

Introducing Manganese-Doped Lead Halide Perovskite Quantum Dots: A Simple Synthesis Illustrating Optoelectronic Properties of Semiconductors

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Supporting Information

ABSTRACT: Quantum dots (QDs) are considered useful for demonstrating quantum phenomena in undergraduate laboratories due to their monodisperse size and excellent optical properties. Although doping has an increasingly important role in QD fabrication in the semiconductor field, it has rarely been discussed in the context of the undergraduate laboratory. In this work, a simple synthesis and characterization method for Mn-doped CsPbCl₃ QDs for an upper-level undergraduate inorganic chemistry laboratory is reported. The Mn-doped CsPbCl₃ system benefits from a simplified synthesis and straightforward characterization. This experiment introduces QD research to students and offers opportunities for instructors to discuss many important concepts in inorganic chemistry, such as energy band theory, particle-in-a-box model, electron paramagnetic resonance, ligand field theory, and nanochemistry.

KEYWORDS: Upper-Division Undergraduate, Inorganic Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Crystal Field/Ligand Field Theory, EPR/ESR Spectroscopy, Nanotechnology

INTRODUCTION

Quantum dots (QD) have been termed as next-generation materials due to their highly tunable electrical, mechanical, electronic, and optical properties, allowing a wide range of applications for displays, photovoltaics, and bioimaging.^{1–3} Specifically, modern synthetic methods produce monodisperse QDs with well-defined shape, size control, and complex structures, thereby allowing the QDs to emit light at desired frequencies.^{4–6} Among the various synthetic techniques used to control QD performance, doping, or the intentional introduction of impurity ions within QD lattice, is considered one of the most useful methods due to its wide range of available doping atoms and orthogonality to intrinsic properties.⁷

Although doping has attracted increasing interest in the nanochemistry field, the concept is yet to be incorporated into undergraduate laboratories due to the complexity in synthesizing doped QDs.^{8,9} Several chemistry undergraduate laboratory experiments pertaining to QDs have been developed, pioneered by Nordell and Winker.^{10,11} Currently, the range of QDs in teaching laboratories includes PbS QDs, carbon QDs, and core–shell QDs, etc.^{12–16} Most of the goals of these laboratory experiments are to demonstrate nanoscale materials to students and discuss size-dependent properties of QDs. Although these laboratory works do vividly present the novelty of QDs and enhance student understanding toward important chemistry ideas, the complex synthesis and characterization methods involved in these works hinder the introduction of the doping concept to the undergraduate audience.

The recent development of lead halide perovskite (LHP) QDs serves as a new platform to present doping to undergraduate laboratory.^{17–19} LHP requires no complex structure to exhibit the unique properties of the dopant,

which makes characterization easy to accomplish under limited access to instruments.^{20–22} Additionally, the synthesis of LHP is less time-consuming, allowing students to complete doping QDs within limited laboratory course time without sacrificing the LHP structural integrity. Recently, Shekhirev et al. provided an excellent example of synthesizing CsPbX₃ nanocubes in ambient conditions using a teaching lab setup.²³ Inspired by the advancements made in LHP studies, we have designed a simple route to synthesize Mn-doped CsPbCl₃ QDs in ambient conditions that is suitable for the setup of an upper-level undergraduate chemistry laboratory. By using a simplified hot-injection reaction, students are able to synthesize high-quality Mn-doped CsPbCl₃ QDs with bright dopant photoluminescence (PL) and a strong electron paramagnetic resonance (EPR) response.

This experiment was developed through the collaboration of a graduate teaching assistant (TA), an undergraduate student, and faculty members. It was initially tested in Spring 2018 with a small number of students and subsequently implemented successfully in a large inorganic chemistry laboratory course in Spring 2019 at Brown University. Pre- and postexperiment surveys were given to students to assess the learning outcomes. Students were asked to rank the extent of their knowledge of QDs, as well as the synthesis process and spectroscopy used in this experiment, before and after the experiment. The learning goals are to ensure that, upon completing the lab activities, students will be able to

- (1) Describe QDs and their basic functions and applications,

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- (2) Identify the differences between nanoparticles and bulk crystals,
- (3) Synthesize doped QDs,
- (4) Draw an energy transfer diagram based on ultraviolet–visible (UV–vis) absorption and PL spectra,
- (5) Interpret PL spectra and explain the color of doped QDs observed under the UV irradiation, and
- (6) Interpret EPR spectra and explain the mechanism for the observed hyperfine splitting pattern.

Student feedback for the experiment was very positive. This experiment not only allowed students to directly observe the impact of doping in QDs but also provided them with a close link to important concepts introduced in inorganic lectures, including nanomaterials, doping, energy bands, photoexcitation, molecular orbitals, and ligand field theory.

■ EXPERIMENTAL SECTION

Overview

This experiment is developed by a graduate student TA, with the help of an undergraduate and supervision of faculties. We have successfully implemented this experiment in a large inorganic chemistry laboratory course of 56 students in Spring 2019 at Brown University after piloting it thoroughly with four students in Spring 2018. In the Spring 2019 Inorganic Chemistry Laboratory course, students were divided into four smaller lab sections with the maximum number of students being 16 for each lab section. Students were divided in pairs of two to conduct the synthesis of Mn-doped CsPbCl₃ QDs with a given doping concentration. A chart in Figure S1 shows the flow of the different experimental components. This experiment spans across 2 weeks of the lab course. During the first week's course, students finished the synthesis and purification of doped QDs. In the second week's course, students characterized their products using UV–vis absorption spectroscopy, PL spectroscopy, and EPR measurements. The detailed lab procedure is provided in Supporting Information. Students were required to read the online lab materials and prepare their lab notebook prior to the start of the lab section. Students were supervised by a graduate teaching assistant (TA) during their 4 h lab section and were given a 30 min prelab lecture by a faculty instructor prior to the experiment. In order to increase the student's critical, analytical, and writing skills, students were required to write their reports in journal article style and their reports were graded following detailed rubrics. The grading criteria include formatting, organization, data presentation and interpretation, citation, and more (see Supporting Information).

Preparation of Cs Oleate

The synthesis of Cs oleate should be conducted prior to the start of the lab by the instructors. A 0.8 g portion of Cs₂CO₃ was mixed with 40 mL of 1-octadecene (ODE) and 2.5 mL of oleic acid (OA). The mixture was heated to 150 °C under nitrogen protection until the solid was fully dissolved. A pale-yellow clear solution was obtained after 30 min. Prior to student use, the Cs oleate solution should be heated to 120 °C to prevent precipitation.

Synthesis of Mn-Doped CsPbCl₃ Quantum Dots

A 108 mg portion of PbCl₂ was mixed with a desirable amount of MnCl₂ with 10 mL of ODE, 1 mL of OA, and 1 mL of oleylamine (OAm) in a three-neck round-bottom flask. The mixture was degassed by bubbling nitrogen gas under vigorous

stirring for 15 min at room temperature. The solution was heated to 120 °C for an hour with continuous nitrogen flow, or until the solid was fully dissolved. The solution was then heated to 180 °C, when 0.8 mL of preheated Cs oleate solution was rapidly injected under vigorous stirring. The reaction was immediately quenched by submerging the product-containing flask in a cold-water bath. As-synthesized QDs were separated from reaction solution by centrifuging at 6000 rpm for 5 min. The precipitate, which contained QDs, was redispersed in hexane or other nonpolar solvents for purification and characterization.

Purification of Mn-Doped CsPbCl₃ Quantum Dots

To facilitate characterization, QDs were purified from high-boiling-point solvents and excess capping ligands. First, ethyl acetate was added to the hexane dispersion of CsPbCl₃:Mn QDs in a volume ratio of 1:1, or until a white precipitate started to form. Then, the mixture was centrifuged at 6000 rpm for 5 min. The supernatant should be discarded, and the resultant QDs in the precipitate were redispersed in hexane. Ideally, arbitrary rounds of purification could be applied to obtain high-boiling-point solvent-free QDs without excess ligand. However, only up to one round was used in order to limit decomposition and preserve enough yield for characterization.

Characterization

QDs were dispersed in hexane for all optical characterizations. During the pilot testing in Spring 2018, an Agilent Technologies Cary 5000 UV–vis–NIR spectrophotometer and an Edinburgh Instruments Fluorescence Spectrometer F55 spectrophotometer were used to obtain UV–vis absorption and PL spectra, respectively. QDs were added to a quartz EPR tube for EPR measurements. In Spring 2019, a Labview UV–vis spectrometer and a custom-made Ocean Optical photoluminescence spectrometer were used to measure the absorption and PL spectra, respectively. Glass test tubes were used for the UV–vis absorption spectroscopy measurement to avoid purchasing expensive quartz cuvettes. In both Springs of 2018 and 2019, QDs were added to a quartz EPR tube at room temperature for EPR measurements using a Bruker EMX Premium-X EPR spectrometer.

Several additional characterizations were carried out to support the uniformity of QDs synthesized using the simplified method. However, the following characterizations should be omitted in a teaching lab due to cost and time. Transmission electron microscopy (TEM) was measured with a CM 20 transmission electron microscope operating at 200 kV. QDs dispersed in hexane were dropped onto a 300 mesh copper TEM grid and dried in ambient conditions. Powder X-ray diffraction (XRD) spectra were obtained on Bruker D8 Discovery high-resolution X-ray diffractometer equipped with Linxeye 1D detector ($U = 40$ kV, $I = 40$ mA, Cu $K\alpha$, $\lambda = 1.5418$ Å). QDs dispersed in hexane were dropped onto a glass slide followed by gentle heating to evaporate solvent to prepare XRD samples.

■ HAZARDS

Due to the harmful nature of the chemicals used in this lab, proper personal protection equipment, including gloves, safety glasses, and lab coats, should always be used. Extra caution should be taken when dealing with high-temperature heaters and containers. Liquid or vapor ODE, OA, or OAM should not come in contact with skin or eyes or be inhaled. Pb-containing

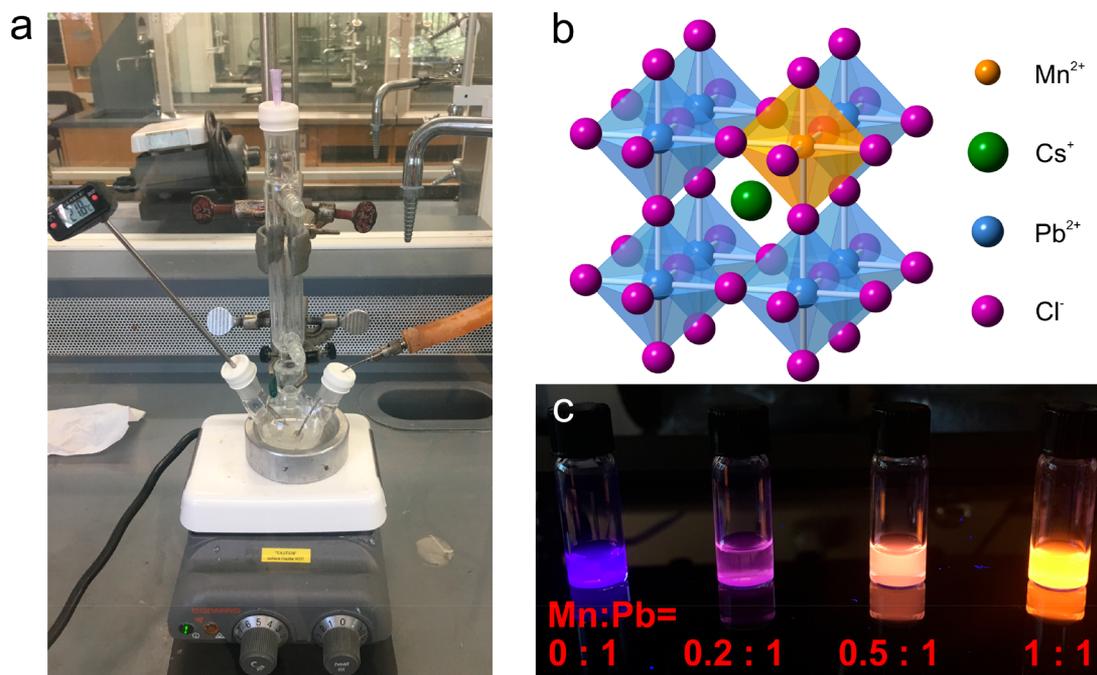


Figure 1. (a) Photograph of the synthesis setup. (b) Schematic illustration of the crystal structure of CsPbCl₃:Mn. (c) Photograph of purified CsPbCl₃:Mn QDs with increasing Mn-doping amount under UV light.

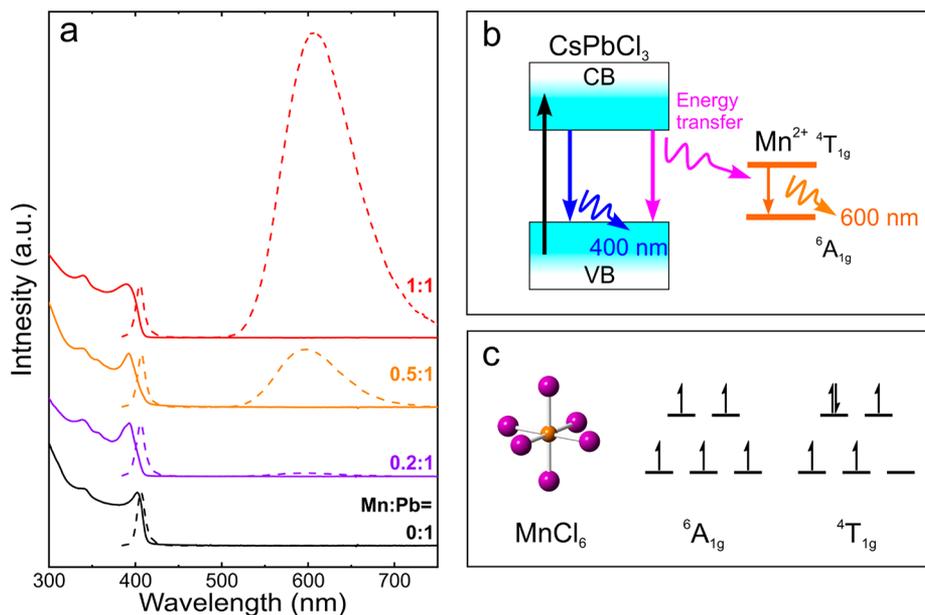


Figure 2. (a) Absorption spectra (solid line) and emission spectra (dashed line) for CsPbCl₃:Mn QDs excited at 325 nm. (b) Energy transfer mechanism for CsPbCl₃:Mn QDs. (c) Electron configuration for ground states and excited states of Mn²⁺.

precursors and products are poisonous and should not be swallowed or inhaled. Most precursors and products should be properly disposed to avoid lead contamination.

RESULTS AND DISCUSSION

Data taken both by TA during the pilot testing and by students in Spring 2019 course are presented in order to better explain and discuss the results from this doped QD experiment.

Synthesis of Mn-Doped CsPbCl₃ QDs

The setup for the synthesis of CsPbCl₃:Mn QDs and their corresponding crystal structure are given in Figure 1a,b,

respectively. The synthesis procedure is adopted with modifications from the work of Liu et al.²¹ PbCl₂ and MnCl₂ are dissolved with capping ligands, OA and OAM, prior to Cs oleate injection, which initiates the QD nucleation and growth. Such synthesis of LHP QDs follows the classic hot-injection technique, which is widely used in the synthesis of nanoparticles. Students interested in this subject should be referred to other resources for furthering their understanding of the mechanism.^{24,25} Due to the air-sensitive nature of both Mn²⁺ and long-chain organic molecules, this reaction has been traditionally carried out under inert conditions to avoid oxidation. In order to adapt to an inexpensive undergraduate

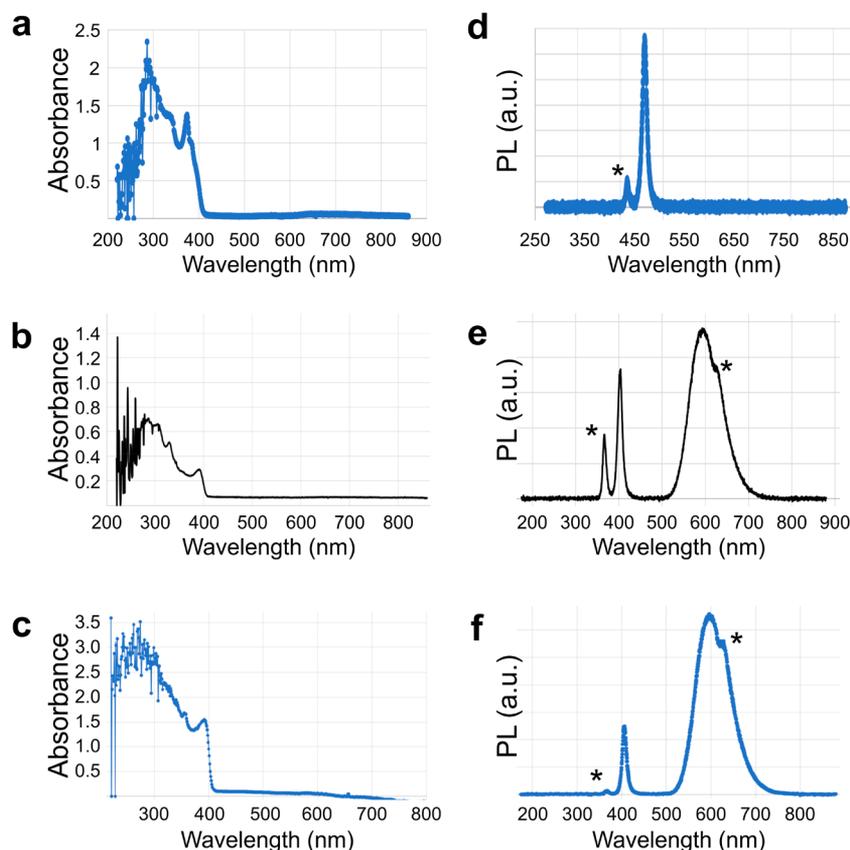


Figure 3. (a–c) Representative UV–vis absorption spectra from student reports. (d–f) Representative PL spectra from student reports for three different Mn:Pb ratios of 0:1, 0.5:1, and 1:1. Asterisks mark instrument artifacts.

lab setup, the Schlenk line setup by Liu et al.²¹ is adapted by bubbling nitrogen throughout the synthesis, removing oxygen and trace amounts of water (shown in Figure 1a). Because the QDs synthesized through our method are capped by organic capping ligands (OA, OAM), they can readily disperse in nonpolar solvents such as hexane. The ligand-capped QDs are also stable enough to undergo two rounds of purification by precipitation using polar solvents (ethyl acetate) and redispersion using nonpolar solvents (hexane). More importantly, the products remain bright with glowing color after purification, allowing direct visualization under the UV lamp. As seen in Figure 1c, the products exhibit bright PL ranging from deep purple to orange, depending on the Mn-doping concentration. The bright PL is a signature of successful syntheses. For a laboratory without further characterization tools, the color of these products can be particularly powerful and useful in demonstrating semiconductor material and their property-modifying techniques by doping.

Dopants and Electronic Properties of QDs

Absorption and PL spectra of CsPbCl₃:Mn QDs taken during the pilot testing by the TA are presented in Figure 2a. The data clearly demonstrate that Mn²⁺ dopants introduce extrinsic electronic states to CsPbCl₃ QDs. Under UV irradiation, the samples of QDs doped with Mn²⁺ exhibit a broad emission peak centered around 600 nm, which is not present in the undoped sample. Hence, the Mn emission peak near 600 nm results from the energy transfer from the CsPbCl₃ host. The scheme in Figure 2b shows the detailed energy transfer mechanism of the system. The unique energy transfer mechanism in CsPbCl₃:Mn QDs correlates to the energy

band model of the CsPbCl₃ semiconductor and the energy structure of Mn²⁺ complexes. This allows students to compare the similarities and differences of electronic and chemical structures in semiconductors and complex molecules. When the CsPbCl₃ host is photoexcited by UV light, electrons that attained enough energy from photon will transit from the valence band of CsPbCl₃ to its conduction band. The band gap energy can be estimated by measuring the cutoff of the absorption spectra. Following photoexcitation, the energy of the excited electron of CsPbCl₃ host can be released in either of the following two pathways. In an undoped CsPbCl₃ QD, the excited electron recombines with a hole in the valence band, releasing a photon whose wavelength around 400 nm corresponds to the electron energy. On the other hand, in Mn-doped CsPbCl₃ QDs, the energy is quickly transferred to the Mn²⁺ dopant ion, while the electron in CsPbCl₃ returns to its ground state without emitting a photon. Through this process, the Mn²⁺ is excited from the ground state ⁶A_{1g} to the spin-forbidden excited state ⁴T_{1g} (Figure 2c).²⁶ The subsequent radiative relaxation from ⁴T_{1g} to ⁶A_{1g} gives the signature bright orange Mn²⁺ emission around 600 nm. Students are expected to attribute the observed wavelength emission to a ⁴T_{1g} to ⁶A_{1g} electronic transition by considering the ground state and excited state of a d⁵ metal complex with weak field ligands. A Tanabe–Sugano diagram could be introduced here to explain the transition. Within our laboratory experiment, the diagram analysis was especially useful in helping undergraduate students understand that the electronic transitions are only allowed if the spin multiplicity remains the same. Thus, the

absence of absorption past 420 nm agrees with the spin-forbidden nature of the ${}^6A_{1g}$ to ${}^4T_{1g}$ transition.

During characterization of the spectra shown in Figure 2a, it is clear that increasing the dopant concentration results in a significant enhancement of emission intensity. This provides evidence for enhanced energy transfer from the exciton to Mn^{2+} . Despite an increasing concentration of dopants, the intrinsic features of the $CsPbCl_3$ QD absorption spectrum are not influenced. This indicates that the optical properties of the $CsPbCl_3$ host are preserved after doping. Students may report observing a slight blue shift in the absorption edge with increasing doping concentration, such as from 404 to 390 nm in Figure 2a. Because there is no significant difference in QD size, this observed phenomenon can be explained by the contraction of the lattice constant due to the smaller radius of Mn^{2+} ions.²⁷ Additionally, students may notice the red shift of the broad Mn^{2+} signature emission peak from 596 to 608 nm. This phenomenon is due to the Mn–Mn exchange interaction, which results in the split of both the ${}^4T_{1g}$ and ${}^6A_{1g}$ energy levels and the decrease of the energy difference between excitation state and ground state.²⁷

The reproducibility of this designed lab was tested through introducing the experiment to a large inorganic chemistry class at Brown University in Spring 2019. All students were able to finish the synthesis of QDs well within the 4 h time frame and produce good products that were characterized during the next lab session that occurred 2 weeks later. If time permits, it is possible to conduct the experiment into one experiment session by running the characterizations right after synthesis. Figure 3a–f includes three sets of optical data chosen from students' lab reports, which include the UV–vis absorption spectra and PL spectra for the samples with Mn:Pb ratios of 0:1, 0.5:1, and 1:1. Compared with data taken by the TA in Figure 2a, the students' optical measurements show similar features and qualities: absorption spectra include a clear absorption edge around 400 nm; PL spectra show strong, distinguishable intrinsic emission and Mn emission. The quality of the students' synthesized products underscores the high reproducibility of the QD synthesis in the teaching lab setup. It is also worth noting that the data were collected after 2 weeks of storage, showing the high stability of as-synthesized QDs.

Application of EPR and Interpretation

Electron paramagnetic resonance (EPR) is a useful tool for studying the structure of paramagnetic species such as transition metal complexes, and organic radicals. EPR can be especially useful in reviewing aspects of inorganic and physical chemistry, such as electron spin and oxidation state. However, probing with EPR is uncommon within undergraduate laboratory and not yet reported in QD experiments. Here, in the described QD-doping experiment, students used X-band EPR to examine the chemical environments of Mn in the $CsPbCl_3$ host. The EPR spectrum of the QDs made by the TA with a doping concentration of 0.5:1 is provided in Figure 4a, and representative EPR spectra taken by students with doping ratio of 0.5:1 and 1:1 are shown in Figure 4b,c. Students were expected to interpret the EPR data and explain the reason for the observed hyperfine splitting pattern (or the number of peaks in EPR spectra) in their reports through examining the electron configuration, spin multiplicity, and nuclear spin of doped Mn^{2+} ions. Specifically, the hyperfine splitting of the

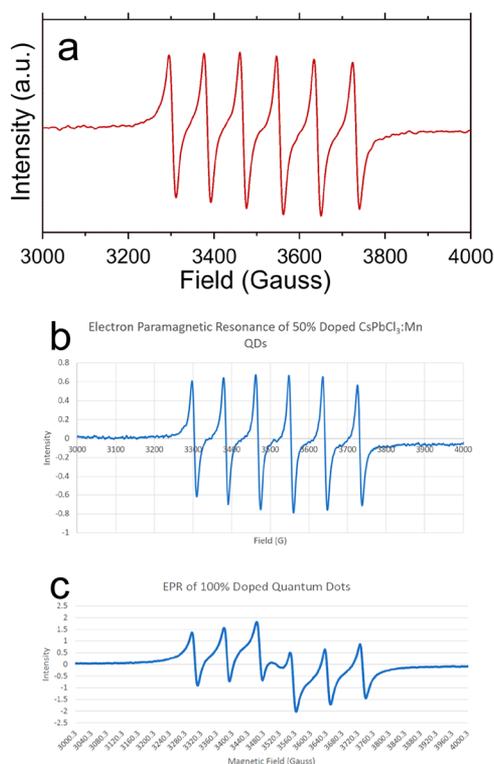


Figure 4. EPR spectra of $CsPbCl_3:Mn$. (a) TA data with the Mn:Pb ratios of 0.5:1. (b, c) Representative student's EPR spectra (taken from their reports without change) with the Mn:Pb ratios of 0.5:1 and 1:1.

EPR signal resulted from the electron–nuclei interaction. The multiplicity can be calculated by

$$n = 2I + 1$$

where “ n ” is the number of peaks and “ I ” is the nuclear spin. To demonstrate their understanding of the laboratory, the students should be able to provide that the electron configuration of Mn^{2+} is $[Ar]d^5$ in a high-spin field and its nuclear spin is $I = 5/2$.²⁸ The number of peaks for Mn^{2+} is 6 based on $n = 2I + 1$. From the EPR spectra in Figure 4 where a 6-fold splitting pattern is observed for all samples, students should be able to understand that the EPR signal is coming from the doped Mn^{2+} ions. On the basis of Figure 4a, the A -value ($A = 86$ G), which corresponds to the splitting distance between adjacent peaks, is in close agreement with previous reports, which shows that most Mn species are inside the NCs in an octahedral environment and remain as Mn^{2+} ions.²⁹ This exercise provides students a useful introduction to the sensitivity of EPR. Students should understand that EPR signals reflect a local environment, such as coordination numbers and valence state,^{30,31} after gaining experience with this sophisticated instrument.

TEM and XRD Characterizations of QD

Transmission electron microscopy (TEM) and X-ray diffraction (XRD) provide data on the morphology, structure, and composition of semiconductor QDs. Limited by time and cost, it is not practical to measure every sample in the teaching lab. Instead, representative images could be provided prior to the start of the lab to help students understand the structure of QDs. This part of the lab involving TEM and XRD is optional depending on the time, facility, and lecture content. Since the

students in the Spring 2019 course were not required to measure these data, they did not discuss these results in their lab reports.

TEM allows direct characterization of the shape and size of the single QD with atomic resolution. As shown in Figure S2a–d, the synthesized CsPbCl₃ QDs are uniform nanocubes with a side-length of approximately 10 nm. The (100) facet is favored by the cubic CsPbCl₃ phase, resulting in the formation of nanocubes, as illustrated in Figure 1b. The Mn-doping does not significantly affect the shape or size distribution of CsPbCl₃ QDs. In fact, on the basis of the TEM images in Figure S2a–d, the uniformity of QDs synthesized through our method is comparable to that of the CsPbCl₃:Mn QDs synthesized using strictly air-free techniques.^{32,33} On the other hand, XRD provides qualitative identification of the crystal structure. The XRD pattern of Mn-doped CsPbCl₃ QDs follows the cubic diffraction pattern for the space group (Figure S2e). The diffraction peaks show a slight shift to higher angles with an increase in the doping concentration of Mn. This is in accordance with Bragg's law, which describes the relationship among X-ray incident angle (θ), wavelength (λ), and lattice spacing (d):

$$\lambda = 2d \sin \theta$$

In prelab lecture, the faculty instructor explains how the larger angle shift confirms the presence of Mn²⁺, which has smaller ionic radius than Pb²⁺. This allows the students to understand that doping involves the uniform replacement of Pb²⁺ with Mn²⁺ in the lattice, rather than a fit of the impurity atoms into the interstitial site. Overall, TEM and XRD data demonstrate that QDs maintain their crystal structure despite doping with Mn²⁺. Additionally, if time permits, the uniform size distribution can provide an opportunity for students to apply the particle-in-box model to estimate the extent of confinement, serving as a link from inorganic chemistry to quantum chemistry.

Learning Outcomes and Student Survey

The learning outcomes were based on student self-assessment of learning gains. Before and after the experiment, the students in the Spring 2019 class took surveys to assess their learning outcomes. Students were asked to rank the extent of their knowledge in QDs, as well as the synthesis process and spectroscopies used in this experiment. The result of the surveys is illustrated in Figure 5 and Table 1. Prior to the experiment, most students had self-identified as lacking knowledge in QDs, optical spectroscopy, EPR measurement, and interpretation of characterization data. The self-identified understanding is significantly improved after the QD lab as illustrated in Figure 5. In the Supporting Information, Figure S3 displays additional postexperiment survey results on the following questions: (a) "How do you enjoy this QD lab?" (b) "Is the doped QD lab engaging and provided new knowledge?" According to this postlab survey that was distributed to 56 students with 54 responses, approximately 90% respondents "agreed" or "strongly agreed" that they enjoyed the QD lab and gained new knowledge through the lab.

In the postexperiment survey, students were also asked to use a few sentences to describe the following:

- What did you enjoy about the doped quantum dot lab and why?
- What are the challenges about the doped quantum dot lab and why?

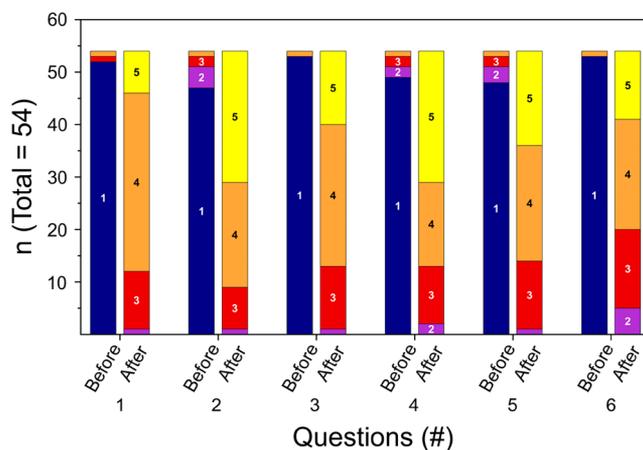


Figure 5. Result of the student survey. Under each question, the result of the pre-experiment survey is shown in the first bar (on the left), and the result of the postexperiment survey is shown in the second bar (on the right). The students respond to the questions by ranking with a number scale 1–5, with 1 representing “least knowledgeable” and 5 representing “most knowledgeable”. Survey questions are summarized in Table 1.

Table 1. Survey Items for Evaluating Students' Knowledge Gains after the Quantum Dots Lab

Item Number	Survey Items for Ranking Students' Perceived Knowledge of the Learning Objectives
1	Describe the quantum dots, their function, and applications.
2	Identify the difference between nanoparticles and bulk crystals.
3	Synthesize quantum dots.
4	Draw an energy transfer diagram based on photoluminescence, ultraviolet absorption, and electron paramagnetic spectra.
5	Interpret PL spectra and explain the color of doped QDs observed under the UV irradiation.
6	Interpret EPR spectra and explain the reason for the observed hyperfine splitting pattern.

- Any comments or suggestions on improving the lab are welcome.

Student feedback was extremely positive. Specifically, students reported that “various methods of characterization [allow] a complete picture of the QDs” and that the lab was “a great way to learn the characterization potential of UV–vis, PL, and EPR”. Students also indicated through the survey that they were able to link the laboratory experiment to concepts learned in the course, including the energy transfer diagram, magnetic properties, and electronic properties. Most students wrote that they enjoyed the QD lab due to the novelty of QDs and the lively colors involved. Some comments included “I enjoyed that we actually synthesized QDs. I have heard them a lot before, but I never truly understand what it was. Now I feel a lot more comfortable with them, and the visual of the difference in emitting light were cool” and “I liked experimenting cutting-edge chemistry. The hot-injection method was exciting, and it was cool to see QD results in the same week.”

Students also wrote about the challenges they faced while conducting this experiment and provided suggestions for the improvement. Since the lecture part of the course did not teach EPR, some students felt that one prelab lecture was not enough for them to fully grasp the new concepts and knowledge. We plan to coordinate the class schedule and content teaching with the lecture instructor to ensure that the

basic concept of EPR is taught in the class lecture prior to the lab. In addition, students suggested that the waiting time for the instrumentation of PL was a bit long since we only had one spectrometer. We plan to set up an additional one for future classes. Our very positive student survey results strongly suggest that our learning objectives are achieved and that this Mn-doped CsPbCl₃ QDs laboratory serves as a great introduction to QDs for the undergraduates.

CONCLUSIONS

In this work, we report the first application of doped QDs in a teaching laboratory for upper-level undergraduate students. Uniformed, Mn-doped LHP QDs with bright dual-color PL are readily synthesized using a simple preparation setup. In addition to providing a vivid presentation of state-of-the-art perovskite technology, the described laboratory experiment provides students with a tangible understanding of several important concepts in inorganic chemistry. The discussion topics proposed in this paper include ligand field theory, energy band theory, electron paramagnetic resonance, and complexation environments. The products can be probed by a variety of characterization tools, ranging from PL, UV-vis, EPR, TEM, to XRD. For these reasons, instructors may direct students to discuss varying topics in inorganic chemistry, depending on the chosen characterization technique. Application of this laboratory experiment in a real-classroom setting shows the ease and reproducibility of the techniques involved. Through in-class survey and laboratory reports, the students showed a significant improvement in the understanding of QD and related spectroscopy after the experiment. Overall, this experiment combines cutting-edge technology with lab-scale practice, offering students a thorough understanding of nanochemistry and quantum phenomena.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.8b00735.

TEM and XRD data, additional student survey results, grading rubrics, and lab manual (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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