Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Photocycloadditions in Disparate Chemical Environments

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Characterization methods and instruments

Innolas Tunable Laser System[1–3]

An Innolas Tunable Laser System SpitLight 600 OPO was applied as a light source. An optical parametric oscillator (OPO) was pumped with a diode pumped Nd:YAG laser (repetition rate 100Hz). The energy of the laser pulses was downregulated by an attenuator (polarizer). The beam is redirected into the vertical cylindrical hole of a custom-made sample holder, which contains the samples during the experiments (**Figure S1**). These glass vials are crimped 0.7 mL vials by LLG Labware, Lab Logistic Group GmbH (Art. Nr. 4-008202). The energy of the incident laser pulses was measured by an Energy Max PC power meter (Coherent) directly above the sample holder. Prism and sample holder are positioned in a way that the complete diameter of the hole of the sample holder is covered by th2e incident laser beam.

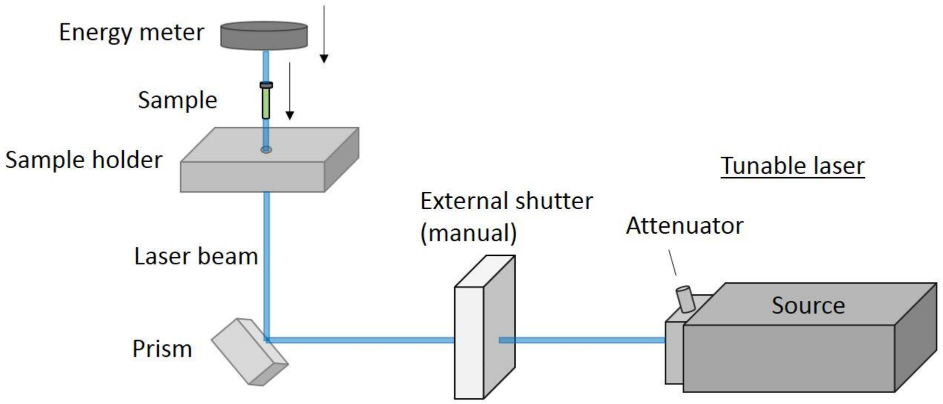


Figure S1. *Experimental setup for the tunable laser experiments. The energy output is regulated with the attenuator and controlled with the energy meter (setup without sample). Measurement of energy and irradiation of samples cannot be carried out simultaneously. An individual setting of the attenuator is necessary before each irradiation experiment.*

Control over the incident number of photons in a tunable laser experiment

The number of photons n_p ($[n_\mathrm{p}]$ = mol) that a monochromatic laser pulse contains can be calculated by application of the Planck-Einstein relation from the energy of the pulse E_pulse, the incident wavelength λ, Planck's constant h and the speed of light c.

$$n_\mathrm{p} = \frac{E_\mathrm{pulse}\ \lambda}{\mathrm{h}\ \ \mathrm{c}\ \mathrm{N_A}}$$

If the absorption of the glass vial and the extent of reflection and scattering at the vial at the respectively relevant wavelength is known, a target energy value can be calculated that must be reached during the above described measurement to guarantee that the desired number of photons penetrates the sample solution during the subsequent irradiation. The wavelength dependent transmittance of the glass vials was determined experimentally using the above setup. Three glass vials were randomly selected as calibration vials. For varying wavelengths and in each case at a constant power output of the laser the energy was measured both with and without the calibration vials fitted into the sample holder. The top parts of these vials were cut off to minimize errors in the procedure, since only the bottom and sides of the glass vials would contribute significantly to the reduction of the photon flux that enters the solution.

The measured energy per pulse without a calibration vial in the sample holder is denoted as E_0 and the measured energy per pulse with a calibration vial in the sample holder as E_n. The transmittance was calculated as the ratio of E_n to E_0. The average transmittance over the measurements of the three vials (T_λ) was plotted together with the respective error (compare **Figure S3**).

$$T_\lambda = \frac{E_\mathrm{n}}{E_0}$$

The target energy per pulse E_0 can be calculated directly from the wavelength λ, the number of pulses k, the transmittance of the glass vial at the respective wavelength T_λ and the desired total photon count n_p.

$$E_0 = \frac{n_\mathrm{p}\,\mathrm{N_A}\,\mathrm{h}\,\mathrm{c}}{k\,T_\lambda\,\lambda}$$

By controlling the target E_0 at the respective wavelength, the number of photons that penetrate each sample solution of one set of experiments as described in the following subsections was guaranteed to be identical despite irradiation at different wavelengths.

Transmittance of the glass vials

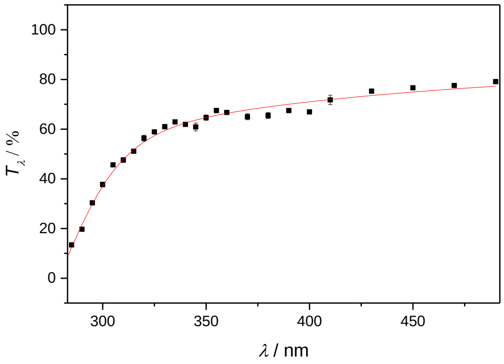
The transmittance of the glass vials that were used for photoreactions with the tunable laser system was determined as follows. Measurement of the energy of laser pulses at a constant energy output was carried out directly above the sample holder first without a glass vial in the sample holder and subsequently with an empty glass vial in the sample holder. The headspace section of the glass vials was removed for these measurements to detect only the absorbance of the bottom of the vial (**Figure S2**). The described procedure was performed for three individual glass vials to account for variabilities between the vials. The obtained averaged values are listed in **Table S1**.

Figure S2. *Left: uncrimped vial; right: vial after removal of the headspace section.*

Table S1. *Transmittance of the glass vials used for the Laser experiments.*

λ / nm	T_λ / %	Mean Deviation / %
285	13.2	0.2
295	19.7	0.6
305	30.3	0.5
315	37.7	1
325	45.6	0.5
335	47.5	1
345	51.1	0.6
355	56.3	1.2
365	58.9	0.8
375	61	0.9
385	62.9	0.9
395	60.4	0.9
405	64.5	1.6
415	60.4	1.1
425	62.1	0.9
435	65.1	0.3
445	65.9	1.2
455	66.3	1.2
465	67.7	3.1
475	68.8	3.0
485	65.6	3.2
495	65.9	4.0

The data was subsequently fitted to obtain values for the wavelengths that have not been measured during the calibration process (compare **Figure S3**).



Model	ExpGro3
Equation	y = A1*exp(x/t1) + A2*exp(x/t2) + A3*exp(x/t3) + y0
Plot	B
y0	85.36613 ± 26.46732
A1	1.63498E14 ± 5.048E15
t1	-9.72709 ± 12.99868
A2	-8.40524E9 ± 2.24463E11
t2	-15.36635 ± 19.4626
A3	-180.78679 ± 656.09892
t3	-157.82413 ± 341.42007
Reduced Chi-Sqr	5.09974
R-Square(COD)	0.99338
Adj. R-Square	0.99149

Figure S3. *Calibration of the glass vial transmittance including a fit to obtain the values that were not determined experimentally.*

Irradiation procedure with control over the photon count

Prior to each irradiation, the respective solution was deoxygenated by purging with a stream of nitrogen for at least five minutes. The tunable laser, including the pump source, was started and the internal shutter was opened several minutes before irradiation to allow the energy output of the laser to stabilize. The direction of the beam was controlled by adjusting the orientation of the prism. The entire cross-sectional area of the sample is irradiated by the laser beam. The intensity of the beam was monitored and adjusted with the built-in polarizer (attenuator). A calculated target energy value was set, which enables the irradiation with the desired number of photons during the irradiation time.

Nuclear magnetic resonance (NMR) spectroscopy

NMR experiments were conducted on a Bruker Ascend 400 instrument, performing at 400 MHz. The δ-scale is referred to the respective deuterated solvents acetonitrile-d_3 or DMSO-d_6, respectively. Abbreviations for the multiplicity of the respective signals are: singlet (s), doublet (d), doublet of the doublet (dd), triplet (t), quartet (q), quintet (qu), multiplet (m).

UV VIS Spectroscopy

The UV/Vis spectra were recorded on a Cary 100 UV-Visible Spectrophotometer (Agilent Technologies, USA) equipped with a tungsten halogen light source (190 to 900 nm, accuracy +/-2 nm) and a R928 PMT detector. The samples were baseline corrected with respect to pure solvent and spectra were recorded between 200 and 800 nm at ambient temperature.

Fluorescence Spectroscopy

Fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence Spectrometer using quartz cuvettes loaded with 700 µL of sample solution. The spectra were recorded in acetonitrile or dimethylsulfoxide at ambient temperature. The excitation wavelength and sample concentration are given in the description of the respective spectra.

Experimental part

Materials

All chemicals and solvents were used as received without further purification.

Acetonitrile-d_3 (> 99 %, Sigma-Aldrich), 4-acetoxystyrene (96 %, Acros Organics), 1-bromopyrene (95 %, Alfa Aesar), dichloromethane (DCM, analytical reagent grade, Fisher Scientific), anhydrous dimethylformamide (DMF (dry), > 99 %, Sigma-Aldrich), dimethylformamide (DMF, analytical grade, Fisher Scientific), ethyl acetate (EA, analytical reagent grade, Fisher Scientific), palladium(II) acetate (47 % Pd, Merck), sodium bicarbonate (> 99 %, Roth), sodium chloride (> 99 %, Thermo Fisher Scientific), triethanolamine (98 %, Alfa Aesar), triethylamine (> 99%, Sigma-Aldrich), triphenylphosphine (99 %, chem-supply).

Hydroxy-styrylpyrene (StyP-OH)

Hydroxy-styrylpyrene was synthesized following a similar reaction procedure published previously in the literature.[4,5]

4-Acetoxystyrene (0.54 mL, 0.58 g, 3.56 mmol, 1.00 eq.), 1-bromopyrene (1.00 g, 3.56 mmol, 1.00 eq.) and palladium(II) acetate (8.00 mg, 35.6 µmol, 0.01 eq.), triphenylphosphine (18.7 mg, 71.1 µmol, 0.02 eq.) and triethylamine (0.73 mL, 1.00 g, 9.88 mmol, 2.78 eq.) were dissolved in DMF (19.8 mL), degassed with nitrogen for 20 minutes and heated to 100 °C. After stirring for 1 day, the solvents were removed under reduced pressure. The obtained solid dissolved in ethyl acetate (ca. 100 mL), subsequently washed with water (3 x 50 mL) and brine (50 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure.

To obtain the final hydroxy-structure the crude product was deprotected via suspension with $NaHCO_3$ (0.79 g, 9.44 mmol, 3.00 eq.) in a mixture of ethanol (100 mL) and water (25 mL) under reflux for 3 hours. The mixture was precipitated into a mixture of 1M HCl (100 mL) and ice water (300 mL), filtered, washed with water and purified using a flash chromatography system (cyclohexane / ethyl acetate from 9 : 1 to 8 : 2) to obtain 0.50 g product (yield 41 %) as a yellow powder.

^{1}H-NMR (400 MHz, Acetonitrile-d_3) δ / ppm = 8.60 (d, J = 9.3 Hz, 1H, l), 8.38 (d, J = 8.1 Hz, 1H, e), 8.25 – 8.20 (m, 3H, h,f), 8.17 (d, J = 9.3 Hz, 1H, k), 8.11 (d, J = 16.1 Hz, 1H, c), 8.10 (s, 2H, g), 8.03 (t, J = 7.7 Hz, 1H, i), 7.66 – 7.62 (m, 2H, b), 7.39 (d, J = 16.1 Hz, 1H, d), 7.1 – 7.2 (bs, 1H, -OH), 6.93 – 6.88 (m, 2H, a).

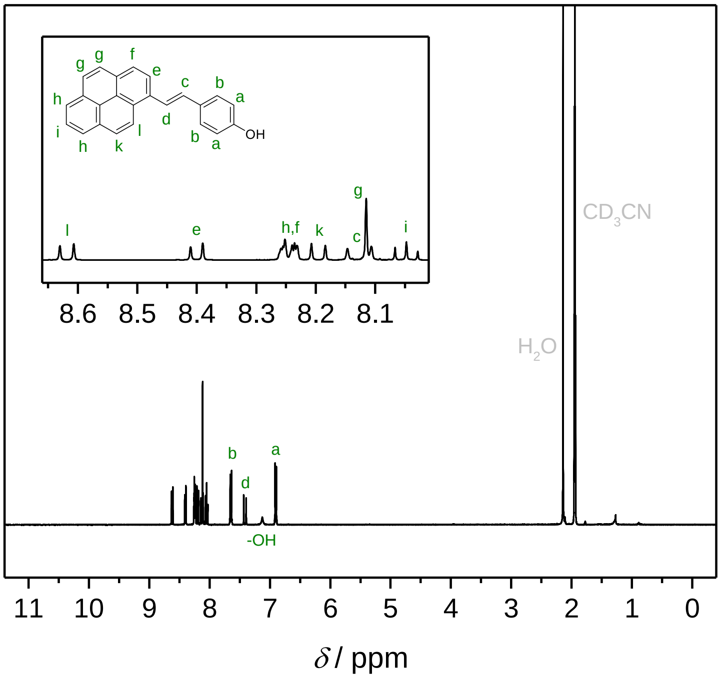


Figure S4. *^{1}H NMR spectrum of StyP-OH recorded in deuterated acetonitrile.*

Irradiation Procedures

For the photochemical experiments, stock solutions were prepared and degassed with nitrogen (ca. 15 min). The stock solution was distributed into with nitrogen (ca. 5 min) flushed laser vials and subsequently irradiated using the Innolas Tunable Laser system.

The stock solutions were prepared with two different concentrations (5 and 10 mM) and two different solvents (**Acetonitrile-*d*$_3$** and **DMSO-*d*$_6$**) to obtain the following samples:

5 mM: 0.80 mg (2.50 µmol) styrylpyrene in 0.5 mL of the respective solvent

10 mM: 1.60 mg (5.00 µmol) styrylpyrene in 0.5 mL of the respective solvent

Irradiation experiments were performed according to the following parameters:

Action Plot for the reactivity relative to the number of absorbed photons

λ [nm]	**Photons [mol]**	**Pulses**	**Energy [mJ]**
310	8.09E-07	1000	656
330	1.44E-06	1000	854
350	5.61E-07	1000	297
370	3.51E-07	500	349
390	3.69E-07	500	336
410	8.34E-07	1000	339
415	1.70E-06	1000	671
420	4.42E-06	3000	571
425	1.19E-05	8000	565
430	2.90E-05	22500	476
435	6.29E-05	45000	514
440	1.16E-04	45000	928
445	1.82E-04	90000	718
450	2.42E-04	90000	931
455	2.95E-04	180000	573
460	3.22E-04	180000	616
465	3.60E-04	180000	679
470	3.80E-04	180000	692

Temperature-dependent reactivity

A number of irradiation experiments at elevated temperature (37 °C) were carried out in a similar setup, however, employing a Coherent Opolette 355 tunable OPO operating at 20 Hz repetition rate, with irradiation times being adjusted accordingly (note that the different energies per pulse have previously been shown to have no significant effect on the 2+2 cycloaddition of styrylpyrene).[6] The glass laser vials were placed in a heated sample holder at constant T = 37 °C and allowed to warm to the respective temperature for 5 min, before starting irradiation.

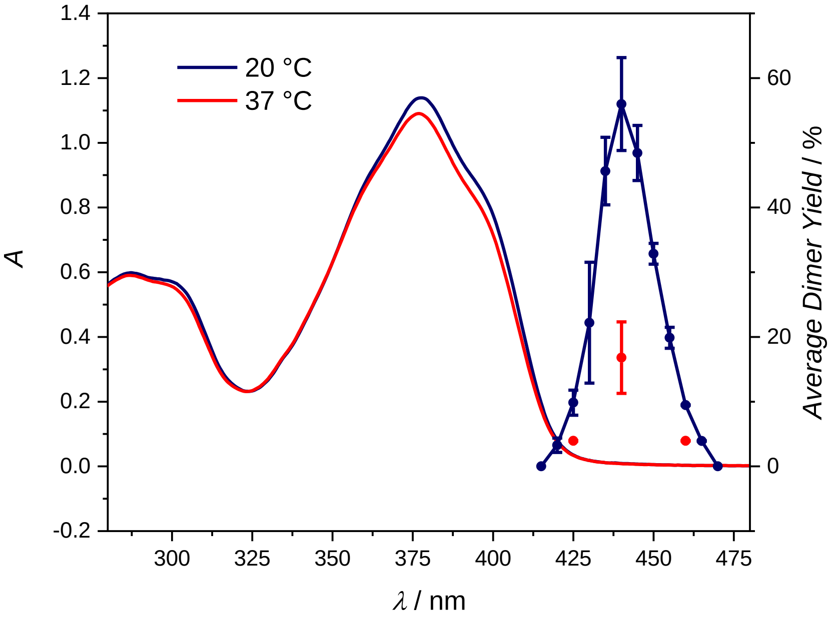


Figure S5: *Absorption spectra of styrylpyrene and wavelength-dependent reactivity map at different temperatures.*

References

(1) Fast, D. E.; Lauer, A.; Menzel, J. P.; Kelterer, A.-M.; Gescheidt, G.; Barner-Kowollik, C. Wavelength-Dependent Photochemistry of Oxime Ester Photoinitiators. *Macromolecules* **2017**, *50* (5), 1815–1823.

(2) Tuten, B. T.; Menzel, J. P.; Pahnke, K.; Blinco, J. P.; Barner-Kowollik, C. Pyreneacyl Sulfides as a Visible Light-Induced Versatile Ligation Platform. *Chem. Commun.* **2017**, *53* (32), 4501–4504.

(3) Menzel, J. P.; Noble, B. B.; Lauer, A.; Coote, M. L.; Blinco, J. P.; Barner-Kowollik, C. Wavelength Dependence of Light-Induced Cycloadditions. *J. Am. Chem. Soc.* **2017**, *139* (44), 15812–15820.

(4) Doi, T.; Kawai, H.; Murayama, K.; Kashida, H.; Asanuma, H. Visible-Light-Triggered Cross-Linking of DNA Duplexes by Reversible [2+2] Photocycloaddition of Styrylpyrene. *Chem. Eur. J.* **2016**, *22* (30), 10533–10538.

(5) Bialas, S.; Michalek, L.; Marschner, D. E.; Krappitz, T.; Wegener, M.; Blinco, J.; Blasco, E.; Frisch, H.; Barner-Kowollik, C. Access to Disparate Soft Matter Materials by Curing with Two Colors of Light. *Adv. Mater.* **2019**, *31*, 1807288.

(6) Marschner, D.; Frisch, H.; Offenloch, J.T.; Tuten, B.T.; Becer, R.; Walther, A.; Goldmann, A.S.; Tzvetkova, P.; Barner-Kowollik, C. Visible Light [2+2] Cycloadditions for Reversible Polymer Ligation. *Macromolecules* **2018**, *51*, 3802-3807.