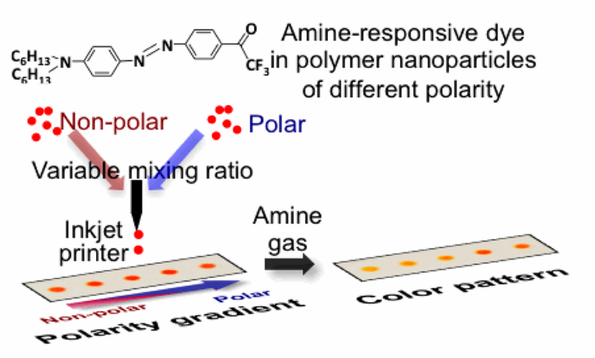
S *Supporting Information*



ABSTRACT: This paper describes a colorimetric sensor array for the discrimination of volatile amines. Analyte discrimination is achieved by combining two functional elements: (1) a "chemical class-selective" single chromogenic sensing dye with selectivity for amines in general, encapsulated into (2) polymer nanoparticles with different polarities. The resulting array has the ability to distinguish one closely related amine from another, relying on a polarity-based approach. In order to achieve reproducible, cost efficient, and flexible sensor array fabrication with the potential for mass production, inkjet-printing technology combined with standard copy paper as a sensor substrate is applied. Printing of 6 types of inks, which are prepared by mixing two dye encapsulating nanoparticles of different polarity in different mixture ratios, results in a colorimetric sensor array with a polarity gradient. Seven primary amines with increasing alkyl chain lengths have been selected to demonstrate the performance of the sensor array. The RGB color differences (ΔR, ΔG, ΔB) of the sensor array spots before and after gas exposure were analyzed by principal component analysis (PCA) and agglomerative hierarchical clustering (AHC) analysis. Under the selected measurement conditions, results of PCA and AHC analysis indicated high discrimination ability with high reproducibility of the sensor array down to amine concentrations of 50 ppm. The discrimination ability was maintained at relative humidities between 10% and 80%. Furthermore, the sensor array showed no significant response to common volatile organic compounds, confirming the high selectivity toward amines. This is, to the best of our knowledge, the first report of a colorimetric sensor array with selectivity for a specific chemical class of analytes and the ability to discriminate compounds of the same class, which is obtained by simply mixing two types of single dye-encapsulating polymer nanoparticles.

Gas sensor arrays operating according to the "electronic nose concept", which in analogy to human olfaction rely on cross-responsive rather than highly selective sensors, have gained significant attention.[1] While gas chromatography coupled with mass spectrometry allows the identification and single component quantification of analytes at even low concentrations in complex mixtures, the desire to obtain analytical results on site and in realtime is, in many cases, better satisfied with simpler, mobile devices. In food and beverage analysis targeting quality control of raw materials and processed products, it is of high interest to have analytical tools that allow for the easy and rapid identification of samples being "different" from a reference sample. Similar requirements apply for the detection of adulteration. These are typical tasks well suited for the application of electronic noses that are able to detect differences in the form of changing response patterns of single sensors in the array. A very simple and low-cost type of electronic nose is the colorimetric sensor array originally developed by Suslick and co-workers.[1,2] The basic system consists of a variety of colorimetric indicators (e.g., pH indicators, solvatochromic dyes, metalloporphyrin derivatives, etc.), all of which being cross-reactive to a number of chemical compounds, spotted on a hydrophobic substrate. Exposure to gaseous analytes results in a sample-specific color change pattern. Several research groups have reported on variations of this concept. Examples include a fluorescent sensor array based on transition-metal complexes,[3] a paper-based colorimetric sensor array using polydiacetylene derivatives,[4,5] and a colorimetric probe array based on push–pull chromophores containing receptor sites for nerve agents,[6] among others. All of these sensor arrays respond to analytes in a non- or semiselective way, resulting in universal analyte discrimination.

In addition to simple pattern recognition, many reports focus on the attempt to achieve enhanced selectivity by using absorbing or fluorescent dyes embedded or covalently linked to functional materials, such as mesoporous silica,[7,8] polymers,[9] or zeolites.[10,11] These composite materials respond to specific analytes or are able to discriminate similar analytes due to their unique structure. Tian et al. have reported a fluorescent sensor

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array fabricated from several porous polymer substrates immersed in a solution of a solvatochromic fluorescent dye.[12] This work is an example of a universal method to identify VOCs with a sensor array fabricated from only one single type of fluorescent dye. Analyte discrimination is due to the different polarities of the polymer substrates and the solvatochromic properties of the dye.

Here, we present a colorimetric sensor array for the discrimination of a specific chemical class of analytes. Focus has been set on volatile amines, which are, for example, present as bacterial metabolic byproducts in a variety of food samples.[13] In contrast to the universal analyte discrimination mentioned above, discrimination of analytes is achieved by combining two functional elements: (1) a "class-selective" chromogenic sensing dye with selectivity for amines in general and (2) polymer nanoparticles with different polarities. A derivative of the amine-responsive azo dye ETH^T 4001 has been selected as the chromogenic sensing element.[14−18] The ability to distinguish one closely related amine from another is achieved by a sensor array with further discrimination, relying on a polarity-based approach.

In order to achieve reproducible, cost-efficient, and flexible sensor array fabrication with the potential for mass production, inkjet-printing technology combined with standard copy paper as sensor substrate is applied. The single amine-selective dye is encapsulated into two types of polymer nanoparticles with different polarity. Printing of inks prepared by mixing the dye incorporating nanoparticles in different mixture ratios is a straightforward approach to colorimetric sensor arrays with a polarity gradient. This is, to the best of our knowledge, the first report of a colorimetric sensor array with selectivity for a specific chemical class of analytes and the ability to discriminate compounds of the same class, which is obtained by simply mixing two types of single dye-encapsulating polymer nanoparticles.

■ EXPERIMENTAL SECTION

Reagents and Instruments. All reagents and solvents used in the preparation of the polymer particles and the synthesis of the amine responsive dye were purchased from commercial suppliers (Wako Pure Chemical Industries, Sigma-Aldrich, Junsei Chemical, Kanto Chemical, and Tokyo Chemical Industry). Monomers used for particle fabrication were purified by passing through a layer of aluminum oxide, while all other reagents were used as received. The synthesis of the amine responsive azo dye (modification of chromoreactant ETH^T 4001[14]) is described in Scheme S1 of the Supporting Information. Its response to amines has been confirmed in solution (Figure S1 of the Supporting Information). The synthesis of the solvatofluorchromic dye KSD-3 has been reported in the literature.[19] The preparation of the polymer nanoparticles is described in the Supporting Information. Encapsulation of the amine responsive dye or the solvatofluorchromic dye into the particles was achieved, according to a previously published method,[20] which is shortly summarized in the Supporting Information.

NMR spectra were recorded on a JEOL-ECA-500 MHz NMR spectrometer (JEOL, Tokyo, Japan) at room temperature. ESI-MS were recorded on a Xevo G2 QTof series mass spectrometer (Waters Corp., Milford, MA). Absorption spectra were measured on a U-2001 double beam spectrophotometer, while fluorescence emission spectra were recorded with a F-4500 instrument (Hitachi, Tokyo, Japan). FE-SEM analysis was performed on an S-4700 microscope (Hitachi High-Technologies, Tokyo, Japan), and the average particle diameter was determined by dynamic light scattering (DLS) on an ELS-8000 instrument (Otsuka Electronics, Osaka, Japan). A DMP-2831 material printer with 10 pL printing cartridges (Fujifilm-Dimatix, Santa Clara, CA) was used for inkjet printing of all materials. A CanoScan 5600F color scanner (Canon, Tokyo, Japan) was used to record images of the sensing array. Recorded images were converted into digital color data by the ImageJ software (NIH, Bethesda, MD) and color difference patterns were created using Microsoft PowerPoint. Principal component analysis and agglomerative hierarchical clustering were performed using the Microsoft Excel extension XLSTAT.

Fabrication of Inkjet-Printed Sensor Arrays. Sensor arrays were fabricated by printing six types of sensing inks (Table S2 of the Supporting Information), which consist of mixtures of dye-encapsulating hydrophobic (pBzMA) and hydrophilic [p(DEGMMA-co-MMA)] polymer nanoparticles in different mixing ratios (100:0, 80:20, 60:40, 40:60, 20:80, and 0:100), on A4 size sheets of copy paper using the inkjet printer. Inks were filtered through a 0.22 μm syringe filter (Millex-GS, Merk Millipore, Billerica, MA) prior to use. Arrays were printed as six spots of 1 mm diameter with 1 mm spacing in a total of 20 printing runs. The drop spacing was set to 20 μm. The prepared arrays were dried for 2 days under vacuum.

Sample Measurements. A schematic image of sample preparation and the measurement system using a gas flow setup is shown in Figure S2 of the Supporting Information. Amine vapors of seven primary amines (*n*-methylamine, *n*-ethylamine, *n*-propylamine, *n*-butylamine, *n*-pentylamine, *n*-hexylamine, and *n*-heptylamine) were generated by passing pure argon at 2 L/min through a bubbler with water and a sealed container with a liquid amine sample, which was heated by a heat gun. The generated gas was collected in a gas-sampling bag. The amount of water was adjusted to generate samples with different relative humidity. The volume of liquid amine was calculated to prepare samples with various concentrations. In addition, samples of 7 common VOCs (methanol, ethanol, toluene, acetone, ethyl acetate, chloroform, and hexane) were generated, according to the same procedure.

For measurements, a printed sensor array was placed in a chamber connected to the gas-sampling bag and a pump. The gas flow rate in the system was set to 200 mL/min. The temperature around the measurement chamber was kept at room temperature (25 ± 2 °C) for 20 min at normal atmospheric pressure. By using the scanner (brightness 20, contrast 50), images of the paper sensor array in the chamber were taken before and after amine exposure. All measurements were performed in triplicate.

Image Conversion and Data Processing. The RGB color-coordinate system was applied to transform the scanned images (JPEG) of the sensor array before and after amine exposure into numerical color values. The software allows the averaging of color values over a freely selectable area using a 256-bit color scale with white corresponding to a color intensity of 255, 255, 255 and black corresponding to a color intensity of 0, 0, 0. Color difference patterns were obtained by calculating the difference of the red, green, and blue (RGB) values at the center of every printed spot before and after exposure to sample gas. For improved visualization, the observed RGB color differences were expanded to the full 0−255 range. Principal component analysis (PCA) was used as the multivariate statistical analysis. To examine the multivariate distances between the analyte responses in this 18-dimensional RGB color space, agglomerative hierarchical clustering (AHC) was performed.

■ RESULTS AND DISCUSSION

Characterization of Polymer Nanoparticles. To fabricate a sensor array for discrimination of analytes based on different polarities, particles made from pBzMA as the more hydrophobic component (benzyl group) and p(DEGMMA-co-MMA) as the more hydrophilic component (diethylene glycol group) were chosen.

The characterization of the prepared polymer nanoparticles is summarized in Table S1 of the Supporting Information. The polarities of pBzMA and p(DEGMMA-co-MMA) were estimated by measuring the fluorescence spectra of the particles with an encapsulated solvatofluorchromic dye (KSD-3) (Figure S3 of the Supporting Information). The correlation between the known $E_T(30)$ values[21] (known as a reliable and widely used scale of solvent polarity) of different organic solvents and the fluorescence maxima of KSD-3 in each solvent was applied to estimate the $E_T(30)$ values of the pBzMA and p(DEGMMA-co-MMA) particles as 34.3 and 38.0 kcal/mol, respectively. From these results, the synthesis of two kinds of polymer nanoparticles with different polarities was confirmed. In addition, the measured hydrodynamic particle diameters of 64 nm (pBzMA) and 45 nm [p(DEGMMA-co-MMA)] were sufficiently small to allow their deposition by inkjet printing.

Fabrication of Inkjet-Printed Sensor Arrays. Colorimetric sensor arrays were prepared by depositing the 6 types of sensing inks containing mixtures of pBzMA and p(DEGMMA-co-MMA) in 6 different mixing ratios (Table S2 of the Supporting Information) onto untreated copy paper by inkjet printing, as schematically shown in Figure 1. All of the particles have the amine responsive dye encapsulated. In order to keep the sensor array size reasonably small and the use of sensing reagents as low as possible, a spot diameter of 1 mm with a spacing of 1 mm between spots was selected. This size is sufficiently large to allow for the readout of colorimetric data from the images obtained by color scanning. Printed sensing arrays were dried under vacuum for two days to remove the ethylene glycol added as an additive to improve printability and then stored in desiccators until use. SEM images taken after sensing ink deposition clearly showed the presence of the polymer particles at high density on the surface of the paper substrate (Figure S4 of the Supporting Information). The dried and ready-to-use sensor arrays showed a uniform red color of all sensing spots before exposure to any gaseous analytes (Figure 2).

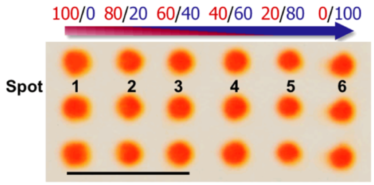

Figure 1. Color scan of a triplicate sensor array (black scale bar indicates a length of 5 mm): the numbers on top of the figure indicate the mixing ratio of the two types of polymer particles [red: lower polarity pBzMA and blue: higher polarity p(DEGMMA-co-MMA)]. The overall polarity of the spots is increasing from left to right.

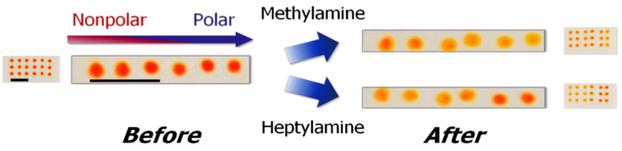

Figure 2. Color- scanned images of sensor arrays before and after exposure to 500 ppm of analyte gas at 50% relative humidity. The images show sets of triplicate sensor arrays used in a single experiment together with an enlarged single sensor array (black scale bars indicate a length of 5 mm).

Colorimetric Discrimination of Primary Aliphatic Amines. The purpose of the present work was to demonstrate the ability of a colorimetric sensor array, obtained by simply mixing two types of dye-encapsulating polymer nanoparticles arrayed by inkjet printing, to selectively recognize and to discriminate gaseous analytes according to their polarities. Primary amines with different alkyl chain lengths have been used as test analytes to characterize the performance of the sensor array.

The use of mixtures of individual polymer particles in contrast to polymer films has several advantages: first, nanoparticles can be deposited by inkjet printing in the form of aqueous emulsion inks, while solvent casting requires the use of an organic solvent. Although inkjet deposition of polymers dissolved in organic solvents is possible, it is not a desirable approach to sensor mass fabrication, since the use of volatile organic compounds (VOCs) could not be prevented. Second, polymers of different polarities cannot be mixed in all possible ratios. It has been reported that film casting could result in polymer demixing and the formation of inhomogeneously distributed separate domains of the different polymer materials.[22]

Upon exposure to primary amines (log P data is shown in Table S3 of the Supporting Information) for 20 min, the six spots of the sensor array showed various degrees of color changes clearly observable by the naked eye. Shorter exposure times of 2 or 10 min have been evaluated (data not shown), but visibly observed color changes were faint. Examples of scanned images of sensor arrays before and after 20 min exposure to analyte gases (raw data) are shown in Figure 2 for the cases of *n*-methylamine and *n*-heptylamine, which represent the lowest and highest polarities of aliphatic amines evaluated. The more polar spots in the sensor array (spots on the right side of the array with a high content of the more hydrophilic copolymer) showed a color change toward yellow upon exposure to polar *n*-methylamine. On the other hand, the more nonpolar spots in the array turned yellow upon the exposure to nonpolar *n*-heptylamine. It is noted here that the amine-responsive azo dye shows a color response (change to yellow color; blue-shift in the absorption spectrum) toward primary amines caused by the weakened π-electron acceptor capacity upon conversion of the trifluoroacetyl group into a hemiaminal.[14] The colorimetric response of the indicator dye is independent of the polarity of the sample gas. Therefore, the observed response behavior of the sensor array demonstrates the possibility for polarity-based analyte discrimination achieved by simple gradient mixing of two types of polymeric particles.

For improved visualization of the color changes, expanded RGB color difference patterns were used, similar to the approach previously described by Suslick and co-workers.[1,2] The color difference patterns obtained as a result of exposing the sensor array to seven primary amines of different polarities are shown in Figure 3. An intense color indicates a strong response toward the respective analyte. As expected based on the sensor array design, the nonpolar spots of the pattern indicated a strong response during the exposure to primary amines with long alkyl chains, such as *n*-heptylamine, *n*-hexylamine, *n*-pentylamine, and *n*-butylamine. In contrast, with higher polarity of the analyte gas, the response of the nonpolar spots decreased, and the polar spots showed an increased signal. All sensing spots responded during the exposure to *n*-propylamine, while the most polar spots responded stronger upon exposure to the most polar samples, *n*-ethylamine and *n*-methylamine. As already mentioned above, these results strongly suggest that the sensor responded differently toward primary amines, depending on their polarity.

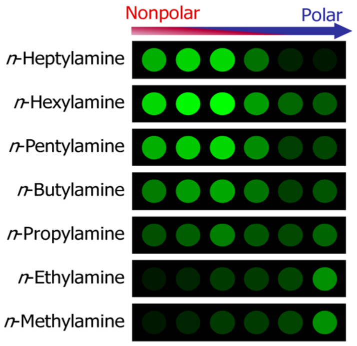

Figure 3. Color difference patterns of sensor arrays after exposure to various amine gases. The color differences as RGB values were expanded to the full 0−255 range (analyte concentration of 500 ppm, 50% relative humidity, and sensing spots according to Figure 1).

Figure 4 shows the total color change (expressed as the Euclidean distance between the two colors measured in the three-dimensional RGB color space before and after gas exposure) for each sensor spot in the array in dependence of the amine analyte. The standard deviation as depicted by the error bars calculated from triplicate experiments was very small. Since every array is used only once, this indicates not only high measurement reproducibility but also high fabrication reproducibility of the sensor arrays obtained by inkjet-printing because triplicate data points are obtained with three independently printed sensor arrays.

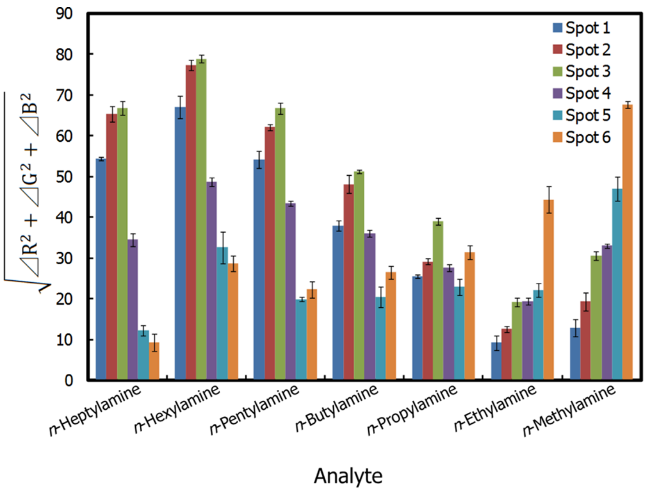

Figure 4. Total color differences observed after exposure to 500 ppm of analyte at 50% relative humidity (error bars represent standard deviations of triplicate measurements). For the composition of sensing spots, refer to Figure 1.

To demonstrate the classification ability of this simple sensor array, further statistical analysis was performed on the pattern response data. First, principal component analysis (PCA) was applied to the set of 378 colorimetric data values (7 primary amines × 3 experimental repeats × 6 sensor spots × 3 values of RGB). The PC score plot showed that the first, second, and third components (F1, F2, and F3) accounted for 57.21%, 15.17%, and 14.17% of the data variance, respectively (Figure 5). Within this PCA plot, clusters corresponding to different primary amines were well-separated, indicating the high discrimination ability of the sensor array.

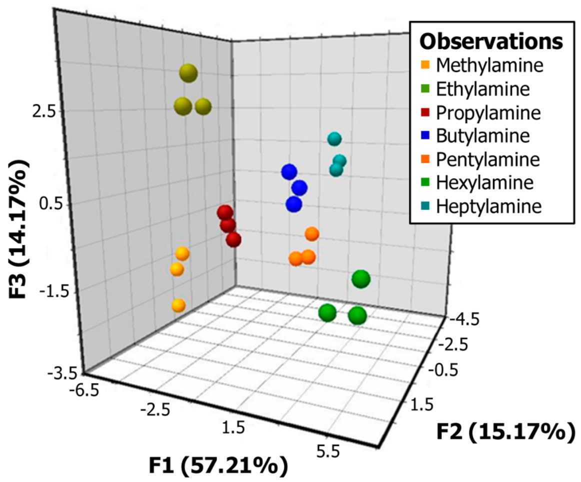

Figure 5. Principle component analysis (PCA) plot for sensor arrays exposed to 500 ppm of analyte at 50% relative humidity (all experiments have been performed in triplicate with separate sensing arrays).

Because of the high dimensionality of the data, agglomerative hierarchical clustering (AHC) analysis was applied in addition to PCA to obtain more quantitative information regarding the differences and similarities of the response patterns (Figure 6). All amines were clearly discriminated from each other, and “families” indicated similarities in terms of alkyl chain length.

In both PCA and AHC analysis, data points obtained in triplicate measurements were in close proximity to each other. Since all sensors are applied in a single-use mode, these results are a good indicator for the high reproducibility of the sensor fabrication method based on the inkjet printing technology.

All discrimination experiments have been performed at 6 different amine gas concentrations (5, 10, 50, 100, 250, and 500 ppm). The sensor array indicated similar discrimination abilities for amine gas concentrations down to 50 ppm. The color difference patterns, total color changes, PCA plots, and AHC dendrograms obtained at 50, 100, and 250 ppm of amines are shown in Figures S5 (panels a−d), S6 (panels a−d), S7 (panels a−d) and S8 (panels a−d) of the Supporting Information. At 10 ppm, the sensor array responded weakly to amines except for *n*-butylamine and *n*-propylamine (Figure S6e of the Supporting Information) but failed in discrimination of the analytes (data not shown). At 5 ppm, all amines lead to only insignificantly weak sensor signals (Figure S6f of the Supporting Information). Therefore, it can be concluded that

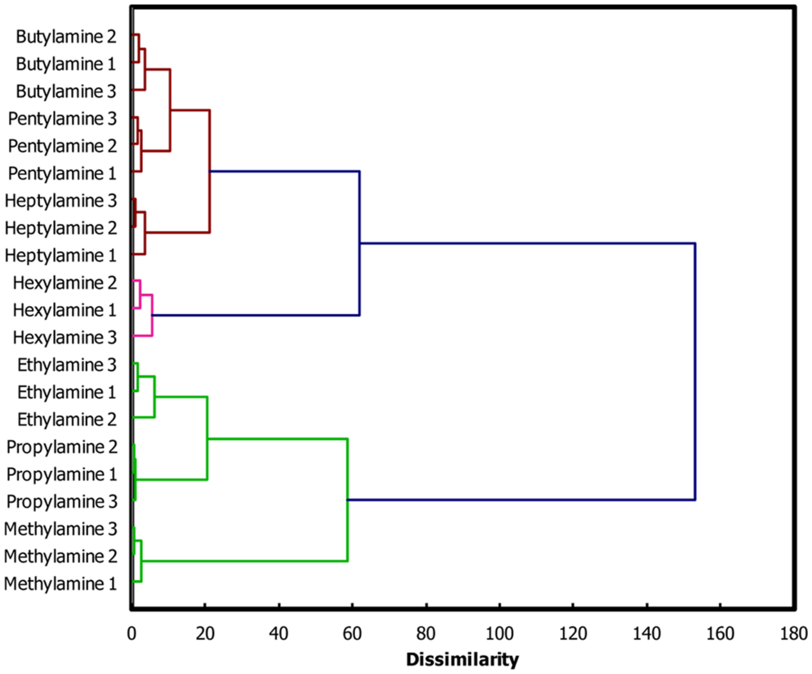

Figure 6. Agglomerative hierarchical clustering (AHC) dendrogram for sensor arrays exposed to 500 ppm of analyte at 50% relative humidity (all experiments have been performed in triplicate with separate sensing arrays).

under the selected measurement conditions, discrimination of amines at concentrations above 50 ppm is achieved.

Selectivity Behavior: Influence of Humidity and VOCs. The used amine selective dye is known to be humidity and alcohol responsive but only in the presence of a catalyst, which is not applied in the present approach.[14,16] In the absence of the catalyst, response times for alcohols and humidity have been reported to be in the order of hours.[16] In order to evaluate the influence of water vapor, the sensor array was exposed to primary amines of 500 ppm concentration at different relative humidities (10, 30, 50, 80 % RH). Although the actual colorimetric pattern changes are slightly different depending on the relative humidity (Figure 3 and Figure S5e-g of the Supporting Information), the sensor array maintained its discrimination ability toward the 7 primary amines under all humidity conditions [Figures S7 (panels e−g) and S8 (panels e−g) of the Supporting Information).

In addition, the chemical class selectivity of the sensor array for amines was confirmed by exposure to seven common volatile organic compounds (VOCs) at a concentration of 1000 ppm and to argon gas of a different relative humidity. By comparing the total color changes recorded upon exposure to the VOCs with the ones obtained in the presence of pure argon at different relative humidity (Figure S6j of the Supporting Information), no significant differences were observed. The signal obtained for 100 ppm of *n*-heptylamine is shown for comparison purposes.

■ CONCLUSION

A simple and low-cost colorimetric sensor array for the discrimination of gaseous amines has been realized. Analyte discrimination was achieved by combining two functional elements: (1) a "class-selective" chromogenic sensing dye with selectivity for amines in general, encapsulated into (2) polymer nanoparticles with different polarities. It has been demonstrated that sensor arrays obtained by simply varying the mixing ratio of polymer nanoparticles with two different polarities allow a reliable polarity-based discrimination of closely related primary aliphatic amines. It has been confirmed that the sensor arrays exhibit (1) visually recognizable sample gas polarity-dependent colorimetric response, (2) high sample discrimination ability, and (3) high fabrication reproducibility. The latter was achieved by selecting inkjet printing as the method to deposit the sensing reagent encapsulating nanoparticles.

It is expected that this very simple approach to colorimetric sensing arrays based on combining a single chromogenic reagent with mixtures of functional nanoparticles can be adapted to become applicable to a variety of sensing systems. While in the present "proof-of-concept", the polarity of the analyte was used to discriminate between compounds of the same chemical functionality (e.g., amines); other systems could include combinations of mesoporous silica particles with different pore diameters for size-selective discrimination or surface molecularly imprinted particles, to name just two examples. On the other hand, the amine selective compound used in the present work could be replaced by a colorimetric reagent with selectivity for a different chemical functional group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis of the amine responsive dye, spectral characterization of the synthesized compound, preparation and characterization of polymer particles and printing inks, measurement system setup, additional experimental results as indicated in the text, raw data of colorimetric signal changes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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