## Solution-Phase Synthesis of CsPbI<sub>3</sub> Nanowire Clusters via Polymer-Induced Anisotropic Growth and Self-Assembly

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## Experimental

**Materials**. All chemical were analytical grade and used without further purification. Cesium iodide (CsI, Sigma-Aldrich, 99%), lead iodide (PbI<sub>2</sub>, Sigma-Aldrich, 99%), N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.9%), Toluene (Sigma-Aldrich, 99.9%).

**Synthesis of CsPbI<sub>3</sub> NWCs**. In a typical experiment, PMMA (0.0125/0.025/0.05/0.1/0.2/0.3 mM) were totally dissolved in 8 mL Toluene. After a period of gentle striring at 25/45/70/95/110 °C, CsI/PbI<sub>2</sub> in DMF (0.06 M, 0.1 mL) was added quickly into the mixture of PMMA/Toluene under vigorous stirring, and the color of the solution changed from transparent to dark brown immediately. The reaction will finish within few mins.

Synthesis of CsPbI<sub>3</sub>-PMMA film. The mixture was centrifuged and re-dispersed in a small amount of solvent for obtaining high-concentration solution of CsPbI<sub>3</sub>-PMMA. The CsPbI<sub>3</sub>-PMMA film was fabricated by dropping high-concentration solution onto a substrate. It is worth noting that CsPbI<sub>3</sub> should be centrifuged immediately, and subsequently fabricated CsPbI<sub>3</sub>-PMMA film within 5 min for obtaining the  $\gamma$ -phase CsPbI<sub>3</sub> when the PMMA concentration below 0.05 mM. The stable  $\gamma$ -phase CsPbI<sub>3</sub> can be obtained as long as the film was fabricated.

Measurement and Characterization. TEM, HAADF, SAED images were measured by a transmission electron microscope (Titan Cubed Themis G2 300, FEI, USA). UV-vis spectra were recorded by UV/Vis/NIR Spectrophotometer (LAMBDA, PerkinElmer, USA). X-ray photoelectron spectrometer (Thermo Scientific ESCALAB 250Xi) with Al K $\alpha$  radiation as the X-ray souce (U=15 kv, I=12.8 mA) and scanning resolution of 0.1 eV. X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV system with Cu K- $\alpha$  radiation (40 kv, 44mA), from 20 to 50°(2 $\theta$ ) with a 0.01° step. Fourier Transform infrared spectroscopy was recorded using a Bruker IFS 66 V/S FTIR spectrometer.



Figure S1. The PL spectra and XRD patterns of CsPbI<sub>3</sub>-PMMA prepared at 0.1 mM concentration of PMMA before and after storing the film under room temperature for 30 days.



**Figure S2**. (a) SEM and (b) TEM images of CsPbI<sub>3</sub> NWCs prepared at high PMMA concentration under room reaction temperature.





Figure S4. The shape of CsPbBr3 and CsPbCl3 prepared with the similar technique.



Figure S5. TEM image of sample fabricated without the adding of PMMA.



**Figure S6**. The PL and UV-vis absorption spectra of CsPbI<sub>3</sub> prepared with different PMMA concentration. In our experiments, the crystal phase of CsPbI<sub>3</sub> perovskite nanocrystals prepared at 0 mM and 0.0125 mM concentration of PMMA will change immediately from orthorhombic ( $\gamma$ ) perovskite phase to non-photoactive yellow orthorhombic ( $\delta$ ) perovskite phase. Therefore, the as-synthesized products should be centrifuged immediately, and subsequently fabricated CsPbI<sub>3</sub>-PMMA film within 5 min for obtaining the  $\gamma$ -phase CsPbI<sub>3</sub> when the PMMA concentration below 0.05 mM.



Figure S7. The average lengths of CsPbI<sub>3</sub> NWCs prepared at different reaction temperature.