Efficient one-pot synthesis of highly monodisperse carbon quantum dots

Keith Linehan and Hugh Doyle*

Tyndall National Institute, University College Cork, Lee Maltings, Cork, Ireland. E-mail: hugh.doyle@tyndall.ie

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) CCl₄ 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 H₂PtCl₆ in isopropyl alcohol as a catalyst, followed by 3 mL of 1-dodecene. 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 hexane and sonicated for 30 min. The solution was then filtered twice using both filter paper and PVDF membrane filters (MILLEX-

HV, Millipore, 0.45 μ M) to remove the surfactant, after which it was washed with 100 mL of deionised water (3 times). Alkyl-terminated CQDs remain in the hexane phase.

Characterization Methods

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 290 nm, and recorded with a total integration time of 50 s, with a "dark" interval of 10 s between successive measurements (83 % duty cycle). All spectra were integrated between 250 and 400 nm for comparison. 1FT-IR spectra were recorded using a liquid cell with NaCl windows on a Perkin Elmer Two spectrometer. Samples were formed by placing an aliquot of carbon crystals dispersed in hexane onto NaCl plates, after which the sample was allowed to evaporate to dryness. Transmission electron microscopy (TEM) images were acquired using a high-resolution JEOL 2100 electron microscope, equipped with a LAB₆ 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 μ L 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.

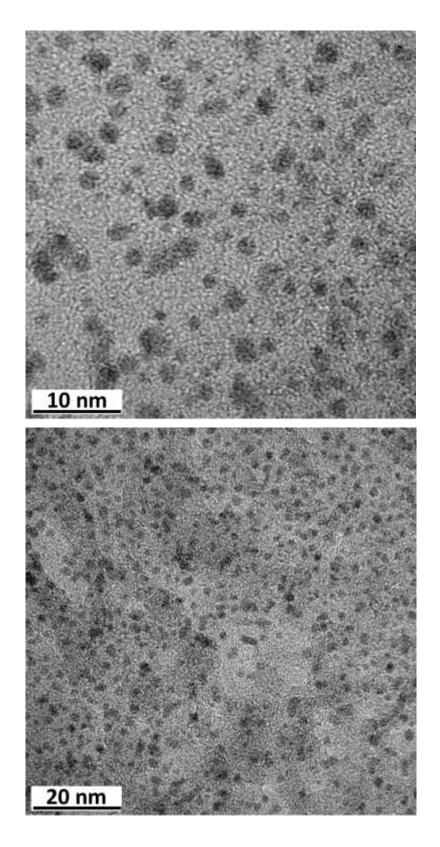


Fig S1. Low magnification TEM images of the carbon quantum dots.

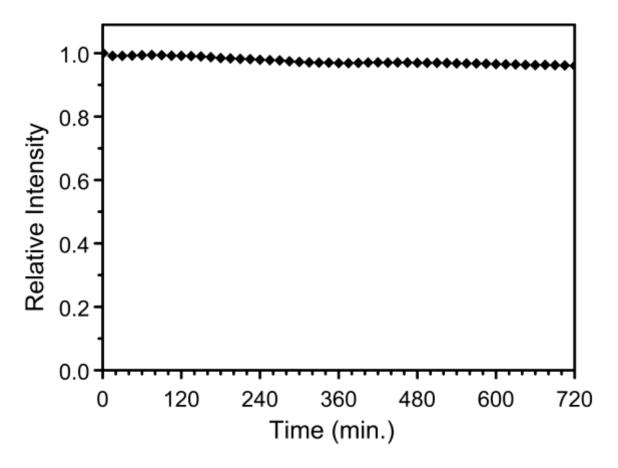


Fig S2. Long term photoluminescence stability of alkyl-capped CQDs recorded over 12 hours. Relative intensity was determined by integrating individual PL spectra, recorded at 1 min. intervals, between 300 and 450 nm. Relative intensities for individual spectra are plotted at 15 min. intervals for clarity.