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Estimating Quantum Dot Size with Pulsed Field Gradient NMR

Hal Van Ryswyk,* Hanna Z. Porter, Connor K. M. Seto, Ixchel Lopez, and Emma Dy

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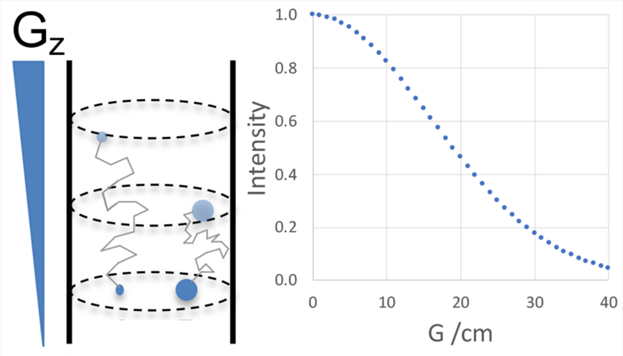
ABSTRACT: Pulsed field gradient nuclear magnetic resonance (NMR) is used to estimate the size of quantum dots (QDs) produced in a simple, fast, small-scale synthesis. This upper-division laboratory experiment teaches the basics of QD synthesis and pulsed field gradient NMR, a powerful technique for measuring diffusion coefficients in solution. The diffusion coefficients are used to calculate hydrodynamic radii, which are compared to core radii obtained from optical absorbance sizing curves, providing insight into the structure of QDs in colloidal suspension and the nature of the information provided by pulsed field gradient NMR.



KEYWORDS: *Upper-Division Undergraduate, Inorganic Chemistry, Physical Chemistry, Interdisciplinary/Multidisciplinary, Laboratory Instruction, Hands-On Learning/Manipulatives, Colloids, Instrumental Methods, Materials Science, Microscale Lab, NMR Spectroscopy, Semiconductors, Synthesis, UV−Vis Spectroscopy*

INTRODUCTION

Quantum dots (QDs) are semiconductor particles ranging from 2 to 16 nm in diameter that often exhibit optical and electronic properties that differ from those of larger particles and bulk materials. Quantum-mechanical considerations can perturb material properties at such short length scales, allowing these properties to be "tuned" by controlling the QD size. This *Journal* has published syntheses and studies of a wide range of QDs, often with an emphasis on producing a range of colored QDs in a single synthesis or across a range of similar syntheses,[1−7] exploiting the effects of quantum confinement,[8−12] or serving as an introduction to nanotechnology.[13,14] A recent report focuses on the synthesis and extensive characterization of PbS QDs as the theme of an undergraduate senior research project designed to teach nanoparticle synthesis and provide insights with advanced instrumental techniques.[15]

The PbS system is amenable to study in undergraduate laboratories because the QDs are relatively easy to synthesize under moderate conditions and a wide range of QD sizes can be made quickly. These QDs are excellent candidates for characterization by solid-state techniques such as transmission electron microscopy, high-resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction. Other techniques commonly associated with liquid or macroscopic solid samples, such as UV−vis and FTIR spectroscopy, can also be applied to good effect.[15] One technique not typically applied to QDs in an undergraduate laboratory is NMR. Recent reports show that ^{1}H NMR of organic ligands on QDs can provide a wealth of information.[16−19]

Pulsed field gradient (PFG) NMR experiments have been applied recently in undergraduate laboratories to measure diffusion of small molecules[20] and the viscosity of solution,[21] illustrating both the power of the technique and helping to fill a dearth of physical chemistry experiments in the area of mass transport.[22] PbS QDs are an interesting system for study via this technique because the diffusion coefficients of QDs can be tracked across a range of easily accessible QD sizes, these sizes work well with the Stokes−Einstein relationship relating diffusion coefficient to hydrodynamic radius, and the hydrodynamic radius can be compared readily with the QD core diameter obtained with optical techniques.

A pulsed field gradient in an NMR experiment is a defined period during which a spatially dependent magnetic field is applied. Several excellent reviews cover the theoretical basis of PFG NMR as a means of measuring diffusion coefficients.[23,24] By way of a brief overview, Figure 1 shows the pulse sequence for one of the simplest experiments designed to measure diffusion coefficients, the pulsed field gradient spin echo. Nuclei are excited by a radiofrequency pulse and then given a

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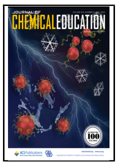

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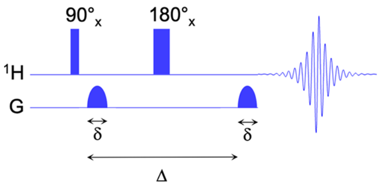

Figure 1. Pulse sequence diagram for a pulsed field gradient spin echo experiment, where the horizontal axis is time. Radiofrequency pulses shown on the ^{1}H channel are applied to the sample, and the spin echo is detected on the same channel at the end of the sequence. Pulsed field gradients are applied along the length (z axis) of the sample by a gradient coil. The diffusion time, Δ, and the gradient length, δ, are also shown on the time axis.

spatially dependent phase label by a subsequent PFG. After a short delay, a second radiofrequency pulse and PFG are applied to refocus the magnetization. Nuclei that are phase-labeled at one position but diffuse to another position along the direction of the field gradient prior to the second PFG pulse are not fully refocused, leading to signal attenuation. The signal shown at the right side of Figure 1, resulting from net magnetization created, dephased, and brought back into focus, is the spin echo.

The spin echo signal intensity is described by the Stejskal−Tanner equation,

$$I = I_0 \exp\left[-(\gamma\delta G)^2 D\left(\Delta - \frac{\delta}{3}\right)\right] \quad (1)$$

where I_0 is the original signal intensity, γ is the proton gyromagnetic ratio, G is the strength of the gradient, Δ is the diffusion time, δ is the gradient length, and D is the diffusion coefficient. In a typical experiment, the signal intensity of a unique proton is plotted as a function of gradient pulse strength (Figure 2) with all other variables held constant, producing a plot that allows the diffusion coefficient to be extracted by fitting the resulting Gaussian curve.

The diffusion coefficient of a molecule depends upon its size and shape, with additional contributions from temperature and solvent viscosity. The Stokes−Einstein equation predicts that for a spherical molecule the diffusion coefficient is

$$D = \frac{k_B T}{6\pi\eta r_H} \quad (2)$$

for a sphere of radius r_H in a solvent of viscosity η, where k_B is the Boltzmann constant and T is the absolute temperature. Thus, for a spherical molecule, measurement of the diffusion coefficient yields an estimate of its hydrodynamic radius.

The Stokes−Einstein relationship holds best when the molecules are spherical and much larger than the solvent molecules. For nonspherical molecules and especially flexible ones, there is no simple relationship between diffusion coefficient and size; attempting to correlate the hydrodynamic radius with the van der Waals radius yields superlinear results for large, nonspherical molecules and sublinear results for smaller molecules on the same order of size as solvent molecules.[25]

In many ways, PbS QDs are the ideal "molecule" for examining diffusion in an instructional laboratory. The PbS core is a truncated octahedron for small QDs, transitioning to a cuboctrahedron for larger QDs.[26] When coated with a monolayer of long-chain aliphatic ligands, the QDs are nearly spherical. Furthermore, they can be synthesized with diameters spanning 2.1−16.5 nm.[27] Thus, using QDs to probe diffusion across a range of sizes sidesteps many of the issues of applying the Stokes−Einstein equation to small molecules of various shapes and uncertain sizes, where the relationship between diffusion coefficient and molecular mass is, in general, quite complex.[28,29]

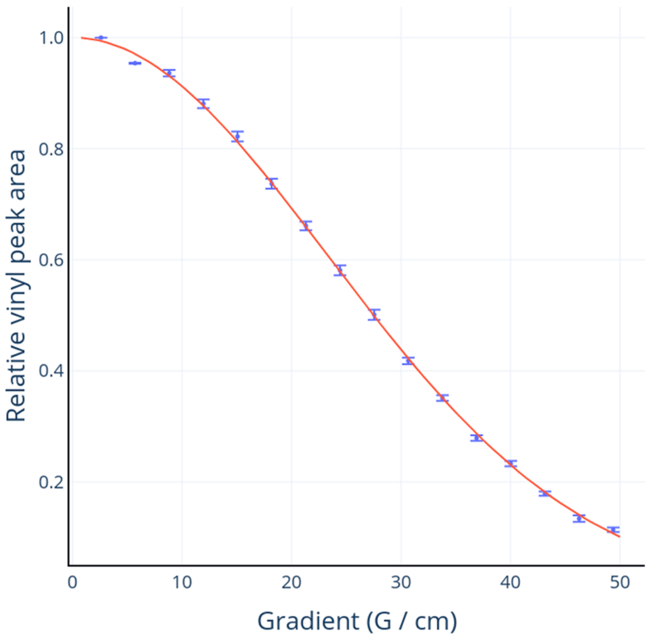

Figure 2. Diffusion curve obtained by PFG NMR for PbS QDs synthesized with 0.3 mL of oleic acid showing the observed area of the vinyl proton peaks in blue and the nonlinear least-squares fit to the Stejskal−Tanner equation in red. Error bars are ±1 standard deviation.

The signal described by eq 1 is a weighted sum over the sample size distribution. As a sample becomes more polydisperse, a single exponential will no longer adequately describe the system, and the fit will suffer.[30] Syntheses like that employed here typically yield QDs with a Gaussian size polydispersity of 0.25 nm.[31] This presents a relatively monodisperse distribution of very large, spherical "molecules" in a sea of relatively small solvent molecules, conditions well-matched to the assumptions in the application of the Stejskal−Tanner and Stokes−Einstein equations.

The "gold standards" for characterizing QD size are transmission electron microscopy (TEM) and, more recently, small-angle X-ray scattering (SAXS). However, such instruments are expensive and not widely available in an undergraduate setting, and the techniques require a good deal of user training to acquire decent results. Fortunately, researchers have produced sizing curves for many QD systems, including PbS.[32] These sizing curves plot the band gap obtained from optical measurements versus QD diameter as characterized by TEM or SAXS. An empirical polynomial equation fit to the sizing curve allows quick conversion between easy-to-obtain optical absorbance measurements of the band gap and the QD diameter.

Figure 3 shows a cross section of an idealized PbS QD. The QD core of lead and sulfide ions is coated in a shell of oleate (OA) ligands that stabilize and protect the surface while presenting hydrophobic tails to the solvent system. These ligands keep the QD in colloidal dispersion in nonpolar solvents. The difference between the QD core radius and the

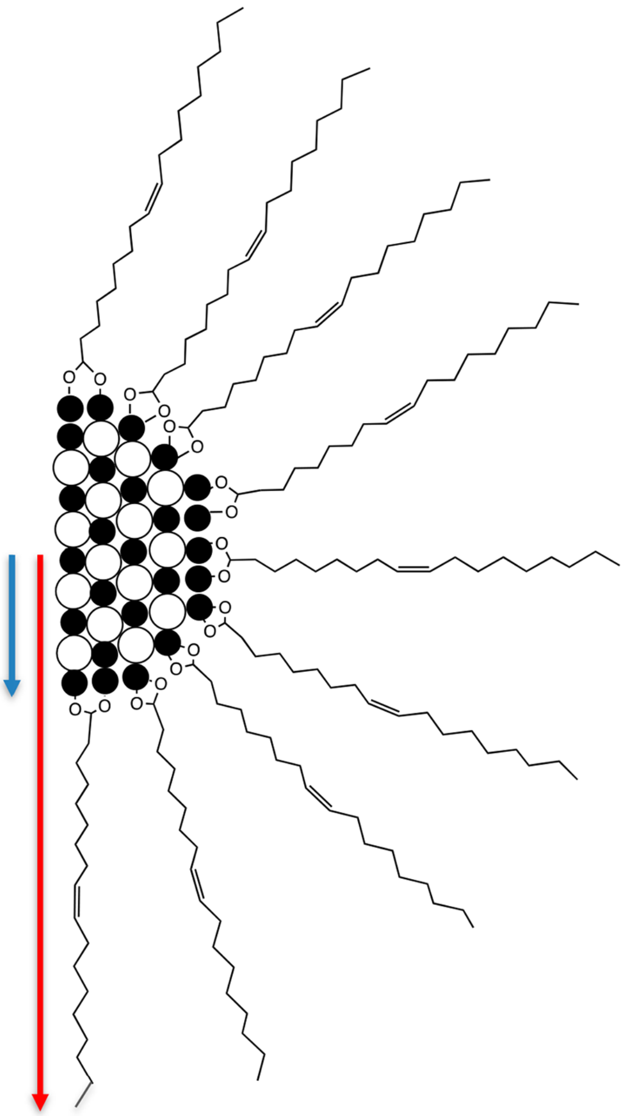

Figure 3. Cartoon cross section of a PbS QD capped with oleate ligands illustrating (blue) the QD core radius and (red) the hydrodynamic radius of the QD with its oleate ligands. Pb^{2+} ions are shown in black and S^{2-} in white.

overall hydrodynamic radius is also shown in Figure 3. Since sizing curves are based upon TEM or SAXS measurements wherein the hydrocarbon ligand shells are invisible, optical measurements provide information only on the QD core radius. PFG NMR experiments, based upon diffusion of the entire QD/ligand shell ensemble, provide information on the hydrodynamic radius.

This experiment describes a quick, small-scale synthesis of PbS QDs of various sizes suitable for PFG NMR and optical measurements. The NMR experiments measure QD diffusion coefficients, and application of the Stokes−Einstein equation provides what should be an excellent estimate of their hydrodynamic radius. A quick optical measurement provides the QD core radius. These two radii can be compared knowing the length of the oleic acid ligand. In the process, students learn about QD synthesis, pulsed field gradient NMR, and the assumptions inherent in the Stokes−Einstein equation. Finally, as PFGs are at the heart of diffusion ordered spectroscopy (DOSY), a powerful two-dimensional form of the PFG experiment used to analyze mixtures of small molecules or oligomers,[33] this experiment provides a basis for a physical understanding of this important technique.

■ EXPERIMENT

QD Synthesis

Monodisperse PbS QDs across a range of sizes in amounts just sufficient for NMR and optical spectroscopy are synthesized via hot injection at a moderate temperature and constant reaction time. In general, 4 mL of a lead precursor solution containing lead oxide in varying amounts of octadecene (ODE) and oleic acid (OA) at 115 °C under nitrogen is injected with 2 mL of a sulfur precursor solution containing hexamethyldisilathiane in ODE, and the reaction proceeds at temperature for 10 min. After cooling to room temperature, the QDs are worked up in a pair of 15 mL conical centrifuge tubes. The resulting QD pellets can be used immediately for NMR and optical absorbance spectroscopy, or the QDs can be redispersed in 1−2 mL of toluene or octane and stored for up to 2 weeks in a sealed vial for later analysis.

The size of the QDs produced is controlled by the amount of OA in the 4.0 mL lead precursor solution. QDs with core diameters spanning 3.5−6.3 nm are synthesized when starting with 0.3−4.0 mL of OA.

Detailed instructions for the synthesis and workup are provided in the student handout.

Pulsed Field Gradient NMR

Half of the reaction yield, which is the contents of one of the 15 mL conical centrifuge tubes used for workup, is sufficient to produce a 0.75 mL NMR sample. The PFG experiments use the standard Bruker pulse program dstebpgp3s, a more sophisticated version of the simple spin echo program shown in Figure 1 that compensates for convection within the sample and suppresses several sampling artifacts. A discussion of this pulse program and how the Stejskal−Tanner equation is modified for its use is provided in Acquiring PFG Diffusion Data for QDs with a Bruker Spectrometer. The signal for the isolated OA vinyl protons at 5.7 ppm as a function of gradient field is fit to the Stejskal−Tanner equation to determine the diffusion coefficient.

Optical Characterization

The QD core diameter can be determined from a single near-infrared spectrophotometric scan with reference to a literature sizing curve that relates the wavelength of maximum absorbance at the band edge to the QD core diameter. Furthermore, if desired, the mass of QDs produced can be determined via quantitative dilution and a single absorbance measurement at 400 nm.

Required Time

The QD synthesis and workup can be accomplished in a single 4 hour laboratory period. If the lead precursor solution is made ahead of time, a process that takes about 15 min, and sealed in a flask to await heating an hour or more in advance of the laboratory period, then the synthesis and workup can be completed in 2 h. Using predetermined values for the diffusion time Δ and the gradient length δ allows each sample to be run in about 28 min. Preparing the sample and determining the size of the QDs with near-infrared spectroscopy requires 30 min. Determining the mass of QDs produced via visible spectroscopy, if desired, requires an additional 60 min. With judicious planning, the entire experiment can be run in two 4 hour laboratory periods. Alternatively, this experiment could be offered as an open-ended, multiperiod project.

Required Instrumentation

QD workup requires a centrifuge capable of spinning 15 mL conical vials at 3500 rpm. A vortex mixer is very useful for redispersion of QDs. A near-infrared spectrophotometer that covers the range of 900−1700 nm and glass cuvettes are needed to measure the QD band gap for use with the sizing curve, while any spectrophotometer capable of measuring absorbance at 400 nm can be used to determine the yield of QDs. An NMR spectrometer and a probe equipped with a *z*-axis gradient coil are necessary to acquire PFG data. Either the proprietary software TopSpin, available without charge to academic users, or the free, open-source General NMR Analysis Toolbox (GNAT)[34] can be used to process NMR data offline.

HAZARDS

Lead oxide, hexamethyldisilathiane, and toluene are toxic. Avoid skin and eye contact with these chemicals. Students should wear eye protection, a lab coat, and gloves throughout the experiment. A fume hood should be used for the QD synthesis. Hexamethyldisilathiane is particularly malodorous and should be used only in a fume hood. Exercise care so that all materials encountering this reagent are either disposed in a sealed solid waste container within the fume hood or treated with a dilute bleach solution prior to removal from the hood. Octadecene and oleic acid are flammable and will catch fire if spilled onto a hot plate. Acetone, methanol, and toluene are flammable as well.

RESULTS AND DISCUSSION

The QD synthesis is easy to tune for differing target QD diameters, reliable, and relatively quick. The choice of ligand in the synthesis and solvents for workup are critical factors in the success of this experiment. OA is the only strongly coordinating ligand present in this synthesis. Oleylamine ligands used in many QD systems, including other popular PbS syntheses,[15] exchange too quickly on the time scale of the NMR experiment, leading to overly large or constant values for the diffusion coefficient. The workup incorporates two methanol washes that effectively remove small lead oleate oligomers and clusters from the product that skew the diffusion results to larger values.[16]

The ^{1}H NMR spectrum of PbS QDs in benzene-d_6 (Figure S2 in the notes for instructors) features broad resonances typical for surface-confined ligands that tumble more slowly than the free ligand in solution on the time scale of the NMR experiment.[18] Figure 2 shows the PFG diffusion decay for the OA vinyl peak associated with QDs synthesized using 0.3 mL of OA. The Gaussian shape of the curve with a signal intensity of roughly 65% of the maximum intensity at 50% of the maximum gradient strength is evidence that the experimental parameters (the diffusion time Δ and the pulse length *δ*) are near optimal.[33] The diffusion coefficient obtained by fitting to the Stejskal−Tanner equation is $(1.13 \pm 0.03) \times 10^{-10}$ m^2 s^{-1} ($\alpha = 0.05$). After correction of the diffusion coefficient by an internal standard,[35] the hydrodynamic radius of the QD with the OA ligand shell as described by the Stokes−Einstein equation is 3.21 ± 0.16 nm ($\alpha = 0.05$).

The QD core diameter *d* (in nm) is determined from the SAXS sizing curve:[32]

$$\frac{hc}{\lambda} = E_g^{\text{bulk}} + \frac{1}{0.0269d^2 + 0.234d} \tag{3}$$

where *h* is Planck's constant (in eV s), *c* is the speed of light (in nm s^{-1}), *λ* is the wavelength of peak band-edge absorbance (in nm), E_g^{bulk} is the band gap of bulk PbS (0.413 eV), and the two empirical constants have units of eV^{-1} nm^{-2} and eV^{-1} nm^{-1}, respectively. (Note that the left-hand side of eq 3 gives the band gap of the QD in eV.) The near-infrared spectrum of the QDs used in Figure 2 has peak absorbance at 981 nm, yielding a QD core radius of 1.78 nm.

Figure 4 summarizes the correlation of PFG-derived QD hydrodynamic radii with QD core radii derived from the sizing curve described by eq 3 across syntheses and measurements completed by seven pairs of students. The QD core radius can be estimated (roughly) from the hydrodynamic radius by subtracting the length of the fully extended OA ligand, 1.97 nm. This undoubtedly underestimates the QD core radius in that lack of full extension of the ligands and solvent infiltration into the ligand shell, both of which change with QD shape, size, and ligand packing, are not considered.

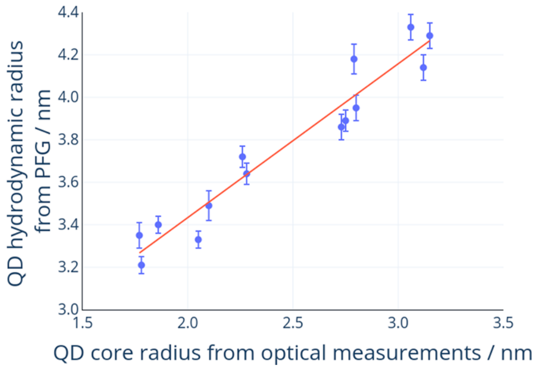

Figure 4. Correlation of PbS QD hydrodynamic radius as determined by PFG with QD core radius obtained by optical/SAXS measurements. PFG-based measurements of the diffusion coefficient for the ligand-clad QDs are corrected by an internal standard and used to calculate the QD hydrodynamic radius via the Stokes−Einstein equation. Error bars are ±1 standard deviation. The line represents a linear regression of the data without forcing a value for the intercept.

Finally, in the PbS system the optical extinction at 400 nm scales with the number of PbS formula units within the quantum dots, meaning that the total amount of PbS in the colloidal suspension, *independent of quantum dot size*, can be calculated readily from a single absorbance measurement:[36]

$$C_{\text{PbS}} = A_{400\text{ nm}} \cdot 0.114 \tag{4}$$

where $A_{400\text{ nm}}$ is the absorbance of a colloidal suspension at 400 nm in a cell with path length of 1 cm and both C_{PbS} and the numerical constant have units of mg mL^{-1}.

STUDENT LEARNING

The experiment, typically run with students working in pairs, has been offered seven times in an upper-division instrumental methods laboratory, an upper-division materials chemistry hybrid laboratory/tutorial, and a first-year introduction to chemical research laboratory.

The focus is on QD synthesis, pulsed field gradient NMR, and the assumptions inherent in the Stokes−Einstein equation. Learning objectives were assessed via a rubric applied to final reports and posters. Students demonstrated a strong understanding of and an ability to explain how the PFG imparts a spatially dependent phase label on the magnetization that can be used to measure diffusion. While their understanding of how a PFG can manipulate the magnetization along the length of a sample was weak in the first offering of this experiment, subsequent revisions in the introductory materials and the addition of an informal whiteboard talk on this subject during downtime on the second day of the experiment greatly enhanced student learning on this point. Finally, students were able to integrate data from PFG and optical/SAXS measurements in support of their arguments regarding the application of the Stokes−Einstein relationship to QDs.

SUMMARY

A quick, small-scale synthesis of PbS QDs of various sizes is combined with pulsed field gradient NMR measurements of diffusion coefficients. Application of the Stokes−Einstein equation provides an excellent estimate of their hydrodynamic radius. In the process, students learn about QD synthesis, pulsed field gradient NMR, and the assumptions inherent in the Stokes−Einstein equation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.3c00155.

Notes for instructors (PDF, DOCX)

Experimental protocol including introduction and student directions (PDF, DOCX)

Acquiring PFG Diffusion Data for QDs with a Bruker Spectrometer (PDF, DOCX)

PFG data template (XLSX)

AUTHOR INFORMATION

Corresponding Author

Hal Van Ryswyk − *Department of Chemistry, Harvey Mudd College, Claremont, California 91711, United States;* orcid.org/0000-0002-1701-6194; Email: vanryswyk@hmc.edu

Authors

Hanna Z. Porter − *Department of Chemistry, Harvey Mudd College, Claremont, California 91711, United States*
Connor K. M. Seto − *Department of Chemistry, Harvey Mudd College, Claremont, California 91711, United States;* orcid.org/0009-0002-3232-7481
Ixchel Lopez − *Department of Chemistry, Harvey Mudd College, Claremont, California 91711, United States*
Emma Dy − *Department of Chemistry, Harvey Mudd College, Claremont, California 91711, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jchemed.3c00155

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Lisensky, G. C.; Dauzvardis, F.; Young, M. M. K. Periodic Properties Illustrated by $CH_3NH_3Pb(I_{1-x}\ Br_x)_3$ Solid Solution Perovskite Semiconductors. *J. Chem. Educ.* **2021**, *98* (7), 2392−2397.

(2) Molvinger, K.; Ayral, R.-M.; Filhol, J.-S. Integrating Lecture and Laboratory Work for a Materials Chemistry Course to Engage and Motivate Students through Highly Visual and Intriguing Syntheses. *J. Chem. Educ.* **2020**, *97* (3), 866−872.

(3) Nordell, K. J.; Boatman, E. M.; Lisensky, G. C. A Safer, Easier, Faster Synthesis for CdSe Quantum Dot Nanocrystals. *J. Chem. Educ.* **2005**, *82* (11), 1697−1699.

(4) Bauer, C. A.; Hamada, T. Y.; Kim, H.; Johnson, M. R.; Voegtle, M. J.; Emrick, M. S. An Integrated, Multipart Experiment: Synthesis, Characterization, and Application of CdS and CdSe Quantum Dots as Sensitizers in Solar Cells. *J. Chem. Educ.* **2018**, *95* (7), 1179−1186.

(5) Landry, M. L.; Morrell, T. E.; Karagounis, T. K.; Hsia, C.-H.; Wang, C.-Y. Simple Syntheses of CdSe Quantum Dots. *J. Chem. Educ.* **2014**, *91* (2), 274−279.

(6) Lisensky, G.; McFarland-Porter, R.; Paquin, W.; Liu, K. Synthesis and Analysis of Zinc Copper Indium Sulfide Quantum Dot Nanoparticles. *J. Chem. Educ.* **2020**, *97* (3), 806−812.

(7) Shekhirev, M.; Goza, J.; Teeter, J. D.; Lipatov, A.; Sinitskii, A. Synthesis of Cesium Lead Halide Perovskite Quantum Dots. *J. Chem. Educ.* **2017**, *94* (8), 1150−1156.

(8) Reid, P. J.; Fujimoto, B.; Gamelin, D. R. A Simple ZnO Nanocrystal Synthesis Illustrating Three-Dimensional Quantum Confinement. *J. Chem. Educ.* **2014**, *91* (2), 280−282.

(9) Harris, C.; Gaster, C.; Gelabert, M. C. Reverse Micelles as Templates for the Fabrication of Size-Controlled Nanoparticles: A Physical Chemistry Experiment. *J. Chem. Educ.* **2019**, *96* (3), 565−570.

(10) Yang, H.; Fan, W.; Hills-Kimball, K.; Chen, O.; Wang, L.-Q. Introducing Manganese-Doped Lead Halide Perovskite Quantum Dots: A Simple Synthesis Illustrating Optoelectronic Properties of Semiconductors. *J. Chem. Educ.* **2019**, *96* (10), 2300−2307.

(11) Frazer, L.; Higginbotham, H. F.; Bell, T. D. M.; Funston, A. M. It's Fundamental": Quantum Dot Blinking Experiment to Teach Critical Thinking. *J. Chem. Educ.* **2020**, *97* (1), 244−252.

(12) Delgado, T.; Villard, M. Spin Crossover Nanoparticles. *J. Chem. Educ.* **2022**, *99* (2), 1026−1035.

(13) Pham, S. N.; Kuether, J. E.; Gallagher, M. J.; Hernandez, R. T.; Williams, D. N.; Zhi, B.; Mensch, A. C.; Hamers, R. J.; Rosenzweig, Z.; Fairbrother, H.; Krause, M. O. P.; Feng, Z. V.; Haynes, C. L. Carbon Dots: A Modular Activity To Teach Fluorescence and Nanotechnology at Multiple Levels. *J. Chem. Educ.* **2017**, *94* (8), 1143−1149.

(14) Schneider, E. M.; Bärtsch, A.; Stark, W. J.; Grass, R. N. Safe One-Pot Synthesis of Fluorescent Carbon Quantum Dots from Lemon Juice for a Hands-On Experience of Nanotechnology. *J. Chem. Educ.* **2019**, *96* (3), 540−545.

(15) Pan, Y.; Li, Y. R.; Zhao, Y.; Akins, D. L. Synthesis and Characterization of Quantum Dots: A Case Study Using PbS. *J. Chem. Educ.* **2015**, *92* (11), 1860−1865.

(16) Cass, L. C.; Malicki, M.; Weiss, E. A. The Chemical Environments of Oleate Species within Samples of Oleate-Coated PbS Quantum Dots. *Anal. Chem.* **2013**, *85* (14), 6974−6979.

(17) Hassinen, A.; Moreels, I.; de Mello Donegá, C.; Martins, J. C.; Hens, Z. Nuclear Magnetic Resonance Spectroscopy Demonstrating Dynamic Stabilization of CdSe Quantum Dots by Alkylamines. *J. Phys. Chem. Lett.* **2010**, *1* (17), 2577−2581.

(18) Fisher, A. A. E.; Osborne, M. A.; Day, I. J.; Lucena Alcalde, G. Measurement of Ligand Coverage on Cadmium Selenide Nanocrystals and Its Influence on Dielectric Dependent Photoluminescence Intermittency. *Commun. Chem.* **2019**, *2* (1), 63.

(19) De Roo, J.; Yazdani, N.; Drijvers, E.; Lauria, A.; Maes, J.; Owen, J. S.; Van Driessche, I.; Niederberger, M.; Wood, V.; Martins, J. C.; Infante, I.; Hens, Z. Probing Solvent−Ligand Interactions in Colloidal Nanocrystals by the NMR Line Broadening. *Chem. Mater.* **2018**, *30* (15), 5485−5492.

(20) Harmon, J.; Coffman, C.; Villarrial, S.; Chabolla, S.; Heisel, K. A.; Krishnan, V. V. Determination of Molecular Self-Diffusion Coefficients Using Pulsed-Field-Gradient NMR: An Experiment for Undergraduate Physical Chemistry Laboratory. *J. Chem. Educ.* **2012**, *89* (6), 780−783.

(21) Li, W.; Kagan, G.; Hopson, R.; Williard, P. G. Measurement of Solution Viscosity via Diffusion-Ordered NMR Spectroscopy (DOSY). *J. Chem. Educ.* **2011**, *88* (9), 1331−1335.

(22) Halpern, A. M.; McBane, G. C. *Experimental Physical Chemistry: A Laboratory Textbook*, 2nd ed.; W.H. Freeman: New York, 2006.

(23) Maki, J. N.; Loening, N. M. Measuring Molecular Motion: Using NMR Spectroscopy to Study Translational Diffusion. *ACS Symp. Ser.* **2007**, *969*, 155−173.

(24) Price, W. S. Pulsed-field Gradient Nuclear Magnetic Resonance as a Tool for Studying Translational Diffusion: Part 1. Basic Theory. *Concept Magn Reson* **1997**, *9* (5), 299−336.

(25) Hoffman, R. E.; Shabtai, E.; Rabinovitz, M.; Iyer, V. S.; Müllen, K.; Rai, A. K.; Bayrd, E.; Scott, L. T. Self-Diffusion Measurements of Polycyclic Aromatic Hydrocarbon Alkali Metal Salts. *J. Chem. Soc., Perkin Trans. 2* **1998**, No. 7, 1659−1664.

(26) Choi, H.; Ko, J.-H.; Kim, Y.-H.; Jeong, S. Steric-Hindrance-Driven Shape Transition in PbS Quantum Dots: Understanding Size-Dependent Stability. *J. Am. Chem. Soc.* **2013**, *135* (14), 5278−5281.

(27) Pan, Y.; Li, Y. R.; Zhao, Y.; Akins, D. L. Synthesis and Characterization of Quantum Dots: A Case Study Using PbS. *J. Chem. Educ.* **2015**, *92* (11), 1860−1865.

(28) Edward, J. T. Molecular Volumes and the Stokes-Einstein Equation. *J. Chem. Educ.* **1970**, *47* (4), 261.

(29) Evans, R.; Dal Poggetto, G.; Nilsson, M.; Morris, G. A. Improving the Interpretation of Small Molecule Diffusion Coefficients. *Anal. Chem.* **2018**, *90* (6), 3987−3994.

(30) Guo, X.; Laryea, E.; Wilhelm, M.; Luy, B.; Nirschl, H.; Guthausen, G. Diffusion in Polymer Solutions: Molecular Weight Distribution by PFG-NMR and Relation to SEC. *Macromol. Chem. Phys.* **2017**, *218* (1), No. 1600440.

(31) Bederak, D.; Sukharevska, N.; Kahmann, S.; Abdu-Aguye, M.; Duim, H.; Dirin, D. N.; Kovalenko, M. V.; Portale, G.; Loi, M. A. On the Colloidal Stability of PbS Quantum Dots Capped with Methylammonium Lead Iodide Ligands. *ACS Appl. Mater. Interfaces* **2020**, *12* (47), 52959−52966.

(32) Maes, J.; Castro, N.; De Nolf, K.; Walravens, W.; Abécassis, B.; Hens, Z. Size and Concentration Determination of Colloidal Nanocrystals by Small-Angle X-ray Scattering. *Chem. Mater.* **2018**, *30* (12), 3952−3962.

(33) Groves, P. Diffusion Ordered Spectroscopy (DOSY) as Applied to Polymers. *Polym. Chem.* **2017**, *8* (44), 6700−6708.

(34) Castañar, L.; Poggetto, G. D.; Colbourne, A. A.; Morris, G. A.; Nilsson, M. The GNAT: A New Tool for Processing NMR Data. *Magn. Reson. Chem.* **2018**, *56* (6), 546−558.

(35) Neufeld, R.; Stalke, D. Accurate Molecular Weight Determination of Small Molecules via DOSY-NMR by Using External Calibration Curves with Normalized Diffusion Coefficients. *Chem. Sci.* **2015**, *6* (6), 3354−3364.

(36) Moreels, I.; Lambert, K.; Smeets, D.; De Muynck, D.; Nollet, T.; Martins, J. C.; Vanhaecke, F.; Vantomme, A.; Delerue, C.; Allan, G.; Hens, Z. Size-Dependent Optical Properties of Colloidal PbS Quantum Dots. *ACS Nano* **2009**, *3* (10), 3023−3030.