Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Quantum Dot photoluminescence lifetime-based pH nanosensor

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Materials

Quantum dots CdSe/ZnS core-shell with maximum emission at 540 nm were purchased from Evident Technologies. The lipophilic long chain surfactant capping the QDs was hexadecylamine. 3-Mercaptopropionic acid was purchased from Fluka. Bovine Serum Albumin (BSA), Ficoll400, and all inorganic salts and buffers were of analytical grade and used as obtained from Sigma-Aldrich (Spain). The pH of solutions and buffers was adjusted using diluted NaOH (Aldrich, Spain) and HCl (Aldrich, Spain) (spectroscopic grade quality) dissolved in Milli-Q water. All standard chemical solutions were protected from sunlight and kept at about 4ºC in a refrigerator.

Synthesis of water-soluble MPA-capped CdSe/ZnS nanoparticles

The lipophilic hexadecylamine-capped QDs (QD-HDA) were modified by 3-mercaptopropionic acid (MPA) to achieve water solubility. The procedure for the surface-ligand exchange was taken from previous reports[1,2]. In brief, 1 ml of QD-HDA dissolved in toluene was left to react overnight with 1 ml of MPA, protected from light. After the ligand exchange, the particles were transferred to an aqueous phase by adding 1 M NaOH solution and shaking. The aqueous phase was separated, and the excess of MPA was removed from the water-soluble CdSe/ZnS QD nanoparticles by precipitation of the particles with acetone and centrifugation (10 min, 13000 rpm), followed by the re-dissolution of the QD-MPA in milli-Q water.

Instruments

Steady-state fluorescence emission spectra were collected on a JASCO FP-6500 spectrofluorometer equipped with a 450 W xenon lamp for excitation, with temperature controller ETC-273T at 25 °C. All measurements were made at 25 ºC, using 5×10 mm cuvettes. Fluorescence decay traces of QD with different capping ligands were recorded in the Time

Correlated Single Photon Counting (TCSPC) mode using the FluoTime 200 fluorometer (PicoQuant, GmbH.) described previously[3]. Briefly, the samples were excited by a 440-nm pulsed laser (LDH-P-C-440 PicoQuant, GmbH.) with a 10 MHz repetition rate. The full width at half maximum of the laser pulse was ~ 80 ps. The fluorescence was collected after crossing through a polarizer set at the magic angle, and a 2 nm bandwidth monochromator. Fluorescence decay histograms were collected using a TimeHarp200 board, with a time increment per channel of 36 ps, at the emission wavelengths of 540 nm. The histograms of the instrument response function (IRF) was determined using LUDOX scatterer, and sample decays were recorded by triplicate until they typically reached 6×10^4 counts in the peak channel.

Methods of analysis

Time resolved fluorescence decay traces were deconvoluted from the signal and fitted using FluoFit 4.4 package (Picoquant GmbH). The experimental decay traces were fitted to multi-exponential functions via a Levenberg-Marquard algorithm-based nonlinear least-squares error minimization deconvolution method. Usually, up to four different exponential terms were used to fit the experimental decay traces. The quality of fittings was judged by the reduced chi-squared method, χ^2, the weighted residuals and the correlation functions. The latter two were checked for random distributions. To compare the emission lifetime of the QD-MPA at different values of pH it was necessary to determinate their average lifetime using the equation 1 in the main text.[4]

References

[1] F. Patolsky, R. Gill, Y. Weizmann, T. Mokari, U. Banin and I. Willner, *J. Am. Chem. Soc*., 2003, **125**, 13918-13919.

[2] M. J. Ruedas-Rama and E. A. H. Hall, *Analyst*, 2008, **133**, 1556-1566.

[3] Ruedas-Rama, M. J.; Orte, A.; Crovetto, L.; Talavera, E. M.; Alvarez-Pez, J. M. *J. Phys. Chem. B,* 2010, **114**, 1094.

[4] Lakowicz, J. R. Principles of Fluorescence Spectroscopy; 3rd ed.; Springer, 2006

Table SI. 1. Lifetimes and normalized pre-exponentials of QD_{540}-MPA at different pH values

pH = 10.24		pH = 9.11		pH = 8.52	
τ (ns)	pre-expon	τ (ns)	pre-expon	τ (ns)	pre-expon
20.89	0.21	20.51	0.18	20.57	0.17
8.51	0.24	8.28	0.24	8.24	0.24
2.00	0.21	1.96	0.23	2.05	0.23
0.30	0.34	0.31	0.35	0.34	0.36
pH = 8.02		pH = 7.57		pH = 7.07	
τ (ns)	pre-expon	τ (ns)	pre-expon	τ (ns)	pre-expon
20.58	0.14	20.34	0.13	20.25	0.11
8.17	0.24	7.99	0.24	8.03	0.23
2.00	0.25	2.05	0.25	2.13	0.28
0.31	0.37	0.32	0.38	0.35	0.38
pH = 6.51		pH = 6.02		pH = 5.35	
τ (ns)	pre-expon	τ (ns)	pre-expon	τ (ns)	pre-expon
19.31	0.11	18.82	0.09	16.89	0.04
7.62	0.24	7.47	0.24	6.72	0.22
2.11	0.27	2.03	0.28	2.03	0.31
0.37	0.38	0.32	0.39	0.36	0.42
pH = 4.38		pH = 3.60			
τ (ns)	pre-expon	τ (ns)	pre-expon		
16.21	0.03	15.11	0.01		
6.39	0.19	5.59	0.13		
2.06	0.32	1.86	0.31		
0.40	0.46	0.36	0.55		

Figure S1. Emission spectra of QD-MPA in 20 mM TRIS buffer at different pH values: 4.38, 5.35, 6.03, 6.52, 7.07, 7.57, 8.02, 8.52, and 9.11.

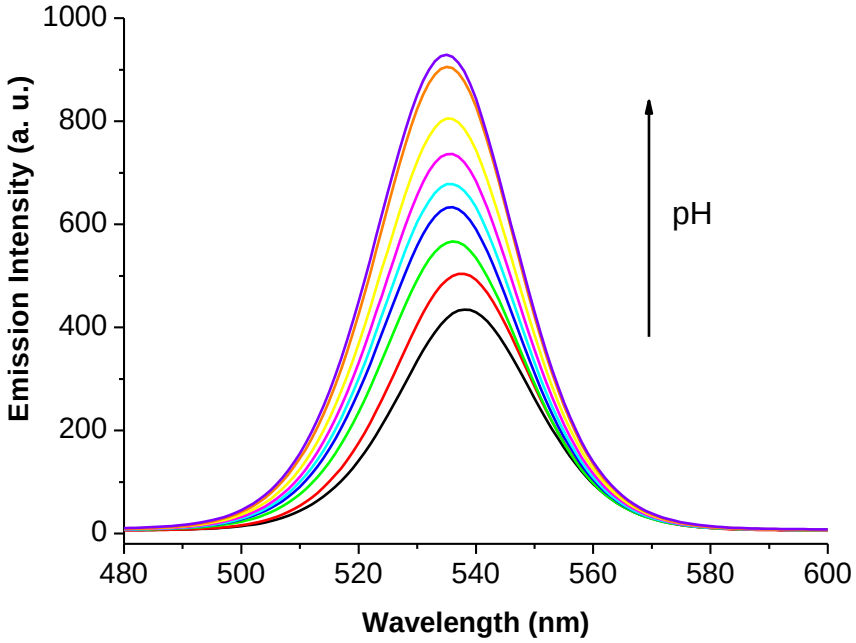

Figure S2. Fluorescence spectra (A) and average PL lifetime (B) of solutions of different concentrations of QD_{540}-MPA (20 mM TRIS buffer, pH 7): 1.25×10^{-8} M (black), 2.5×10^{-8} M (red), 5×10^{-8} M (green),and 1×10^{-7} M (blue) (λ_{ex} = 400 nm). While the emission intensity is highly dependent on the QD-MPA concentration, the average PL lifetime of the same samples is almost invariable.

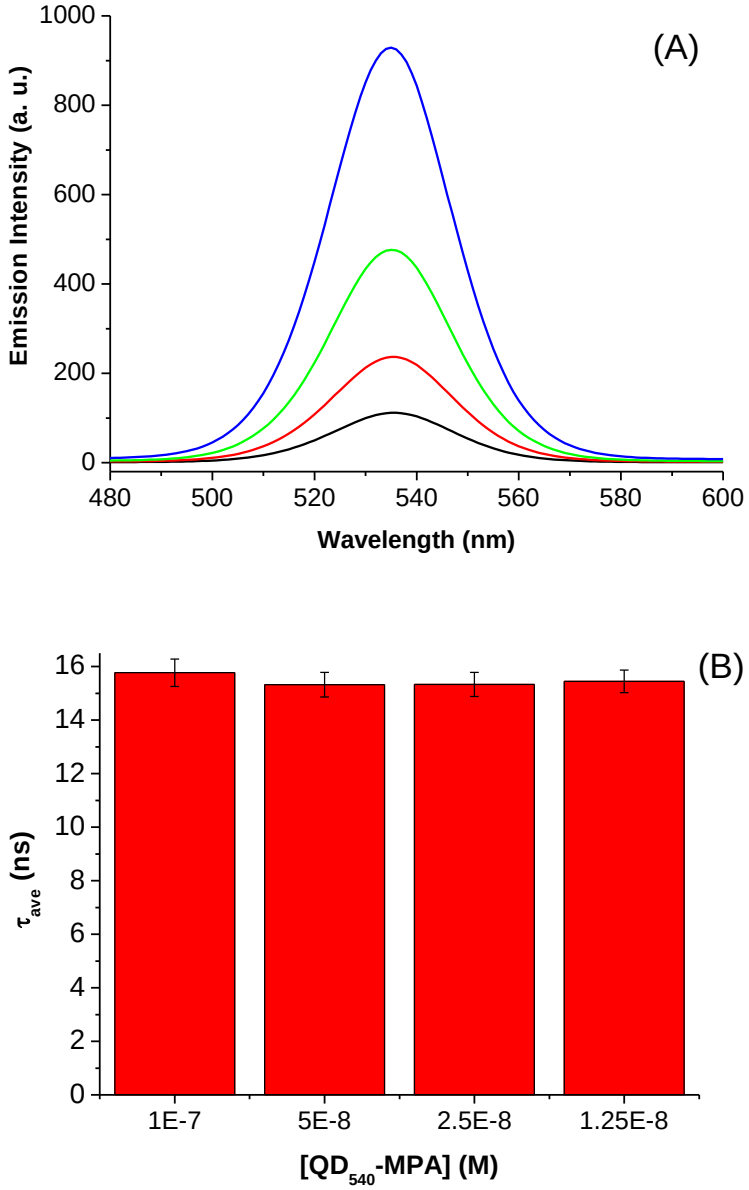

Figure S3. Average lifetime of 1×10^{-8} M QD_{540}-MPA at different laser power (20 mM TRIS buffer, pH 6.7).