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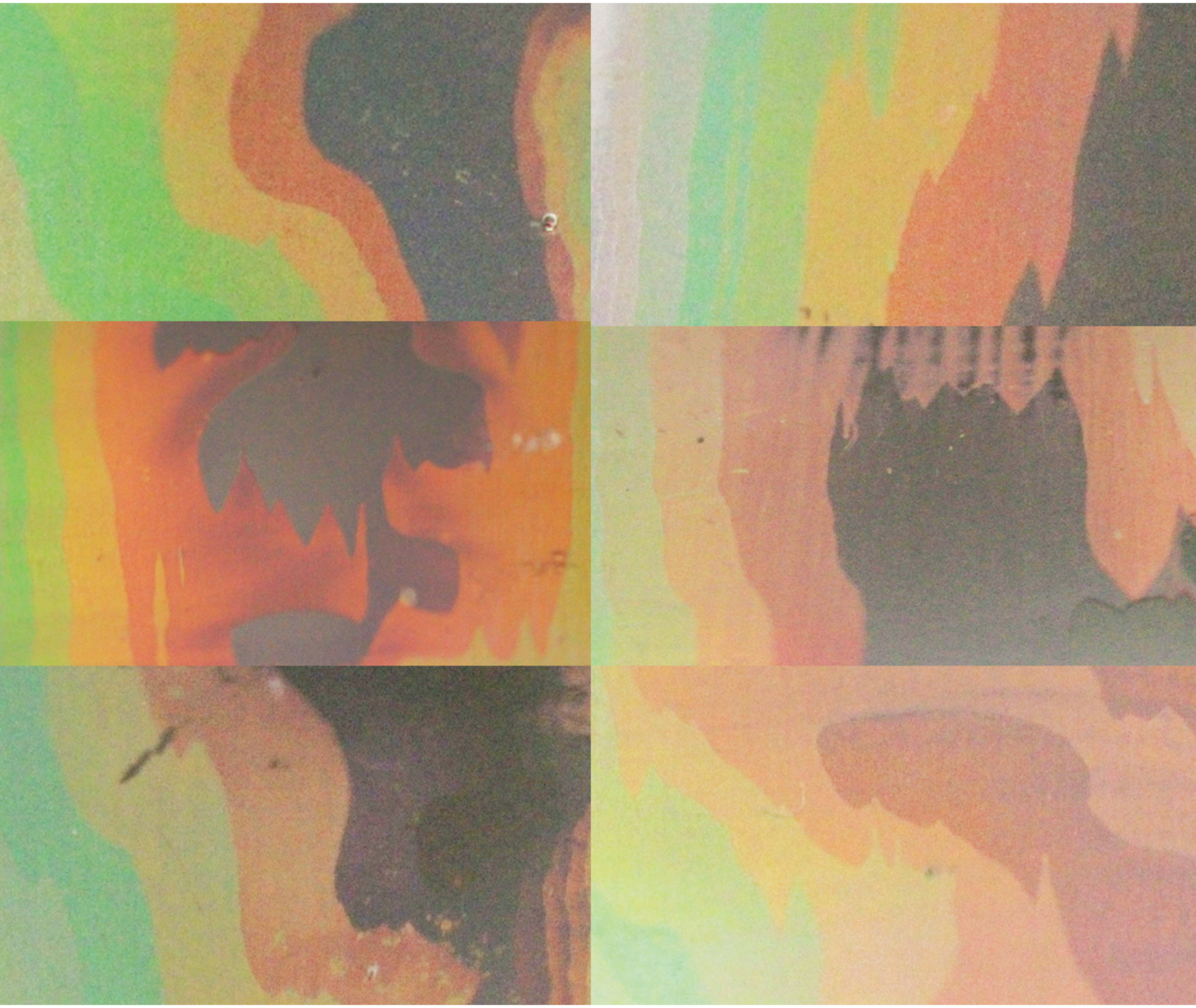

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COMMUNICATION

Combinatorial wetting in colour: an optofluidic nose†‡

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We present a colourimetric litmus test for simple differentiation of organic liquids based on wetting, which achieves chemical specificity without a significant sacrifice in portability or ease-of-use. Chemical specificity is derived from the combination of colourimetric wetting patterns produced by liquids in an array of inverse opal films, each having a graded wettability, but using different surface groups to define that gradient.

Colourimetry is a powerful form of chemical sensing. Without expensive equipment or extensive training, a colourimetric test gives a user at-home access to increasingly sophisticated chemical and biological diagnostic methods.[1] The colour response provides an elegant visualization to this class of sensor, but also poses the greatest challenge to its development. While some target properties of an unknown can be easily coupled to colour change in an indicator material (*e.g.* pH), it is generally challenging to couple a colourimetric response that is sensitive to a general physical or chemical property.

Recently, we developed a platform for colourimetry based on wetting in silica inverse-opal films (IOFs), whose surface chemistry was graded such that the lyophobicity of the porous network increased with depth, which we called a Wetting In Colour Kit (WICK).[2] When immersed in a liquid, the structure is infiltrated up to a fixed depth, and displays a structural colour pattern that is highly sensitive to the liquid's wettability to the surface chemistry.[2] When this procedure is applied to an IOF that varies in total thickness laterally across the sample (and where the individual layers steps can be seen as regions of distinct colour), distinct depths of infiltration can be visualized by a shift in the rainbow pattern corresponding to the number of unfilled layers, as shown in Fig. 1A. Intuitively, this shift will proceed in the direction of the thicker area as more of the lattice is filled.

A scheme of colourimetry that is sensitive to wettability (a generic property of liquids) can be applied in principle to any sensing problem that involves liquids. However, the sensitivity of WICK to such a generic property of liquids also means that no chemical information about the unknown can be discerned without any prior-given information. Fig. 1B illustrates this principle in a WICK, whose vertical gradient of wettability is applied by first functionalizing the IOF with 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl (13FS) groups (by exposure to vapours of the corresponding trichlorosilane), then exposing it to oxygen plasma for a short time (30 s), and then functionalizing it with 3,3,3-trifluoropropylsilyl (3FS) groups (this type of functionalization will hereafter be abbreviated 3FS→13FS, see Supplementary Methods and Ref. 2 for a more detailed description of this method). While the two ethanol-water mixtures shown (80%EtOH, 90%EtOH) produce visibly distinct colour patterns, it is relatively easy to find different liquids whose wetting behaviour exactly mimics those of the above ethanol-water mixtures. In this WICK, n-octane and acetone mimic the response of 80% EtOH and 90% EtOH respectively, as shown in Fig. 1B. In this example, if it is known beforehand that the unknown is a mixture of ethanol and water, WICK would be able to measure the ethanol concentration colourimetrically (with up to 2.5% sensitivity[2]). However, if no information is given beforehand, then it is impossible to identify the unknown.

Here we show that chemically specific information can be extracted from a combination of colourimetric wetting responses displayed by a WICK array, with each element displaying a vertically graded wettability that is designed to exhibit a partial wetting response in most organic liquids (*e.g.* surface tension in the 20–30 mN m^{-1} range), but each using distinct types of surface groups to achieve the wetting gradient. Combinatorial sensing, exploited in our olfactory system as well as by several synthetic systems, is a useful approach to extracting chemically specific responses from an array of individual weakly-specific sensors.[3] A wetting-based response is potentially ideal for combinatorial sensing because of the broad range of materials that can elicit the response (any liquid) and its weakly specific dependence on the chemical interactions between the liquid components and the surface chemistry (the solid-liquid interfacial tension is influenced by the chemical affinity of the liquid to the solid surface). Fig. 1C shows how chemical specificity is added by comparing the responses of two different WICKs employing different surface groups to achieve the wetting gradient (left: DEC→13FS, DEC = n-decylsilyl groups; right: 3FS→13FS) in methanol (γ = 22.1 mN

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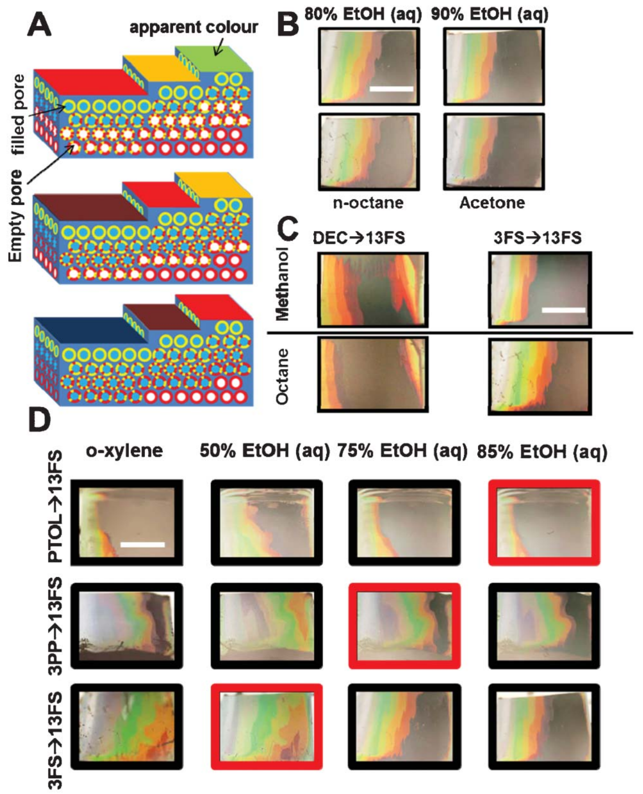

Fig. 1 (A) Schematic depicting the colour response to partial infiltration of liquids in IOFs with vertically graded wettability. Blue pores indicate pores filled with liquid, white pores indicate air-filled pores, and the colour of the top of the structure represents the macroscopic colour observed by eye. The colour in a given region is determined by the number of layers that remain air-filled. (B) Illustration of the chemical non-specificity of WICK: while the sample (3FS→13FS functionalization) shows distinct patterns in 80% and 90% ethanol (aq), these two colour patterns can also be reproduced in entirely different liquids (n-octane, and acetone, here). (C) Chemical specificity derived from a WICK array: Comparison of the colour responses of two WICKs (left: DEC→13FS, right: 3FS→13FS) in methanol and octane. Methanol penetrates fewer layers than octane in the DEC→13FS WICK, but penetrates more layers than octane in the 3FS→13FS WICK. (D) Using reference liquids to assign numerical values to the colourimetric response: The colour response of a test liquid (*o*-xylene shown) in an element in the array is quantified by identifying an ethanol-water mixture that produces the same degree of wetting. In this example, *o*-xylene is given the following scores: PTOL→13FS: 85, 3PP→13FS: 75, 3FS→13FS: 50. Scale bars: 5 mm.

m^{-1}) and octane ($\gamma = 21.4$ mN m^{-1}).[2] In the sample on the right (3FS→13FS) the octane is less wetting than the methanol, showing more coloured layers, while the trend is reversed on the left. The combination of patterns in the two samples gives more information about the liquid than one sample alone. For example, a water-dilution of methanol could have produced the pattern mimicking octane at right, but not the one on the left.

We produced WICK arrays consisting of six samples, whose chemistry was vertically graded, each using different surface groups. When choosing the surface groups for IOF functionalization, it was important that all elements produce non-trivial wetting responses in most organic liquids (*i.e.* partially filled IOFs; trivial responses occur when all layers are filled or all layers are unfilled). To ensure that this condition was satisfied, we used 13FS as the first group deposited on all IOFs, since this functionality by itself facilitates a nonwetting response to nearly all liquids.[2] After the oxygen plasma exposure, each element of the array was functionalized with a different (less lyophobic than 13FS) surface group: pentafluorophenylpropyl (5FP), 3,3,3-trifluoropropyl (3FS), n-decyl (DEC), *p*-tolyl (PTOL), trimethylsilyl (TMS), 3-phenylpropyl (3PP). The plasma exposure time (30 s) was chosen to eliminate trivial responses and maximize the range of penetration depths observed in our library of organic liquids.

To facilitate interpretation of the results, we developed a system to translate qualitative wetting patterns to numerical values. Each element of the WICK array was first characterized in a series of reference liquids. To serve as ideal reference liquids, a set of liquids would have to induce a wide range of wetting responses in each element, ideally covering the broad range of penetration depths observed in test liquids. Most importantly, the relative order of wettability of the reference liquids would ideally be the same in each element in the array. For example, methanol and octane would make a bad set of reference liquids because methanol wets more than octane in 3FS→13FS samples, while the reverse is true in DEC→13FS samples (shown in Fig. 1C). As reference liquids, we chose the set of water-ethanol mixtures (in increments of 5% EtOH by volume) and isopropyl alcohol (IPA). IPA was found to wet more than ethanol in all elements, and is thus a suitable addition to extend the effective range of detectable responses covered by the reference liquids. Colour patterns produced by unknown liquids (test liquids) were then assigned a numerical score for each element of the array based on the reference liquid(s) that produced the most similar pattern. The scoring system is illustrated in Fig. 1D for *o*-xylene as a test liquid, having scores of 50 (3FS→13FS), 75 (3PP→13FS), and 85 (PTOL→13FS) in three elements of the array. To integrate IPA into the scoring system, it was assigned the numerical value of 110. When a test liquid produced a wetting response that fell in between that of adjacent reference liquids, a midpoint score (ending in 2 or 7) was assigned (*e.g.* a liquid that wet more than 80% EtOH but less than 85% EtOH in a given element would be assigned a score of 82, or 87 for a liquid whose response fell in between 85% EtOH and 90% EtOH).

Fig. S1 (Supplementary Information) shows the complete sample set of colour patterns and reference liquid scores from an array tested in 17 different organic solvents. Notably, each liquid yielded a unique combinatorial colour response and thus a unique set of scores. Fig. S2A (Supplementary Information) shows the reference liquid scores for a wide range of organic solvents in the 3FS→13FS and DEC→13FS elements of the array. Aliphatic compounds displayed higher scores (*i.e.* more wetting relative to reference liquids) in the DEC→13FS element than they displayed in the 3FS→13FS element. As a general trend, the elements of the array with fluorinated surface groups (3FS, 5FP) produced lower scores relative to the other elements of the array in the nonpolar hydrocarbons, with deviation from the reference line (given by the reference liquids) negatively correlating with polarity of the liquid. Also as expected, the scores of the linear alkanes in all elements decreased monotonically with increasing chain length (increasing surface tension), since the chemical affinity for the different surface groups should be of the same type. The monotonically varying scores of the linear alkanes form a nearly straight line in this plot.

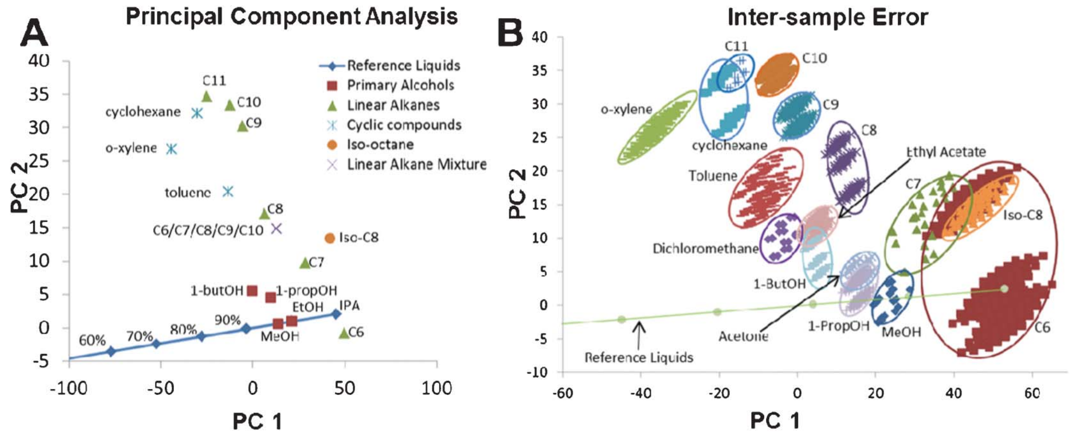

Fig. 2 A) 2D principal component analysis of the reference liquid scores of all six elements of an array, showing differentiation of the different liquid classes. (B) Estimation of inter-sample variability using the reference liquid scoring system. Three WICKs with each type of chemistry gradient were tested. All mutually distinct combinations of scores from every possible "array" combination (made by one sample with each chemical functionality) are plotted. There are 729 such combinations possible, however not all produce distinct combinations of scores. Although the plot shows the presence of some variability from array to array, the scoring system preserves the general trends that provide chemical information about the unknowns from one array to the next (there are relatively few areas of overlap between different liquids).

Fig. 2A shows a two-dimensional principal component analysis (PCA),[3] where the aforementioned 6-dimensional set of numerical wetting scores are projected onto a new two-dimensional set of principal component axes, accounting for 98% of the total variance. Qualitatively Fig. S2A and Fig. 2A look similar, indicative of the fact that the contrast between the wetting behaviour in fluorinated and non-fluorinated elements of the array was the largest source of variability between the different liquids (see Supplementary Information for a more detailed discussion of our PCA). However, the consideration of all six elements (Fig. 2A) allows us to distinguish iso-octane and cyclohexane from the linear alkane line. In Fig. S2B–D, analyses using fewer elements of the array are done, showing that even three elements are able to differentiate the 17 test liquids successfully, thus suggesting that the 6-dimensional set is largely redundant.

A hallmark of ideal combinatorial sensors is that they give information as to what the chemical makeup of an unknown (not previously entered in the library) is likely to be.[3] To test the applicability of this principle to our WICK sensor, we tested the array in a randomized mixture of the linear alkanes between C6 and C10. Its response is shown in Fig. 2A. Naïvely, we would expect that its response should fall along the arc (nearly straight line) connecting the responses of consecutive linear alkanes and this is exactly what is observed.

While the sophistication and selectivity of this array-based sensor is below that of many other previously reported "artificial noses" that have a much higher effective dimensionality of the variability,[3] the value of WICK array lies in its ease of use and technical simplicity relative to the information it is able to extract. Unlike most artificial noses,[3] the reference-liquid scoring system allows measurements to be done easily by eye, by simply comparing the response produced by a test liquid to that of reference liquids. Shown in Fig. 2B, the relative nature of the reference-liquid scoring system also facilitates measurements that are fairly robust against sample-sample variability, potentially eliminating the need for costly quality-control procedures. Notably, unlike previously reported colour-based combinatorial sensors,[3] it does not require image analysis, RGB subtraction, or any other complex analysis technique that places constraints on the type of equipment amenable for use in the field. Furthermore, as shown in Fig. S2, a significant enhancement of chemical specificity can be achieved by using an array with only two or three elements. This requires a minimal increase in complexity compared to the original WICK litmus paper concept.[2]

Conclusions

Using arrays of WICKs, each with distinct chemical functionality, but exhibiting a nontrivial wetting response over a common range of liquids, we are able to extract chemical specificity from a sensing platform whose widespread applicability is derived from sensitivity to wettability, a general (non-chemically specific) property of all liquids. Furthermore, through the use of a simple-to-use reference-based scoring system, we are able to translate qualitatively perceptible degrees of wetting to numerical values that can be assigned by eye (using a reference card) without the need for sophisticated equipment or software in a manner that simultaneously desensitizes the system to inter-sample variability. In addition to the ability to differentiate a wider range of liquids, our WICK arrays also allow users to make rough predictions about the chemical nature of a previously uncharacterized unknown liquid by comparing relative degrees of wetting of the different elements.

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