

## Direct Synthesis of Highly Efficient NIR-I Emitting Core-Only InP Quantum Dots via Multiligand Synergy

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### INTRODUCTION & AIM

Colloidal InP quantum dots (QDs) are promising candidates for optoelectronics due to their size-tunable emission, high spectral purity, and RoHS compliance. Among these properties, near-infrared (NIR) emission is particularly important for applications in displays, detection, and imaging. Among abundant alternatives, InP-based QDs offer notable advantages in material accessibility and synthesis cost. While typical strategies like Cu doping, heterostructure engineering (including type-II and inverse type-I), and template-assisted synthesis enable NIR emission, they often compromise color purity or efficiency. Recently, large-sized InP QDs have been synthesized using InCl<sub>3</sub>-based methods, achieving both high color purity and moderate luminous efficiency through multi-shell passivation. To simplify the synthesis process and exploit the advantages of shell-less QDs for carrier transport in further optoelectronic devices, post-treatments such as HF etching and ligand exchange are widely applied to improve luminescence efficiency. However, these methods are often complex or hazardous.

Herein, we present a simple and post-treatment-free method for preparing high-efficiency, NIR-I emitting core-only InP QDs. The synergistic coordination effects of ZnCl<sub>2</sub> and NH<sub>4</sub>PF<sub>6</sub> enable two key processes: removal of detrimental surface oxidation and effective surface passivation by ligands, along with a competitive adsorption reaction that promotes rapid formation and growth of InP monomers, facilitating the fast synthesis of large-sized QDs. Further optimization of Z-type ZnCl<sub>2</sub> content leads to more effective passivation of trap sites, ultimately achieving an enhanced PLQY of up to 74%. The feasibility of applying these QDs in display technology is preliminarily demonstrated through photolithographic patterning.

### METHOD

**Synthesis of core-only InP QDs:** 0.5 mmol of In(I)Cl<sub>3</sub>, X (0.5 to 2.5) mmol of ZnCl<sub>2</sub>, 0.5 mmol NH<sub>4</sub>PF<sub>6</sub>, 0.4 mL of TOP, and 5 mL of OLA were added into a 50 mL three-necked flask. The cationic solution was degassed at 50 °C for 30 minutes and flooded with N<sub>2</sub>, with the color of solution changes from light yellow to black. Afterward, the solution was quickly heated to 230 °C. Once the temperature reached 230 °C, 0.36 mL (DMA)<sub>3</sub>P diluted in 0.36 mL ODE was immediately injected. After 40 min, the reaction was quenched by removing the heating mantle. The resulting crude was purified with a combination of hexane and ethanol. Specifically, the crude solution was mixed with 10 ml hexane and 30 ml of ethanol, followed by centrifugation at 8000 rpm for 4 minutes. This procedure was repeated three times. The purified QDs were then dissolved in hexane for further characterization.

**Fabrication of fluorescent optical pattern:** To prepare the QD ink, TFB was first dissolved in toluene to form a TFB-toluene solution. Subsequently, 25 mg of QDs were added to this TFB-toluene solution, followed by the incorporation of DMPA. The mixture was then stirred on a 70 °C hotplate until complete dissolution. The resulting QD ink was spin-coated onto a substrate at 2000 rpm for 30 seconds. For photolithography patterning, the spin-coated QD film was exposed under UV light (365 nm, 50 mW/cm<sup>2</sup>) through a pre-designed mask for 30 seconds. Finally, the exposed film was developed by spin-coating with toluene as the developer at 2000 rpm to form the desired pattern.

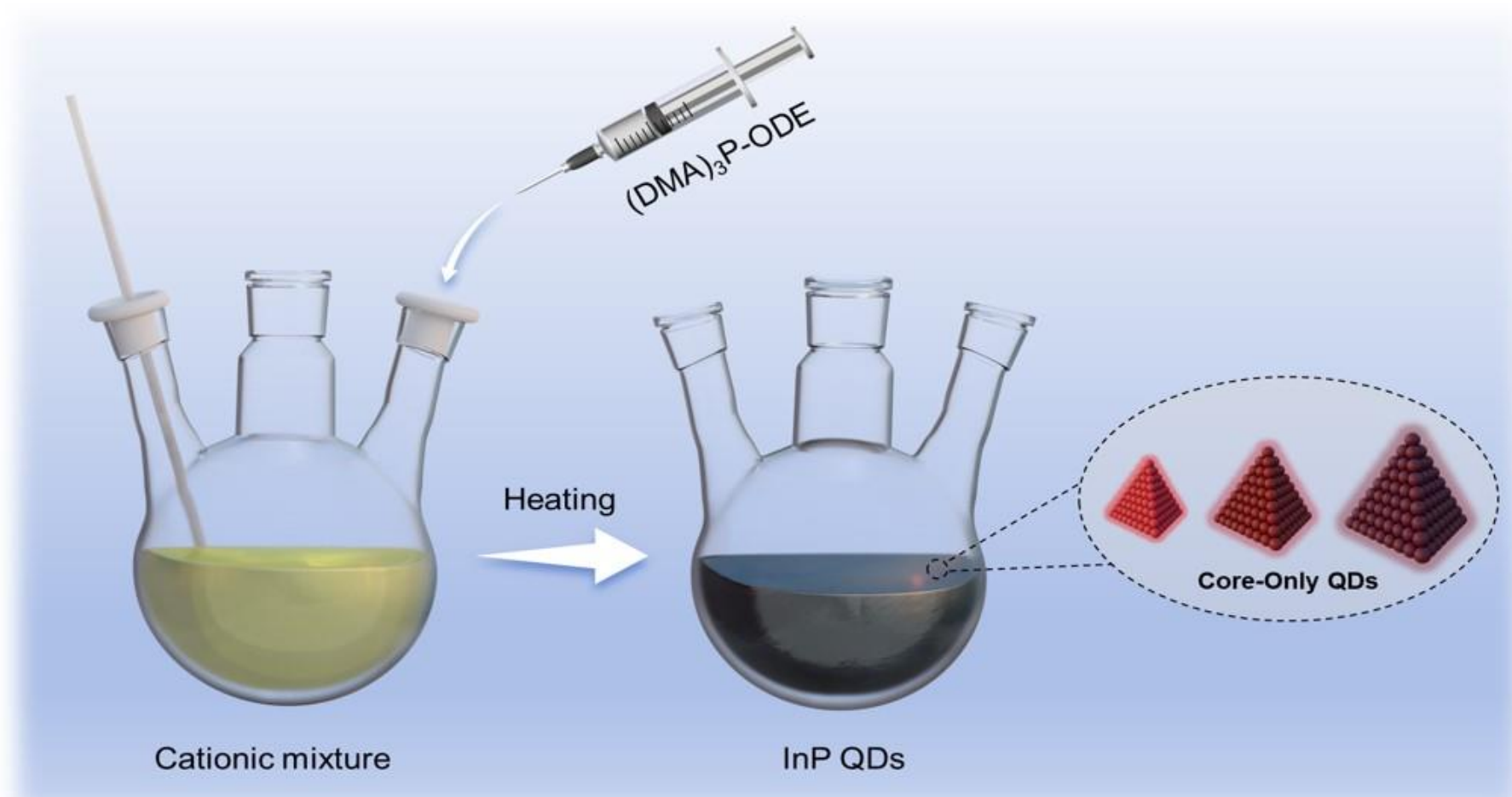


Figure 1. Schematic of the synthesis process for core-only InP QDs

### RESULTS & DISCUSSION

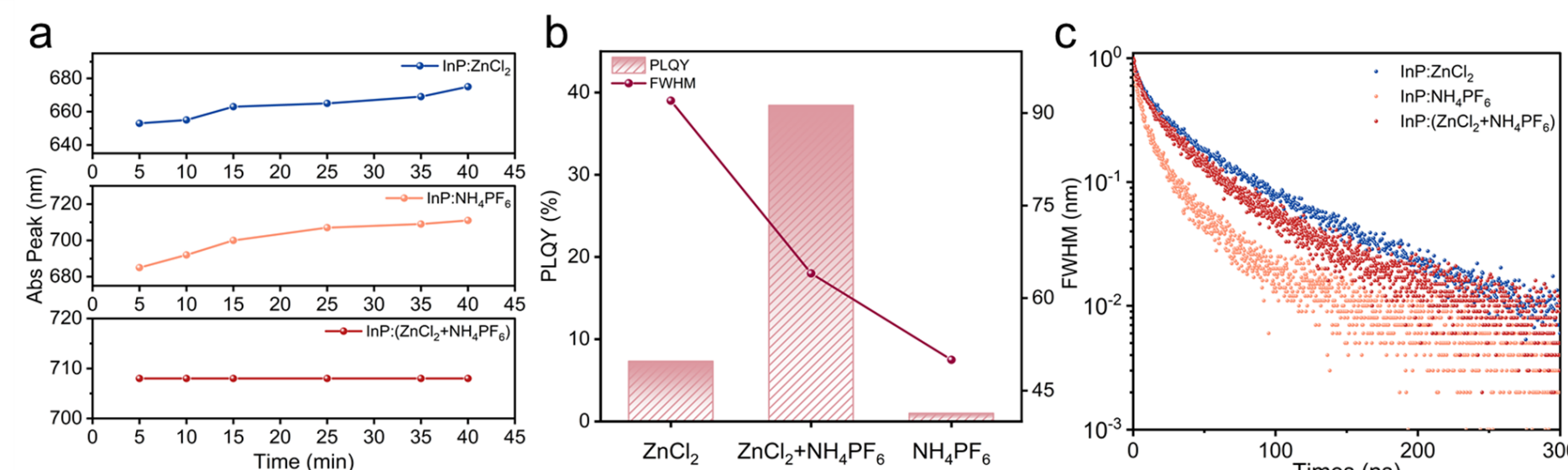


Figure 2. The comparison of optical properties for core-only InP QDs synthesized with ZnCl<sub>2</sub> only (blue), NH<sub>4</sub>PF<sub>6</sub> only (orange), and the combination of ZnCl<sub>2</sub> and NH<sub>4</sub>PF<sub>6</sub> (red)

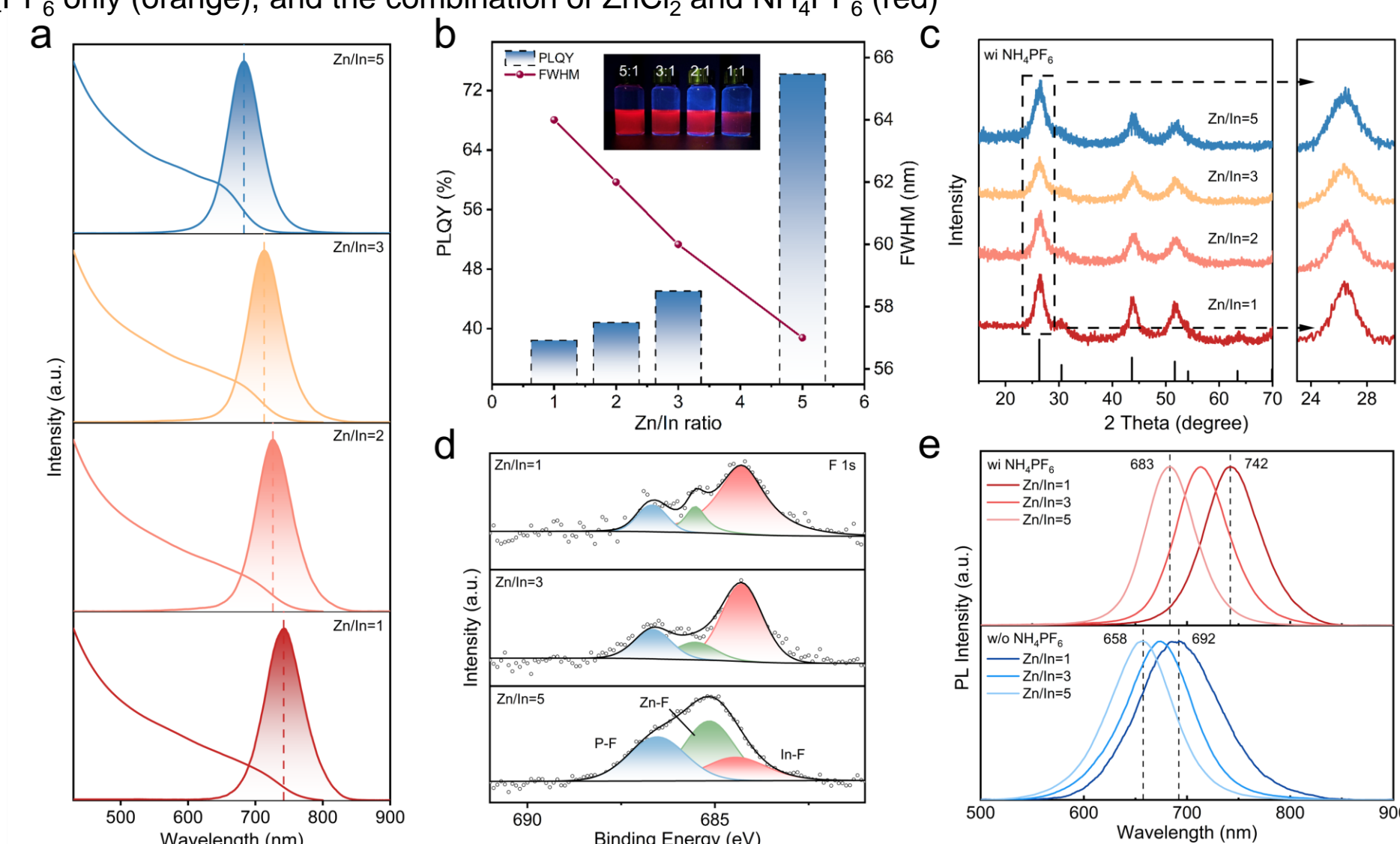


Figure 3. (a) Optical properties of core-only InP QDs synthesized with ZnCl<sub>2</sub> and NH<sub>4</sub>PF<sub>6</sub> at varying Zn/In ratios; (b) Corresponding PLQY and FWHM of core-only InP QDs; (c) Overall and magnified XRD patterns for core-only QDs prepared with different Zn contents; (d) High-resolution F 1s XPS spectra as a function of Zn precursor concentration; (e) Normalized PL spectra of QDs synthesized with (upper panel) and without (lower panel) NH<sub>4</sub>PF<sub>6</sub> across varying Zn/In feed ratios.

InP:(ZnCl<sub>2</sub>+NH<sub>4</sub>PF<sub>6</sub>) demonstrated a competitive adsorption among multiple ligands, which accelerates the formation of monomers and subsequent growth. The enhancement in PL intensity is due to the progressive surface passivation through the adsorption of multiple ligands on size-locked QDs. The resulting ZnCl<sub>2</sub> and NH<sub>4</sub>PF<sub>6</sub> co-treated InP QDs exhibited a PLQY of nearly 40%, outperforming control group prepared with ZnCl<sub>2</sub> or NH<sub>4</sub>PF<sub>6</sub> alone. The synergistic effect of this dual-salt strategy was further confirmed by TRPL results, which indicated a more suppressed trapping process in the co-treated InP QDs.

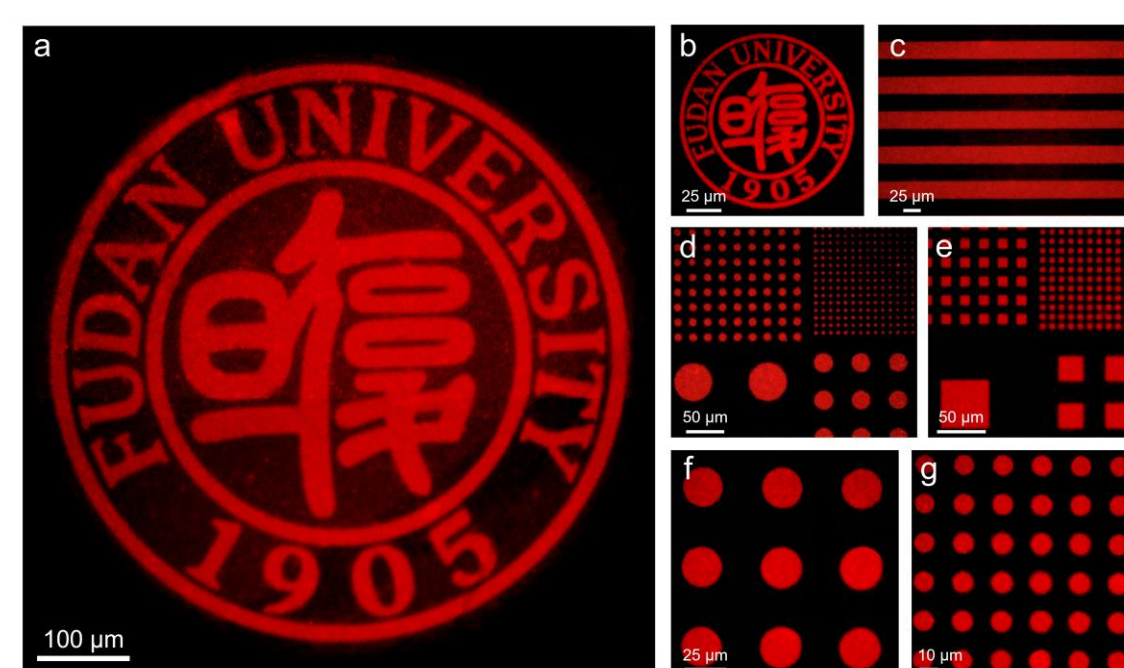


Figure 4. Fluorescence microscopic images of InP QDs.

Zn incorporation enables efficient passivation of bulk defects while simultaneously promoting the adsorption of NH<sub>4</sub><sup>+</sup> on the surface, thereby enhancing surface defect passivation. With the most optimal NIR-I emissive InP QDs, QD films were deposited via spin-coating and subsequently irradiated under UV exposure through various photomasks. Well-defined patterns with resolution ranging from 500 μm to as small as 5 μm were successfully obtained.

### CONCLUSION

In conclusion, we present a simple, direct dual-salt-mediated strategy for synthesizing high-performance, NIR-I emitting core-only InP QDs with tunable emission wavelengths ranging from 683 to 742 nm and a PLQY of up to 74%. The exceptional performance of these core-only InP QDs was further demonstrated by fabricating fluorescence microscopic images with a spatial resolution down to 5 μm. This work provides valuable insights into the preparation of highly efficient NIR-emitting core-only InP QDs and highlights their potential to advance commercial applications of InP QDs in next-generation optoelectronic devices.

### FUTURE WORK / REFERENCES

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