Solution reduction synthesis of amine terminated carbon quantum dots

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S1. Experimental details

All reagents and solvents were purchased from Sigma-Aldrich Ltd. and used as received. In an inert atmosphere glove-box, 5.49 mmol of tetraoctyl ammonium bromide (TOAB was dissolved in 100 mL anhydrous toluene. 0.2 mL (2.07 mmol) CCl_4 was then added to the solution and left to stir for 30 min. Carbon quantum dots (CQDs) were then formed by the dropwise addition of 4 mL of 1 M lithium aluminium hydride in THF over a period of 5 min. The solution was then left to stir for 30 min. The excess reducing agent was quenched with the addition of 30 mL of methanol, upon which the dispersion became transparent. At this stage of the reaction the CQDs are terminated by hydrogen and encapsulated within the reverse micelle. Chemically passivated CQDs were formed by modifying the carbon-hydrogen bonds at the surface *via* the addition of 200 μL of a 0.1 M H_2PtCl_6 in isopropyl alcohol as a catalyst, followed by 3 mL of Allylamine. After stirring for 30 min, the CQDs were removed from the glove box and the organic solvent removed by rotary evaporation. The resulting dry powder (consisting mainly of surfactant) was then re-dispersed in 50 mL deionised water and sonicated for 30 min. The solution was then filtered twice using both filter paper and PVDF membrane filters

(MILLEX-HV, Millipore, 0.45 μM) to remove the surfactant. The solution was then concentrated down to 20 mLs.

Characterization Methods

Transmission electron microscopy (TEM) images were acquired using a high-resolution JEOL 2100 electron microscope, equipped with a LAB_6 electron source and a Gatan DualVision 600 Charge-Coupled Device (CCD), operating at an accelerating voltage of 200 keV. TEM samples were prepared by depositing 100 μL of CQDs dispersion, onto a holey carbon coated TEM grid (400-mesh, #S147-3H, Agar Scientific). Particle size analysis of TEM images was carried out using the Particle Size Analzyer macro (r12, available online at http://code.google.com/p/psa-macro/), running on Image J software. FT-IR spectra were recorded using a liquid cell with CaF_2 windows on a Perkin Elmer Two spectrometer. Samples were formed by placing an aliquot of carbon crystals dispersed in Chloroform onto CaF_2 plates, after which the sample was allowed to evaporate to dryness. UV-Vis absorption spectra were recorded using a Shimadzu UV PC-2401 spectrophotometer equipped with a 60 mm integrating sphere (ISR-240A, Shimadzu). Spectra were recorded at room temperature using a quartz cuvette (1 cm) and corrected for the solvent absorption. Photoluminescence (PL) spectra of optically dilute solutions (optical density 0.01 - 0.1) were acquired on a Cary Eclipse luminescence spectrophotometer. Long-term PL stability measurements on CQDs were carried out using an excitation wavelength of 380 nm, and recorded with a total integration time of 60 s. All spectra were integrated between 400 and 550 nm for comparison. Quantum yield were measurements were carried out using the comparative method described by

Williams *et al.*[1] Dilute dispersions of the CQDs in water were prepared with optical densities between 0.01 – 0.1 and compared against 9,10 diphenyl anthracene (literature quantum yield of 90 % at 320 nm)[2] as the standard. Linear aggression analysis was employed to determine the relative PL intensities of the sample and references solutions over the range of concentrations. The quantum yield of the water soluble CQDs were recorded using the following equation.

$$\Phi_x = \Phi_R \left(\frac{m_x}{m_R} \right) \left(\frac{\eta_x^2}{\eta_R^2} \right)$$

Where Φ is the quantum yield, m is the slope from the plot of integrated fluorescence intensity versus absorbance. The subscript R refers to the reference material of the known standard while x indicates the unknown species to be calculated.

1. A. T. R. Williams, S. A. Winfield, and J. N. Miller, *Analyst*, 1983, **108**, 1067-1071.
2. S. Hamai and F. Hirayama, *J. Phys. Chem.*, 1985, **89**, 294-300

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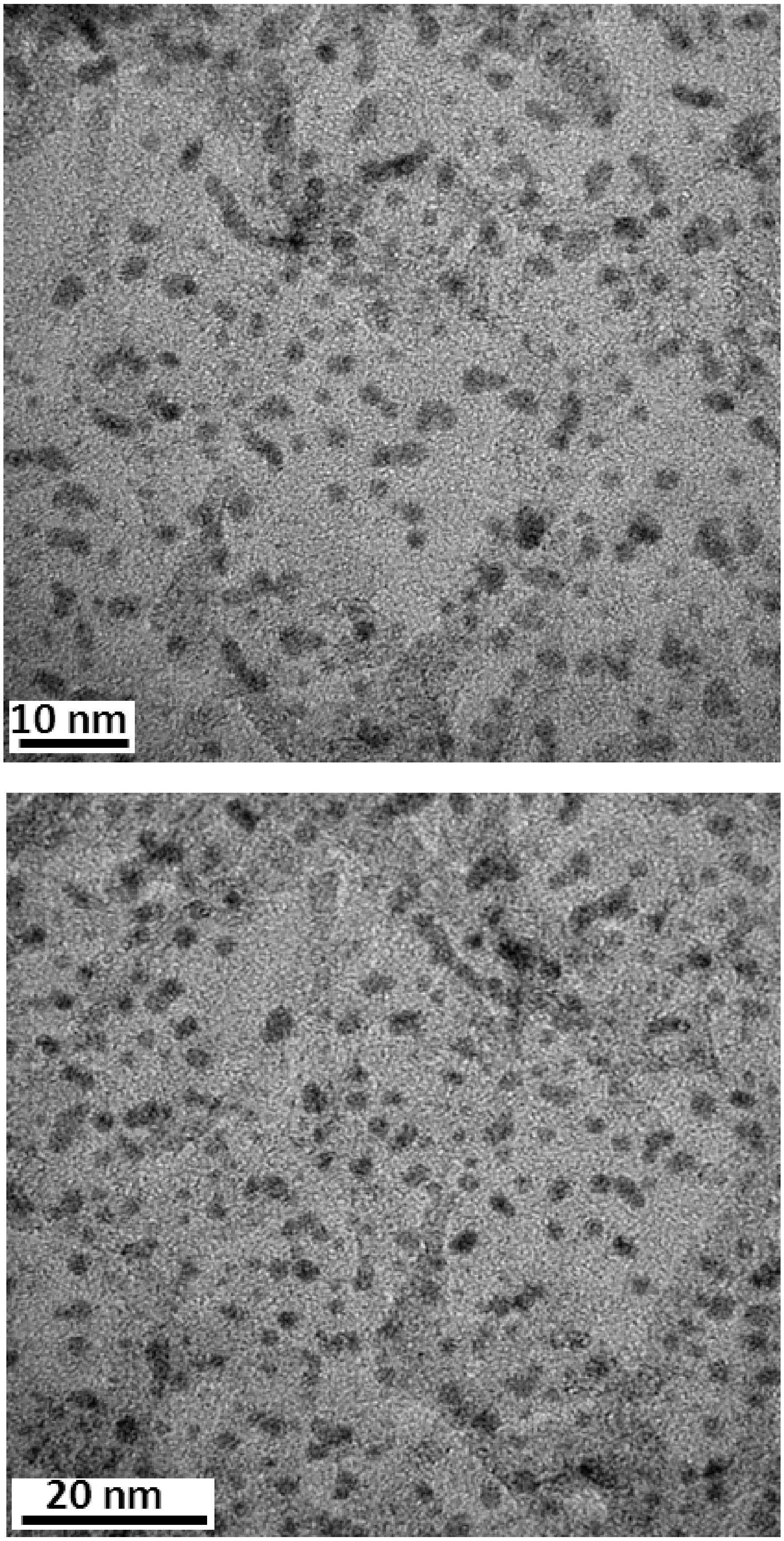

Fig S1. Low magnification TEM images of the carbon quantum dots.

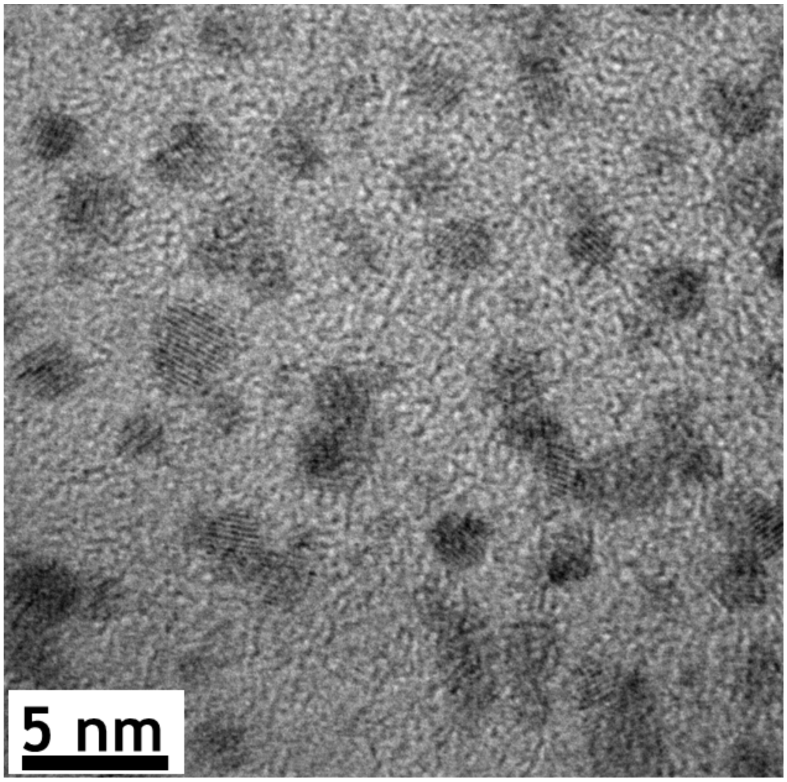

Fig. S2 High resolution TEM images of the carbon quantum dots.

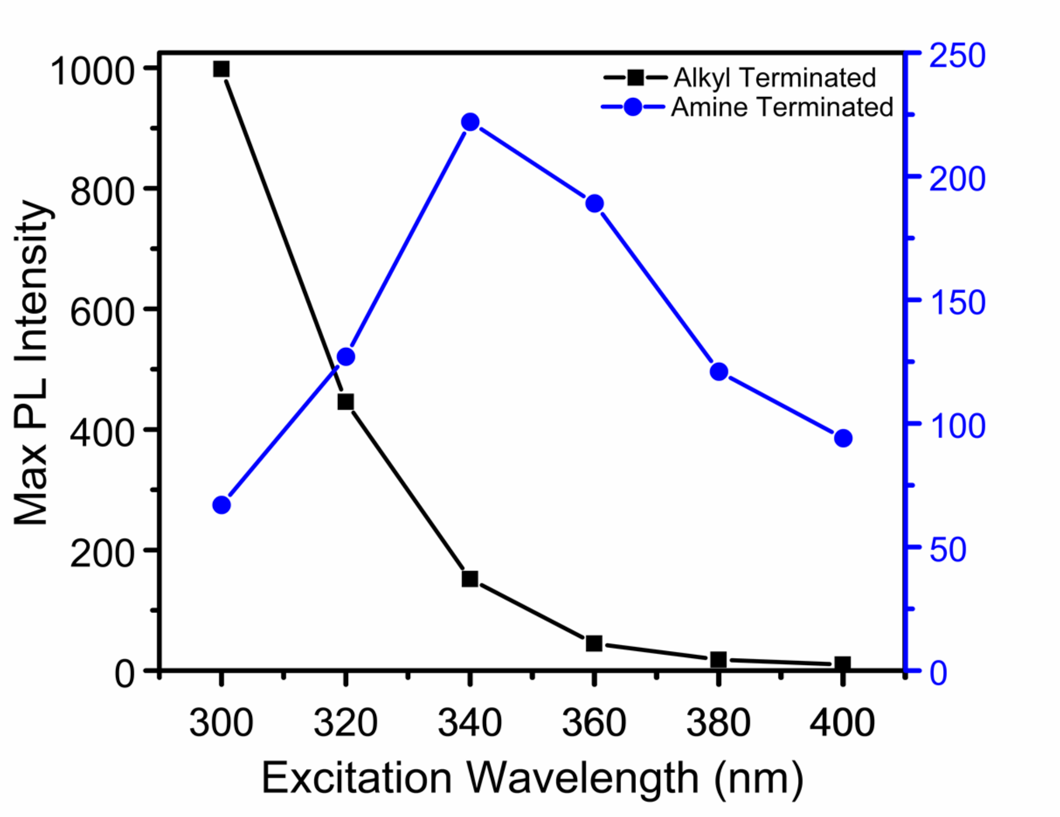

Fig. S3 Photoluminescence spectra of alkyl capped (black) and amine capped carbon quantum dots as a function of PL intensity.

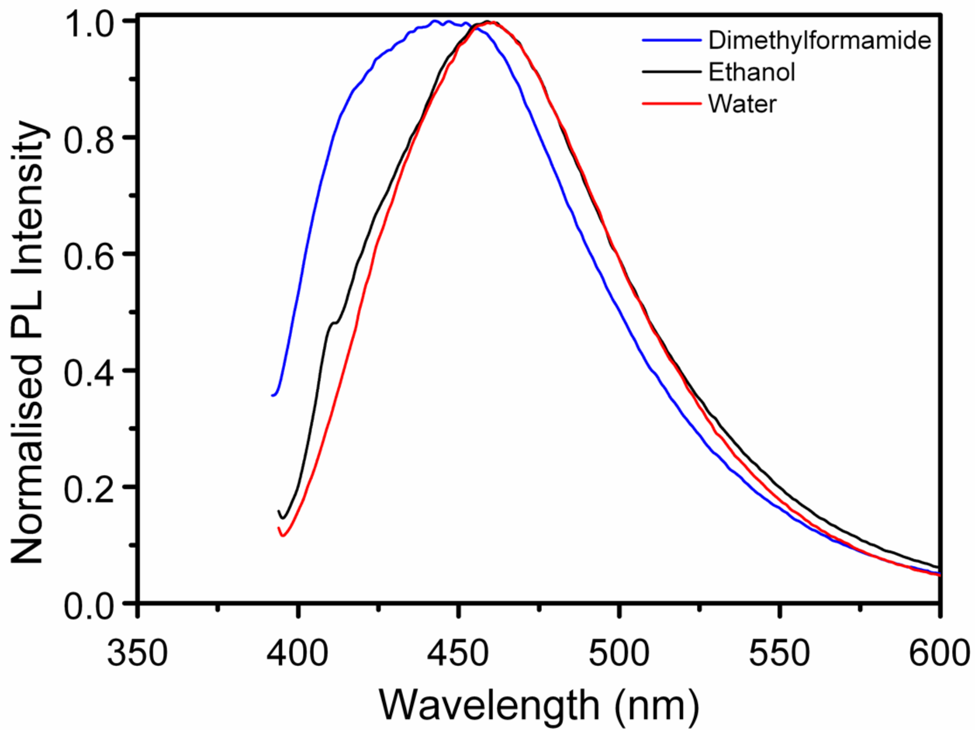

Fig. S4 Normalised photoluminescence spectra of the amine capped carbon quantum dots in dimethylformamide, ethanol and water.

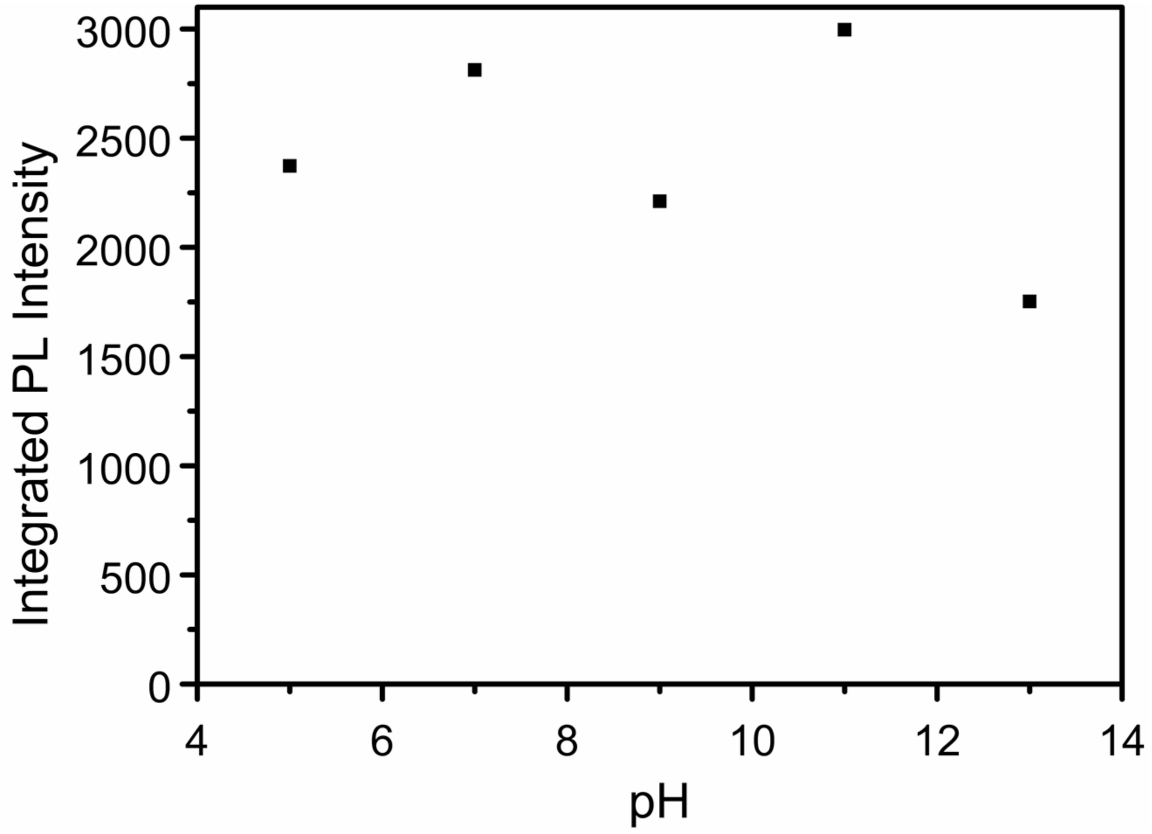

Fig. S5 Integrated PL intensity of allylamine-terminated CQDs recorded in different pH environments.