Shedding light on the effective fluorophore structure of high quantum yield carbon nanodots

The supporting information

CD synthesis.

In a typical synthesis, 18.9 g citric acid and 16.2 g urea (both obtained from Carl Roth, Germany) was dissolved in 150 mL of deionized water. The solution was then transferred to a 250 mL poly tetrafluoroethylene (Teflon)-lined autoclave, heated to 180~210°C for 3~17 h under stirring and subsequently cooled to room temperature in air. The product was filtered through a membrane with a pore size of 0.22 μm to remove bulk impurities. A dialysis membrane with a molecular weight cut-off of 1000 g/mol, obtained from Spectrum Laboratories Inc., USA, was used to purify and separate the CD suspensions from residuals of the starting materials, their low molecular condensation products and not bond fluorophore molecules. The obtained aqueous CD suspension was translucent and brown in color. The production yield was about 60%.

Characterization and devices.

In-situ UV-Vis absorption spectra were recorded with a transmission dip probe in reflection mode with 6 illumination fibers, 1 detection fiber, an optical path length of 10 mm and a deuterium halogen light source. The spectrophotometer was coupled with an AvaSpec-Fast detector with a 10 ms integration time and an averaging of 100 measurements. In-situ fluorescence spectra were recorded by a fluorescence probe with 12,200 μm diameter fibers, a LED light source with a 365 nm (FWHM 9 nm) emission wavelength and 1 mW output power, and an AvaSpec-Fast detector with 1 ms integration time and an averaging of 500 measurements. The excitation light source was obtained from Ocean Optics (USA) and other light sources, probes and spectrometers were obtained from Avantes (Netherlands).

Ex-situ UV-Vis absorption spectra from 200 to 800 nm were recorded with a Cary 100 (Varian) spectrometer. Ex-situ fluorescence spectra were recorded with a Jobin–Yvon photoluminescence

spectrometer (Horiba, Japan). All absorbance and fluorescence spectra were measured at room temperature using quartz cuvettes with a path length of 10 mm. The absolute fluorescence quantum yield (QY) of the CDs was determined by the slope method described in Ref [Jones, G., Solvent effects on emission yield and lifetime for coumarin laser dyes. Requirements for a rotatory decay mechanism. The Journal of Physical Chemistry 1985, 89, 294-300] using quinine sulfate as standard (Sigma-Aldrich, America, QY: 54.6%), Figure S2. UV illumination from an UV-8 SL ultraviolet lamp (Konrad Benda, Germany) with a wavelength of 365 nm, a power output of 8 W and light intensity of 950 $\mu W/cm^2$ at the sample's place was applied to induce CD photobleaching.

Solid-phase Fourier transform infrared (FTIR) spectra of CDs samples, compressed to KBr pellets, were recorded with a "Digilab FTS3100" FTIR spectrometer. Liquid-phase FTIR spectra were recorded with an FTIR dip probe manufactured by Art Photonics.

Transient absorption experiments were carried out with an amplified Ti: Sapphire CPA-2110 fs laser system (ClarkMXR: output 775 nm, 1 kHz, 150 fs pulse width) using transient absorption pump/probe detection systems (Helios and Eos, Ultrafast Systems). All samples were measured in a fused quartz glass cuvette with a thickness of 2 mm. Data was acquired with the HELIOS Visible / NIR software (Newport / Ultrafast Systems).

Time-correlated single photon counting (TCSPC) spectra were taken with a Fluorolog system (HORIBA Jobin Yvon). Signal acquisition was gathered by a Hamamatsu MCP photomultiplier (type R3809U-50). The time profiles were recorded at the emission maxima. All samples were measured in a quartz glass cuvette with a width of 10 mm.

DFT simulation

For the DFT simulation the software BioChem3D (BioChem office) was used. GAMESS was used as simulation interface and works similar to a Gaussian algorithm.

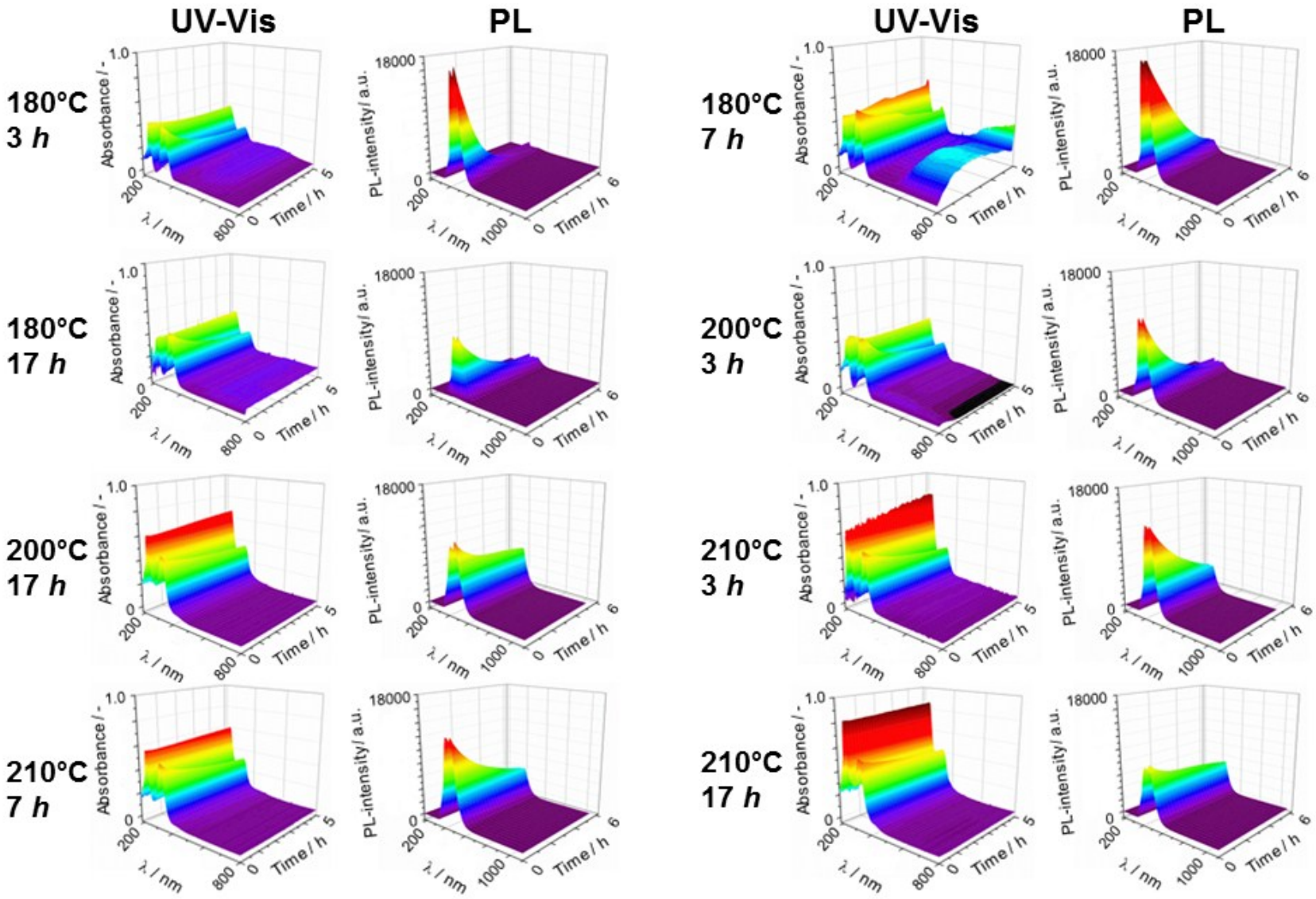

Figure S1. UV-Vis absorption and fluorescence spectra of aqueous CD suspensions synthesized under the conditions mentioned in the figure as a function of UV light exposure time.

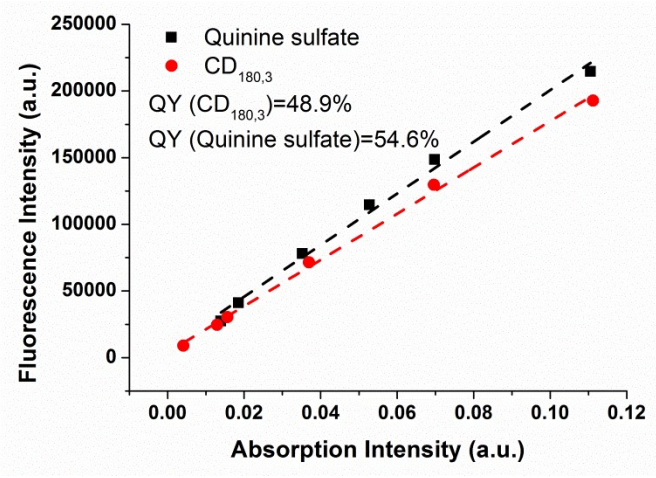

Figure S2. Integrated fluorescence intensity versus absorbance for quinine sulfate (standard) and a CD-sample synthesized at 180°C for 3h. The quantum yield of this CD-sample is determined to be 48.9%.

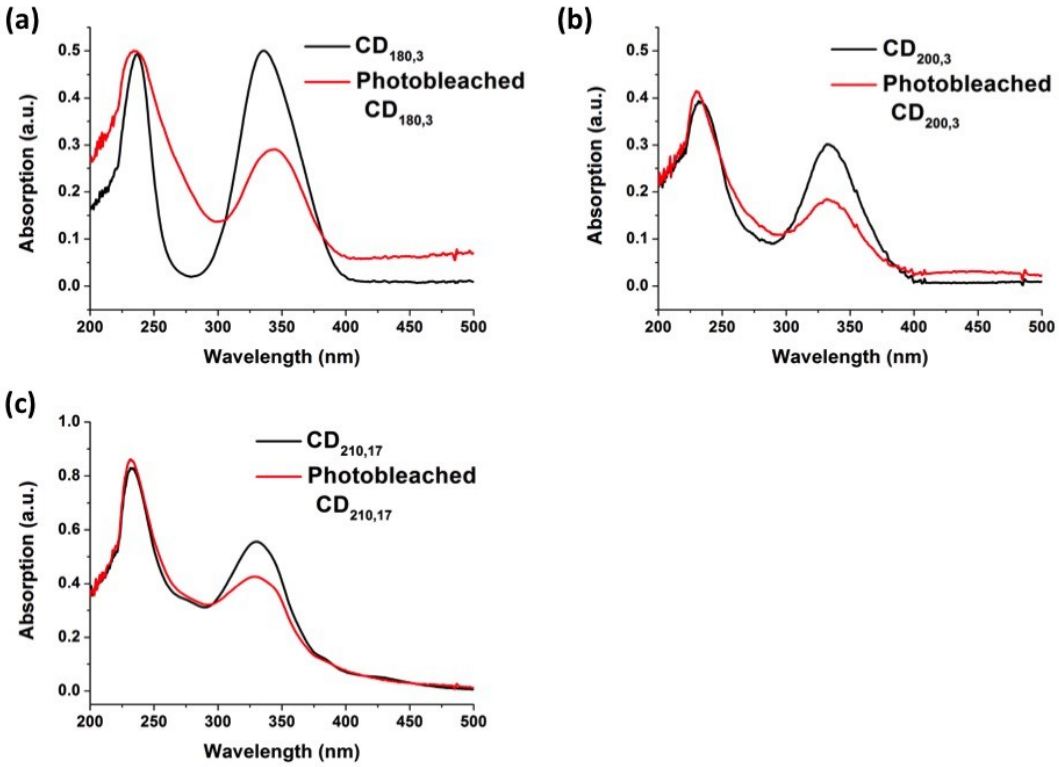

Figure S3. UV-Vis absorption spectra of CDs synthesized at 180°C for 3h (a), 200°C for 3 h (b) and 210°C for 17 h (c) before and after UV exposure. The absorption around 270 nm, which is more pronounced in the CDs samples synthesized at lower temperature or shorter reaction time, and, which is formed due to photobleaching, implies the formation of new sp^2 domains.

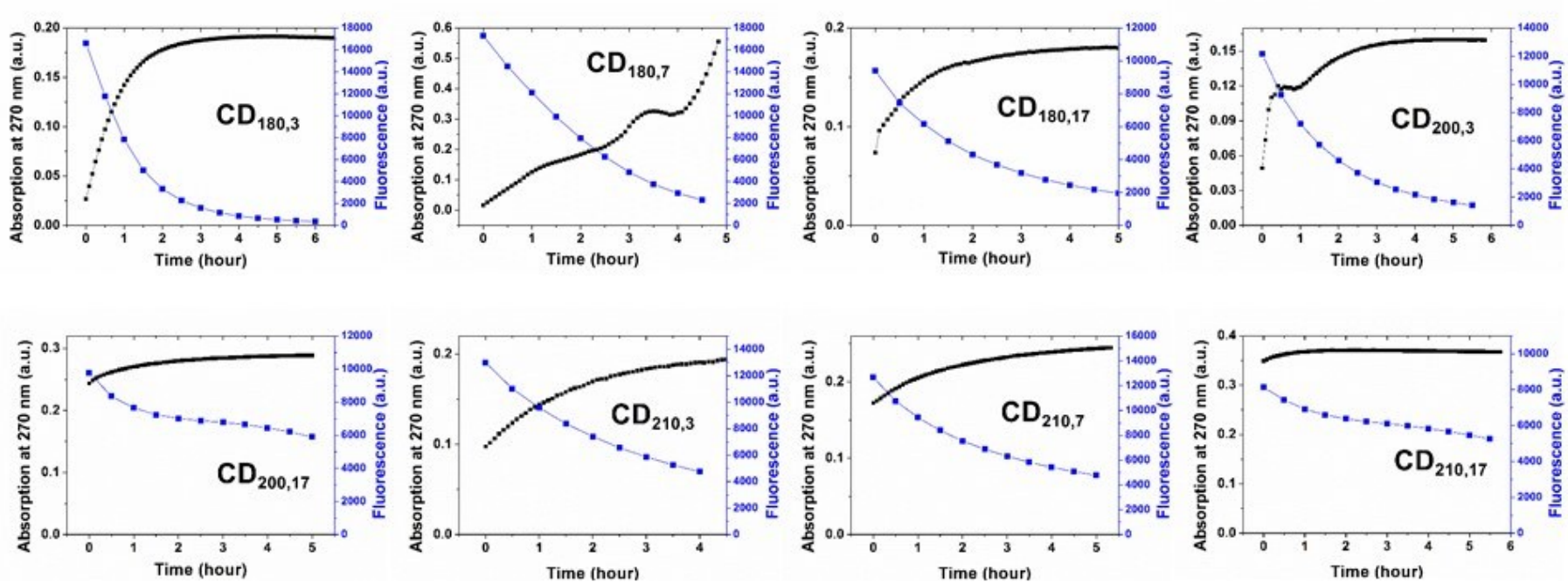

Figure S4. Inverse correlations between temporal evolution under UV light exposure of the absorption at 270 nm and the fluorescence intensity of CD suspensions synthesized under different conditions.

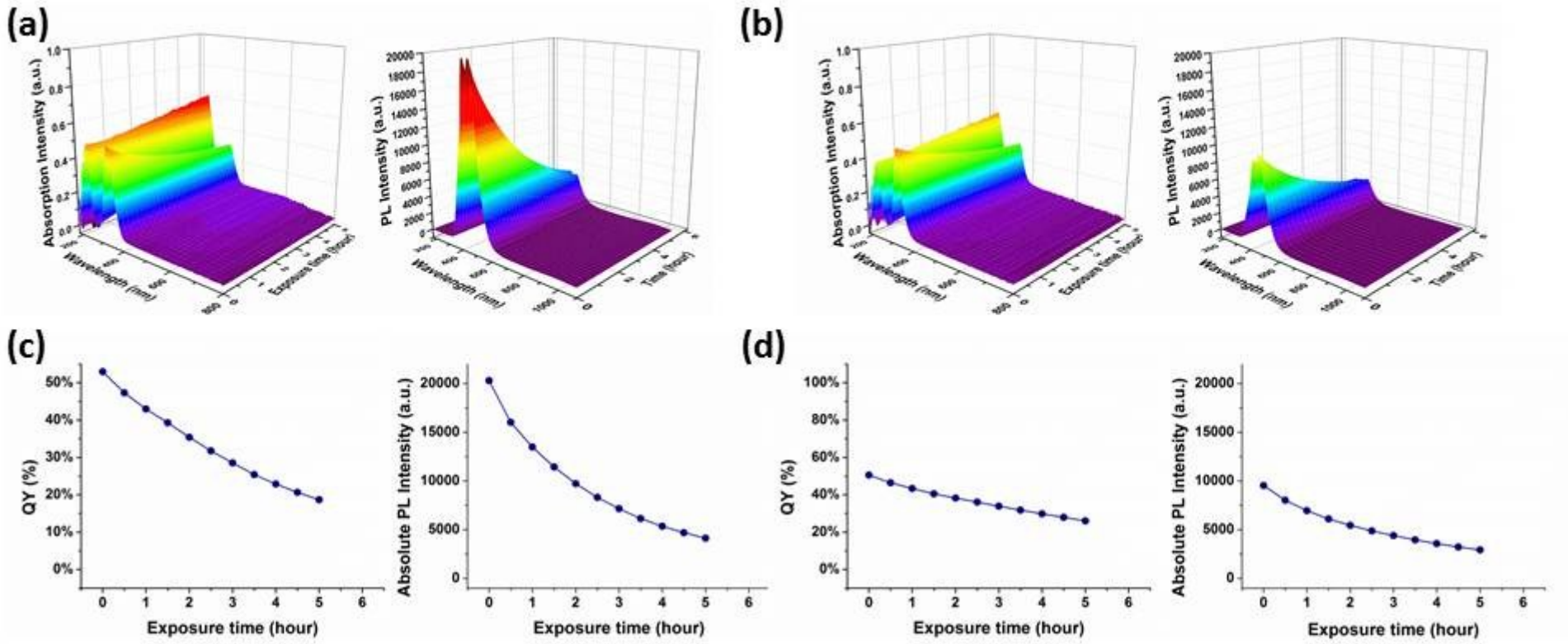

Figure S5. UV-Vis absorption and fluorescence spectra of a CD suspension separated by dialysis as a function of UV exposure time (a) dissolved fluorophores and (b) purified CD suspension synthesized at 200°C for 3 h. The declining trends of relative quantum yield and absolute PL of (c) free fluorophores and (d) CDs.

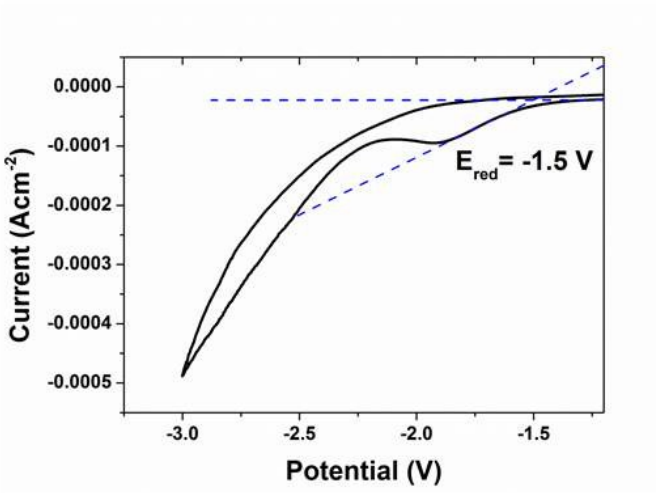

Figure S6. Cyclic voltammogram of CDs measured at room temperature in acetonitrile-H_2O (20 : 1 v/v) with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte *versus* Ag/AgCl, with 0.05 V s^{-1} scan rate.

LUMO and HOMO energy level of carbon dots are possible to be estimated according to the following empirical formulas: (Biosensors & Bioelectronics, 2016, 79, 822-828. Analytical chemistry, 2014, 86, 9846-9852. UPB Sci Bull Ser B, 2013, 75, 111-118.)

E_{LUMO}=-e(E_{red}+4.4)

E_{HOMO}=-e(E_{ox}+4.4)

Where E_{red} and E_{ox} are the onset of reduction and oxidation potential for CDs, respectively. The E_{red} was determined to be −1.5 V. The corresponding E_{LUMO} was calculated to be −2.9 eV. However, the HOMO energy could not be obtained because the oxidation of CDs is irreversible. To determine the HOMO, we approximate the optical band gap as the HOMO-LUMO gap. The optical band gap E_g was estimated from absorption edge according to Tauc plot, and E_g was determined to be 3.3 eV. So the E_{HOMO} was calculated to be -6.2 eV.

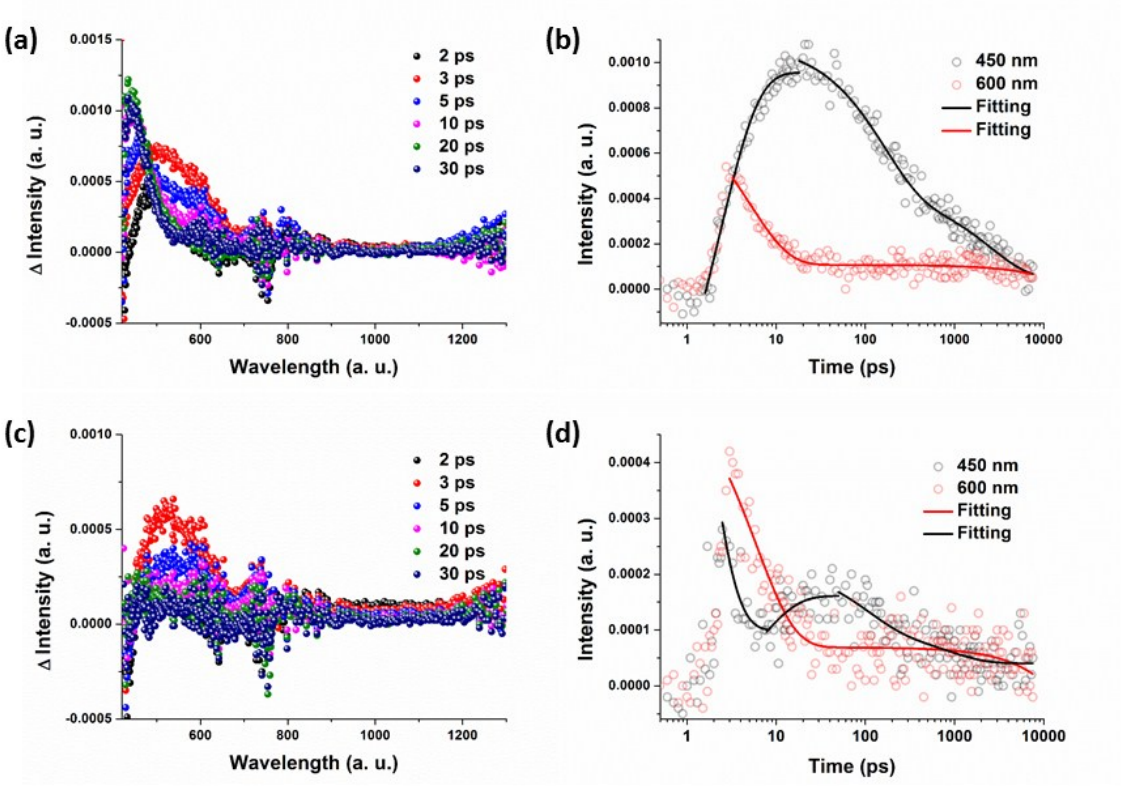

Figure S7. (a) Differential absorption spectra obtained upon femtosecond pump probe experiments (320 nm and 500 nJ) of (a) freshly synthesized CDs with time delays between 2 and 30 ps at room temperature. (b) Time absorption profiles at 450 and 600 nm. (c) Differential absorption spectra obtained upon femtosecond pump probe experiments (320 nm and 500 nJ) of photobleached CDs with time delays between 2 and 30 ps at room temperature. (d) Time absorption profiles at 450 and 600 nm.

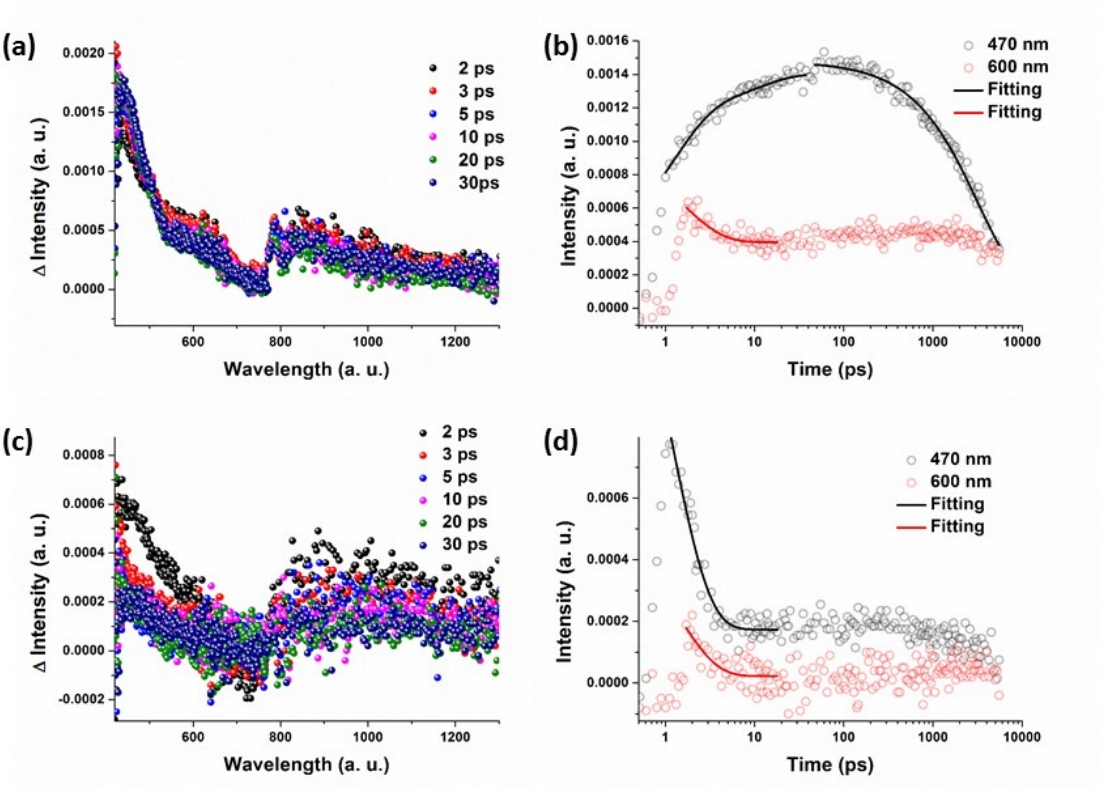

Figure S8. (a) Differential absorption spectra obtained upon femtosecond pump probe experiments (387 nm and 500 nJ) of (a) freshly synthesized CDs with time delays between 2 and 30 ps at room temperature. (b) Time absorption profiles at 470 and 600 nm. (c) Differential absorption spectra obtained upon femtosecond pump probe experiments (387 nm and 500 nJ) of photobleached CDs with time delays between 2 and 30 ps at room temperature. (d) Time absorption profiles at 470 and 600 nm.

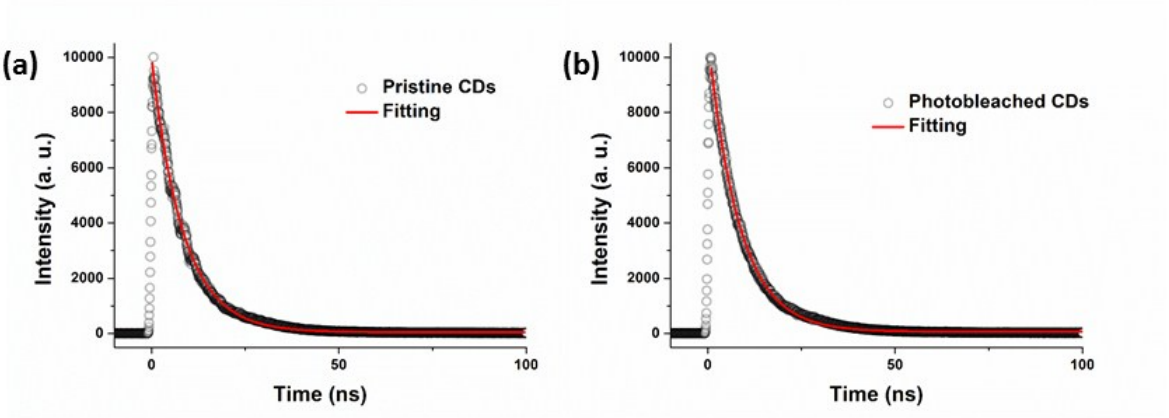

Figure S9. Time fluorescence profiles at 450 nm of (a) freshly synthesized CDs and (b) photobleached CDs upon 361 nm photoexcitation with lifetimes of 8.3 and 8.4 ns, respectively.

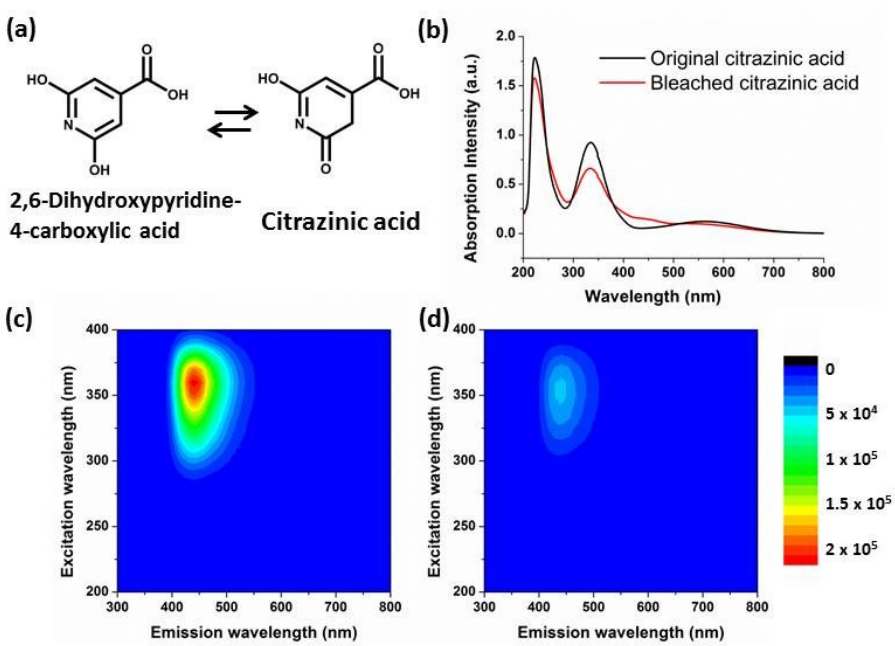

Figure S10. (a) Tautomerization scheme between 2,6-Dihydroxypyridine-4-carboxylic acid and citrazinic acid (Pesticide Science, 1972, 3, 113-120.). (b) UV-Vis absorption spectra of citrazinic acid in water before and after UV exposure. (c) 3D fluorescence spectra of citrazinic acid in water before UV exposure. (d) 3D fluorescence spectra of citrazinic acid in water after UV exposure.

In the range > 400 nm the spectrum of citrazinic acid differs slightly from the spectra of the CDs (Fig. S3), because in the CDs the pyridone structure is bound to a carbon core leading to electronic coupling. Moreover, citrazinic acid was selected just as model pyridone compound, because it matches most of the properties of CDs like fluorescence spectrum, photobleaching and excited state deactivation pathways. The exact structure of the pyridone-based fluorophore in the CDs, however, can deviate slightly from citrazinic acid leading to marginal differences in the UV/Vis-spectra.

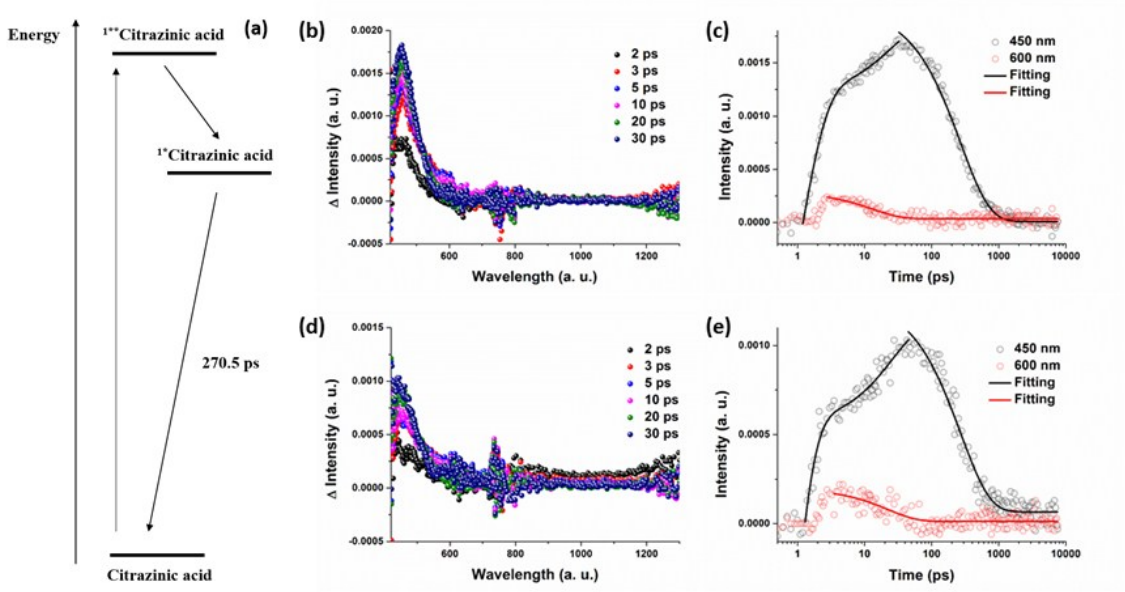

Figure S11. (a) Energy level diagram and excited state deactivation pathways for citrazinic acid. (b) Differential absorption spectra obtained upon femtosecond pump probe experiments (320 nm and 500 nJ) of citrazinic acid with time delays between 2 and 30 ps at room temperature. (c) Time absorption profiles at 450 and 600 nm. (d) Differential absorption spectra obtained upon femtosecond pump probe experiments (320 nm and 500 nJ) of photobleached citrazinic acid with time delays between 2 and 30 ps at room temperature. (e) Time absorption profiles at 450 and 600 nm.

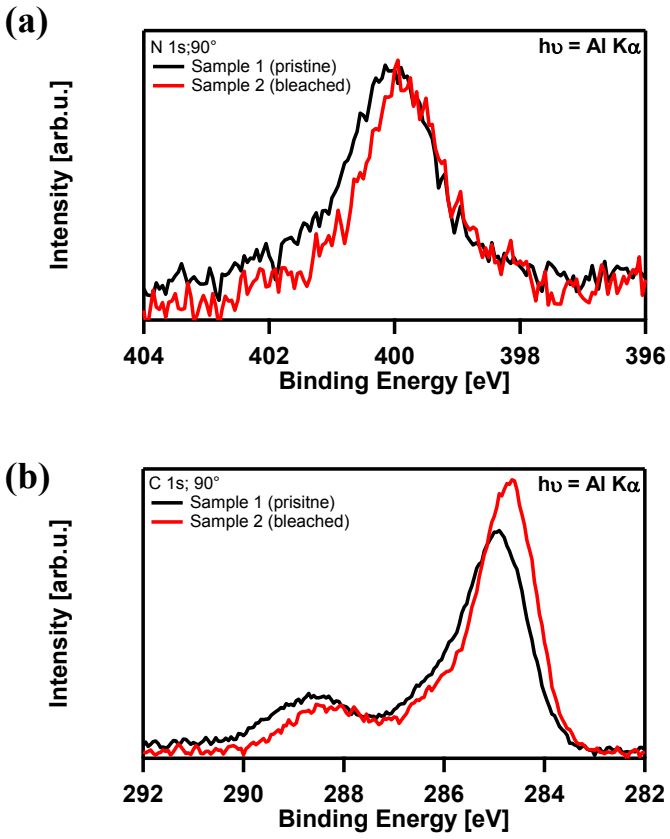

Figure S12. XPS spectra of fresh (black line) and photobleached CDs (red line), (a) N 1s spectrum, (b) C 1s spectrum: the peak at around 289 eV corresponds to C=O bonds, the peak at around 285 eV can be assigned to C-C and C=C bonds.

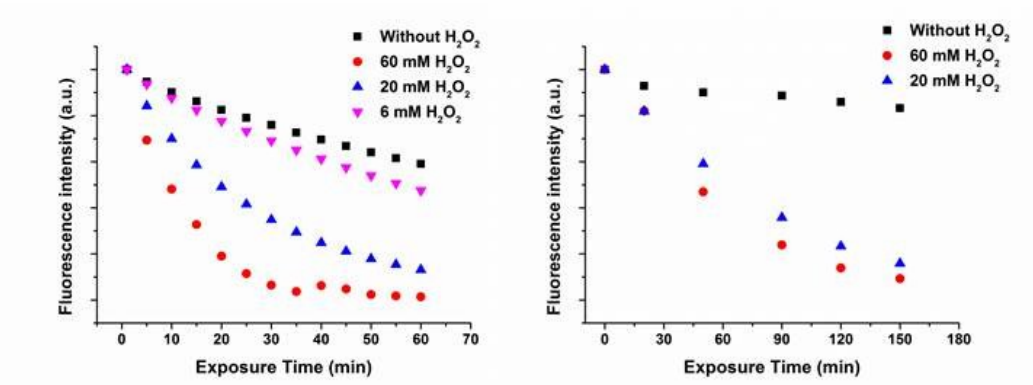

Figure S13. The H_2O_2 influence on photobleaching speed of (a) a CD suspension in water synthesized at 200°C for 3 h and (b) citrazinic acid aqueous solution.