Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Ultrafast spectroscopy, superluminescence and theoretical modeling for a two-photon absorbing fluorene derivative

S. A. Kurhuzenkau,[a] A. W. Woodward,[b] S. Yao,[b] K. D. Belfield,[c] Y. O. Shaydyuk,[d] C. Sissa,[a] M. V. Bondar*[d] and A. Painelli*[a]

[a.] *Department of Chemistry, University of Parma, Parco Area delle Scienze 17/A, Parma, 43124, Italy. E-mail: anna.painelli@unipr.it*
[b.] *Department of Chemistry, University of Central Florida, Orlando, FL 32816-2366, United States*
[c.] *College of Science and Liberal Arts, New Jersey Institute of Technology, University Heights, Newark, NJ 07102, United States*
[d.] *Institute of Physics National Academy of Science of Ukraine, Prospect Nauki, 46, Kiev-28, 03028, Ukraine. E-mail: mike_bondar@hotmail.com*

Description of the pump-probe setup

As schematically shown in Figure S1, the fundamental output of a Ti:sapphire mode-locked laser (Mira 900-F, 800 nm, repetition rate f = 78 MHz, pulse duration $\tau_p \approx 200$ fs), pumped by the Nd^{3+}:YAG Verdi V10 laser, was amplified by the regenerative amplifier Legend F-1K-HE. The resulting laser beam consisting of a train of short pulses (pulse duration $\tau_p \approx 140$ fs, repetition rate of 1 kHz and average power 1 W) was split in a pump and probe beam by a beam splitter. To generate a broadband white-light supercontinuum probe one of the two beams was focused into LiF or sapphire plate. The pump beam was sent through a mechanically controlled optical delay line (M-531.DD, PI Inc.) and then frequency-doubled to the 400 nm pump pulses by second harmonic generation in a BBO crystal. The generated pump and probe beams were overlapped at a small angle within the 1 mm flow cell containing the sample solution, whose concentration was adjusted to obtain an absorbance of about 1 at the pump wavelength. The spectrum of the probe beam after the sample was recorded by the Acton SP500i spectrometer with a CCD detector and transferred to the computer. Results are shown in terms of the differential absorbance: $\Delta D(\lambda, \Delta t) = D(\lambda, \Delta t) - D_0(\lambda)$, where $D_0(\lambda)$ is the absorbance at wavelength λ in the absence of the pump and $D(\lambda,\Delta t)$ is the same quantity measured at time Δt after the pump excitation.

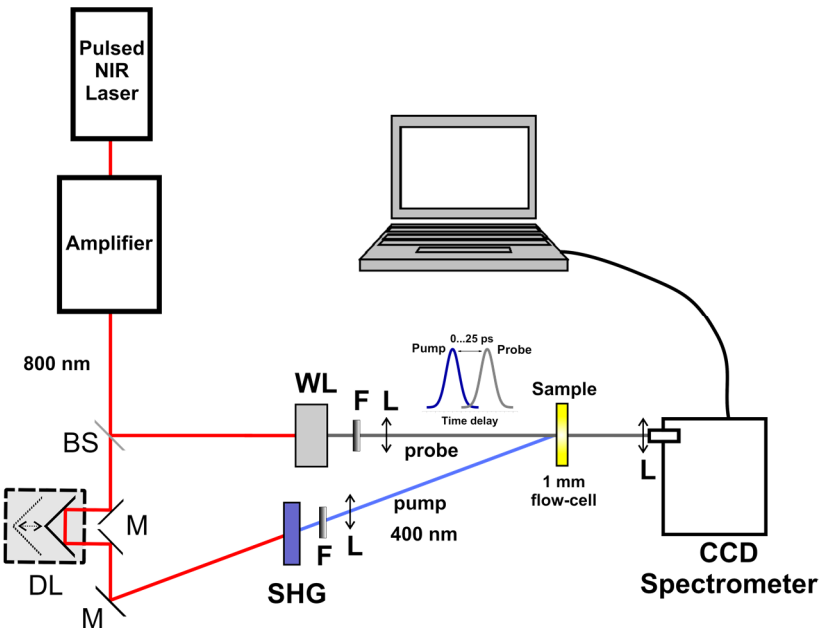

Figure S1. Schematic diagram of the experimental pump-probe setup. BS – beam splitter; DL – optical delay line; M – 100% reflection mirror; L, F – set of focusing lenses, neutral density and/or interferometer filters; WL – LiF or sapphire plate for generating white-light supercontinuum; SHG – BBO crystal for second harmonic generation.

The optimized molecular geometry in Figure S2 suggests a small deviation from linearity of the molecular structure. A precise definition of the angle α between the DA and DR molecular arm is not univocal, mainly because of the extended nature of the D, A and R groups. However the value α ~ 10°, extracted from the analysis of anisotropy spectra is well compatible with the calculated geometry. We underline that α mainly affects anisotropy results, all other spectral properties being marginally affected by small α variations.

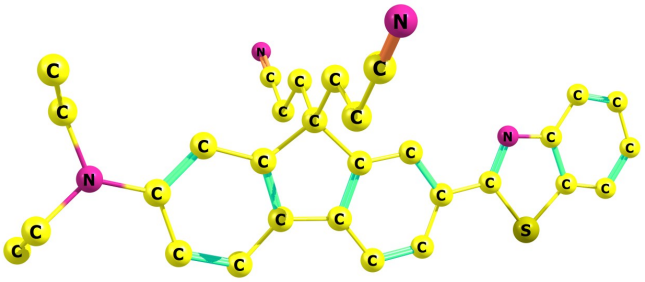

Figure S2. Optmized geometry of **1** (DFT\B3LYP with a 6-31G(d,p) basis set, Gaussian G09).

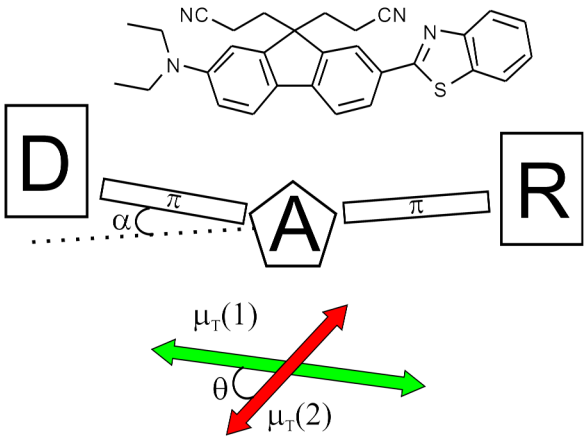

Figure S3. Definition of angle: α is the angle between the DA and AR molecular arms; θ is the angle between the transition dipole moment from the ground to the first excited state $\mu_T(1)$ and from the ground to the second excited state $\mu_T(2)$.