## **Electronic Supplementary Information**

## The interaction of photoexcited Carbon nanodots with metal ions disclosed down to the femtosecond scale.

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**Figure S1**: Emission spectra excited at 440 nm of solutions of bare CDs (purple line) and of CDs with different amounts of  $Cu(NO_3)_2$  (dashed lines) and  $CuSO_4$  (continuous lines).



Time (ns)

**Figure S2**: Normalized decay kinetics at different emission wavelengths (indicated in the legend) extracted from Figure 2b, with the least-square fitting curves.



**Figure S3**: Transient absorption spectra of an aqueous solution of CDs at 300 fs, 400 fs, 600 fs, 800 fs, 1 ps, 3 ps, 5 ps, 8 ps, 12 ps (continuously from purple line to red line) from photoexcitation at 400 nm.



**Figure S4**: Transient Absorption time traces at 550 nm (excitation at 400 nm) in a long time range of carbon nanodots with no copper ions in solution (dark red), 4 mM (green), 20 mM (orange), 500 mM (blue).



**Figure S5**: *TA spectra measured in water (red and orange curves) and ethanol (blue and light blue curves) solution of CDs at fixed delay times.* 



**Figure S6**: Normalized absorption spectrum (red line) and normalized emission spectrum excited at 440 nm (green line) of a solution of CDs compared with the normalized absorption spectrum of a 1 M aqueous solution of  $Cu(NO_3)_2$ .



**Figure S7**: *TA* 2D-plot of an aqueous solution of CDs+30 mM of  $Zn^{2+}$  ions (a). Kinetics at 550 nm of bare CDs (red curve, extracted from data in figure 3a) and  $CDs+Zn^{2+}$  (green curve, extracted from data in panel a).



**Figure S8**: Infrared absorption spectra of bare CDs (black line) and of CDs with 400  $\mu$ M Cu(NO<sub>3</sub>)<sub>2</sub> (red line) and of pure Cu(NO<sub>3</sub>)<sub>2</sub> (blue line). The arrows point at the signals and their attributions.



**Figure S9**: Total amplitudes obtained by the sum of all the amplitudes in Table 1, extrapolated from the fitting procedures. The independence of the value from increasing copper concentration indicates that the nature of the excited state at time zero is independent from the presence of copper.