Electronic Supplementary Information for

Photocyclization Reaction and Related Photodynamics in the Photoproducts of a Tetraphenylethylene Derivative with Bulky Substituents: Unexpected Solvent Viscosity Effect

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1. General

Time-Correlated Single-Photon Counting (TCSPC): The picosecond (ps) time-resolved emission experiments were carried out by employing a time-correlated single-photon counting (TSCPC) system. The samples were excited by 325 nm from the output of a femtosecond (fs) optical parametric oscillator (OPO, Inspire Auto 100, Radiantis). The fluorescence signal was collected at the magic angle (54.7°) and monitored at a 90° angle to the excitation beam at discrete emission wavelengths.

Transient Absorption: The fs-transient absorption experiments were realized using a chirped pulse amplification setup that consists of a Ti:Sapphire oscillator (TISSA 50, CDP Systems) pumped by a 5 W diode laser (Verdi 5, Coherent). The seed pulse (30 fs, 450 mW at 86 MHz) centered at 800 nm is directed to a chirped pulse amplification system (Legend-USP, Coherent). The amplified fundamental beam (50 fs, ~3.1 W at 1 kHz) is then split by a beam splitter and the main portion (2.7 W) is directed through an optical parametric amplifier for wavelength conversion (TOPAS, Light Conversion). A small portion of the remaining fundamental beam (~200 μW) goes through a delay line S2 (7.8 fs step and 2 ns of maximum delay) and is focused on a 3-mm thick sapphire crystal for white light continuum (WLC) generation. The produced WLC is split into two parts to form probe and reference beams, which are directed to the sample, where the probe and the pump beams are overlapped. The polarization of the pump is set to the magic angle in respect to the probe. The transmitted light is focused to light guides, directed to a spectrograph, and collected by a pair of photodiode arrays (1024 elements, for spectral measurements). To avoid photo degradation and re-excitation by consecutive pulses, the samples were placed in a 0.8-mm thick rotating quartz cell.
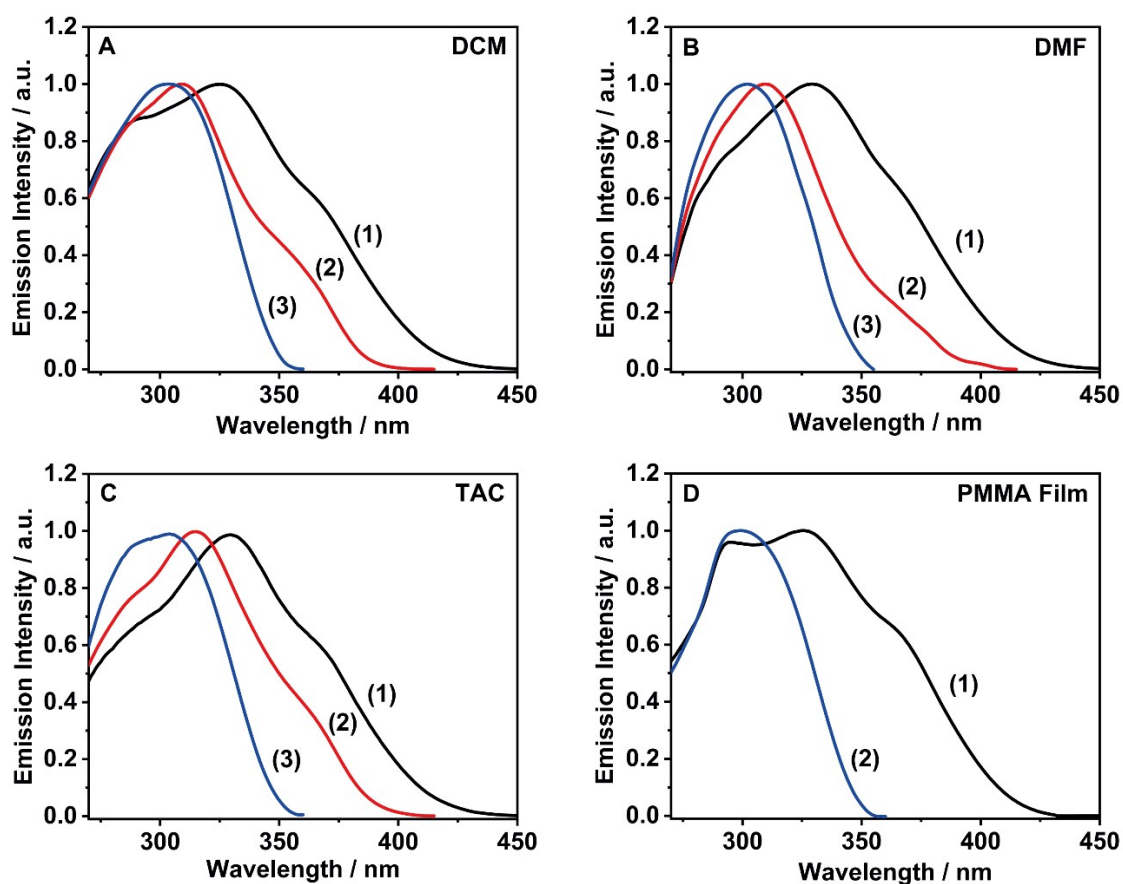
2. Photochemical reaction of TTECOOBu

Figure S1. Changes of the excitation spectra of **TTECOOBu** in (A) DCM, (B) DMF, (C) TAC and (D) PMMA Film with different periods of UV-light irradiation: (1) 0, (2) 60 and (3) 150 min. The observation wavelength for the excitation spectra was 550 nm (black line), 425 nm (red line) and 375 nm (blue line).
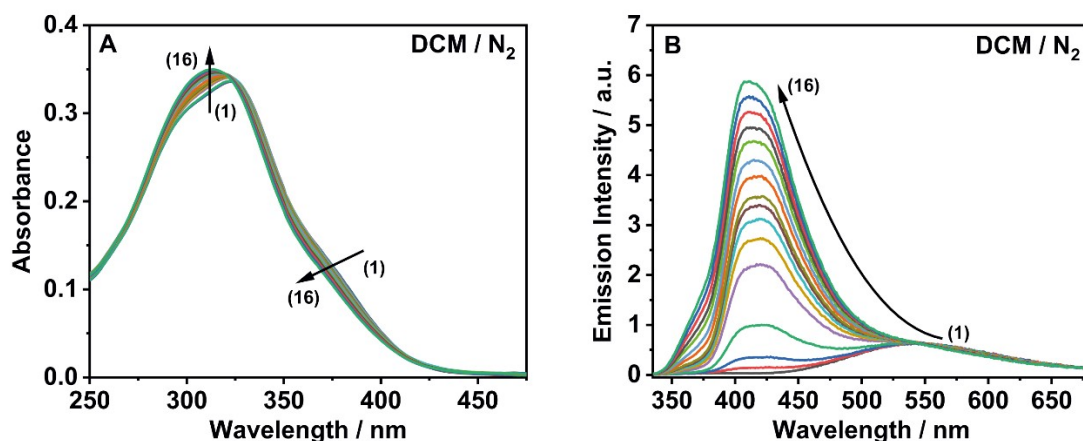
Figure S2. Changes in the absorption (A) and emission (B) spectra of **TTECOOBu** in DCM solutions with different periods of UV-light at 365 nm ($UV_{MAX} = \sim 0.3$ W cm^{-2}). The sample was irradiated under N_2 atmosphere. The irradiation times with UV-light was 0, 2, 5, 10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240 and 270 min. The excitation wavelength for the emission spectra was 325 nm.
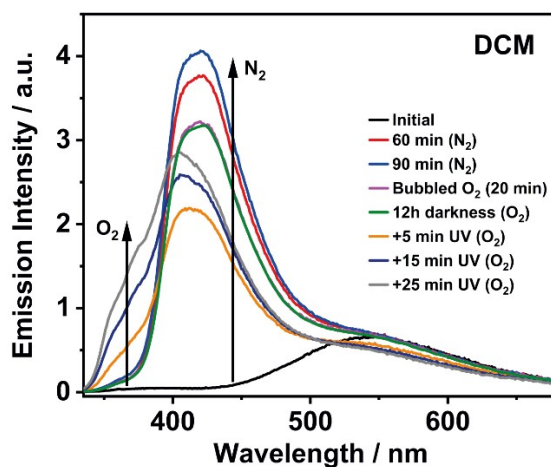

Figure S3. Changes of the emission spectra of **TTECOOBu** in DCM solutions with different periods of UV-light at 365 nm ($UV_{MAX} = \sim 0.3$ W cm^{-2}). The sample was firstly irradiated under N_2 atmosphere for 90 min and then under O_2 atmosphere. The excitation wavelength for the emission spectra was 325 nm.
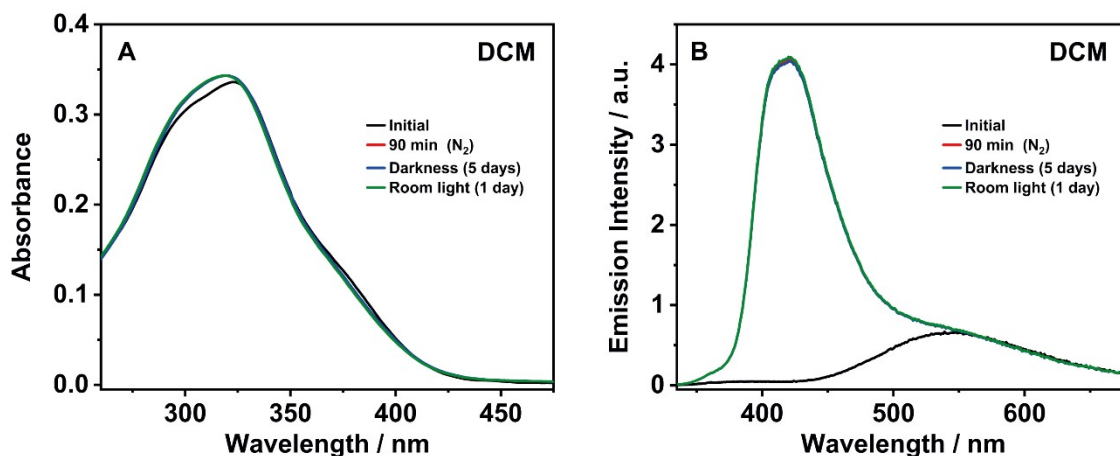
Figure S4. Changes in the absorption (A) and emission (B) spectra of **TTECOOBu** in DCM solutions upon irradiation under N_2 atmosphere for 90 minutes (red line), stored in darkness for 5 days (blue line) and at room light for 1 day (green line). The sample was irradiated with UV-light at 365 nm ($UV_{MAX} = \sim 0.3$ W cm^{-2}). The excitation wavelength for the emission spectra was 325 nm.

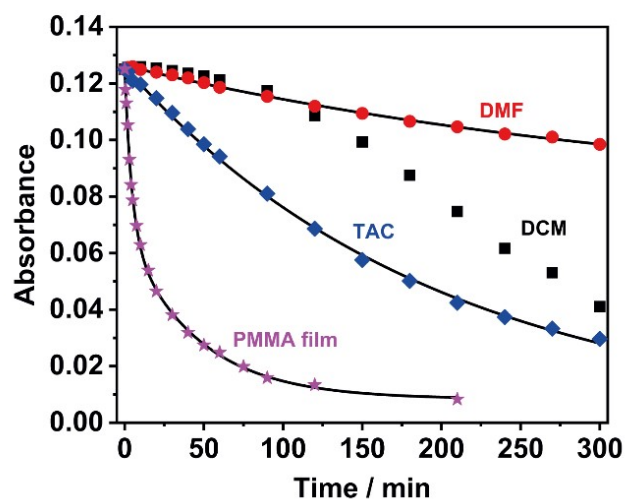**Figure S5.** Kinetics fits for the photocyclization reaction of **TTECOOBu** obtained from the changes observed in the absorption intensity at 370 nm.
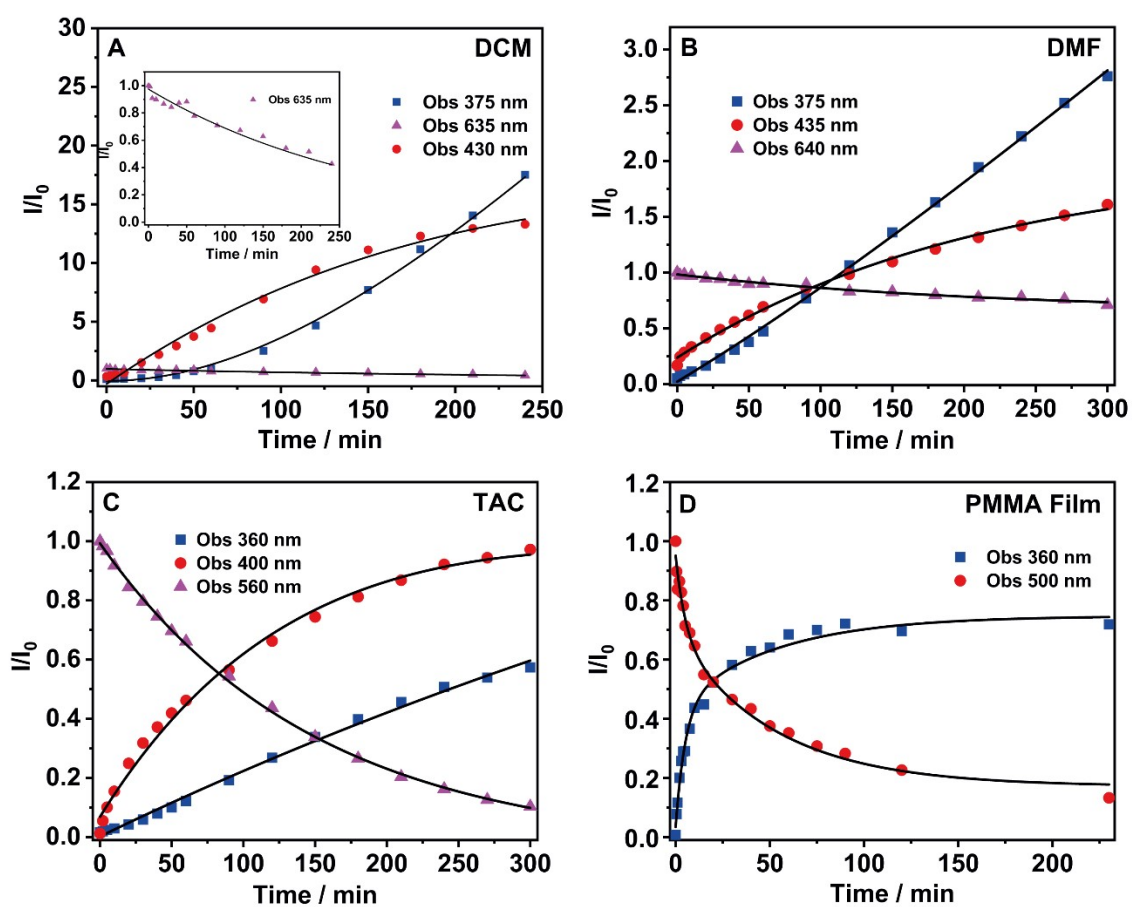
Figure S6. Kinetics fits for the photocyclization reaction of **TTECOOBu** in DCM (A), DMF (B), TAC (C) and in PMMA film (D) obtained from the changes observed in the emission intensity as indicated in the insets.
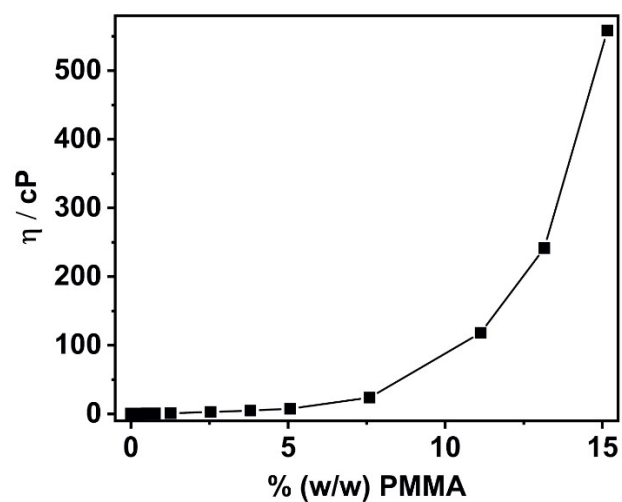
Figure S7. Values of the viscosity of TFH-PMMA solutions as a function of PMMA weight percent.
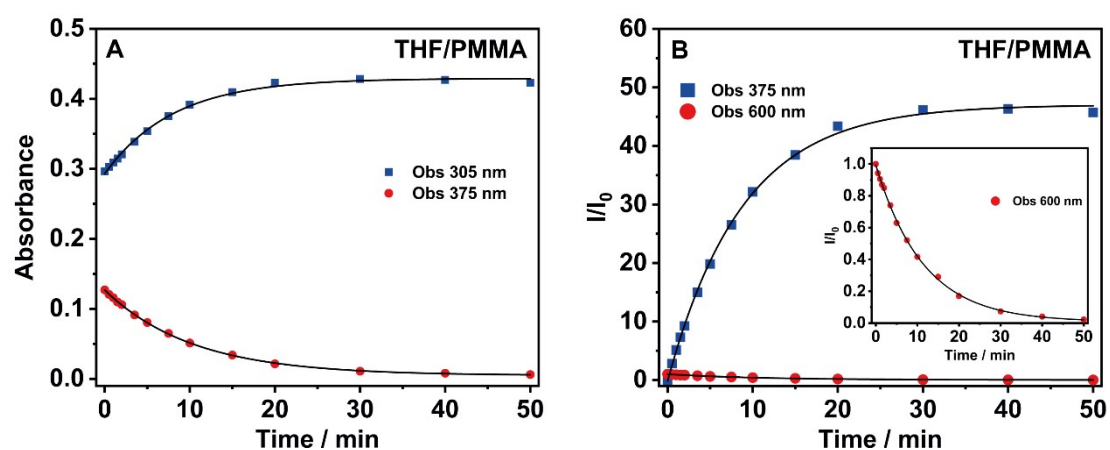

Figure S8. Kinetics fits for the photocyclization reaction of **TTECOOBu** in mixed THF/PMMA solutions obtained from the changes observed in absorption (A) and emission spectra (B) at the indicated wavelengths.
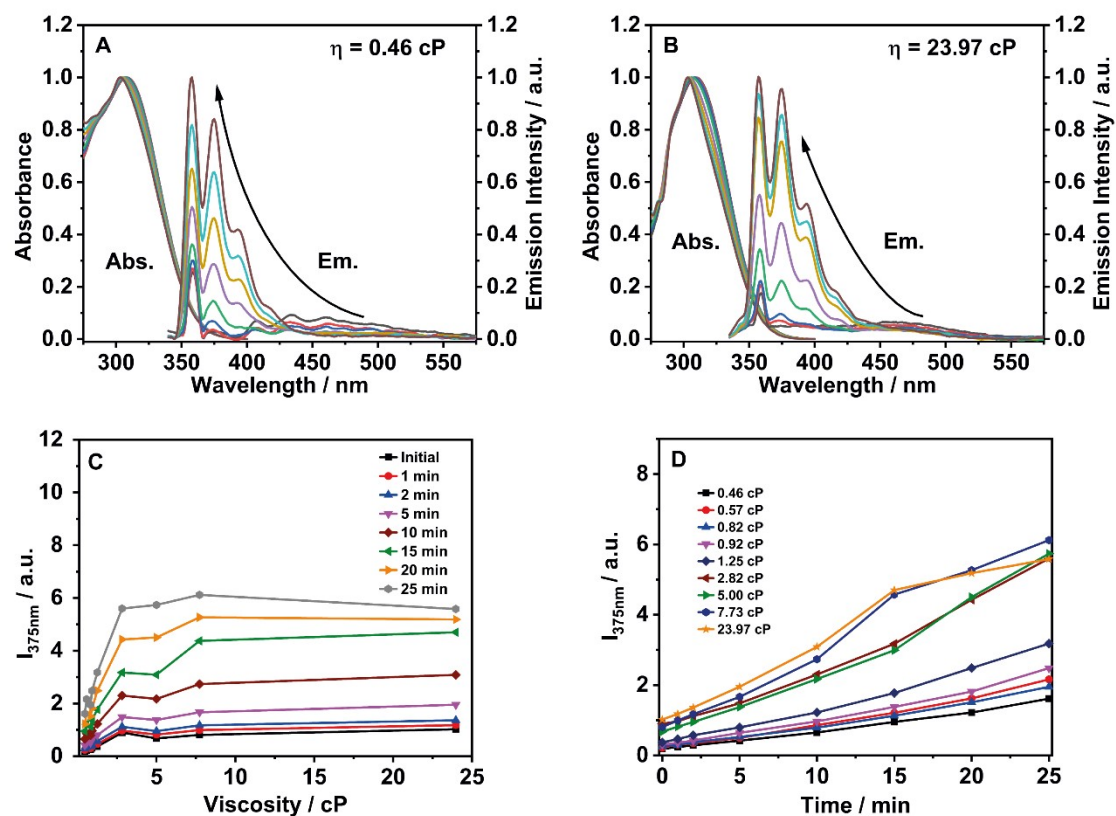
Figure S9. (A, B) Changes in the absorption and emission spectra of **TPE** in mixed THF/PMMA solutions with different viscosities at different irradiation times with UV-light at 365 nm ($UV_{power} = \sim 0.18$ W cm^{-2}). Final photoproduct emission intensity at 375 nm vs (C) viscosity value of the mixture and (D) irradiation time. The viscosity of each sample is indicated in the inset. For emission spectra, the excitation wavelength was 325 nm.
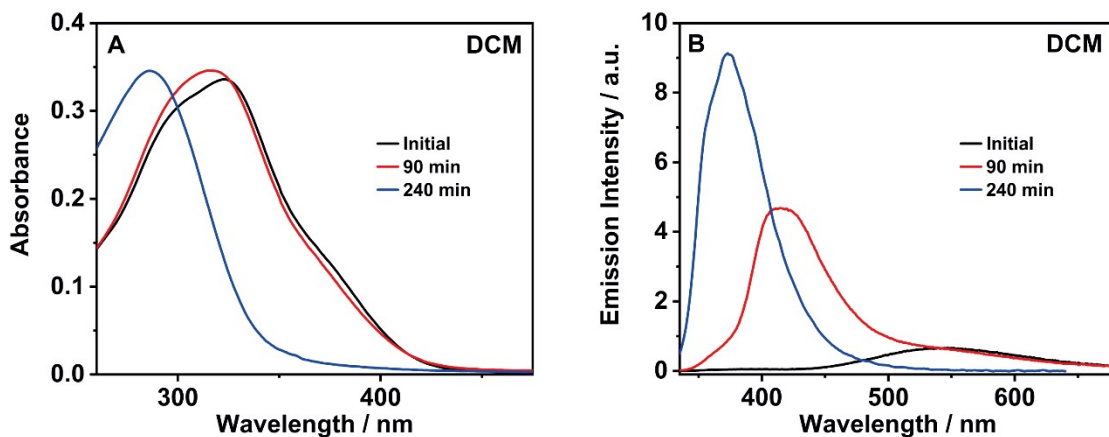
Figure S10. Absorption (A) and emission (B) spectra of the initial (black solid line, t_{irr} = 0min), intermediate (red solid line, t_{irr} = 90 min) and final (blue solid line, t_{irr} = 240 min) species of **TTECOOBu** in DCM solutions. The samples were irradiated at different times (as indicated) with UV-light at 365 nm (UV_{power} = ~ 0.3 W cm^{-2}). For emission spectra, the excitation wavelength was 325 nm.
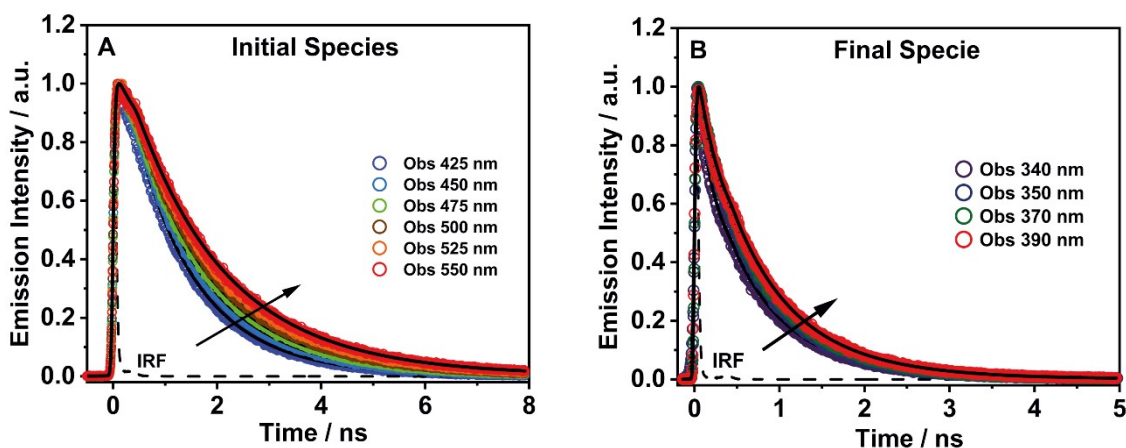
Figure S11. Magic-angle emission decays of (A) initial (t_{irr} = 0 min) and (B) final (t_{irr} = 210 min) species of **TTECOOBu** in PMMA Film upon excitation 325 nm and observation as indicated in the inset. The solid lines are from the best multiexponential fits, and the IRF is the instrumental response function. **Figure S11-A** adapted from reference.[1] The samples were irradiated at different times with UV-light at 365 nm (UV_{MAX} = ~ 0.3 W cm^{-2})

Figure S12. Absorption (A) and emission (B) spectra of initial (black solid line, t_{irr} = 0min), intermediate (magenta solid line, t_{irr} = 6 min) and final (grey solid line, t_{irr} = 40 min) species of **TTECOOBu** in DCM solutions. The samples were irradiated at different times with a pump laser source at 355 nm (UV_{MAX} = ~ 3 mJ cm^{-2}). For emission spectra, the excitation wavelength was 325 nm.

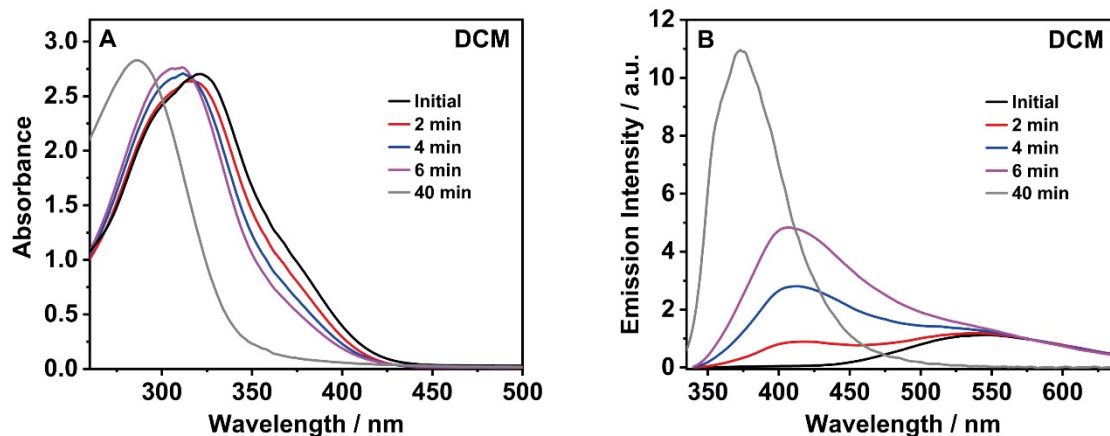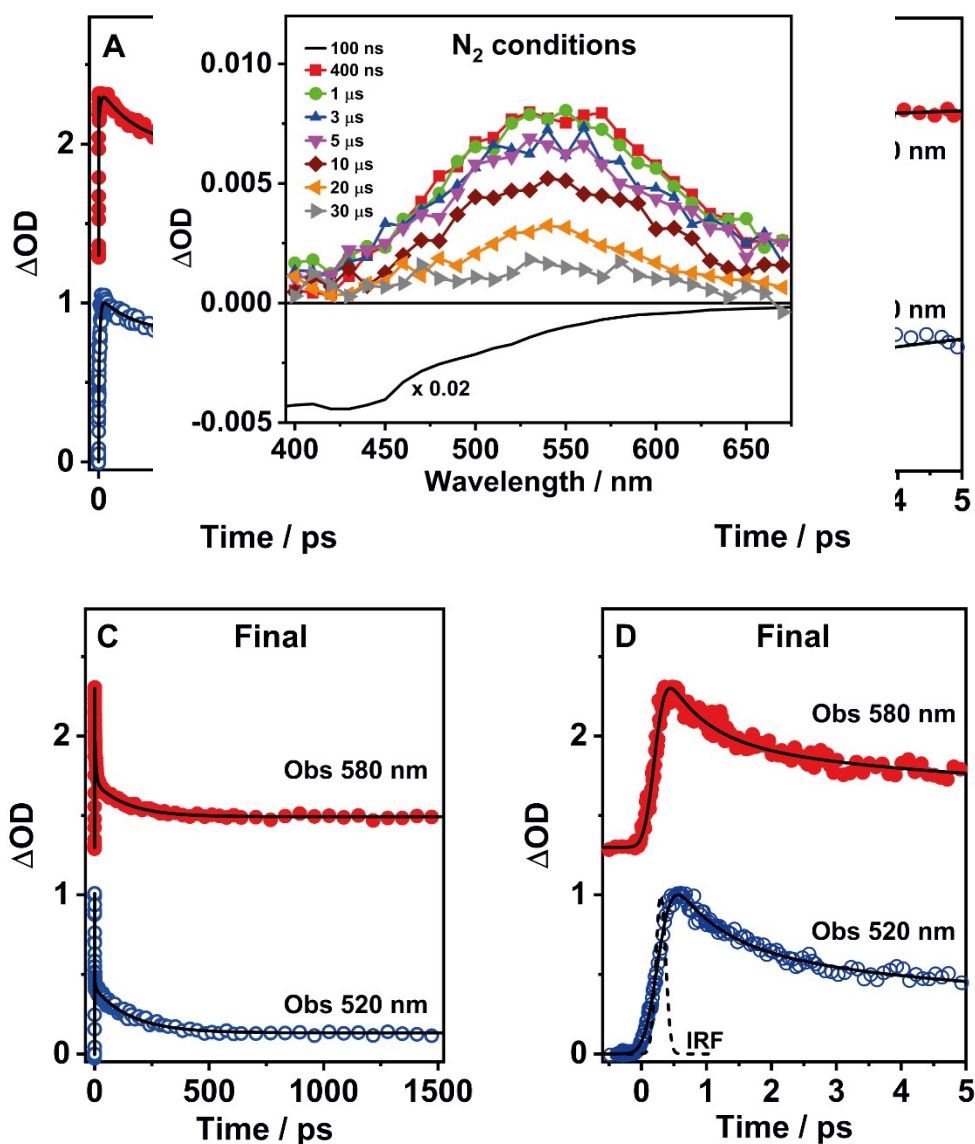**Figure S13.** Representative transient absorption decays of intermediate (A, B) and final (C, D) species of **TTECOOBu** in DCM solutions exciting at 325 nm and observing as indicated at the inset. The solid lines are from the best multiexponential fits, and the IRF is the instrumental response function.

Figure S14. Time-resolved transient absorption spectra of **TTECOOBu** photoproduct in DCM solutions and under nitrogen conditions at different delay times. The excitation wavelength was 355 nm.

Table S1. Values of the photochemical parameters of **TTECOOBu** in the selected media. k_1 are the rate constants for the first step obtained by applying the kinetic model for irreversible consecutive reactions. The kinetic was obtained from the changes observed in absorption spectra at 370 nm.[a]

Medium	k_1 / 10^{-3} (min^{-1})
DCM	-
DMF	0.86
TAC	6.99
PMMA film*	224.21 / 22.33
THF/PMMA	111.98

[a]The data obtained from the kinetic model refer only to the disappearance of I*. *For PMMA film, the disappearance of the initial species decays biexponentially.

Table S2. Weight percent of PMMA and viscosity values of the different mixed TFH-PMMA solutions.

% (w/w) PMMA	Viscosity at 295 K / η (cP)
0	0.46
0.25	0.57
0.50	0.82
0.76	0.92
1.27	1.25
2.54	2.82
3.80	5.00
5.06	7.73
7.59	23.97
11.13	118.27
13.15	241.67
15.16	558.33

Table S3. Values of time constants (τ_i), contribution (c_i), and normalized (to 100) pre-exponential factor (a_i) obtained from the best fit of the emission ps-ns decays of the initial and the final photoproduct of **TTECOOBu** in PMMA Film upon excitation at 325 nm and observation as indicated. The error in τ_i is 10 - 15%. Data from the initial species adapted from reference.[1]

Sample	λ_{obs} (nm)	τ_1 (ns)	a_1	c_1	τ_2 (ns)	a_2	c_2	τ_3 (ns)	a_3	c_3
Initial Species	380	0.40	40	20		59	80		-	
	400		17	8		74	92			
	425					74	65		26	35
	450				1.10	44	34		56	66
	475					23	17		77	83
	500		-			2	2	1.90	98	98
	525					1	1		99	99
	550					-			100	100
	570								100	100
Final Species	340		26	5		50	52		24	43
	350		22	4		58	62		20	34
	370	0.12	19	3	0.66	52	52	1.22	29	45
	390		15	3		41	35		44	62
	410		18	3		67	68		15	29
	430		14	2		50	40		36	58

References:

(1)   M. de la Hoz Tomás, M. Yamaguchi, B. Cohen, I. Hisaki and A. Douhal, *Phys. Chem. Chem. Phys.,* 2023, **25**, 1755.