Sustainable Materials Acceleration Platform Reveals Stable and Efficient Wide Bandgap Metal Halide Perovskite Alloys

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Summary

The vast chemical space of emerging semiconductors, like metal halide perovskites, and their varied requirements for semiconductor applications have rendered trial-and-error environmentally unsustainable. In this work, we demonstrate RoboMapper, a materials acceleration platform (MAP), that achieves tenfold data intensification by formulating and palletizing semiconductors on a chip, thereby allowing high-throughput (HT) measurements to generate quantitative structure-property relationships (QSPRs) considerably more efficiently and sustainably. We leverage the RoboMapper to construct QSPR maps for the mixed ion $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ halide perovskite in terms of structure, bandgap and photostability with respect to its composition. We identify wide bandgap alloys suitable for perovskite-Si hybrid tandem solar cells exhibiting a pure cubic perovskite phase with favorable defect chemistry while achieving superior stability at the target bandgap of ~1.7 eV. RoboMapper's palletization strategy reduces environmental impacts of data generation in materials research by more than an order of magnitude, paving the way for sustainable data-driven materials research.

Keywords

materials acceleration platforms; high throughput experimentation; metal halide perovskites; wide bandgap hybrid perovskites; stability; photostability; defect chemistry; halide vacancy; halide segregation; solar cell; hybrid tandem; perovskite-Si; quantitative structure-property relationships; phase diagram; life cycle assessment; sustainable laboratory practices.

Introduction

The proliferation of quantitative structure-property relationships (QSPRs) is revolutionizing the design of use-based compounds including pharmaceuticals and energy materials by providing pragmatic property predictions which dramatically accelerate the time frames of discovery.[1-4] Such rapid and disruptive advancements have inspired the materials research community to adopt QSPR models to accelerate use-based material design, synthesis optimization, and discovery.[5-7] However, the issues of experimental data sparsity and reproducibility continue to hamper the materials community's adoption of rapidly emerging data science tools[8,9] and are symptomatic of a wider problem: only a small fraction of data generated in research labs is communicated, a smaller fraction still is made available in databases,[5,10] and what data is mined from the literature is often unreliable and/or lacks sufficient protocol details.[11-14] Chemistry and biology have shown that adoption of automation, robotics and high-throughput (HT) infrastructures are proven pathways to successful digitization of experimental datasets.[10,12,15,16-18] Moreover, the experience of these disciplines has shown that adoption of informatics and QSPR models can make data collection repetitive and labor intensive,[16-18] which favors adoption of automation in materials research.[19-31]

In recent years, the materials research community has seen the emergence of materials acceleration platforms (MAPs). MAPs automate repetitive materials research tasks, facilitate digitization of materials laboratory data, and have increasingly facilitated generation of QSPR models in chemical and materials research,[22,29-35] in line with the Materials Genome Initiative 2.0 strategic plan.[36,37] MAPs automate data generation by emulating tasks performed in materials laboratories,[24,38] such as formulation of precursors or feedstocks,[19,23,25] processing or fabrication of compositionally and structurally diverse materials,[22,27] and characterization of synthesized/processed materials.[20,22,26,27] Additional design considerations for MAPs is the environmental impact and material research sustainably associated to generation of QSPR maps. While automation is a proven path toward reduction of labor intensive tasks, repeating wasteful and environmentally harmful practices is likely to exacerbate environmental problems associated to already wasteful practices.[39-41] An opportunity therefore exists to design MAPs that establish QSPRs more sustainably by reducing waste, greenhouse gas emissions (GHGEs) and other environmental impact categories of experimental research. In addition to generating data with efficiency and reduced environmental impact, next-generation MAPs have the opportunity to overcome the lack of information-rich data characteristic of many MAPS which integrate a fixed number of characterization methods.[19,20,26,27] We take the view that MAPs are ripe for innovation: they can be designed to generate information-rich data by enabling multi-modal characterization that is automated and decentralized; the generated sample layouts can reduce operational steps of research, as well as energy, GHGEs, waste and time. Evaluating environmental impacts of existing materials research workflows via methods, such as life cycle assessment (LCA),[42,43] provides insights into the bottlenecks of state-of-the-art materials research and creates opportunities to reduce GHGEs and make design improvements that will maximize data intensity. Industrial palletization approaches have improved supply chain productivity and provide inspiration for challenging human-centric laboratory workflows by reducing operational steps by placing multiple materials on a common pallet or substrate to achieve considerable efficiency gains,[44,45] reducing cost and energy.[16,28,30] Recent advances in capillary printing[46] combined with liquid handling[19,23,25,27] make it possible to design MAPs that can robotically palletize materials by formulating materials on-the-fly and depositing miniaturized pixels on a common substrate, similar to how chemists and biologists parallelize samples in well plates.[16] Pallets can thus be mapped efficiently via HT characterization methods to generate multi-modal QSPR models with reduced operational steps and material waste.

A priority area of materials research that can benefit from rapid developments in MAPs is the area of metal halide perovskites (MHPs).[19-21,23-27] MHPs are emerging semiconductors with compositionally tunable structure and properties and a very large design space.[47,48] To date, over two thousand unique MHPs have been demonstrated or predicted, with orders of magnitude more compounds and alloys possible.[10,49,50] MHP semiconductors have allowed single junction perovskite solar cells to match the power conversion efficiency (PCE) of monocrystalline Si photovoltaics close to 26%.[51] However, a new challenge in this field is the development of new wide bandgap MHP alloy with a bandgap of ~1.7 eV toward development of perovskite-Si hybrid tandem solar cells, which have recently achieved a PCE of 33.2%.[51] A number of studies have shown that the bandgap tuning through the mixed halide alloying comes at the expense of light-induced halide segregation, which causes photodegradation of the material and device under illumination.[52,53] Thus, compositional tuning with multi-component alloying (through mixing of both cations and halides) has been widely used to design the desired MHPs that exhibit thermodynamically stabilized perovskite phases and are photostable.[54-59] It is therefore essential to develop multi-modal QSPR maps that relate the phase diagram, bandgap, and photostability to the composition of MHPs to zero in on ideal alloys.

Here, we introduce the RoboMapper (Figure 1), a new concept in MAPs that palletizes materials on demand and uses decentralized HT characterization facilities to generate multi-modal QSPR maps efficiently. The RoboMapper integrates on-the-fly formulation with micro-printing and micro-coating of MHPs directly on a chip and accelerates QSPR mapping 14-fold compared to manual workflows and 9-fold compared to serial automation MAPs. We utilize the RoboMapper platform to construct a comprehensive phase diagram of the quaternary $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ hybrid perovskite system using synchrotron-based HT wide angle X-ray scattering (HT-WAXS). We focus on a photovoltaic region of interest in the iodine-rich quadrant (FA and I rich phases with $0 \leq x \leq 0.35$ and $0 \leq y \leq 0.45$) to search for a pure cubic perovskite alloy exhibiting an ideal bandgap of ~1.7 eV target bandgap suitable for perovskite-Si hybrid tandem solar cells. To do so, we construct QSPR models for bandgap and photostability. Photostability is a powerful screening tool as demonstrated by recently developed diffusion-stability framework which relates material photostability to solar cell device hysteresis.[60] Using the developed QSPRs, we predict new wide bandgap compounds and validate these results with spin-cast thin films with remarkable consistency, proving the reliability and fidelity of the platform and our model. The predicted ideal compound ($FA_{0.775}Cs_{0.225}Pb(I_{0.749}Br_{0.251})_3$) is translated to single junction p-i-n solar cells with PCE of 19.20 ± 0.45%, low hysteresis and far better photostability than other compounds evaluated within the QSPR map at 1.7 eV. We evaluate the scientific link between photostability and the vacancy concentration and show the ideal composition exhibits low halide vacancy concentration. This can explain why photo-induced halide segregation and photobleaching of the ideal compound were considerably slower. We evaluate the cost, energy requirements and environmental impact of this approach via LCA in contrast to manual labor and serial automation MAPs. The RoboMapper generates QSPR datasets with 1/50th the cost and 1/25th the energy of manual workflows even when excluding labor costs. Importantly, the palletization approach slashes environmental impact on ecosystems, human toxicity and GHGEs by 1/10th by reducing the electricity consumption of characterization and by reducing waste generation. Our palletization strategy paves the way for materials research to be accelerated while remaining sustainable by making MAPs considerably more data intensive and information-rich in their quest for QSPR models for material design.

Results and discussion

RoboMapper: Automated formulation and on-chip palletization

Figure 1 illustrates the RoboMapper platform we have developed in-house and its workflow. The RoboMapper platform (Figure 1B and S1) is a compact, benchtop multi-robot platform consisting of an ink formulation bot based on liquid handling technology working in tandem with a dispensing bot consisting of a gantry-based hollow capillary that allows micro-printing and micro-coating with volumes ranging from 0.6 pL to 0.5 nL (See the SI part I for details). This coating approach builds upon the similarity between hollow capillary coating/printing and slot-die coating, which is the premier scalable manufacturing method used in solution-processed semiconductors, including HMH materials, and the low material utilization rate of the process. In contrast, MAPs currently in use employ spin coating or drop casting on traditionally sized coating areas.[22,27,31] The tedious substrate cleaning procedures and challenges in substate handling and storage limit the size of these campaigns to what manual workflows would typically achieve[24,38] (see Figure S2 for details). The nature of spin-coating, which requires relatively large sample areas (> 1 cm^2) to achieve uniformity and large ink volumes owing to >95% ink waste, also makes large QSPR datasets expensive and environmentally unsustainable to obtain, as will be discussed below. The RoboMapper's home-built user interface designs the palletization of materials (Figure 1A) by defining the boundaries of QSPR campaign in terms of materials composition and ink formulation, the layout of these compounds on the substrate, and their size and geometric patterns (dots, lines, patches, etc.) and spacings. A key design consideration of multi-modal characterization campaigns on material pallets is the necessity to meet the requirements of every intended characterization method. This includes measurement footprint and spatial resolution, as well as choice of substrate (e.g., conducting vs insulating, optically transparent vs opaque, x-ray transparent, etc.).

Given the spatial resolution of the RoboMapper, our robotic palletization approach can theoretically integrate up to 2,500 pixels/cm^2 with an average size per pixel of 50 μm along a square lattice arrangement and a center-to-center spacing of 200 μm. This highlights that a very large number of materials and associated data can be encoded on a single pallet. This in turn requires spatially resolved analytical probes that can scan samples automatically to conduct HT characterization and construct QSPR maps. In this study, we conducted QSPR campaigns focused on optical characterizations performed on-site as well as off-site structural characterizations at NSLS II synchrotron to establish QSPR models of hybrid perovskite phase diagram, composition-dependent bandgap and photostability. For this study, we have palletized up to 150 compositions (and multiple copies thereof for verification of reproducibility). We conducted laboratory-based HT optical microscopy, HT micro-photoluminescence (HT-μPL) spectroscopy mapping, as well as synchrotron-based HT-WAXS mapping. These experimental campaigns were conducted in a closed loop, where needed, to refine the dataset and validate QSPR models. The resulting information from these characterization techniques helped us create a high-fidelity data stack (Figure 1C) towards construction of QSPRs that link the bandgap and photostability of hybrid perovskites to their composition and crystalline phase.

The RoboMapper workflow adapted to hybrid perovskites research is summarized in Figure 2. A library of AX and BX_2 precursor salts in various solvents (Figure 2A) is used as stock solutions, together with blank solvents, to create mixtures resulting in hybrid perovskite ink formulations, including all 150 compositions that are evaluated in this study. The RoboMapper aspirates (Figure 2B i) the prescribed stoichiometric volume of stock precursor through its steel tube and carefully rinses itself prior to switching to another stock precursor. Once all components are aspirated, mixing is conducted (Figure 2B ii) directly in the tube by pulsing the liquid controllably several times resulting in the desired formulation. Once ready, the mixture is ready to be dispensed into the well plate (Figure 2B iii) at a designated position, the tube is flushed with pure solvent and the formulation bot prepares the next ink. The deposition bot moves in to immediately load the hollow capillary with the ready-made ink (Figure 2B iv) and approaches the substrate to deposit the ink at a designated location on one or more substrates according to a pre-determined pattern (Figure 2B v). The capillary is cleaned automatically (Figure 2B vi) before performing the next deposition. The cooperative workflow between the two bots should enable the seamless formulation and deposition of a large composition set of hybrid perovskite materials from their precursor and solvent libraries onto a single substrate. The substrate can be placed on a computer-controlled hotplate during deposition or moved to a hotplate to be annealed after all materials are deposited.

As a basic proof of concept of this workflow, we demonstrate how $MAPbBr_3$ is formulated and deposited in a step-by-step manner by the RoboMapper starting from MABr and $PbBr_2$ precursor salts in stock solutions (Video S1 and Figure S3A show). The entire process is completed within 8 minutes in a 30% humidity controlled dry lab. We demonstrate the versatility of the deposition head to satisfy the resolution and requirements for different HT-characterizations by creating different patterns of $MAPbBr_3$, including dot arrays (50 μm diameter), lines (1.5 mm length), and square patches (500 by 500 μm) with 600 nm thickness (Figure 2C). The square patches are evaluated by UV-Vis absorption measurements, the lines are ideal for grazing incidence wide angle X-ray scattering (GIWAXS), whereas HT μPL (Figure S4A) and synchrotron-based HT WAXS measurements (Figure S4B) can be conducted on dot arrays. We confirm the resulting material is $MAPbBr_3$ by comparing its bandgap to previous reports (Figure S3B),[61,62] and its diffraction pattern to $MAPbBr_3$ powders (Figure S3C).

To demonstrate multi-material processing, we continuously formulate and deposit dot arrays of 5 commonly studied HMH compounds on the same substrate, namely the hybrid perovskites $MAPbBr_3$, $FAPbBr_3$, $MAPbBr_{2.4}Cl_{0.6}$, $MAPbBr_{1.5}Cl_{1.5}$ (mixed halide), and the Ruddlesden-Popper layered perovskite $(PEA)_2PbBr_4$. Figure 2D shows optical and fluorescence micrographs of each material printed on the substate. Different emission colors for each material agree with previous reports based on material bandgaps.[61,63] HT WAXS and μPL results revealing the structure and optical properties of the different compounds are plotted in Figure 2E. The (100) peak positions of $MAPbBr_3$ (1.056 $Å^{-1}$), $MAPbBr_{2.4}Cl_{0.6}$ (1.065 $Å^{-1}$) $MAPbBr_{1.5}Cl_{1.5}$ (1.075 $Å^{-1}$) and $FAPbBr_3$ (1.042 $Å^{-1}$) and the trends of (100) peak shift with cation and halide substitution/doping are in agreement with expectations.[61,64,65] The absence of (00*l*) peaks in WAXS from $(PEA)_2PbBr_4$ can be explained by the transmission geometry of WAXS and the formation of the layered perovskite structure with quantum wells parallel to the substrate plane.[66,67] Likewise, the emission peak positions of $MAPbBr_3$ (538 nm), $MAPbBr_{2.4}Cl_{0.6}$ (515 nm), $MAPbBr_{1.5}Cl_{1.5}$ (482 nm), $FAPbBr_3$ (550 nm) and $(PEA)_2PbBr_4$ (410 nm) obtained from μPL measurements are consistent with the fluorescence color observed in Figure 2E and with prior reports for these materials.[61,65,68] The structural and spectral results indicate compositional and phase purity indicative of success rinsing and cleaning protocols between successive ink formulations and depositions (see SI and Figure S5 for further details). These results highlight the proof of concept of the distributed RoboMapper workflow that can be expanded toward even more flexible and advanced implementations.

Palletization benefits: Acceleration, sustainability and scalability to big data

We evaluate the RoboMapper workflow's benefits from the perspectives of experimental cost, energy consumption, environmental impacts and scalability to large datasets in comparison to manual research and existing MAPs built on serial automation, as depicted in Figure S2. To do so, we have applied the LCA methodology specified in the ISO 14040-14044 series by considering all aspects of sample preparation from cradle to grave. The functional unit selected to compare the three workflows is the experimental investigation of 500 mixed ion perovskite compositions, a relatively large dataset by current standards. The characterizations include optical microscopy, PL, XRD, and photostability evaluations. The details of LCA including definition of the system boundary (Figure S6), the full life cycle inventory (Table S1-S5) and the results (Table S6-S13) are presented and discussed in SI. We have broken down the total time needed to conduct tasks into smaller rate-determining steps (see pie charts in Figure 3A) during formulation, processing, and characterization, we are able to estimate the average time for each step, from similar evaluations conducted in the literature[24,27,31] as well as a decade of experience conducting such workflows in our lab.

Time savings. Our analysis (Figure 3A) reveals the RoboMapper workflow and traditional MAPs save considerable time during ink formulation and sample preparation compared with the manual workflow because of the more efficient, continuous, and automated procedures done by robots. While both RoboMapper and current generation MAPs are comparable in sample preparation time, considerable time savings by the RoboMapper are observed when it comes to characterization, primarily thanks to reduction of the number of operational steps associated with sample loading, alignment, and calibration. These time savings are considerable when palletizing 500 compositions. As a result, it can take as little as 6 days for 500 compositions palletized by the RoboMapper to be fully screened while the same task requires at least 54 days via serial automation and upwards of 84 days for manual workflow using full time labor. This constitutes a 9-fold acceleration in data generation for RoboMapper compared to existing MAP workflows and a 14-fold acceleration compared to manual experimentation (see inset of Figure 3D).

Cost and energy savings. Besides time savings, we also evaluate the amount of waste, cost (excluding labor and equipment) and energy demand for all three workflows (Figure 3B). We find that automation in general reduces waste, cost and energy demand compared with the manual workflow. However, the palletization feature of the RoboMapper further reduces these categories by more than an order of magnitude thanks to micro-printing/coating capabilities. We estimate a sample dataset generated by RoboMapper workflow will only cost \$0.34 and 0.344 kWh, in contrast to \$17.61 and 8.936 kWh for the manual workflow, and \$2.82 and 6.284 kWh for existing MAPs, respectively (Table S13). This leads to impressive saving ratios (see inset of Figure 3D) by the RoboMapper workflow, including 8 times cheaper and 18 times more energy efficient than existing MAPs and 52 times cheaper and 26 times more energy efficient than manual workflows.

Environmental Impact. Figure 3C displays the environmental impacts of the three workflows on the selected five categories that are most concerning or dominant calculated by LCA from all impacts (Figure S7A). Clearly, the environmental categories related with toxicity are being affected the most for all three workflows. Nevertheless, the RoboMapper workflow reduces the freshwater ecotoxicity, marine ecotoxicity and human carcinogenic toxicity impact categories (0.11, 0.08, 0.05) by more than 24 times and 18 times compared with the manual workflow (2.69, 1.98, 1.20) and serial MAPs (2.04, 1.44, 0.91), respectively. Even more impressive, the RoboMapper workflow yields almost negligible effects on global warming and fossil resource scarcity, with a score of 0.0025 and 0.0075, respectively, which correspond to only 19.8 kg CO_2 emitted and 7.3 kg of oil consumed, equivalently, compared with 536.4 kg CO_2 and 224.8 kg oil for manual workflow, and 350.8 kg CO_2 and 123.6 kg oil for serial MAPs (Figure S7B).

Environmental impact of characterization. We further looked into what aspects of materials research contribute the most to each impact category by further sub-dividing the workflow into six categories and assessing their associated LCA: perovskite materials, solvents, supplies, electricity consumption during material processing (electricity-P), electricity consumption during characterization (electricity-C), and waste, as summarized in Figure 3C and Figures S9-13(A-D). Our analysis shows that electricity usage by materials characterization is by far the dominant factor across all impact categories for all three workflows, mainly because of the use of high-power instrumentation, such as XRD, lasers and solar simulators. Remarkably, HT characterization of palletized materials saves considerable time and reduces operational steps, including alignment and calibration which result in considerable reduction in electricity consumption. This in turn reduces the environmental impact of RoboMapper materials research quite dramatically.

Waste reduction due to palletization. In the interest of evaluating the environmental impacts of the sample preparation method in terms of material utilization without characterization, we have analyzed the impacts excluding the characterization (Figure S8). As expected, the absolute and relative impacts of the three factors (perovskite materials, supplies and waste) decrease considerably compared to manual workflows (Figure S8 and Figure S9-13F) with adoption of serial MAPs (Figure S9-13G) and RoboMapper (Figure S9-13H), primarily because of reductions in material and supply utilization. However, for the MAPs with serial automated workflow, the consumption of solvents that primarily comes from the cleaning steps during sample preparation begins to play a big role, especially in global warming and fossil resource scarcity (Figure S9&13G) and the increased power consumption from the automated platform makes electricity the secondary contributor to the freshwater and marine ecotoxicity (Figure S14-15G). Only the RoboMapper benefits from miniaturization of materials quantities, where the influence of the perovskite materials, solvents, supplies and waste are comparably negligible along most categories (Figure S8). As a result, the increased usage of electricity by the robots and instruments becomes a more significant factor although the total environmental impacts are still lower than MAPs and manual workflow (Figure S9-13E&H).

Scalability toward big data. We have sought to evaluate the scaling differences among the three workflows to large datasets consisting of thousands of experiments in terms of required research time, energy demand, and cost. Figure 3D reveals the long-term benefits of palletization in materials research: the RoboMapper workflow can scale much more easily and effectively to large datasets than serial MAPs. For instance, completing a large dataset of 10,000 experiments can take nearly 2.9 years with serial MAPs, requiring 60 MWh of energy and costing >$28,000 just in terms of materials and supplies. Compared to manual workflows, this requires considerably less time (4.6 years), energy (90 MWh), and costs considerably less ($170,000). However, these savings pale in comparison to what can be achieved by the RoboMapper workflow which completes 10,000 experiments in 4 months, consumes just over 3 MWh of energy and is estimated to cost $3,000. Overall, our analysis indicates tremendous benefits of the RoboMapper palletization approach in terms of efficiency, sustainability, and economy especially for generating medium to large materials datasets.

Multi-modal QSPR mapping in metal halide perovskites

For our main demonstration, we seek to map the double cation and double halide quaternary system $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ and preliminarily identify compounds which meet the requirements for hybrid tandem photovoltaics with Si. This alloy is one of the most consequential mixed ion HMHs investigated to date as it contains the $FA_{0.83}Cs_{0.17}Pb(I_{0.83}Br_{0.17})_3$ (x=0.17, y=0.17) hybrid perovskite popularized in photovoltaics[54,56,59] and and the inorganic perovskite $CsPb(I_{1-x}Br_x)_3$ (x, y=1) desirable in light emission applications.[69] However, the experimental phase diagram and phase boundaries for this alloy have not been established with sufficient detail,[38,58] the boundaries of the single phase regions are not known, and QSPRs that relate these phases to their properties of relevance to photovoltaics are sparse or have not been established. Our search will focus initially on creating a coarse phase diagram, from which we will identify the boundaries of the iodine-rich single-phase compound. In a subsequent round we will refine the phase boundary and map the bandgap and photostability in the region of interest to construct QSPRs. We will use the predictive power of QSPRs to identify new compositions which achieve the target bandgap of 1.7 eV and rank them in terms of photostability. For the purposes of this study, all thermal processing (150°C for 10 minutes) and measurement conditions (room temperature) are selected to resemble those of typical thin film preparation and characterization.[58,64,70] This will ensure high fidelity with phases typically observed in thin film devices, however the reader is reminded that measured phase diagrams should be considered nonequilibrium.

$FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ quaternary phase diagram. To build the phase diagram of $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$, 61 individual compounds in the compositional space by varying x and y discretely from 0 to 1 were synthesized and palletized across one substrate spaced by 500 μm (Figure S14 and Table S14). The palletized sample was packaged in nitrogen and shipped to the CMS beamline at NSLS II, where it was subject to HT WAXS mapping (Fig S4B).

Phase identification begins with the 4 unary compounds at the corners. The circular average of the scattering patterns shown in Figure 4A are identified as those of the α phase $FAPbI_3$ (cubic), δ phase $CsPbI_3$ (orthorhombic), α phase $FAPbBr_3$ (cubic), and γ phase $CsPbBr_3$ (orthorhombic), respectively, matching our expectations and previous reports.[38,61] To facilitate the analysis and categorization of phases present in the mixed phase domains later, we label as 1C the cubic α phase that is FA- and I-rich, 1O the orthorhombic δ phase that is Cs- and I-rich, 2C the cubic α phase that is as FA- and Br-rich, and 2O the orthorhombic γ phase that is Cs- and Br-rich. In Figure 4B, we present the 4 binary subsets of the quaternary system (full range in Figure S15) showing structural trends with change of compositions along the four edges of the phase diagram. Using the labeling scheme, we see the (101) peaks of 1O phase shifting to higher q values with the increasing Br contents when x ≤ 0.4 for $CsPb(I_{1-x}Br_x)_3$ due to the decreased X site radius with substitution of the small Br^- ion with I^- (Figure 4B i). At x=0.4, we observe the co-existence of both the (101) peak of 1O phase at q~0.7 $Å^{-1}$ and the (101) peak of 2O phase at q~1.02 $Å^{-1}$. With further increase of Br contents, the peaks belonging to the 1O phases disappear and a shifting towards higher q values of (101) peaks in 2O phases is observed. Similarly, substitution of FA^+ with smaller Cs^+ also results in the shift towards higher q values of (100) peak in 1C phases, as well as (101) and (102) peaks in 1O phases for $FA_{1-y}Cs_yPbI_3$ (Figure 4B ii). Interestingly, when the 1O and 1C phases co-exist for 0.2 ≤ y ≤ 0.8, we observe a more obvious shift of peak positions in 1O phases, possibly because of more Cs^+ doped into 1O phases. Very similar transitions from 1C to 2C ($FAPb(I_{1-x}Br_x)_3$), and 2C to 2O phase (FA_{1-}

${}_yCs_yPbBr_3$) are also observed in Figure 4B iii-iv. The complete phase diagram (Figure 4C) is built by analyzing the fingerprint peaks representing each phase for all the compositions (Figure S16). The circles with different colors indicate the phases of measured compositions. The phase boundaries are determined from the middle of two adjacent clusters of data points with different phases.

In the absence of an actionable phase diagram like in Figure 4C, the community has tended to rely on basic calculations using the Goldschmidt tolerance factor, t, and octahedral factor, μ, to predict the formation of stable structures at room temperature.[71-74] The predicted phase diagram for $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ is presented in Figure 4D for comparison (see supporting information for details). We estimate $0.464 < \mu < 0.521$ across the entire composition, which suggests that all compounds meet the minimum criterion for perovskite structure formation ($\mu > 0.41$).[71-74] Meanwhile, $0.849 < t < 1.066$ and therefore some compositions should be cubic ($0.9 < t < 1$), while others are likely to be distorted orthorhombic perovskites ($0.849 < t < 0.9$). For $t > 1$, the A-site cations are too large to support the perovskite structure and a hexagonal structure is predicted to form instead.[71-74] Evaluating the differences between our actual and computed phase diagrams, we find that the latter neither captures the mixed phase regions nor does it predict the specific phase boundaries accurately. This is not entirely surprising given the tolerance factor is designed to predict thermodynamically stable structures. Moreover, the correct ionic radii are difficult to measure or calculate and different values have been reported.[71-74] This varies the tolerance factor values and affects the prediction of the actual structures. Thus, experimental phase diagrams are essential for practitioners of the field to understand the structure and phases of their materials and begin to establish structure-property relationships.

QSPRs in a perovskite PV region of interest. Having obtained an initial coarse phase diagram, we now focus our attention on the FA- and I-rich region ($0 \leq x \leq 0.35$, $0 \leq y \leq 0.45$) of interest to the PV community.[54,56,59,75] We have refined the phase diagram (Figure 5A) with 20 additional compositions palletized by the RoboMapper for HT WAXS evaluation (Figure S17 and Table S15). The close-up view of the phase diagram in the region of interest (Figure S18) shows the refined phase boundaries and reveal the compositions with a small amount of Cs (<25%) are ones most likely to form a solid solution giving rise to a single photoactive phase (1C phase), the so-called “black phase” desired in photovoltaic applications. For compositions with higher Cs and low Br contents, the 1O phase, also known as “yellow phase”, forms together with 1C, which is highly undesirable for photovoltaics. Increasing the amount of Cs requires higher Br contents to suppress the 1O phase formation. At low Cs concentration, all the compositions are within the single-phase region, for example at y=0.1, as illustrated in Figure 5B i and ii, the (100) peaks and the lattice constants change linearly with Br content. However, at higher Cs concentration, for example at y=0.3 as indicated in Figure 5B iii and iv, a sudden shift of the (100) peak position and a decrease of lattice constant are observed when crossing the phase boundary. This is associated to an incongruent inclusion of the added Cs and Br into the lattice of 1C phase owing to formation of a second phase (1O), whereas all the Cs and Br are incorporated into the single-phase solid solution within the 1C phase field.

To get a better overall understanding of the composition-structure relationship and derive our first QSPR, we have quantitatively analyzed the lattice constants of the 1C phase field obtained from the (100) peaks of all the compositions within the region. Figure 5C shows a 2D color map of the 1C lattice constant for the entire photovoltaic region of interest. A monotonic color evolution with varying Br and Cs contents and the linear contour lines (black dashed lines) within the 1C phase region highlights the evolution expected within the phase field. The color band in 5C deviates when crossing the phase boundary into the mixed phase region, as do the contour lines. The contour line within the 1C phase field is obtained by linearly fitting the lattice constant (Table S16) , a (R^2=0.992). As a result, we obtain the QSPR of the 1C phase lattice constant with the Br (x) and Cs (y) contents for the 1C phase within the single-phase region, as expressed below:

$$a(\text{Å}) = 6.399 - 0.369x - 0.154y \qquad (1)$$

The scatter plot in Figure S19B also demonstrates that the lattice constants of the 1C phase changing with Cs content for all the measured compositions follow the same general trend, where all the lattice constants of the compositions with pure 1C phase fall along the linear trend line (calculated with equation (1)) while those with mixed phases (in the red circles) are above the trend line.

We turn our attention to the relationship between the bandgap and composition within the photovoltaic region of interest and seek to establish a QSPR within the single-phase region. To do so, the RoboMapper was used to palletize the wider region of interest near the 1C phase with 80 compositions (Figure S20 and Table S17) allowing HT-μPL mapping to evaluate the emission properties, including bandgap (Figure S22A). In general, we observe the expected blue shift of emission peaks with both increasing amount of Cs and Br, with a significantly stronger blueshift with addition of the latter. Figure 5E features two examples of the influences of varying Cs at fixed Br content (i) and varying Br with fixed Cs content (ii) on the PL spectra. We extract the bandgap by fitting emission spectra and establish a bandgap map across the composition region of interest (Figure 5D). The bandgap mapping of the composition space reveals the compositions which achieve the same bandgap within the 1C phase field by finely tuning the Br and Cs contents. Isolines indicating equal bandgap are established by surface fitting the bandgap map (Figure S22B) for both x and y (R^2 = 0.952; Table S18) using Vegard's model, which is a commonly used physics-based model for compound semiconductions.[76,77] We thus come up with a QSPR model fit to express the effects of Br (x) and Cs (y) contents on the bandgap of the quaternary system as expressed in equation (2):

$$E_g = 1.54 + 0.412x + 0.0799y - 1.40 \times 10^{-3}x^2$$
$$-2.16 \times 10^{-3}y^2 + 9.63 \times 10^{-3}xy \qquad (2)$$

The obtained QSPR model relating bandgap to composition is a valuable tool to identify eligible compositions achieving target bandgaps within the mapped composition space.

Next, we seek to link the ambient photostability of $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ compounds within the same region of interest to evaluate the influence of the 1C phase composition and the presence of the phase boundary on photostability. To do so, a copy of the palletized samples in Fig. 5D was exposed to 1 sun in ambient air (30%RH) for a duration of 1h (Figure S23A), after which the sample was mapped once again by μPL immediately thereafter. By comparing the normalized PL spectra before (Figure S22A) and after (Figure S23B) 1 sun exposure, we observed three categories of photodegradation (Figure 5F): single emission peak undergoes red shift (Type 1); double emission peaks form and undergo shift (Type 2); total loss of emission peaks (Type 3). We visualize the distribution of these three types of photodegradation behavior across the composition map (Figure S23C). Most compositions undergo Type 1 photodegradation. To quantify the relative photostability of the compositions, we define an "instability score" which relates to spectral shifts (see SI for information). Figure 5G visualizes the composition-dependent photo-stability map based on the instability score. Our investigation reveals that photostability varies somewhat monotonously in certain regions while exhibiting islands of stability and instability. For instance, considering the location of the 1C phase boundary, it is noteworthy that the compositions within the 1C phase space are considerably more stable than those in the mixed phase region 1C+1O. Moreover, compositions exhibiting lowest stability tend to be in the mixed phase region with high Cs content and low Br content. We further validate the conclusions of the photo-stability map by performing time-dependent μPL on 4 additional representative compositions exhibiting different stability behaviors (See Figure S24 and S25 for details). The results are consistent with the photostability map and confirm its reliability. So far, we have demonstrated a multi-dimensional data framework (Figure 5H) created by our RoboMapper workflow to reveal the QSPRs of the quaternary mixed ion $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ perovskites.

Data-driven wide bandgap hybrid perovskite screening. To further validate our established QSPRs as well as demonstrate the practical use case, we predict 14 compositions (Table S19) achieving the same bandgap but with very different A-site and X-site compositions as per QSPR calculations (Figure 6A inset). For this case study we have selected ~1.70 eV which is the optimal bandgap for the top cell of perovskite/Si tandem solar cells. The RoboMapper was used to formulate and print these compositions for QSPR validation with μPL mapping. All the predicted materials have similar and overlapping PL spectra (Figure S26). The measured bandgaps achieve an average value of 1.710 eV with a narrow distribution of 0.007 eV (Figure 6A), very close to the target/predicted 1.70 eV with only small deviations. To examine the transferability of the observed properties and correlations from RoboMapper samples to traditional thin films, we selected 7 compositions to make spin-coated thin films and compare the bandgap and photostability results with RoboMapper samples (Figure S27). Remarkably, we observe similar bandgap results for each composition among the RoboMapper samples and thin films (Figure S27) and the average bandgap for thin films is 1.707 eV with a standard deviation of 0.010 eV, almost the same as RoboMapper results (1.713 ± 0.006 eV) (Figure 6B). Similarly, photostability of the compositions achieving ~1.7 eV for both RoboMapper and thin film samples show an identical general trend (Figure 6B inset) and a good match with the predicted stability (Figure S27A). The compositions with high Br content show intermediate instability scores with obvious red shifts of PL spectra, whereas the compositions with high Cs content exhibit high instability scores with double emission peaks formation. Only the compositions with ideal Br and Cs contents present low instability scores with very small shifts (Figure 6C and Figure S27C). It is worth mentioning that the discrepancy of the absolute value of the bandgap and instability score between the RoboMapper samples and the thin films may come from the difference of morphology and grain size due to different processing methods and need further study in the future.

To prove the relevance for device application, we fabricated the perovskite solar cells (PSCs) in inverted p-i-n architecture (Figure 6D) with three representative high Cs, ideal and high Br compositions that show the same bandgap but very different photo-stability (Figure 6C). Interestingly, we found the devices with ideal composition exhibit the best device performance and reproducibility with an average power conversion efficiency (PCE) of 19.20 ± 0.45%, overperforming the high Br (17.75 ± 0.59%) and high Cs (14.36 ± 1.65%) devices (Figure 6E). The other device parameters like open circuit voltage (V_{OC}), short circuit current density (J_{SC}), and fill factor (FF) also present the same trend (Figure S28 and Table S20). The champion device for the ideal composition has a V_{OC} of 1.18 V, a J_{SC} of 21.54 mA/cm^2, and an FF of 78.83%, resulting in a PCE of 20.06% (Figure S29 and Table S21). We further monitored the PCE evolution of the three types of devices under 1 sun illumination at the open circuit condition within one hour (Figure 6F). As expected, the devices with ideal composition show the best photo-stability and can maintain 93.2 ± 5.9% of their initial value, while the high Br devices drop to about a half (53.6 ± 5.9%) and the high Cs devices only retain 23.2 ± 2.4% of the initial PCE. These results are in great consistent with the prediction of our QSPR models. We also notice that the devices with ideal composition display almost negligible hysteresis compared with the other two compositions (Figure 6G and Figure S30). According to previous reports, it has been shown that the hysteresis is directly related to the migration of halide ions/vacancies[60,78] while the halide migration and the halide vacancy density are also responsible for the photo-induced phase segregation[53,79] and photodegradation.[60,80,81] This is in good agreement with our observations and provides us a pathway to understand the reasons for the different performance and photostability of the three compositions. Thus, we experimentally measured the rate of superoxide generation using the dihydroethidium fluorescent probe (Figure S31), which has been shown the higher rate of superoxide generation is linked to the higher density of vacancies in the hybrid perovskites.[60,80,81] As indicated in Figure 6H, we did find the ideal composition exhibits a significantly lower superoxide yield and generation rate, being reduced by almost 50% compared to the high Cs composition and by 30% compared to the high Br composition, providing evidence that the ideal composition has the lowest vacancy density. This conclusion is further verified by the different light-induced degradation rates of the thin films of the three compositions in the presence of oxygen and moisture (Figure 6H inset and Figure S32). We found the high Cs thin film degraded very quickly and totally turned yellow after 7 hours when the high Br thin film began to show obvious color change, while the thin film with ideal composition could still maintain most of its black phases after 12 hours. These are consistent with our hypothesis that the low vacancy density in the ideal thin film can suppress the diffusion of halide ions and oxygen, which in turn limits the transport of halide ions to form iodide- and bromide-rich domain as well as slows down the rate of superoxide species formation, resulting in inhibited light-induced phase separation and a slow degradation rate (Figure 6I).

Conclusions

In this work, we have developed a robotic platform-RoboMapper and demonstrated an end-to-end miniaturized, automated workflow from on chip experimental design to ink formulation and micro-printing multi-materials on a single chip for high-throughput multi-modal characterization with a wide range of laboratory- and synchrotron-based microprobes. The unique RoboMapper workflow is shown by the life cycle assessment to be more eco-friendly than the manual and existing automated workflow by yielding significantly less environmental impact on ecosystems, human toxicity and GHGEs, and decreasing time, energy consumption and cost by 9 to 52 times. A state-of-the-art case study on a quaternary $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ perovskite system proves the ability of RoboMapper to rapidly establish the quantitative structure-property relationships in a large and complex compositional space. The constructed quaternary phase diagram based on experimental results provided more accurate and practical guidance to the composition-structure relationship than theoretical predictions. The quantitative lattice constant, bandgap, and photo-stability maps focusing on the photovoltaic region of interest provide insights into the screening and prediction of compositions among a wide range of options for target applications. Using the developed QSPR models, we searched for the phase pure and photostable perovskite alloy exhibiting an ideal bandgap of ~1.7 eV suitable for perovskite-Si hybrid tandem solar cells. The predicted new wide bandgap compounds are validated with both RoboMapper samples and spin-cast thin films, matching the predictions with remarkable consistency, proving the reliability and fidelity of the platform and our model. The predicted ideal compound was translated to single junction p-i-n solar cells with a PCE of 19.20 ± 0.45%, low hysteresis, and far better photostability than other compounds evaluated within the QSPR map at 1.7 eV. Furthermore, we evaluated the scientific link between photostability and the vacancy concentration and showed that the ideal composition exhibits low halide vacancy concentration, which can explain why photo-induced halide segregation and photobleaching of the ideal compound were considerably slower. This platform could also be applied to other solution processable materials such as organic semiconductors, quantum dots, and nanoparticles to pave the way towards the fully autonomous experimentation of ink-based semiconductor materials, ink formulations and (opto)electronic devices co-design with the guidance of artificial intelligence (AI).

Experimental Procedures

Resource availability

Lead contact

Further information and request for resources and reagents should be directed to and will be fulfilled by the lead contact, Aram Amassian (aamassi@ncsu.edu).

Materials availability

This study did not generate new reagents. All the reagents used are commercially available as described in Materials subsection.

Data and code availability

All the data needed to evaluate the conclusions are available in the files in the Supplementary information section. All other data and the code related to this work are available upon reasonable request from the authors.

Materials

Formamidinium iodide (>99.99%), formamidinium bromide (>99.99%), methylammonium bromide (>99.99%), phenylethylammonium bromide (>99.99%) were purchased from GreatCell Solar. Cesium iodide (99.999%), cesium bromide (99.999%), lead iodide (99.999%), lead bromide (99.999%), lead chloride (99.999%), dimethylformamide (> 99.8%, anhydrous), dimethyl sulfoxide (>99.9%, anhydrous) were purchased from Sigma Aldrich. All the materials and solvents were used as received without further purification.

Inks and RoboMapper sample preparation

The Si/SiO_2 substrates were pre-cleaned with soap, acetone, IPA and rinsed with DI water followed with nitrogen drying. 1 M FAI, FABr, CsI, PbI_2, $PbBr_2$ were dissolved in DMF/DMSO(4:1) as stock solutions and stirred in the nitrogen filled glove box overnight. 0.5M $CsPbBr_3$ was used as the stock solution directly by dissolving equal molar of CsBr and $PbBr_2$ in pure DMSO due to the very low solubility of CsBr in the polar solvent. The different ink formulations were made automatically by the liquid handler through mixing certain volumes of the stock solutions controlled by the home-built LabVIEW software. After each ink was formed, it would be deposited in the 384 well plate in order. Then the inks were loaded into a 50 μm diameter hollow capillary and directly printed on the substrates by the dispensing robot. 0.5 V applied voltage and 0.5 s dispensing time were applied during the printing and the array has 300 μm center to center distance. All the experiments were conducted in a 30% humidity controlled dry lab at room temperature. After the printing was done, the samples were transferred to the glove box and annealed at 150 °C for 10 mins.

Perovskite precursor solution and device fabrication

To make $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ perovskite thin films, 1.4 M precursor solutions were prepared by weighing the stochiometric amount of FAI, CsI, FABr, $PbBr_2$, and PbI_2 in precleaned glass vials and dissolved into 800 μL DMF and 200 μL DMSO (4:1 volume ratio). After stirring for 4 hours, fresh solutions were used to fabricate thin films and devices. For the device fabrication, ITO glasses were sonicated in a sequence of soap water, DI water, acetone, and IPA for 15 min, respectively. The N_2-dried ITO glasses were transferred into glovebox after UV-ozone for 15 min. 50 μL MeO-2PACz (0.5 mg mL^{-1}) was spin-coated onto ITO substrates at 5000 rpm for 30s and then being annealed at 100 °C for 10 min. After cooling for 5 min, 1.4 M wide-bandgap perovskite solution (with 30 mol % MACl additive) was spun coated at 5000 rpm for 30s with 200 μL ethyl acetate antisolvent dripped onto the spinning substrates at 15s and was then annealed at 150 °C for 10 min. After cooling to room temperature, the substrates were transferred into the chamber of thermal evaporator. LiF (1 nm), C_{60} (25 nm), BCP (6 nm) and Ag (100 nm) were deposited in sequence to finish the device fabrication.

Characterization and stability test of solar cell device

J-V characteristics were measured with a Keithley 2400 source meter under 100 mW cm^{-2} illumination by the AM 1.5G solar simulator (Class 3A, Newport). The light intensity was calibrated by the KG5 silicon reference cell before the measurement. All the solar cell measurements were conducted in the nitrogen filled glove box (O_2, $H_2O < 0.1$ ppm) with a scan rate of 0.2 V s^{-1} (0.02 V voltage step and 100 ms delay time). The device area is 0.076 cm^2 and is determined by the shadow mask during the thermal evaporation of contact. No mask/aperture is used during the solar cell testing. The photostability test was also performed in the glovebox with the home-built setup without any encapsulation. The light source consists of a white LED array (TX 100W LED Chip) and a 120° concentration lens. The light intensity is calibrated by the KG5 silicon reference cell and equivalent to 1 sun AM 1.5 G illumination. A fan is used to cool the sample and maintain the temperature around 30-35° under 1 sun illumination.

High-throughput wide angle X-ray scattering measurement (HT-WAXS)

HT-WAXS was performed in the transmission geometry at the Complex Materials Scattering (11-BM CMS) beamline of National Synchrotron Light Source II (NSLS-II), Brookhaven National Lab. The double side polished Si substrate with high-throughput printed arrays was mounted on a motorized x-y translation stage. The x-ray beam with the wavelength of 0.918A, 13.5k eV energy, perpendicularly penetrated through the printed samples. The x-ray beam size was set to 0.2x0.2mm in order to cover isolated printed grains. The scattering signal was collected by an area detector, Pilatus 800K, placed 259mm away from the sample. The exposure time was 10s. All the measurements were done automatically with the python software controlling the automated sample translations and data collection.

Steady-state and time-dependent micro photoluminescence measurement (μPL)

The steady-state and time-dependent photoluminescence measurements were performed in a home-built μ-PL setup. For $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ compositions, 532 nm laser beam was focused to a ~50 μm spot to excite the whole individual pixel on the sample mounted on a x-y translation stage with the power of 20 μW. The reflected light was then collected with the same focusing lens and after passing through a 550 nm edge pass filter, the PL was spectrally resolved by a spectrometer (Acton SP2300i) and detected by a deep cooled CCD camera (PIXIS) with 2s exposure time. The Br and Cl based compositions are measured with the same setup, except that 400 nm laser beam and 450 nm long pass filter was used. The μPL spectrum of 2D perovskite PEA_2PbBr_4 were taken using an Edinburgh Instruments FS-920 photoluminescence spectrometer with 360 nm excitation.

Time-dependent μPL was conducted by keep illuminating the pixel for 30 minutes with 532 nm CW laser with adjusted power density close to 1 sun (~ 100 mW/cm^2). The μPL spectra was collected every 1 min with LabView controlled program.

Optical and fluorescence microscopy

Optical microscopy images were obtained on a Nikon Eclipse LV100POL microscope equipped with motorized XYZ stage with 20X-, 50X and 100X objectives via automated stitching controlled by the NIS-Elements software. The fluorescence images were excited with a solid-state white light source (SOLA SM II 365) and collected through a BV-2A long-pass filter cube. The exposure time was 100 ms.

UV-visible spectroscopy

The UV–vis transmittance measurements were performed using an F40-UVX (Filmetrics) for thin films. The home-built UV-vis set up modified from the Nikon Eclipse 80i microscope was used for material arrays and the spectra were collected with Ocean Insight flame UV-vis spectrometer.

Superoxide generation

Superoxide probe testing was performed by dissolving 1mg of Dihydroethidium probe (ThermoFisher) in 1ml of chlorobenzene. Sonication was used to facilitate the dissolution. Perovskite films were submerged into this solution. The film was illuminated with visible light source using 520 nm long pass optical filter. The solution was exposed to xenon lamp with approximate light intensity of ~10 mWcm^{-2} (~ 0.1 sun). Photoluminescence spectra were recorded using an excitation wavelength of 520nm and bandwidth of 10 on Edinburgh Instruments FLS920 spectrofluorometer. The excitation light source for the fluorimeter was a 450 W Xe arc lamp equipped with a monochromator.

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Author Contributions

A.A. and T.W. conceived the project and designed the experiments. A.A., M.A., K.G., and D.S. supervised the project. T.W. and M.R. developed the robotic hardware and software. T.W. led the data collection and analysis. T.W., K.D., and B.G. performed robotic experiments for sample preparation. R.L. performed the structural characterization (WAXS) at Beamline 11-BM, NSLS II. H.A. and R.W. developed the μPL setup and performed the mapping. H.A. also carried out the time-dependent μPL experiments. L.S.L. performed the LCA study and analysis. J.W. and T.W. fabricated the solar cell devices and performed the device characterizations. M.C. and B.G. conducted the superoxide generation measurement. R.W.E. assisted with the data visualization. T.W. and A.A wrote the manuscript. All authors contributed to the discussion of the work and editing of this manuscript.

Declaration of Interests

TW and AA have filed a provisional patent related to the work.

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Figure Titles and Legends

Figure 1. Schematic of the RoboMapper platform and workflow
(A) Illustration of the experimental design of inks formulated from different AX, BX_2 stock solutions and solvents and mapped on a chip.
(B) Schematic of the RoboMapper micro-experimentation platform enabling automated ink formulation and micro-printing of a wide variety of solution-processable materials from a library of precursors onto a common substrate. The materials array is then subject to multi-modal characterization and mapping using a wide range of laboratory- and synchrotron-based microprobes.
(C) Demonstration of multi-layer data stacks linking the materials, structures and properties to establish the quantitative structure-property relationship (QSPR).

Figure 2. Illustration of the RoboMapper platform for solution processing hybrid perovskite materials and multimodal micro-characterization
(A) Precursor (AX, BX_2) and solvent library used to formulate inks for different ABX_3 and $A_{n+1}B_nX_{3n+1}$ metal halide perovskites.
(B) Step by step illustration of the platform's workflow from ink preparation (i-iii) to micro-printing (iv-v) on a common substrate, as well as carefully optimized flushing (iii) and cleaning (vi) steps to eliminate cross-contamination while allowing reuse of syringe and capillary.
(C) Photographs of (i) the dot array with 50 µm diameter of $MAPbBr_3$ being printed; (ii) the line array consisting of 30 lines of $FAPbBr_3$, $MAPbBr_3$ and $CsPbBr_3$ with 1.5 mm length; and (iii) the square patches of $MAPbBr_3$ (500 by 500 µm) with 600 nm thickness printed using RoboMapper. Scale bars are 200 µm (i), 2mm (ii), 250µm (iii).
(D) Optical microscopy (OM) and fluorescence OM (FOM) images with 50X magnification of multiple HMH compounds micro-printed by the RoboMapper on the same substrate; the scale bar is 20 µm.
(E) High-throughput wide angle x-ray scattering patterns (HT-WAXS) and micro-photoluminescence (HT-µPL) spectra of pixelated samples in (D) confirming the structure and optical properties of the pixels correspond to the compounds.

Figure 3. Life cycle assessment on the manual, automated and RoboMapper workflow
(A) Comparison of accumulated time to screen (formulate, process and characterize) 500 individual formulations by the three workflows. Inset: Pie charts representing the fraction of time allocated to the most time-consuming steps in each workflow.
(B) Comparison of total time, waste, cost and energy demand required for all three workflows to screen 500 perovskite formulations. Labor and capital costs are excluded.
(C) Accumulated column plot of the normalized environmental impact of three workflows on global warming, freshwater ecotoxicity, marine ecotoxicity, human carcinogenic toxicity, and fossil resource scarcity in terms of perovskites, solvents, supplies, electricity of the process (electricity-P), electricity of the characterization (electricity-C) and waste.
(D) Scaling of time, energy demand, and costs with the increasing number of experiments for the three workflow scenarios. The inset table shows the relative saving ratio in terms of time,

energy demand and cost when comparing the RoboMapper workflow with manual and automated workflows.

Figure 4. On-chip Robo-Mapping of quaternary phase diagrams: Demonstration of the $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ mixed ion perovskite system's non-equilibrium phase diagram

(A) Circular average of WAXS patterns and phase identification of the unary compounds at the four vertices of the phase diagram: $FAPbI_3$ (x=0, y=0) in the 1C (cubic) perovskite phase; $CsPbI_3$ (x=0, y=1) in the 1O (orthorhombic) non-perovskite phase; $FAPbBr_3$ (x=1, y=0) in the 2C (cubic) perovskite phase; CsPbBr3 (x=1, y=1) in the 2O (orthorhombic) perovskite phase.

(B) Structural evolution from WAXS measurements along the four edges of the $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ phase diagram with a $\Delta x=\Delta y=0.2$ step size, corresponding to four binary systems: $CsPb(I_{1-x}Br_x)_3$ (y=1; i), $FA_{1-y}Cs_yPbI_3$ (x=0; ii), $FAPb(I_{1-x}Br_x)_3$ (y=0; iii) and $FA_{1-y}Cs_yPbBr_3$ (x=1; iv).

(C) Quaternary phase diagram of the $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ system constructed from HT-WAXS measurements of 61 compositions. The substrate with all compounds was annealed at 150 ˚C for 10 mins and allowed to cool. HT-WAXS mapping was performed at room temperature in a vacuum.

(D) Predicted phase diagram based on the Goldschmidt tolerance factor, *TF,* and Octahedral factor, *OF.* The compound is expected to be tetragonal or hexagonal when $TF > 1$; cubic when $0.9 < TF < 1$, and orthorhombic when $TF < 0.9$. All compositions are eligible to be perovskites as $\mu > 0.41$.

Figure 5. Phase boundary refinement and optical analysis of a photovoltaic region of interest

(A) Refined phase map of the 1C phase region consisting of 20 additional compositions ($0 < x < 0.35$; $0 < y < 0.45$).

(B) The evolutions of (100) peaks of the 1C phase with varying Br content (x) for low Cs (y=0.1) and high Cs (y=0.3) concentrations. At low Cs concentration, a monotonic increase of the q value and lattice parameter with increasing Br (x) indicate single phase solid-solution alloy, whereas at higher Cs content, the (100) peak and lattice constant variation with increasing amount of Br are not monotonous when crossing the phase boundary, which also corresponds with formation of an additional 1O phase ($0.05 < x < 0.2$).

(C) 2D color map of 1C phase lattice constant showing monotonous trend within the phase boundary and deviations outside the 1C single phase boundary. The black dashed contour lines are obtained by fitting all the lattice constants within the single-phase region linearly for both x and y ($R^2 = 0.992$). The grey dashed line is the approximate phase boundary separating the single and double phase regions.

(D) 2D color map of bandgaps extracted from µPL measurements for a sample set RoboMapped with 0.05 increments in x and y. The solid dots denote the actual compositions measured while the dashed contour lines denote equal bandgap compositions as obtained by fitting the global data with a quadratic function for both x and y according to Vegard's law ($R^2 = 0.952$). The model therefore links the bandgap to x and y values corresponding to halide and cation composition.

(E) Examples of the µPL spectra with fixed halide composition and changing cation composition (left, x=0.25, varying y) or fixed cation composition and varying halide (right, y=0.1, varying x).

(F) Photodegradation in air under 1 sun for 1 hour reveals three types of PL spectral changes, which we classify as type 1 (a single peak undergoes red shift), type 2 (formation of double peak), and type 3 (loss of PL signal).

(G) A photo-stability map obtained by ascribing an instability score according to the peak wavelength shift values ($\Delta\lambda$) before and after exposure under 1 sun for 1 hour. For Type 1, $\Delta\lambda$ is used directly as the instability score; for Type 2, since obvious photo-induced phase segregation can be observed, the maximum shift value $\Delta\lambda_{max}$ was used in the equation $0.46*\Delta\lambda_{max} + 43.6$ to make sure the instability score distributed between 50 and 90; Type 3 was ascribed with a score of 100; the black dashed contour lines indicate the bandgaps while the grey dashed line is the approximate phase boundary separating the single 1C phase and 1C+1O phase regions.

(H) The full data stacks from the morphology, phase, structure, bandgap and photostability mapping of $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ compounds, demonstrating the QSPRs.

Figure 6. Screening of $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ wide bandgap hybrid perovskite alloy for device application

(A) The measured bandgaps from µPL of 14 predicted compounds with ~ 1.7 eV bandgap showing a narrow distribution of 1.710 ± 0.007 eV. The x axis indicates the specific compositions with Br percentage(x)/Cs percentage (y). The inset shows the predicted bandgap map by our model and a total of 14 compositions with the same 1.7 eV bandgap extracted from the map.

(B) Comparison of the statistical bandgap results from the same 7 compounds of RoboMapper samples (1.713 ± 0.006 eV) and spin-coated thin film samples (1.707 ± 0.010 eV). The inset shows the instability score of the 7 compounds of RoboMapper samples and spin-coated thin films.

(C) The PL spectra of three representative compounds with high Br content ($FA_{0.9}Cs_{0.1}Pb(I_{0.675}Br_{0.325})_3$), ideal Br and Cs contents ($FA_{0.775}Cs_{0.225}Pb(I_{0.749}Br_{0.251})_3$) and high Cs content ($FA_{0.575}Cs_{0.425}Pb(I_{0.796}Br_{0.205})_3$) before and after photodegradation in air under 1 sun for 1 hour, showing the same bandgaps and very different photo-stability, consistent with the trend predicted by the photostability map.

(D) Schematic of the inverted p-i-n perovskite solar cell device structure. BCP, bathocuproine.

(E) The statistical power conversion efficiency results from 20 devices for each compound: high Cs (14.36 ± 1.65%); ideal (19.20 ± 0.45%); high Br (17.75 ± 0.59%).

(F) Evolution of the normalized PCE of three types of solar cells at the open circuit condition under 1 sun illumination at 35 °C in the nitrogen filled glove box within one hour. The error bars denote the standard deviation of the PCE from 3-9 cells.

(G) Hysteresis indexes of the three types of devices extracted from the forward and reverse scans with 0.2 V/s scan rate.

(H) Normalized PL intensity of the probe solution (0.01 mg/ml of dihydroethidium in chlorobenzene) as a function of perovskite films aging time under continuous light illumination (0.1 sun) and constant oxygen flow at 620 nm, representing the yield of superoxide generation.

The inset shows the images of three films under 1 sun illumination in ambient air, indicating the different photo-degradation behavior.

(I) Schematic of the influence of vacancy density on the photostability of mixed halide perovskites. The higher density of vacancies promotes the halide ion migration and leads to faster photo-induced halide segregation by forming I-rich (red square region) and Br-Rich (green square) domains. Also, more vacancies are favorable for oxygen ingress into the volume of grains and causes a higher superoxide formation rate, resulting in faster photobleaching rate of the perovskite.

Supplemental Video Titles and Legends

Video S1. The demonstration of the RoboMapper platform automatic workflow with $MAPbBr_3$ as an example including ink formulation, mixing, on-chip printing and cleaning.