Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information: Evidence for Ultrafast Formation of Tribenzoylgermyl Radicals Originating from Tetraacylgermane Photoinitiators

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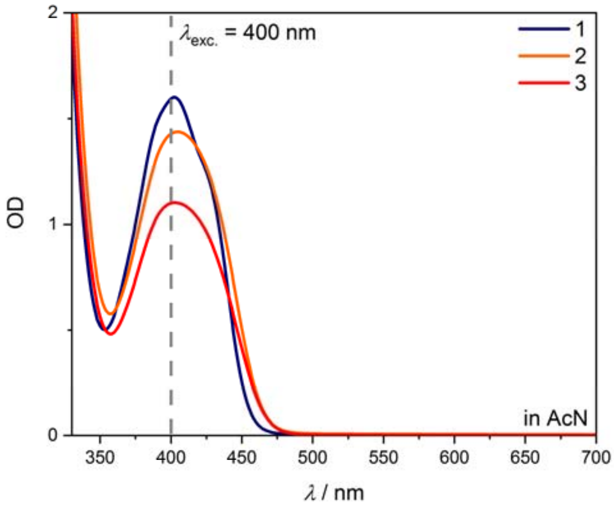
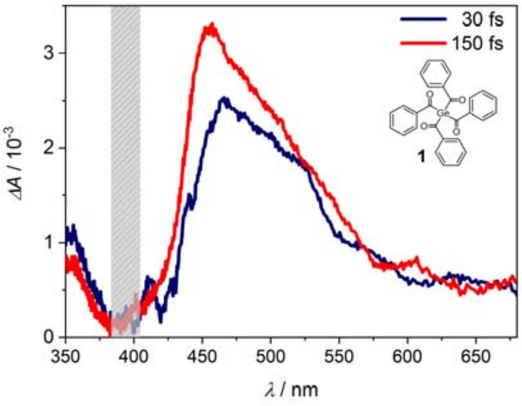
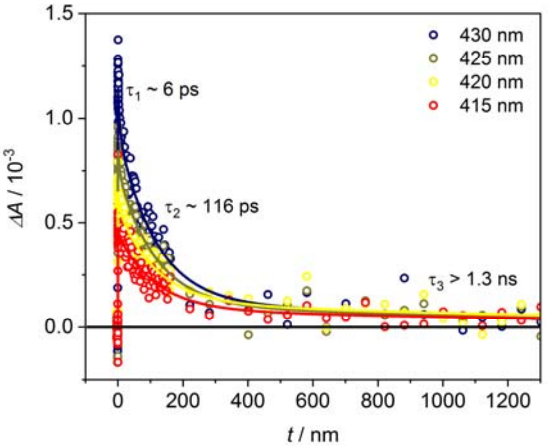


Figure S1. Steady-state UV/Vis absorption spectra of investigated photoinitiators samples as used for fs-transient broadband absorption spectroscopy after 400 nm excitation: **1** tetrabenzoylgermane, **2** tetra-*ortho*-methyl-benzoylgermane, **3** tetra-*ortho*-ethyl-benzoyl-germane.

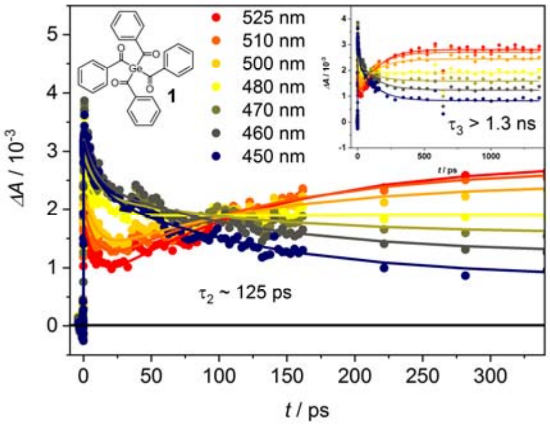
a)


30 fs
150 fs
1
ΔA / 10-3
λ / nm
350
400
450
500
550
600
650
0
1
2
3

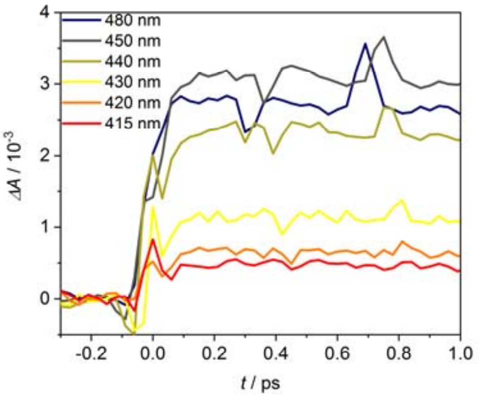
b)


430 nm
425 nm
420 nm
415 nm
τ1 ~ 6 ps
τ2 ~ 116 ps
τ3 > 1.3 ns
ΔA / 10-3
t / nm
0
200
400
600
800
1000
1200
0.0
0.5
1.0
1.5

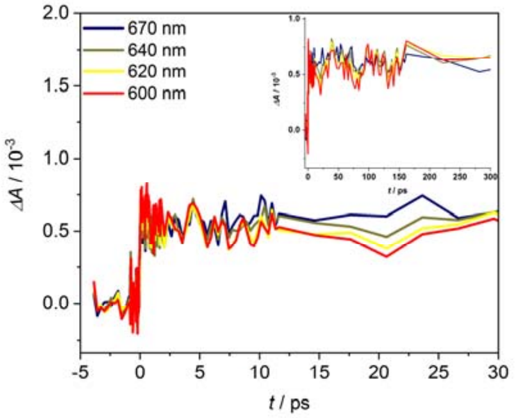
c)


525 nm
510 nm
500 nm
480 nm
470 nm
460 nm
450 nm
1
τ3 > 1.3 ns
τ2 ~ 125 ps
ΔA / 10-3
t / ps
0
50
100
150
200
250
300
0
1
2
3
4
5

d)


480 nm
450 nm
440 nm
430 nm
420 nm
415 nm
ΔA / 10-3
t / ps
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
0
1
2
3
4

e)


670 nm
640 nm
620 nm
600 nm
ΔA / 10-3
t / ps
-5
0
5
10
15
20
25
30
0.0
0.5
1.0
1.5
2.0

f)

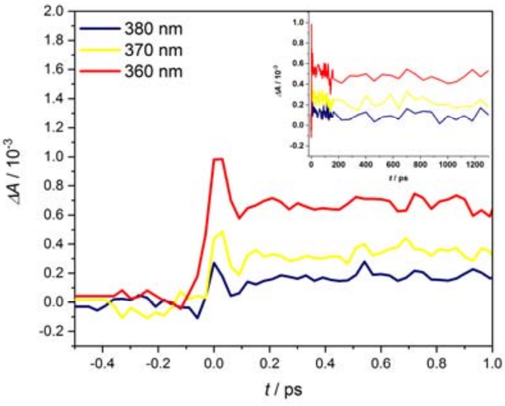

380 nm
370 nm
360 nm
ΔA / 10-3
t / ps
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

Figure S2. a) Transient broadband absorption spectra of **1** for very early delay times after pumping at 400 nm as indicated. Transient responses in the range of 400 nm has been omitted due to scattering of the pump pulse. **b)** Single transients probed between 415-430 nm show a remaining ESA for long delay times > 1.3 ns. **c)** Illustration of the isosbestic point according to the radical formation within ~125 ps by single transients probed between 450-525 nm. Differences between the same time constants in plots **b)** and **c)** accord to different numbers of single transients used for global analysis, which reflects the error of the experiment of ~40 %. **d)** Single transients probed between 415-480 nm reveal negligible GSB-recovery. Single transients **e)** and **f)** probed between 600-670 nm and 360-380 nm, respectively, show an ultrafast rise and remaining ESA for long times > 1.3 ns.

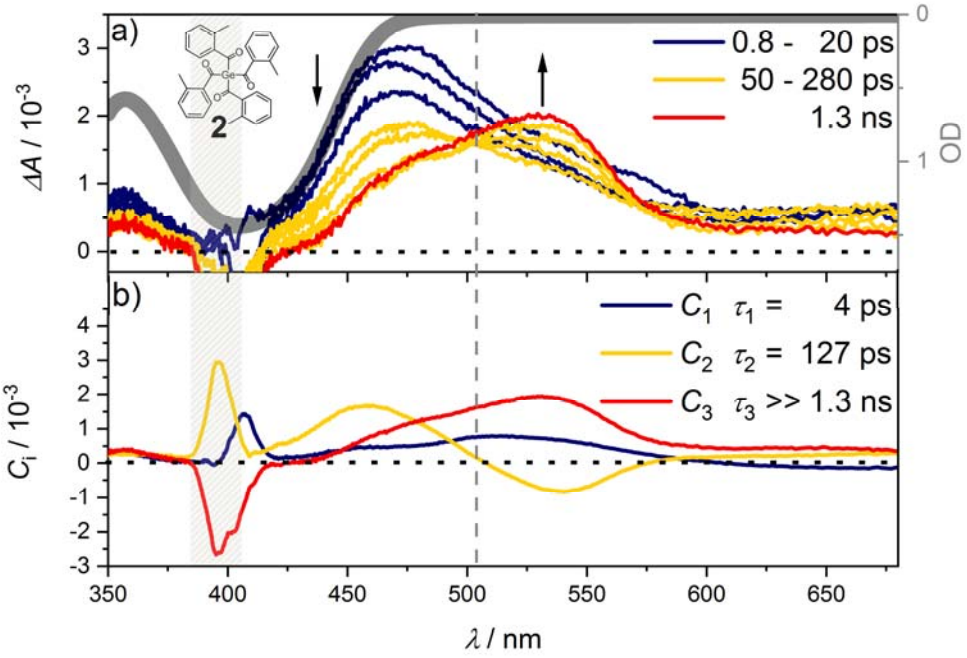


Figure S3. a) TA-spectra of **2** dissolved in AcN recorded after excitation at 400 nm and probed by CaF_2-white light continuum between 350 and 680 nm. The corresponding steady-state UV/Vis absorption spectrum is plotted upside down in grey. A decay associated difference spectrum (DAS) obtained by global analysis of the TA-spectrum is presented in **b)**. The color code of blue, yellow, and red depicts time frames for early, mid, and late delay times as indicated. Horizontal dashed lines indicate zero, while vertical dashed lines guide the eye to isosbestic points. Transient response in the range of 400 nm has been omitted due to scattering of the pump pulse.

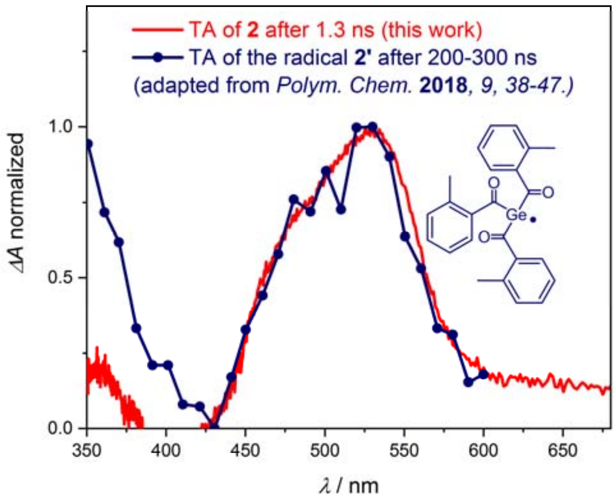


Figure S4. Comparison of transient absorption spectra of the tri *ortho*-methyl-benzoylgermyl radical fragment observed after ~1.3 ns within this work and after 200-300 ns within a recently published laser flash photolysis study.[1]

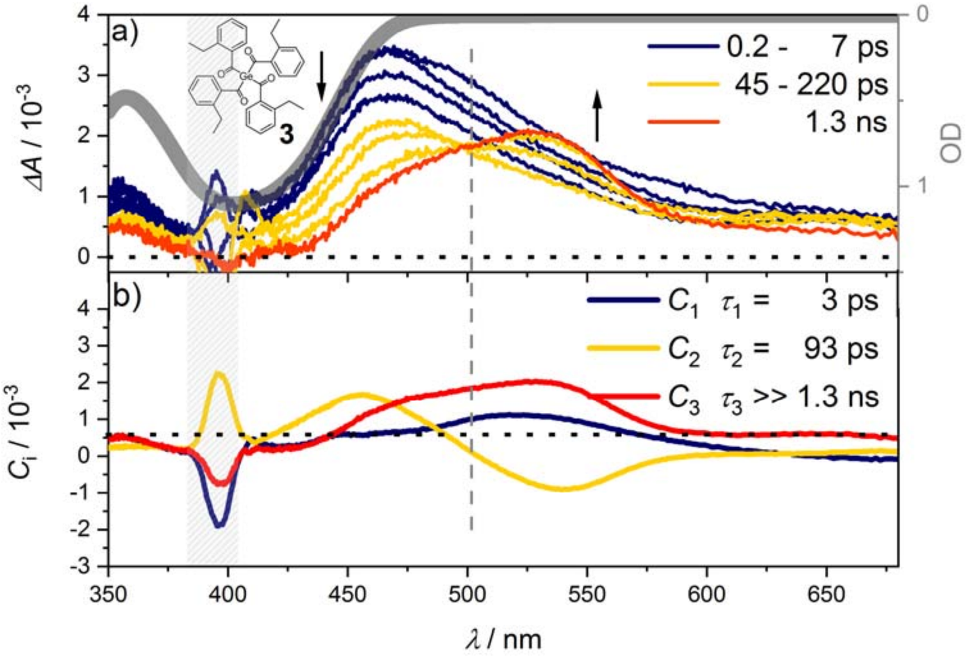


Figure S5. a) TA-spectra of **3** dissolved in AcN recorded after excitation at 400 nm and probed by CaF_2-white light continuum between 350 and 680 nm. The corresponding steady-state UV/Vis absorption spectrum is plotted upside down in grey. decay associated difference spectrum (DAS) obtained by global analysis of the TA-spectrum is presented in **b)**. The color code of blue, yellow, and red depicts time frames for early, mid, and late delay times as indicated. Horizontal dashed lines indicate zero, while vertical dashed lines guide the eye to isosbestic points. Transient response in the range of 400 nm has been omitted due to scattering of the pump pulse.

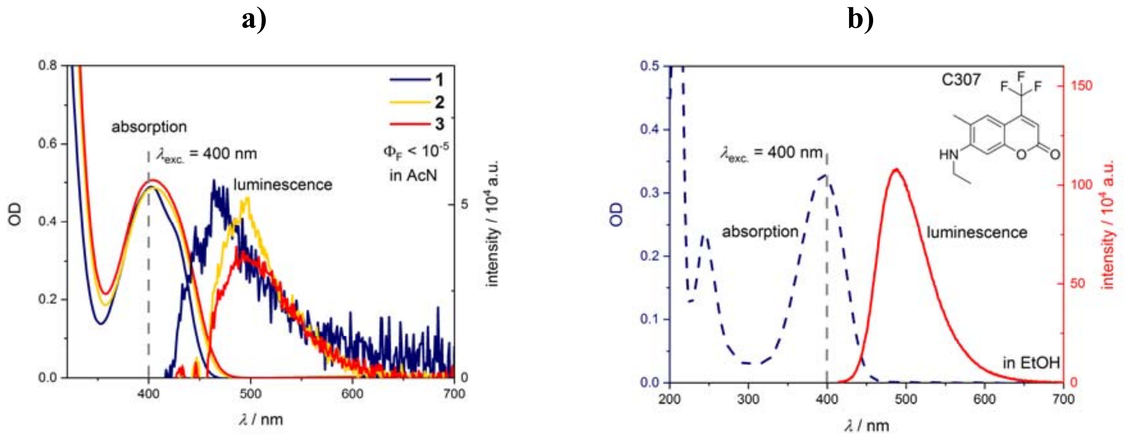


Figure S6. a) Steady-state absorption and luminescence spectra of all investigated tetraacylgermanes used for the determination of quantum yields (refer to **Table S1**). **b)** Reference spectrum of Coumarin 307 (C307) in ethanol. The luminescence spectrum was measured after diluting the sample by factor 5000. The resultant quantum yields were calculated with a reference OD of 6.5×10^{-5} at 400 nm and the following equation.[2]

$$\phi_{\mathrm{F}}^{\mathrm{i}} = \phi_{\mathrm{F}}^{\mathrm{ref}} \frac{f_{\mathrm{OD}}^{\mathrm{ref}}(\lambda_{\mathrm{exc.}})}{f_{\mathrm{OD}}^{\mathrm{i}}(\lambda_{\mathrm{exc.}})} \frac{\int_{\lambda_{\mathrm{em.}}} I_{\mathrm{em.}}^{i}(\lambda_{\mathrm{em.}})\mathrm{d}\lambda_{\mathrm{em.}}}{\int_{\lambda_{\mathrm{em.}}} I_{\mathrm{em.}}^{\mathrm{ref}}(\lambda_{\mathrm{em.}})\mathrm{d}\lambda_{\mathrm{em.}}} \frac{n_{\mathrm{i}}^2}{n_{\mathrm{ref}}^2},$$

$$\text{with } f_{\mathrm{OD}}^{\mathrm{ref/i}}(\lambda_{\mathrm{exc.}}) = 1 - 10^{-\mathrm{OD}_{\mathrm{ref/i}}(\lambda_{\mathrm{exc.}})}.$$

Herein, $\phi_{\mathrm{F}}^{\mathrm{i}}$, $\phi_{\mathrm{F}}^{\mathrm{ref}}$ are the fluorescence quantum yield of the investigated and reference sample, respectively. $f_{\mathrm{OD}}^{\mathrm{ref/i}}$ is the absorption factor given by the $\mathrm{OD}_{\mathrm{ref/i}}$ at the excitation wavelength $\lambda_{\mathrm{exc.}}$. $I_{\mathrm{em.}}^{\mathrm{i/ref}}(\lambda_{\mathrm{em.}})$ represents the emission spectrum summarized for all emission wavelengths, $\mathrm{d}\lambda_{\mathrm{em.}}$, and $n_{\mathrm{i/ref}}^2$ is the refractive index of the applied solvent.

Table S1. Fluorescence quantum yields of investigated tetraacylgermanes determined at an excitation wavelength of 400 nm. C307 in EtOH was used as a standard.

derivative dissolved in AcN	fluorescence quantum yield ϕ_F
1	$8{\cdot}10^{-6}$
2	$5{\cdot}10^{-6}$
3	$4{\cdot}10^{-6}$

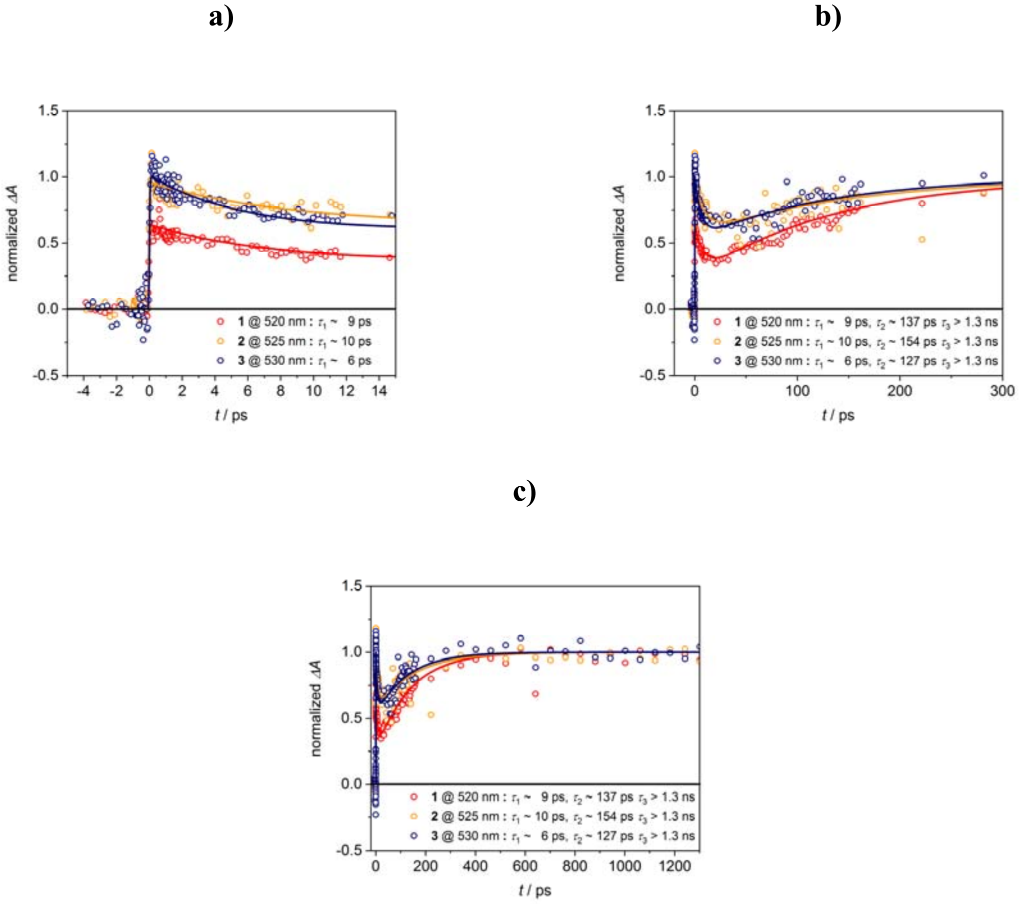
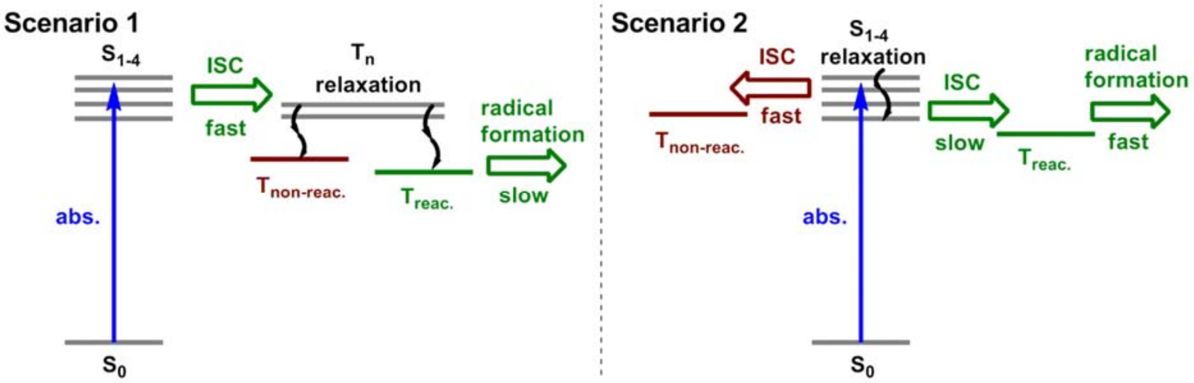


Figure S7. Single transient responses of **1**, **2** and **3** probed at 520, 525, and 530 nm, respectively, after 400 nm excitation presented at **a)** short, **b)** mid, and **c)** long times. The chosen wavelengths correspond to the TA maximum of the formed radicals. Time constants as presented in the bottom of the figures were obtained from triexponential fitting routines. In comparison to time constants determined by global analysis, deviations up to 40 % were observed, which reflect the error of the experiment.

Scheme S1. Two Jabłoński diagrams are postulated for investigated tetraacylgermanes showing a branching between non-reactive and reactive triplet states either via ultrafast ISC and subsequent relaxation processes within the triplet state (Scenario I) or via ISC on different time-scales accompanied by relaxation processes within singlet states (Scenario II). Relaxation processes are IVR, IC, VR and reorganization of the geometry. More details provided in main text.



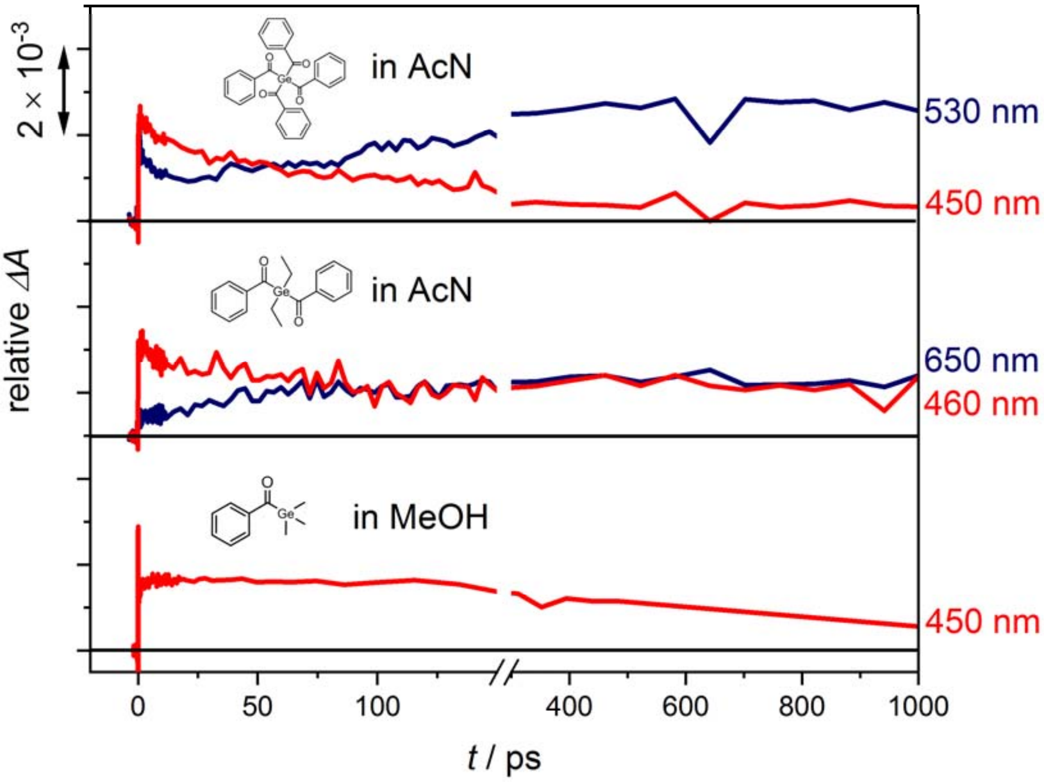


Figure S8. From top to bottom: Single transient responses of tetra- (**1**), bis- and monoacylgermanes recorded with the same laser system by our group are presented for specific probing wavelengths, where the maxima of relevant transient absorption bands after 400 nm excitation are located. The in-depth interpretation of the ultrafast dynamics of tetraacylgermanes is presented in the main paper. For a detailed discussion of bisacylgermanes refer to Vauthey and coworkers.[3] For monoacylgermanes refer to our earlier publication.[4] In contrast to monoacylgermanes dissolved in methanol, bis- and tetraacylgermanes were investigated in acetonitrile (AcN) due to solubility reasons. In the following, the transient responses are discussed from top to bottom.

Top (Tetra), Tetrabenzoylgermane (**1**): The decrease of ESA at 450 nm (response of triplet state) is related to an increase of ESA at 530 nm (response of radical fragment) within ~100 ps. The rise of the additional band at 530 nm is a strong evidence for the ultrafast formation of the tribenzoylgermyl radical fragment as discussed in detail in the main text.

Middle (Bis), the ESA-decay at 460 nm is related to ESA-rise at 650 nm in less than 100 ps according to the population of an excited triplet state. Both bands remain at the same positive relative absorbance level within the recorded time window, which is interpreted as the transient response of the same long-lived triplet state in line with Vauthey and coworkers.[3] Thus, no radical formation is observed within the first ns.

Bottom (Mono),

After excitation of benzoyltrimethylgermane dissolved in MeOH at 400 nm, an ultrafast rise at 450 nm according to excited triplet states is observed, which remains within the recorded time window. For long times, a slight decay is observed, which is not fully resolved within the time window of ~1 ns. In our previous publication from 2017, the slight decay was interpreted as (i) triplet−triplet relaxation from T_2 to T_1, (ii) radical formation, and/or (iii) additional relaxation from quenching processes.[4] Thus, no clear signature of a radical formation was found, but is expected to occur on a post-ps time scale. The example shows that more studies with improved detection methods, e.g. covering the ps to hundreds of ns range without gaps, are needed as briefly discussed in the main paper.

References

1. A. Eibel, J. Radebner, M. Haas, D. E. Fast, H. Freißmuth, E. Stadler, P. Faschauner, A. Torvisco, I. Lamparth, N. Moszner, H. Stueger and G. Gescheidt, *Polym. Chem.*, 2018, **9**, 38-47.
2. K. Rurack and M. Spieles, *J. Anal. Chem.*, 2011, **83**, 1232-1242.

3. D. Neshchadin, A. Rosspeintner, M. Griesser, B. Lang, S. Mosquera-Vazquez, E. Vauthey, V. Gorelik, R. Liska, C. Hametner, B. Ganster, R. Saf, N. Moszner and G. Gescheidt, *J. Am. Chem. Soc.*, 2013, **135**, 17314-17321.
4. P. Jöckle, C. Schweigert, I. Lamparth, N. Moszner, A.-N. Unterreiner and C. Barner-Kowollik, *Macromolecules*, 2017, **50**, 8894-8906.