Supplementary Material : Efficient Time Sampling Strategy for Transient Absorption Spectroscopy

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Index Terms—Transient Absorption Spectroscopy, Transient Imaging, Femtochemistry, Non-linear Curve Fitting

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1 EXPERIMENTAL DETAILS

1.1 Sample

In this paper we used a solution of 4CzIPN in Dichloromethane (DCM). The solution had a concentration of $2\frac{mmol}{L}$ in $12\,\text{mL}$. 4CzIPN is shown in 1. The solution was done under air conditions and was not degassed to remove any oxygen contamination.

It was flown through a Harrick's cell with a path length of $200\,\mu\text{m}$. It was circulated by using a peristaltic pump in a continuos flow system. The Harrick's cell was build with CaF_2 windows and $200\,\mu\text{m}$ PTFE spacers. The cell's position was continuously adjusted in the plane perpendicular to the directory of the laser beam's propagation to avoid photodamage to the sample. All experimental measurements were done at ambient laboratory temperature of $20\,^\circ\text{C}$. The solutions were all prepared at the Rutherford Appleton Laboratories.

1.2 TRIR data collection

All data was measured using the LIFEtime facility at the Rutherford Appleton Laboratories (RAL) in Didcot, United Kingdom.

In the LIFEtime laser system, a laser oscillator with a $1030\,\text{nm}$ output frequency (operating at $80\,\text{MHz}$) seeded two Yb:KGW amplifiers (Light Conversion, Pharos, $15\,\text{W}$, $100\,\text{kHz}$, $260\,\text{fs}$ output and Light Conversion, Pharos SP, $6\,\text{W}$, $100\,\text{KHz}$, $180\,\text{fs}$ output). The Pharos amplifier was used to pump an optical parametric amplifier (OPA; Light Conversion, Orpheus HP) for generating the UV-Vis pump excitation wavelength, while the Pharos SP amplifier pumped two OPAs (Light Conversion, Orpheus ONE) to produce independently tunable mid-infrared (IR) probe beams through difference frequency generation. These two probe beams were then focused by a $f = 7.5\,\text{cm}$ gold parabolic mirror to achieve identical spot sizes. To implement multiple-probe-pulse measurements following each excitation pulse, the repetition rate of the UV pump pulses was reduced to $1\,\text{kHz}$ using pulse picking. The timing between the UV-Vis pump pulses and the multiple IR probe pulses was controlled using a combination of an optical delay stage with a range of $0 - 16\,\text{ns}$ and electronic pulse selection, allowing for efficient
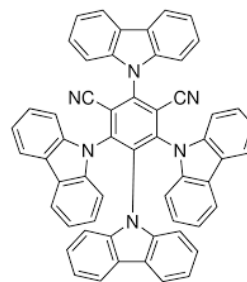

Fig. 1. Molecular structure of 4CzIPN or 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 2,4,5,6-Tetrakis(9H-carbazol-9-yl) isophthalonitrile

S4 measurement of time delays ranging from less than $1\,\text{ps}$ to $100\,\text{µs}$. The pulse energy for the $425\,\text{nm}$ UV-Vis pump was kept below $300\,\text{nJ/pulse}$ to avoid multiphoton excitations, and both IR probe beam energies were maintained at $50\,\text{nJ/pulse}$.

For TRIR measurements, the UV-Vis pump and two IR probe beams were spatially overlapped at the sample and the transmitted IR beams were spatially dispersed by gratings onto a pair of 128-element MCT array detectors (InfraRed Associates, Inc.) to generate a TAS spectrum. The The probe IR region was selected within the range of $1400 - 1600\,\text{cm}^{-1}$ ($6200 - 7100\,\text{nm}$), with the center wavenumbers of the two probe pulses detuned to cover separate spectral windows, each pulse spanning approximately 200^{-1}. Reference spectra of polystyrene and 1,4-dioxane were used for calibrating the pixel-to-wavenumber conversion of the TRIR data post-acquisition.

2 MORE DETAILED TRIR AND TAS DESCRIPTION

We include more detailed explanation on TAS and TRIR (Time-resolved infrared spectroscopy) in Fig. 2, which was not covered in the main manuscript. Please refer to the caption of Fig. 2.

(A) Pump-probe spectroscopy

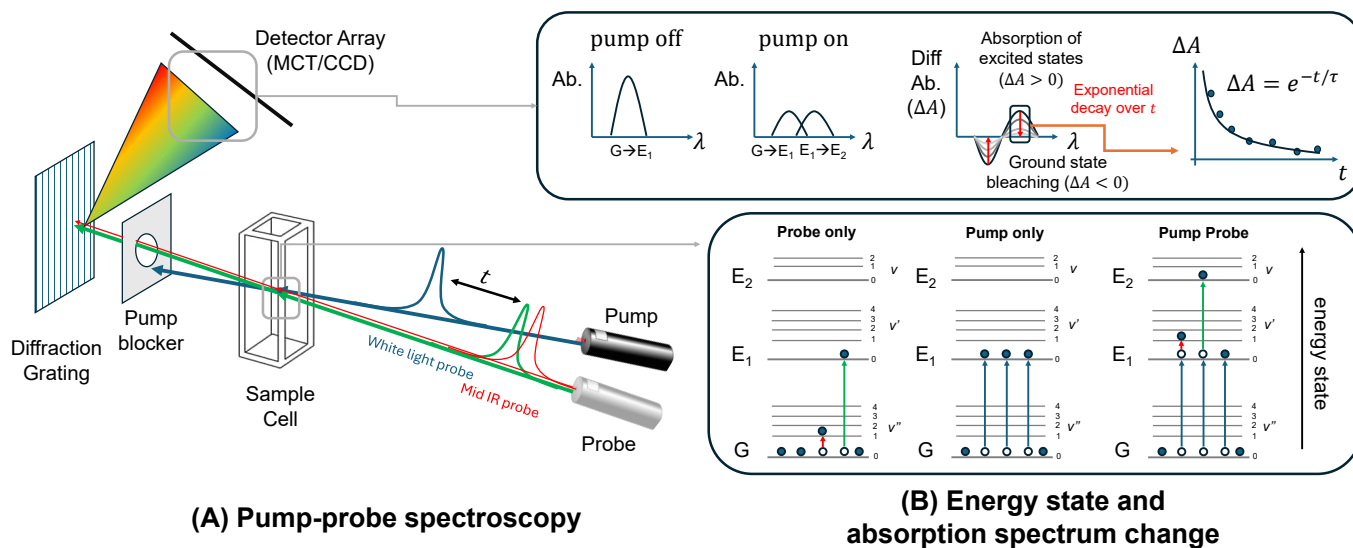**(B) Energy state and absorption spectrum change**

Fig. 2. (A) Illustration of transient absorption spectroscopy. A narrow bandwidth pump pulse [blue] is used to excite the electrons and a broad probe pulse (either white light [green] or mid IR [red]) after time delay of t to measure the absorption over wavelength. (B) Probe only shows the energy level of the electrons/molecules, that got excited by either the Mid-IR pulse [red] or the white light probe [green]. The excitation from a IR-pulse excites the vibrations from the molecule in the overall ground state ($\nu_0'' \rightarrow \nu_1''$). If the excitation is happening with white light we excite from ground state to the first electronic excited state (G→E$_1$ or $\nu_0'' \rightarrow \nu_0'$). The pump pulse excites large numbers of the electrons to the E$_1$ state ($\nu_0'' \rightarrow \nu_0'$). When using pump probe ($t > 0$) many molecules are electronically excited. This means the second excitation from the probe pulse lifts the molecules into an even higher energy state. For a IR-probe $\nu_0'' \rightarrow \nu_0' \rightarrow \nu_1'$, for white light probe $\nu_0'' \rightarrow \nu_0' \rightarrow \nu_0$. Only a few molecules are left at the ground state (ν_0') so the excitation from either probe will be less than with pump off. This phenomenon can be seen in the spectra as ground state bleaching (a dip at the position where the peak of $\nu_0'' \rightarrow \nu_1''$ or $\nu_0'' \rightarrow \nu_0'$ would appear. By calculating absorption spectra difference at pump-off and pump-on, one can calculate differential absorbance ΔA. Lack of ground state electrons (ground state bleaching) is represented as $\Delta A < 0$, while absorption of excited state shows $\Delta A > 0$.