Supporting Information to: "Excited-State Dynamics in a DNA-Stabilized Ag$_{16}$ Cluster with Near-Infrared Emission"

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Technical Experimental Details
Sample preparation

The NIR emissive DNA-AgNCs used in this study were synthesized and HPLC-purified based on the protocol described in reference 17 of the main text[1]. Briefly, the hydrated DNA (5'-*CACCTAGCGA*-3') was mixed with AgNO3 in 10 mM ammonium acetate (pH 7). The solution was then vortexed and after 15 minutes, freshly prepared NaBH$_4$ was added in order to reduce the silver cations and promote the formation of the clusters. The ratio of the components in the final mixture was [DNA]:[AgNO$_3$]:[NaBH$_4$] = 25 µM: 187.5 µM: 93.75 µM.

The sample was stored at 4 $^{\circ}$C for three days prior to HPLC purification. The HPLC method and chromatograms are reported in reference 17. In the end, the purified fraction was solvent exchanged to 10 mM ammonium acetate by spin-filtration with 3 kDa cut-off membrane centrifugal filters.

Transient Absorption spectroscopy

fs-TA experiments were performed by using a femtosecond pump-probe setup. Laser pulses (796 nm, 60 fs pulse length, 4 kHz repetition rate) were generated by a regenerative amplifier (Solstice Ace) seeded by a femtosecond oscillator (Mai Tai SP, both Spectra Physics). For the pump we used the Topas C (Light Conversion) to obtain pulses with central wavelength located at 520 nm. Pump pulse energy was set to 0.5 µJ per pulse. The spot size was approximately 0.2 mm^2. For the probe we used the super-continuum generation from a thin CaF$_2$ plate. The mutual polarization between pump and probe beams was set to the magic angle (54.7°) by placing a Berek compensator in the pump beam.

HCF Transient Absorption Spectroscopy

A commercial Ti:Sapphire laser amplifier (Coherent Legend ElitecDuo), delivering 25 fs laser pulses at 800 nm central wavelength with 2.4 mJ per pulse at 5 kHz repetition rate, is used as a fundamental light source. Pulse energies are attenuated down to 240 µJ by a combination of λ /2 plate and a thin film polarizer. This

light is focused into a 1 m Hollow-Core Fiber (Ultrafast Innovations). The efficiency of the HCF output was measured to more than 60%. An uncoated fused silica wedge pair is used as a broadband beam splitter. The reflection from the wedge, approx. 5% of the total HCF output, is sufficient for the pump pulses. The pump beam passes via an all-reflective telescope consisting of a pair of two concave mirrors with focal lengths of 300 and 150 mm. The reflecting telescope reduces the beam waist by a factor of two, resulting in a pump beam diameter approx. four times larger than the probe at the sample position. Spectrally filtered pump pulses were compressed to 14 fs using chirp-mirror compressor, and a measured autocorrelation curve is shown in Figure S1b. Using a broadband half-wave plate, the polarization of the pump pulse is set at magic angle (54.7°) with respect to the probe pulse. The spectrally filtered pump spectrum is shown in Figure S1a.

The transmitted beam through the wedge pair passes through a 900 nm long-pass filter and is used to seed a 5 mm thick CaF_2 crystal to generate broadband super-continuum probe pulses (Figure S1a). After super-continuum generation, aluminum mirrors are used to steer the beam to the sample position. A double chopping scheme was used, where both pump and probe pulses are modulated at a sub-harmonic frequency of the fundamental using two mechanical choppers synchronized to the laser's repetition rate. This scheme is highly efficient in removal of scattered pump light.

Both pump and probe pulses hit a spherical mirror (250 mm focal length) at an angle of incidence of approx. 0°. The pulses reflected from the spherical mirror hit a folding mirror, steering them through a hole in the center of the spherical mirror. This optical design minimizes aberrations such as astigmatism. The $1/e^2$ beam waist of the focused pump and probe beam at the sample position is approximately 200 and 65 μm respectively, as determined by a beam profiler (CMOS-1201, Cinogy). After the sample, the transmitted probe pulses are detected using a CMOS camera (ANDOR Kymera 328i).
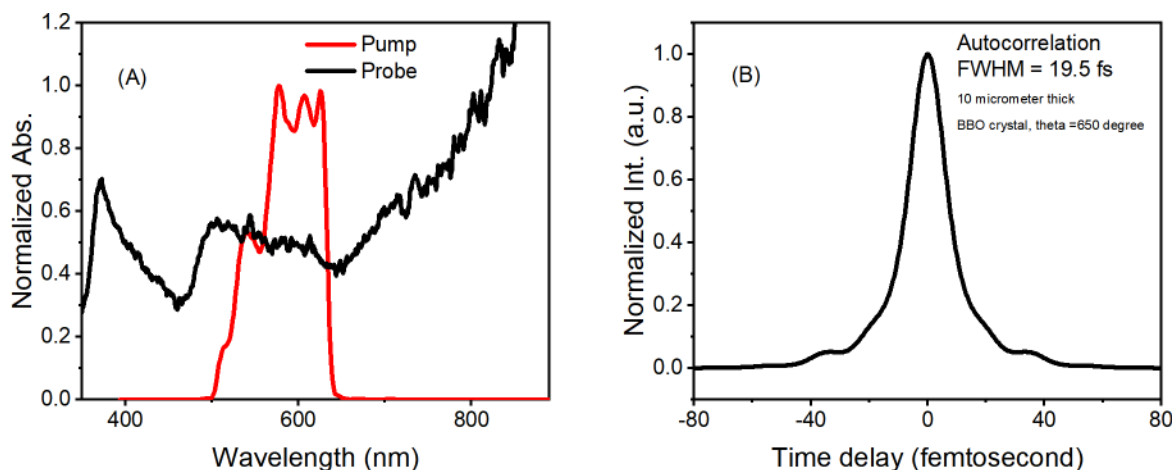

Figure S1. a) Spectral characteristics of the HCF-TA pump- and probe- pulses. **b)** Autocorrelation trace of the HCF-TA pump pulse.

Coherent two-dimensional spectroscopy

The diffractive optics-based, fully non-collinear instrument used for one- and two- color 2D spectroscopy has been described in detail elsewhere[2]. Briefly; the ≈1030 nm, 250 fs output pulses from a Yb:KGW amplified laser (Pharos, Light Conversion ltd.) where used to drive two independent non-collinear OPAs. In the one-color experiments, visible light was generated using a commercial NOPA (Orpheus-N, Light Conversion ltd.), which provided ≈15 fs and ≈60 nm FWHM pulses centered at 540 nm. The energy of the excitation pulses was attenuated to 3 nJ/pulse, and the experiment was performed at 20 KHz repetition rate. To record the 2D interferograms, the coherence time t_1 was scanned from -36 to + 36 fs in 1 fs steps,

which was both sufficient to avoid aliasing artifacts, and for the signal to decay below the noise level. The resulting excitation frequency resolution was ≈460 cm^{-1} (≈15 nm), while the detection frequency resolution set by the spectrometer was ≈145 cm^{-1} (≈5 nm).

In the two-color experiments, the commercial NOPA provided visible "pump" light as described above, whereas the near-infrared "probe" light was supplied by a lab-constructed NOPA. This provided ≈14 fs and ≈140 nm FWHM pulses centered at approximately 740 nm. The visible pulses were attenuated to 2 nJ/pulse, while the near-infrared pulses were 8 nJ/pulse. The coherence time t_1 was scanned from -36 to +36 fs in 1 fs steps, resulting in an excitation frequency resolution of ≈460 cm^{-1} (≈15 nm), while the detection frequency resolution was ≈85 cm^{-1} (≈5 nm).

The focal spot at the sample was approximately 160 µm, and all experiments were performed under magic-angle polarization conditions in order to avoid depolarization artifacts.
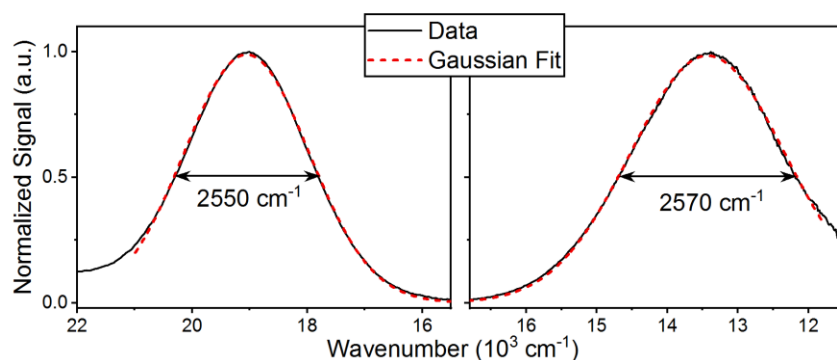
Supplementary Spectra

Figure S2. Normalized absorption (left) and emission (right) spectra overlaid with Gaussian fits to the data (red dashed lines). The full-width at half-maximum (FWHM) values extracted from the fits are reported below the arrows. The intensity distribution of the emission spectrum was corrected in the standard way with the square of the wavelength on conversion to wavenumber scale.
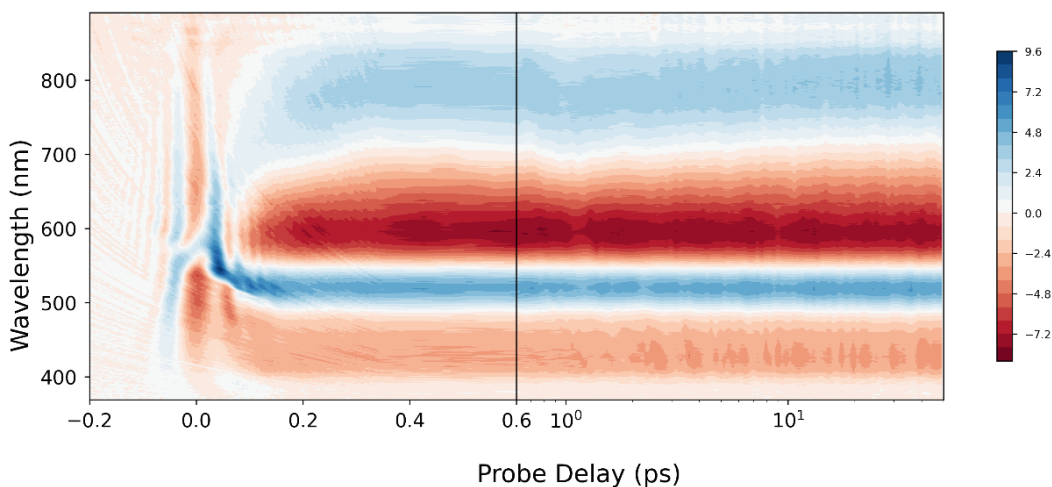

Figure S3. TA data from HCF-TA experiment shown over the full probe-delay range of the experiment. The color scale represents the differential absorption signal in mOD. Note change from linear- to log- timescale at 0.6 ps (solid black line).
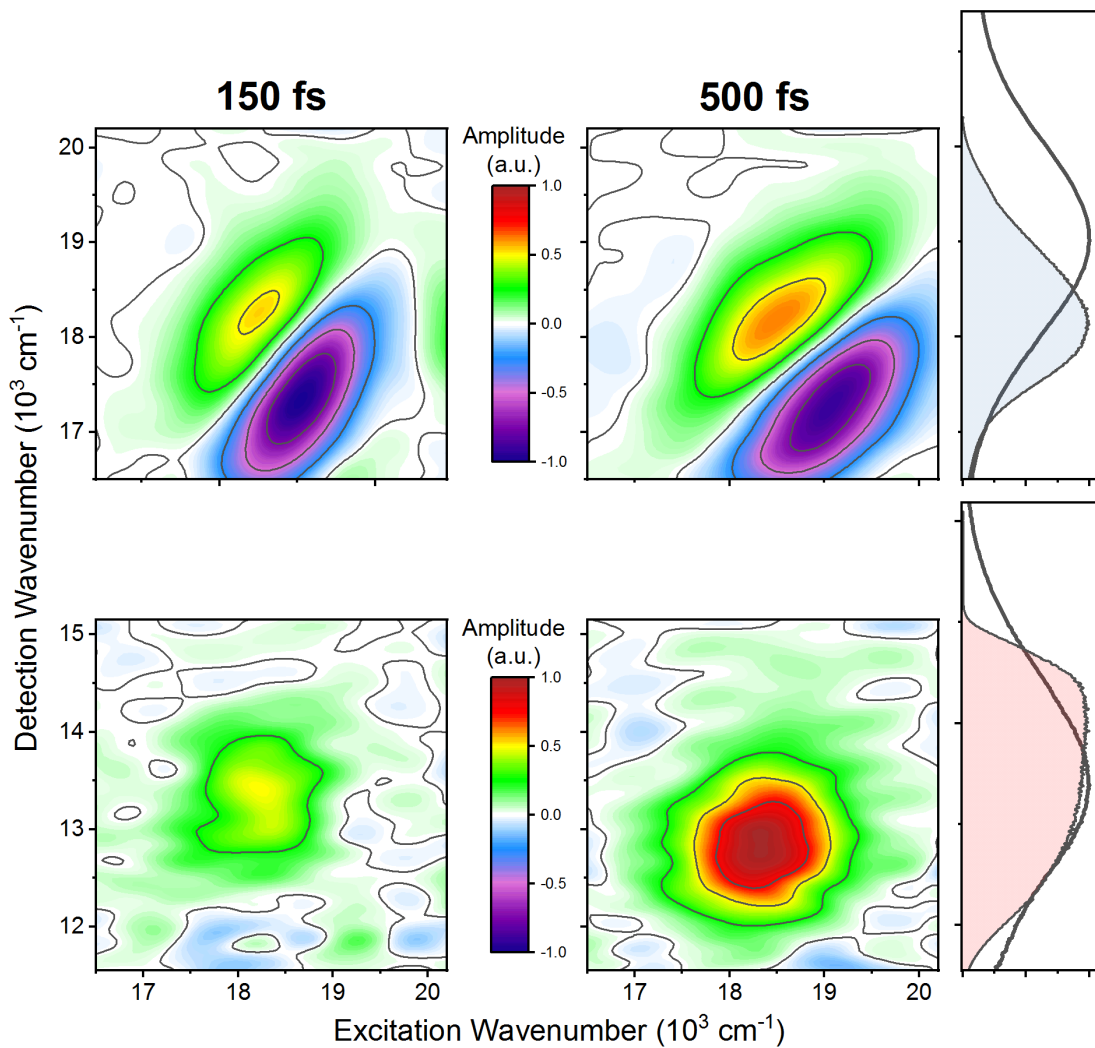
Figure S4. Selected one- and two-color 2D spectra. The one-color experiment shows only minor spectral dynamics on timescales >150 fs, while a clear increase of stimulated emission in the two-color experiment is observable over the first few hundred femtoseconds. The spectra are normalized: the signals are normalized to be directly comparable at different times, but the amplitudes of one- and two- color experiments are not directly comparable due to the different intensities of the visible and NIR laser pulses. The linear absorption spectrum, the emission spectrum, and the spectra of the laser pulses are shown for reference in the right-most panels. Note that the sign-convention of 2DES signals is opposite to that of TA, as one detects electric field amplitude rather than differential absorption.
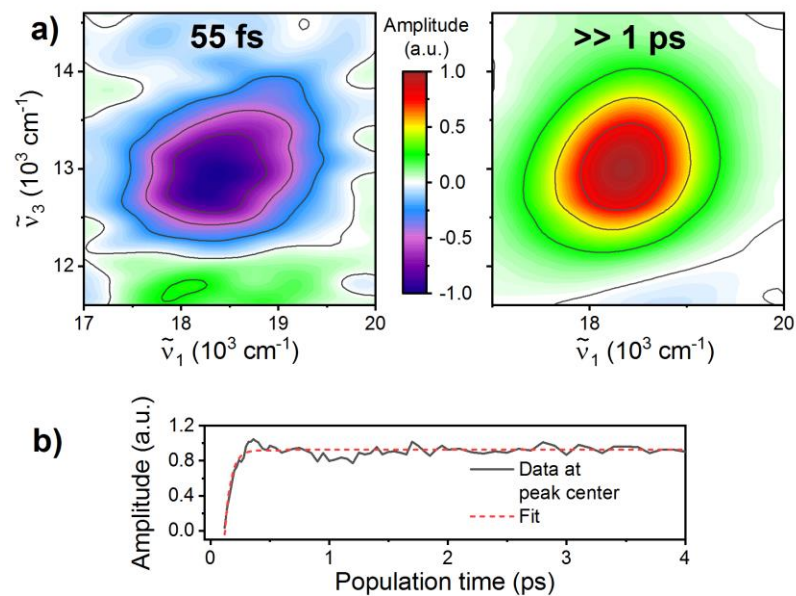
Figure S5. Global spectra extracted from kinetic fits to early-time of two-color 2DES data. **a)** 2D-DAS for the two components necessary to fit the data in this range. The negative-amplitude ≈55 fs component corresponds to a rise in the signal near the fluorescence maximum, while the "long" component corresponds to an overall decay of the signal on timescales much longer than the time window used here. **b)** Representative measured kinetics and corresponding fit. The data shown is extracted from the approximate center of the 2DES feature. All data are shown on normalized amplitude scale.
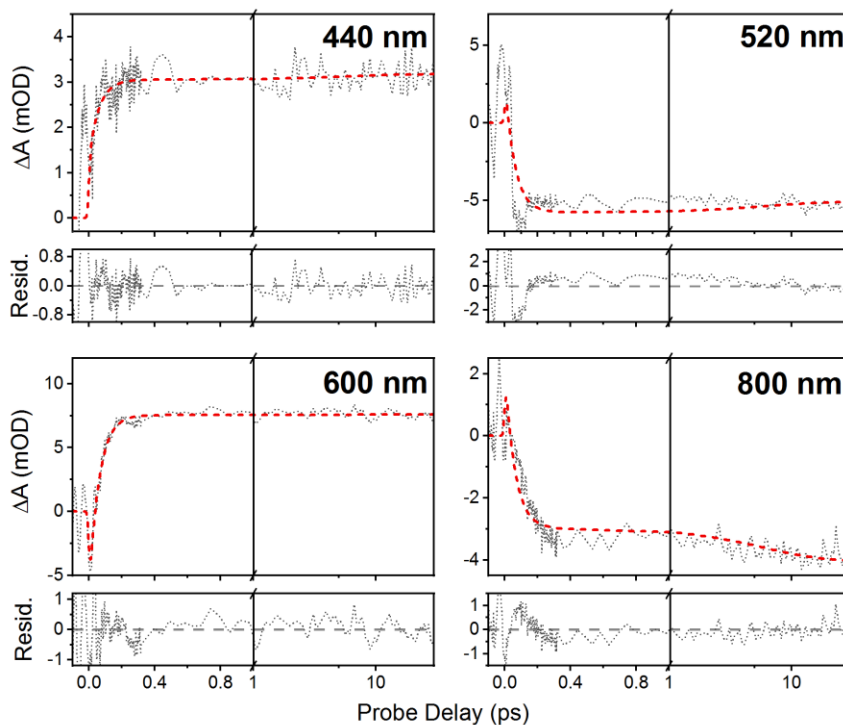

Figure S6. Kinetic traces (grey, dotted) extracted at representative detection wavelengths from the HCF-TA experiment. Data overlaid by the corresponding kinetic trace extracted from the global fit (red, dashed). Residuals shown in separate panels.
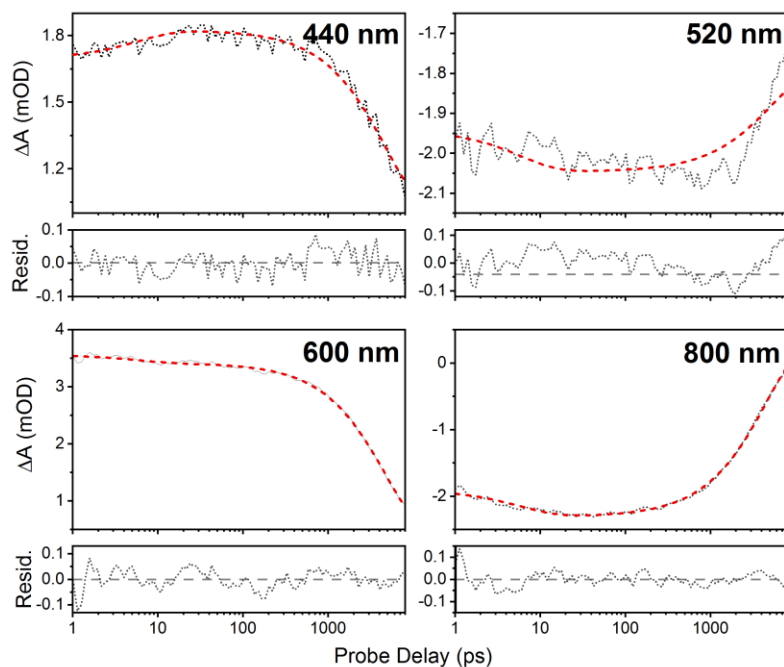
Figure S7. Kinetic traces (gray, dotted) and corresponding fits (red, dashed) at selected detection wavelengths in the WL-TA experiments. Residuals shown in separate panels.
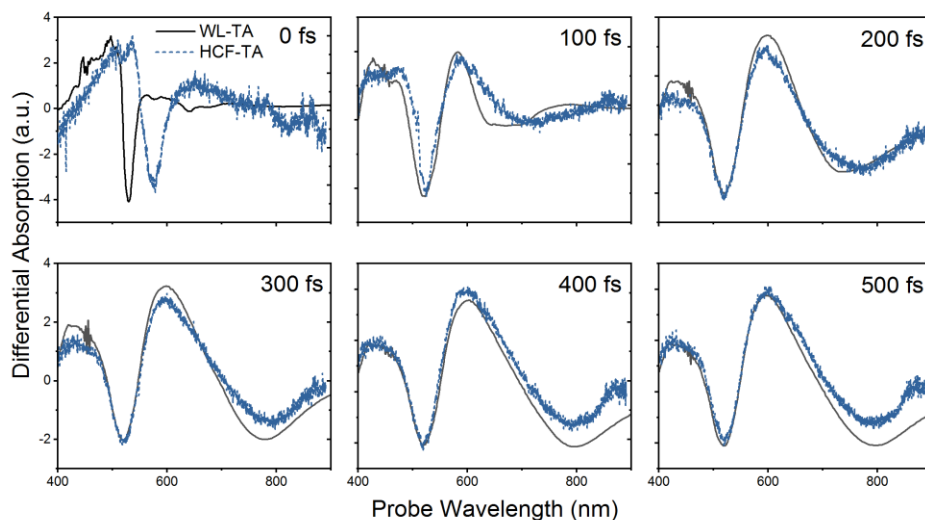

Figure S8. Comparison of normalized WL-TA (black) and HCF-TA (blue) spectra at short probe delays.

(1) Bogh, S. A.; Carro-Temboury, M. R.; Cerretani, C.; Swasey, S. M.; Copp, S. M.; Gwinn, E. G.; Vosch, T. Unusually Large Stokes Shift for a Near-Infrared Emitting DNA-Stabilized Silver Nanocluster. *Methods Appl. Fluoresc.* **2018**, *6* (2), 024004.

(2) Augulis, R.; Zigmantas, D. Two-Dimensional Electronic Spectroscopy With Double Modulation Lock-In Detection: Enhancement of Sensitivity and Noise Resistance. *Opt. Express* **2011**, *19* (14), 13126-13133.