Electronic Supplementary Information (ESI):

Fluorescent nitrogen-rich carbon nanodots with an unexpected β-C_3N_4 nanocrystalline structure.

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Supplementary Figures

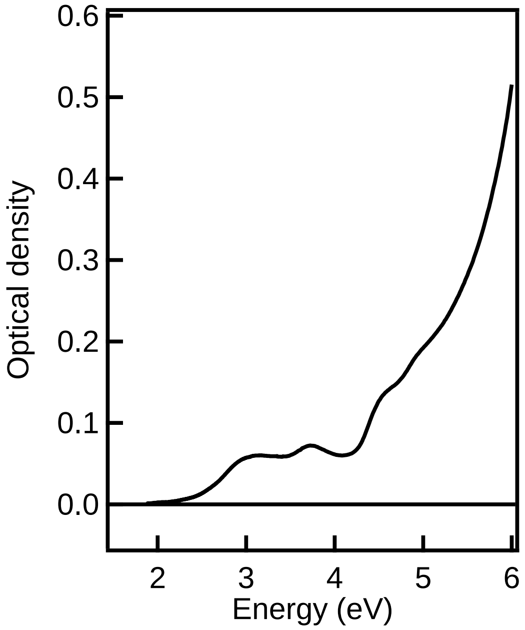

Figure S1: Optical absorption spectrum of a sample of N-CDs dispersed in water. Data are the same as in Fig. 1 of the manuscript, plotted in a different scale to better show the steep increase of the absorption coefficient for E>4 eV.

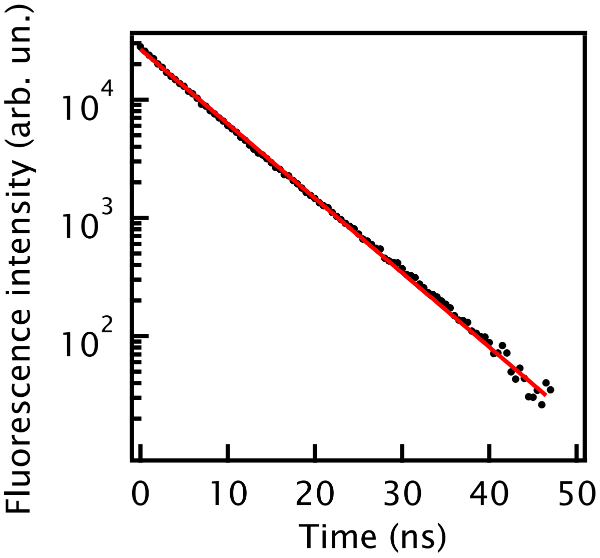

Figure S2: Fluorescence intensity detected after laser excitation at 2.6 eV as a function of the time delay from the excitation laser pulse (black points). Least-square fitting of the data with an exponential decay function (red line). The lifetime extracted from these data is 6.9±0.5 ns.

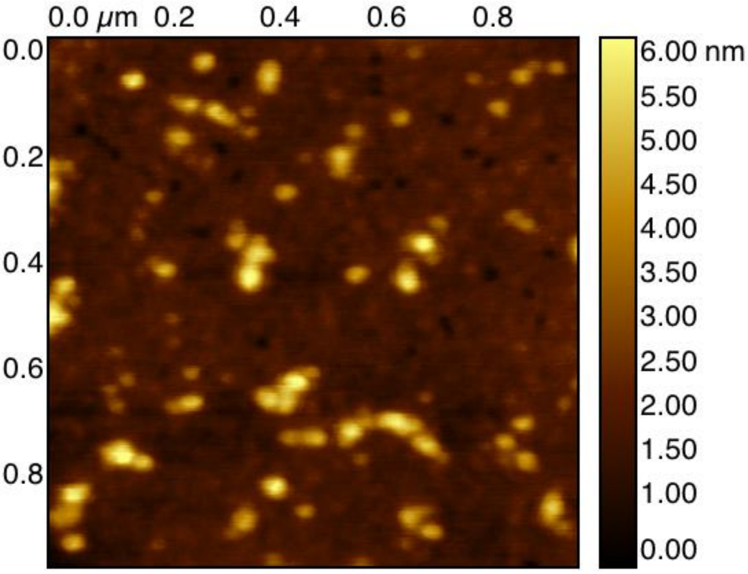

Figure S3. AFM image of N-CDs deposited on a mica substrate. The statistical distribution of topographic heights obtained by a set of such images is reported in Fig. 2a of the main paper.

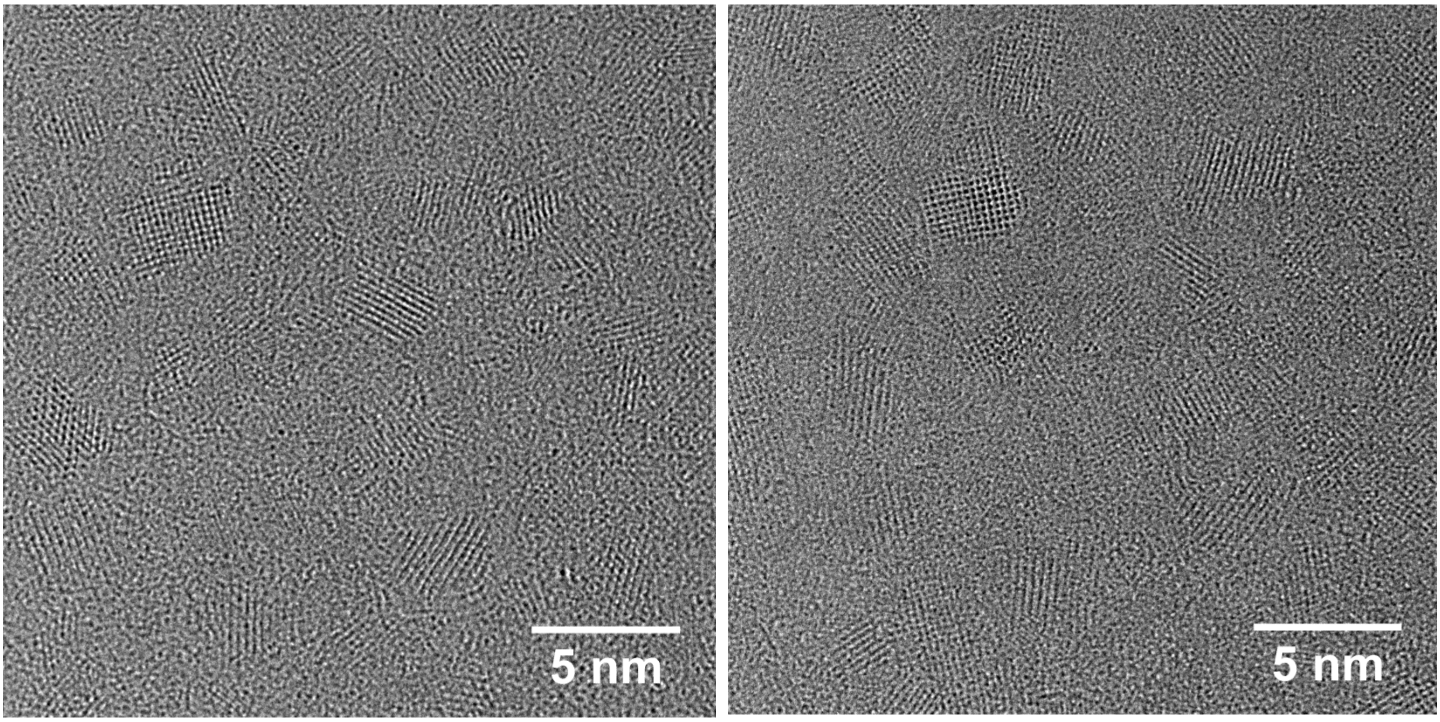

Figure S4: Two HRTEM images of the sample, showing many small dots with crystalline structure and typical diameters of ∼3 nm.

(h k l)	k (nm^{-1})	d (Å)
(1 1 0)	3.138	3.19
(2 0 0)	3.573	2.80
(1 0 1)	4.619	2.16
(2 1 0)	4.889	2.05
(1 1 1)	5.125	1.95
(3 0 0)	5.370	1.86
(2 2 0)	6.270	1.59

Table S1: Miller indices (hkl), diffraction peak positions k and the corresponding lattice-plane distances d_{hkl} of all reflections used to fit the radial scan (left panel of Figure 3, main paper) calculated from the SAED pattern shown on the right panel of Figure 3 of the main paper. All the reported diffraction peaks can be attributed to β-C_3N_4 (space group P6_3/m, space group number 176, characterized by a=6.38 Å and c=2.395 Å). From the peak positions lattice parameters of a=6.37±0.06 nm and c=2.40±0.02 nm were calculated.

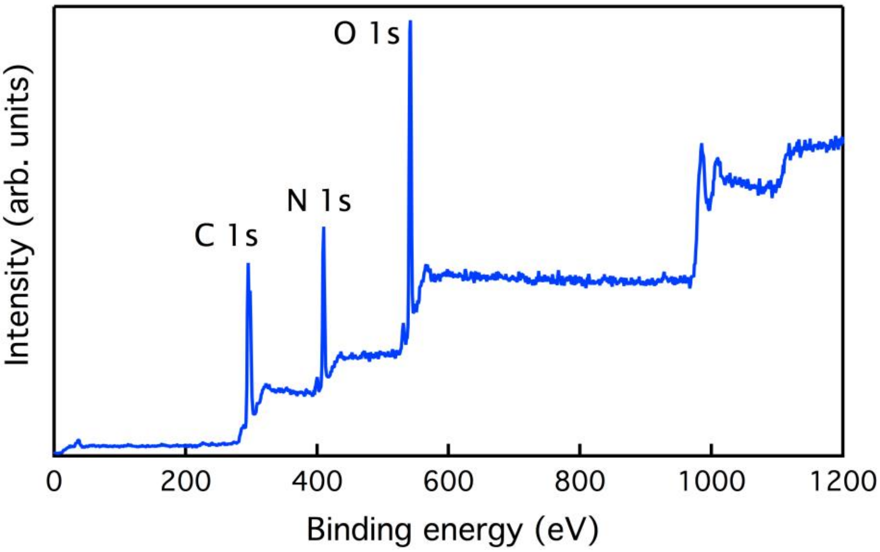

Figure S5: XPS survey spectrum of N-CDs. Here the relative intensity of the peaks, even corrected by the atomic sensitivity factors, do not reflect the stoichiometric ratio between the carbon and the nitrogen of the N-CD, due to the presence of adventitious carbon. However, as discussed in the paper, a C/N atomic ratio very close to the C_3N_4 composition is obtained when considering only the components arising from the β-C_3N_4 nanocrystalline core of the dots, which can be isolated by proper fitting of the high resolution C 1s and N 1s regions.

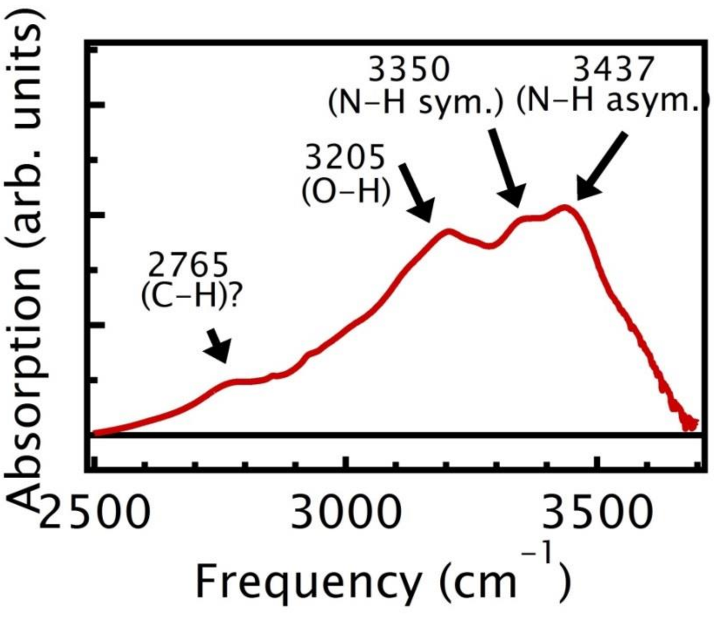

Figure S6: Infrared absorption spectrum of N-CDs in the spectral region beyond 2500 cm^{-1}. The arrows highlight our attributions of the signals, as discussed in more detail in the main paper.

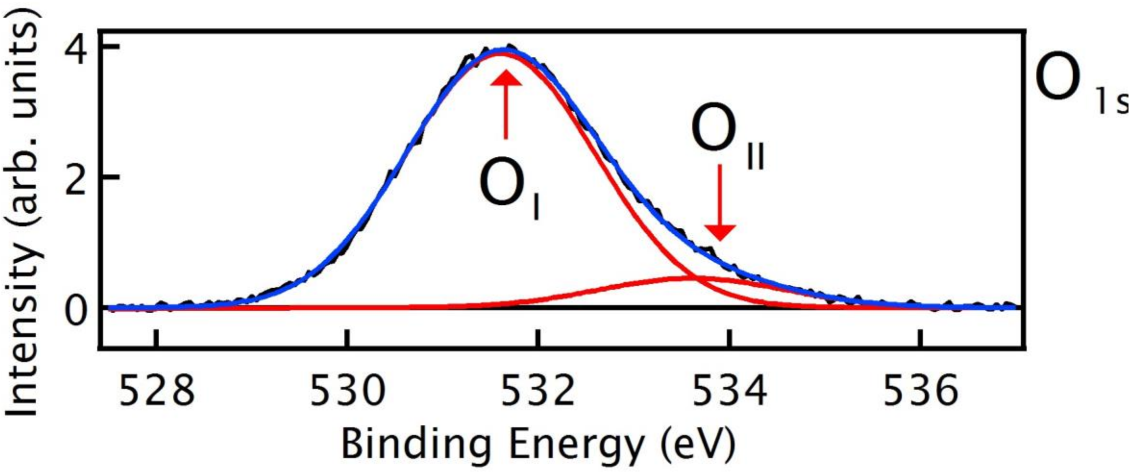

Figure S7: XPS O_{1s} signal detected in N-CDs (black lines), its decomposition in different contributions, as described in the text (red lines), and the resulting fits of the experimental data (blue lines).

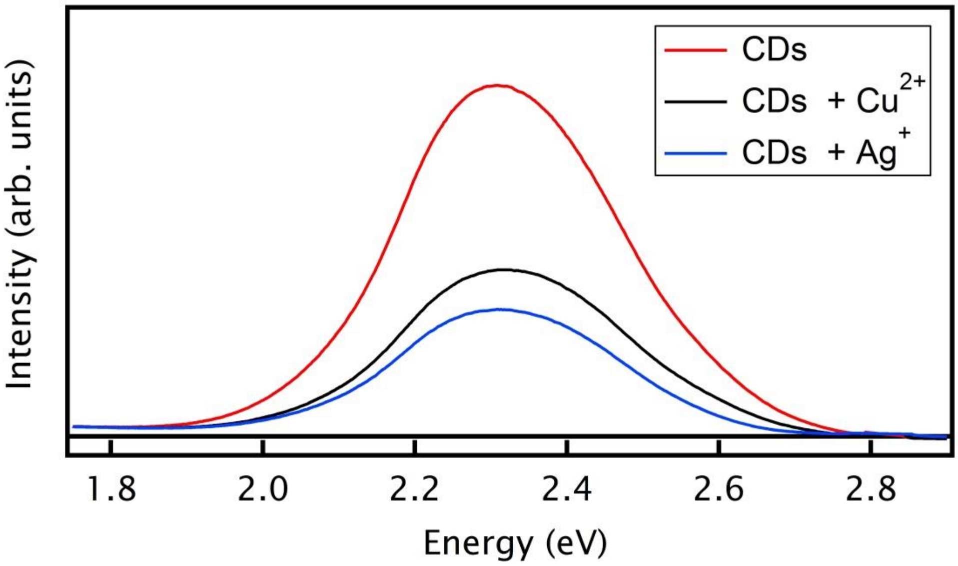

Figure S8: Quenching of the N-CD fluorescence intensity induced by the presence of Cu^{2+} or Ag^{+} in solution. The measurements were carried out in aqueous solutions of CDs (dispersed in a 0.02 g/L concentration) excited at 2.8 eV photon energy, with and without the addition of Cu^{2+} or Ag^{+} ions in a 5 mM concentration.

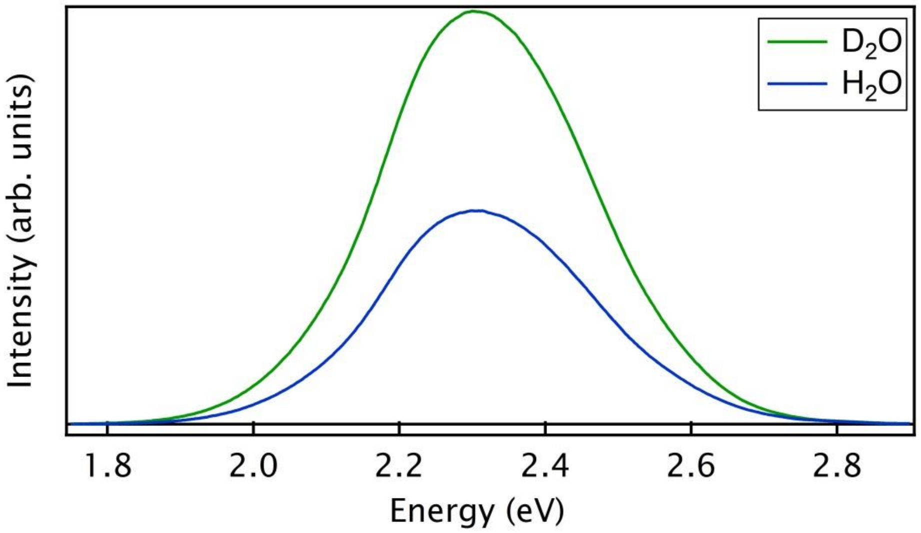

Figure S9: Comparison between the emission spectra registered in a sample of N-CDs in H_2O and D_2O, both excited at 2.8 eV photon energy. The two solutions were prepared in the same concentration (∼0.02 g/L), and the emission spectra carefully scaled by the optical density at the excitation wavelength (as measured by an absorption spectrum). Thus, the areas of the emission bands directly reflect the emission quantum yields, highlighting an increase of a factor ∼2 from H_2O to D_2O.

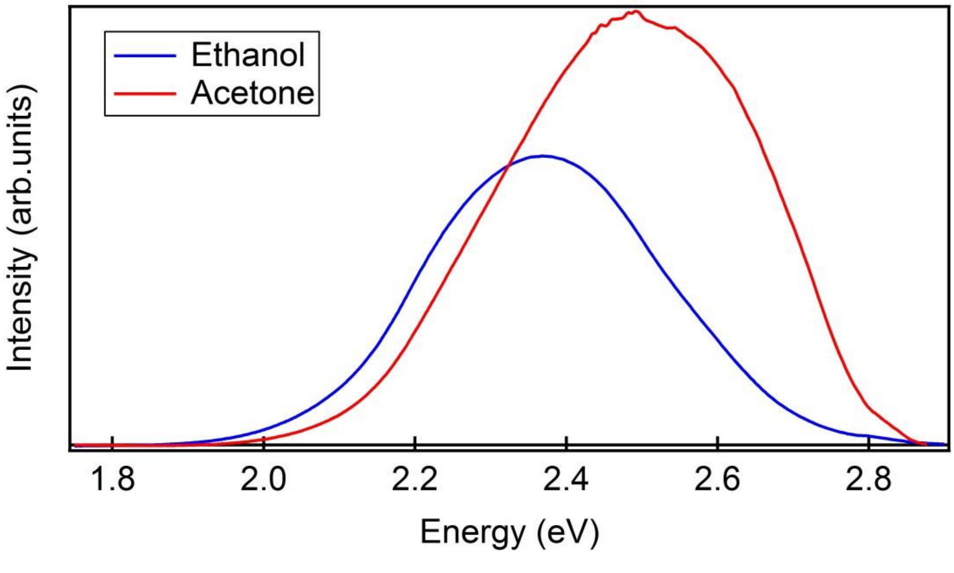

Figure S10: Comparison between the emission spectra registered in a sample of N-CDs in ethanol and acetone, both excited at 2.8 eV photon energy. The two solutions were prepared in the same concentration (0.02 g/L), and the emission spectra carefully scaled by the optical density at the excitation wavelength (as measured by an absorption spectrum). Thus, the areas of the emission bands directly reflect the emission quantum yields, highlighting an increase of a factor ∼1.6 from Ethanol (protic polar solvent) to acetone (aprotic polar solvent). The absolute intensity in Ethanol roughly equals that in D_2O reported in Fig. S9.