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The Fascinating Chemistry of Perovskite Quantum Dots

The rise of quantum dots

The rapidly increasing demand for smaller and faster optoelectronic devices has led to a growing need for nanometer-sized semiconductors [1]. This need can be fulfilled with quantum dots (QDs) - an exciting group of nm-sized semiconductors whose optical properties can be tuned via their respective sizes. These QDs have attracted the attention of diverse materials scientists due to their unique optical versatility, including widely tunable light absorption, bright emission of pure colors, control over electronic transport, and a wide tuning of chemical and physical functions across the visible and infrared wavelengths and coherent single photon emission [1]. This makes them promising materials for technologies such as displays and lighting, lasers, sensing, electronics, solar energy conversion, photocatalysis, and quantum information [1-4]. Additionally, QDs are crucial materials in the fundamental studies of quantum effects on the optical and electronic properties of semiconductors. Thus, the development of QDs was a milestone in the field of nanotechnology, as was recognized by the Nobel Prize for Chemistry in 2023, highlighting the pioneering work of Alexey Ekimov [5], Louis E. Brus [6], and Moungi Bawendi [7], as well as many others in the 80s and 90s [8, 9]. Colloidal QDs offer the most precise tuning of their quantum properties. These consist of small semicon-

ductive crystalline domains (from several tens of nanometers down to several nanometers) that are covered with organic ligands that are not only needed to control their size, but also grant them colloidal and chemical stability.

Nanosized lead halide perovskites

Among the many possible semiconductors, such as CdSe, InP, PbS or HgTe [1], the latest class of materials within the field of QDs are those made of perovskites [10]. These are composed of the ABX_3 perovskite crystal structure, with $A = Cs^+$, methylammonium or formamidinium, $B = Pb^{2+}$ or Sn^{2+} , and $X = Cl^-$, Br^- , or I^- (Figure 1a) [11]. These tiny semiconductors, first introduced in 2014 and 2015 as nanocrystals [12, 13] and later also as QDs (Figure 1b and c) [10], are gaining a significant interest due to their highly defect tolerance [14] allowing for easily obtainable unity photoluminescence quantum yields (PLQYs) [15]. In addition, they exhibit extremely fast radiative recombination rates, highly excitonic absorbance, a bright emission, near-unity PLQYs, a PL peak that is tailorable across the visible spectral range, a small PL full-width at half-maximum (FWHM), and easy and accessible syntheses (Figure 1d) [14]. Therefore, perovskite QDs will play a crucial role in the next generation

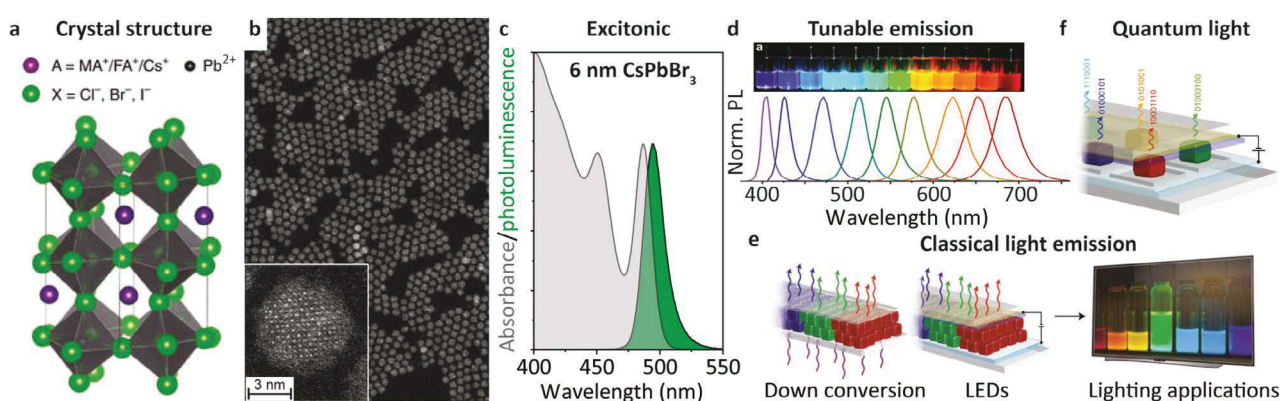


Fig. 1: Overview of perovskite quantum dots. a) A diagram of a lead halide perovskite crystal structure. b) Electron microscopy images of monodisperse 7 nm $CsPbBr_3$ QDs. c) Absorption and PL spectra of 6 nm $CsPbBr_3$ QD with sharp excitonic resonances. d) Emission spectra of various LHP NCs demonstrating tunability spreading the complete visible spectrum. e) Perovskite QDs in classical and (f) quantum light sources. Reprinted with permission: a, f, e) from [14], Copyright 2018, Springer Nature, b) from [20], Copyright 2022 American Chemical Society, and d) from [13], Copyright 2015 American Chemical Society.

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of optoelectronic devices such as LEDs (Figure 1e) [16]. Perovskite QDs are also promising building blocks for future quantum technologies, which require precise control over individual photons (Figure 1f) [4, 17]. Our work focusses on the size and shape control of perovskite QDs [10, 18], understanding their underlying surface chemistry [19], as well as their excitonic quantum properties [20].

Size and composition control of perovskite QDs

One of the most exciting features of QDs is their ease of optical tunability, allowing us to finely tune their absorption and emission with nm precision by tuning their size, shape and composition. To achieve this, one must first understand the underlying chemistry that drives the formation of these tiny nanometer sized semiconductors. To this end, our work has a strong focus on understanding how the chemistry of these systems dictate their growth dynamics, which in turn, controls the size, shape and composition of the QDs [10, 18, 21]. For this, we for instance use in-situ spectroscopy to monitor the growth of QDs [10, 18, 19]. From this, we can learn which parameters specifically control the nucleation and growth, which controls the final size and monodispersity of the colloidal QDs. For example, in the case of CsPbBr₃ QDs, it is crucial to use the right ligands to precisely, and atomically, control the growth of the QDs. We recently demonstrated that using weakly coordinating ligands, such as trioctylphosphine oxide (TOPO) and diisooctyl phosphinates (DOPA), allows us to grow these QDs at room temperature, with nm precise control over their final size (Figure 2a and b) [10]. Additionally, we can tune the composition of the QDs post synthesis via a controlled anion exchange process (Figure 2a), in which halides of pre-synthesized QDs can be replaced, with the full preservation of the QDs' size and size dispersion [21]. This allows us to precisely, for instance in the case of an exchange from CsPbBr₃ to CsPb(Br:Cl)₃, tune the excitonic absorption of the QDs from green to blue, without losing the size and monodispersity of the parents CsPbBr₃ QDs [18]. This gives us a powerful tool to tune the properties of these QDs for their respective optoelectrical and quantum devices.

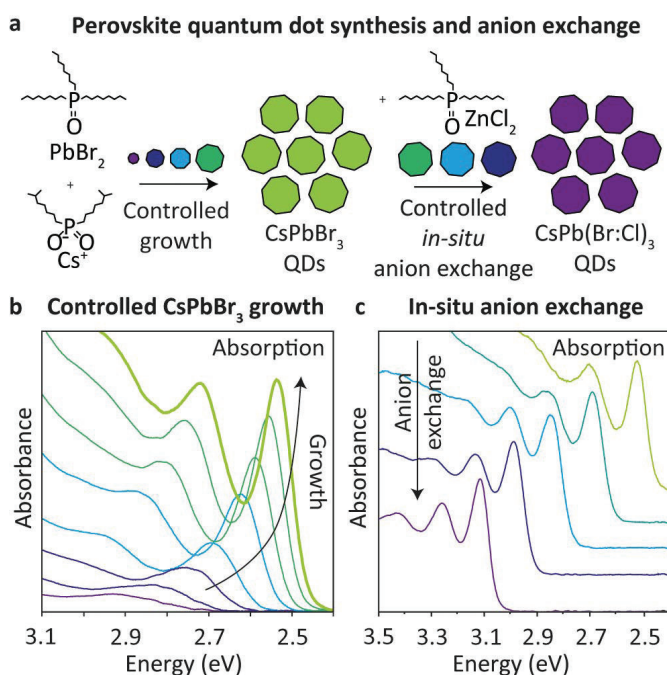


Fig. 2: Controlling the growth and composition of perovskite quantum dots. a) A reaction scheme of the synthesis and post-synthesis anion exchange of lead halide perovskite QDs. b) In-situ absorption spectra of growing CsPbBr₃ QDs. c) Absorption spectra of various CsPb(Br:Cl)₃ QDs with different halide compositions archived via anion exchange. Reprinted with permission from [18]. Copyright 2022 American Chemical Society.

A closer look at the QDs' surface

Due to their extremely small size, QDs have a very high surface area to volume ratio. Additionally, colloidal QDs are covered with ligands. This means that the surface of QDs and their respective surface chemistry play a crucial role in both the optical and chemical properties of QDs. Therefore, we also focus our work on detailed studies of what happens at the surface of QDs and how we can use this to optimize the QDs' properties [19, 22]. For instance, we recently developed a "sphere of action" model for metal salts adsorbing to the surface of perovskite QDs [19]. With this approach, we can use molecular species (such as BiBr₃), which strongly quenches the photoluminescence of CsPbBr₃ QDs (Figure 3a), as a tool to "look" at the surface of the QDs. Using concentration dependent quenching (Figure 3b), we show that a single surface bound BiBr₃ molecule can completely switch off a perovskite QD, resulting in a negligible PLQY, without altering the absorption of the QD. Using these quenching dynamics, we identified key parameters of the adsorption of metal salts towards the QDs' surface, demonstrating an enhanced surface reactivity at the corners of QDs (Figure 3c) where the QD is the most exposed, and a "Langmuir"-type surface coverage with ligands (Figure 3d), which can be better passivate with the addition of additional ligands. These quenching studies are relevant for a controlled surface engineering of perovskite QDs for optoelectronic applications and they hold promise for further studies on surface modification such as ligand exchange reactions or charge transfer mechanisms with additives.

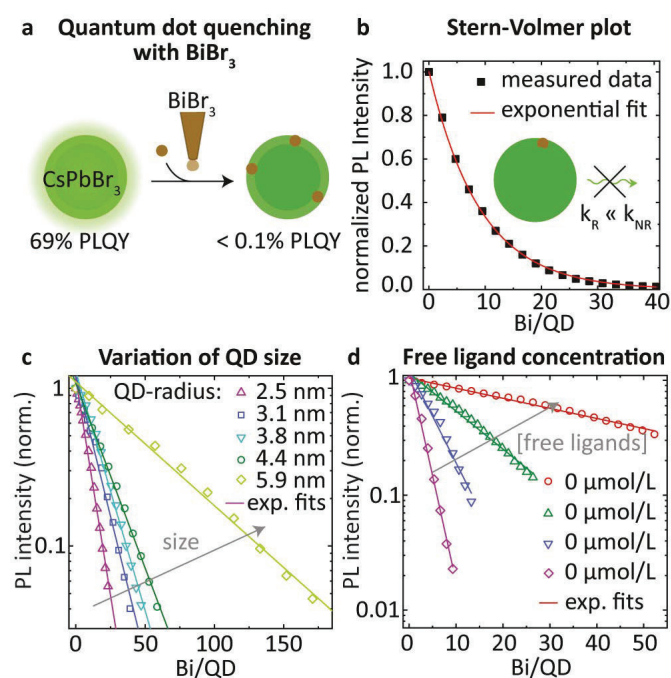


Fig. 3: Quenching studies of perovskite QDs. a) A reaction scheme of the quenching of CsPbBr₃ QDs with BiBr₃. b) Stern-Volmer plot of the QD quenching, showing a clear exponential quenching, originating from the Poisson distribution of quencher among the QDs, combined with the strong non-radiative (NR) quenching of the BiBr₃. c) Stern-Volmer plots of different sized QDs, showing a stronger quenching for smaller QDs, originating from their increased corners. d) Stern-Volmer plots of QDs with varying free ligand concentration, showing a strong decrease in quenching with increasing free ligands, originating from the increased surface coverage of the QDs. Reprinted with permission from [19]. Copyright 2023 American Chemical Society.

A bright but challenging future for perovskite quantum dots

Although there are still many challenges up ahead for perovskite QDs, it is clear that their bright, narrow and tunable emission will be important for the next generation of classical and quantum light sources. Within the field of physical chemistry, several important questions need to be answered; Can we make perovskite QD based heterostructures like core shell QDs? How do we control the perovskite's homogeneous and heterogeneous nucleation at the nanoscale? Can we understand their underlying, fast, ionic and complex reaction mechanisms? Likewise, better ligands need to be developed which requires a better understanding of the ionic inorganic-organic interface of the perovskite QDs and their ligand shell. To this end, our group continues to develop in-situ techniques to monitor the synthesis and ligand exchanges of peQDs and use this to gain a better understanding of their underlying physical chemistry. With these powerful tools we will answer many of these questions and develop new synthesis routes for better ligands shells, leading to a better integration into future peQD based devices.

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References

- [1] Arquer, F. P. G. d. et al. Semiconductor Quantum Dots: Technological Progress and Future Challenges. *Science* **373**, eaaz8541 (2021).
- [2] Park, Y.-S., Roh, J., Diroll, B. T., Schaller, R. D. & Klimov, V. I. Colloidal Quantum Dot Lasers. *Nat. Rev. Mater.* **6**, 382-401 (2021).
- [3] Won, Y.-H. et al. Highly Efficient and Stable InP/ZnSe/ZnS Quantum Dot Light-Emitting Diodes. *Nature* **575**, 634-638 (2019).
- [4] Kagan, C. R., Bassett, L. C., Murray, C. B. & Thompson, S. M. Colloidal Quantum Dots as Platforms for Quantum Information Science. *Chem. Rev.* **121**, 3186-3233 (2021).
- [5] Ekimov, A. I., Efros, A. L. & Onushchenko, A. A. Quantum Size Effect in Semiconductor Microcrystals. *Solid State Communications* **56**, 921-924 (1985).
- [6] Brus, L. E. A Simple Model for the Ionization Potential, Electron Affinity, and Aqueous Redox Potentials of Small Semiconductor Crystallites. *J. Chem. Phys.* **79**, 5566-5571 (1983).
- [7] Murray, C. B., Norris, D. J. & Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse Cde (E = Sulfur, Selenium, Tellurium) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **115**, 8706-8715 (1993).
- [8] Efros, A. L. & Brus, L. E. Nanocrystal Quantum Dots: From Discovery to Modern Development. *ACS Nano* **15**, 6192-6210 (2021).
- [9] Alivisatos, A. P. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science* **271**, 933-937 (1996).
- [10] Akkerman, Q. A. et al. Controlling the Nucleation and Growth Kinetics of Lead Halide Perovskite Quantum Dots. *Science* **377**, 1406-1412 (2022).
- [11] Akkerman, Q. A. & Manna, L. What Defines a Halide Perovskite? *ACS Energy Lett.* **5**, 604-610 (2020).
- [12] Schmidt, L. C. et al. Nontemplate Synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskite Nanoparticles. *J. Am. Chem. Soc.* **136**, 850-853 (2014).
- [13] Protesescu, L. et al. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **15**, 3692-3696 (2015).
- [14] Akkerman, Q. A., Rainò, G., Kovalenko, M. V. & Manna, L. Genesis, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. *Nat. Mater.* **17**, 394-405 (2018).
- [15] Dey, A. et al. State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **15**, 10775-10981 (2021).
- [16] Kim, J. S. et al. Ultra-Bright, Efficient and Stable Perovskite Light-Emitting Diodes. *Nature* **611**, 688-694 (2022).
- [17] Utzat, H. et al. Coherent Single-Photon Emission from Colloidal Lead Halide Perovskite Quantum Dots. *Science* **363**, eaau7392 (2019).
- [18] Akkerman, Q. A. Spheroidal Cesium Lead Chloride-Bromide Quantum Dots and a Fast Determination of Their Size and Halide Content. *Nano Lett.* **22**, 8168-8173 (2022).
- [19] Vinçon, I., Barfüßer, A., Feldmann, J. & Akkerman, Q. A. Quantum Dot Metal Salt Interactions Unraveled by the Sphere of Action Model. *J. Am. Chem. Soc.* **145**, 14395-14403 (2023).
- [20] Barfusser, A. et al. Confined Excitons in Spherical-Like Halide Perovskite Quantum Dots. *Nano Lett.* **22**, 8810-8817 (2022).
- [21] Akkerman, Q. A. et al. Tuning the Optical Properties of Cesium Lead Halide Perovskite Nanocrystals by Anion Exchange Reactions. *J. Am. Chem. Soc.* **137**, 10276-10281 (2015).
- [22] Akkerman, Q. A. et al. Strongly Emissive Perovskite Nanocrystal Inks for High-Voltage Solar Cells. *Nat. Energy* **2**, 16194 (2016).

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Quinten Akkerman studied Chemistry at the University of Utrecht and obtained his PhD at the Istituto Italiano di Tecnologia. After this, he was a postdoctoral research at the Eidgenössische Technische Hochschule Zürich. Since 2021 he is a group leader at the department of physics at the Ludwig-Maximilians-University. His work focusses on developing novel quantum dots systems, as well as understanding their underlying chemistry using in-situ methods. This is combined with ultrafast spectroscopy to investigate their excitonic photophysical properties.

