Electronic Supplementary Information

Synthesis of KIT-6 gyroidal mesoporous silica

Pluronic® P123 (4.0 g) was dissolved in 150 mL of dilute HCl solution (6 mL 37 wt% HCl in 144 mL deionized water). Then n-butanol was added to reach a concentration of 0.36 M, and the solution was stirred for 1 hour at 35 °C. 8.6 g of tetraethoxysilane was added dropwise and the solution was kept under vigorous stirring for 24 hours at 35 °C. This suspension was divided between several Teflon liners and heated at different temperatures (T_H = 60, 80, 100, 120 and 140 °C) in hydrothermal autoclaves. Finally, the products were washed several times with deionized water and ethanol using a vacuum microfiltration system before being dried and calcined at 550 °C for 6 h.

Synthesis of $MAPbBr_3$@KIT-6 and $MAPbI_3$@KIT-6

The procedure is similar to what was reported previously.[1] In brief, methylammonium iodide/bromide (MAX, X = I, Br) was prepared by mixing equimolar ratios of methylamine solution (40 % in methanol) and HBr (48 % in water) or HI (57 % in water) under constant argon flow, with the flask sitting in an ice bath for 2 h. The precipitate was then rinsed with diethyl ether three times and recrystallized from ethanol. Each perovskite solution was prepared by dissolving 0.2M lead halide $PbBr_2$ (or PbI_2) and 0.2M MABr (or MAI) in N,N-dimethylformamide solvent.
Both the solution and the empty silica template were heated to 80 °C prior to the impregnation. Then the solution was added to the powders in 5 µL increments, each followed by vigorous vortex mixing (2000 rpm), to reach a final concentration of 0.5 µL/mg. The powders were then placed on a hot plate and dried at 100 °C for 30 min. During that period, the color of the $MAPbBr_3$@KIT-6 samples changed from white to yellow (from yellow to brown for $MAPbI_3$@KIT-6).

Characterization

The nitrogen adsorption-desorption isotherms were obtained with a high-precision Belsorp-mini apparatus (Bel Japan, Inc.) at 77 K and the Barrett-Joyner-Halenda (BJH) method was used to calculate the pore size distribution of each silica template. Low-angle XRD profiles were acquired on a NANO VIEWER (Rigaku, Japan) equipped with a Micro Max-007 HF high-intensity micro-focus rotating anode X-ray generator. The wide-angle powder X-ray diffraction patterns (XRD) were obtained with a Rigaku Rint 2500 diffractometer with monochromated Cu Kα radiation at a rate of $0.2°\cdot min^{-1}$. The high-resolution transmission electron microscope (HR-TEM) and scanning transmission electron microscope high-angle annular dark-field (STEM HAADF) images were obtained with a JEM-2100F TEM (JEOL, Japan) operated at an accelerating voltage of 200 kV with a spot size of 0.7 nm. The UV-Vis-NIR reflectance data was acquired with a JASCO V-570 at a scan rate of 400 $nm\cdot min^{-1}$ from 220 to 1000 nm using a deuterium or halogen lamp as a light source (for the 220-350 nm range and 350-1000 nm range, respectively). Photoluminescence (PL) spectroscopy was performed on a JASCO FP8500 at a scan rate of 500 $nm\cdot min^{-1}$, with 10 nm bandwidth.

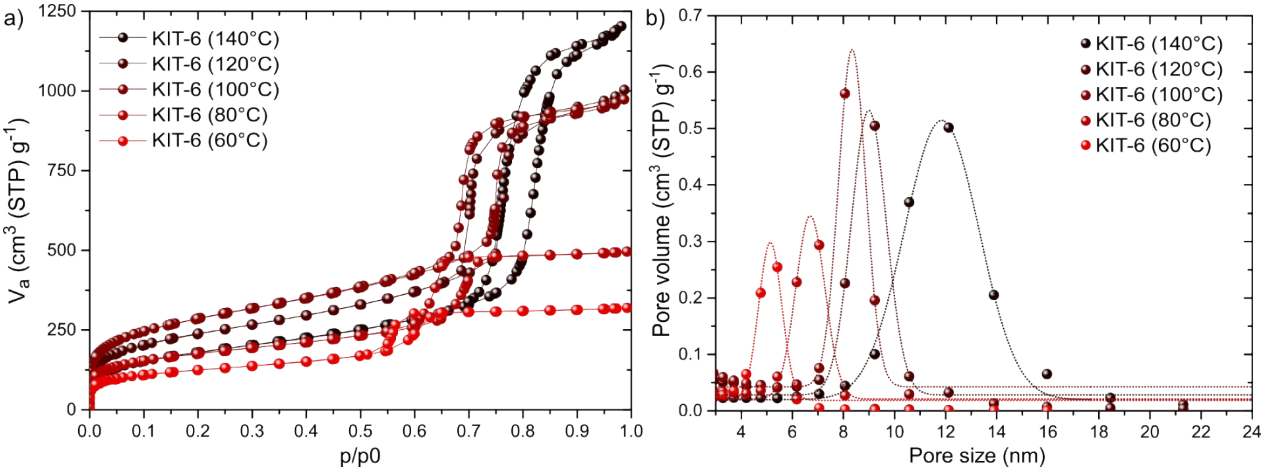

Figure S1. a) Adsorption-desorption isotherms from each KIT-6 mesoporous template and b) the pore size distribution calculated from the BJH method.

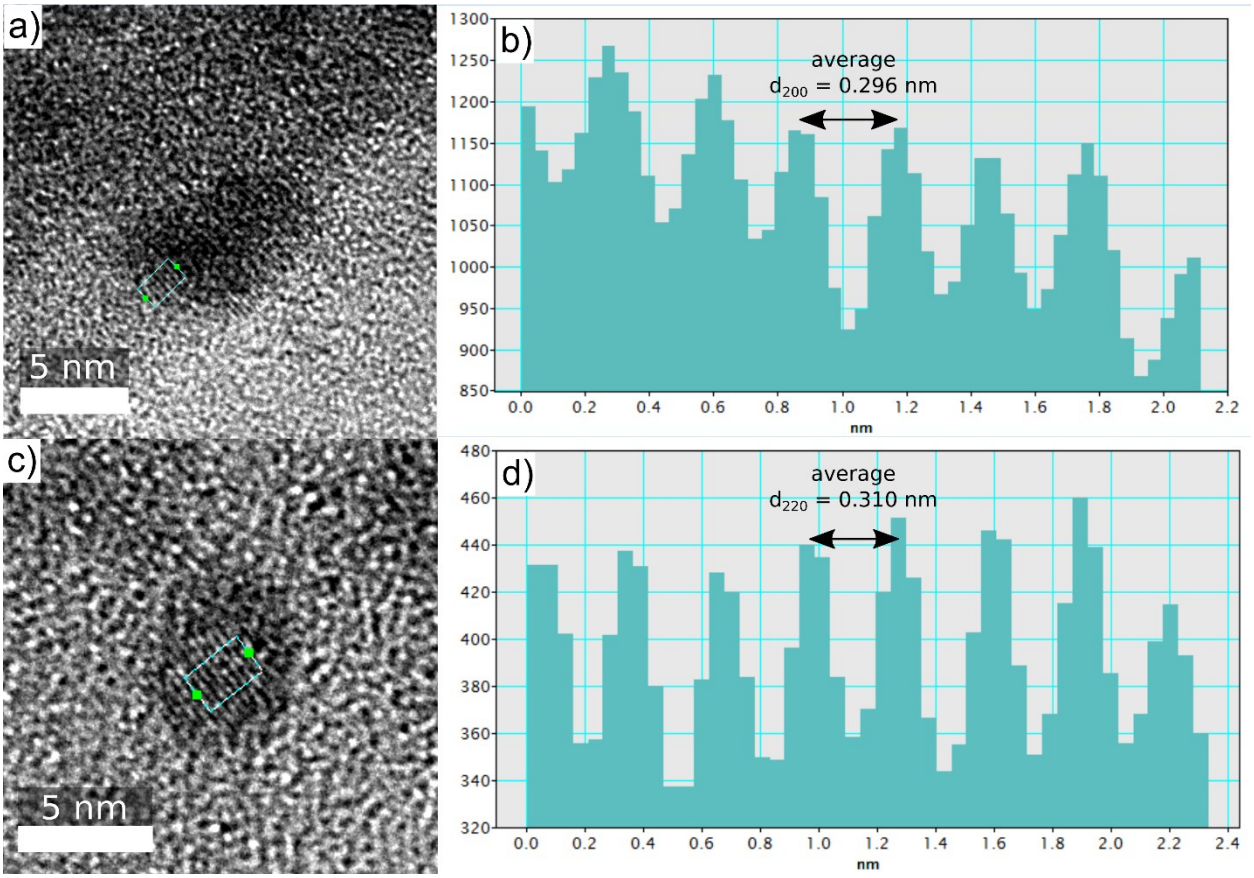

Figure S2: HR-TEM image and corresponding profile highlighting the a) and b) Fourier transforms from the HR-TEM images displayed in Figure 2c and 2d, respectively.

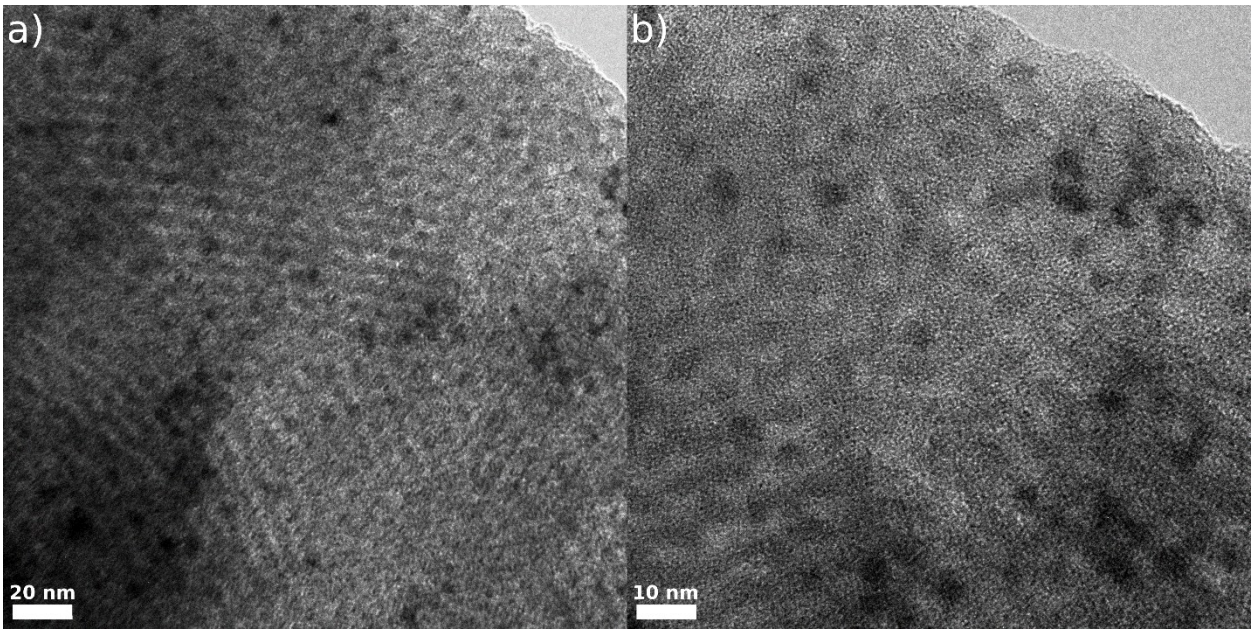

Figure S3. a) Low- and b) high-magnification TEM image of $MAPbI_3$@KIT-6 (T_H = 60 °C)

References

[1] V. Malgras, S. Tominaka, J. W. Ryan, J. Henzie, T. Takei, K. Ohara and Y. Yamauchi, *Journal of the American Chemical Society*, 2016, **138**, 13874-13881.