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PAPER

Polydiacetylene paper-based colorimetric sensor array for vapor phase detection and identification of volatile organic compounds†

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Detection and identification of VOCs in their vapor phase is essential for safety and quality assessment. In this work, a novel platform of a paper-based polydiacetylene (PDA) colorimetric sensor array is prepared from eight diacetylene monomers, six of which are amphiphilic and the other two are bolaamphiphilic. To fabricate the sensors, monomers are coated onto a filter paper surface using the drop-casting technique and converted to PDAs by UV irradiation. The PDA sensors show solvent induced irreversible color transition upon exposure to VOC vapors. When combined into a sensing array, the color change pattern as measured by RGB values and statistically analyzed by principal component analysis (PCA) is capable of distinguishing 18 distinct VOCs in the vapor phase. The PCA score and loading plots also allow the reduction of the sensing elements in the array from eight to three PDAs that are capable of classifying 18 VOCs. Utilizing an array containing only two PDAs, various types of automotive fuels including gasoline, gasohol and diesel are successfully classified.

Introduction

During the last decade, monitoring of volatile organic compounds (VOCs) has gained enormous interest due to environmental and public safety concerns posed by exposure to these substances. Therefore, many researchers have been focusing on the development of VOC sensors.[1–4] Changes of electrochemical properties,[5–9] fluorescence[10–15] and color[16–20] of those sensing materials after exposure to VOCs provide signals for the detection and identification of the analytes. Among output signals, the colorimetric mode is considered as the most convenient sensing platform for developing a simple naked-eye VOC detector because it minimizes the need for extensive signal transduction hardware. Such an advantage will lead to practical on-site analysis that can be delivered to non-technicians or end-users. Reported colorimetric sensing materials for VOC sensors include small organic compounds,[21–24] metal complexes[25–30] and conjugated polymers.[31–36] Among these sensing materials, polydiacetylenes (PDAs) are one of the most promising due to their unique chromism properties. PDAs are a class of conjugated polymers which can undergo distinct color changes from blue to red under various external stimuli such as heat (thermochromism),[37–42] mechanical stress (mechanochromism),[43,44] ligand–receptor interactions (affinochromism)[45–51] and solvents (solvatochromism)[33,52–54] that make them invaluable transducers for many optical sensing systems.[55–59] The latter property has recently drawn attention for the development of PDAs in sensors for VOCs. Those reports share the same strategy in the preparation of a PDA library embedded in a polymer matrix in various forms such as polyethyleneoxide or polystyrene electrospun fibers as well as polydimethylsiloxane or poly(4-vinylpyridine) spin-coating films.[31–36] Moreover, PDAs have also been incorporated into arrays generating color change patterns to each VOC analyte leading to the detection and qualitative recognition of VOCs. The sensing systems reported so far have been tested successfully only with the liquid form of VOCs but not their vapor phase. Some of these fabrication techniques are rather time-consuming and require complicated instrument set up. Furthermore, all the VOC discrimination was based only on the visual observation of the color change without any statistical analysis. Therefore, there remains a great challenge to improve the fabrication and analysis method of these PDA sensing systems. More diacetylene monomers should also be investigated for an optimal array, which can efficiently detect and identify the vapor of VOCs.

As a continuation of our previous works on PDA sensors,[60–62] we would like to report herein the preparation of a VOC sensor array from eight PDAs coated on filter paper. Filter paper is selected as a sensing platform due to its many advantageous

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† Electronic Supplementary Information (ESI) available: characterization data of compounds **3–8**; PCA loading plot; PCA score plot; color change profile. See DOI: 10.1039/c2jm16273c

features *i.e.* (i) it is widely available, easy to use, store and transport; (ii) it is thin and lightweight; (iii) it is biodegradable and biocompatible; (iv) its white surface provides strong contrast with colored substrates, making it a good medium for colorimetric tests. The fabrication technique is fast and scalable giving a stable and sensitive paper based sensor array, which can be used for the detection and identification of 18 different VOC vapors using a statistical pattern recognition method. Numerical data of colorimetric responses to VOCs were conveniently obtained from a flatbed scanner and an image processing program. Principal component analysis (PCA) was used for the multivariate statistical analysis. This paper based PDA sensor array and the analysis method can also be applied successfully to distinguish vapors of various automotive fuels such as gasoline, gasohol and diesel.

Results and discussion

Synthesis of diacetylene monomers 1–8

In this work, eight diacetylene monomers (DA) such as amphiphilic (**1–6**) and bolaamphiphilic (**7–8**) compounds were utilized as precursors for preparation of PDA sensing elements in the paper based array sensor for VOCs (Fig. 1). The monomers **1** (PCDA) and **2** (TCDA) are well known and commercially available while the others were prepared according to reported procedures. Briefly, diacetylene lipid **3** was synthesized through the Cadiot–Chodkiewicz coupling reaction between the corresponding alkynoic acid with terminal alkyne in the presence of copper iodide.[38] Diacetylene monomers **4** and **5** were prepared from the condensation reaction between PCDA (**1**) with appropriate diamines.[63] The addition of HBr to secondary amine **5** gave ammonium salt **6** in reasonable yield.[63] Finally, bolaamphiphilic monomers **7** and **8** were synthesized from a copper catalyzed Glasser homocoupling reaction between the corresponding terminal alkynoic acids.[64,65] Detail synthetic procedures and characterization data of compounds **3–8** are available in the ESI.†

Preparation of PDA coated paper

With the panel of diacetylene monomers (DA) in hand, we next focused on their fabrication onto filter paper sheets. The fabrication was started by dropping a solution of the DA monomer in an appropriate solvent on filter paper (Fig. 2a) and allowing it to dry in the dark at room temperature. The size of the DA dot can be easily controlled by the solution volume using an auto pipette and the desired numbers of DA dots are created simply by repeating the drop casting process at different locations on the filter paper. The resulting filter paper coated with multiple dots of the DA monomer was irradiated with UV light (254 nm, 500 μW cm^{-2}) for 1 min to produce the replicated PDA sensing dots (Fig. 2a). All DA monomers except **7** gave the typical blue color of ene-yne π-conjugated PDAs indicating good packing of the DA molecules. The color of PDA derived from **7** appeared as red, which is perhaps due to its unusual packing in the molecular self-assembly.[66] Pleasingly, the PDA prepared by this method was very stable in that their color did not change upon storage in a refrigerator over several months. It is thus important to emphasize that this preparation technique is very convenient and economical to construct a robust solid-state PDA sensor array as shown in Fig. 2b. The microscopic images obtained from an optical microscope also revealed that most of the PDA pigments are deposited on the surface of the cellulose fibers with little or no fiber penetration (Fig. 2c). This surface coating behavior is desirable for colorimetric detection because it requires less sensing material and provides better sensitivity.

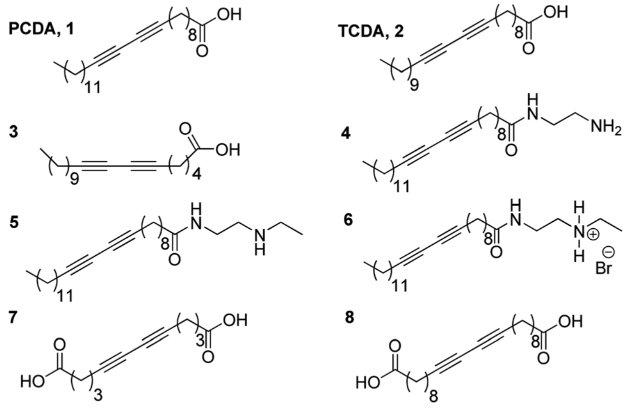

Fig. 1 Structures of diacetylene monomers (**1–8**).

Colorimetric detection of VOC vapors

Although the solvent dependent color transition of PDAs has been well-investigated in many literature works,[31–36] the sensing application of PDAs for VOCs in the vapor phase have never been reported. Therefore, the PDA coated filter papers were tested for this application by attaching them on the inner surface of a lid of a chamber saturated with a wide range of VOC vapors *i.e.* pentane, hexane, cyclohexane, toluene, *o*-xylene, benzene, diethyl ether, dichloromethane (DCM), 2-propanol,

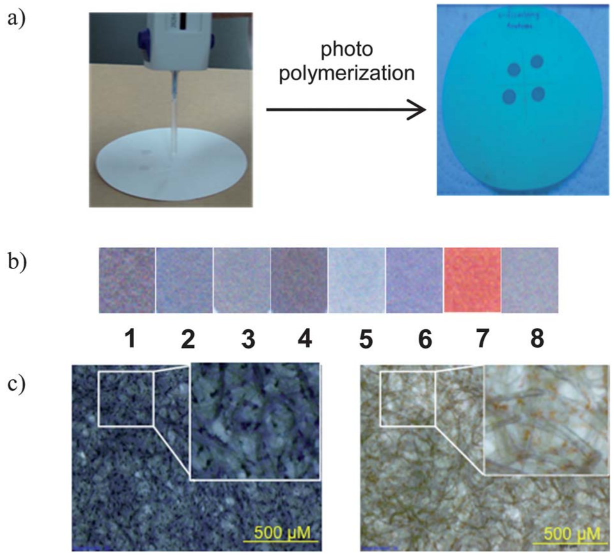

Fig. 2 (a) Preparation of paper-based PDA sensor and (b) scanned images of sensor array constructed from **1–8** exposed with UV light (1 min, 500 μW cm^{-2}). (c) Microscopic images of a paper based PDA sensor from **8** before (left) and after exposure to THF vapor (right).

tetrahydrofuran (THF), chloroform ($CHCl_3$), ethanol (EtOH), ethyl acetate (EtOAc), acetone, methanol (MeOH), acetonitrile (MeCN), dimethylformamide (DMF) and dimethylsulfoxide (DMSO). To monitor the color changes of the PDA sensor array, fa latbed scanner was chosen as the optical recorder as the images are always in focus and not affected by lighting conditions.[67,68] Upon exposure to vapors for 1 h, the PDA dots displayed various degrees of color transition as shown in Fig. 3. Due to its high solvent sensitivity, poly(PCDA) was used for mixing with less sensitive PDAs to generate solvent sensor arrays with a wide range of solvent responses.[69] However, in this work, poly(PCDA) coated paper was colorimetrically insensitive toward most VOC vapors except THF (Fig. 3, row 1). The results strongly suggested that PDAs with higher sensitivity are required for construction of an effective vapor-sensing array. Among the diacetylene monomers tested in this work, **3** gave blue PDA coated paper with the highest sensitivity, as it turned red upon the exposure to vapors of most VOCs (Fig. 3, row 3). We believe that the high sensitivity of this PDA is derived from weaker hydrophobic interaction between its shorter side chains.[38,54,60] The PDAs obtained from other monomers gave lower but variable sensitivities toward various VOC vapors that provided an array of different color patterns. These variable sensitivities of PDAs are governed by the interactions among PDA side chains. The combination of different alkyl chain lengths with various functional groups *i.e.* carboxylic, dicarboxylic, amido, amino and ammonium groups was proven to be effective for tuning the VOC sensitivity. Notably, the color transition of this PDA array is irreversible so that the color record by a flatbed scanner can be conveniently conducted after the removal of the VOCs.

Evaluation of colorimetric response patterns

To evaluate 144 colorimetric responses of 8 PDA sensors against 18 VOC vapors, we converted the scanned images (TIF format) into the RGB values (R = red, G = green and B = blue) using a conventional image-processing program. A three-dimensional vector (ΔR, ΔG, ΔB) of each PDA sensor was determined from the RGB values before and after exposure to the VOC vapors. The histogram plot of these vectors against the VOC vapors generated a color change profile of the array (Fig. 4), which illustrated distinguishable color change patterns of the VOC vapors. To highlight the discrimination efficiency of our PDA array, the responses of VOCs with similar structures and polarity are mentioned here. For example, hydrocarbon VOCs (pentane, hexane, cyclohexane, toluene, *o*-xylene and benzene) induced different response patterns on PDAs **2** and **3**. PDA **2** is also effective for discriminating between two chlorinated VOCs such as chloroform and dichloromethane. Due to their significant difference in solvating power nature, the ethereal solvents such as ether and THF are readily distinguished by several PDAs including **1**, **5**, **6** and **8**. For solvents containing carbonyl groups such as ethyl acetate, acetone and DMF, PDA **8** seemed to be the most efficient sensing element for differentiating these VOCs. For vapors of alcohols such as 2-propanol, ethanol and methanol, PDAs **2** and **6** gave diverse responses. Notably, the quantitative color change profile (Fig. 4) is in good agreement with the photographic images (Fig. 3). Importantly, the standard deviation as depicted by the error bars in Fig. 4, calculated from 12 measurements (4 dots of PDA × 3 scans), was very small which demonstrates the high precision of this method of measurement. We attribute the high reproducibility of this method to the fact that the PDA sensing spots are not in direct contact with the liquid solvents, which can cause PDA detachment from the paper surface.

Since the colorimetric response patterns were based on 24 dimensions (8 polymers × 3 values of RGB), effective pattern recognition and comparison require a statistical multivariate analysis. In this work, we utilize principal component analysis (PCA), a non-supervised method, to generate coordinates (PC scores) recognizable within the lowest dimension represented by the principal component (PCs) from the set of 5184 colorimetric

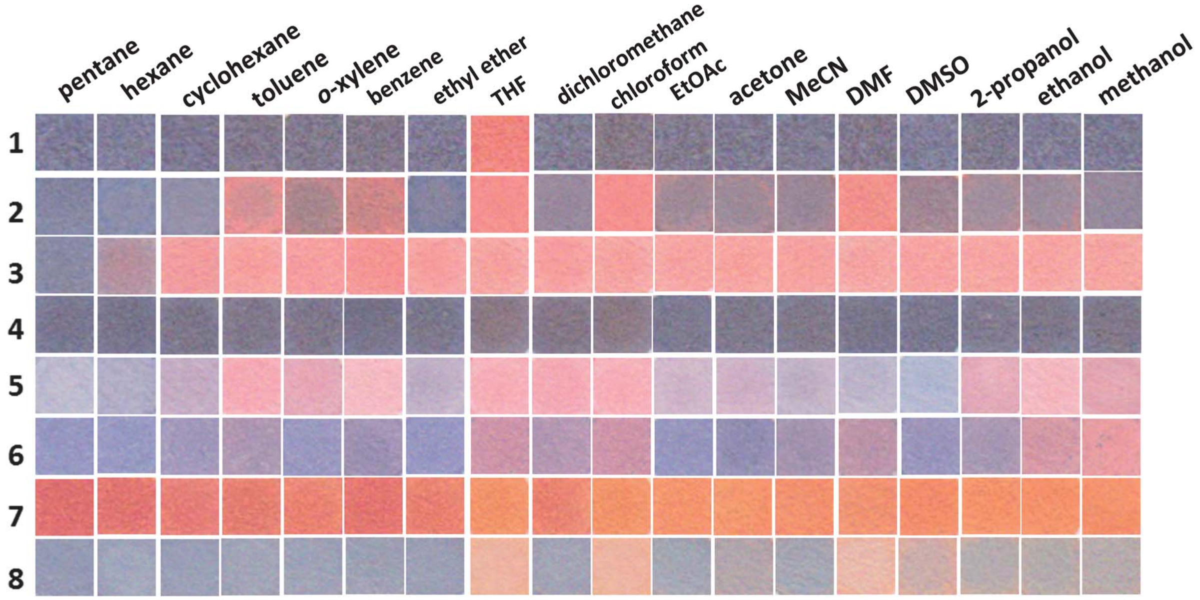

Fig. 3 Scanned images of the paper-based PDA sensor array prepared from **1–8** exposed to various saturated vapors of volatile organic solvents.

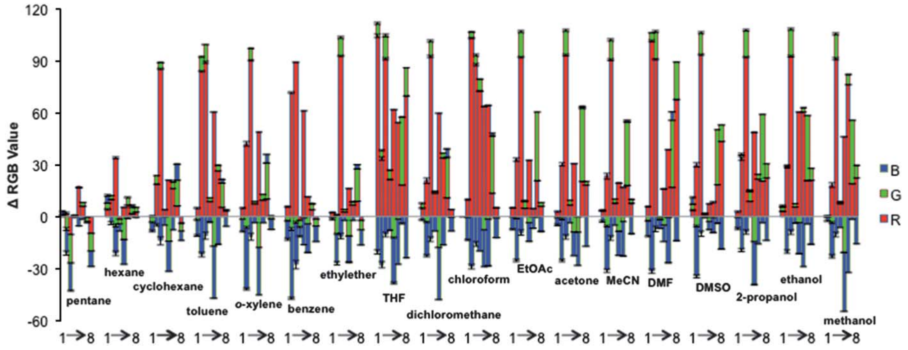

Fig. 4 RGB color change profile of a paper-based PDA sensor array prepared from **1–8** after exposure to saturated vapors of VOCs.

data set (18 VOCs × 12 repeats × 8 polymers × 3 values of RGB). The PC score plot showed that the first and second components (PC1 and PC2) accounted for 47.33% and 14.62% of the data variance, respectively (Fig. 5). Within this 2D plot, 18 discrete clusters corresponding to all VOCs tested were clearly observed. The results indicated high discriminating ability of this paper based PDA sensor array. To evaluate the classification accuracy, factorial discriminant analysis (FDA), a supervised method, was applied on the PC scores to cross validate the discriminating ability using a leave-one-out technique.[70] The FDA cross validation gave 100% classification accuracy confirming the high efficiency of this sensor array.

For a sensor array, if the numbers of sensing elements can be reduced without deterioration of the discriminating performance, its application will be more user friendly. In order to reduce the redundant and negative sensing elements in the studied array, the plots of loading factors associated with PC1 and PC2 for each individual PDA sensor were evaluated (see ESI† Fig. S19). The plots showed that sensors **2**, **3** and **8** had higher influence in the PC scores than sensors **1**, **4**, **5**, **6** and **7** of which the loading factors appear close to the origin point. Therefore, three PC score plots of the data from each pair of sensing elements selected from sensors **2**, **3** and **8** were generated. Again, FDA was used to cross validate the classification accuracy of the PCA score plots. Interestingly, both **2/8** and **3/8** sensor pairs provided the classification accuracy of 100% while the **2/3** sensor pair gave a lower accuracy of 88% (see ESI† Fig. S20–22). These outcomes imply that the combination of the sensors from amphiphilic (**2** or **3**) and bolaamphiphilic monomers (**8**) provides greater sensitivity variance toward the VOCs compared with the sensor pair from only amphiphilic monomers (**2/3** pair). The high sensitivity variance in turn benefits the discriminating efficiency of the sensor array.

Application in classification of automotive fuels

Due to the current price hike of petroleum fuels, several bio-fuels such as ethanol and fatty acid esters have been added to create

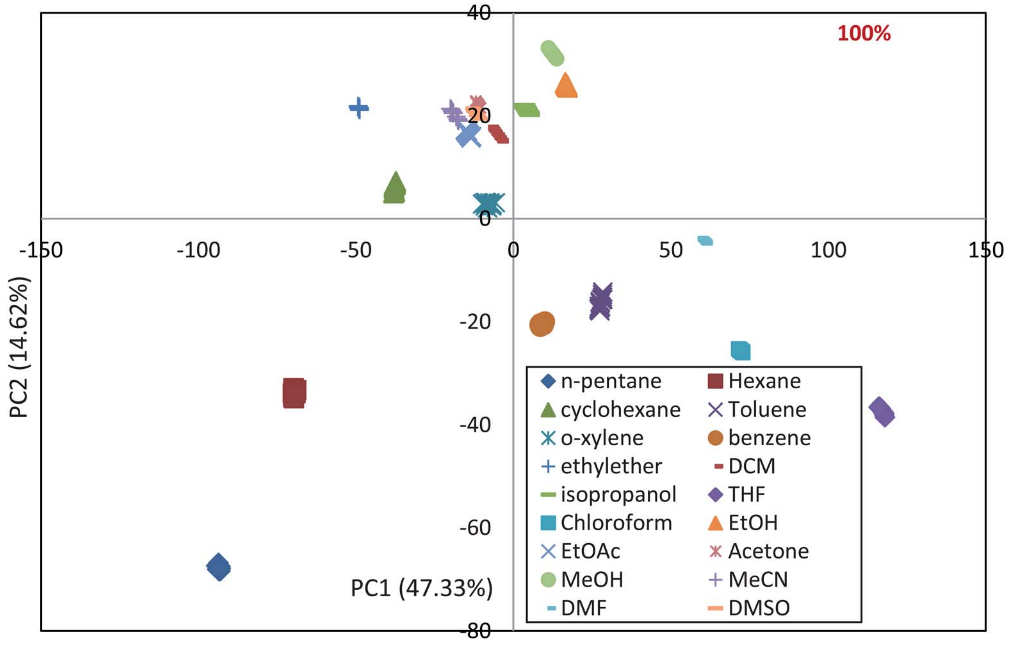

Fig. 5 PCA score plot of RGB color changes obtained from the paper-based PDA sensor array upon exposure to 18 VOC vapors (8 PDAs × 4 replicates × 18 VOCs × 3 measurements).

a variety of alternative fuels. In Thailand, for example, many types of automotive fuel have been commercialized such as gasoline octane 91 (G91), 10% ethanol blended gasoline widely known as gasohol octane 91 and 95 (H91 and 95), 20% ethanol blended gasoline (E20), diesel (D) and biodiesel (B5). Authentication and identification of these fuels are of commercial and legal importance. Presently, the authentication and identification of different types of gasoline are performed by direct observation of the color generated by different additives (see the their appearance in ESI† Fig. S23). However, this easy and simple method does not prevent misuse and intentionally fake gasoline because the color of the additive does not reflect the chemical component within the fuel. Therefore, there remains a need for an inexpensive on-site method for automotive fuel testing. Along this line, we extended the scope of our paper based PDA sensor array to identify these commercial automotive fuels.

Having identified that PDAs **2**, **3** and **8** are the most informative sensing elements for the identification of VOC vapors, ten automotive fuel samples (G91, H91, H95, E20, D and B5) from two leading oil companies in Thailand (A and B) were tested with selected PDA sensors by the same procedure as those performed with the solvent vapors described above. Clearly, the PDA from **2** showed blue to red color transition upon the exposure to vapors of fuels containing ethanol (H95(A), H95(B), H91(A), H91(B) and E20) and the PDA from **3** gave the response to both gasohol and gasoline while the PDA from **8** was insensitive to all type of fuels (Fig. 6(top)). None of these PDAs showed any colorimetric response to diesel (D) and biodiesel (B5). The fuel dependent color transitions described above are the results of the difference in solvating power and vapor pressure of the fuels.

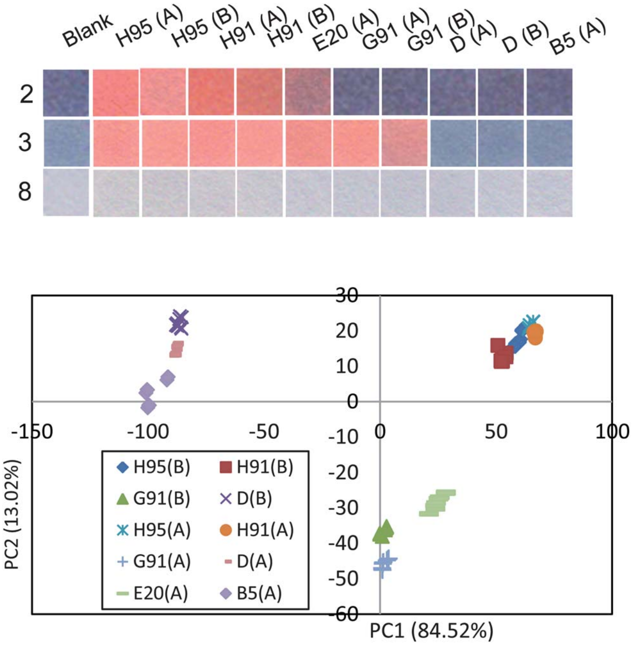

Fig. 6 (Top) Scanned images of the paper-based PDA sensor array prepared from **2**, **3** and **8** before (blank) and after exposure to 10 automotive fuel vapors. (Bottom) PCA score plot of RGB color changes obtained from the paper-based PDA sensor array derived from **2** and **3** upon exposure to automotive fuels (2 PDAs × 3 replicates × 10 automotive fuels × 3 measurements of each RGB).

From Fig. 6(top), the classification of fuels into gasohol (including E20), gasoline and diesel (including biodiesel) is possible by the color pattern of sensors **2** and **3**. To ensure the robustness of this sensor array, the reproducibility and discriminating ability were evaluated using the PCA technique. The RGB color-change values (see ESI† Fig. S24) were again converted into a PCA score plot (Fig. 6(bottom)). From the plot, a total variance of 97.54% can be obtained from the first two PCs in which PC1 and PC2 contributed 84.52% and 13.02%, respectively. The plot also showed well-separated clusters of diesel (D), biodiesel (B5), E20, gasohol (H), gasoline (G) confirming the high fuel discrimination ability of sensors **2** and **3**.

It is also important to note that all the data points in each cluster are very tight indicating a high reproducibility of this sensing platform. In fact, the data points were so reproducible that even the same type of fuels obtained from different companies could be differentiated. These dissimilarities may be attributed to different additives used by the oil companies.

Conclusions

Paper-based PDA sensors were prepared by drop casting of diacetylene monomers followed by UV photopolymerization, a very simple and economical method. An array constructed from 8 different diacetylene monomers was capable of distinguishing 18 VOCs in the vapor phase when utilized in combination with principle component analysis. In its optimal form, an array containing 3 chosen PDAs was capable of classifying 18 VOCs with high reproducibility and discriminating ability. In addition, a sensor array containing two PDAs was effective at distinguishing various types of automotive fuels. Thus, this is the first platform truly proven to be effective for detection and identification of a large numbers of VOCs in their vapor phase.

Experimental section

General information

10,12-Pentacosadiynoic acid (PCDA) and 10,12-tricosadiynoic acid (TCDA) were purchased from GFS Chemical and other reagents were obtained from Sigma-Aldrich and Fluka. All organic solvents for monomer synthesis and purification were purchased from TSL chemicals (Thailand) and were used without further purification. For VOCs tested, all solvents are high purity grade (HPLC grade). ^{1}H and ^{13}C spectra were collected on a 400 MHz NMR spectrometer (Mercury 400, Varian). Photographic images were recorded using a CanoScanner LiDE 200.

Preparation of diacetylene monomers (3–8)

6,8-Nonadecadiynoic acid (3). To a stirred solution of 6-heptynoic acid (3.0 mmol) and 1-iodo-1-dodecyne (3.6 mmol) in pyrrolidine (15.0 mmol) was added copper(I) iodide (0.05 mmol). Then the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was then added to an saturated aqueous solution of ammonium chloride (50 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed by a rotary evaporator. The crude product was purified by column chromatography with hexane and ethyl acetate (90:10) as an eluent to give 6,8-nonadecadiynoic acid (**3**) (650.00 mg, 75% yield) as a white powder: mp 57–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.31 (t, J = 7.4 Hz, 2H), 2.22 (t, J = 6.9 Hz, 2H), 2.17 (t, J = 7.1), 1.68 (m, 2H), 1.52 (m, 2H), 1.43 (m, 2H), 1.30–1.28 (m, 14H), 0.81 (t, J = 6.8 Hz, 3H); ESIMS m/z = 289.26 $[M - H]^-$ (calcd for $C_{19}H_{30}O_2$, 290.44). Anal. Found: C, 78.71; H, 10.53 (calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41).

***N*-(2-Aminoethyl)pentacosa-10,12-diynamide (4).** A solution of 1-ethyl-3-(3′-dimethylamino) carbodiimide HCl salt (EDC) (246.14 mg, 1.28 mmol) in methylene chloride (2 mL) was added dropwise into a solution of 10,12-pentacosadiynoic acid (PCDA) (400.00 mg, 1.07 mmol) in methylene chloride (5 mL). The mixture was stirred for 1 h at room temperature and was then added dropwise into a solution of *N*-hydroxysuccinimide (NHS) (147.77 mg, 1.28 mmol) in methylene chloride (2 mL) at room temperature. After the reaction mixture was stirred at room temperature overnight, water (20 mL) was added and extracted with methylene chloride (25 × 3 mL). The organic phase was dried with sodium sulfate and rotary evaporated to yield the crude product as a white powder. Then the crude product was dissolved in methylene chloride (10 mL) and added dropwise into a solution of ethylenediamine in methylene chloride (2 mL). The mixture was then kept stirring for 4 h at room temperature. The mixture was extracted with methylene chloride (25 × 3 mL) and the organic phase was dried with sodium sulfate and rotary evaporated to yield the crude product as a white powder. The crude product was purified by column chromatography on silica gel eluted with a mixture of ethyl acetate and methanol (70:30) to give *N*-(2-aminoethyl)pentacosa-10,12-diynamide (**4**, 325.00 mg, 92% yield) as a white powder: mp 111–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.87 (t, J = 6.8 Hz, 3H), 1.42 (m, 32H), 2.18 (t, J = 7.6 Hz, 2H), 2.23 (t, J = 6.8 Hz, 4H), 2.84 (t, J = 5.7 Hz, 2H), 3.31 (q, J = 5.8 Hz, 2H), 5.94 (brs, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 173.6, 77.6, 77.5, 65.3, 65.3, 41.6, 41.6, 41.3, 36.8, 31.9, 29.6, 29.6, 29.5, 29.3, 29.2, 29.2, 29.1, 28.9, 28.9, 28.7, 28.3, 25.7, 22.7, 19.2, 19.2, 14.1; ESIMS m/z = 416.50 $[M]^+$, 438.47 $[M - H + Na]^+$ and 439.34 $[M + Na]^+$.

***N*-(2-(Ethylamino)ethyl)pentacosa-10,12-diynamide (5).** *N,N′*-Dicyclohexylcarbodiimide (DCC) (264.18 mg, 1.28 mmol) in methylene chloride (4 mL) was added dropwise into a solution of 10,12-pentacosadiynoic acid (PCDA) (400.00 mg, 1.07 mmol) in methylene chloride (7 mL). The mixture was stirred at 0 °C for 1 h. *N*-Ethylethylenediamine (146 µL, 1.38 mmol) was added dropwise into the reaction mixture at room temperature. The reaction mixture was stirred at room temperature overnight. The mixture was extracted with methylene chloride (25 × 3 mL). The organic phase was dried with sodium sulfate and evaporated to yield the crude product as a white powder. The crude product was purified by column chromatography on silica gel eluted with a mixture of ethyl acetate and methanol (70:30) to give *N*-(2-(ethylamino)ethyl)pentacosa-10,12-diynamide (**5**, (417.00 mg, 88% yield) as a white powder: mp 64–66 °C;^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.86 (t, J = 6.8 Hz, 3H; CH_3), 1.09 (t, J = 7.1 Hz, 3H; CH_3), 1.33 (m, 16H, 32H; CH_2), 2.15 (t, J = 7.6 Hz, 2H: CH_2), 2.21 (t, J = 6.9 Hz, 4H; CH_2), 2.64 (q, J = 7.2 Hz, 2H; CH_2), 2.74 (t, J = 7.6 Hz, 2H; CH_2), 3.33 (q, J = 5.7 Hz, 2H; CH_2), 4.75 (brs, 1H, NH), 6.11, (brs, 1H; NH); ^{13}C NMR (400 MHz,$CDCl_3$): δ (ppm) = 173.5, 77.6, 77.5, 65.3, 65.2, 48.4, 43.7, 38.7, 31.9, 29.6, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 29.1, 29.2, 29.1, 28.9, 28.9, 28.8, 28.4, 28.3, 25.7, 22.7, 19.2. ESIMS m/z = 444.58 $[M]^+$ and 445.48 $[M + H]^+$.

***N*-Ethyl-2-pentacosa-10,12-diynamidoethanaminium bromide (6).** *N*-(2-(Ethylamino)ethyl)pentacosa-10,12-diynamide (400.00 mg, 0.90 mmol) was dissolved in chloroform and hydrobromic acid (HBr) (97.00 µL, 1.80 mmol). The mixture was stirred at room temperature for 1 h. Water (20 mL) was added and the mixture was extracted with chloroform. The organic phase was dried with sodium sulfate and rotary evaporated to yield the crude product as a white powder. The crude product was recrystallized by chloroform to give *N*-ethyl-2-pentacosa-10,12-diynamidoethanaminium bromide (**6**, 307.00 mg, 65% yield) as a white powder: mp 115–118 °C; ^{1}H NMR (400 MHz,$CDCl_3$): δ (ppm) = 0.88 (t, J = 6.8 Hz, 3H; CH_3), 1.40, (m, 32H; CH_2), 1.62 (t, J = 7.2 Hz, 3H; CH_3), 2.25 (m, H3; CH_2), 3.12 (m, 4H; CH_2), 3.68 (q, J = 4.4 Hz, 2H; CH_2), 7.65 (brs, 1H; NHC═O); ^{13}C NMR (400 MHz,$CDCl_3$): δ (ppm) = 175.5, 77.7, 77.4, 65.3, 65.2, 47.9, 43.5, 36.5, 36.3, 31.9, 29.7, 29.6, 29.7, 29.5, 29.4, 29.2, 29.2, 29.1, 28.9, 28.9, 28.9, 28.3, 28.4, 25.6, 22.7, 19.2, 19.2, 14.1, 11.3. ESIMS m/z = 444.62 $[M]^+$ and 445.50 $[M + H]^+$.

5,7-Dodecadiynedioic acid (7). A solution of 5-hexynoic acid (400 µL, 3.60 mmol) in DI water (15 mL) in a three-neck round bottom flask was bubbled with oxygen gas at room temperature. Then copper(I) chloride (1790 mg, 18.10 mmol) and ammonium chloride (1930 mg, 36.00 mmol) were successfully added. After the reaction mixture was vigorously stirred for overnight, 10 mL of 1 M hydrochloric acid cold solution was poured into the mixture and the precipitate was collected and dried under vacuum oven at room temperature to give 5,7-dodecadiynedioic acid (**7**, 393.00 mg, 98% yield) as a white powder: mp 137–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.79 (m, 4H; CH_2), 2.32 (t, J = 2.33 Hz, 4H; CH_2), 2.43 (t, J = 2.43 Hz, 4H; CH_2); ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 19.4, 25.0, 33.8, 51.7, 51.9, 67.1, 77.4, 175.5. ESIMS m/z = 220.46 $[M]^-$.

10,12-Docosadiynedioic acid (8). A solution of 10-undecynoic acid (200 mg, 1.1 mmol) in tetrahydrofuran (15 mL) in a three-neck round bottom flask was bubbled with oxygen gas at room temperature. Then copper(I) chloride (545 mg, 5.50 mmol) and ammonium chloride (590 mg, 11.00 mmol) were successfully added. After the reaction mixture was vigorously stirred overnight, 10 mL of 1 M hydrochloric acid cold solution was poured into the mixture and the precipitate was collected and dried under vacuum oven at room temperature to give 10,12-docosadiynedioic acid (**8**, 179.00 mg, 90% yield) as a white powder: mp 100–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.51 (m, 12H; CH_2), 2.42 (t, J = 2.24 Hz, 4H; CH_2), 2.28 (m, J = 2.28 Hz; 4H; CH_2). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 19.5, 25.8, 29.3, 29.6, 29.8, 29.9, 30.0, 34.6, 66.2, 77.7, 175.9. ESIMS m/z = 360.51 $[M]^-$.

Fabrication of PDA coated paper

A diacetylene solution (2 µL) in 2-propanol or THF (1% w/v) was dropped on a piece of filter paper (Whatman No.1

chromatography paper). The paper was allowed to dry in the air at room temperature for 60 min. A hand-held UV lamp has 500 μW cm^{-2} at 254 nm, hung 10 cm above the dotted white filter paper, and was used for UV-polymerization for 1 min to provide PDA coated papers.

Detection of VOCs and colorimetric measurements

The organic solvents (10 mL) were poured into chambers and kept for 60 minutes before placing the dotted blue filter paper within the chamber. The chambers were then placed in a fume hood. Filter papers containing the blue PDA dots were attached on the inside surface of a cover of a chamber containing the VOC being tested. The cover was then used to close the chamber tightly for 60 min at room temperature. The cover was removed from the chamber and the photographic images of the PDA dots were recorded using a scanner. Each image of PDA dots was saved in TIF format and cropped into 0.5 × 0.5 cm^2 areas. The RGB values of the cropped images were obtained from Adobe Photoshop®. The ΔR, ΔG and ΔB values were determined from the RGB values before and after exposure to VOC saturated vapors and were used for the histogram plot.

Data analysis for vapors of VOC discrimination

The set data of 5184 RGB numerical data (3 RGB values × 18 solvents × 8 PDAs × 4 pieces of paper × 3 scans) were then tabulated and analyzed by principal component analysis (PCA; Unscrambler 9.7 software version) to generate clusters of data in the PCA score plot.

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