Electronic Supplementary Information (ESI) for

Size-Controllable and Stable Organometallic Halide Quantum Dots/Polymer Film

Wonhee Cha,[a] Hae-Jin Kim,[b] Songhee Lee,[c] and Jiwon Kim[c,d*]

[*]Corresponding author, E-mail: jiwon.kim@yonsei.ac.kr

a. Department of Chemistry, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea.
b. Department of Mechanical Engineering, University of Houston, 4800 Calhoun Road, Houston, Texas 77204, USA.
c. Underwood International College, Yonsei University, 85 Songdogwahak-ro, Yeonsu-gu, Incheon 21983, Republic of Korea.
d. School of Integrated Technology, Yonsei University, 85 Songdogwahak-ro, Yeonsu-gu, Incheon 21983, Republic of Korea.

EXPERIMENTAL SECTION

General Methods

All chemicals were acquired from commercial sources (except for methylammonium bromide, MABr) and used unless other treatments. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 at 200 kV. The absorption spectra were recorded using UV/Vis spectrometer SCINCO MEGA 2100 in 350 nm – 900 nm range. X-ray diffraction pattern were obtained using Rigaku SmartLab and Rigaku Ultima IV equipped with a graphite-monochromated Cu Ka radiation source (40 kV, 40 mA). The time-correlated single-photon-counting (TCSPC) system was used for measuring the fluorescence decay profiles. [S1] A photoluminescence confocal microscope Carl Zeiss LSM 700 was used to structural analysis.

Materials

Preparation of Methylammonium bromide (CH_3NH_3Br, MABr)

MABr was synthesized according to reported method. [S2] Methylamine (30 mL, 40 wt% in methanol, TCI) was reacted with hydrobromic acid (50 mL, 48 wt% in water, Aldrich) at 0 ℃ for 2h. CH_3NH_3Br was recovered by rotary evaporation at 50℃ for 1h. The product was washed with diethyl ether and dried in vacuum oven at 60℃ for 24h.

Synthesis of gold nanoparticles (AuNPs)

AuNPs were synthesized as previously reported. [S3]

Purification of AuNPs

AuNP solution and methanol (4 times in volume) was mixed for 1 hour. The upper part of solution was dumped, then pure toluene with the same volume of dumped solution was added. Repeat the same processes and at the final step, n-hexane was added instead of toluene.

Preparation of AuNP/PDMS film

1.0 g of silicone elastomer base (PDMS pre-polymer) and 0.4 mL of prepurified AuNp solution (concentration: 8.05 x 10^{14}/mL) were mixed. 0.2 mL of n-hexane (extra pure grade) was added for preventing further aggregation. 0.1 g of silicone elastomer curing agent (cross-linker) was added to the mixture. The mixture was degassed in dynamic vacuum for several hours. The final mixture was heated at 65 ℃ for overnight in the oven.

Preparation porous PDMS template (etching gold nanoparticles)

AuNPs within AuNP/PDMS film could be removed by using aqua regia (mixture of nitric acid and hydrochloric acid) as etching solvent. For effective etching process, AuNP/PDMS film was swelled in THF solution before dipping into the aqua regia. After etching process, the reddish colored AuNP/PDMS film became transparent porous PDMS.

Growth of $MAPbX_3$ in porous PDMS template

The porous PDMS template was swelled in THF solution. Then, the template was dipped into 1 M precursor solution (Methylammonium halide and lead halide in anhyrous DMF or mixture of DMF and DMSO with 1:1 ratio) for several hours. Then, the template was dried at 65 ℃ in vacuum oven for several hours. Transparent porous template became colored $MAPbX_3$ QDs/PDMS film. Bulk materials formed on the film surface was washed by clean DMF solution and then the $MAPbX_3$ QDs/PDMS film was dried at 65 ℃ in vacuum oven for several hours.

$MAPbBr_3$ QDs Synthesized by Using Ligand-Assisted Re-Precipitation (LARP) Method

Three different sized $MAPbBr_3$ QDs were synthesized by LARP method at 20 ℃, 30 ℃, and 40 ℃. As synthesis temperature increased, the larger $MAPbBr_3$ QDs were synthesized. Absorption and photoluminescence peak of $MAPbBr_3$ QDs were blue-shifted as the size decreased owing to the quantum confinement effect.

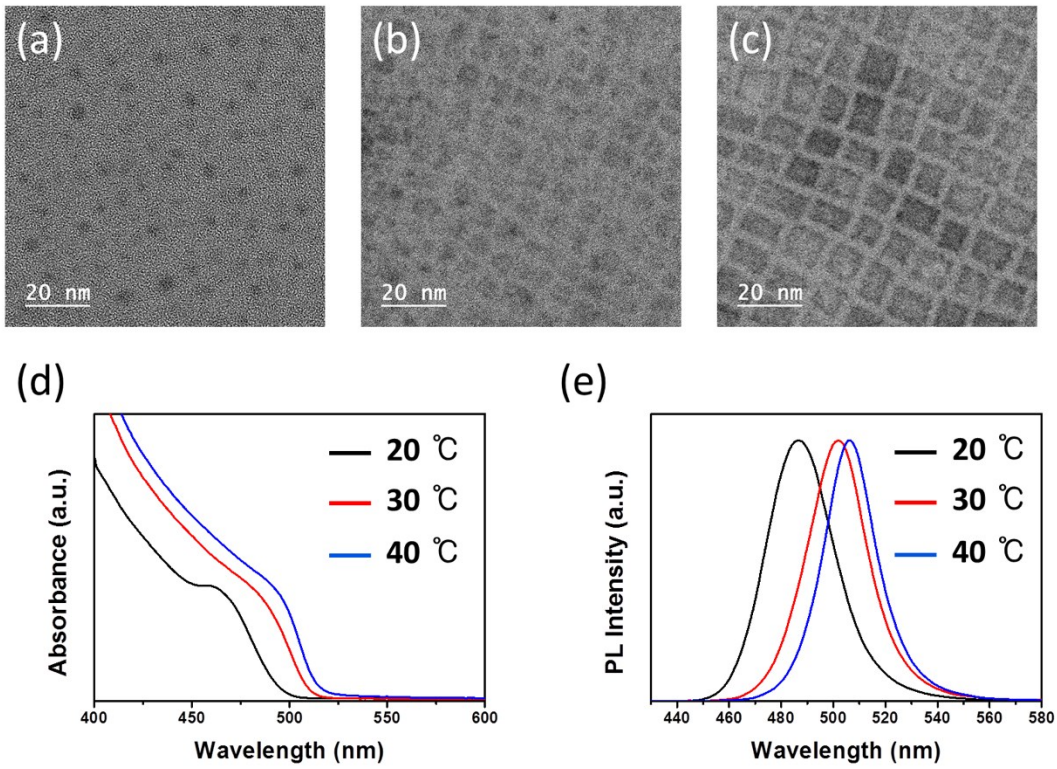

Figure S1. **$MAPbBr_3$ QDs synthesized by using LARP strategy.** (a)-(c) TEM image of $MAPbBr_3$ QDs synthesized by using LARP strategy at 20℃, 30℃, and 40℃, respectively. [S2] (d)-(e) Absorption and PL spectra of $MAPbBr_3$ QDs.

Photoluminescence of Three Different Sizes of $MAPbBr_3$ QDs/PDMS Films

Three different sized AuNPs whose diameter was 5.6 nm, 7.8 nm, and 9.8 nm were used to prepare $MAPbBr_3$ QDs/PDMS films. Under UV lamp excitation at 365 nm, these films exhibited green emission. When the diameter of AuNPs was 9.8 nm, it showed the strongest photoluminescence.

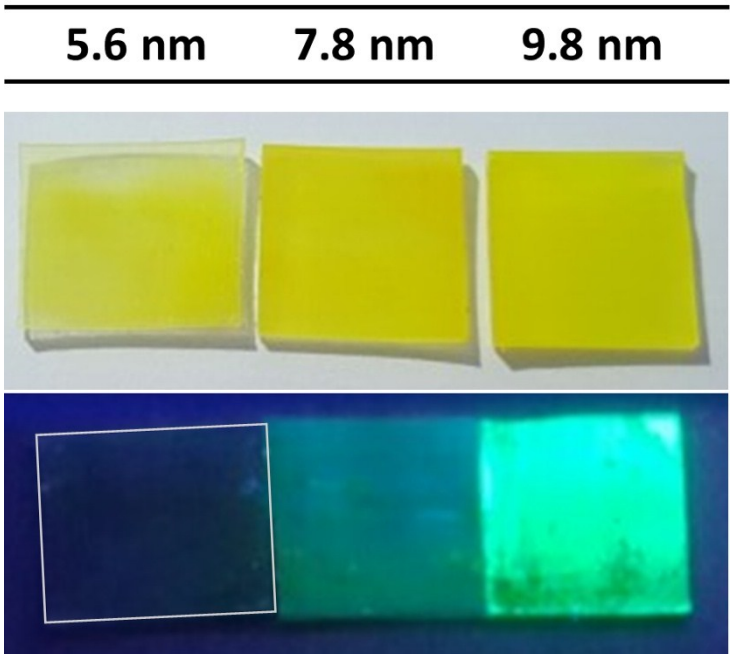

***Figure S2*. Images of size-controlled $MAPbBr_3$ QDs/PDMS film.** Photograph of three different sizes $MAPbBr_3$ QDs/PDMS film (top) and under UV lamp excitation at 365 nm (bottom).

Fluorescence Decay of $MAPbBr_3$ QDs/PDMS Film

The time-correlated single-photon-counting (TCSPC) system was used for measuring the fluorescence decay profiles. [S1] We can assign the fast time component (τ_1) as a decay related to recombination of biexcitons and the slow time component (τ_2) as a decay related to recombination of single exciton. As $MAPbBr_3$ QD size increased, the ratio of τ_2 amplitude to τ_1 amplitude (A_2 / A_1) increased from 0.14 to 0.27, and 0.43 for D_1, D_2, and D_3, respectively.

	D_1	D_2	D_3
τ_1 (ns)	0.6	0.9	0.6
A_1 (%)	88	79	70
τ_2 (ns)	10	12	10
A_2 (%)	12	21	30
A_2/A_1	0.14	0.27	0.43

Table S1. **Photoluminescence lifetime of different sizes of $MAPbBr_3$ QDs/PDMS films.** Decay lifetimes (τ_1 and τ_2) and A_2/A_1 of different sized $MAPbBr_3$ QDs within the $MAPbBr_3$ QDs/PDMS film.

Fluorescence Decay of $MAPbBr_3$ QDs/PDMS Film at weak photo-excitation (<20 μJ/cm²)

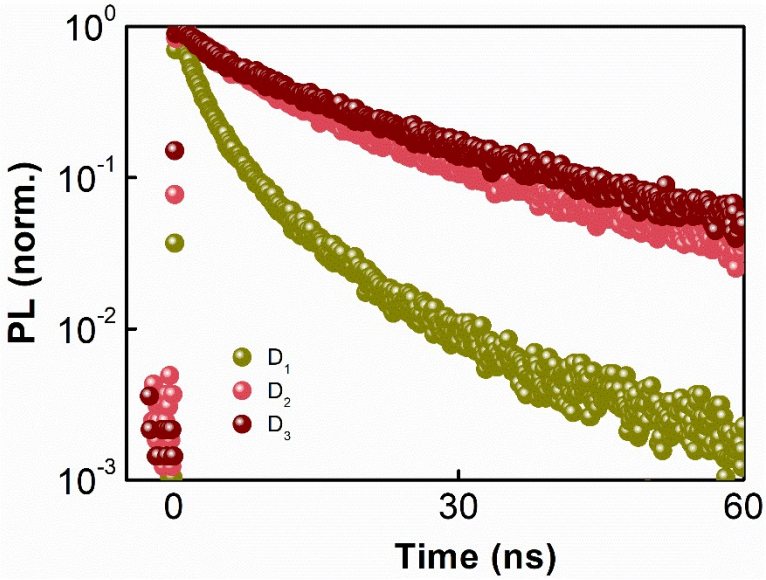

Figure S3. **Fluorescence Decay of $MAPbBr_3$ QDs/PDMS Film at weak photo-excitation.** Time-correlated single photon counting (TCSPC) measurements of three different sizes of $MAPbBr_3$ QDs in PDMS films at weak photo-excitation (<20 μJ/cm²).

	D_1	D_2	D_3
τ_1 (ns)	2.3	5.3	3.4
A_1 (%)	81	50	30
τ_2 (ns)	9.8	19.3	18.4
A_2 (%)	19	50	70

Table S2. **Photoluminescence lifetime of different sizes of $MAPbBr_3$ QDs in PDMS films.** Decay lifetimes (τ_1 and τ_2) and amplitude (A_1 and A_2) of different sized $MAPbBr_3$ QDs within the $MAPbBr_3$ QDs/PDMS film with weak photo-excitations.

References

[S1] D. Shimizu, J. Oh, H. Uoyama, H. Watanabe, K. Tagawa, H. Uno, D. Kim, *Phys. Chem. Chem. Phys.* 2013, **15**, 10612-10615.

[S2] H. Huang, A. S. Susha, S. V. Kershaw, T. F. Hung and A. L. Rogach, *Adv. Sci.* 2015, **2**, 1500194.

[S3] R. Klajn, K. J. M. Bishop, M. Fialkowski, M. Paszewski, C. J. Campbell, and T. P. Gray, *Science* 2007, **316**, 261-264