Pyridine-induced Dimensionality Change in Hybrid Perovskite Nanocrystals

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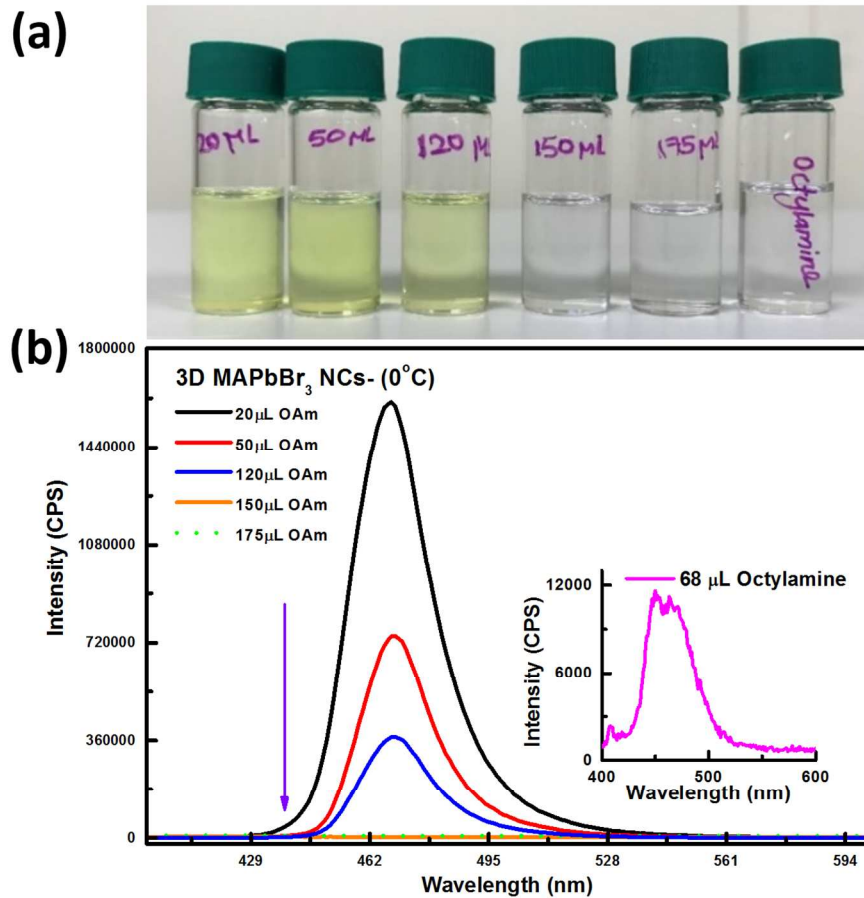
Figure S1. (a) The synthesis procedure of 2D nanostructures where we did vary the oleylamine concentration without adding pyridine, and adding similar molar amount of octylamine instead of pyridine (rightmost). (b) PL spectra of the 0°C-3D MAPbBr$_3$ NCs obtained by varying the amount of oleylamine to optimize the NCs synthesis procedure.
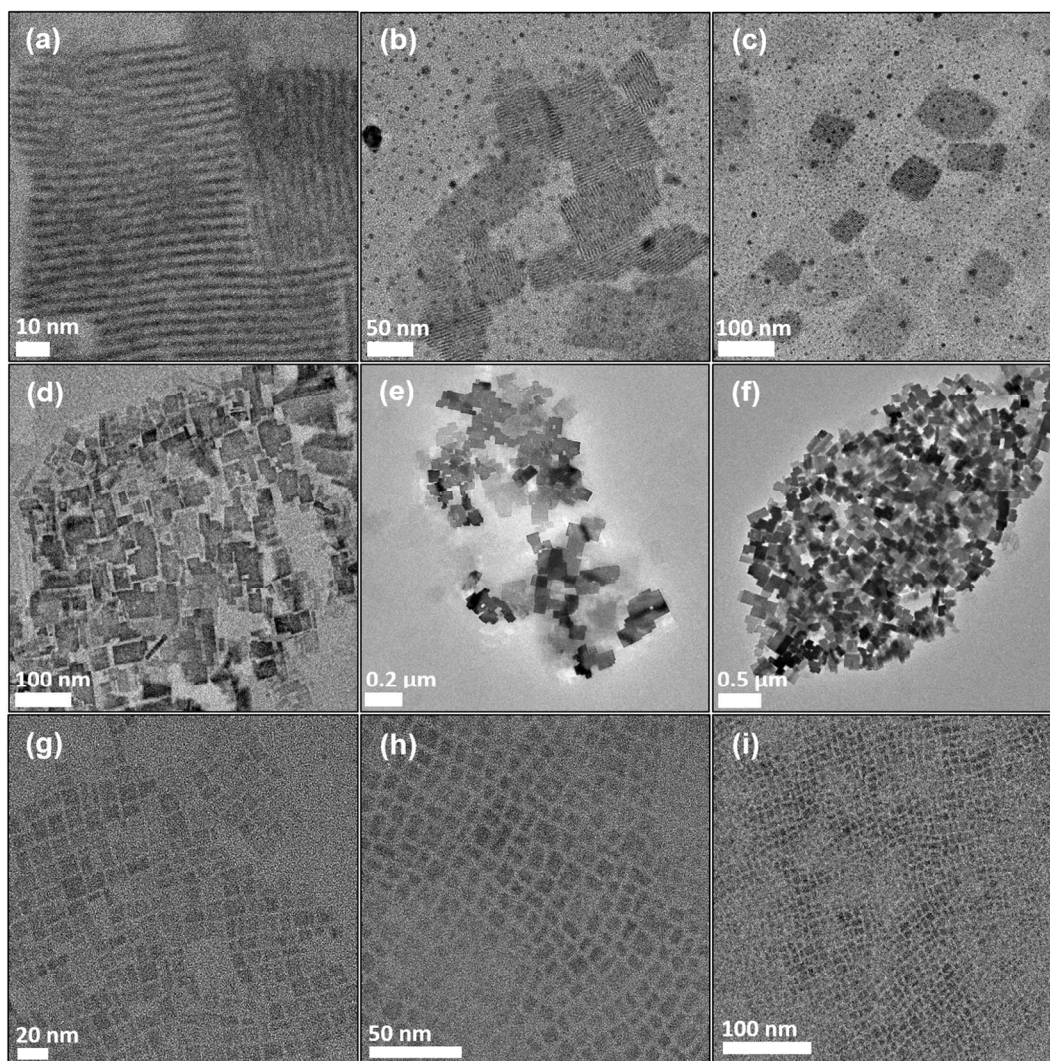
Figure S2. TEM images of (a,b,c) 0$^\text{o}$C, (d,e,f) 25$^\text{o}$C and (g,h,i) 60$^\text{o}$C synthesized MAPbBr$_3$ 2D-nanostructures after pyridine modifications presented at different magnifications.
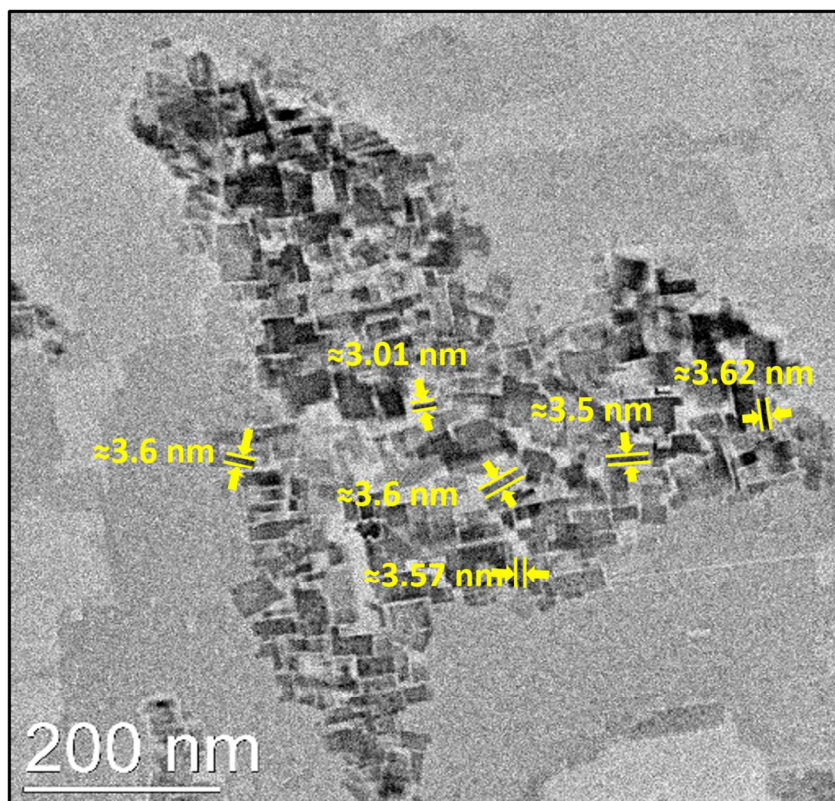
Figure S3. TEM image of the 2D MAPbBr$_3$ nanostructures synthesized at 25°C in the presence of pyridine. The thickness of the nanostructures is measured from the vertically standing nanostructures on the TEM grid.

(a) 2D NCs selected	n	2θ periodicity (º)	d-spacing
0ºC-py	2	5.54	1.59
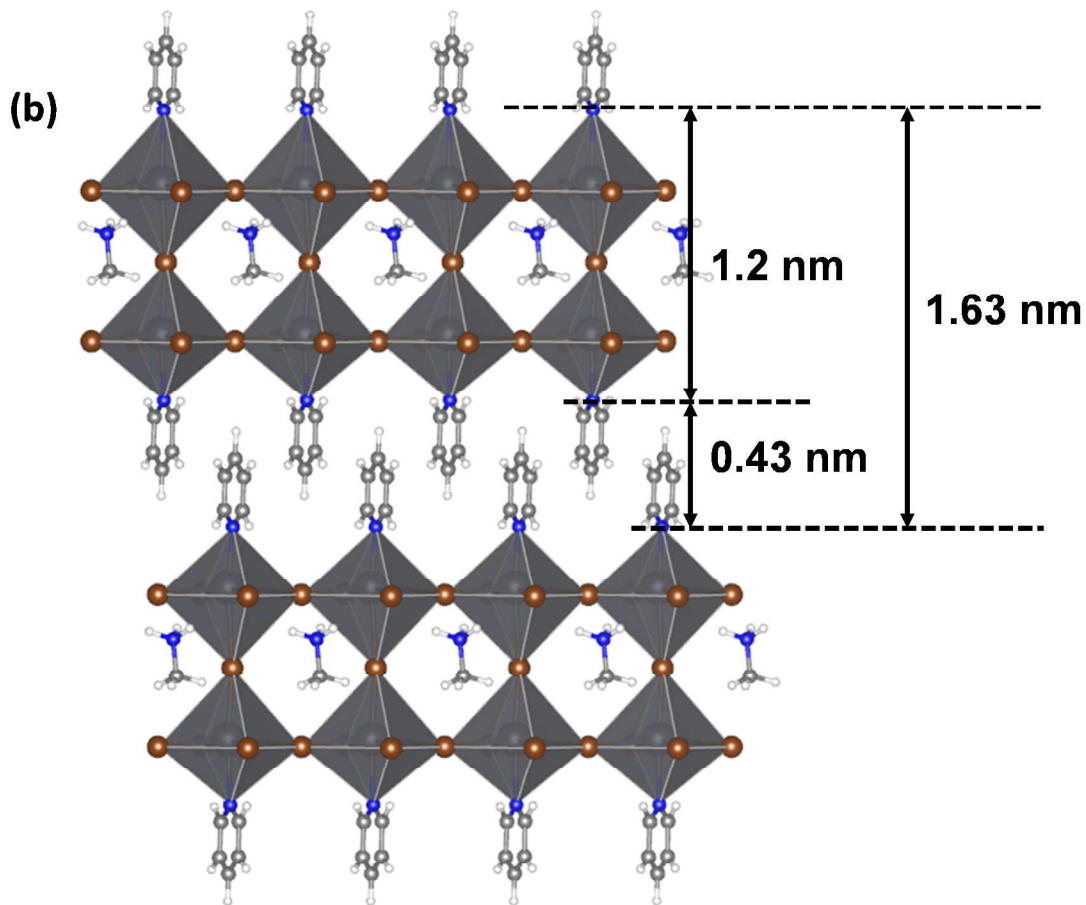
Figure S4: The average distance between the stacked 2D layers has been estimated from the XRD reflections periodicity measured in Figure 3a (blue line-highlighted part) for 0ºC-py MAPbBr$_3$ NCs of (n=2). The peak obtained from nanostructures stacking is obtained at 5.54º for n = 2 nanoplatelets, which corresponds to average layer spacing of 1.59 nm. Knowing the fact that the metal-halide octahedron unit is approximately 0.6 nm as reported in the literature,[1] the n=2 nanostructures are ~1.2 nm thick. In our case, the length of pyridine being ~0.39 nm, and with interdigitation between ligands in neighboring nanoplatelets (as shown in the Figure),[2] the ligand spacing is simulated to be ~0.43 nm, so the total distance of the octahedron units and ligand spacing is consistent with the layer spacing obtained from XRD.
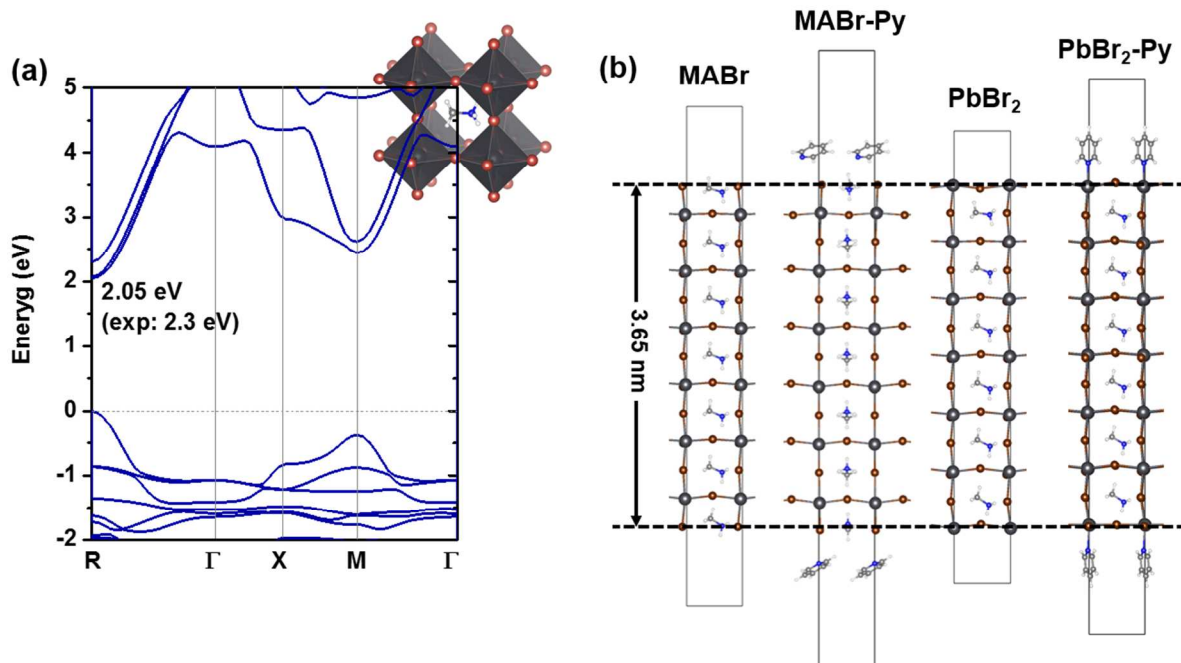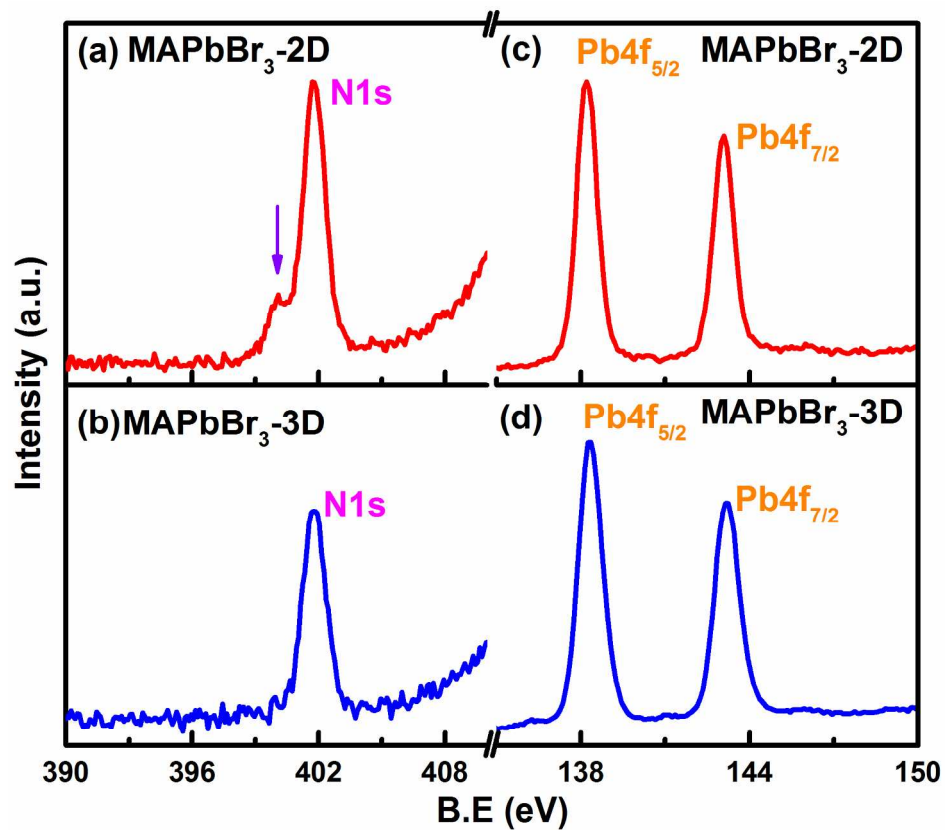
Figure S5. (a) Band structure of cubic-phase bulk MAPbBr$_3$ calculated at the DFT-PBE level of theory; (b) optimized MAPbBr$_3$ (001) slab structures (thickness= 3.65 nm) with MABr- and PbBr$_2$-rich terminations before and after pyridine addition.
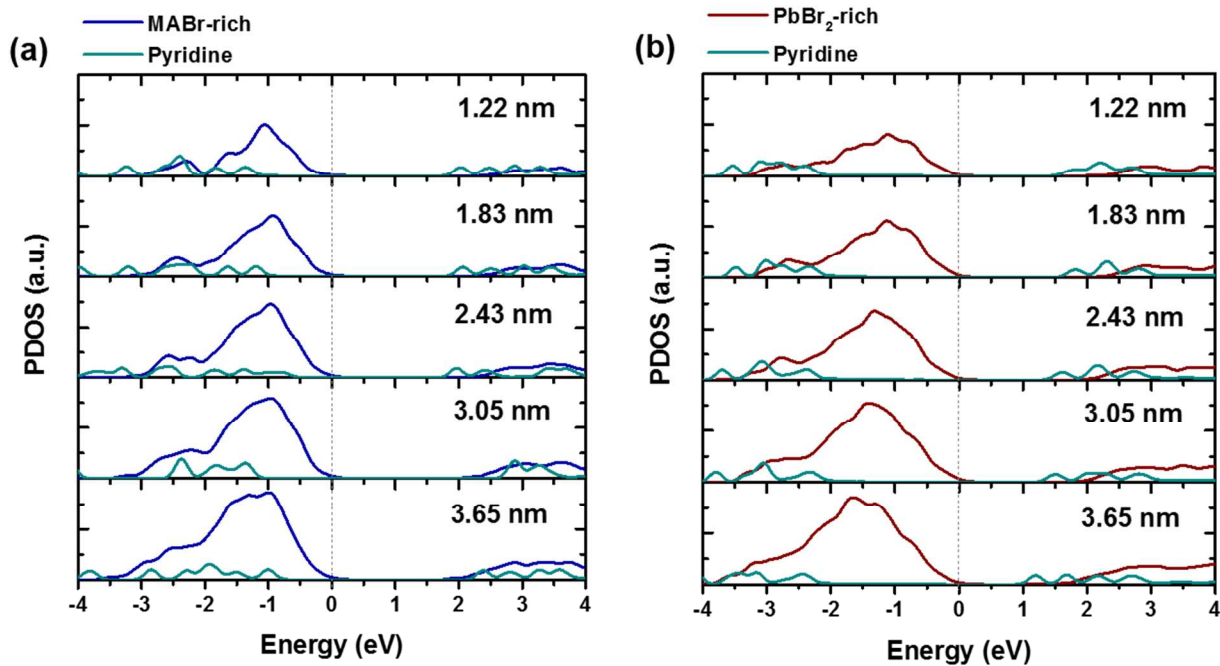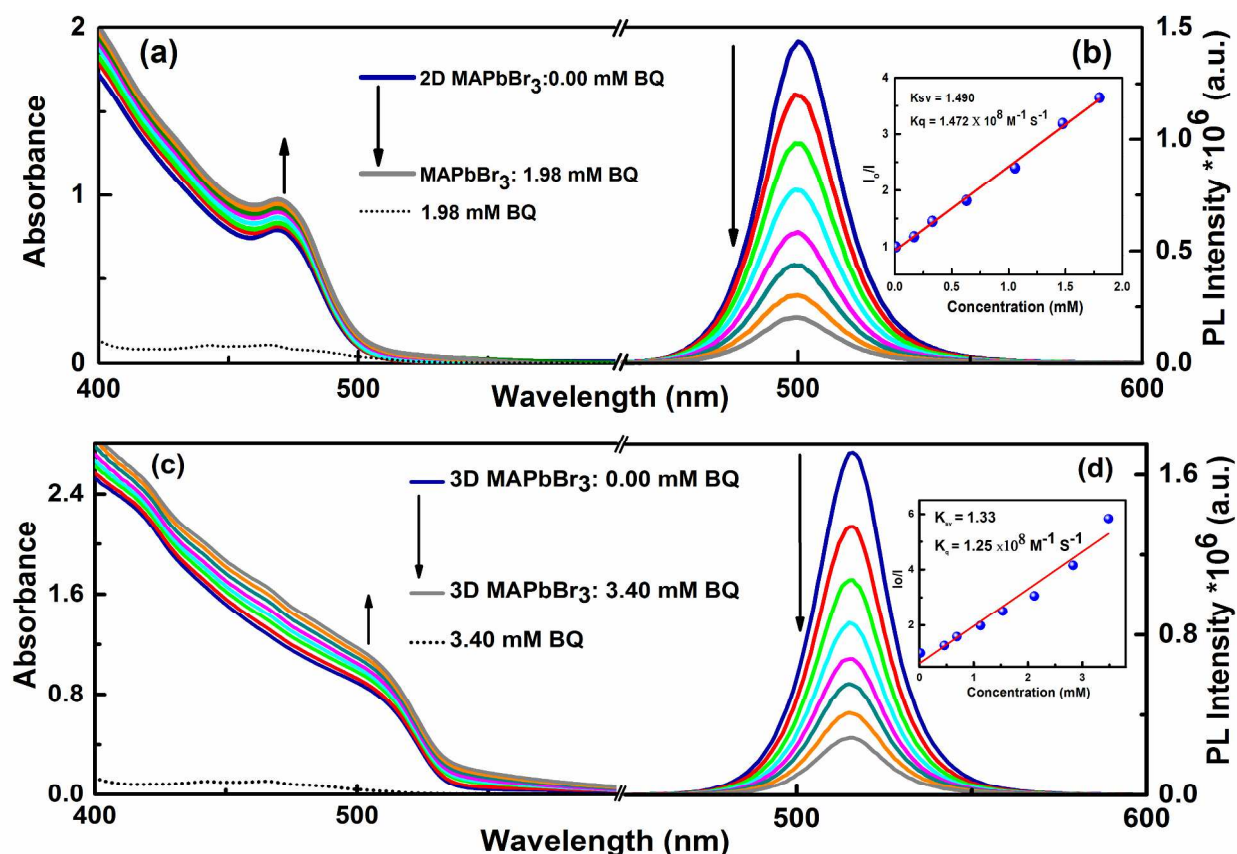

Figure S6. Projected density of states of (a) MABr-rich and (b) PbBr$_2$-rich MAPbBr$_3$ (001) surfaces after pyridine-ligand modifications.

Figure S7. XPS data comparison of 3D and 2D MAPbBr$_3$ nanostructures synthesized at o$^{\circ}$C. The purple arrow refers to the N1S signal located at 399.8 eV which indicates the presence of the pyridine on the 2D nanostructures surface.

Figure S8. (a,c) Steady-state absorption and (b,d) photoluminescence spectra of the 2D and 3D MAPbBr$_3$ nanostructures synthesized at 60°C with successive additions of benzoquinone (BQ), respectively. Inset is the Stern-Volmer plot showing the photoluminescence intensity of the perovskite nanocrystals as a function of the concentration of the quencher (BQ). The progressive increase in the absorption intensity after the addition of BQ is due to the absorption spectra of BQ, which overlaps with that of the nanostructures. From the photoluminescence quenching rate, it is obvious that the 2D nanostructures show more efficient charge transfer to BQ. Almost double the BQ concentration is required to the quench the photoluminescence intensity of 3D nanostructures to similar extent.

Lifetime (τ_e, ns)	3D	2D
without BQ	7.67	8.6
with BQ	5.8	6.2

Table S1. The 1/e decay times for the 3D and 2D MAPbBr$_3$ nanostructures synthesized at 60°C in the absence and in the presence of benzoquinone (BQ).[3]

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