Supporting Information

Combining Ligand Design with Photoligation to Provide Compact, Colloidally Stable, and Easy to Conjugate Quantum Dots

Naiqian Zhan,[a] Goutam Palui,[a] Henry Grise,[b] Hengli Tang,[b] Igor Alabugin,[a] and Hedi Mattoussi[a]

[a] Florida State University, Department of Chemistry and Biochemistry, 95 Chieftan Way, Tallahassee, FL 32306

[b] Florida State University, Department of Biological Science, Stadium Drive, Tallahassee, FL 32306

Synthesis of DHLA-zwitterion, reduction of the dithiolane ring (Compound 3).

LA-zwitterion (compound **2**; 3 g, ~7 mmol) was solubilized in 60 mL methanol and cooled to 0 °C under N_2. $NaBH_4$ (1.1 g, ~29 mmol) dissolved in DI water (5 mL) was added dropwise and the reaction mixture was left stirring for ~ 6-8 hours at room temperature. Methanol was removed under vacuum and the pH of the aqueous solution was adjusted to 7 by adding a few drops of 1M HCl solution. DI water was evaporated and the obtained compound was re-dispersed in anhydrous MeOH followed by removal of salts by filtration. The solution was dried over Na_2SO_4 and solvent was evaporated yielding DHLA-ZW (compound **3**) as white solid powder. The reaction yield is ~90%. We should note that the purification of this compound is tedious due to difficulties associated with the full removal of NaCl.

Dynamic light scattering setup and analysis.

We used ALV/CGS-3 Compact Goniometer System equipped with a HeNe laser (illumination at 633 nm) and a single-photon counting avalanche photodiode for signal detection (ALV-GmbH, Langen, Germany). The autocorrelation function was performed by APD-based single photon detector, ALV/LSE-5004 Electronics and ALV-5000/EPP correlator and the analysis was done using ALV-7004 correlator software (Version 3.0). The sample was filtered through a 0.22 μm filter before data collection; here we used

green-emitting quantum dots, λ_{em}= 540 and a concentration of ~ 3 µM. Sample temperature was maintained at 21°C. The autocorrelation function was the average of 20 runs of 20s each. We performed the DLS measurement at different angles ranging from 50 to 100 degrees, and the values for the hydrodynamic radius (R_H) obtained at these angles were essentially identical. Here we have provided plots of the electric field autocorrelation function along with the Laplace transform profile of intensity versus the hydrodynamic radius, $R_{H,}$ measured at 90 degrees.

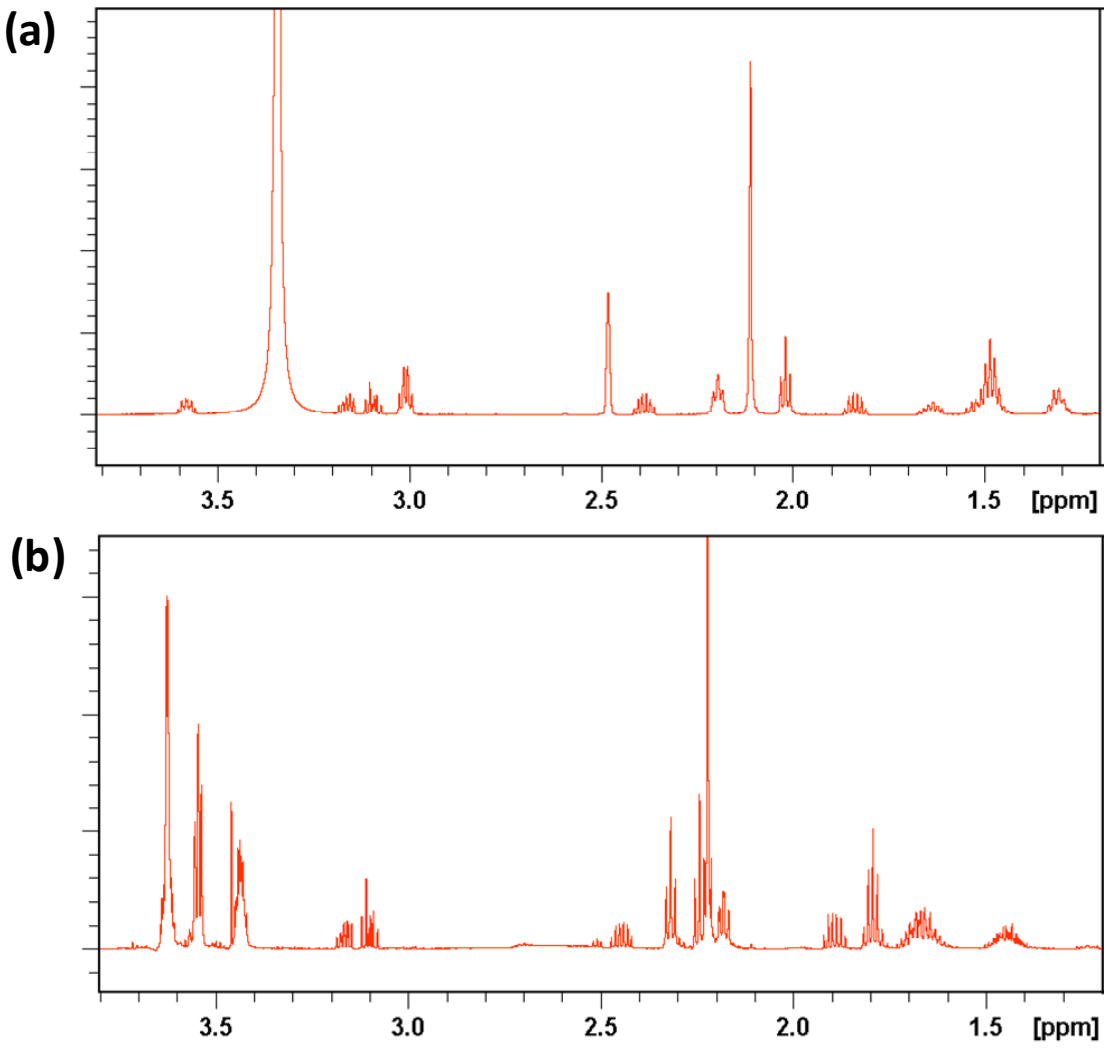

Figure S1. ^{1}HNMR spectra of (a) LA-N,N-dimethyl-1,3-propanediamine (compound **1**) in DMSO-d_6 and (b) LA-TEG-4-(dimethylamino)butyric acid (compound **4**) in $CDCl_3$.

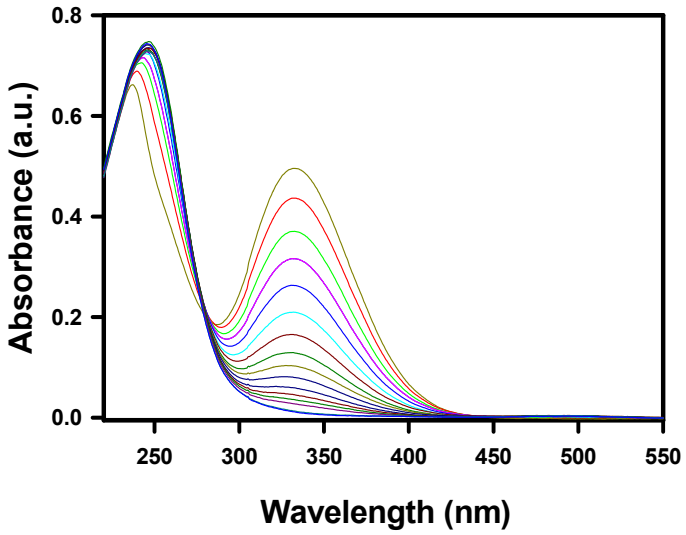

Figure S2. Time-dependent progression of the UV-Vis spectra of a solution of LA-ZW ligand in methanol (in a 10 mm optical path cell) at ~3.3 mM. Sample was irradiated using UV signal (at 340 nm) under nitrogen atmosphere.

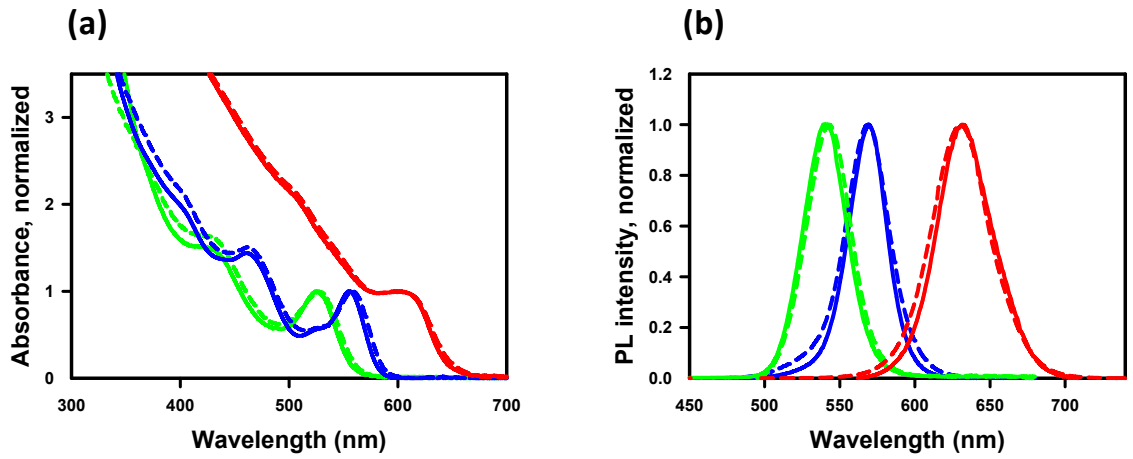

Figure S3. (a) UV-Vis absorption and (b) PL Spectra of QDs with different sizes (λ_{em} = 540 nm, 568 nm and 624 nm); dotted lines represent hydrophobic QDs in hexane and the solid lines represent hydrophilic QDs photoligated with LA-TEG-ZW ligand. The absorption and PL spectra were normalized with respect to the band edge peak and the emission maximum, respectively.

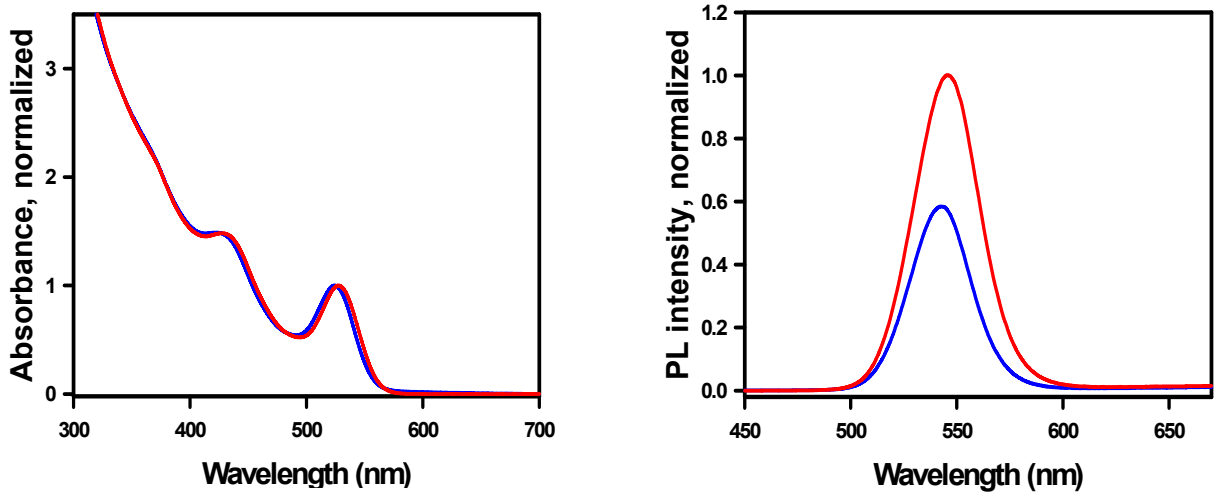

Figure S4. Normalized UV−Vis absorption (left) and PL spectra (right) of QDs photoligated using LA-ZW (red line) and LA-PEG_{750}-OCH_3 (blue line) dispersed in aqueous solutions; the dispersions have the same concentration (~1 μM).

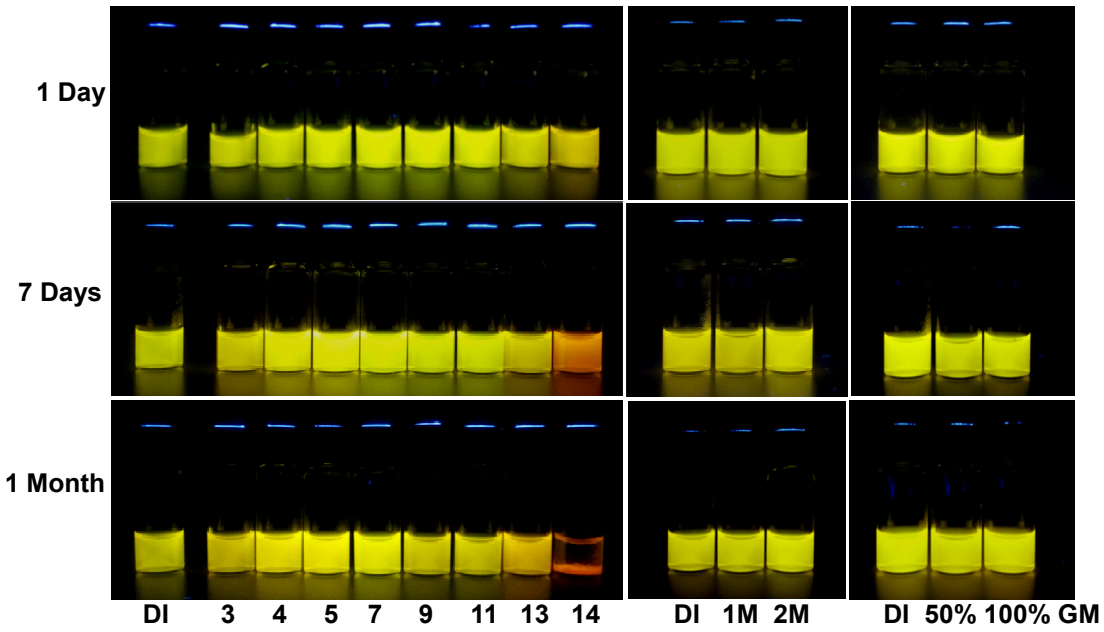

Figure S5. PL images of yellow QDs photoligated with LA-ZW (λ_{em} = 574 nm) dispersed in phosphate buffer at different pHs, in the presence of 1M NaCl and 2M NaCl, and in the presence of 50% and 100% growth media (GM); control dispersions in DI water are also shown.

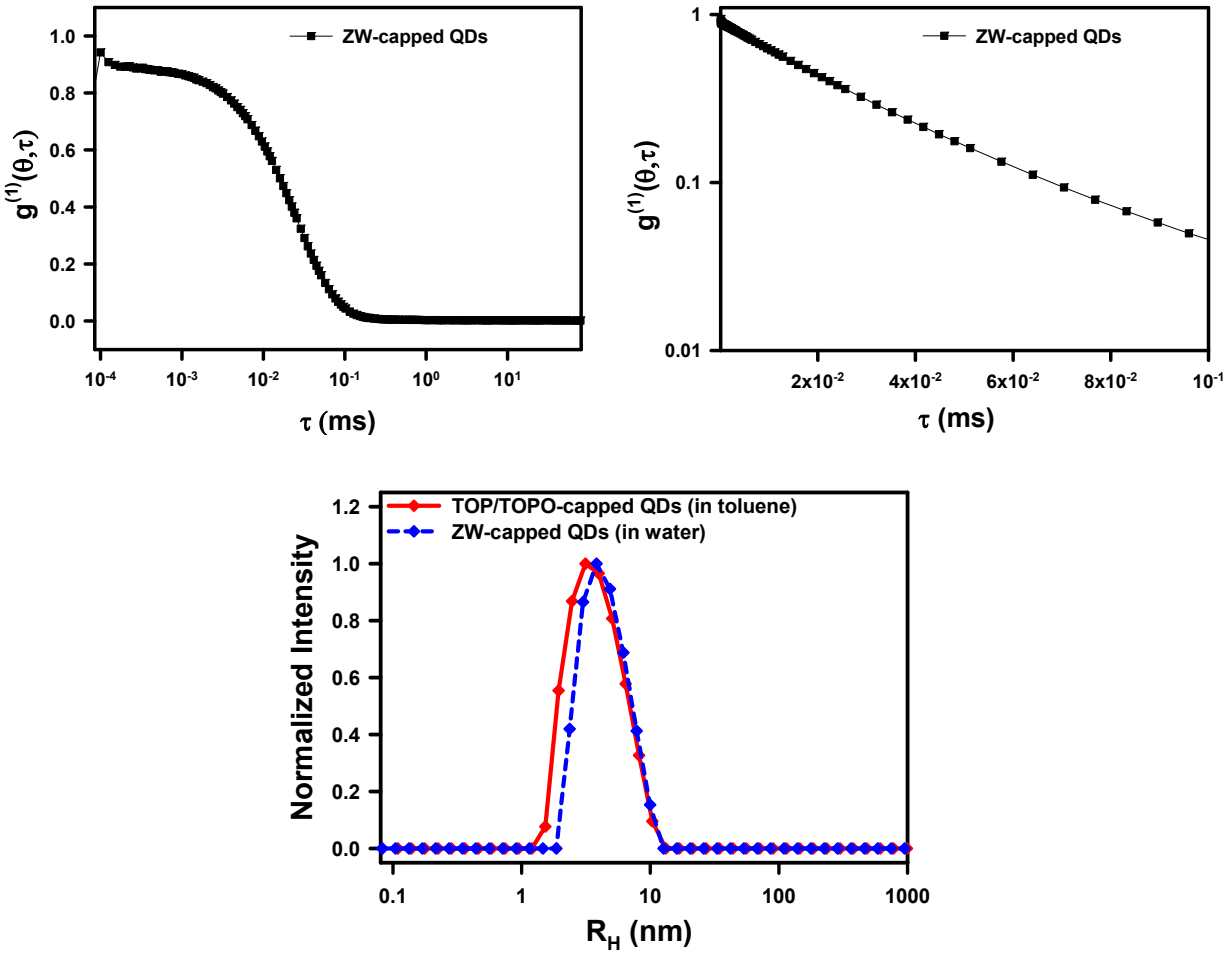

Figure S6. Dynamic Light Scattering Data. Shown are the electric field autocorrelation function $g^{(1)}(\theta,\tau)$ vs log (τ) (top left), log ($g^{(1)}(\theta,\tau)$) vs. τ (top right), and the Laplace transform profile of the intensity versus hydrodynamic size, R_H (bottom), for 540 nm-emitting QDs before (R_H = 3.8 nm) and after phase transfer (R_H = 4.8 nm). We should note that the signal-to-noise ratio was weaker for the dispersion in toluene, presumably due to weaker contrast.