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

Electronic Supplementary Information (ESI)

The Role of Twisting in Driving Excited-State Symmetry Breaking and Enhanced Two Photon Absorption in Quadrupolar Cationic Pyridinium Derivatives

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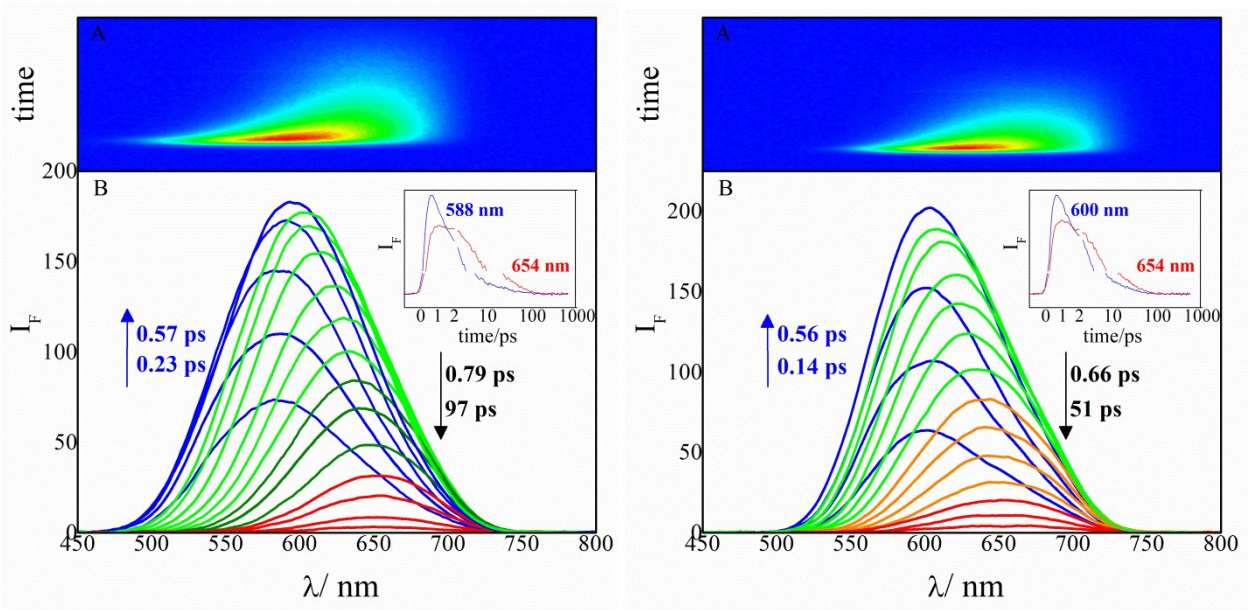

Figure S1. *Broadband fluorescence up-conversion (λ_{exc}=400 nm) of 1DPA (left graph) and 2DPA (right graph) in MeOH: A) contour plot of the experimental data, B) time resolved emission spectra recorded at different delays after the laser pulse. Insets: decay kinetics recorded at meaningful wavelengths.*

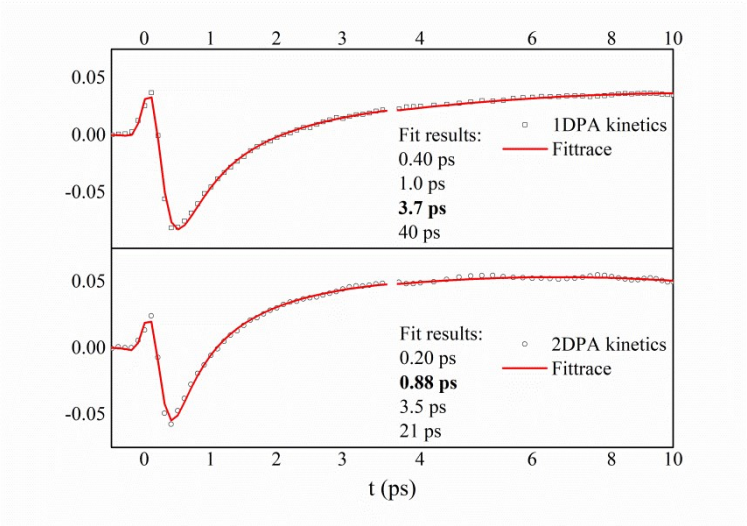

Figure S2. *Kinetic traces of 1DPA (upper panel) and 2DPA (lower panel) recorded at 600 nm, as obtained by TA measurements in MeOH, and their fitting in the first 10 ps time interval. In the Fit results, the transient which most contributes to the rise is marked in bold.*

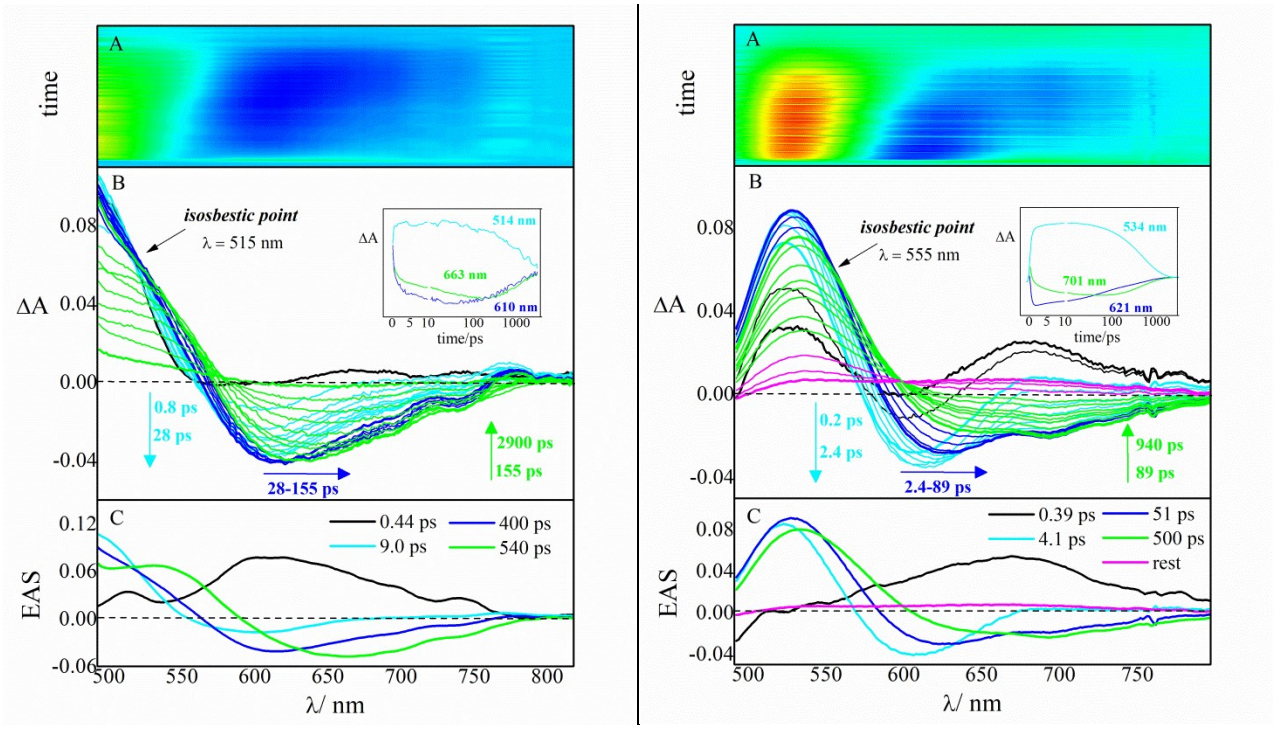

Figure S3. *Pump−probe absorption (λ_{exc}=400 nm) of 1DPA (left graph) and 2DPA (right graph) in hydrogel: A) contour plot of the experimental data, B) time resolved absorption spectra recorded at different delays after the laser pulse. Insets: decay kinetics recorded at meaningful wavelengths C) Evolution Associated Spectra (EAS) of the decay components obtained by Global Analysis.*

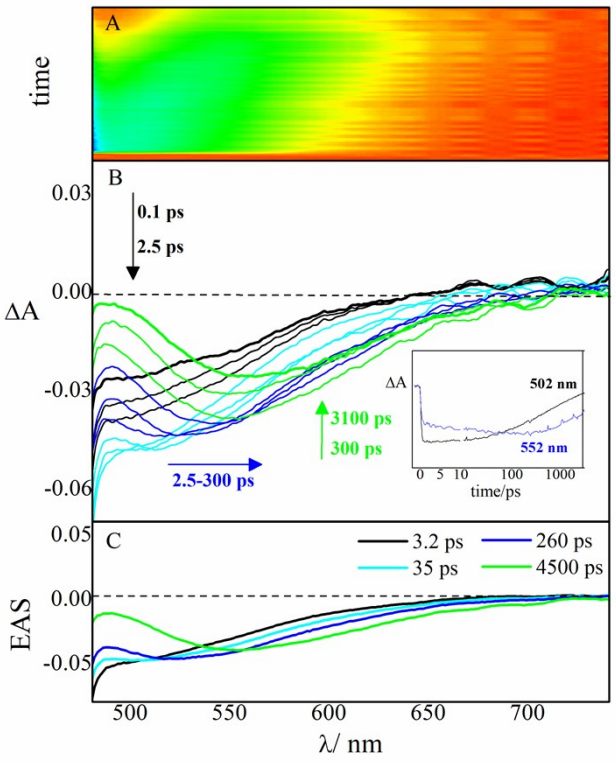

Figure S4. *Pump−probe absorption (λ_{exc}=400 nm) of C153 in hydrogel: A) contour plot of the experimental data, B) time resolved absorption spectra recorded at different delays after the laser pulse. Insets: decay kinetics recorded at meaningful wavelengths C) Evolution Associated Spectra (EAS) of the decay components obtained by Global Analysis.*

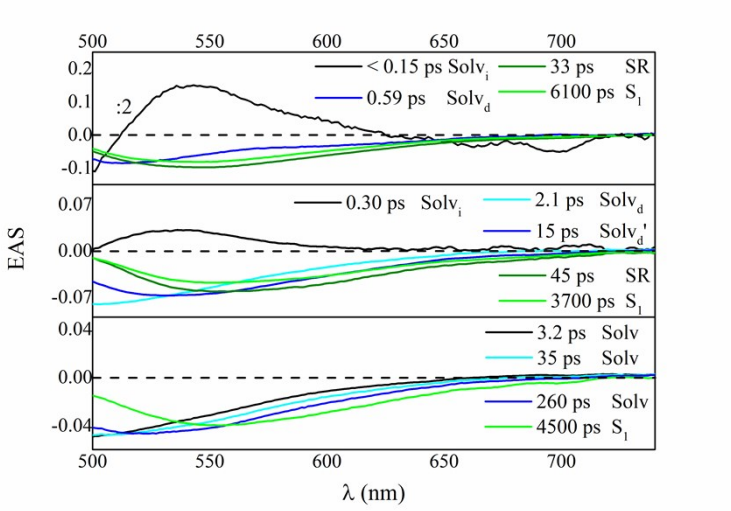

Figure S5. *Comparison between the transient spectra describing the excited state dynamics of C153 as obtained by the Global Analysis of the TA measurements in MeCN (upper panel), MeOH (middle panel), and hydrogel (lower panel).*

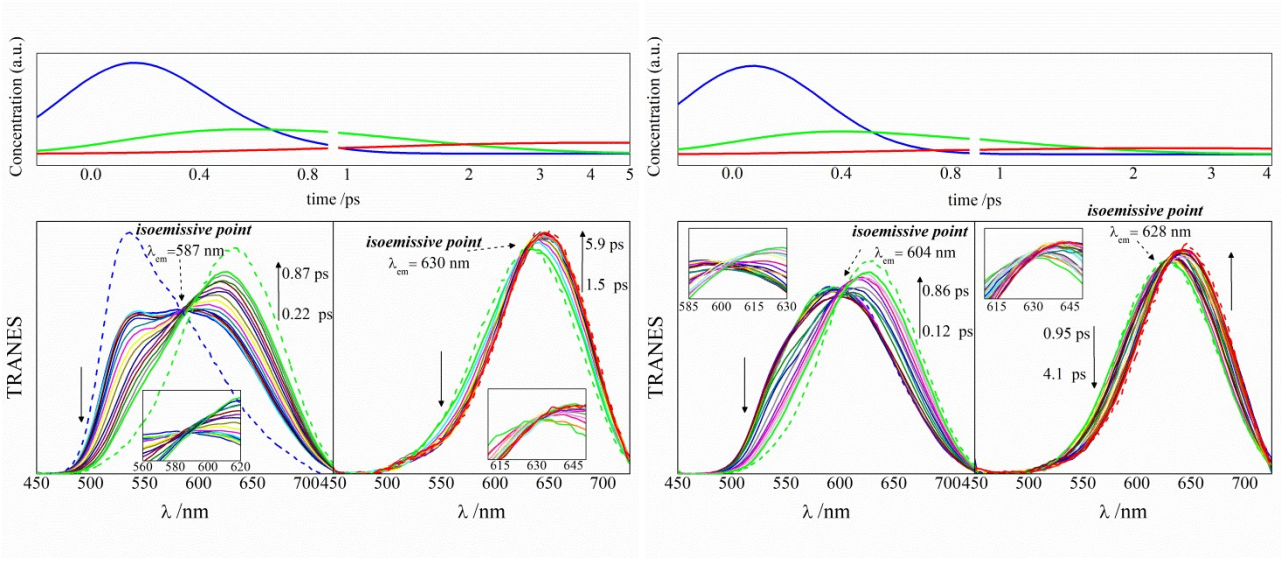

Figure S6. *TRANES analysis of 1DPA (left graph) and 2DPA (right graph) in MeCN: concentration profiles of the transients obtained by Global Analysis (upper panels) and TRANES evolution over time (lower panels) in proper delay time intervals.*

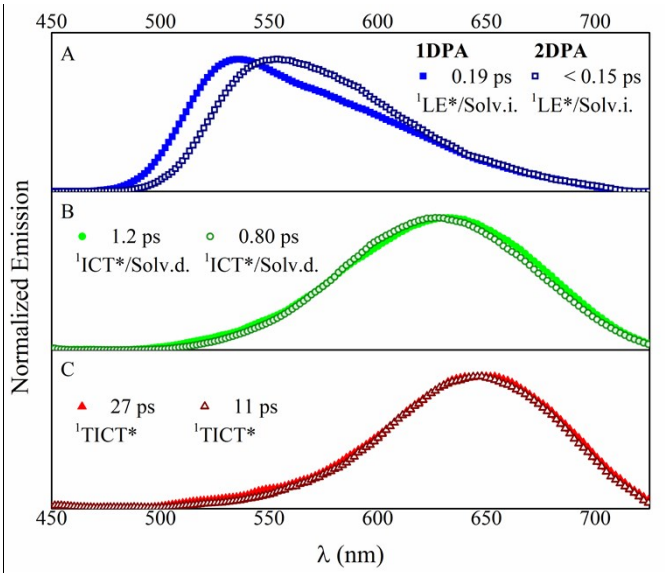

Figure S7. *Comparison between the transient emission spectra describing the excited state dynamics of 1DPA (filled symbols) and 2DPA (void symbols), as obtained by the Global Analysis of the broadband fluorescence up-conversion measurements in MeCN.*

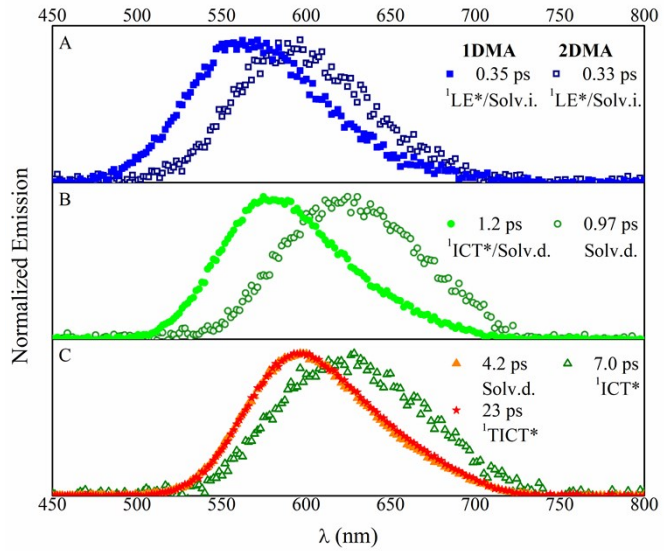

Figure S8. *Comparison between the transient emission spectra describing the excited state dynamics of 1DMA (filled symbols) and 2DMA (void symbols), as obtained by the Global Analysis of the broadband fluorescence up-conversion measurements in W/EtOH (70/30) mixture.*

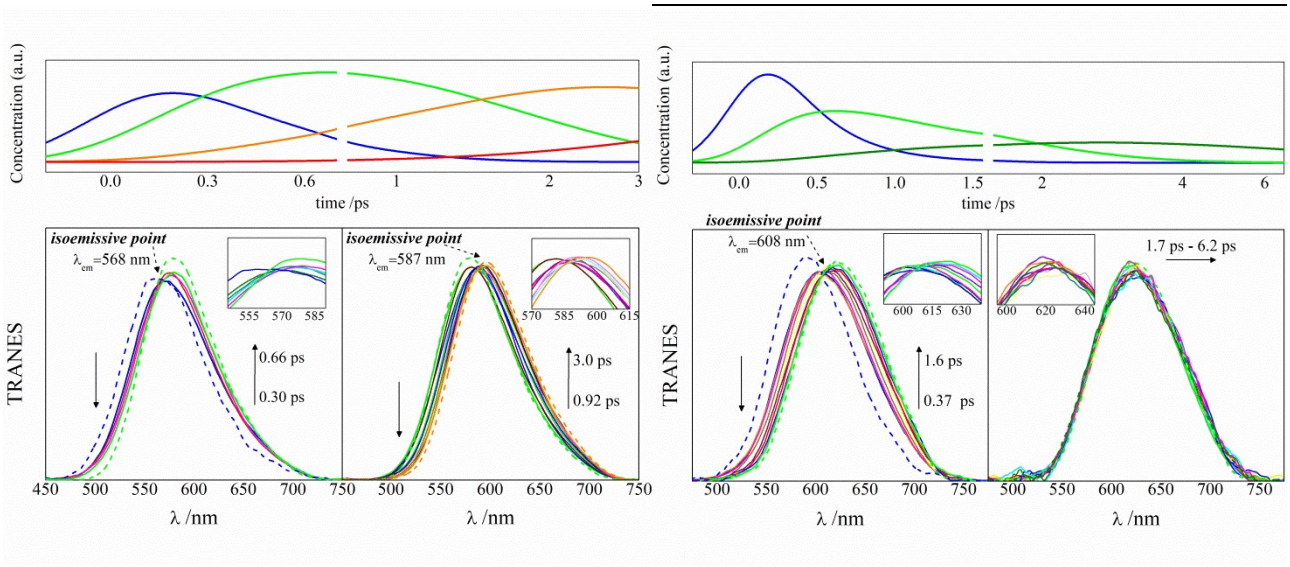

Figure S9. *TRANES analysis of 1DMA (left graph) and 2DMA (right graph) in W/EtOH (70/30) mixture: concentration profiles of the transients obtained by Global Analysis (upper panels) and TRANES evolution over time (lower panels) in proper delay time intervals.*

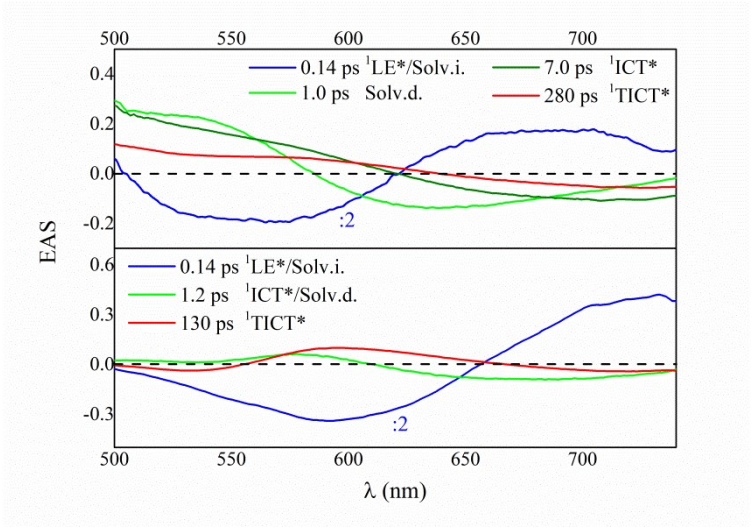

Figure S10. *Comparison between the transient spectra describing the excited state dynamics of 1DPA (upper panel) and 2DPA (lower panel), as obtained by the Global Analysis of the TA measurements in DCM. Raw data were retrieved from ref. 50 and analyzed through a refined fitting.*

Table S1*. Results of the Global Analysis of the femtosecond transient absorption (TA) experiments for 1DPA and 2DPA in DCM: exponential components revealed by the fitting with their lifetime (τ) and assignment.*

Solvent	TA	Assignment
	τ / ps	

	1DPA	2DPA	
DCM	0.14	0.14	^{1}LE*/Solv.$_{i.}$
	1.0		Solv.$_{d.}$
	7.0	1.2	^{1}ICT*
	280	130	^{1}TICT*