Hierarchical assemblies of functional nanoparticles can have applications exceeding those of individual constituents. Arranging components in a certain order, even at the atomic scale, can result in emergent effects. We demonstrate that printed atomic ordering is achieved in multiscale hierarchical structures, including nanoparticles, superlattices, and macroarrays. The CsPbBr₃ perovskite nanocubes self-assembly into superlattices in ordered arrays controlled across 10 scales. These structures behave as single nanoparticles, with diffraction patterns similar to those of single crystals. The assemblies repeat as two-dimensional planar unit cells, forming crystalline superlattice arrays. The fluorescence intensity of these arrays is 5.2 times higher than those of random aggregate arrays. The multiscale coherent states can be printed on a meter-scale panel as a micropixel light-producing layer lattice arrays. The fluorescence intensity of these arrays is 5.2 times higher than those of random aggregate arrays. The multiscale coherent states can be printed on a meter-scale panel as a micropixel light-producing layer.
align the nanocubes. The well-resolved interfringe distances of 0.29 and 0.41 nm were also indexed to the (220) and (020) lattice planes, respectively, of orthorhombic CsPbBr$_3$ (Fig. 1, C and D, and fig. S4). Fast Fourier transform (FFT) analyses suggested that the square basal plane in each CsPbBr$_3$ nanocube was normal with respect to the <001> direction, wherein the four faces were formed by (220) planes (Fig. 1D and fig. S4).

The NP superlattices were induced by slow evaporation of the solvent in an airtight storage tank filled with n-hexane vapor (see Materials and Methods for details). This procedure led to the aggregation of nanocubes and the gradual formation of individual superlattices with a square geometry, as well as the eventual precipitation of nanocubes and the gradual formation of individual superlattices. Scale bar, 10 nm. (I and J) The corresponding FFT patterns of superlattice located at the positions of the red and blue squares in (H).

To obtain detailed understanding of the formation process for NP superlattice, both real time and in situ, we performed GISAXS to obtain structural information (Fig. 2A). Structure formation progresses in four stages: amorphous phase (I), simple cubic phase (II), transitional phase (III), and simple tetragonal phase (IV) (Fig. 2, B to D, and fig. S12). In stage I, there were no rings or dots displayed for the long-range NP orientation or atomic arrangement. After 1.5 min, when the assembly process moved to stage II, diffraction rings appeared at an equal distance in $q_x$, $q_y$, and $q_z$, which was indexed as simple cubic superlattices with lattice parameters of $a = b = c = 10.8 \pm 0.1$ nm (see fig. S13 and table S2 for indexation). After a long interval, there was a transition from the simple cubic structure to the final simple tetragonal phase at stage III. The diffraction rings began to transform into arcs, indicating a better crystallographic orientation. A new bright spot gradually appeared at a larger $q_z$ value, owing to the decrease in the interparticle distance.
along the $z$ direction. At stage IV, the NP superlattices reached their final simple tetragonal structure, where a significant contraction occurred along the $c$ axis, whereas the distances between the nanocrystals along the $a$ and $b$ axes remained equal (fig. S14). The drastic decrease in length along the $c$ axis can be attributed to ligand interdigitation owing to the detachment of partial ligands in the (001) facets of the nanocubes (Fig. 2D). The simple tetragonal superlattices had unit cell constants $a = b = 10.2 \pm 0.1$ nm and $c = 9.0 \pm 0.1$ nm (see fig. S15 and table S3 for indexation). The grazing-incidence wide-angle x-ray (GIWAXS) patterns of the NP superlattices demonstrated sharp, sporadic Bragg spots, whereas the out-of-plane mode of the XRD patterns showed clear periodic crystallographic planes, indicating the vertical crystallographic orientation of the $z$ axis with respect to the substrate (fig. S16, A to D). Pre-adlayers of bromine anions on the surface increased the dipole–dipole attraction between the CsPbBr$_3$ nanocrystals and substrates, which may have played a key role in guiding the preferential NPs orientation. In contrast, the crystallographic planes disappeared when NP superlattices were formed on the substrate without pre-adlayers of bromine anions. Furthermore, the GIWAXS patterns switched to diffraction rings, accompanied by randomly oriented crystals (fig. S16, E to H).

The adjusted $z$ axis of the superlattice features inspired us to print large-area crystalline superlattice arrays by a droplet splitting method using a dispensing machine and by a lithography etching technique (Fig. 3A). We first designed a variety of micrometer-level grooves on the substrate by photolithography etching, after which the liquid in the needle of the dispensing machine was injected into the appropriate groove sites by controlling the dispensing pressure level during the up and down movement of the needle along the $z$ axis (Fig. 3B). During the injection process, solvent evaporation control caused the NPs to nucleate in the cube grooves and eventually aggregated (17, 29). The concave structure provided a confined environment that drastically decreased the nucleation barrier for the assembly of nanocubes in topographical traps (Fig. 3B) (15). The

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**Fig. 2. Different stages of progress toward a simple tetragonal superlattice.** (A) Schematic of the sample placed in the grazing-incidence small-angle scattering (GISAXS). The incident beam of wave vector $k_i$ makes a small incident angle $\beta_i$ with respect to the sample surface. GISAXS probes the scattered intensity close to the specularly reflected beam. The top left inset is a typical TEM image of NPs projected along the $z$ direction showing equal interdistances along the $x$ and $y$ axes. The top right inset is a typical TEM image of NPs projected along the $x$ direction showing shorter interdistance along the $z$ axis of the superlattices than along the $y$ axis. The right inset contains the typical GISAXS pattern: arc with a high $q$ spot in the $z$ direction and obliquely superior spots on both sides. Scale bars, 20 nm. (B) Interdistance between NPs along $y$ and $z$ axes directions as a function of time. (C) Temporal evolution of GISAXS patterns during the in situ measurement of the self-assembly of the NPs, showing the transition from a colloidal suspension to an equal spacing superlattice to a compressed superlattice via contraction of the $c$ axis. (D) Overall depiction of the consecutive phase transitions during the self-assembly of NPs. The black arrows represent the dipole moment direction of single NPs along the $c$ axis. The blue rectangle regions represent the range of the interligand interdigitation.
precision spitting tip of the needle was moved in the \( xy \) plane with tens of thousands of repetitive injections to splice the micrometer arrays and then the meter-scale panel. When the cubic grooves in the substrate were densely functionalized by bromine anions, the nanocubes tended to form crystalline superlattice arrays (Fig. 3, C and D). The size and shape of the grooves and the pressure of the injection of the dispensing machine were not the main factors influencing the atomic ordering of the superlattice arrays (fig. S17). The presence of crystalline superlattice arrays was further confirmed using a polarizing microscope with a conoscope lens. For the NP superlattices, a Maltese cross birefringence with an interference color circle was observed (Fig. 3E) when the \( z \) axis was perpendicular to the substrate. In contrast, no Maltese cross birefringence was observed when the orientation of the \( z \) axis was changed (Fig. 3G). Anisotropic NP-superlattice arrays with Maltese cross birefringence extending over the micrometer scale were visible on the surface of the pattern zone (Fig. 3F). Each cube groove contained, on average, tens of thousands of uniformly aligned nanocubes, with the NP-superlattice arrays spanning the entire range of the wafer, and the \( z \) axis orientations aligned vertically toward the substrate (fig. S18).

The hierarchical assemblies were composed of crystalline arrays of anisotropic ordered superlattices packed with NPs that had consistent atomic orientations. These assemblies can be used as the basis of a promising strategy for enhancing the performance of microlight-emitting devices (30, 31). We found that this structure increases the brightness of backlight panels of NPs. The NPs normally exhibit excellent brightness characteristics at the single-particle level; however, the brightness decreases if the NPs are aggregated in a disorderly fashion into films. Currently, the pixels of backlight panels are typically composed of randomly aggregated NPs (30). Random NP aggregates typically emit photons in all directions and exhibit low brightness owing to insufficient convergence (Fig. 4A). However, when the NPs in this study were assembled into anisotropic simple tetragonal superlattices, the resulting crystalline superlattice arrays were approximately 5.2 times brighter than arrays of random NP aggregates, after normalizing the quality (Fig. 4B and figs. S19 to S21). This brightness enhancement can be attributed to a combination of the directional dielectric-antenna effect inside the uniaxially coupled superlattice patterns and photon redistribution induced by oriented transition dipoles in macro panels (32–34). To verify this conjecture, we performed a linearly polarized photoluminescence (PL) emission test at 517 nm. A typical emission polarization ratio calculated using \( P_{\text{emi}} = (I_{\text{max}} - I_{\text{min}})/(I_{\text{max}} + I_{\text{min}}) \) was approximately 0.66 (Fig. 4C); this value is comparable to that of individual CdSe-CdS nanorods (0.75) (35, 36). This suggests that the transition dipole in the arrays was highly oriented (fig. S22).

Various programmable metamaterials with ultrahigh-brightness crystalline superlattice arrays were fabricated using lithography to

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Fig. 3. Packing of superlattices into crystalline superlattice arrays with \( z \) axis pointing upward. (A) Photograph of optimized dispensing machine for specific site arrays in operation. (B) The combination of the dispensing process and the grooved substrate to obtain the array. The NP solution was injected into the groove at the specific site of the substrate through the up and down movement of the high-precision needle along the \( z \) direction. (C) Photograph of the assembled meter-level crystalline superlattice array. Because of the low content, the luminous layer cannot be seen by the naked eye under the sunlight. (D) Schematic of the formation of crystalline superlattice array and aggregate array when patterned cube grooves are functionalized with or without adlayers of bromine anions, respectively. The insets are the corresponding fluorescence micrographs. The high brightness of the crystalline superlattice array panel can be recognized. Scale bars, 1 cm. Schematic of the flat superlattices along a \( z \) axis perpendicular to the sample stage plane (E) and random nanocube aggregates arrays (G) placed into crossed polarizers with the conoscope lens (top) and the corresponding polarized optical microscopes (bottom). Scale bars, 2 \( \mu \)m. Polarized optical microscopy of crystalline superlattices array chips (F) and random nanocube aggregates array chips (H). Scale bars, 10 \( \mu \)m.
adjust the topographical structure of silicon wafers. These materials exhibited large-scale topology regulation (Fig. 4, D and E, and fig. S23). We also assembled red and blue arrays of the crystalline superlattice with enhanced PL by tuning the precursor mixture ratios of Br⁻/I⁻ and Br⁻/Cl⁻ for other halogen-type nanocubes. Three monochromatic primary PL colors were successfully achieved using the Commission Internationale de l’Eclairage (CIE) 1931 color coordinates of (0.37, 0.63) for ultrapure blue, (0.174, 0.779) for ultrapure green, and (0.712, 0.287) for ultrapure red, which represents 97.2% color saturation per the Rec. 2100 standard (100.4% per the CIE 1976 color space), thereby demonstrating the ultrawide color display (Fig. 4F, fig. S24, and table S4). These results can be attributed to the superperfect superlattice arrays with lattice consistency produced by hierarchical transformation of the NPs, superlattices, and macroarrays (fig. S25).

DISCUSSION
From a fundamental perspective, superperfect assemblies with uniaxial orientation displayed previously unachieved accurate spatial placement across the centimeter, nanometer, and atomic scales, resulting in strong emission bursts. Transformations from simple cubic to simple tetragonal crystalline structures have been achieved. An understanding of the successive stages of assembly dynamics was gained through in situ monitoring. Crystalline superlattice arrays have proven emergent effects along the c axis, resulting in optical properties that exceed those of the individual building blocks and random aggregates. Parallels in the behavior of green, red, and blue perovskite nanocubes suggest a possible fundamental universality. The large-area ordering of NP assemblies can be regulated by the substrate components, which is conducive to the development of long-range ordering of other semiconductors and metal or dielectric NP assemblies. Theoretically, template-assisted printing assemblies can be used to engineer sophisticated superperfect assembled systems, which will help meet the demand for high-brightness and multiphoton quantum light sources, as well as potentially exploit the next-generation miniaturization of light-emitting displays toward arbitrary surface patterns, high polarization, ultrahigh brightness, and an ultrawide color gamut.

MATERIALS AND METHODS

Synthesis and purification of CsPbBr₃, CsPbCl₃, and CsPbI₃ NPs

In the typical synthesis of CsPbBr₃, 15.0 ml of octadecene (ODE), 207.0 mg of PbBr₂, 1.5 ml of oleylamine, and 1.5 ml of oleic acid in a three-neck flask were mixed under vacuum and heated up to 120°C for 1 hour (25, 26). The above mixture was subsequently heated to 170°C under argon and kept for 20 min, which was followed by a swift injection of 1.2 ml of the cesium oleate solution. The crude solution was cooled immediately to room temperature with the cold air gun and subsequently centrifuged at 7000 rpm for 4 min. After centrifugation, the precipitation was discarded. The supernatant solution was mixed with 60 ml of toluene, forming stable colloidal solutions, and stored at 22°C for 3 days. The resulting solution was purified by antisolvent ethyl acetate with a ratio of 1:3 to achieve precipitation of the NPs. The purified NPs were stored for the next preparation of superlattices.

As for CsPbCl₃ NPs, 20.0 ml of ODE, 241.3 mg of PbCl₂, 1.0 ml of oleic acid, 20.4 mg of 2,2’-iminodibenzoic acid (IDA), and 2.0 ml of oleylamine in a three-neck flask were mixed and heated up to 120°C under vacuum for 45 min. The above mixture was subsequently heated to 170°C under argon and kept for 20 min, which is followed by a swift injection of 1.2 ml of the cesium oleate solution. The other steps are the same as CsPbBr₃.

As for CsPbI₃ NPs, 15.0 ml of ODE, 402 mg of PbI₂, 3.5 ml of oleylamine, 20 mg of IDA, and 1.5 ml of oleic acid in a three-neck flask were mixed and heated up to 120°C under vacuum for 45 min. The above mixture was subsequently heated to 170°C under argon and kept for 20 min, which is followed by a swift injection of 1.2 ml of the cesium oleate solution. The other steps are the same as CsPbBr₃.
Assembly of NPs
The superlattices were created through solvent (hexane) evaporation in an airtight storage tank. Different lateral size superlattices were prepared by tuning the evaporation speed solvent and the concentration of the nanocrystals.

For the lateral 0.5-μm by 0.5-μm superlattices, an n-hexane solution containing NPs with sizes of side length = 7.2 nm (2 mg/ml, 5 μl) was dropped onto the carbon support film. The evaporation was complete within 30 min. For the lateral 1-μm by 1-μm superlattices, 30 μl of solution of NPs in n-hexane (6 mg/ml) was dropped onto the 1.5-cm by 1.5-cm silicon wafer under the atmosphere of n-hexane vapor and volatilized slowly for 24 hours. For the lateral 5-μm by 5-μm superlattices, 30 μl of solution of NPs in n-hexane (6 mg/ml) was dropped onto the 1.5-cm by 1.5-cm silicon wafer under the atmosphere of n-hexane vapor and volatilized slowly for 72 hours. For the lateral 10-μm by 10-μm superlattices, 30 μl of solution of NPs in n-hexane (6 mg/ml) was dropped onto the 1.5-cm by 1.5-cm silicon wafer under the atmosphere of n-hexane vapor and volatilized slowly for 96 hours.

Crystalline superlattice arrays
The topographic structure substrate of P <100> silicon with the mask was treated by the reactive ion etching of HBr. After the process of removing the mask, 30 μl of solution of NPs in n-hexane (10 mg/ml) was dropped onto the various topographic structure of a 1.5-cm by 1.5-cm wafer under the atmosphere of n-hexane vapor and volatilized slowly for 96 hours.

Random nanocube aggregates arrays
Ten microliters of solution of NPs in n-hexane (10 mg/ml) was directly dropped onto the topographic structure of a 1.5-cm by 1.5-cm substrate wafer under the atmosphere of n-hexane vapor. The above operation was repeated three times at intervals of 5 min. Then, they were volatilized for 96 hours.

Large-area crystalline superlattice arrays by optimized dispensing and photolithography etching technology
The inner diameter of the needle of the injection cavity of the dispensing machine was preferably 60 μm, and the length of the flow channel was preferably 55 mm. The tip of the needle was further ground before use. The pressure of the dispensing machine is set to 1 kPa. To control the volatilization rate, the dispensing device is covered by a closed acrylic shell. Two n-hexane atomizers were placed around the confined space. The solvent is preferably n-undecane. The topographic structure substrate with the mask was treated by the reactive ion etching of HBr. After the process of removing the mask, a solution of NPs in n-undecane (10 mg/ml) in the injection cavity was injected onto the various topographic structure of the substrate during the up and down movement of the needle along the z axis. The precision spit tip moves in the xy plane with tens of thousands of repetitive injections to achieve the splicing of micrometer arrays and then meter-level panels. The panels were then volatilized slowly for 96 hours.

Characterization and measurement
The morphology of the obtained products was performed using TEM on JEOL JEM-1011 with a thermionic gun operating at 100 kV of accelerating voltage and HR-TEM images on JEOL JEM-2100F working at an accelerating voltage of 200 kV. SAED patterns were taken with TEM on JEM-1011 with different camera lengths. Samples were prepared by dropping washed and diluted NP solutions onto carbon-coated 200-mesh copper grids with subsequent solvent evaporation in a vacuum.

Scanning electron micrographs together with energy-dispersed x-ray spectroscopy measurements were performed on a Hitachi S-4800 field-emission scanning electron microscope. Electron energy loss spectroscopy was recorded using a Gatan Quantum spectrometer installed on a Themis 300 microscope.

Powder XRD patterns of the obtained products were measured on a PANalytical Empyrean-2 x-ray diffractometer using Cu Kα source with a 1/2° fixed diffraction slit and a 1-mm receiver slit. Ultraviolet-visible absorbance spectra were recorded with a Shimadzu UV-1800 spectrophotometer. The PL measurements were acquired using an RF-5301PC spectrofluorophotometer with emission and excitation slit widths of 1.5 nm and an excitation wavelength of 360 nm. Cross-polarized optical images were collected using Olympus BX51-P. Fluorescence micrographs were collected using Olympus IX 83. PL emission polarization was conducted on the FLS 980 spectrofluorometer. Raman spectra and PL emission spectra of single pixel were conducted on the Horiba LabRAM HR Evolution.

The GISAXS measurements under the experimental conditions of a 0.154-nm incident x-ray wavelength and a distance of 250 cm between the sample chamber and the two-dimensional charge-coupled device (CCD) camera (Mar 165) were carried out in a 1W2A beamline at BSRF (Beijing Synchrotron Radiation Facility). A thin Pb strip was used to be a beam stop. Spot size is 10 mm by 5 mm. The GIWAXS measurements were also performed at the 1W2A beamline of BSRF. Spot size is 10 mm by 5 mm. The transmission mode small-angle x-ray scattering measurements were conducted at the Xeuss 2.0 with a PILATUS3 300K CCD camera. The distance between the sample and the detector was set to 250 cm.

The in situ GISAXS measurements were also conducted using the Xeuss 2.0 with the PILATUS3 300K CCD camera. The sample-to-detector distances were calibrated from the theoretical value of the characteristic peak of the standard silver behenate (AgC 22 H 43 O 2 ) crystal, q(001) = 1.07 nm⁻¹. The grazing angle was set as 0.8° for achieving the optimal signal-to-noise ratio. The x-ray exposure time of the sample was set to 60 s. The sample compartment was a custom-made, vacuum-able, sealed aluminum chamber with windows that enabled the x-ray beam to be directed at the sample while allowing the scattered signal to enter the detector through another window. The sample compartment had a viewing window for ease of observation. A weighing bottle containing 2 ml of hexane was placed at the corners of the chamber before the sample was placed, and the entire chamber was sealed and allowed to stand for 20 min to saturate the chamber with hexane vapor. The NP dispersion was then added dropwise to the substrate. To slow down the volatilization of the NP dispersion, a trace amount of ODE was usually added to the NP dispersion, allowing us to obtain the NP packing information until up to 40 min.

SUPPLEMENTARY MATERIALS
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