Electronic Supplementary Material for PCCP

Supporting Information

PbS Quantum Dot Synthesis:

All reagents were purchased from Sigma–Aldrich. In a typical synthesis of the 3.2-nm diameter PbS QDs, a flask containing 220 mg of lead(II) oxide (1 mmol), 0.25 mL of oleic acid (tech grade), and 9.75 mL of 1-octadecene (ODE, tech grade) was heated at 150 °C for 1 h under N_2 flow. After cooling the reaction flask to 90–100 °C, 5 mL of 0.1 M hexamethyldisilathiane (0.5 mmol) dissolved in ODE was quickly injected with a syringe into the reaction flask, which was immediately cooled with an ice bath. The solution turned brown in color within 1 s after injection, indicating the formation of QDs. Larger diameter QDs can be synthesized by varying the injection temperature (120 °C for both the 3.8- and 5.4-nm diameter samples) and by changing the Pb:oleic acid molar ratio (4:1 and 32:1 for the 3.8- and 5.4-nm diameter samples, respectively). The resulting nanoparticles were precipitated with a methanol/butanol mixture, centrifuged to remove excess oleic acid and ODE, re-dissolved in tetrachloroethylene or toluene, and stored in a nitrogen glovebox.

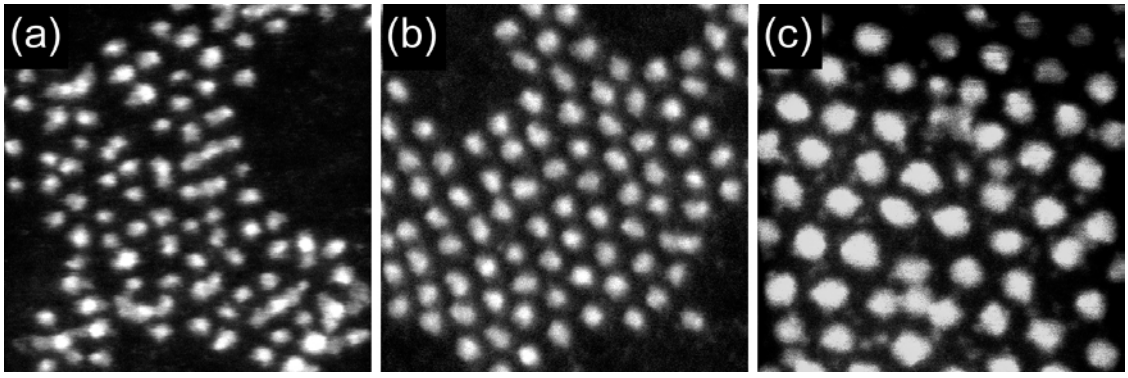

Figure S1. Scanning transmission electron micrographs of PbS QDs with average diameters 3.2 ± 0.5 (a), 3.8 ± 0.4 (b), and 5.4 ± 0.7 nm (c).

Kinetic Regime		3.2 nm Air	3.2 nm N_2	3.8 nm Air	3.8 nm N_2	5.4 nm Air	5.4 nm N_2
Fast, initial decrease	Present (Y/N)	Y	Y	Y	Y	Y	Y
	Magnitude (% decrease)	71	--	80	52	62	71
	Time scale (s)	< 3	--	< 3	< 3	< 3	< 3
Nonexponential increase	Present (Y/N)	N	Y	Y	Y	N	N
	Magnitude (% increase)	--	200	80	60	--	--
	Time scale (s)	--	60	100	50	--	--
Multiexponential decrease	Present (Y/N)	Y	Y	Y	N	N	N
	Magnitude (% decrease)	98	48	42	--	--	--
	Time constant (s)	50	390	350	--	--	--
Steady state	Present (Y/N)	N	N	N	Y	Y	Y

Table S1. Characterization of fluorescence intensity kinetics in 3.2-, 3.8-, and 5.4-nm diameter PbS QDs prepared as a spun-cast sample in a polymer film measured in both air and in N_2.

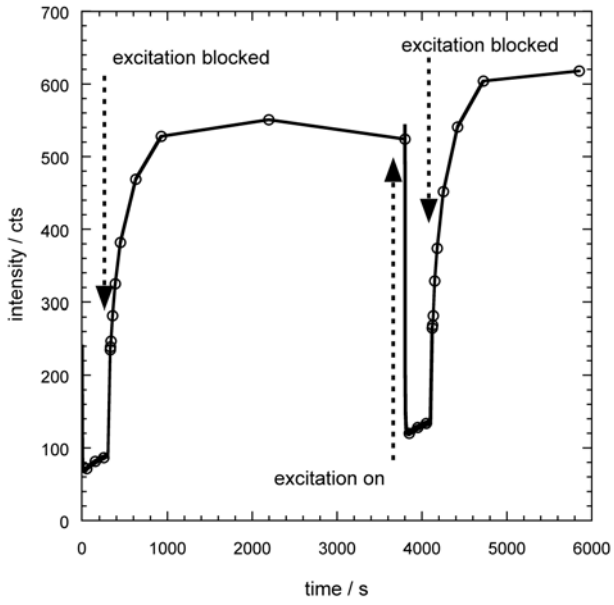

Figure S2. Fluorescence intensity time trace of 5.4-nm PbS QDs exhibiting a complete recovery of initial intensity levels after sitting in darkness for ~10 min. The beginning of excitation and recovery are marked on the plot and are cycled a total of two times.