

## Supporting Information

### Photo-Induced Phase Transfer of Luminescent Quantum Dots to Polar and Aqueous Media

Goutam Palui,<sup>a</sup> Tommaso Avellini,<sup>a</sup> Naiqian Zhan, Feng Pan,<sup>b</sup> David Gray,<sup>b</sup> Igor Alabugin,<sup>a</sup> and Hedi Mattoussi<sup>a</sup>

<sup>a</sup> Florida State University, Department of Chemistry and Biochemistry, 95 Chieftan Way, Tallahassee, FL 32306

<sup>b</sup> Neuroscience Research Unit, Pfizer Global Research & Development, Eastern Point Rd, Groton, CT 06340

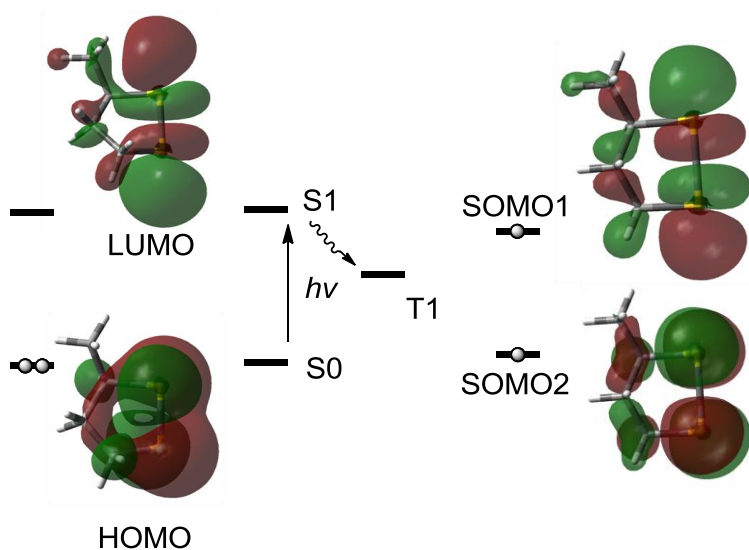
**Materials.** The chemical compounds required for the synthesis: poly(ethylene glycol) (molecular weight average of 600 and 750), triphenylphosphine, thiocetic acid, DMAP (4-(N,N-dimethylamino)pyridine), DCC (N,N-dicyclohexylcarbodiimide), triethylamine, sodium borohydride, methanesulfonyl chloride, organic solvents (DMF, CHCl<sub>3</sub>, etc.), PBS buffer, and salts (such as NaCl, Na<sub>2</sub>SO<sub>4</sub>, Mg<sub>2</sub>SO<sub>4</sub>), were purchased from Sigma Chemicals (St. Louis, MO). Sodium azide, N,N-dimethyl propanediamine, and 1,3-propane sultone were purchased from Alfa Aesar (Ward Hill, MA). Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA). The chemicals and solvents were used as purchased unless otherwise specified.

**Instrumentation.** The UV-irradiation experiments were performed using a UV photo-reactor Model LZC-4V (Luzchem Research Inc., Ottawa, Canada). It is equipped with fourteen lamps, one set of 6 lamps illuminating from the top and two sets of 4 lamps providing lateral illumination. The optical absorption and PL measurements were, respectively, carried out using an UV-Vis absorption spectrophotometer (UV 2450 model from Shimadzu), and Fluorolog-3

spectrometer (HORIBA Jobin Yvon Inc., Edison, NJ), equipped with a TBX PMT detector and an air cooled CCD camera. The  $^1\text{H}$  NMR spectra were collected using a 600 MHz spectrometer (Bruker SpectroSpin 600 MHz).

**Gel electrophoresis experiment.** The gel electrophoresis experiments were carried out using QDs phase-transferred in the presence of a ligand mixture (using PEG-NH<sub>2</sub> or PEG-COOH mixed with PEG-OCH<sub>3</sub>). A dispersion made of QDs capped with pure PEG-OCH<sub>3</sub> was used as control. The QD dispersion were diluted in a 20% glycerol, 1X TBE (Tris borate EDTA), and loaded into 1% agarose gel media. The gel experiments were run at 7.5 V/cm using TBE (pH 8.3) as running buffer for ~20 min. The image was captured using a High Performance Transilluminator (UVP, Upland, CA) equipped with digital camera.

**DFT Calculation.** The singlet excited state electronic structure was analyzed at the TD-B3LYP/6-31+G(d,p) level of theory. Solvent effects were modeled using CPCM dielectric continuum solvent model for methanol at the B3LYP/6-31+G(d,p) gas phase geometry.<sup>1,2</sup> This method accurately reproduced the  $S_0 \rightarrow S_1$  excitation energy ( $\lambda_{\max}(\text{calc})=349$  nm vs. ( $\lambda_{\max}(\text{exp})=345$  nm). The experimentally observed photochemical S-S bond cleavage is fully consistent with the  $n, \sigma^*$ -nature of excitation which transfers electron density from the lone pairs of sulfur atoms into the  $\sigma^*_{S-S}$  orbital. The resulting increase in the antibonding orbital population weakens the S-S bond and facilitates its cleavage.



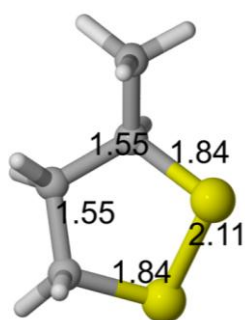
**Figure S1.** Photochemical excitation corresponds to the one-electron transfer from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). 3-Methyl-1,2-dithiacyclopentane was used as the model compound to represent the 3-alkyl-1,2-dithiacyclopentane chromophore of lipoic acid.

Computational data:

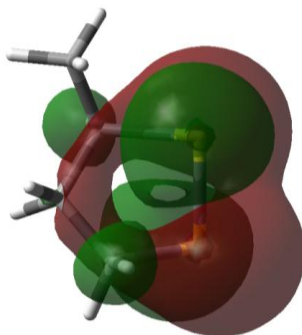
All calculations were performed at B3LYP/6-31+G(d,p) level of theory

### 3-methyl-1,2-dithiacyclopentane

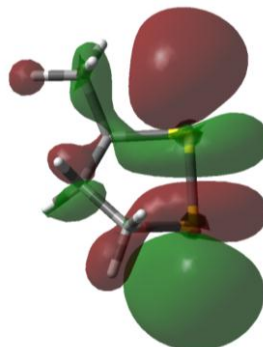
Geometry



HOMO



LUMO



S<sub>0</sub> Energy: E(RB+HF-LYP)-953.64519353

Dipole Moment 4.0309

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.068238	0.129781	-0.469216
2	6	0	-1.049406	1.305626	0.405747
3	6	0	0.419286	1.479699	-0.061521
4	1	0	1.082577	0.018231	-1.555985
5	1	0	-1.698550	2.102945	0.032561
6	1	0	-1.110784	1.284351	1.496455
7	1	0	0.461186	2.158319	-0.919322
8	1	0	0.990467	1.940921	0.750547
9	16	0	0.092201	-1.263760	0.238065
10	16	0	-1.712424	-0.288480	-0.236017
11	6	0	2.507755	-0.007158	0.060537
12	1	0	2.920379	-0.939247	-0.264809
13	1	0	3.104266	0.797612	-0.315520
14	1	0	2.498802	0.025015	1.130016

**S1 (vertical excitation at S0 geometry):**

Excited State 1: Singlet-A 3.5502 eV 349.23 nm f=0.0056

32 -> 33 0.67727

This state for optimization and/or second-order correction.

Copying the excited state density for this state as the 1-particle RhoCl density.

Excited State 2: Singlet-A 4.9581 eV 250.07 nm f=0.0004

31 -> 33 0.56595

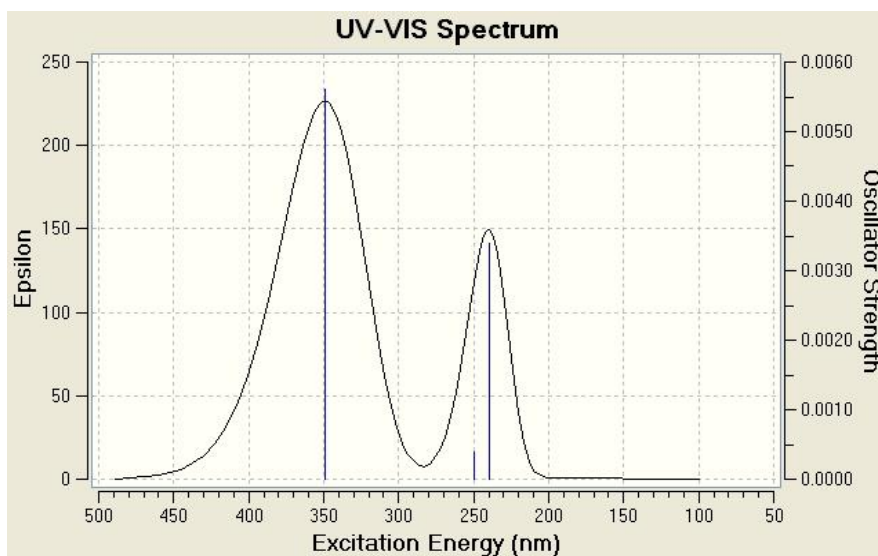
32 -> 34 0.37446

32 -> 35 0.10295

Excited State 3: Singlet-A 5.1823 eV 239.25 nm f=0.0034

31 -> 33 -0.38035

32 -> 34 0.58082



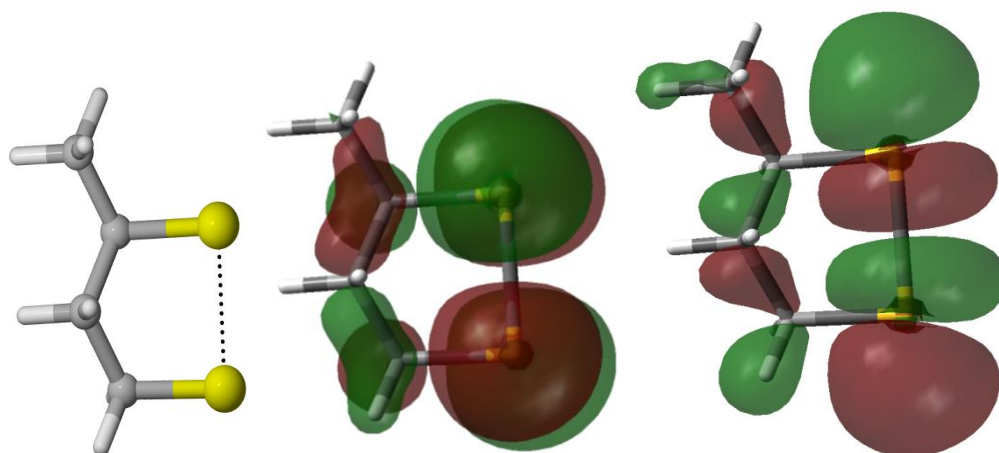
**Figure S2.** Calculated UV-Vis Spectrum of 3-methyl-1,2-dithiacyclopentane at TD-B3LYP/6-31+G(d,p) level of theory at B3LYP/6-31+G(d,p)-geometry. Solvation was approximated using CPCM method in methanol.

**Triplet:** Fully optimized at UB3LYP/6-31+G(d,p) level:

Geometry

SOMO1

SOMO-2

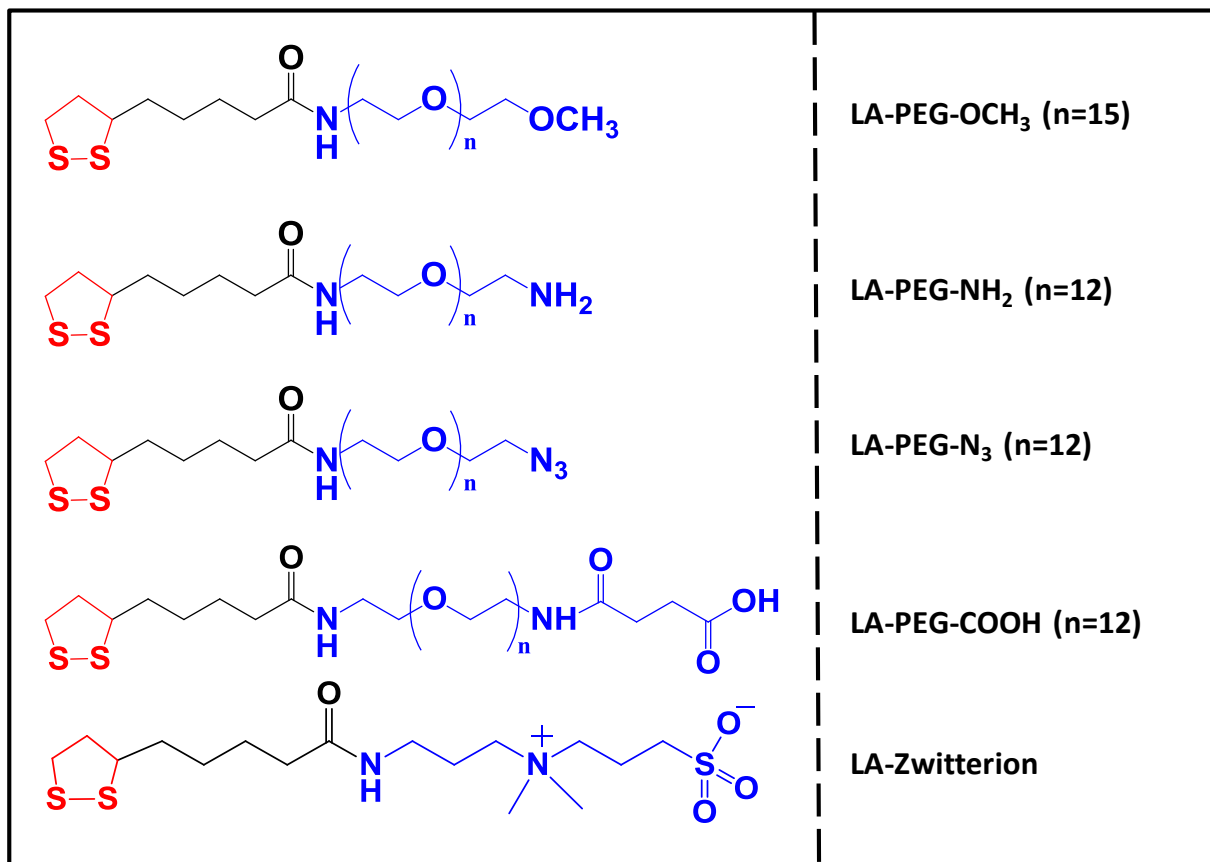


Energy: E(UB+HF-LYP) -953.58391174

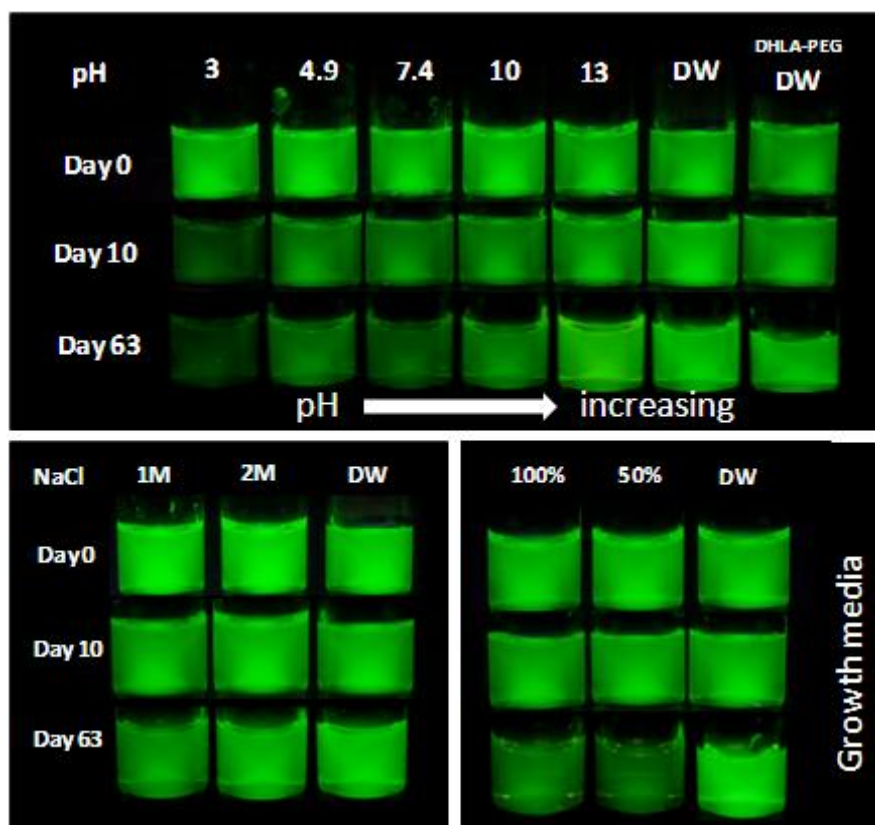
Geometry:

Input orientation:

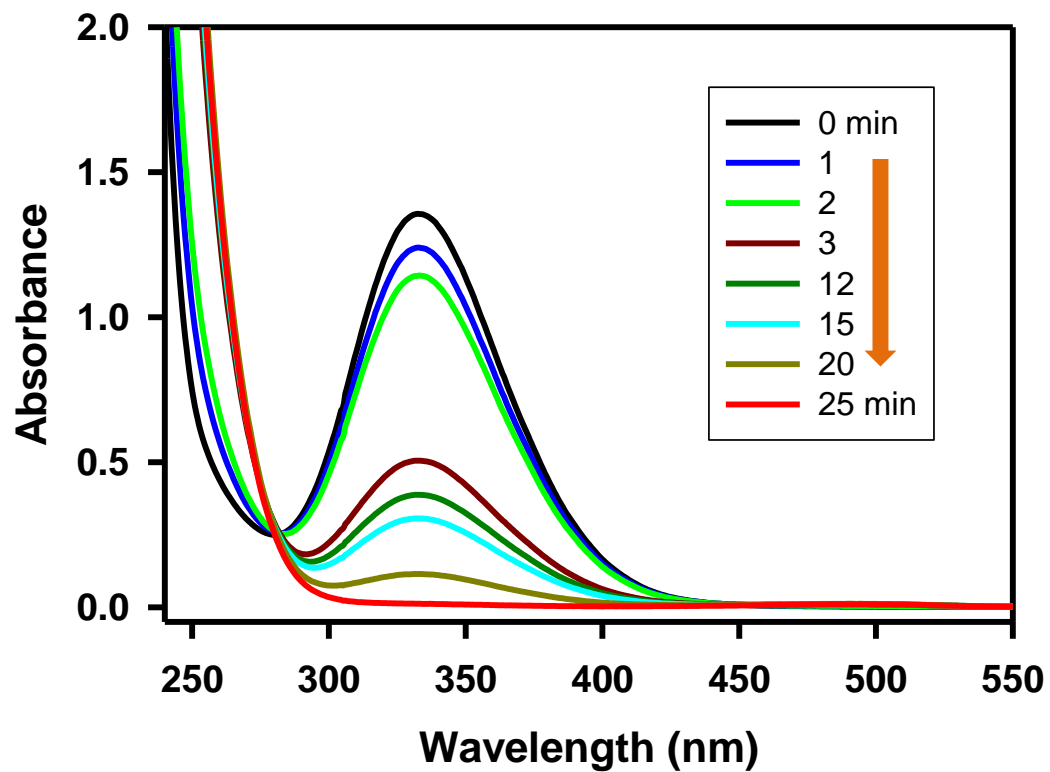
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.059031	0.121218	-0.377167
2	6	0	-1.109977	1.353678	0.169358
3	6	0	0.405843	1.295815	0.362838
4	1	0	0.849917	0.221452	-1.452038
5	1	0	-1.359164	1.521001	-0.886514
6	1	0	-1.545713	2.176008	0.745102
7	1	0	0.846785	2.233391	-0.005173
8	1	0	0.638782	1.223743	1.432662
9	16	0	0.271246	-1.469749	0.120288
10	16	0	-1.942308	-0.192541	0.688129
11	6	0	2.577071	0.069920	-0.166055
12	1	0	3.028773	-0.754167	-0.724620
13	1	0	3.033457	1.006934	-0.508487
14	1	0	2.820251	-0.062846	0.893215



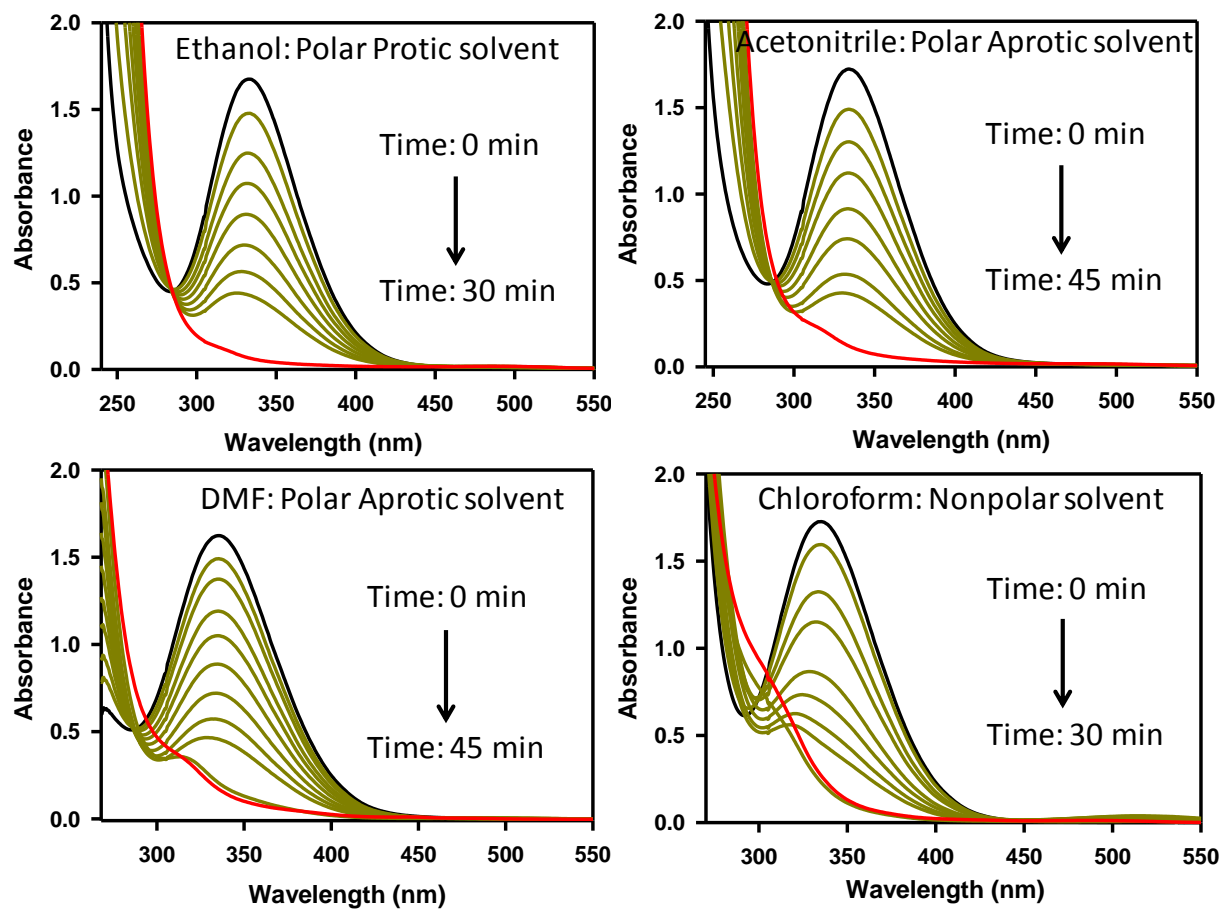
**Figure S3.** Chemical structures of the compounds (both zwitterions and PEGylated ligands) used in our study.



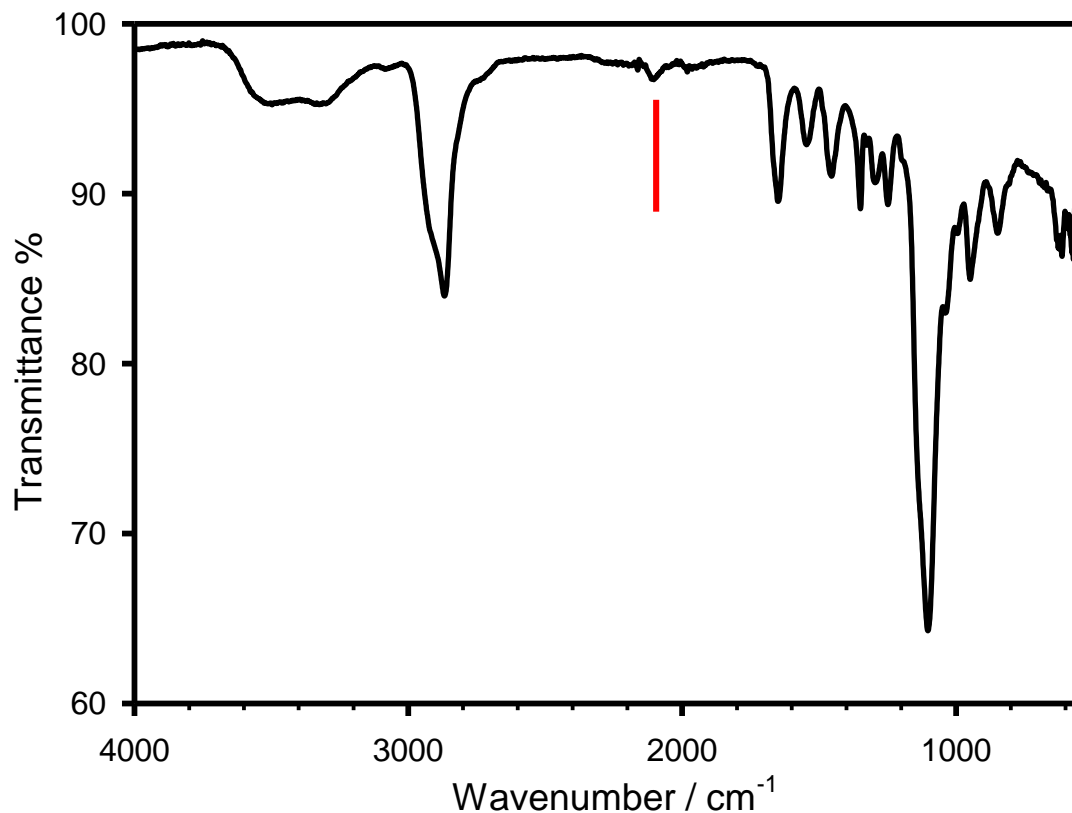
**Figure S4.** (Top) Fluorescence images of vials containing green-emitting CdSe-ZnS QDs phase transferred UV irradiation with LA-PEG ligands dispersed in different phosphate pH buffers along with one control sample in deionized water. A second control sample is prepared using  $\text{NaBH}_4$ -reduced ligand (conventional route) is also shown. (Bottom) Fluorescence images of vials containing QDs dispersed in growth media and in buffer plus 1M and 2M NaCl. Images were collected on freshly prepared and after 10 and 63 days of storage. The QD concentration is  $0.5 \mu\text{M}$  in all dispersions.



**Figure S5.** Progression of the UV-vis absorption spectra collected from lipoic acid dissolved in methanol (2.5 mL at  $10^{-2}$ M) following UV-irradiation at several time periods. The sample was irradiated at 350 nm with a power of  $4.5 \text{ mW/cm}^2$ .



**Figure S6.** Progression of the UV-vis absorption spectra of LA-PEG-OCH<sub>3</sub> (dispersed in various solvents) with UV-irradiation time. The solution volume and ligand concentration were 2.5 mL and  $1.23 \times 10^{-2} \text{M}$ , respectively. Samples were irradiated at 350 nm with a power of  $4.5 \text{ mW/cm}^2$ .



**Figure S7.** FT-IR spectra of QDs dispersion in DI water (phase transferred via UV-irradiation) surface-functionalized with a mixture of LA-PEG<sub>750</sub>-OCH<sub>3</sub>/LA-PEG<sub>600</sub>-N<sub>3</sub> (85%/15%). The arrow shows the typical azide signal at 2100 cm<sup>-1</sup>.

## References

1. Miertus, S., Scrocco, E. & Tomasi, J. Electrostatic Interaction of a Solute with a Continuum - a Direct Utilization of Abinitio Molecular Potentials for the Prevision of Solvent Effects. *Chem Phys* **55**, 117-129 (1981).
2. Cossi, M., Rega, N., Scalmani, G. & Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J Comput Chem* **24**, 669-681 (2003).