

Supplementary Information

Ligand-Flexible Synthesis of Strongly Confined Perovskite Nanocrystals: A Microwave Synthetic Approach

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Experimental section

Materials

Oleylamine 70%, Hydrobromic acid 48%, Oleic acid 90%, Cesium carbonate 99.9%, Lead bromide 98%, Trimethylsilyl bromide 97%, Diethylphosphate, Tert-Butyl acrylate, and Tri-octylphosphine oxide 99% were bought from Sigma Aldrich and used without further purification. Ethyl acetate 99.9%, Mesitylene 98%, Toluene 99.5%, Methyl acetate 99%, and Lead acetate trihydrate 99% were bought from Fisher Scientific and used without further purification. Ethanol 95% from Commercial Alcohols. Oleyl alcohol (80-85%) and sodium hydride (57-63%) were purchased from Alfa Aesar. The carboxyl capped polystyrene was purchased from Scientific Polymer Products, Inc. The polydispersity was established by

SEC/GPC and it was found to be equal to 1.08.

Oleylammonium bromide preparation

Oleylamine (30mL) and ethyl acetate (100mL) were placed in a three necked flask. The mixture was cooled down with an ice bath and 18mL of HBr were added under constant stirring. The reaction mixture was placed under argon and left overnight to react. The product was placed in an ice bath, then centrifuged at 10k rpm for 10 min at 5°C. The supernatant was discarded and the precipitate was recrystallized in with ethyl acetate and recovered by vacuum filtration.

OLPA synthesis

The synthesis of oleylphosphonic acid was performed following the procedure of Zhang et al..¹ See Figure S 1.

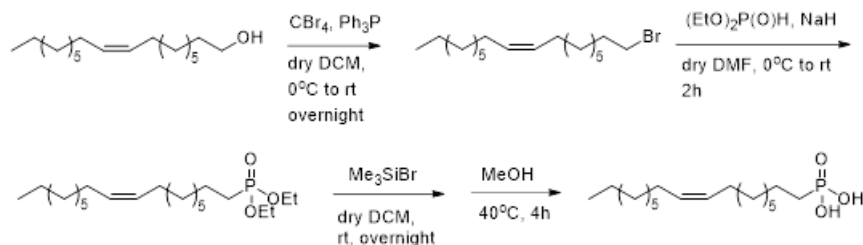


Figure S 1: Scheme of OLPA synthesis.

PSPA synthesis

The ω -phosphonic acid terminated polystyrene was obtained in a three steps procedure, see Figure S 2). The starting material was subjected first to bromination carried under the conditions described by Zhao et al..² The syntheses of the diethyl phosphonate and phosphonate derivatives were performed by adaptation of the reported literature procedure of Demortiere et al..³ The functionalization was confirmed by ^1H NMR and FTIR.

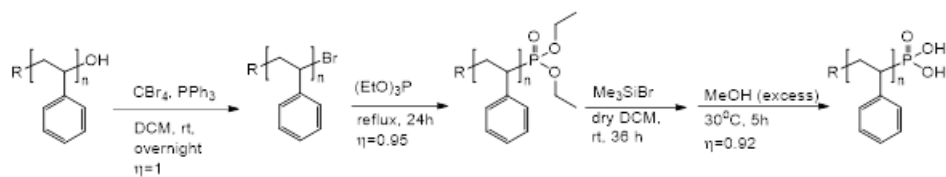


Figure S 2: Scheme of PSPA synthesis.

HI Synthesis of OA/OLABr PNC

A typical synthesis involved adding 0.3mmol of $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ and 0.18mmol of Cs_2CO_3 in a 3-necked flask along with 125 mg of trioctylphosphine oxide (TOPO), 500 μL of OA, and 6mL of mesitylene. The solution was degassed at 120°C for ~20 min under vacuum, then placed on argon atmosphere and heated up to 140-150°C. 1mL of a warm OLABr (224 mg) solution in mesitylene was then injected into the reaction mixture. The reaction was quenched with ice water after 5 s growth time and the product was centrifuged at 3000 rpm for 5min, the precipitate was discarded and the supernatant was added twice its volume in MeAc, then centrifuged again at 10k rpm for 10 min. The supernatant was discarded, and the precipitate was resuspended in 5 mL of toluene and centrifuged one last time at 6k rpm for 2 min to precipitate large or unstable PNC. The final green solution was stored for later use.

MW Synthesis of OA/OLABr and OLPA/OLABr PNC

In a typical synthesis, 0.3 mmol $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ 1.8 mmol Cs_2CO_3 and 125 mg of TOPO were loaded in a 5 mL MW vial, along with 500 μL of OA (or 470 mg of OLPA) and 224 mg of OLABr. Mesitylene was used as the reaction solvent, so enough of it was used to reach a 5 mL volume. Once in the MW reactor, the temperature was set at 110-170°C and kept for 5 min, the whole synthesis process took about 10 min to complete, including heating and cooling processes. The product was then centrifuged at 3000 rpm for 5 min to remove unreacted species and big PNCs. The clear green suspension obtained was kept and a 1:1 ratio of methyl acetate (MeAc) was added to it. The PNC immediately started crashing out

and the mixture was centrifuged again at 10k rpm for 10 min. The clear supernatant was discarded and the precipitate was resuspended in 5mL of toluene. Finally, the suspension was centrifuged at 6000 rpm for 2 min to remove remaining big or damaged PNCs, the clear green supernatant was labeled and saved for characterization analysis.

The MW synthesis process involves placing the solid precursors in the vial along with the ligands and the solvent. Without pre-dissolving any of them the reaction vial is sealed and placed in the MW reactor. The MW reactor heats up the reaction using 400W until the reaction temperature is met, then it controls the power to keep that temperature for 5 min and finally it cools the reaction down with a cool breeze of air. TOPO was used as a MW absorbent species, thus, it helped the reaction mixture reach the desired temperature in a short period of time (around 2 min), and reduced the power needed to keep the temperature. Mesitylene was used as a solvent instead of the most commonly used octadecene (ODE) because it is a high boiling point solvent whose $^1\text{H-NMR}$ signals don't superimpose with the ligand ones, it is a good solvent for the PNCs, and it is also a non-viscous liquid which helps its removal during the washing processes. The amount of OA and OLPA to use was determined by comparing overall synthesis yield with different amounts of acid present (data not shown here). The amount selected was enough to completely dissolve the precursors during the short heating process while still allowing the PNC formation. The amount of OLABr was fixed to a 1:2 molar ratio with Pb as it also provides the Br precursor, no OLA was added as it reduced the yield of the synthesis (data not shown here).

Synthesis of PSPA/OLABr PNC

A typical MW polymer synthesis was different than for the shorter ligands. The Pb and Cs precursors had to be predissolved by the PSPA before placing them in the MW reactor, which is why using $\text{Pb}(\text{OAc})_2$ as a Pb precursor came in handy. The PSPA/OLABr samples were made at a lower temperature range because temperatures above 115°C yielded only non-colloidally stable samples. Polystyrene also has a glass transition temperature of $\sim 100^\circ\text{C}$,

before which the polymer has a more rigid structure, so reactions below this temperature didn't work out. Normally, 0.1 mmol $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ and 0.06 mmol Cs_2CO_3 were placed in a 5 mL MW vial along with 125 mg TOPO and 1000 mg of PSPA, 4 mL of mesitylene were added as solvent. The vial was heated to 130°C in air and under constant stirring for 2h, until all the precursors were dissolved. The solution was allowed to cool to room temperature, no precipitate was observed, and 75 mg of OLABr were added to the vial. The Reaction flask was then sealed and placed in the MW reactor, the temperature was set (100-115°C) and kept for 5 min before cooling. The obtained product was centrifuged at 3000 rpm for 5 min to remove unreacted precursors and large PNCs. Then a mixture of hexanes and ethanol was used to crash out the PNC. The cloudy solution was centrifuged again at 10k rpm for 10 min, the clear supernatant was discarded and the solid was placed under vacuum for 2h to remove all excess ethanol. Then the product was resuspended in 5 mL of toluene and centrifuged once more at 6000 rpm for 2 min. A clear green solution was obtained.

Characterization

Absorption and PL spectra were measured using a Cary UV-Vis spectrometer and Cary fluorescence spectrometer, respectively. Quantum yields were calculated using coumarin 6 as the standard dye of reference with a quantum yield of 78%⁴ and an excitation wavelength of 450nm. Time-resolved PL measurements were obtained using a time-correlated single-photon counting (TCSPC) unit from Edinburgh Instruments with a 340nm picosecond-pulsed laser. Transmission electron microscopy (TEM) images were obtained with a Thermo Scientific Talos F200X G2 S/TEM for Materials Sciences on drop-casted and overnight-vacuumed TEM grids. Infrared spectra was obtained in a Spectrum II FT-IR Spectrometer from Perkin Elmer on PNC thin films.

Nuclear magnetic resonance (NMR) ^1H , ^{31}P and NOESY spectra were performed on a Bruker AVIIIHD NMR Spectrometer operating at a ^1H frequency of 500 MHz, while DOSY measurements were obtained on a Varian Inova NMR Spectrometer operating at

the same frequency. For sample preparation, the PNC dispersions were precipitated with MeAc, except PSPA/OLABr PNC which were precipitated with a hexanes/ethanol mixture, and placed under vacuum for 2h, then they were dispersed in deuterated chloroform and transferred to an NMR tube. Standard pulse sequences from Bruker and Varian libraries were used to acquire both 1D and 2D spectra. ^1H relaxation delay time was set to 30s and NOESY mixing time as 300ms. DOSY's gradient pulse duration was set to 2.5ms and the delay was modified as required to get a 90% decrease of the initial signal.

FTIR of free ligands and ligand mixture

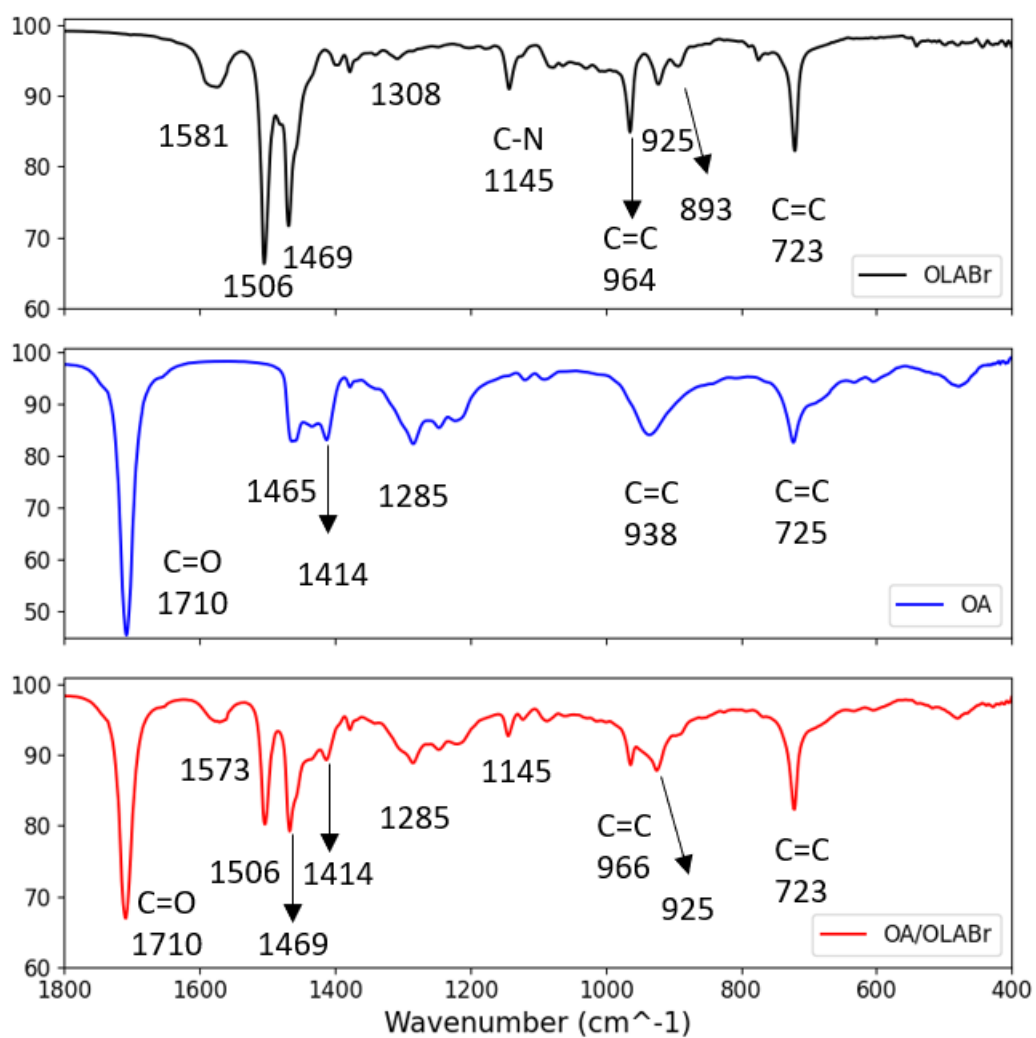
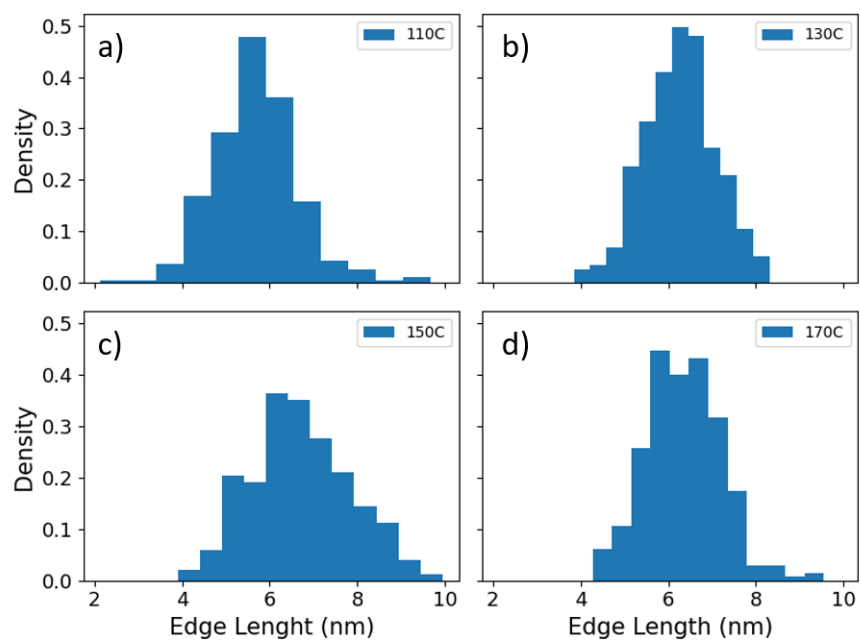


Figure S 3: FTIR of free ligands and ligand mixture in CDCl_3 .

Size histograms OA/OLABr samples



e)

Synthesis Temp	110°C	130°C	150°C	170°C
Average Size	6	6.3	7	6.3
Standard Deviation	1	0.8	1	0.9

Figure S 4: Size histogram of OA/OLABr samples with increasing temperature 110°C a), 130°C b), 150°C c), 170°C d). Sizes are not significantly different from each other.

Effect of time

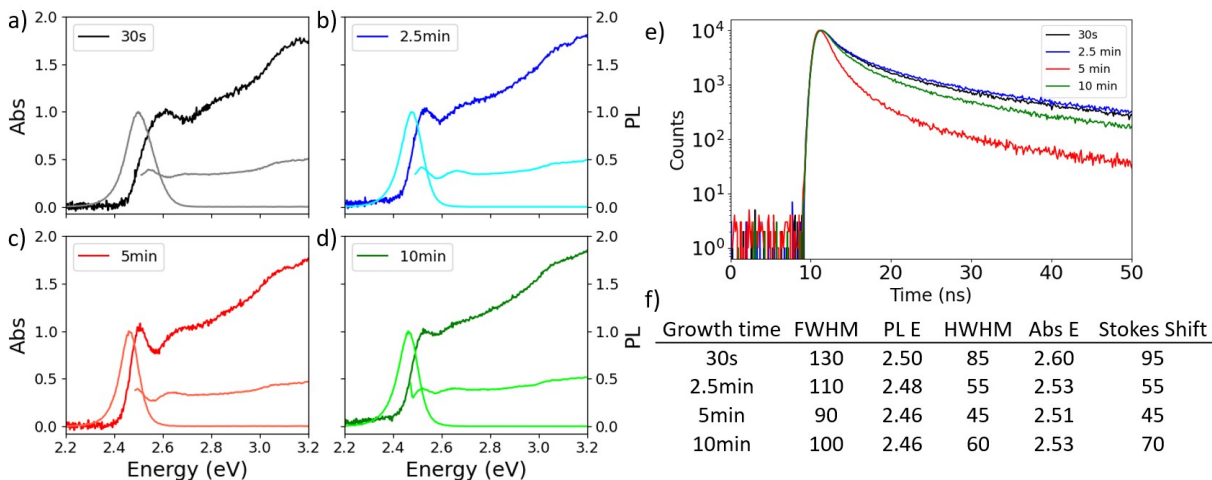


Figure S 5: Absorption, PL and PLE spectra(a-d), as well as PL decay lifetime profiles (e) of MW synthesized PNCs with different growth periods, using the OA/OLABr ligand system. Summary of the optical properties is included in f. As growth time increases the samples' exciton definition improves and the FWHM and HWHM decreases. However, growth times longer than 5 min become detrimental for the sample, reducing the yield and exciton definition. The PL decay lifetimes show a distinct difference between shorter and longer growth times compared to the optimal value of 5 min, indicating different recombination pathways.

Effect of Bromine Source

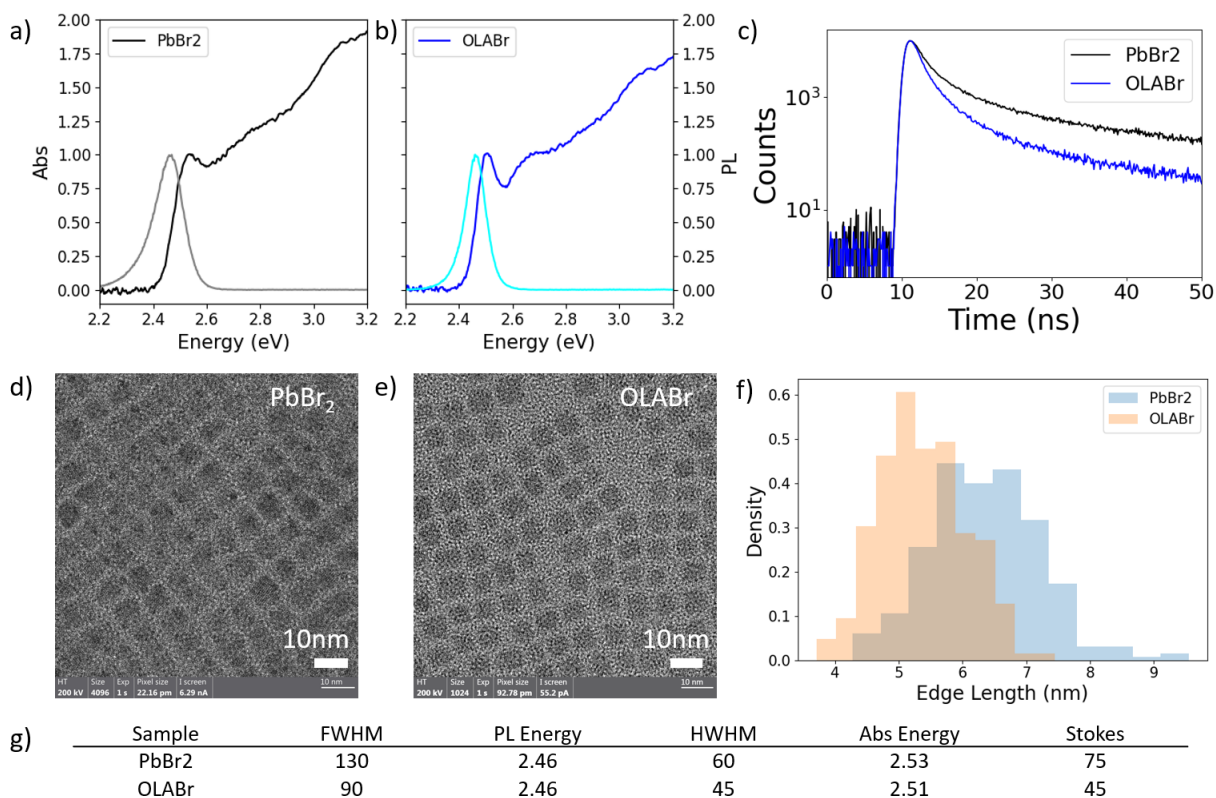


Figure S 6: Effect of bromine source on PNCs. Absorption and PL and PL decay lifetime spectra of PNCs prepared with PbBr₂ and OLABr (a-c), TEM images and size histograms (d-e), and table of summary of optical properties (g).

Figure S 6 shows a comparison of PNCs made by MW synthesis with different bromine (Br) sources. Panels a) and b) show the absorption and PL spectra of PNC prepared with PbBr₂ and OLABr, which show the former manages less exciton definition and broader FWHM, also the yield of the synthesis was lower than for OLABr. The size distribution, as shown in the size histograms in panel f) indicate the PbBr₂ has a higher polydispersity and manages a larger PNC size. These results can be due to PbBr₂'s lower solubility which reduces the kinetics of the reaction. Finally, the shorter decay lifetime of the OLABr sample could indicate shallower traps achieved by a better passivation layer on the PNCs.⁵ These results suggest that the OLABr ligand is better suited for PNC synthesis using the microwave method.

Additionally, although PbBr_2 is a commonly used Pb and Br precursor for both HI and MW synthesis, it requires both acid and basic ligands to be present for complete dissolution, which proved inefficient for the PSPA ligand, as it requires pre-dissolution of precursors. Then OLABr becomes a promising alternative since it has been previously recognized as the binding ligand for PNCs,⁶ has been used for comparison purposes with other bromine sources,^{7,8} and allows the pre-dissolution of Pb and Cs precursors by PSPA. Here OLABr proved to be a fast dissolving ligand that achieved a better control of PNC growth.

DOSY

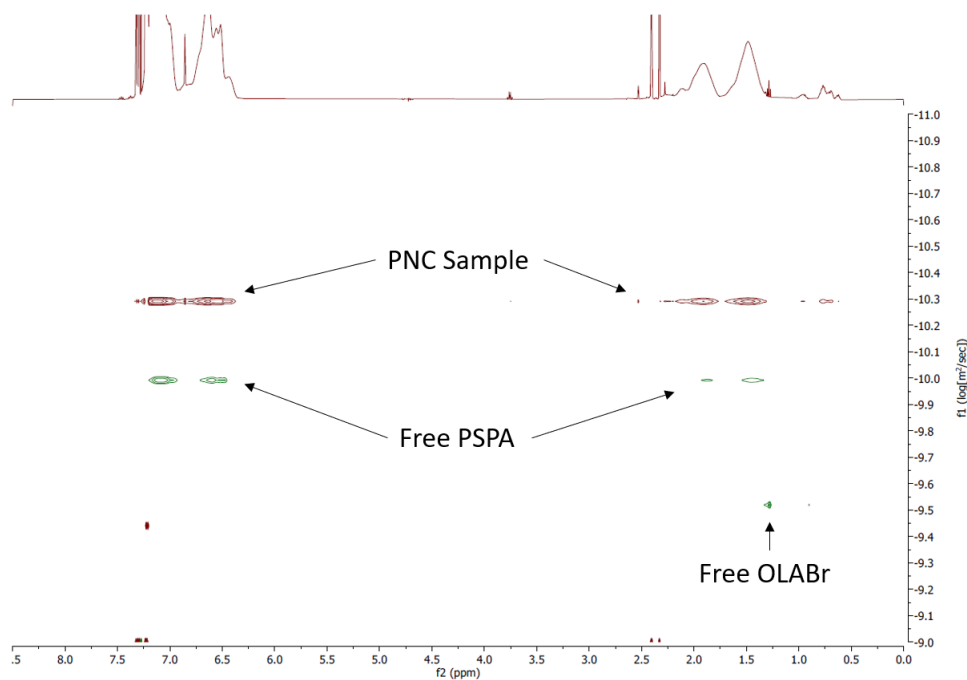


Figure S 7: Example of DOSY NMR. Superimposed DOSY spectra of the free ligand mixture PSPA/OLABr and PSPA/OLABr-coated PNCs.

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