

Trialkylsulfonium Ligands for the Robust Surface Passivation of Lead Halide Perovskite Nanocrystals

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Abstract: This study introduces a structurally diverse library of long-chain trialkylsulfonium ligands designed to provide surface stabilization of lead halide perovskite nanocrystals (LHP NCs). We evaluate the influence of ligand structure on binding affinity and demonstrate that sulfonium-based ligands offer effective passivation compared to traditional ammonium ligands. Notably, the resulting NCs exhibit exceptional stability at high dilutions and maintain integrity in industrially relevant manufacturing solvents for down-conversion layer production. This work highlights the potential of sulfonium-based ligands to stabilize and produce robust, high-performance perovskite NCs for photonics and optoelectronics.

Keywords: Capping ligands · Colloids · Nanocrystals · Perovskites



Oleksandr Kolomiets received his Bachelor's degree in chemistry from V. N. Karazin Kharkiv National University. In 2022, he moved to Switzerland and became an Alfred Werner Scholar, and started working in Prof. Dr. Maksym Kovalenko's group as a Master's student. Oleksandr received his Master's degree in chemistry from ETH Zurich in 2024. He continued working in the Kovalenko group as a PhD student.

His research focuses on the development and synthesis of novel ligands to stabilize lead halide perovskite quantum dots and their subsequent applications.

1. Introduction

Defect tolerance is a key property that positions lead halide perovskite nanocrystals (LHP NCs) as materials with exceptional optical characteristics, particularly their tuneable narrow-band photoluminescence (PL) with near-unity PL quantum yield (PLQY) across the entire visible spectrum.^[1–4] Since their discovery, one of the most significant challenges has been effective surface passivation. The ionic and labile structure of these NCs,^[5] combined with the highly dynamic nature of conventional surface-passivating ligands,^[6] necessitates new ligand design – headgroup and tail optimization.

Using hydrophobic, fully methylated ammonium^[7] or phosphonium^[8] headgroups (Fig. 1a) significantly improved the stability of LHP NCs by minimizing their interaction with polar solvent molecules.^[7,9,10] Nevertheless, while improved ligand stability against deprotonation and interactions with polar molecules is beneficial, it can lead to a non-ideal structural fit at the binding sites of LHP NCs.^[9,11] The more compact pyramidal structure of sulfonium, arising from the elimination of one substituent on its headgroup (Fig. 1a), is thought to provide a better fit at the A-site on the LHP NC surface.

This concept, along with the recent demonstration of sulfonium species in stabilizing FAPbI₃ (FA = formamidinium) solar cells and quasi-2D perovskites with high power conversion efficiency,^[12,13] has sparked our interest in exploring long-chain trialkylsulfonium organic salts, and the result is presented in a recently published work.^[14]

2. Structural Diversity of Organic Sulfoniums

A simple (*via* S_N2 substitution) and robust synthesis of long-chain aliphatic sulfoniums has been developed to create a diverse library of cationic and zwitterionic ligands with tuneable lengths and structures for the aliphatic tail, in conjunction with their headgroups (Fig. 1b). These diverse organic sulfoniums were screened as ligands for LHP NC surfaces.

3. Surface Passivation of LHP NCs with Sulfonium Ligands

Fully inorganic (CsPbBr₃, CsPb(Br/Cl)₃) and hybrid (MAPbBr₃) (MA = methylammonium) NCs capped with sulfonium ligands, synthesized *via* a scalable, room-temperature colloidal approach,^[15] exhibit monodispersity and optical brightness on par with, or exceeding, state-of-the-art ammonium-capped systems. Specifically, cationic sulfonium ligands yield PLQYs approaching 90%, while zwitterionic ligands yield PLQYs exceeding 90% (Fig. 1c and d).

The excellent colloidal stability of NCs with organic sulfoniums prompted us to pursue further studies of sulfonium ligands. A combination of experimental (stability to purification), computational (*ab initio* molecular dynamics (MD) of ligand competition), and temperature-dependent diffusion NMR (DOSY) studies revealed that the sulfonium headgroup provides passivation comparable to that of the ammonium headgroup, whereas the conformational entropy and packing density of the hydrophobic tails are the key factors governing the binding of cationic ligands.

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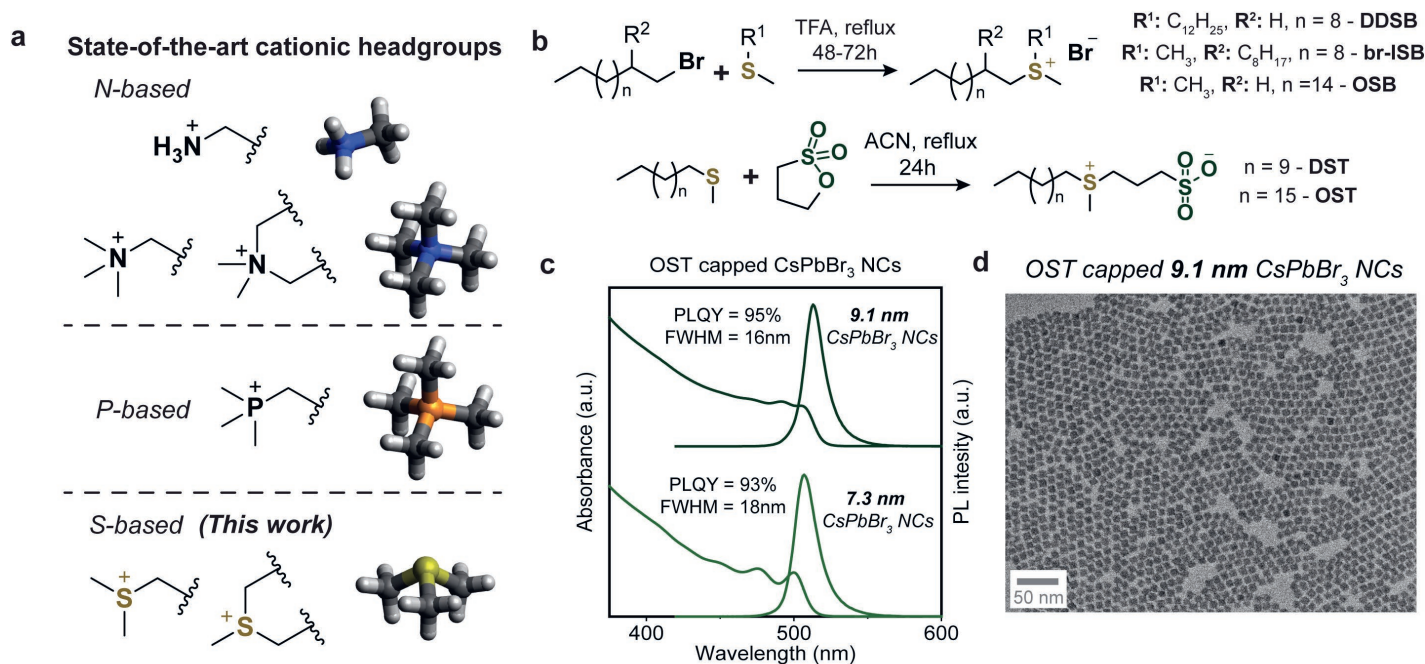


Fig. 1. a) Structural formulas and space filling models of common cationic head groups - traditional alkylammonium, recently introduced trimethylalkylphosphonium, and the sulfonium head groups studied in this work; (b) general reaction scheme for the synthesis of cationic and zwitterionic alkyl sulfonium ligands; (c) optical absorption and PL spectra of single-purified 7.3 nm and 9.1 nm CsPbBr_3 NCs capped with OST; (d) TEM images 9.1 nm CsPbBr_3 NCs capped with OST ligands. Adapted with permission from Ref. [14]. Copyright 2026 American Chemical Society.

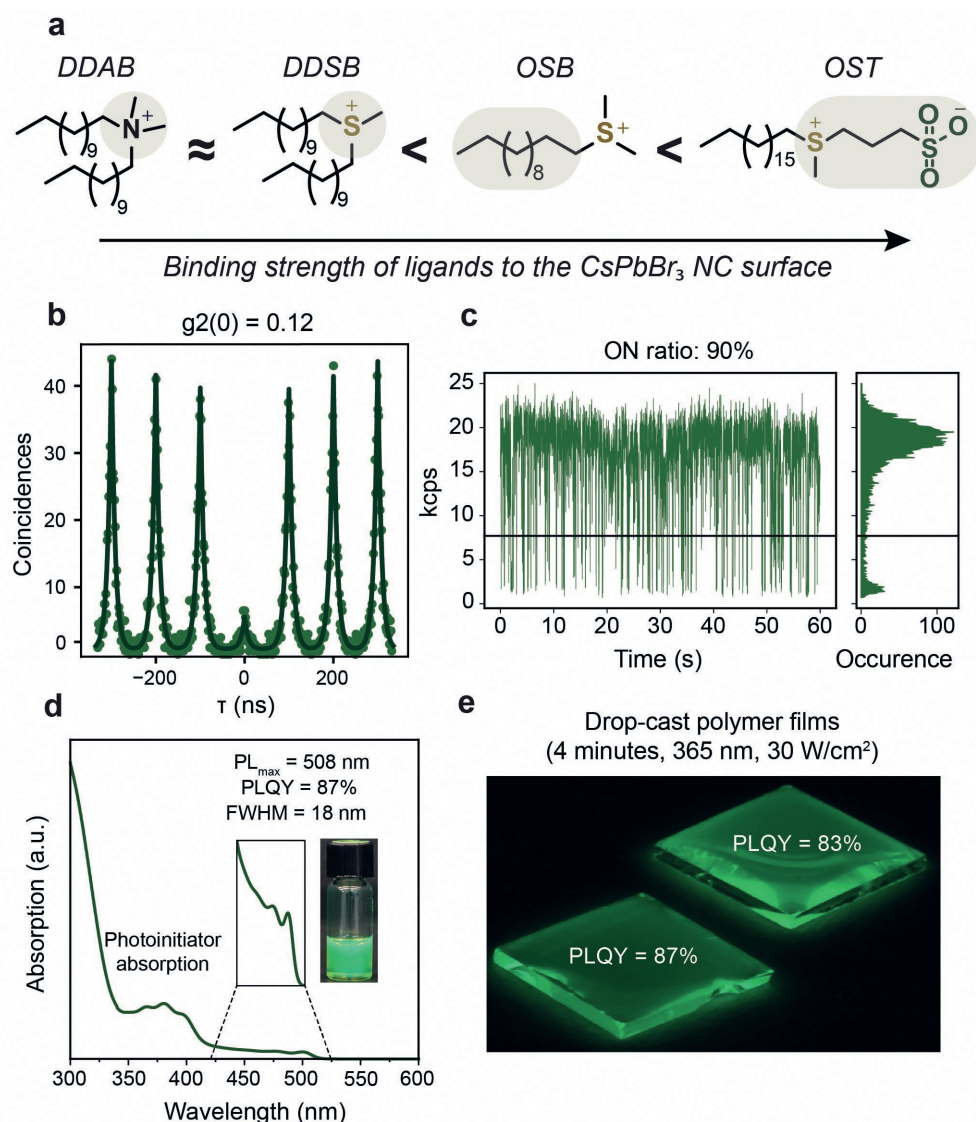


Fig. 2 a) Trend in ligand binding affinities (DDAB, DDSB, OSB, and OST) based on purification stability, MD simulations, and DOSY measurements; (b) second-order photon-photon correlation of an OST-capped CsPbBr_3 NC displaying high single-photon purity ($g^{(2)}(0) = 0.12$); (c) representative PL blinking traces (10 ms binning time) of an NC capped with the OST ligand; (d) absorption spectrum of CsPbBr_3 NCs dispersed in UV-curable inks (monomers and photoinitiator); (e) UV-polymerized films of different thicknesses obtained from the NC ink. Adapted with permission from Ref. [14]. Copyright 2026 American Chemical Society.

Single-tail cationic and zwitterionic sulfonium ligands enabled a more densely packed and less dynamic organic shell on the NC surface, significantly suppressing ligand desorption during multiple purification cycles and at high dilution (Fig. 2a).

4. Implication of Sulfonium-Based Ligands

Further implementation of 'sulfobetaine-like' zwitterionic ligands, featuring both sulfonium and sulfonate moieties, led to the development of bright (PLQY > 90%) CsPbBr₃ and CsPb(Br/Cl)₃ NCs. These NCs demonstrated suppressed blinking rate (on-time fraction ~ 90%) and high single-photon purity ($g^2(0) = 0.12$) (Fig. 2b and c), as well as enhanced colloidal stability and monodispersity during ink formulation and polymerization to produce bright (PLQY > 80%) films (Fig. 2d and e). These properties make them applicable for diverse applications, including quantum photonics and down conversion layers for displays.

5. Conclusion

In summary, the resulting sulfonium-capped NCs exhibited high PLQY of up to 90%, narrow size dispersion, and narrow emission spectra comparable to those achieved with state-of-the-art cationic and zwitterionic ligands. Stability at both the assembly level and in formulation solvents such as acrylates and methacrylates, as well as under a harsh high-dilution regime, benchmark sulfonium-based ligands as practically applicable for diverse LHP NC applications.

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