

Supporting information

Solvatochromism Unravels the Emission Mechanism of Carbon Nanodots

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Experimental procedures

The CDs used in this study were synthesized by a one-step synthesis, already reported¹² in a previous paper, and similar to previous studies in the literature.³⁷ In short, a solution of urea (3 g), citric acid monohydrate (3 g), both obtained from Sigma-Aldrich, dispersed in Milli-Q water (10 mL) was heated up to the boiling point. Once water completely evaporated, an aggregate of CDs appearing as a dark powder was collected. The CD nanopowder was further dried in a vacuum for 30-60 min, in order to remove small organic molecules which may be occasionally formed as contaminants of the nanomaterial during bottom-up CD synthesis.^{37,43} These CDs are highly N-doped and show the typically bright and tunable photoluminescence reported for many other N-doped CDs in the literature.^{6,8,9,37}

We recently studied in depth the structure of these CDs by a combination of high-resolution transmission electron microscopy, electron diffraction, atomic force microscopy, X-ray photoelectron spectroscopy and Fourier-transform infrared absorption.¹² All the results point to describe the endproduct of the synthesis as consisting in a collection of quasispherical nanoparticles with sizes ranging from 1 to 5 nm, with an average of 3 nm. These carbon dots are found to have a well-defined, β - C_3N_4 crystalline core structure surrounded by a subnanometric shell hosting amide, carboxylic and hydroxyl groups. In particular, we demonstrated that the N/C ratio estimated by XPS closely matches the stoichiometric ratio expected for a carbon nitride structure, and all electron diffraction Debye-Sherrer rings can be assigned to the β - C_3N_4 structure. These results have been published in detail elsewhere.¹²

Here, we dispersed these CDs in 14 different solvents obtained from Sigma-Aldrich, Merck and Fluka. Specifically, we used eight protic solvents: water, methanol (MeOH), ethanol (EtOH), 2-propanol (IsOH), glycerol, ethylene glycol (EG), polyethylene glycol 400 (PEG400) and deuterated water (D_2O), and six aprotic solvents: acetone, acetonitrile (ACN), dimethyl sulfoxide (DMSO), dichloromethane (DCM), 1,4-dioxane, and

toluene. Depending on the solubility, all the solutions were prepared at concentrations of 0.02 *mg/mL* or smaller. Anyway, we found that neither the peak position or the QY depend on CD concentration (at least below 0.1 *mg/mL*). In all solvents we used for this experiment, CD form stable solutions which cannot be separated by centrifugation up to a RCF of 18000 g.

The absorption spectra were recorded with a double beam spectrophotometer (JASCO V-560) operating in the 200-900 nm range (4.30-1.50 eV). For a concentration of 0.02 *mg/mL* we measure an absolute absorption of ~ 0.25 OD at 3.05 eV in a 1 cm cuvette. During this work we used two different instruments to record photoluminescence measurements: a commercial spectrofluorometer, and a laser-excited photoluminescence setup. Time-resolved photoluminescence measurements and most of the steady-state photoluminescence (PL) spectra were recorded on an intensified charge coupled device (CCD) camera while exciting the sample by a tunable laser system consisting in an optical parametric oscillator pumped by a Q-switched Nd:YAG laser (5 ns pulses at 10 Hz repetition rate). The energy of laser pulses was about 0.1 mJ and the spectral resolution is 4 nm (guaranteed by using an appropriate monochromator and a slit). The CCD camera records the emission spectra after variable delays respect to laser pulses in a fixed time window of 0.5 ns. When using this setup, steady-state PL spectra were obtained by time-integrating the spectra captured within a temporal window extending from before photoexcitation to a few hundreds of nanoseconds after excitation. The decay kinetics of the fluorescence was measured by extracting the time dependence of the spectrally-integrated emission intensity and the decay curves were least-squares fitted to a single exponential fitting function ($I(t) \propto \exp(-t/\tau)$) or to a stretched exponential fitting function ($I(t) \propto \exp(-(t/\tau)^\beta)$). The accuracy on the lifetime value is about 0.5 ns.

We also used a JASCO FP6500 spectrofluorometer to record some of the steady-state PL spectra, all the photoluminescence excitation (PLE) spectra, and to measure the

emission quantum yield (QY). This instrument is equipped with a xenon lamp as a source and a photomultiplier as detector. The accuracy on the peak's position is about 0.01 eV. We measured the QY by comparing the steady-state emission intensity with that obtained from an aqueous solution (pH=13) of fluorescein excited at 470 nm, used as a reference of known QY=0.95. To this aim, the fluorescence from the sample and the reference were measured in exactly the same conditions and geometry. Then, the quantum yield values were calculated according the following equation (the subscripts *R* indicate the reference quantities)

$$QY = QY_R \frac{A}{A_R} \frac{1 - 10^{-OD_R}}{1 - 10^{-OD}} \frac{n^2}{n_R^2} \quad (1)$$

where *A* is the area of the photoluminescence band, *OD* is the value of absorbance, and *n* is the refractive index. The accuracy on the QY value is about 0.01. All the optical measurements were carried out at room temperature in 1 cm quartz cuvettes. To perform single molecule spectroscopy measurements, quartz coverslips (Structure Probe Inc.) were cleaned by sonication in an alkaline cleaning solution (Hellma Analytics, Hellmanex III), followed by sonication in and rinsing with demineralized water, drying by nitrogen flow and an ozone dry- cleaning procedure (UVP, PR-100) for 30 min. Samples with a low average particle density ($< 1/\mu m^2$) were prepared by drop-casting a dilute solution ($\sim 0.5 \mu g/mL$) of CDs in water on a coverslip. Single molecule spectroscopy measurements were carried out using an inverted microscope (Zeiss, AxioObserver Z1) coupled to a spectrometer (Princeton Instruments, Acton SP2300) and a CCD (Princeton instruments, Pylon 400B) in a wide-field scheme. Continuous wave excitation was provided by the 488 nm ($\sim 90 W/cm^2$) line of an Ar+ laser (Spectra-Physics, Stabillite 2017) and the emitted light was collected using a 100x air objective (Zeiss, Epiplan-Neofluar NA 0.75). The emission from CDs, as observed under the microscope, remained stable under laser exposure over a typical

time of a few minutes. Each single-dot spectrum shown in Figure 2d required an acquisition time of ~ 8 min.

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- (43) Zhu, S.; Zhao, X.; Song, Y.; Lu, S.; Yang, Y. Beyond Bottom-up Carbon Nanodots: Citric-Acid Derived Organic Molecules. *Nano Today* **2016**, *11*, 128–132

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Table S1: Protic (upper part of the table) and aprotic (lower part) solvents used in this study. Dielectric constant, E_T^N polarity parameter, and Kamlet-Taft polarity parameters of the solvents (second to sixth column). Fluorescence quantum yield, decay lifetime (b is the stretching parameter, if smaller than one), radiative and non-radiative decay rate measured for CDs dispersed in each solvent and excited at 2.82 eV (seventh to last column). QY measurements (and, in turn, K_R and K_{NR}) were not possible in some of the most apolar solvents where a low solubility hindered a reliable estimate of the absorption coefficient, needed to calculate the QY. In the table, these cases are indicated as ND - not determined.

Solvent	ϵ	E_T^N	α	β	π^*	QY	τ (ns)	$1/K_R$ (ns)	$1/K_{NR}$ (ns)
H ₂ O	80	1.00	1.17	0.47	1.09	0.09	4.8 (b=0.85)	53	5
D ₂ O	79	1.00	1.09	0.18	1.09	0.18	10.7	61	13
Glycerol	43	0.81	1.21	0.51	0.62	0.25	8.0	31	10
Ethylene Glycol	37	0.79	0.9	0.52	0.92	0.27	9.0	33	12
Methanol	33	0.76	0.98	0.66	0.6	0.22	9.7	45	12
Ethanol	24	0.65	0.86	0.75	0.54	0.28	10.5	38	14
2-propanol	18	0.55	0.76	0.84	0.48	0.33	11.5	34	17
PEG400	14	0.57	0.31	0.75	0.75	0.41	13.5	33	23
DMSO	47	0.76	0	0.76	1	0.44	12.5	29	22
Acetonitrile	38	0.47	0.19	0.4	0.75	0.24	5.7 (b=0.85)	24	8
Acetone	21	0.35	0.08	0.43	0.71	0.45	9.5	21	17
Dichloromethane	9.1	0.32	0.13	0.1	0.82	ND	5.2 (b=0.75)	ND	ND
Toluene	2.4	0.10	0	0.11	0.54	ND	5.7 (b=0.54)	ND	ND
1,4-Dioxane	2.3	0.16	0	0.37	0.55	0.13	7.6	58	9

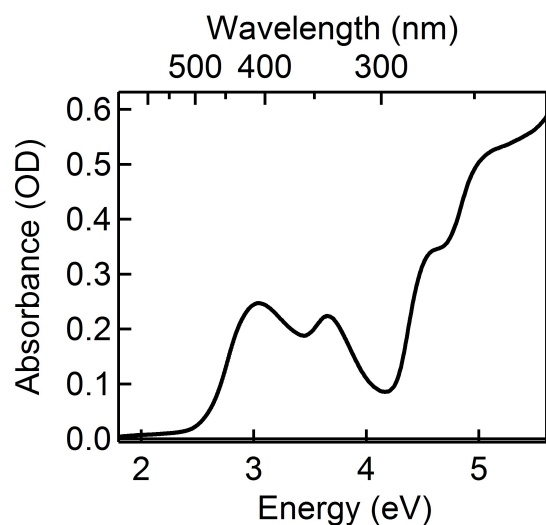


Figure S1: Absorption spectrum of CDs dissolved in H₂O. The absorption bands below 4.00 eV are associated to midgap states whereas the steep increase of the absorption above 4.00 eV is due to band-to-band transitions of the β - C₃N₄ crystalline core.^{12,33}

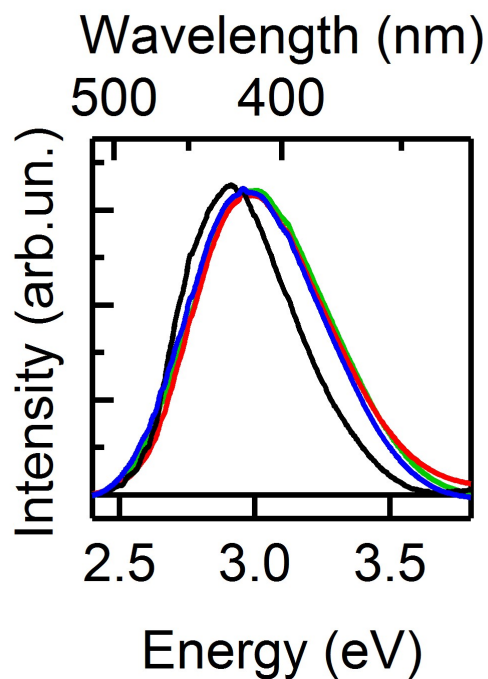


Figure S2: Normalized excitation spectra of the emission at 2.30 eV in dioxane (black), 2-propanol (red), methanol (green) and ethylene glycol (blue).

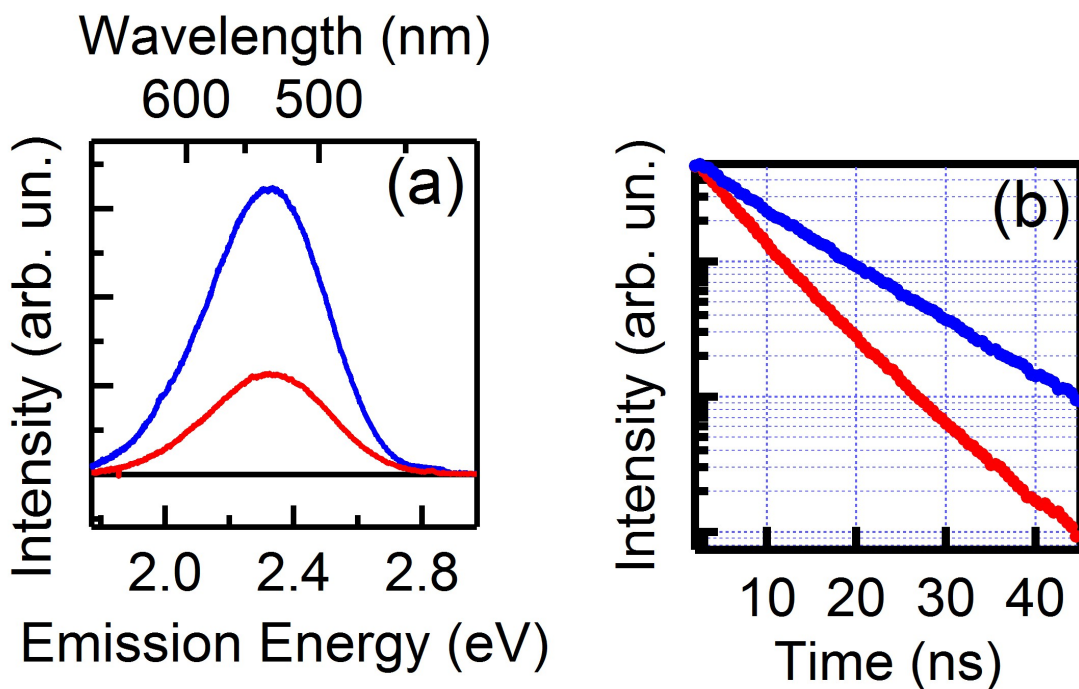


Figure S3: Emission spectra of CDs (panel a) and their decay kinetics (panel b) in water ($\tau = 4.8$ ns) (red line) and in deuterated water ($\tau = 10.7$ ns) (blue line). Measurements were obtained upon excitation at 2.82 eV photon energy (440 nm wavelength). Having the two samples been prepared in the same concentration, the intensities of the two spectra in panel a reflect the different emission QYs. From the measured values of lifetime and QY, we obtain radiative and non-radiative rates reported in Table S1.

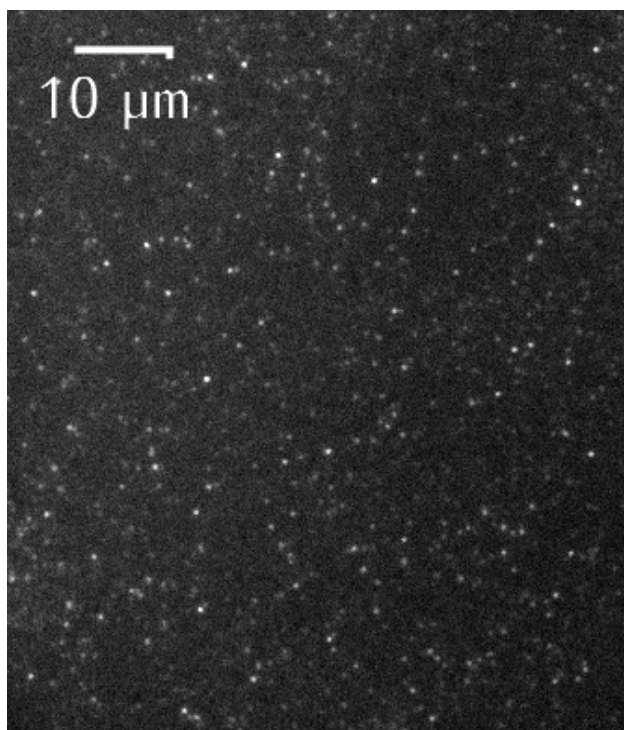


Figure S4: Micro-photograph of a sample of CDs deposited on a quartz substrate and excited at 2.54 eV. Spectra recorded from isolated dots are reported in Figure 2d.

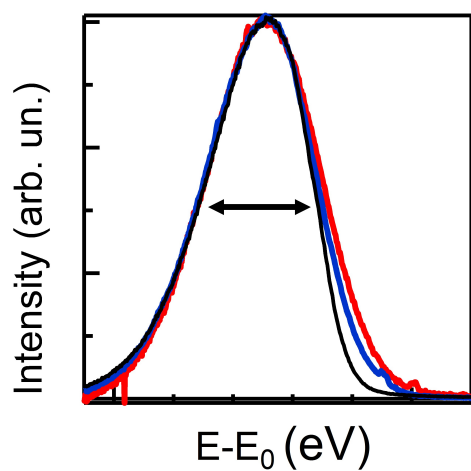


Figure S5: Normalized emission spectra of CDs in dioxane (black), 2-propanol (blue) and water (red). The spectra have been horizontally shifted in order to compare their widths. The arrow is a guide to the eye to emphasize the almost complete absence of solvatochromic broadenings.

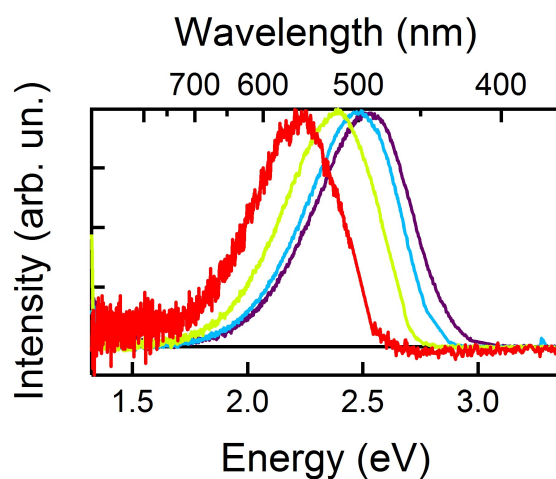


Figure S6: Normalized photoluminescence spectra of CDs in 1,4-dioxane at excitation energies of 3.02 eV (purple), 2.82 eV (pale blue), 2.64 eV (yellow), 2.48 eV (red), highlighting the fluorescence tunability of CDs in 1,4-dioxane.