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NIR-Emitting Colloidal Quantum Dots Having 26% Luminescence Quantum Yield in Buffer Solution

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Efficient infrared lumophores are urgently needed in a host of biological sensing applications.[1] Such applications demand light emitters that meet a number of requirements simultaneously. First, the light-emitting species must be stable and bright (quantum yield >10%) under biologically relevant conditions including buffered conditions. In addition, emission in the near-IR (NIR) and short-wavelength IR (SWIR) range of 800−1300 nm allows greatly reduced absorption of emitted light in biological samples: optical penetration depths as high as 1 cm have been reported in tissue.[2] Finally, lumophores must have hydrodynamic diameters smaller than ∼10 nm to promote circulation transport in living organisms.[3]

To date, no single material displaying all of these attributes simultaneously has been reported. Instead, >10% quantum yield (QY) has been reported at tissue-penetrating SWIR emission wavelengths, but these materials were unstable in physiologically relevant buffer.[4−6] IR-emitting quantum dots with hydrodynamic diameters <10 nm were reported following a III−V/II−VI core−shell colloidal synthesis; however, these particles exhibited sub-10% QY in water.[3] Efficient size-effect tunable >10% QY nanoparticle suspensions in water have been achieved using TOPO-copolymer-PEGylation of II−VI core−shell nanoparticles; however, this approach produced nanoparticles with 15−30 nm hydrodynamic diameters.[8]

Here we report high QY infrared lumophores that are stable under buffered conditions for greater than 5 days. The result was achieved through straightforward mercaptan-PEGylation ligand exchange which rendered organometallically synthesized lead sulfide (PbS) quantum dots stable in aqueous solution.

The infrared lumophores described simultaneously meet requirements on brightness, stability, wavelength, and hydrodynamic diameter. The PbS quantum dots were synthesized using an organometallic route previously described.[9] The particles exhibited hydrodynamic diameters less than 10 nm and, through quantum size effect tuning readily accessed in the organometallic route synthesis, have emission peaks tunable from 700 to 1600 nm.

The material was transferred from organic solvent into aqueous solution by replacing oleate capping ligands with (1-mercaptoundec-11-yl)tetra(ethylene glycol) (MTPEG). A solution of MTPEG in HEPES, Tris, or PBS buffer was mixed with oleic acid capped PbS nanocrystals (∼80 mg/mL) in toluene. An aqueous phase containing nanoparticles was separable from the toluene phase that previously solubilized the PbS. These results contrast with previous reports describing aqueous suspension of organometallic lead sulfide nanocrystals using carboxylic acid or amino mercaptan strategy. Experimentally, we found that thioglycerol, 6-mercapto-1-hexanol, and 2,3-dimercapto-1-propanol all produce high QY stable colloids in polar solvents following this strategy; however, only when we used MTPEG did we obtain high QY PbS nanocrystals stable in biologically relevant buffer.

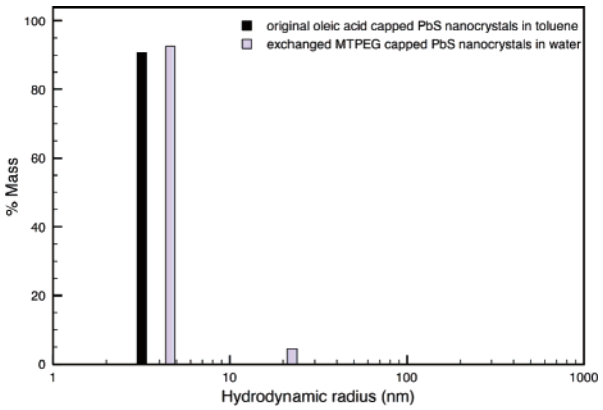

Figure 1. Dynamic light scattering measurements of hydrodynamic radius, by % mass modeled as solid Rayleigh spheres, of unexchanged PbS nanocrystals with oleic acid ligands (solid bars) in toluene, and PbS nanocrystals exchanged to having MTPEG ligands (shaded bars) in water.

We selected the MTPEG ligand for three reasons. First, monodentate complexation of the thiol group is expected to achieve good passivation of PbS nanocrystals in view of thiol−Pb binding affinity (strong thiol-metal affinity has been widely exploited in, for example, Au nanoparticle functionalization).[7] Second, its hydrophobic single-bonded carbon chain was expected to conserve QY. Third, its polar terminal group was expected to yield stable suspensions in aqueous solutions at physiological pH. Finally, these compact ligands enable hydrodynamically small nanoparticles that are comparable in size with a single antibody.

Dynamic light scattering (DLS) was used to investigate nanoparticle hydrodynamic diameters before and after exchange, as shown in Figure 1. Prior to ligand exchange, oleate-capped nanoparticles in toluene constitute a monodispersed colloid with hydrodynamic diameter of ∼6 nm. Following exchange, 90% by mass of these particles have 10 ± 0.5 nm hydrodynamic diameter. The remaining 10% of these nanoparticles have formed small 40−60 nm and larger aggregates. Ligand exchange is also supported by density phase segregation of MTPEG-exchanged nanocrystals in 20 mM HEPES buffer from fresh excess addition of organic solvent.

Figure 2 reports the absorbance and photoluminescence spectra for the nanoparticles prior to and following exchange. The excitonic structure remains but is somewhat reduced in sharpness following exchange. There is a red shift of ∼70 meV in the photoluminescence and a ∼60 meV red shift in absorbance as a result of the exchange

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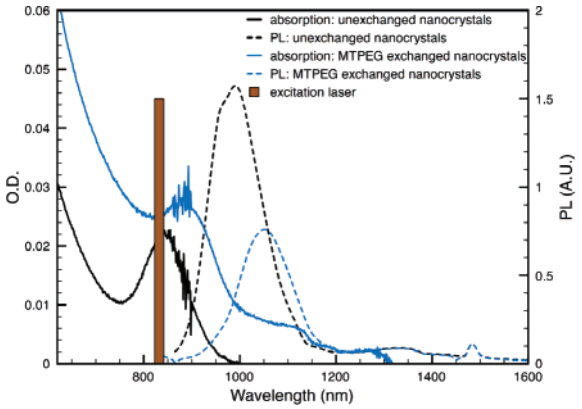

Figure 2. Absorption and luminescence spectra of (~10 mg/mL) PbS quantum dots prior to and following exchange to aqueous solution. Solid lines represent absorption spectra. Dashed lines represent photoluminescence spectra. Dark lines represent original OA capped PbS nanocrystals in toluene. Gray lines represent MTPEG-exchanged capped PbS nanocrystals in 20 mM HEPES buffer. Solid bar represents excitation wavelength used for PL spectra collection.

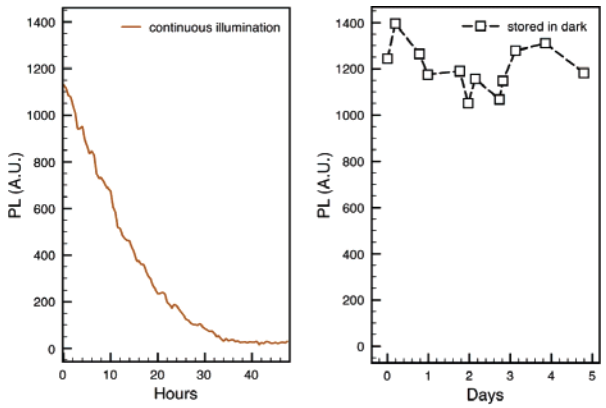

Figure 3. Photoluminescence intensity of lumophores in buffer. The dashed line is for a sample stored in the dark and periodically measured. The solid line is for a sample that was illuminated continuously using a 6 mW, 300 μm excitation spot from a HeNe laser.

procedure. One mechanism that may explain the observed red shifts is an effective growth in the nanocrystal size upon exchange.[10]

We measured QY of luminescence in the infrared using the 2-port integrating sphere approach of Mello.[11] Two sample positions, corresponding to direct and indirect excitation regimes, were used, with collected power spectra acquired using a calibrated monochromator, lock-in amplifier, and liquid nitrogen-cooled infrared sensitive germanium detector. We chose excitation sources to be slightly blue shifted relative to the first excitonic peak of all nanocrystals studied. Oleate-capped nanocrystals suspended in toluene were found to have QY lying between 40 and 50%. Following exchange, typical batches of nanoparticles had QY as high as 26%.

We used time-resolved single-photon counting measurement to investigate the origins of the decrease in QY. A Horiba−Jobin−Yvon time-resolved fluorometer was used with a 785 nm nanosecond pulsed excitation source, with the emission monochromator tuned to the luminescence peak of the nanocrystal samples. The luminescence excited-state lifetime of oleate-capped nanoparticles was 1550 ± 10 ns, while that of exchanged nanoparticles was 920 ± 10 ns. The reduction in lifetime between unexchanged and exchanged samples scales proportionally with the ~twofold reduction in their QY within the interpretation that the radiative lifetimes stayed approximately fixed at ~3.5 μs. We attribute the reduction in QY following exchange to an increased nonradiative rate.

The stability of exchanged colloids under dark storage and illuminated conditions was investigated for quantum dots dispersed in 20 mM HEPES buffer. Figure 3 reports the evolution over 5 days of the materials' photoluminescence intensity. Illuminated samples experienced 6 mW HeNe laser continuous excitation and degraded in photoluminescence intensity with a half-life of 10.6 h over 1 day's active use. Samples stored in the dark were periodically characterized for brief periods under these same excitation conditions; these samples demonstrated no appreciable loss in PL over 5 days.

The modification of organometallic route synthesized nanocrystals presented herein results in hydrodynamically small, bright nanoparticles emitting in the short-wavelength infrared. The aqueous suspensions are stable over days at physiological pH. Future work must include experimental determination of the concentration regime of lumophores that is compatible with cell survival.

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Supporting Information Available: Experimental procedures, STEM data, and additional optical characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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