<u>**SUPPLEMENTARY INFORMATION**</u>

Combinatorial strategies for material screening/discovery

Array-based strategies typically deal with functionally graded samples that are designed to represent the grading granularity in the form of a matrix which can then be directly probed for optima. These methods are generally used to study material systems whose functional response is not simply a proportional sum of its components but also involves complex interactions such as phase and morphological changes in polymer blends (33), nonlinear catalytic effects (34) and polymeric cross-linking (35) to name a few. Parallel strategies are employed in situations where the functional response of the material system is usually a linearly proportional sum of its components. However, the sheer number of combinations of components and process parameters result in extremely large sample pools if considered exhaustively. Despite the fact that these methods make meticulous use of experimental data on similar material systems to optimize their respective processes, it is not possible to know exactly how a new material or blend will behave when probed by different characterization tools at different levels of processing. Consequently, the compositional variation between any two samples has to be minimal to begin with in order to cover the relevant spectrum of compositions without missing key aspects of the observed quantity and such high process parameter granularity makes the size of the sample set unavoidably large. Similarly, in the case of entirely new material systems, combinatorial strategies are applied but with certain bounds that are generally set at the outset of such a developmental initiative. Some commonly established bounds on combinatorial experimental design include, and are not limited to, minimization of the number of experimental runs, capping of component fractions, equipment-related constraints among others. Implementation of these bounds involve experimental methods like blocking, machine learning (ML) tools and software-assisted generation of sample compositions, process parameters and sample sizes necessary to draw meaningful conclusions. In essence, these bounds are imposed to limit the total sample pool from exploding which is impractical in terms of resource investment and in that sense, are quite similar to some of the more conventionally combinatorial (parallel) strategies.

Table S1: Common evaluation and screening methodologies for materials research and development.

Types	Implemented methodologies	Remarks
Array strategies	Gradient arrays (36, 37)	Rapid sample generation for evaluation
	Masked arrays (38, 39)	
	High-speed conventional arrays (40)	
Parallel strategies	Representational approach (41)	Selective evaluation of pool subsets
	Indexed library approach (42)	
	n-way combinations approach (43)	
Minimalist strategies	Randomized runs (44, 45)	Unknown sample/process parameters
	Metaheuristic approaches (46, 47)	
	Software/ML methods (48, 49)	

General CPH structure

A generalized CPH structure consists of N fluid inputs (F_1, F_2, … , F_N) as shown in Fig. S1. These fluid inputs feed to the pre-processing unit(s) of choice W (mixer, heater etc.) and from there, the processed fluid mixture is fed to the dispenser V (inkjet, ultrasonic etc.).
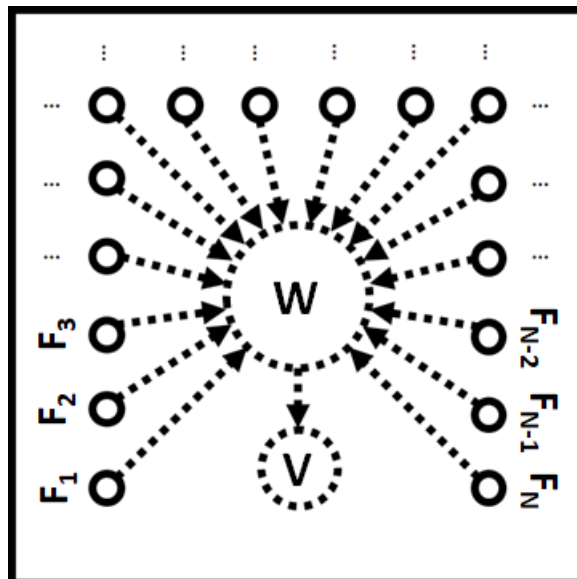

Fig. S1: Schematic of the general CPH structure showing the requisite fundamental components

Chemical compatibility of silicone-based elastomers

The specific elastomer (RTV 615) used in the CPH application presented in this article is a silicone which has good chemical compatibility with organic solvents like alcohols (methanol, ethanol, isopropanol etc.), glycerol, ethylene glycols (mono-, di-, poly- etc.), dilute acids (acetic, citric etc.), dimethyl sulfoxide, dimethyl formamide, N-methyl-2-pyrrolidone, hydrogen peroxide, ethyl acetate among others. Other commonly used organic solvents such as chloroform, carbon tetrachloride, chlorobenzene, tetrahydrofuran and oils (with some exceptions) cause swelling and are considered incompatible with silicones. In this article, all chemicals used belong to the former category and the platform design and fabrication can be modified for elastomer-like materials to accommodate the latter category of chemicals depending upon the application. Please refer to the database provided in https://www.coleparmer.com/chemical-resistance for corroboration.

Sources of measurement variability

Volumetric variability in droplets

Droplet-to-droplet size variation can result in variability in conductivity measurements under the premise that droplet volume and solute volume carried in the droplet are directly related. Sparsely populated (in terms of droplet count) printed features are more susceptible to such variations and as such, these variations are expected to decrease as the number of droplets used to print a particular feature increase.

The ejected droplet volume measured using two identical 80 µm Microfab dispensers (https://pubs.rsc.org/en/content/articlelanding/2016/lc/c6lc00636a/unauth, Bsoul *et al.*, 2016) varies between ~1 pl and ~2 pl with coefficients of variation ~2.6% and ~3.5% respectively.

Intrinsic variabilities such as these cannot be controlled and can only be circumvented by printing features that are not sparse (in terms of droplets).
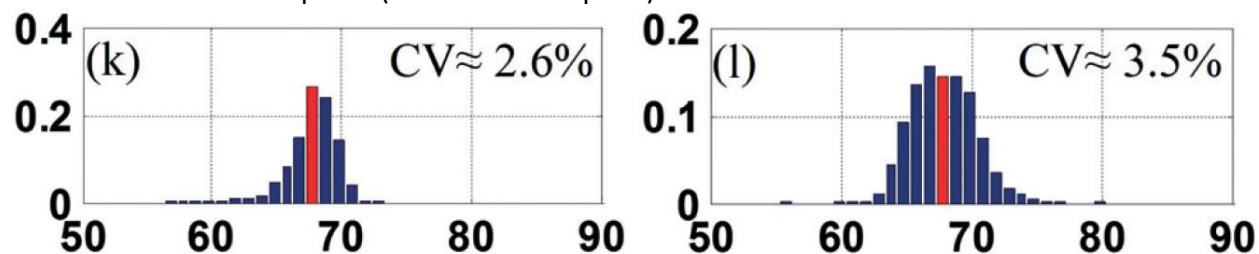

Fig. S2: Droplet diameter variability of the Microfab dispensers used in this work (adapted from Fig. 13 of https://pubs.rsc.org/en/content/articlelanding/2016/lc/c6lc00636a/unauth, Bsoul *et al.*, 2016 cited as reference 60 in the article).

Solute composition variability in droplets

Aqueous PEDOT:PSS dispersions are not perfect solutions and have a general propensity to form aggregates while resting in reservoirs or undergoing very low Reynolds number (0.05 in our case) flows through microfluidic channels. This property has also been mentioned briefly on page 6 in the subsection discussing the formulation of binary ink systems. Consequently, the PEDOT and PSS (non-stoichiometric excess) fractions in each droplet can understandably vary. This leads to compositional and by extension, morphological inhomogeneity which accumulates droplet by droplet within the print and is manifested in the conductivity measurement as variations. This is an intrinsic property of the ink and cannot be circumvented except by modifying the ink.

Mixing fluids with higher viscosity contrast

In this article, we have used electrical conductivity of secondary doped PEDOT:PSS (coded as "A") as a measure of mixing efficiency which has greater relevance to practical applications. We have conducted CPH print tests using 75 vol.% PEG-400 (coded as "D") in aqueous solution as the conductivity-modulating additive whose viscosity is ~50 cP (~10× that of the PEDOT:PSS dispersion used) as an upper limit of viscosity contrast between two fluids being mixed using our platform. For reference, the viscosity of 100% PEG-400 is ~90 cP. The increase in conductivity, although of the same order of magnitude, is quantitatively lower due to (i) use of a diluted additive resulting in a greater fraction of water and (ii) the nature of the additive as not all additives give rise to equal conductivity enhancement (Chapter 9 of PEDOT: Principles and Applications of an Intrinsically Conductive Polymer, Elschner et al., 2010).
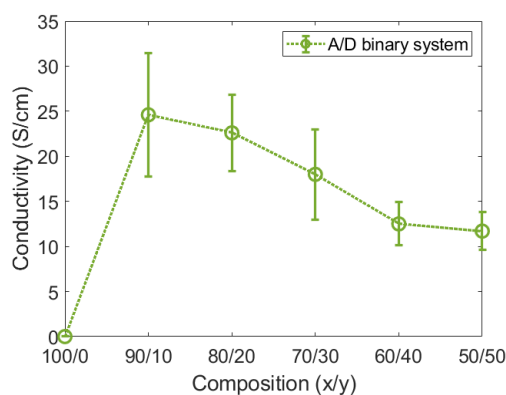

Fig. S3: Electrical conductivity trends in binary mixture of PEDOT:PSS (A) and PEG-400 (D) using our CPH platform.