Supporting Information

Thermo-Responsive microgels based in encapsulated carbon quantum dots

Bruno B. Campos[a], Dragosav Mutavdžić[b], Mira Stanković[b], Ksenija Radotić[b], Juan M. Lázaro-Martínez[c], Joaquim C.G. Esteves da Silva[a], Rafael Contreras-Cáceres[d*], M. Soledad Pino-González[d], E. Rodriguez-Castellón[e], Manuel Algarra[e*]

[a]*Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Porto, Portugal.*
[b]*Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava1, 11000 Beograd, Serbia.*
[c]*CONICET, Av. Rivadavia 1917 (1033), CABA, Argentina & Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Junín, 956 (1113) CABA, Argentina.*
[d]*Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos s/n, 29071 Málaga, Spain.*
[e]*Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos s/n, 29071 Málaga, Spain.*

Details of TG/DSC experiments

TG/DSC curves were measured in Pt crucibles, in N_2 flow (20 mL/min) and using a heating rate of 5 °C min^{-1} in the range of 25-1600 °C by a HT1600 oven connected to a MX5 microbalance (thermostatic at 22 °C). The process was controlled by STARe software v.10.0 (Mettler Toledo STARe system). All the samples were air dried in an oven at a temperature of 60 °C for one week to remove water.

DTG curves measured in air show the occurrence of various processes on the surface during thermal treatment (Fig. S1A). On the DTG curve of CQDs@PEG a low temperature peak below 100 °C represents the loss of residual moisture (0.52%). The main weight loss for CQDs@PEG takes place between 210 and 300 °C. It represents an endothermic process (see DSC curve in supplementary information, Fig. S1B) with a weight loss of 14.22 %. We linked it to the decomposition of PEG grafted to the surface of CQDs@PEG. That loss for CQDs is smaller (about 12%) in this temperature. This supports the incorporation of PEG to the surface of CQDs.[1] The weight loss between 397-630 ºC is attributed to the loss of C due to the slow combustion of carbon in the CQDs (*see* Fig S1). The results of thermal analysis indicate that CQDs@PEG material does not decompose up to 300 °C and residual water is easily removed from the surface, and useful for the aim of the work.

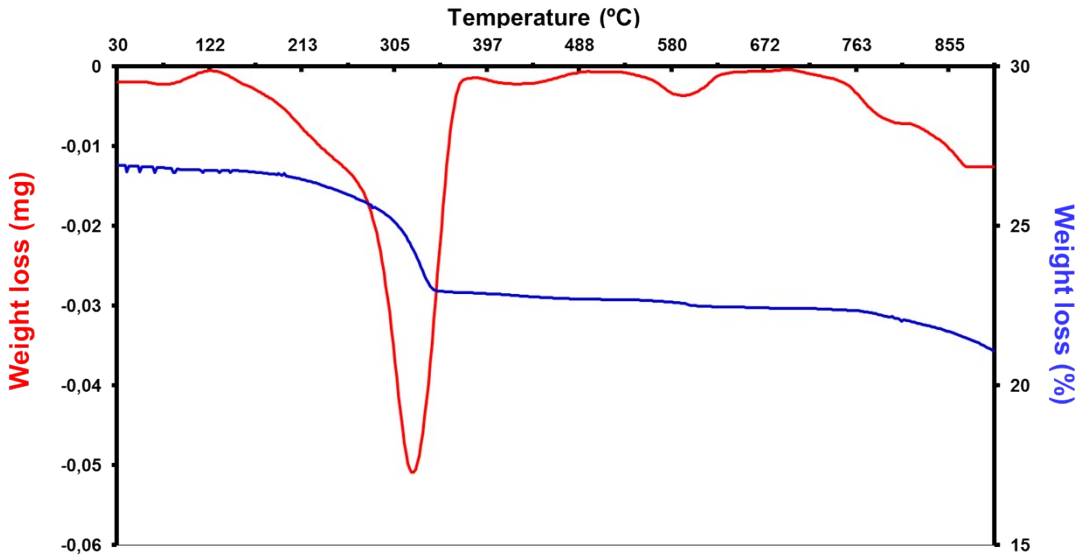

Figure S1A. TGA (red line) and DTG (blue line) curves of CQDs@PEG

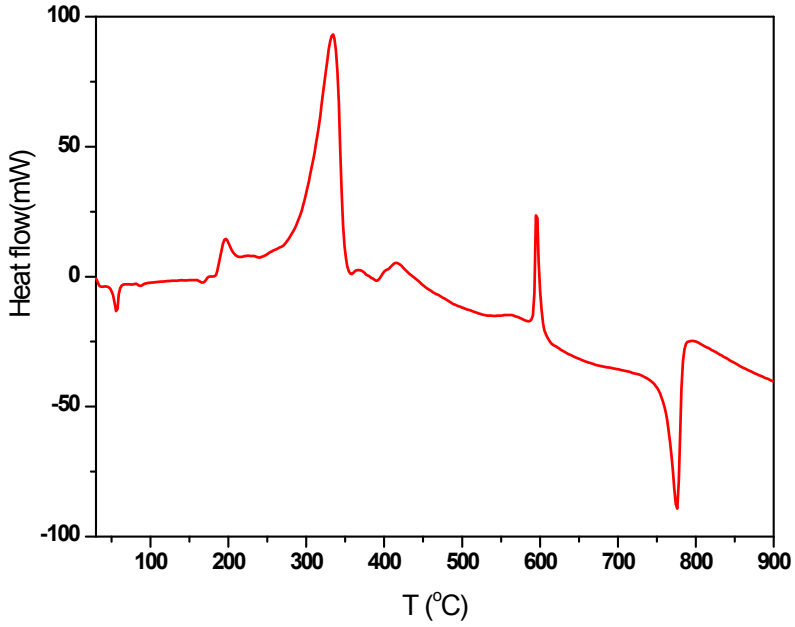

Figure S1B. DSC curve obtained for CQDs@PEG

Details of fluorescence spectra

The spectra of CQDs@PEG compound were measured in the front-face configuration of the measuring cavity. The slits on the excitation and emission beams were fixed at 4 and 2 nm respectively. The integration time was 0.1 s. The spectra were corrected for dark counts. In each measurement three scans were averaged. For each compound a series of emission spectra was collected, by excitation at different wavelengths. The fluorescence of CQDs@PEG was measured in the wavelength 310-340 nm range. For each compound a series of 11 emission spectra were collected, by excitation at different wavelengths, in the range 350-380 nm, with 3 nm step. The emission spectra were measured in the range 400-670 nm, with 1 nm increment. In the analysis we used two matrices, corresponding to the pure carbon dot (CQDs) and CQDs@PEG. Each matrix was analyzed by using Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) method, [2] which extracted the number of components, as well as their emission profiles. All analyses were performed using The UNSCRAMBLER software package (Camo ASA)..All measurements were performed at controlled temperature of 25 °C. Fluorescence lifetime analysis was done using an Edinburgh Instruments FLS920, equipped with a Xe lamp (450 W) as excitation source for steady state fluorescence measurements and monochromatic LEDs (PicoQuant PLS), controlled by a PDL 880-B system. Fluorescence decays were interpreted in terms of a multi-exponential equation: $\mathbf{I(t)} = \mathbf{A}+\Sigma\mathbf{B}_i\exp^{-t/\tau i}$, where A is the pre-exponential factor; B_i are the relative amplitude and $\langle\tau_i\rangle$ are the average component lifetimes, respectively, calculated according to the above equation

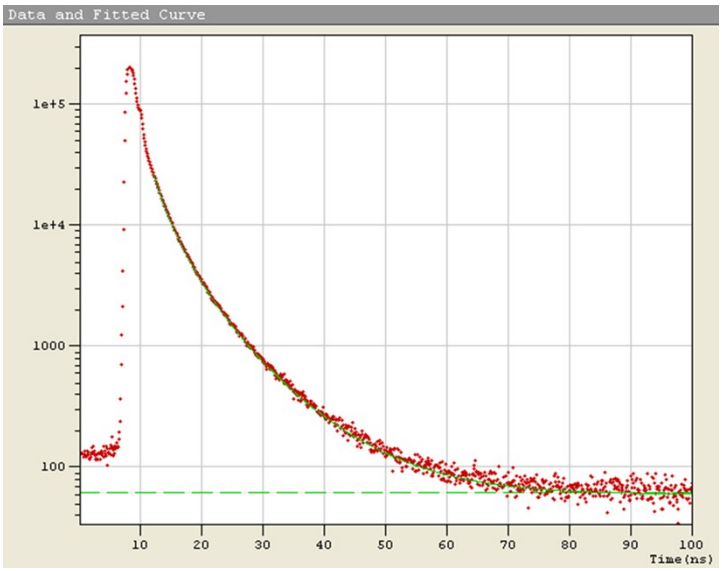

Figure S2. Fluorescence decay curve of CQDs@PEG (λ_{ex} = 365 nm; λ_{em} = 465 nm).

Nuclear Magnetic Resonance Spectroscopy (NMR)

High-resolution ^{13}C solid-state spectra for the pure PEG polymer and CQDs@PEG material were recorded using the ramp ^{1}H-^{13}C CP-MAS sequence (cross-polarization and magic angle spinning) with proton decoupling during acquisition. All the solid-state NMR experiments were performed at room temperature in a Bruker Avance II-300 spectrometer equipped with a 4-mm MAS probe. The operating frequencies for protons and carbons were 300.13 and 75.46 MHz, respectively. The recycling time was 4 s. The contact time during CP was 1500 μs for ^{13}C spectra. The SPINAL64 sequence (small phase incremental alternation with 64 steps) was used for heteronuclear decoupling during acquisition with a proton field H_{1H} satisfying $\omega_{1H}/2\pi = \gamma_H H_{1H} = 62$ kHz. [3] The spinning rate for all the samples was 10 kHz. The non-quaternary suppression (NQS) and cross-polarization with polarization inversion (CPPI) spectral editing experiments were recorded as in previous reports.[4] The 2D ^{1}H-^{13}C HETCOR experiments in the solid state[4,5] were recorded following the sequence presented by van Rossum *et* al. [5] The contact time for the CP was 200 μs to avoid relayed homonuclear spin-diffusion-type processes. The magic angle pulse length was 2.55 μs. To obtain the ^{1}H spectra, 64 points were collected with a dwell time of 35.5 μs. The acquisition time was 1.14 ms and the spinning rate was 10 kHz.

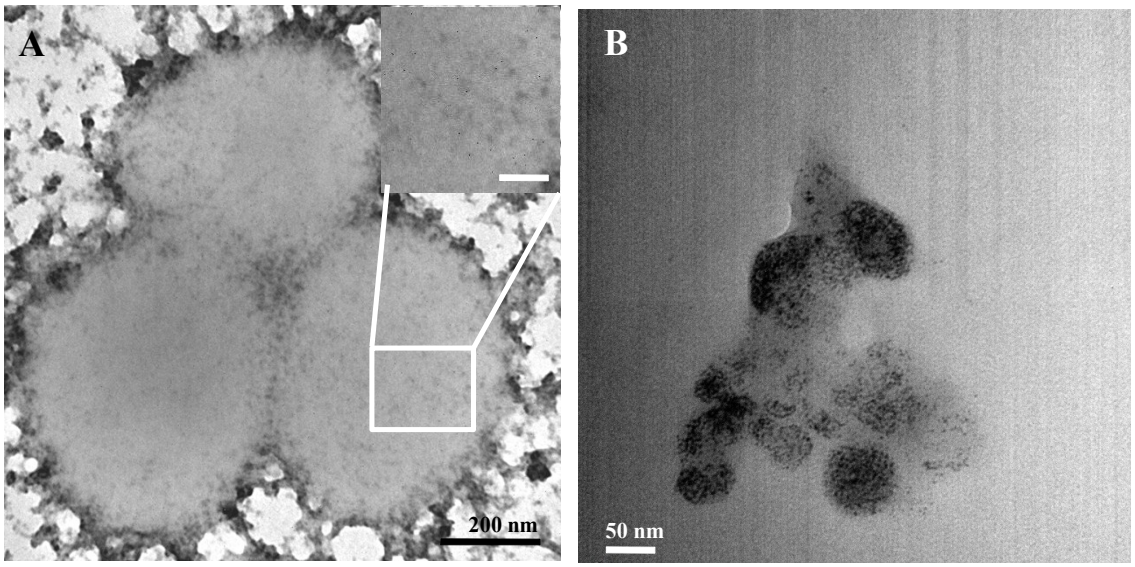

Figure S3. A) TEM images of the CQDs@pNIPAM particles at high magnification level B) TEM images of the CQDs@pNIPAM particles synthesized in absence of 3-butenoic acid The scale bar in the inset of figure S3A is 20 nm

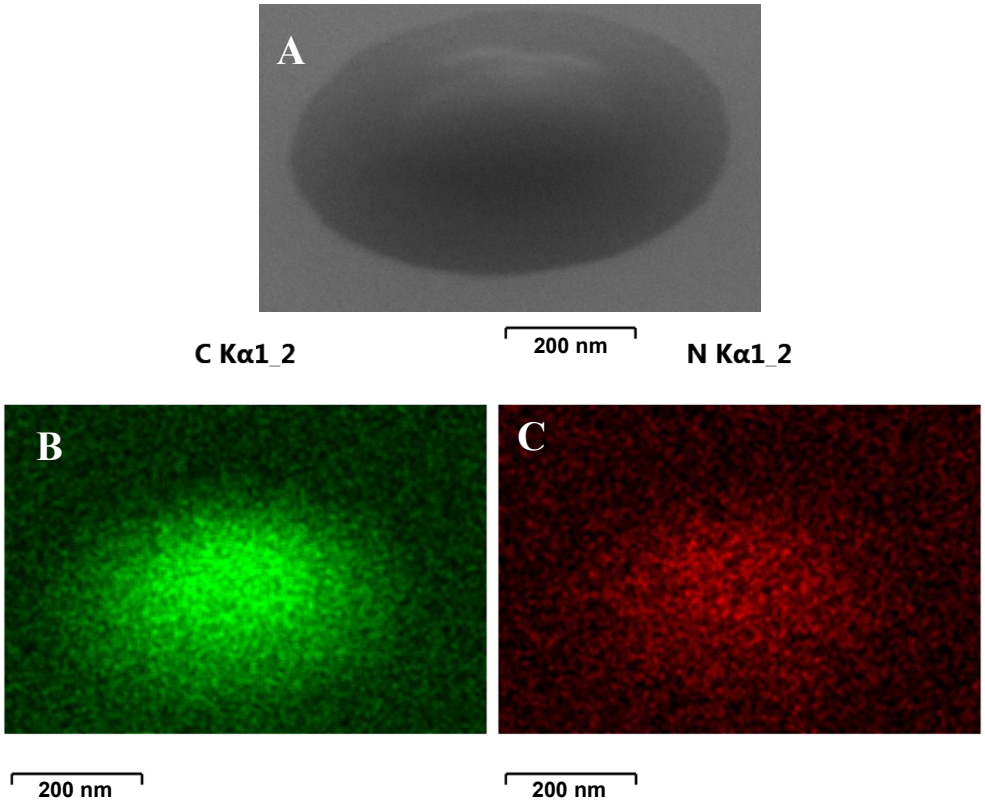

Figure S4. A) FESEM image of a CQDs@pNIPAM particles. EDX mapping (elemental distribution) for B) Carbon and C) Nitrogen.

References

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