Supporting Information

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

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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 τp ≈ 200 fs), pumped by the Nd3+: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 τp ≈ 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: ∆D(λ, Δt) = D(λ, Δt) – D0(λ), where D0(λ) is the absorbance at wavelength λ in the absence of the pump and D(λ, Δt) 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.](image)
The optimized molecular geometry in Figure S2 suggests a small deviation from linearity of the molecular structure. A precise definition of the angle $\alpha$ 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 $\alpha \sim 10^\circ$, extracted from the analysis of anisotropy spectra is well compatible with the calculated geometry. We underline that $\alpha$ mainly affects anisotropy results, all other spectral properties being marginally affected by small $\alpha$ variations.

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

Figure S3. Definition of angle: $\alpha$ is the angle between the DA and AR molecular arms; $\theta$ is the angle between the transition dipole moment from the ground to the first excited state $\mu_1(1)$ and from the ground to the second excited state $\mu_1(2)$. 