Lead–Salt Quantum-Dot Ionic Liquids**

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The electronic energies of lead-salt quantum dots (QDs) are determined primarily by quantum confinement due to their large exciton Bohr radii.^[1] The fundamental electronic structure of the QDs (PbS and PbSe) has been worked out by Kang et al.,^[2] and now research with these materials is turning towards applications. For instance, lead-salt QDs have been used as active materials in photovoltaic devices^[3,4] due to their size-tunable infrared (IR) absorption. They are also efficient IR emitters and could be used in biomedical imaging^[5] and in electroluminescent devices.^[6,7] In order for QDs to realize their full potential, their stability (e.g., photostability) and compatibility with other materials must be improved. Accordingly, much effort is devoted to surface passivation and functionalization of QDs, with increasing attention being paid to the use of ionic liquids to passivate the QD surface.^[8-13] Using certain ionic liquid ligands, solid materials can be transferred to a new state that exhibits liquidlike behavior at room temperature.^[12,13] To date, metal nanoparticles^[12] and oxide nanoparticles^[9-11] have been functionalized using a polymer ionic liquid. Some semiconductor nanoparticles (e.g., CdSe) functionalized using small-molecule ionic ligands have been reported.^[13] In this work, we report the first lead-salt (PbS, PbSe, and PbTe) QD ionic liquid where polymer ionic liquid ligands are used as capping ligands for QDs. The resulting amphiphilic QD ionic liquids exhibit fluidlike behavior at room temperature, even in the absence of solvents. The ionic liquid capping ligands also dramatically improve the photostability of

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the QDs. This approach provides an effective method to tailor the physical properties of lead–salt QDs. We demonstrate the approach using PbS QDs as a model system.

Colloidal PbS QDs were synthesized using organometallic precursors.^[14,15] Ionic liquid ligands were synthesized by protonating sodium 3-mercapto-1-propanesulfonate followed by neutralizing with polyetheramine, as shown in Scheme 1. 0.5 mL of a PbS QD suspension in toluene (concentration \approx 50 mg mL⁻¹) was added to 0.5 mL of thiol-capped ionic liquid in a centrifuge tube. The molar ratio of PbS QDs to the ionic liquid ligand was about 1:10⁴. The excess ligands prevent the QDs from aggregating. The ionic liquid and QD toluene solution were phase separated, as evidenced by a layer of brown QD toluene solution on top of a layer of transparent ionic liquid. The thiol moiety in the ionic liquid serves as the anchor to bind ionic liquid ligands to the PbS QD surface. After vigorous shaking, the mixture became uniformly brown in color. The solution was then centrifuged at a speed of 14500 rpm for five minutes. No separation or precipitation was observed. The mixed solution was then loaded into a vacuum oven and dried at room temperature until all the toluene was removed. The final volume of the solution was about 0.5 mL, which is the same as the volume of the original ionic liquid. It is believed that the ODs were capped by ionic liquid instead of oleic acid due to the much stronger binding strength of a thiol than a carboxylic group to a QD.^[5,16] In a separate experiment, we observed that the original hydrophobic QDs capped by oleic acid were attracted to water where more hydrophilic ionic liquid was dissolved (see Supporting Information), showing the completeness of ligand exchange. Figure 1c shows a transmission electron microscopy (TEM) image of the original PbS QDs, where QDs of about 2.5 nm in size are observed. After capping the QDs with ionic liquid ligands, a much higher interparticle separation is observed in the TEM image (Figure 1c, left inset), which is expected based on the sizes of the oleic acid and the ionic liquid ligand. Larger QD clusters (size $\approx 7 \text{ nm}$) are also observed in QD ionic liquid, which consist of a few small dots, as resolved in the high-resolution TEM (HRTEM) image (Figure 1c, right inset). The small dots form a cluster but do not fuse together. Thermal gravimetric analysis (TGA) measurements (see Supporting Information) showed that there was about 4.5% weight residue when the PbS QD ionic liquid was heated to 540 °C, corresponding to the inorganic portion of the hybrid. The resulting QD ionic liquid is a viscous, brown fluid, as shown in Figure 1b. The fluidity of the material is affected by both the electrostatic and the van der Waals forces among the ions (shown in Figure 1a). By carefully tuning the size of the ions, which in turn changes the relative magnitude of



Scheme 1. Schematic image showing the synthesis of ionic liquid with a thiol moiety.

the two forces, the fluidity can be varied at fixed temperature.^[16] In other words, the glass-transition temperature T_g of the material can be changed by tuning the size of the ions.

The amphiphilic nature of the PbS QD ionic liquid was demonstrated using contact-angle measurements. As shown in Figure 2a, the contact angle of PbS QD ionic liquid on a silicon wafer is about 12° , which is much less than that of water (58°) on the same substrate. The low contact angle indicates that the PbS QD ionic liquid easily wets a hydrophilic substrate. On a Teflon film, the PbS QD ionic liquid shows a contact angle of 40° , while the contact angle of water on the same substrate is about 106° . Thus the PbS QD ionic liquid wets reasonably well both a hydrophilic and a hydrophobic substrate.

Both the ionic liquid used for surface functionalization and the QD ionic liquid are electrically conducting, although their conductivities are low. At temperatures above T_{g} measured by differential scanning calorimetry (DSC; see Supporting Information), the conductivity-temperature relation of the pure ionic liquid follows the Vogel-Tammann-Fulcher (VTF) model,^[22] as shown in Figure 3. However, the conductivity of the QD ionic liquid has more features (shown in Figure 3) and is about an order of magnitude lower. The conductivity is probably reduced because the heavy QD cores reduce the fluidity of the fluid, which in turn reduces the mobility of the ligands binding to the QDs. At temperatures below T_{g} , the conductivities of the pure ionic liquid and the QD ionic liquid overlap (shown in Figure 3). Since the materials are in the solid phase, the fluidity has no contribution to the conductivity. The mechanism of the conductivity below T_g is explained in terms of many-body interactions^[18,19] and is "universal" for a wide range of materials.^[18] The theory^[18,19] also predicts that the dependence of the conductivity on frequency follows a power law $\sigma(\omega) \propto \omega^n$, with $n \approx 1$, consistent with our experiment (see Supporting Information). Further studies using different types of ionic liquids and/or different sizes of QDs are underway to elucidate charge-transport phenomena in these systems.

The optical properties of PbS QDs were preserved and in some cases enhanced after being capped by the ionic liquid ligands. These properties were investigated by measuring the optical absorption, photoluminescence (PL), and absolute quantum yield. A solid-state laser that emits 635-nm light was used to excite the samples. The power of the laser was kept lower than 100 μ W to avoid degrading the sample. The QD



C)



Figure 1. a) Schematic image of an ionically modified QD. b) A photograph of a PbS QD ionic liquid. c) TEM image of the original PbS QDs. Left inset: TEM image of the QD ionic liquid. Right inset: HRTEM of the QD ionic liquid.



Figure 2. Contact angle of PbS QD ionic liquid on a silicon wafer (a) and on Teflon (c); contact angle of water on a silicon wafer (b) and on Teflon (d).



Figure 3. Temperature-dependent conductivity of ionic liquid (solid squares) and QD ionic liquid (dots), measured at a frequency of 1 Hz.

ionic liquid was prepared by sandwiching a thin layer ($\approx 10 \,\mu m$) of the liquid between two cover glass slides. The original QDs in toluene (concentration is about 0.5 mg mL^{-1}) were prepared in a glass cuvette (optical path, 3 mm). The QD film was prepared by spin-coating a layer of QDs on a glass slide. The purpose of the different sample preparation methods is to keep the optical density low (close to or less than 0.1 at the lowest energyabsorption peak) to reduce self-absorption on the PL spectra. Both the lowest energy-absorption peak (see Supporting Information) and PL emission peak of the QD ionic liquid were red-shifted by \approx 65 nm relative to those of the original QDs (shown in Figure 4), as observed previously with different thiol ligands.^[16,5] No noticeable absorption or PL peak shift was observed from a spin-coated QD film. The absolute quantum yield of each sample was measured using an integrating sphere, which is based on the design proposed by Friend et al.^[23] As shown in Table 1, the PL quantum yield from the original QDs dispersed in toluene is about 40%, while it is only about 3% for the QD film. The quantum yield from QD ionic liquid is about 22%, which is lower than that of the original QDs but still larger than a typical IR dye (e.g., 13% from IR125^[24]). The decrease of the quantum yield in the QD ionic liquid might be caused by low levels of aggregation, as observed in the TEM image (Figure 1c, right inset), or possibly the effect of the ligand on the electronic properties. The small peak at around 1300 nm in the PL spectrum of the QD ionic liquid likely indicates cluster formation after ligand exchange. If that is true, there is the

Table 1. Absolute quantum yield of each sample.

	Absolute quantum yield [%]
QDs in toluene	40 ± 2
QD ionic liquid	22 ± 2
QD film	3±2

potential that the efficiency of PL from QD ionic liquids can be improved, if cluster formation can be prevented during synthesis.

The photostability of the PbS QD ionic liquid was measured by shining a solid-state laser (4 mW, 635 nm) onto the sample in ambient air, while PbS QDs in toluene were used as the control. A small amount of the sample ($\approx 50 \,\mu$ L) was loaded into a cuvette $(3 \times 3 \times 30 \text{ mm} \text{ in width} \times \text{length} \times \text{height for the})$ interior dimensions). By using small volumes, most of the sample can be exposed under the \approx 3-mm-diameter laser spot while minimizing the convection effect in the liquid, which brings/removes fresh/exposed QDs in/out of the laser spot. The PL from the PbS QDs in toluene decreased rapidly in the first few seconds and then slowly decreased in the following 20 minutes. In contrast, there is virtually no change in the PL intensity of the PbS QD ionic liquid (Figure 5). For the QDs in toluene, the fast decrease is quite reversible, which is thought to be caused by the trapping of photoexcited charge in the QDs,^[25] while the slow decrease is not reversible on the timescale of a few hours (see Supporting Information). We also observed spectrum blue-shift after long-term laser exposure. The blue-shift could be caused by photo-oxidation, which causes a shrink in QD size, as suggested by Krauss et al.^[25] It might also be caused by ionization of large QDs followed by a long-term charge trapping. The PL spectra of the PbS QD ionic liquid before and after laser exposure were almost identical (see Supporting Information), which indicates that no photo-oxidation or long-term charge trapping occurred. This may be attributed to the surface passivation by the thiol moieties of the ionic liquid. The QD ionic liquid could be developed further for a dye-sensitized solar cell, where QDs serve as the sensitizer dye molecules. It has an absorption band that is tunable from the visible to IR, ionic conductivity, and negligible vapor pressure, which are favorable for a practical dye-sensitized solar cell.^[26]

In summary, we have synthesized a new kind of ionic liquid consisting of lead-salt semiconductor QDs. The method



Figure 4. a) PL intensity of PbS QDs in toluene (solid squares), PbS QD ionic liquid (solid circles), and PbS QD film (solid triangles).



Figure 5. Time-dependent PL from PbS QDs in toluene (solid squares) and PbS QD ionic liquid (dots).

developed is a simple yet general way to functionalize nanoparticles. In ambient environment, the QD ionic liquids are solvent free and more stable than the same QDs dispersed in a solvent.

Experimental Section

Synthesis of colloidal PbS QDs: Lead (II) oxide (220 mg, 1 mmol, 99.999%), oleic acid (0.64 mL, 2 mmol, 90%), and 1-octadecene (ODE, 9.36 mL, 90%) are mixed and stirred at 150 °C under pure nitrogen environment. At the same time, a 0.1 μ hexamethyldisilathiane ((TMS)₂S, 126 μ L, 0.6mmol) in ODE (6 mL) is stirred in a glove box for at least 30 minutes. After the reaction solution (containing PbO) turns clear, the temperature is set to 90 °C and allowed to stabilize. Then, 5 mL of the (TMS)₂S/ODE solution (0.5 mmol sulfur) is drawn into a syringe and injected into the reaction solution. After reacting for 1 min, the reaction solution is rapidly cooled with an ice bath. The growth solution is then mixed with 5 mL hexane. Excess oleic acid and unreacted precursors are removed by precipitating the particles using incompatible solvents, for example, methanol. The NCs are redispersed in toluene and stored in the dark under an inert atmosphere.

Synthesis of ionic liquid ligands: Sodium 3-mercapto-1-propanesulfonate (0.2 g, 1.12 mmol, technical grade, 90%) is dissolved in 4 mL deionized water. The solution is run through an ion exchange column (Dowex, HCR-W2 ion exchange resin) to remove Na⁺ ions and fully protonate the sulfonate groups present. The fully protonated solution shows a distinct pH value change (from 2.75 to 0). Polyetheramine (0.67 g, 1.12 mmol, Jeffamine XTJ505, XTJ506) is mixed with 3 mL deionized water and then added dropwise to the mercaptosulfuric solution while monitoring the pH increase. Once the equivalence point is reached, the reaction mixture is kept at room temperature overnight under shaking. Then the solvent is evaporated by placing the solution in a vacuum oven for drying at 35 °C until all the solvent is removed. Equivalence point plots are used to determine the necessary amount of reagents to achieve a 1:1 ratio of mercaptosulfonic acid to amine.

Absolute quantum yield measurement: An integrating sphere (IS; IS200, Thorlabs) that has its inner surface coated with a diffusely reflecting material - PTFE - is used to redistribute the light isotropically over the sphere interior surface. A solid-state laser (wavelength 635 nm) beam enter the IS through the input port. At the output port of the IS, an optical-fiber bundle is used to collect and send the light to a spectrometer (SpectraPro 275, Acton). A femtowatt photoreceiver (Model 2151, New Focus) is mounted on the exit side of the spectrometer to measure the dispersed light power. The laser beam is chopped by a fan and a lock-in amplifier is used to depress the background noise during measurements. The spectral response of the entire system is calibrated using a quartz tungsten halogen lamp (20 W QTH, Newport). The sample is loaded into a small glass cuvette or dropcast onto a glass slide and then mounted to a sample holder that allows the sample to pass in and out of the laser beam. Three spectra are taken: a) laser beam only, b) sample in IS but off the laser beam, and c) sample in the laser beam. In each photonnumber spectrum (intensity \times wavelength verus wavelength), five parameters are calculated, L_a , L_b , L_c (area under laser peak), P_b

and P_c (area under PL peak), where the subscripts a, b, and c denote the measurements aforementioned. The quantum yield is then calculated by the simple equation^[23]

$$\eta = \frac{P_{\rm c}L_{\rm b} - P_{\rm b}L_{\rm c}}{L_{\rm a}(L_{\rm b} - L_{\rm c})}.$$

We verified that the accuracy of this method is about $\pm 2\%$.

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conductivity \cdot ionic liquids \cdot lead salts \cdot photostability \cdot quantum dots

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