Supporting Information:

“Combinatorial Wetting in Colour: An Optofluidic Nose”

Kevin P. Raymond, Ian B. Burgess, Mackenzie H. Kinney, Marko Lončar and Joanna Aizenberg

Methods

IOF Synthesis. Large-area, crack-free inverse-opal films (IOFs) were fabricated according to the procedure previously detailed in refs S1-S3.

Cleaning. After calcination, IOFs were cleaned in acid piranha solution (3:1 H_2SO_4:30% H_2O_2) for 4h (90 °C). IOFs were then exposed to oxygen plasma (5-10 sccm, 100W) for 1 h, followed by 24hrs of dialysis cleaning in DI water.

Storage. While IOFs were not in use, they were stored in closed petri dishes under ambient conditions to shield them from dust. Significant sensitivity to changes in ambient conditions (i.e. temperature, humidity, etc.) was not observed during storage.

Applying Vertical Gradients of Wettability. Since 13FS was used as the base group in all elements of the array, all IOFs were first exposed under vacuum to vapours of 1H,1H,2H,2H-tridecafluoroocytl (13FS) – trichlorosilane for 24hrs. To remove potential sensitivity of the protocol to ambient humidity, IOFs were exposed after silanization to a saturated atmosphere of water vapour (done simply by submerging the hydrophobic porous IOFs in a dish filled with DI water). IOFs were then baked for 20 minutes at 150 °C under atmospheric pressure and ambient humidity. To apply the gradient, IOFs were then exposed to oxygen plasma (5-10 sccm O_2 flow, 100W) for 30s. Samples were then functionalized with one of: n-decyl -(DEC), 3-phenylpropyl- (3PP), 3,3,3-trifluoropropyl- (3FS), pentafluorophenylpropyl- (5FP), p-tolyl- (PTOL), or trimethylsilyl (TMS) groups. Functionalization with DEC, 3PP, 3FS, 5FP and PTOL groups was done by exposing the IOF to vapours of the corresponding alkyltrichlorosilane according to the same procedure as described for 13FS. TMS-functionalization was accomplished by exposing the IOF to vapours of chlorotrimethylsilane under atmospheric pressure and ambient humidity for 20 minutes. After silanization, all samples were post-treated as described for 13FS functionalization. All trichlorosilanes were purchased from Gelest Inc. and used without further purification. Chlorotrimethylsilane was purchased from Alfa Aesar and used without further purification. Finally, before testing, all samples are vigorously rinsed in ethanol, and air dried.

Testing. Each sample is placed in a dish of desired liquid and its colourimetric wetting response photographed. Initially, samples were photographed in ethanol-water mixtures to be used as references, beginning at 100% ethanol and decreasing in increments of 5% until all samples were completely non-wetted. Each element of the array was then photographed in a variety of solvents. Importantly, to ensure that the previous solvent does not affect the wetting response of the next, all samples were carefully cleaned and re-standardized in order to verify reliability of the response. Cleaning consisted of acetone and ethanol rinsing, baking at 150°C and then a further rinsing with ethanol (air drying). To verify the quality of the cleaning, all samples were re-immersed in the 100% ethanol and 90% ethanol references and their wetting patterns were verified to exactly match the patterns produced in the original reference-liquid testing stage. This indicated passing of quality control. If quality control step failed (e.g. one of the reference liquids did not produce the expected wetting pattern in the array), the cleaning process was repeated until all samples passed before continuing on to next liquid.

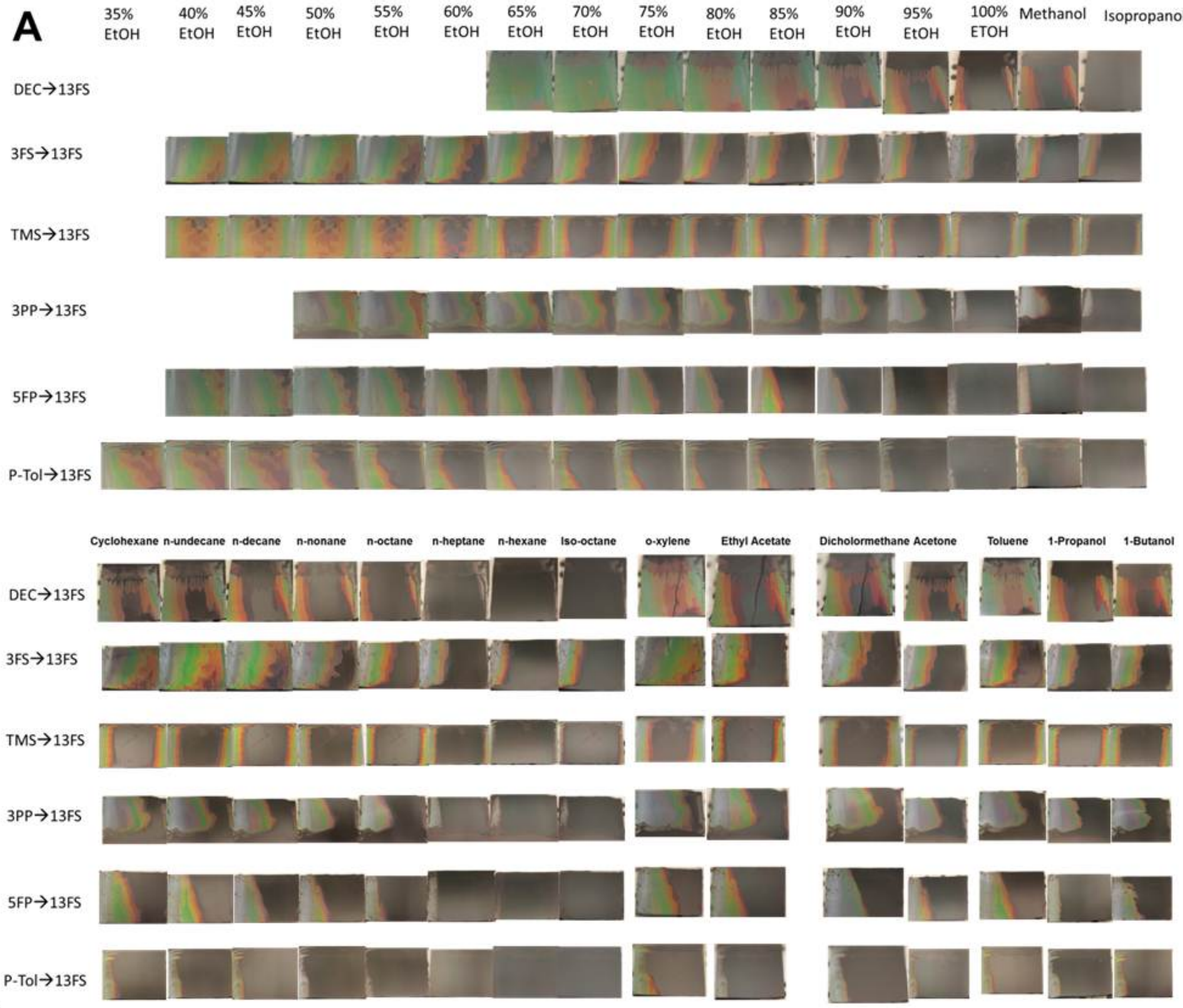
Data Capture. Optical images were captured using a Canon EOS Rebel T2i Digital SLR camera equipped with a macro lens, and fixed to a tripod. All images were taken under zero magnification and at roughly the same angle under consistent ambient lighting conditions. It should be noted that while all images were captured under roughly the same conditions, this is not strictly a necessary step since all subsequent analysis is based on *countable* differences in wettability (visualized by a shift in the rainbow pattern corresponding to the number of unfilled layers), which are independent of angle or lighting conditions.

Reference Liquid Scoring. The reference liquids used were the ethanol-water mixtures (increments of 5% volume fraction) and isopropyl alcohol (IPA). Since IPA wetted to a greater extent than 100% ethanol in all elements of the array, the set of reference liquids produced a consistent monotonic relative wetting trend. The colourimetric wetting pattern produced by a test liquid (e.g. n-octane) in each element of the array was compared to each of the reference liquids. For a given element (e.g. 5FP→13FS) if one of the reference liquids (e.g. 85% ethanol) produced an identical wetting pattern to the test liquid, then the test liquid was assigned a score corresponding to the ethanol concentration of the matching reference liquid (e.g. a score of 85). If a test liquid produced a pattern that matched none of the reference liquids, the score was interpolated to a value ending with 2 or 7. For example, if a test liquid wets more than 85% ethanol, but less than 90% ethanol, then a score of 87 would be assigned. A liquid whose wetting pattern matched IPA was assigned a score of 110. If a liquid wetted more than 100% ethanol, but less than IPA, then a score of 105 was assigned. If a liquid wetted more than IPA, a score of 115 was assigned.

2D Principal Component Analysis. Performing a 2D principal component analysis (PCA) facilitates graphical sorting of the different liquid types by performing a mathematical optimization of a 2D projection plane that maximizes the variability in the 6D dataset of reference liquid scores for each element in the array. The goal is to look at the smallest number of variables that preserves most of the information from the higher-dimensional complete set of axes. The first principal component is the linear axis on-which the data is projected that gives the maximum possible variance to the data set. The second principal component is the linear axis, under the constraint of being orthogonal to the first principal component axis, which maximizes the variance of the projected data. The same optimization is done for the third axis, except it must now be orthogonal to the first two, and so on [see ref S4]. The first two principal components of our system, accounting for 98% of the variance of the data, provide some insight into which elements of the array provide the most information. In the co-ordinate system of [5FP→13FS, 3FS→13FS, DEC→13FS, PTOL→13FS, TMS→13FS, 3PP→13FS], the first two principal components axes are PC1=[0.389638, 0.448862, 0.374264, 0.393558, 0.423698, 0.414998], PC2=[0.041843, -0.86808, 0.314051, 0.306926, 0.166533, 0.155311] (the global mean of 88.4057971 was subtracted from the whole data set to center the data before transforming to the principal component axes). The first principal component weights all elements nearly equally. The maximum variance in this direction reflects the trend that the degree of wetting (and thus the reference liquid scores) has a general negative correlation with surface tension of the liquids for all surface chemistry combinations. The second principal component primarily looks at the contrast between the 3FS→13FS score and the scores of the non-fluorinated elements of the array (this axis is nearly orthogonal to the 5FP→13FS axis). The principal components reflect the strong degree of correlation between the scores in the DEC→13FS, PTOL→13FS, TMS→13FS and 3PP→13FS elements of the array (indicates redundancy in these elements), and that the 3FS→13FS element provides the most distinct information from the others. This is also reflected in the qualitative similarity between the 2D 3FS→13FS vs. DEC→13FS plot (Fig. S2A) and the 2D principal component plot including all 6 elements (Fig. S2D).

References:

S1. B.D. Hatton, L. Mishchenko, S. Davis, K.H. Sandhage, J. Aizenberg, *Proc. Natl. Acad. Sci., U.S.A.* 2010, 107, 10354.
S2. I.B. Burgess, L. Mishchenko, B.D. Hatton, M. Kolle, M. Lončar, J. Aizenberg, *J. Am. Chem. Soc.*, 2011, 133, 12430.
S3. I.B. Burgess, N. Koay, K.P. Raymond, M. Kolle, M. Lončar, J. Aizenberg, *ACS Nano*, 2012, 6, 1427.
S4. I.T. Jolliffe *Principal Component Analysis*, *2nd ed*., (Springer, NY, 2002).



B

	o-Xylene	Dichloromethane	Cyclohexane	Iso-octane	Acetone	Ethyl Acetate
5FP	70	85	80	110	92	87
3F	50	77	50	97	90	82
DEC	87	92	92	105	95	95
P-Tol	85	92	87	110	97	97
TMS	77	87	87	115	97	95
3PP	75	90	82	115	95	95

	n-hexane	n-heptane	n-octane	n-nonane	n-decane	n-undecane
5FP	105	97	92	92	87	82
3F	115	97	80	62	57	50
DEC	110	105	100	97	97	92
P-Tol	110	110	100	97	97	92
TMS	115	110	97	95	92	85
3PP	115	100	97	95	92	90

	Isopropanol	Methanol	1-Butanol	1-Propanol	Toluene
5FP	110	97	87	95	85
3F	110	97	87	92	67
DEC	110	97	95	97	85
P-Tol	110	97	92	97	95
TMS	110	97	95	95	95
3PP	110	97	92	97	90

Figure S1 – Reference liquid scoring system: (A) Photographs of a six-element array, tested in reference liquids (ethanol-water mixtures and isopropyl alcohol) and several organic test liquids. (B) Reference-liquid scores for each liquid extracted from the photographs in (A).

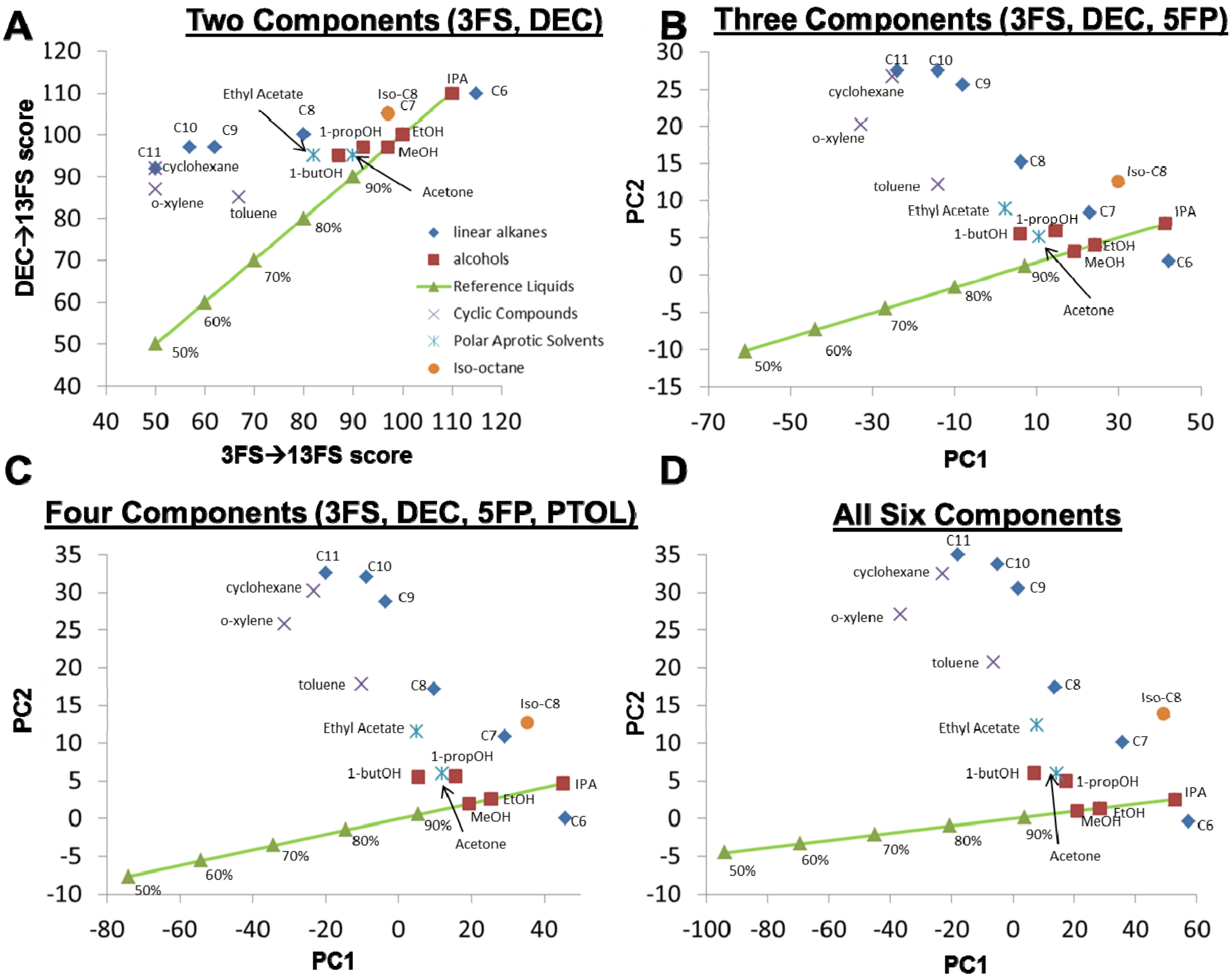


Figure S2 – Redundancy of the Array: Comparison of the information given from just two components of a WICK array (3FS→13FS, and DEC→13FS, A) and 2D Principal component projections of arrays where three (B), four (C), and all six (D) elements are included. Much of the information distinguishing the different types of liquids can be obtained from relatively few elements, meaning that the increased specificity garnered by an array versus a single element can come at a minimal sacrifice in simplicity.