

Ultrafast energy relaxation and transfer dynamics in fluorescent carbon nanodots

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Carbon nanodots (CDs) are a novel family of optically-active carbon-based nanomaterials discovered only a few years ago.^[1] They are 1-10 nm nanoparticles composed by carbon, oxygen and hydrogen and endowed with a rather appealing combination of properties, such as “tunable” and strong fluorescence in the visible,^[2,7] excellent solubility in aqueous environments,^[3] photo- and chemical stability, sensitivity to perturbations like the presence of metal cations, and the capability of behaving as efficient photo-activated acceptors or donors of electrons and protons.^[4] Because of this unique combination of properties, CDs have the potential to complement or even replace semiconductor nanoparticles in several applications and domains, in particular where bio-toxicity is an issue.^[5] Understanding their optical properties at a fundamental level and the interplay between core and surface groups is crucial to move towards applications such as optoelectronics, bio-imaging, physicochemical sensors and markers.^[6]

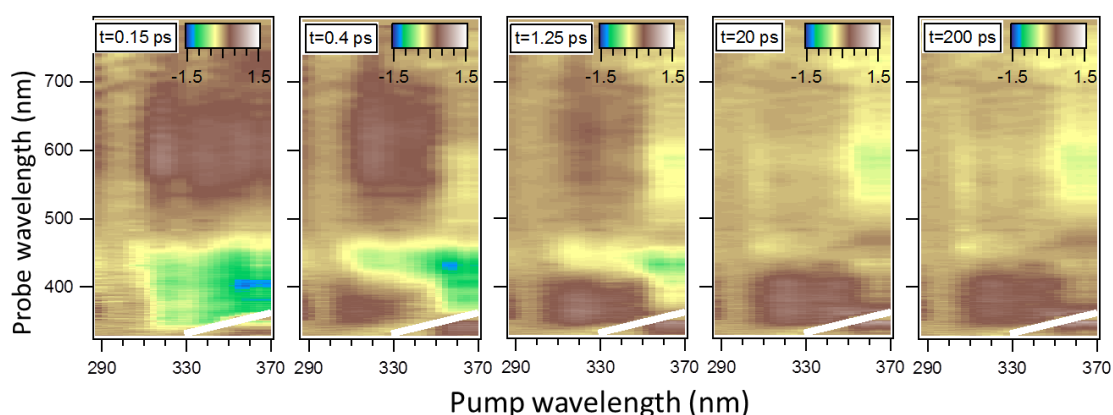


Figure 1. A representative selection of 2D-UV spectra on C-dots at different population times: 0.1, 0.4, 1.25, 20 and 200 ps.

We carried out an extensive study with DUV-to-Vis femtosecond transient absorption spectroscopy on N-rich CDs in water solution, also in presence of metal ions.^[8] These dots are particularly interesting because of their enhanced fluorescence, whose fundamental properties are subject of strong debate in literature.^[7] Transient absorption studies, performed varying pump wavelength and polarization allows to gain deeper understanding of the photophysical properties and the higher excited states dynamics of such systems. 2D-UV transient absorption was performed to disentangle the dynamic of the different bands contributing to the emission activity (Fig. 1).

Our results provide unanticipated insight on the photocycle of carbon nanodots in aqueous solution, unravelling the relaxation steps of photo-excited CDs and their characteristic timescales, as shown in Fig. 2. In particular, we observed rotational diffusion of the transition dipole moments on timescales (10s ps) much faster than the rotational diffusion of the entire nanoparticles (10s ns). This finding reveals a diffusional energy transfer occurring through surface electronic states of the nanodots, making them potentially suitable for chemical sensing or as light harvester antennas. Modelling and further experimental evidences are underway to rationalize such an unexpected behaviour.

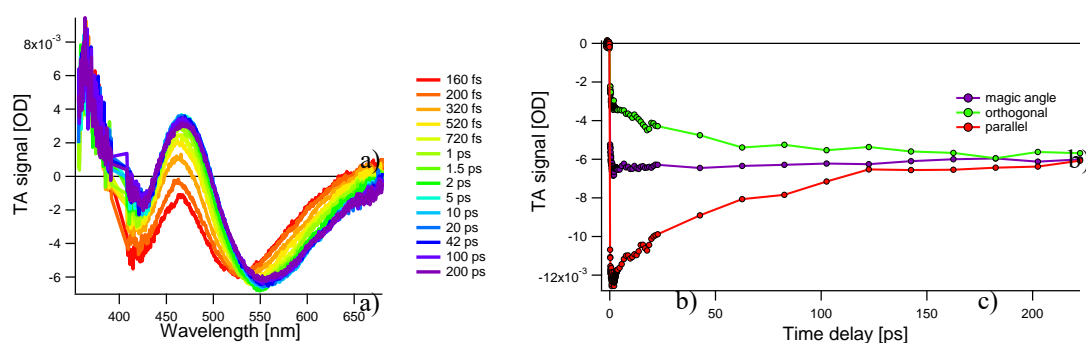


Figure 2. a) The selected spectra from transient absorption measurements, performed here with 400 nm pumping wavelength and broadband probe with magic angle polarization respect to the pump, show the relaxation mechanism of the dots. b) The kinetic traces at 550 nm (emission wavelength) from transient absorption measurement performed with magic angle, orthogonal and parallel polarization of the probe respect to the pump pulse, show the rotational dynamic.

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