Supporting Information

Redox Modification of CdSe-ZnS-Polymer Quantum Dots: Photoassisted Fluorescence Quenching and Recovery

X.X. Yu,[1,2] J. Li,[2] K.C. Kwok,[2] M.C. Paau,[3] Martin M.F. Choi,[3] K.K. Shiu,[3] J.Y. Chen,[1,*] and N.H. Cheung[2,*]

[1] State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Handan Road 220, Shanghai 200433, China.
[2] Department of Physics, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China.
[3] Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China.

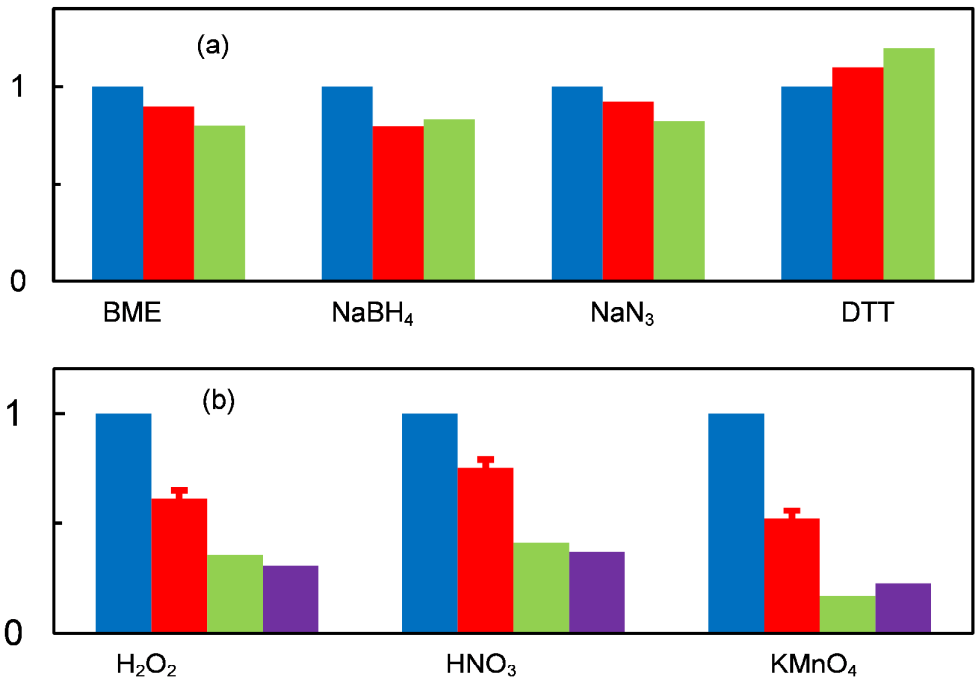

Fig. S1. Effects of redox chemicals on QD fluorescence. Fluorescence intensities of QD samples in 96-well plates were measured on a micro-plate reader (Tecan), using 590 nm excitation light and 635 ± 17 nm emission. [QD] ~ 2.5 nM. Fluorescence intensity before redox treatment was normalized to 1 (blue) in all cases. (a) Effects of reducing agents: beta-mercapto-ethanol (BME), sodium borohydride ($NaBH_4$), and sodium azide (NaN_3) at 10 μM (red) and 100 μM (green); and dithiothreitol (DTT) at 20 μM (red) and 200 μM (green). (b) Effects of oxidizing agents: hydrogen peroxide (H_2O_2) and nitric acid (HNO_3) at 6 μM (red) and 16 μM (green); and potassium permanganate ($KMnO_4$) at 4 μM (red) and 10 μM (green). For each last oxidized sample, DTT was then added to make 35 μM. Effect is shown in purple. Representative error bars based on three or more measurements are also shown.

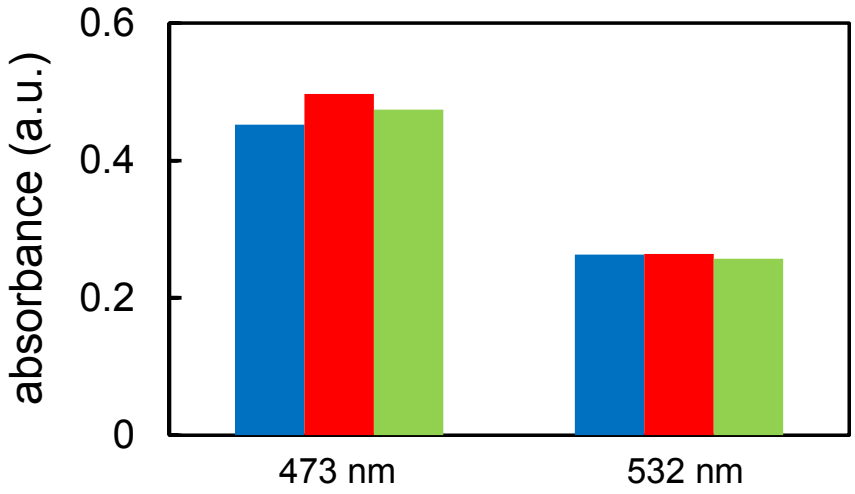

Fig. S2. Absorbance of oxidized QDs. Absorbance of 1 μM QD samples was measured using a micro-volume spectrophotometer (NanoDrop) at 532 and 473 nm under three conditions: (1) in water (blue), (2) in 500 μM $KMnO_4$ for 15 min (red), and (3) in 500 μM $KMnO_4$ with 473 nm irradiation at 160 mW cm^{-2} for 30 s. Absorbance due to $KMnO_4$ alone was corrected. Measurement uncertainty was about ± 5%. The sample prepared under condition (2) was also measured for fluorescence brightness. It was 6 % of that before oxidation.

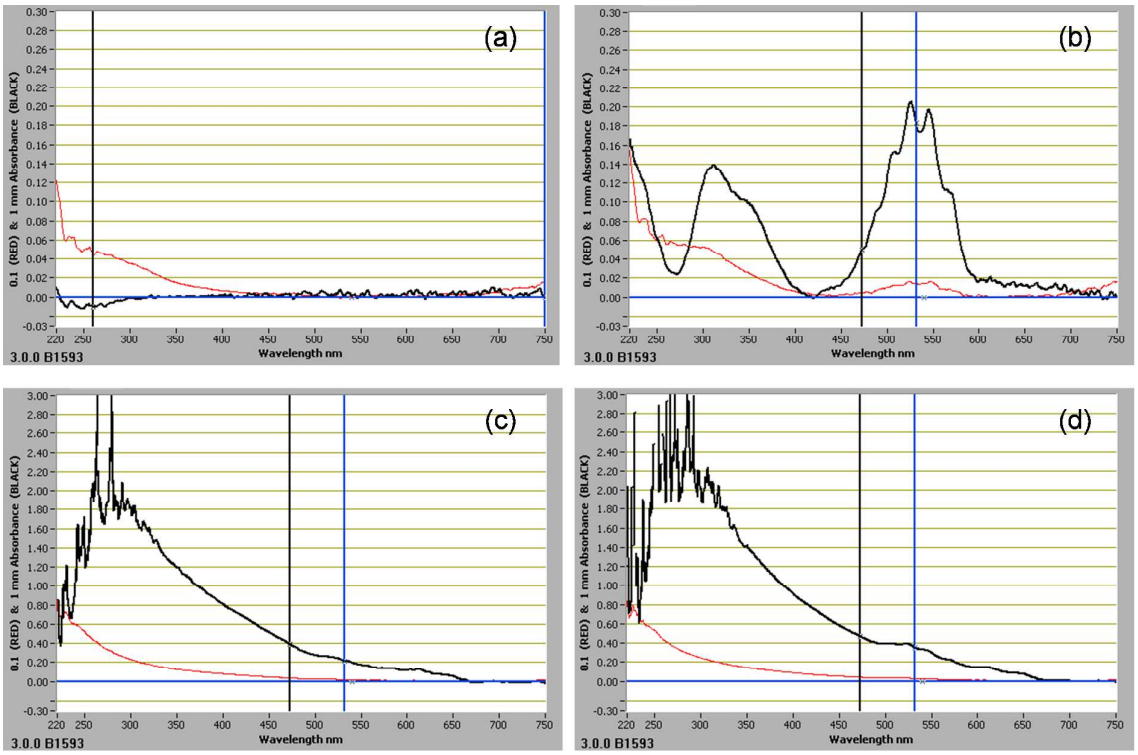

Fig. S3. Absorption spectra of four samples measured with NanoDrop ND 1000. (a) Blank water, (b) 1 mM $KMnO_4$, (c) 1 μM of QDs in water, and (d) 1 μM of QDs in 1 mM $KMnO_4$. Plotted are the absorbance for two sample thicknesses, 0.1 mm (red curves) and 1 mm (black curves). Note that the absorbance curves shown in (d) was approximately (± 5%) the superposition of the corresponding curves shown in (b) and (c).

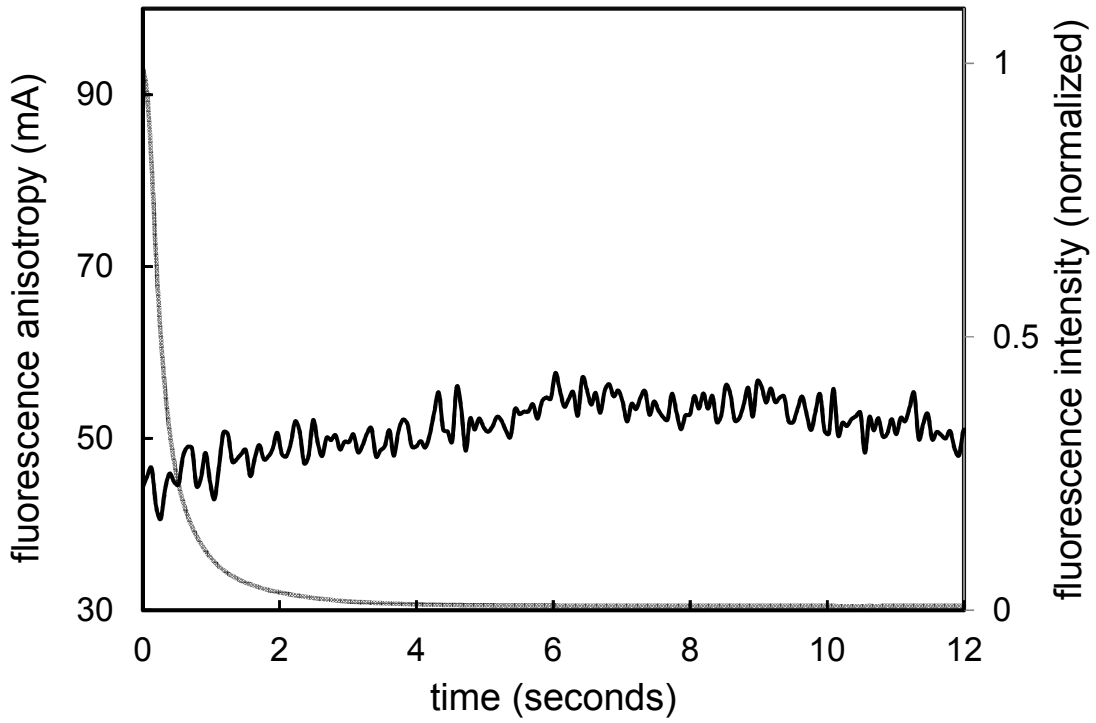

Fig. S4. Change in fluorescence anisotropy as QDs were bleached. QDs were treated with 20 μM $KMnO_4$ and irradiated with 532 nm laser at 350 mW cm^{-2}. Plotted are fluorescence anisotropy change (black curve, left-hand axis) and normalized intensity (gray curve, right-hand axis).

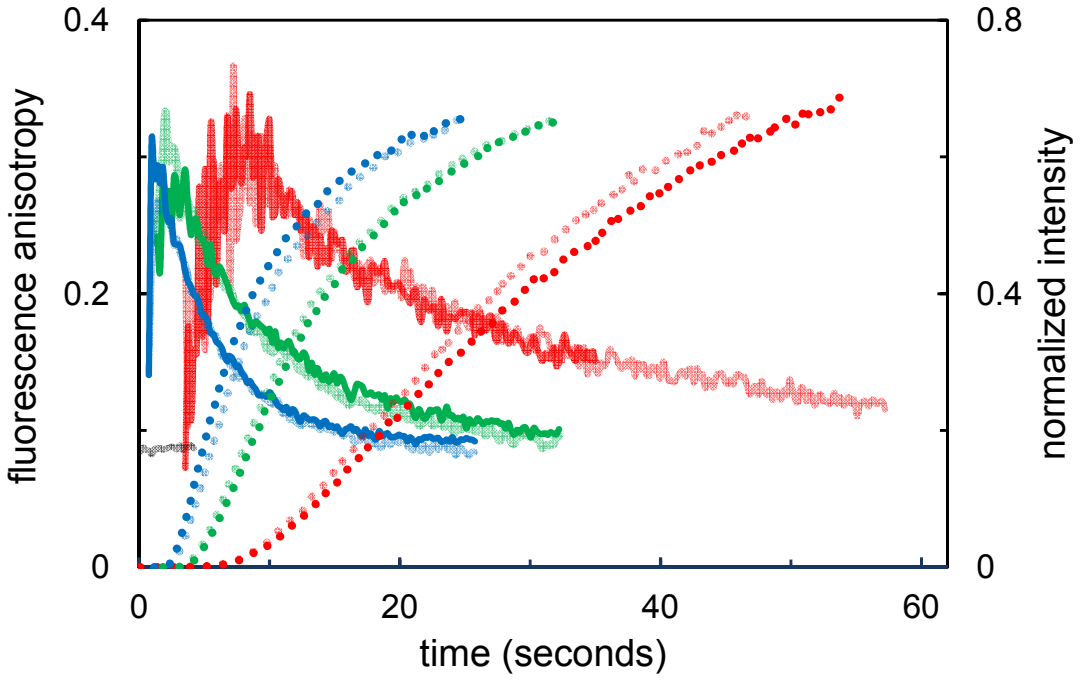

Fig. S5. Photo-activated relaxation of fluorescence anisotropy. The solid curves are fluorescence anisotropies (left-hand axis) versus exposure time for 473 nm laser illumination at three irradiances: 6.8 (red pair), 22 (green pair), and 43 (blue pair) mW cm^{-2}. For each irradiance, two data sets are shown. The dotted curves show the corresponding normalized fluorescence intensities (right-hand axis). As can be seen, the fluorescence at the early times was very weak; the anisotropy value was therefore poorly defined and was not plotted. A brief trace of the fluorescence anisotropy of untreated QDs is shown in gray. It was based on the average of 4 data sets; the standard deviation is about twice the line thickness.

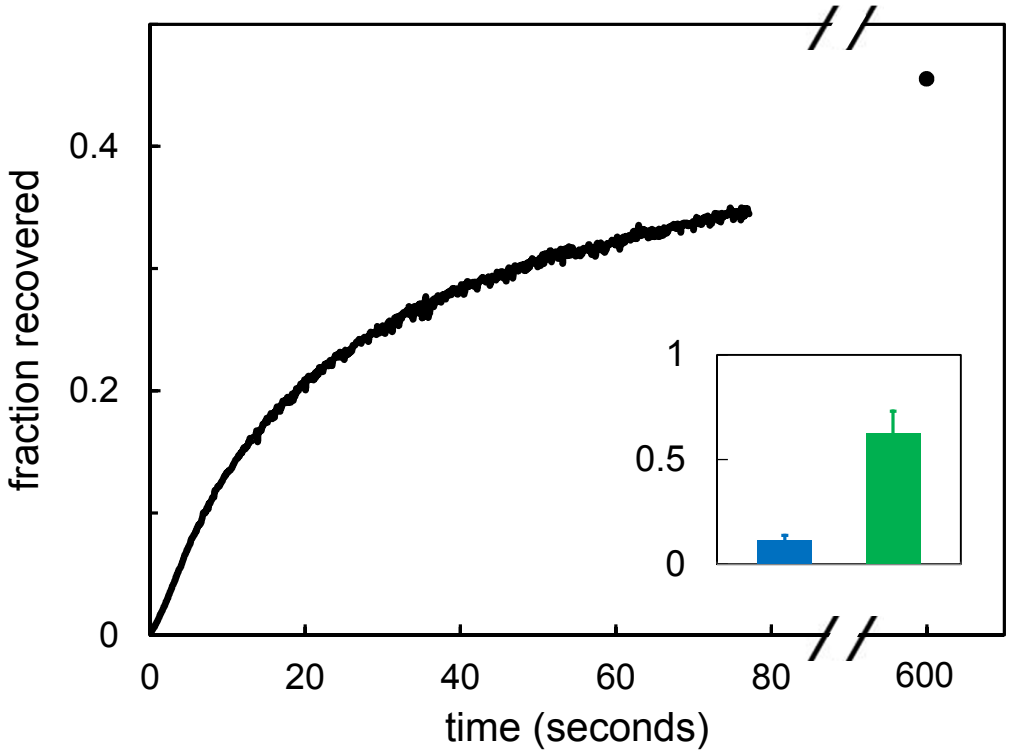

Fig. S6. Fluorescence recovery of QDs. QDs were treated with 20 μM $KMnO_4$ and 910 mW cm^{-2} irradiation at 532 nm for 5 seconds. Permanganate was flushed and QDs were photo-activated with 532 nm laser at 910 mW cm^{-2} to recover. Final recovered fraction after 10 min was about 46%. Inset: Fluorescence finally recovered for QDs treated with 20 μM $KMnO_4$ and 160 mW cm^{-2} irradiation for 10 s at 473 nm (blue) and 532 nm (green).

TABLE S1. pH values of various concentrations of $KMnO_4$ in MilliQ water at T = 19.5 ± 0.5 °C

Solvent	pH
MilliQ water	5.6 (4)
1 mM $KMnO_4$	5.9 (3)
400 nM $KMnO_4$	5.3 (3)

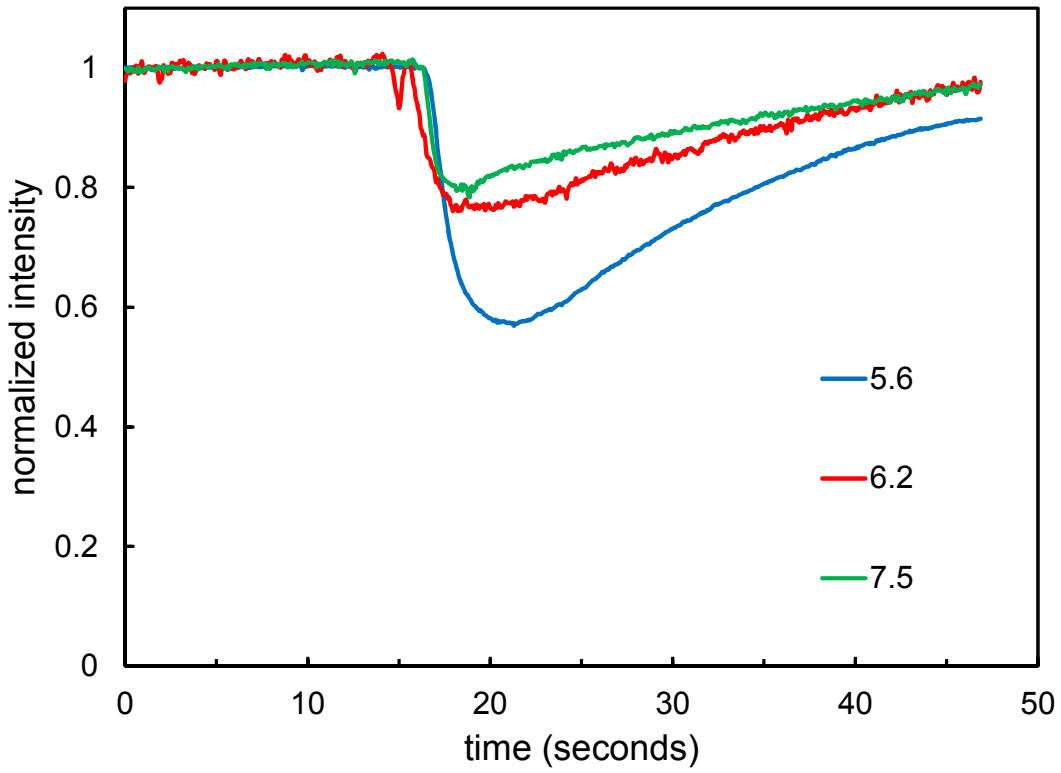

Fig. S7. Effect of pH on oxidative bleaching of QDs. 400 nM $KMnO_4$ and 1.6 W cm^{-2} at 532 nm, at three different pH values, 5.6 (blue curve), 6.2 (red curve) and 7.5 (green curve). Evidently, oxidative bleaching was more extensive at lower pH.

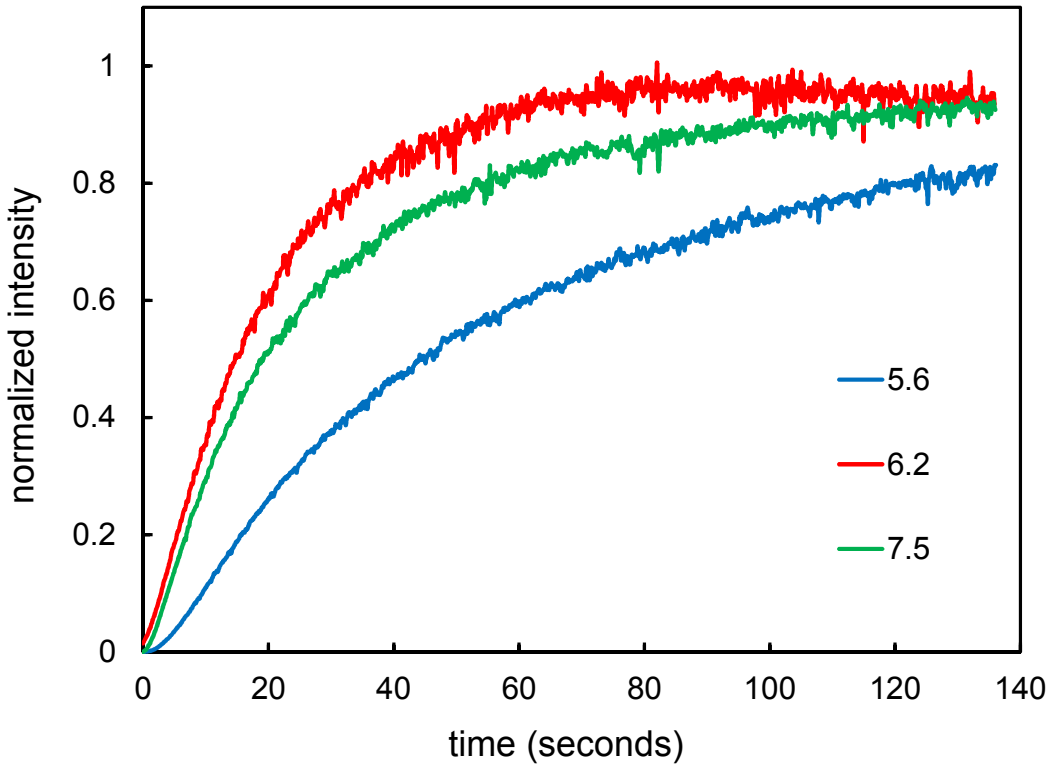

Fig. S8. Effect of pH on photo-activated recovery of dark-bleached QDs. Plotted is the normalized fluorescence intensity against irradiated time at 532 nm irradiance of 1.6 W cm^{-2} and at three different pH values, 5.6 (blue curve), 6.2 (red curve) and 7.5 (green curve). The pH 5.6 solution was MilliQ water. The pH 7.5 solution was phosphate buffered saline. The pH 6.2 solution was prepared by adding citric acid to phosphate buffered saline. Citric acid was a reducing agent. That explained the accelerated recovery.