Supporting Information

Fully Independent Photochemical Reactivity in One Molecule

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1 Additional Data

1.1 Small Molecule Study

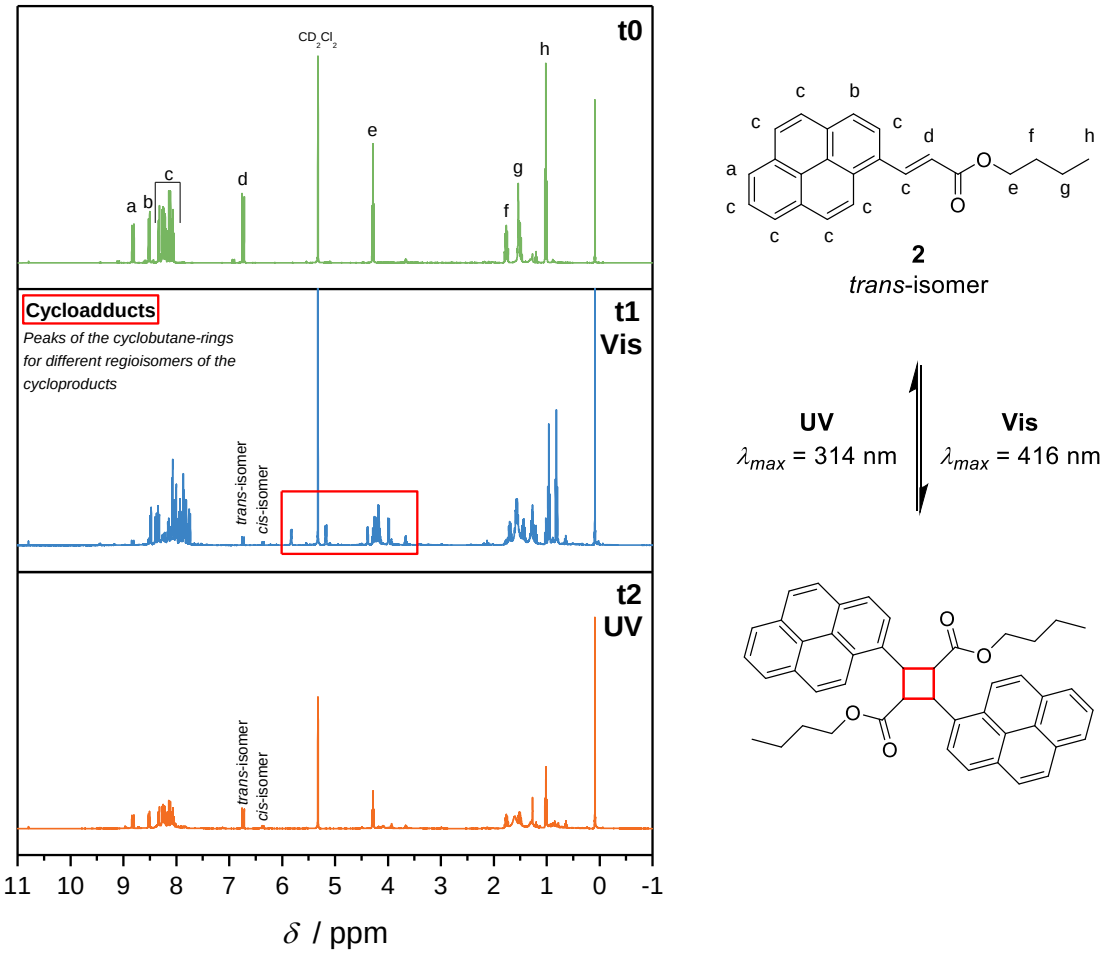


Figure S1. *Proton NMR (recorded in deuterated dichloromethane, 400 MHz) of* ***2*** *before irradiation (t0), after irradiation with visible light (*λ_{max} *= 416 nm, t1), and subsequent UV light irradiation (*λ_{max} *= 314 nm, t2). An enlarged version which is highlighting the crucial magnetic resonances is depicted in Figure S2.*

Comparing the proton NMR spectra of **2** before and after irradiation with visible light (Figure S1 and S2), new magnetic resonances can be detected (close to δ = 5.82, 5.17, 4.38, 4.22 and 3.98 ppm), which can be assigned to the expected photoproducts and are comparable to known systems.[6] In addition, the NMR measurement revealed that **2** is able to undergo photoisomerisation from the starting *trans*-form (δ = 6.74 ppm) to its *cis*-isomer, resulting in a new doublet at δ = 6.36 ppm. Subsequent irradiation with UV-A light (Figure S1 and S2) shows the complete reversion of the photoproducts (close to δ = 5.82, 5.17, 4.38, 4.22 and 3.98 ppm) but not only to the starting *trans*-isomer of **2** but a mixture of *trans*-**2** and its *cis*-structure.

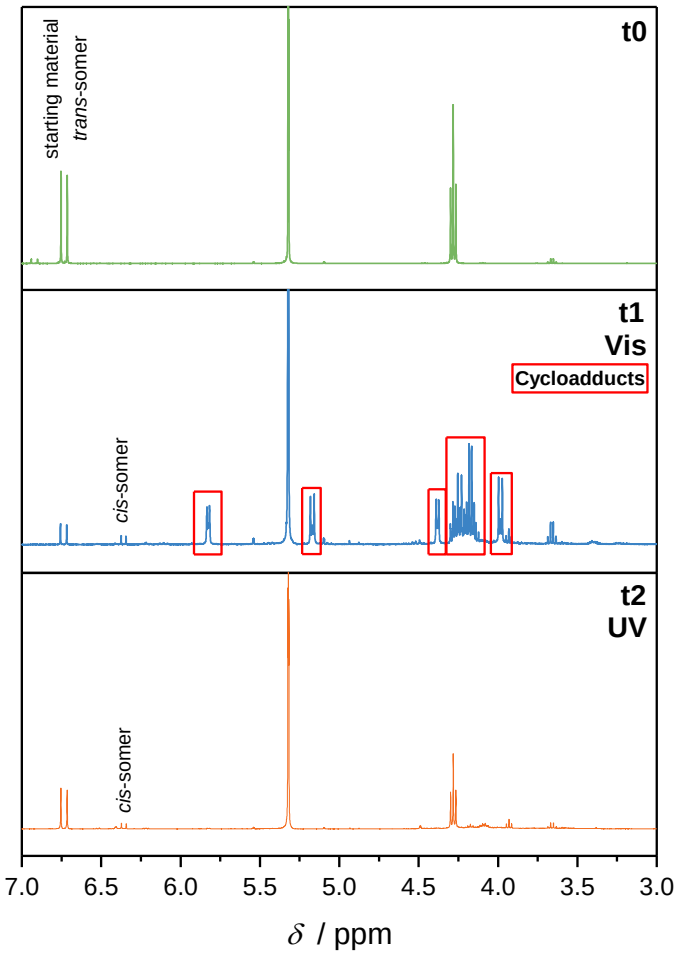
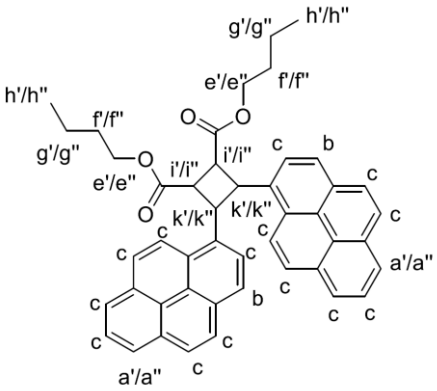


Figure S2. *Enlarged proton NMR spectrum (recorded in deuterated dichloromethane, 400 MHz) of* ***2*** *before irradiation (t0), after irradiation with visible light (λ_{max} = 416 nm, t1), and subsequent UV light irradiation (λ_{max} = 314 nm, t2). A complete NMR spectrum which is highlighting the crucial magnetic resonances is depicted in Figure S1.*



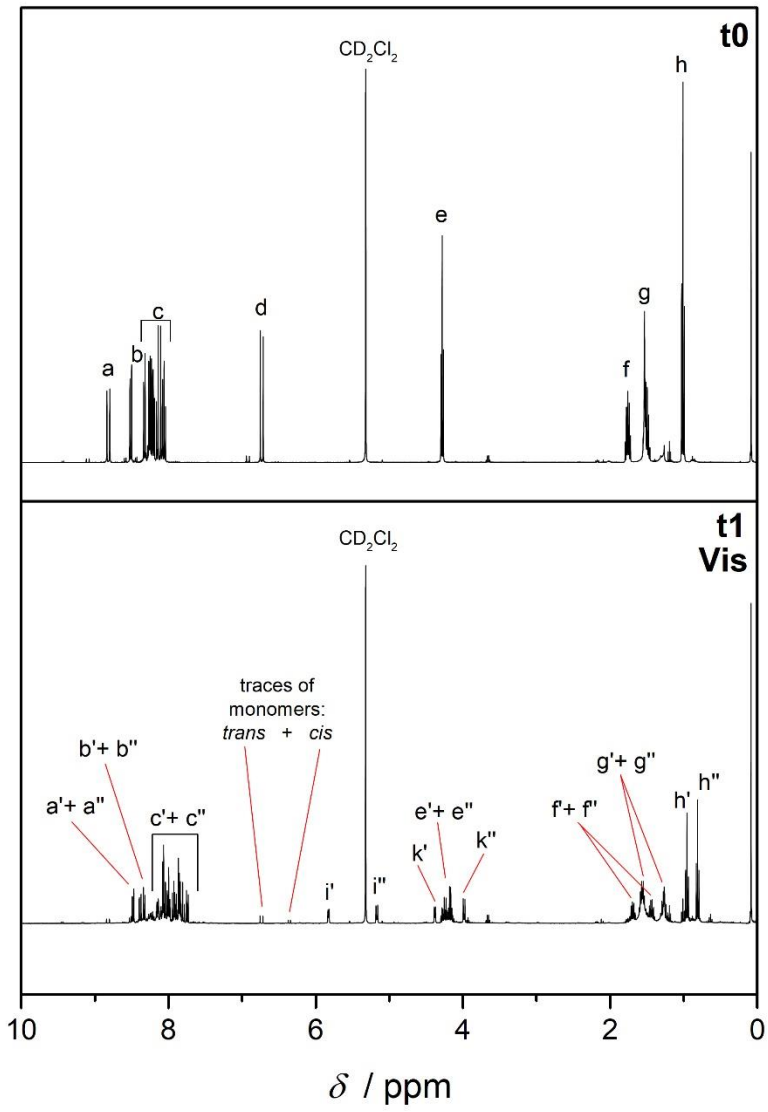


Figure S3*. Comparison of the proton NMR spectra of* ***1*** *before (t0) and after irradiation for 1 h (t1), both in deuterated dichloromethane. The curve in t1 indicates visible light-induced formation of two different cyclobutane-dimers of* ***1****.*

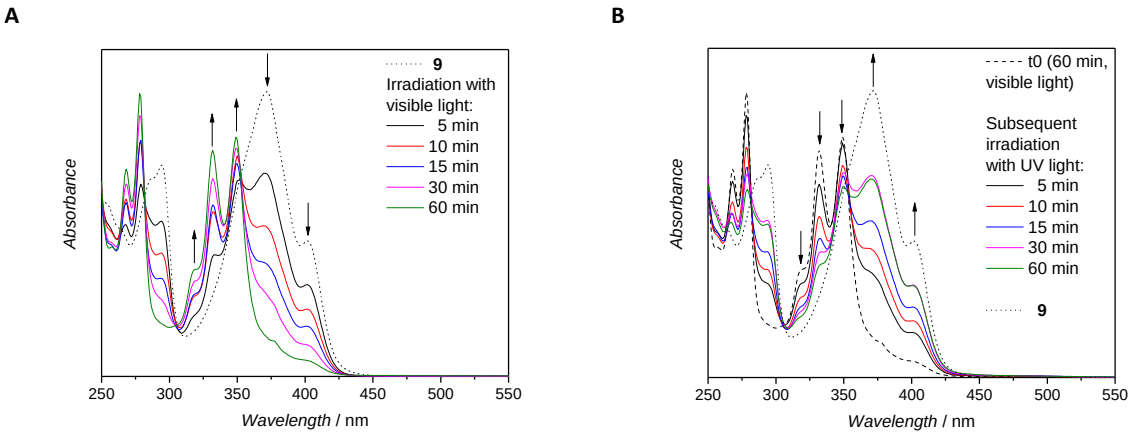


***Figure S4**. Conversion of **1** under irradiation with visible and subsequently UV light indicating the time at which maximum conversion is obtained.*

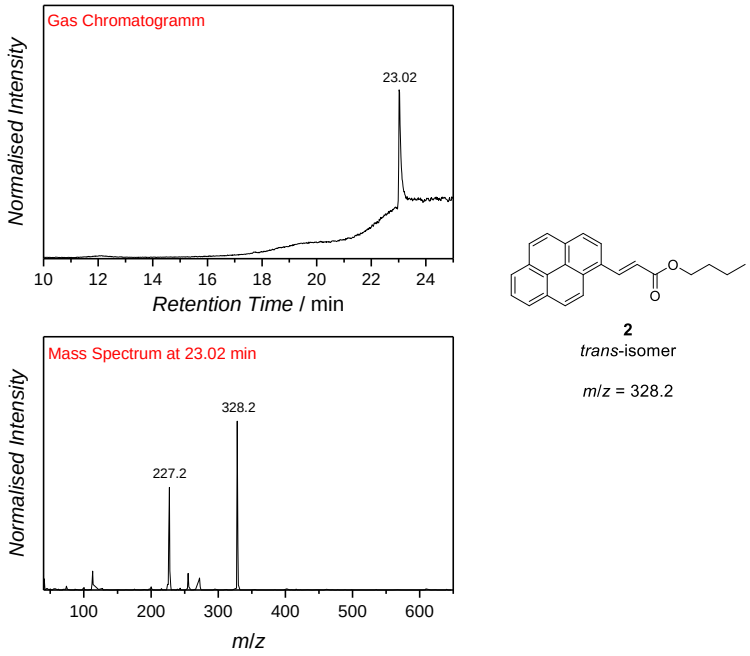


***Figure S5**. GC-MS measurement of **2** before irradiation.*

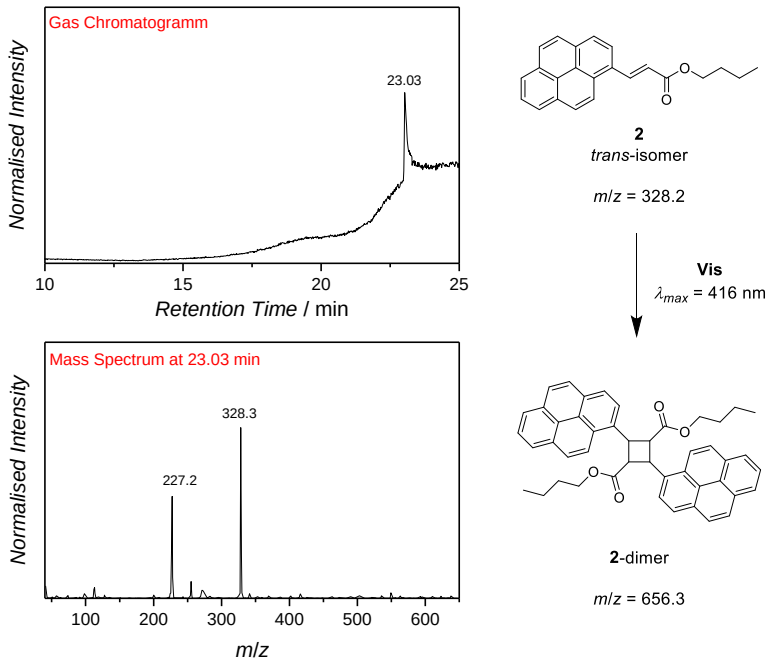


***Figure S6.** GC-MS of **2** after irradiation with visible light (λ_{max} = 416 nm). No photodamage is observed during this reaction since no new peaks are arising in the gas chromatogram or the mass spectrum in comparison with Figure **S5**.*

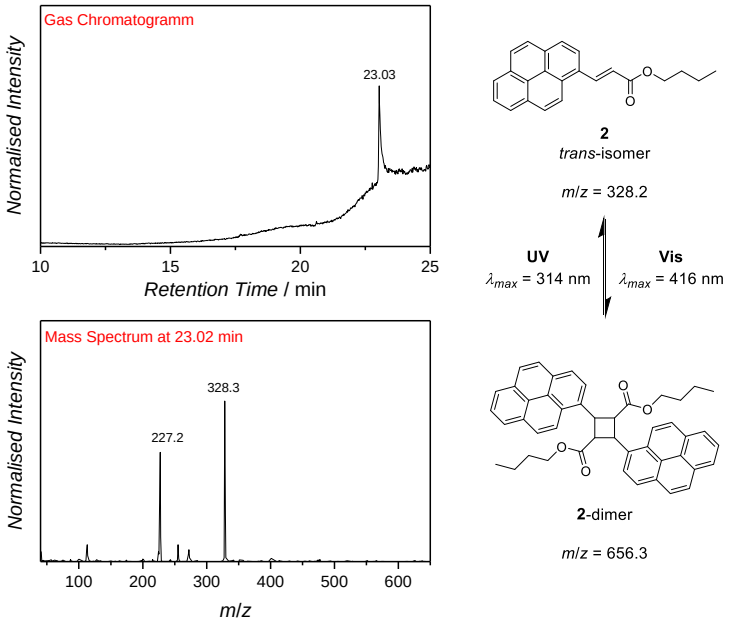


Figure S7. *GC-MS of* ***2*** *after irradiation with visible light (λ_{max} = 416 nm) und subsequent irradiation with UV light (λ_{max} = 314 nm). No photodamage is observed during this reaction, since no new peaks are arising in the gas chromatogram or the mass spectrum in comparison with Figure S5 and Figure S6.*

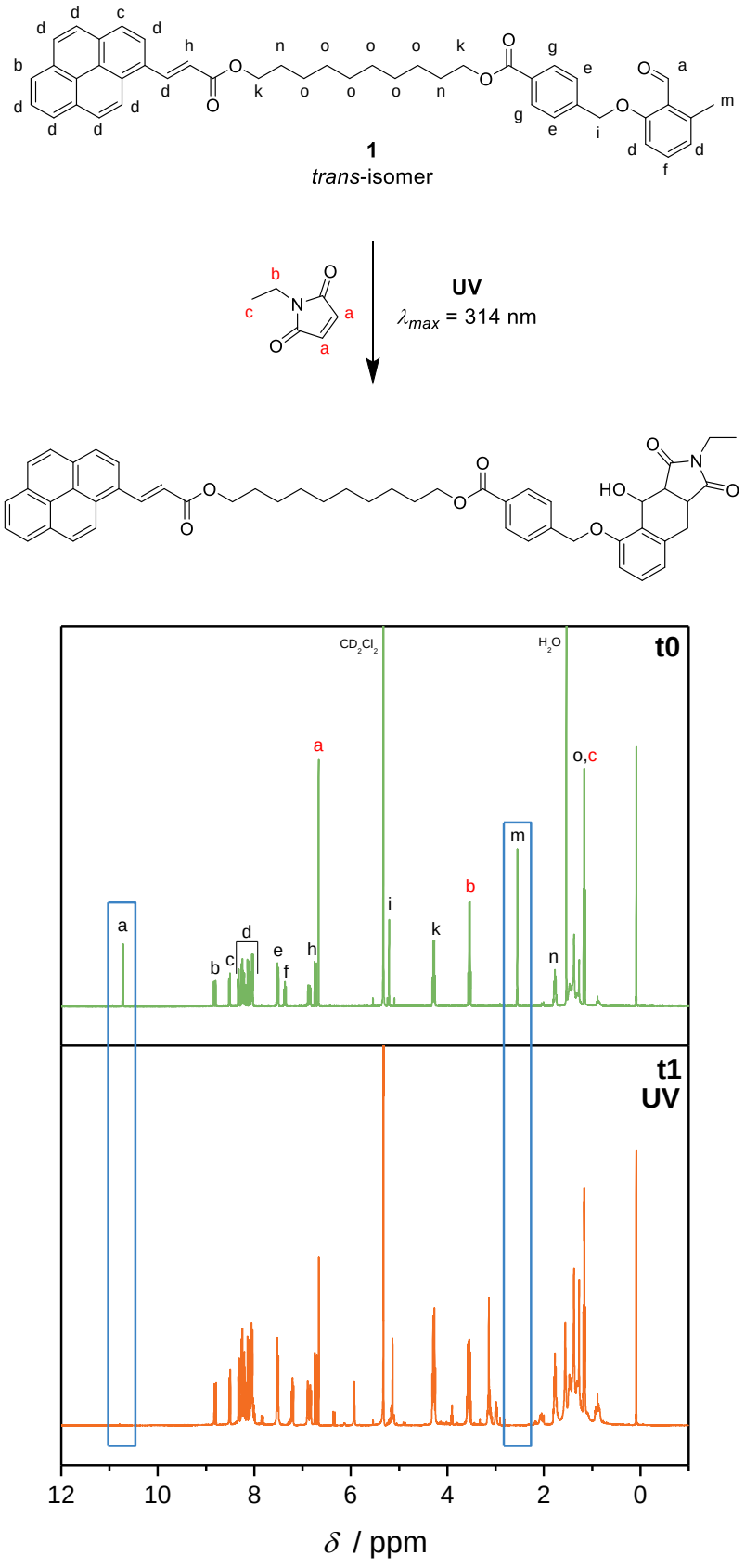


Figure S8. *Proton NMR (recorded in deuterated dichloromethane, 400 MHz) of* ***1*** *before irradiation (t0) and after irradiation with UV light (*λ_{max} *= 314 nm, t1). The disappearance of the magnetic resonances* a *and* m *proves the complete consumption of the o-MBA group.*

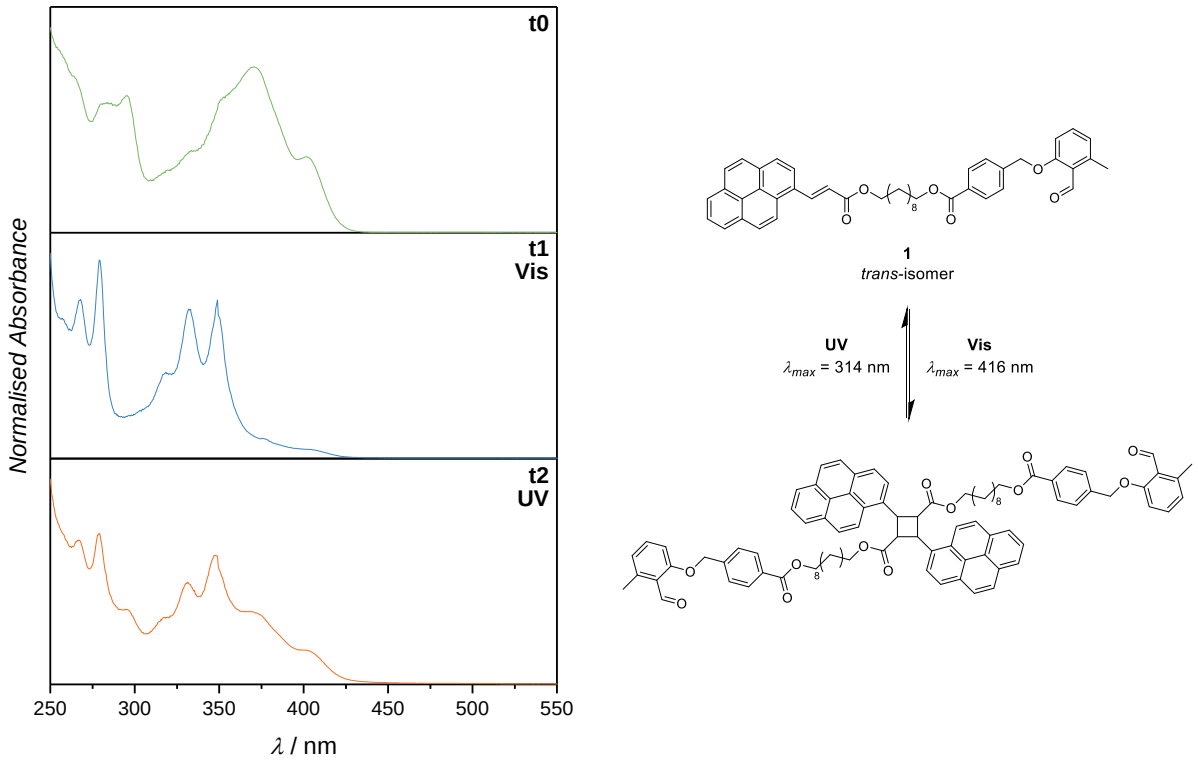


Figure S9. *UV/Vis spectra of* ***1*** *before irradiation (t0), after irradiation with visible light (λ_{max} = 416 nm, t1), and subsequent UV light irradiation (λ_{max} = 314 nm, t2).*

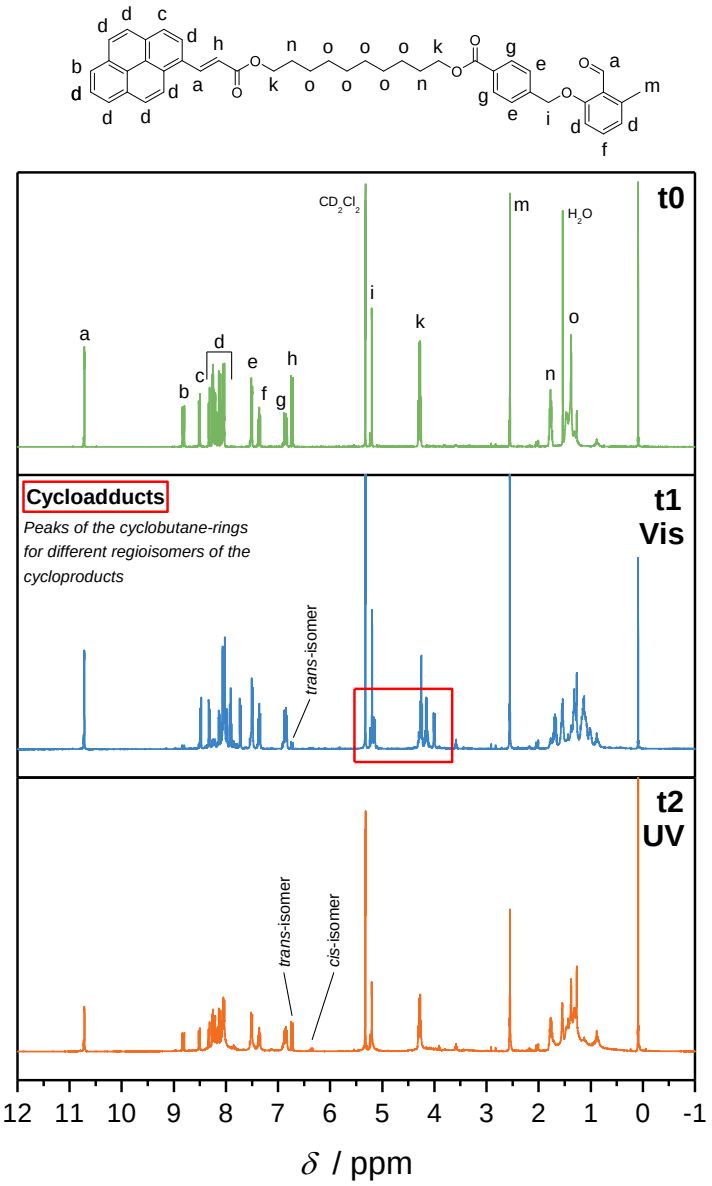


Figure S10. *Proton NMR (recorded in deuterated dichloromethane, 400 MHz) of* ***1*** *before irradiation (t0) after irradiation with visible light (λ_{max} = 416 nm, t1, dimerisation), and subsequent irradiation with UV light (λ_{max} = 314 nm, t2, dissociation).*

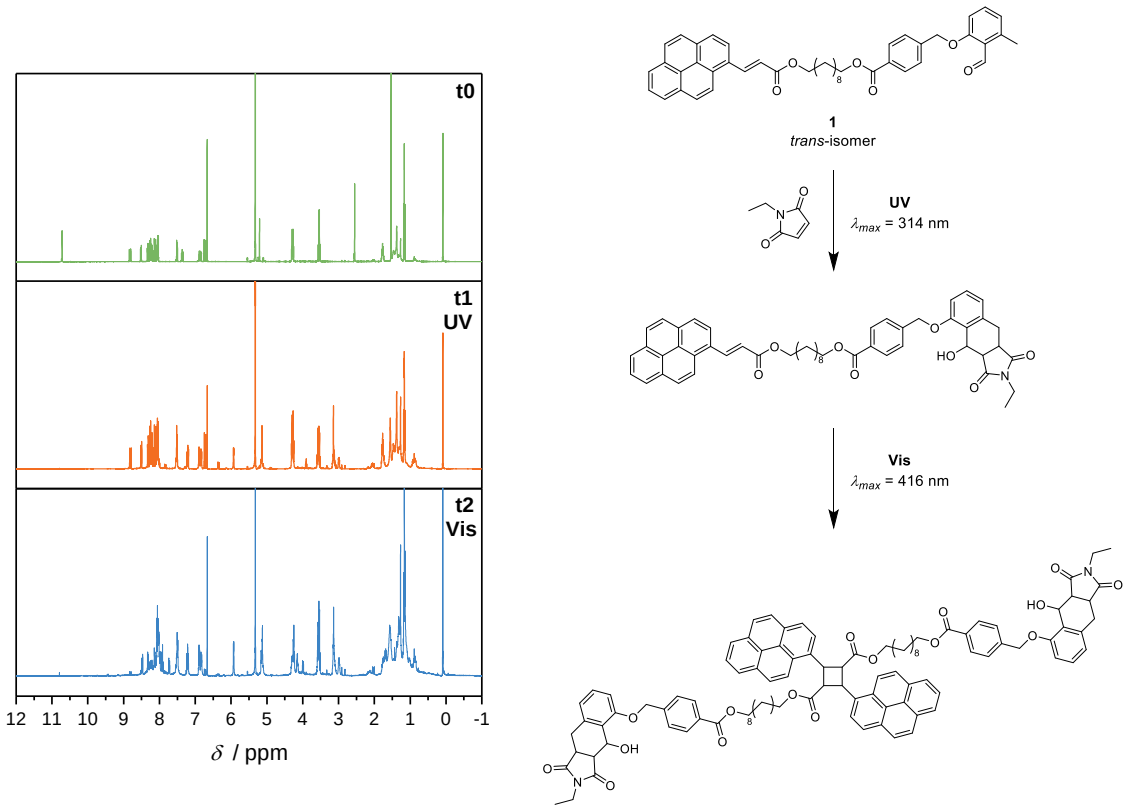


Figure S11. *Proton NMR (recorded in deuterated dichloromethane, 400 MHz) of* ***1*** *before irradiation (t0), after irradiation with UV light (*λ_{max} *= 314 nm, t1), and subsequent visible light irradiation (*λ_{max} *=614 nm, t2).*

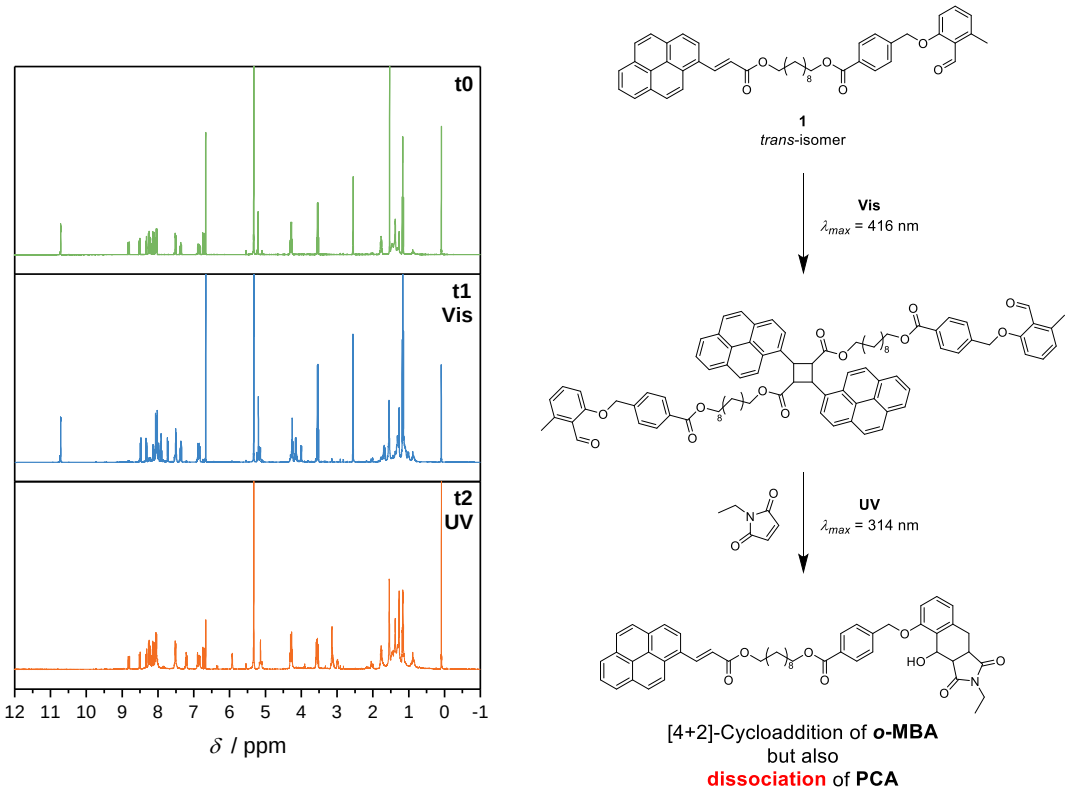


Figure S12. *Proton NMR (recorded in deuterated dichloromethane) of* ***1*** *before irradiation (t0), after irradiation with visible light (*λ_{max} *= 416 nm, t1), and subsequent UV light irradiation (*λ_{max} *= 314 nm, t2). Upon irradiation not only the [4+2] cycloaddition of o-MBA occurs but the unexpectedly the in the first step formed cyclobutane structure also dissociated back to the double bond of PCA.*

1.2 Preliminary Tests for Polymer Ligation

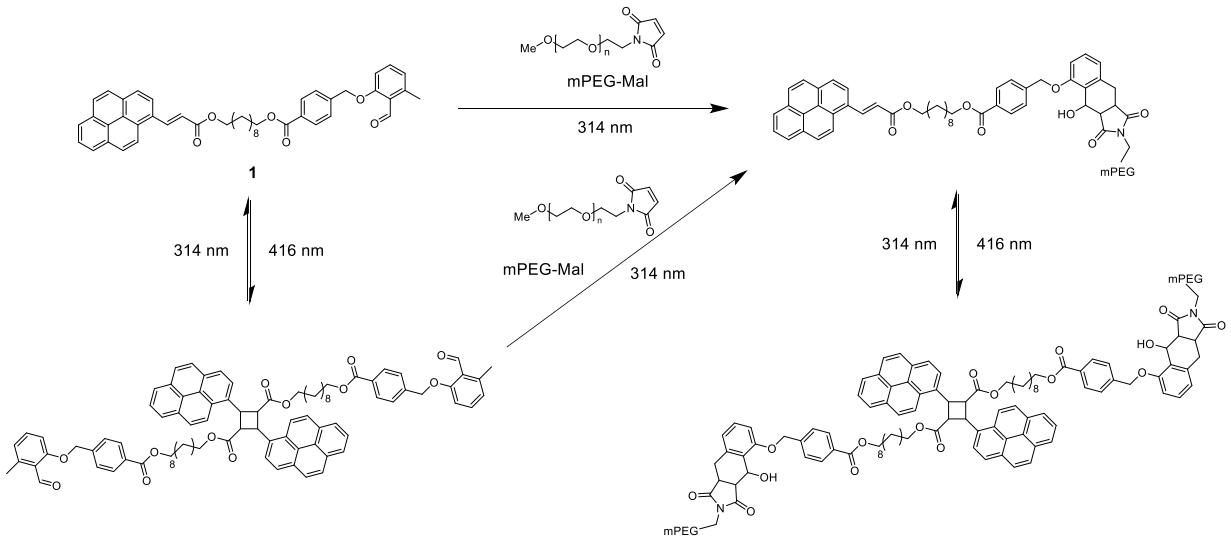


Figure S13. *Reaction scheme depicting the wavelength orthogonal pathways for the reaction between **1** and mPEG-Mal.*

As an additional application of the concept, the counter reactive group for the UV reaction, i.e. Et-Mal, was replaced with a maleimide end-functionalised polyethylene glycol derivative (e.g. mPEG-Mal, 2000 g mol^{-1}), and reacted with **1** in a similar manner (as for the small molecule study) under the optimized reactions conditions (compare Figure S13). Analysis via UV/Vis spectroscopy (Figure S14) showed identical results as previously observed for the study with Et-Mal (refer to Figures 5 and 6 in the main text).

Further analysis via SEC returned the anticipated SEC traces (Figure S15), however they were featuring small shoulders to higher molecular weights (i.e. smaller retention time). The SEC measurement after irradiation with visible light (λ_{max} = 416 nm, blue line) represented in Figure S15 A shows an additional peak (***A***, 1100 g mol^{-1}) along the main peak (***B***, 3000 g mol^{-1}) which is arising at lower molecular weights. This peak ***A*** can be assigned to the cyclobutane dimer formed via dimerisation of **1**. The starting material of **1** is not presented in this graph since it is overlaying with the system peaks of the SEC. Comparing the blue SEC trace to the starting material (green line, Figure S15 A), the mPEG-Mal peak ***B*** remains intact, hence confirming that mPEG-Mal is not participating in the reaction performed under visible light. On the other hand, there is a small shoulder to higher molecular weights (***C***, starting at around 8200 g mol^{-1} with broad tailing to even higher molecular weights) that could not be explained.

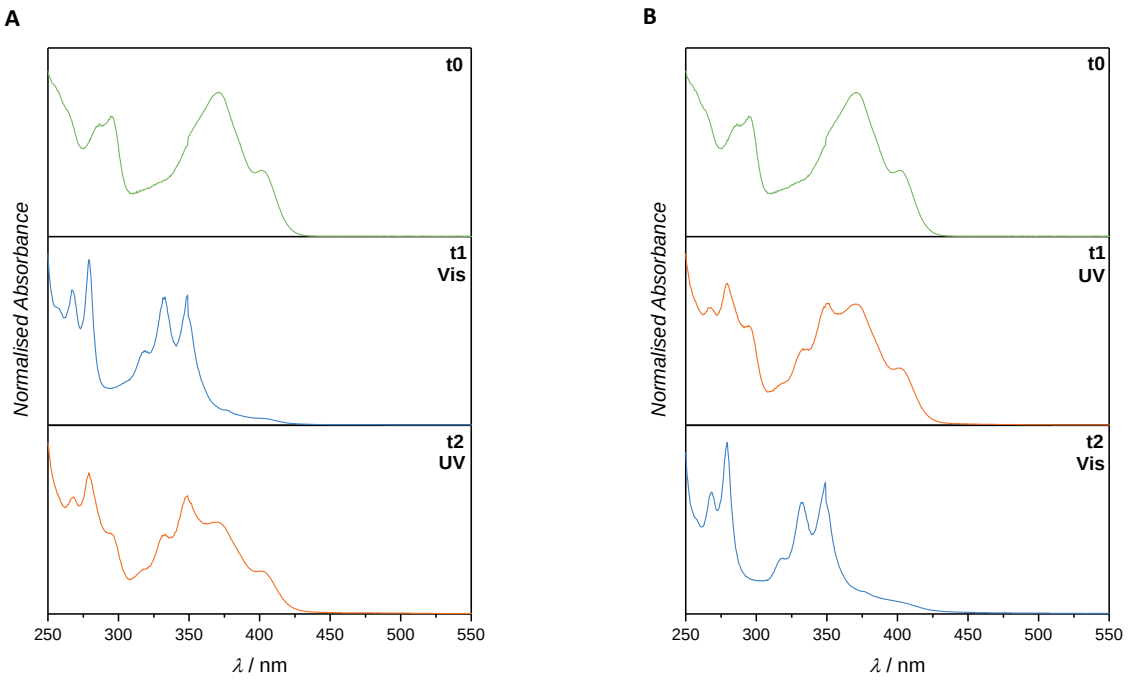


Figure S14. *UV/Vis spectra of **1** with mPEG-Mal: A) before irradiation (t0), after irradiation with visible light (λ_{max} = 416 nm, t1), and subsequent UV light irradiation (λ_{max} = 314 nm, t2). B) before irradiation (t0), after irradiation with UV light (λ_{max} = 314 nm, t1) and subsequent visible light irradiation (λ_{max} = 416 nm, t2).*

Subsequent irradiation with UV light (λ_{max} = 312 nm, orange line, Figure S15 A) displayed the disappearance of the peak to lower molecular weights (***A***, 1100 g mol^{-1}), and a small shift of the main peak (from peak ***B*** at 3000 g mol^{-1} to peak ***C*** at 3600 g mol^{-1}), which confirms the successful reaction of **2** with the mPEG-Mal. In detail, the present **1**-dimer undergoes cycloreversion as well as a reaction with mPEG-Mal. This reaction sequence is in accordance with the study in the presence of Et-Mal (compare Figure S12, and Figure 6 in the main text), since UV light should not only trigger the reaction with *o*-MBA, yet also the PCA dissociation. The shoulder to higher molecular weights (***E***) however increased in size. Shoulder ***E*** could be due to small amounts of **1**-dimer undergoing the *o*-MBA reaction, while the PCA dissociation is not taking place. Such a behaviour could not be confirmed by analysing the NMR spectra of the small molecule study (compare Figure S1). In addition, the SEC trace features another peak ***F*** at even higher molecular weights which, at this point, could not be explained. Further studies are being performed to clarify this phenomenon.

By examining Figure S15 B, one can observe similar shoulders (***F***). Indeed, upon irradiation with UV light (λ_{max} = 314 nm, orange line), the starting material **1** reacts with mPEG-Mal (***B***, 3000 g mol^{-1}), and a small shift can be seen (***C***, 3600 g mol^{-1}). Whereas, a subsequent irradiation with visible light (blue line, Figure S15 B) triggers the PCA dimerisation, hence increasing the molecular weight of the molecule (E, 8100 g mol^{-1}). Nevertheless, after irradiation both traces feature unclear shoulders (***F***) along with tailing towards high molecular weight, which are not in accordance to previous results.

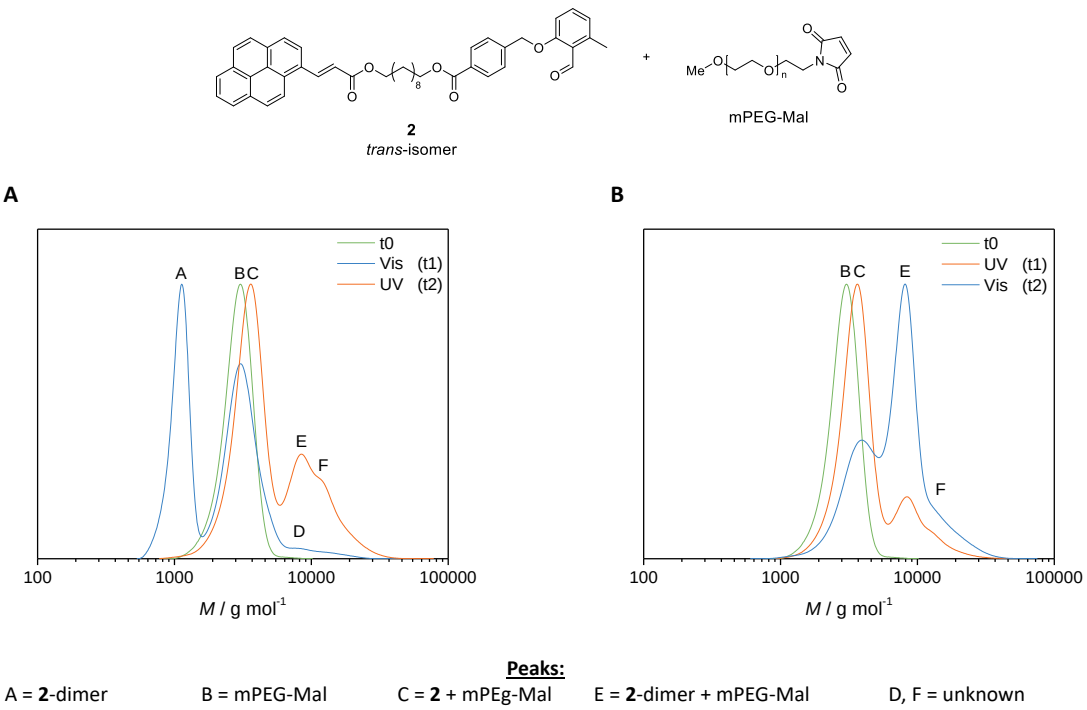


Figure S15. *THF SEC traces of **1** with mPEG-Mal: A) before irradiation (t0), after irradiation with visible light (t1) subsequent UV light irradiation (t2). B) before irradiation (t0), after irradiation with UV light (t1) and subsequent visible light irradiation (t2).*

For further investigation, all conducted experiments in this study were submitted to SEC analysis (compare with Figure S16 to Figure S19). The unknown shoulders and tailing towards higher molecular weights are very well visible in all measured spectra. Since these shoulders also appear in the SEC measurements of **1** with Et-Mal, it can be ruled out that these side effects are due to the use of PEG (Figure S16). However, measuring **1** after irradiation in absence of Et-Mal also results in shoulders (Figure S17). Since these shoulders are apparent in all the SEC traces even for the molecules not featuring a *o*-MBA group (Figure S18), the latter can be ruled out as a cause. In fact, the pyrene moiety itself features a shoulder at higher molecular weights when irradiated with UV or visible light (Figure **S19**) – while its NMR spectra remain the same (Figure S20) – which leads to the conclusion that these shoulders are actually arising due to pyrene-pyrene stacking, and not as side reactions interfering with the λ-orthogonal bichromophore presented in this study.

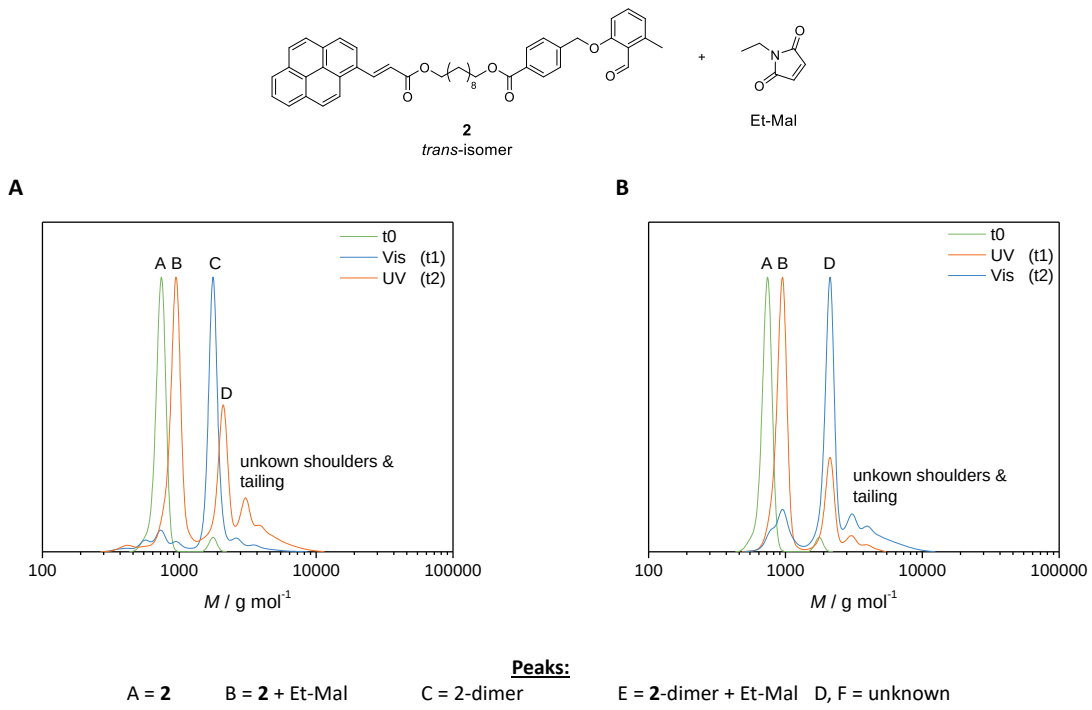


Figure S16. *SEC traces (with THF as the eluent) of* ***1*** *with Et-Mal: A) before irradiation (t0), after irradiation with visible light (t1), and subsequent UV light irradiation (t2). B) before irradiation (t0), after irradiation with UV light (t1) and subsequent visible light irradiation (t2).*

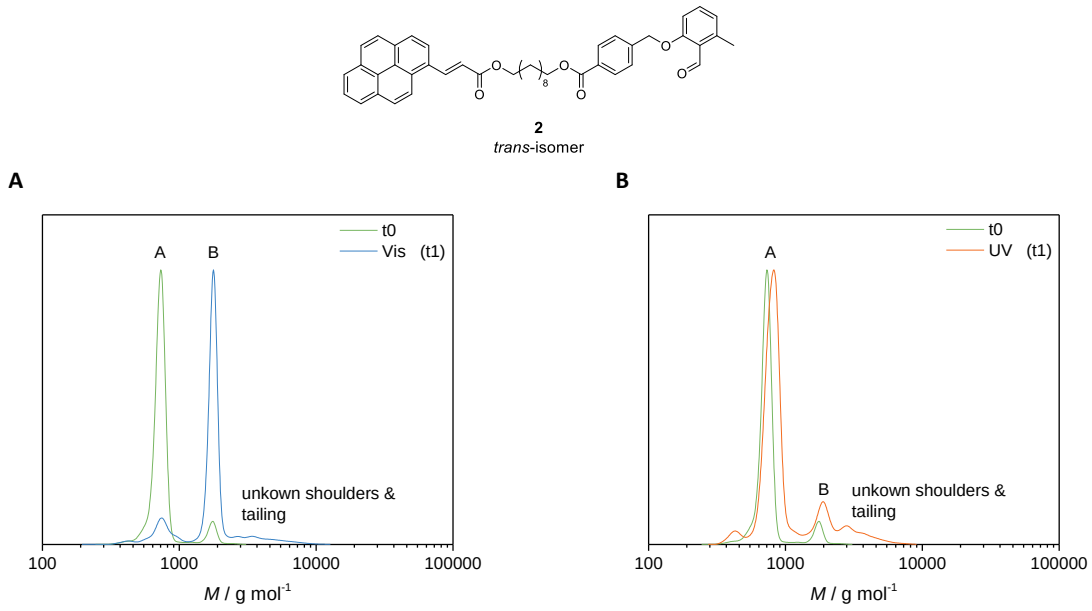


Figure S17. *SEC traces (with THF as the eluent) of* ***1****: before irradiation and after irradiation with visible light (A) or UV light (B).*

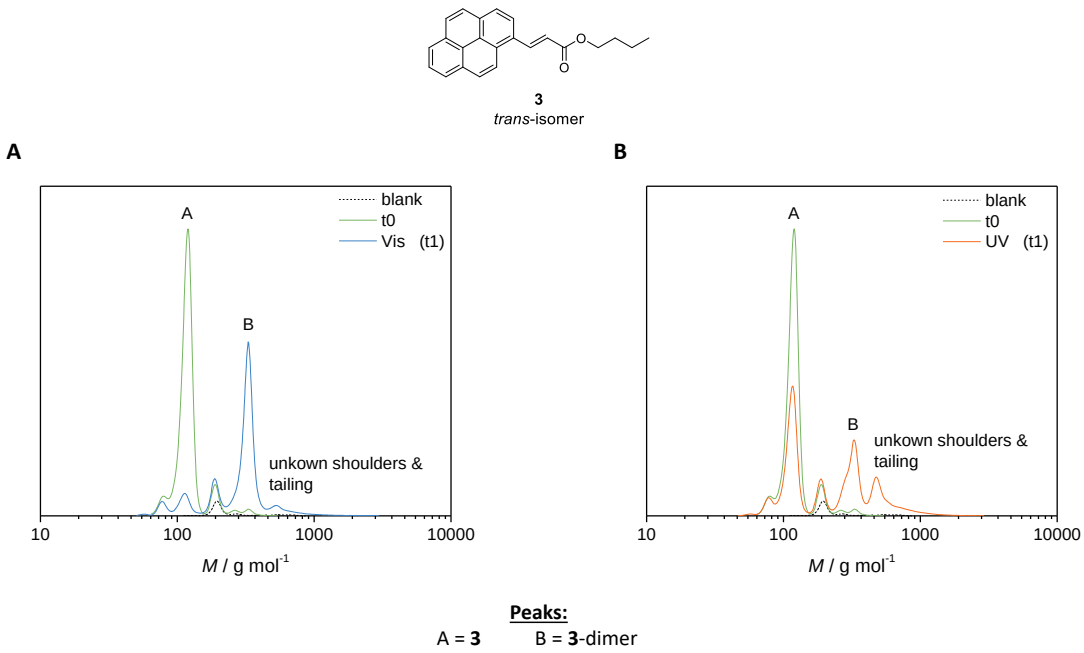


Figure S18. *SEC traces (with THF as the eluent) of* ***2****: before irradiation and after irradiation with visible light (A) or UV light (B). Measured on a Tosoh SEC system.*

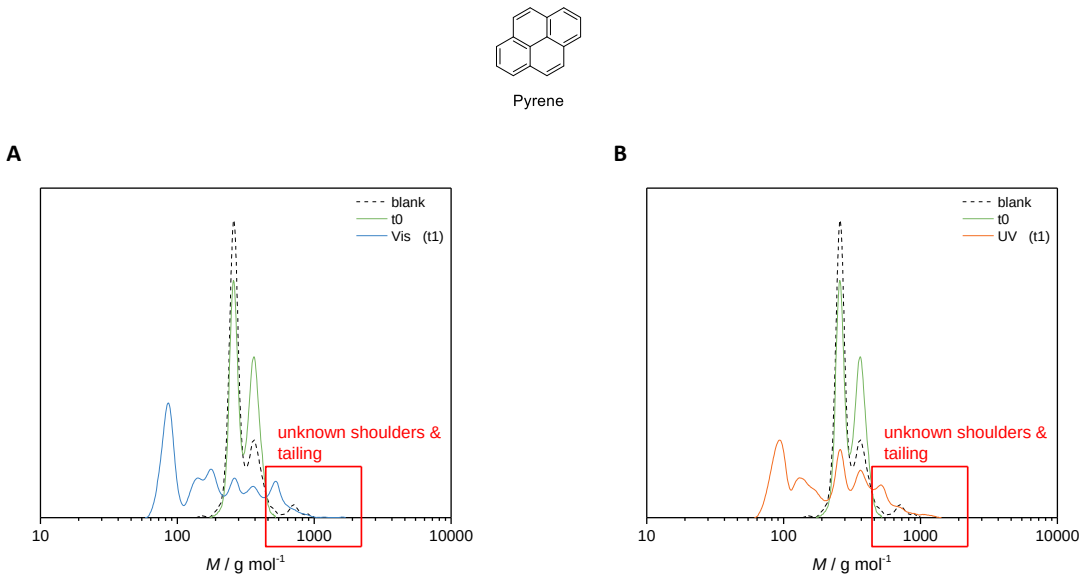


Figure S19. *SEC traces (with THF as the eluent) of pyrene: before irradiation and after irradiation with visible light (A) or UV light (B). Measured on a Tosoh SEC system.*

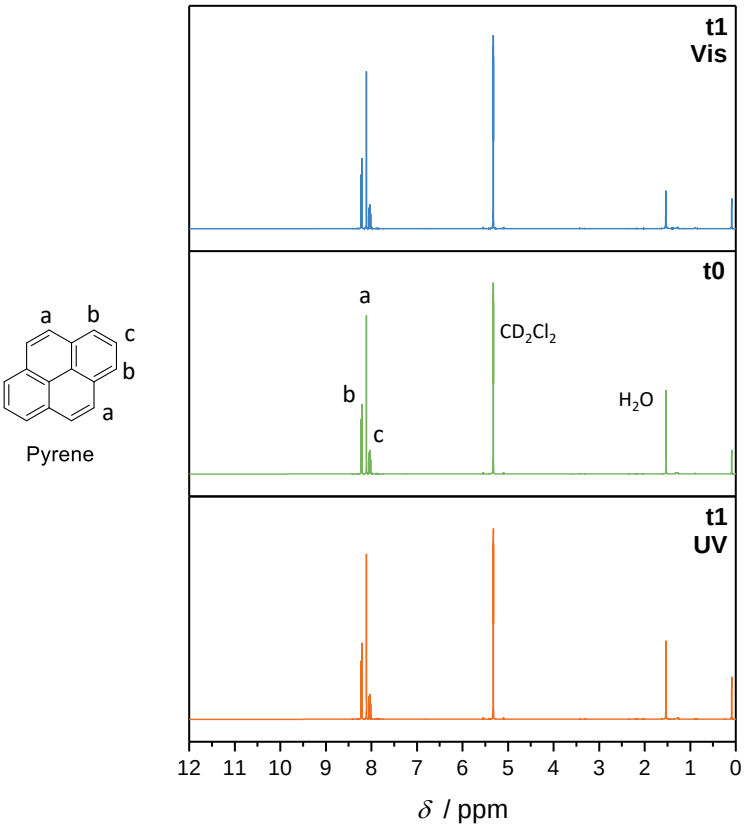


Figure S20. *Proton NMR (recorded in deuterated dichloromethane, 400 MHz) of pyrene before irradiation (middle) and after irradiation with visible light (top) or UV light (bottom).*

1.3 ESI-MS measurements

To further evidence both λ-orthogonal reactions, a mixture of **1** in presence of a five-fold excess of Et-Mal was irradiated with UV (λ_{max} = 314 nm) and subsequently visible light (λ_{max} = 416 nm). The excess of Et-Mal was chosen to ensure a complete reaction of the *o*-MBA moiety. Next, the reaction mixture was thoroughly investigated for the **1**-dimer via ESI-MS measurements (refer to **Figure S21** and **Table S1**), which could prove that the desired structure (❑) was formed, thus evidencing that **1** is capable of undergoing λ-orthogonal ligation. In addition, a chemical structure was identified, which had reacted with Et-Mal on both the PE and [2+2]-moiety (❖), due to the excess of Et-Mal Thus, it can be inferred that the respective moieties can be addressed in λ-orthogonal reactions, but not in chemically orthogonal procedures. Therefore, either product ❑ or ❖ and not both structures would have been detected. However, a product simulation of ❑ ultimately demonstrated the formation of the desired product. Thus, the small molecule study reveals that compound **1** was able of undergoing λ-orthogonal ligation in the UV as well as the visible light spectrum.

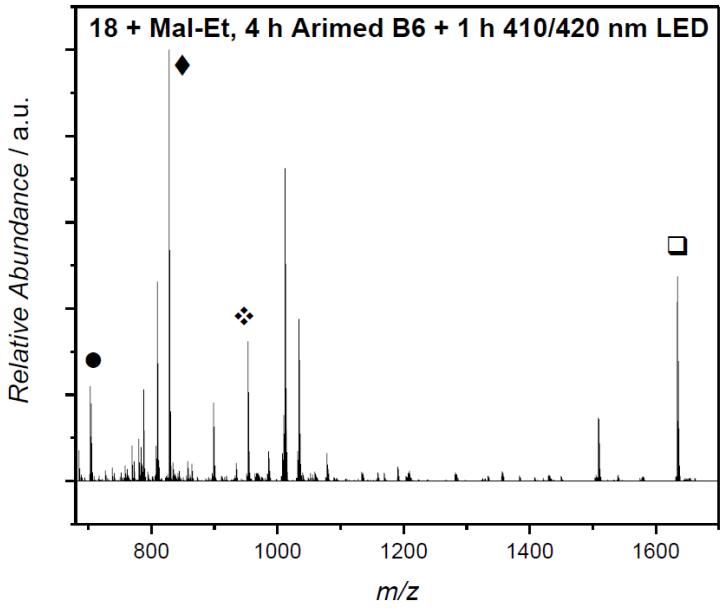
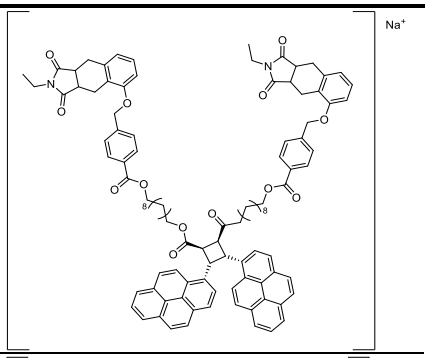
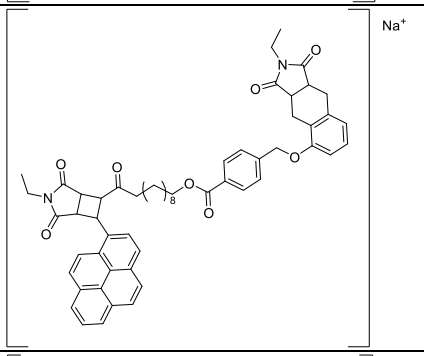
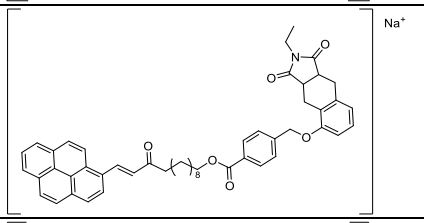
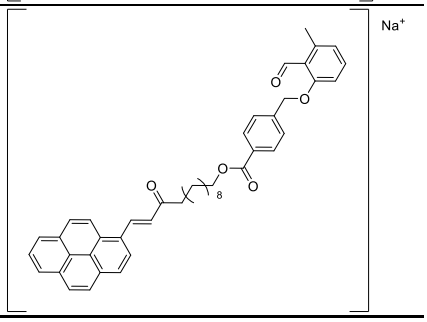


***Figure S21**. Overview ESI mass spectrum of the reaction mixture of **1** (1 eq.) and Et-Mal (5 eq.) after 4 h irradiation with UV (λ_{max} = 314 nm, 4 h) and subsequently visible light (λ_{max} = 416 nm, 1 h) in DCM-d2, recorded from m/z 690 to 1700.*

***Table S1**. Peak assignment of the ESI Orbitrap mass spectrum of the reaction mixture (**1** + Et-MaI after 4 h irradiation with UV (λ_{max} = 314 nm, 4 h) and subsequently visible light (λ_{max} = 416 nm, 1 h), showing the respective labels (corresponding to the peaks in **Figure S21**), the resolution, the experimental and simulated m/z values, Δm/z as well as the proposed chemical structure.*

Label	Resolution	m/z (experimental)	m/z theoretical	Δ m/z	Structure
❑	55506	1634.7156	1634.7155	0.0001	
❖	72109	953.4001	953.3984	0.0017	
♦	79206	828.3516	828.3507	0.0009	
●	83102	703.3037	703.3030	0.0007	

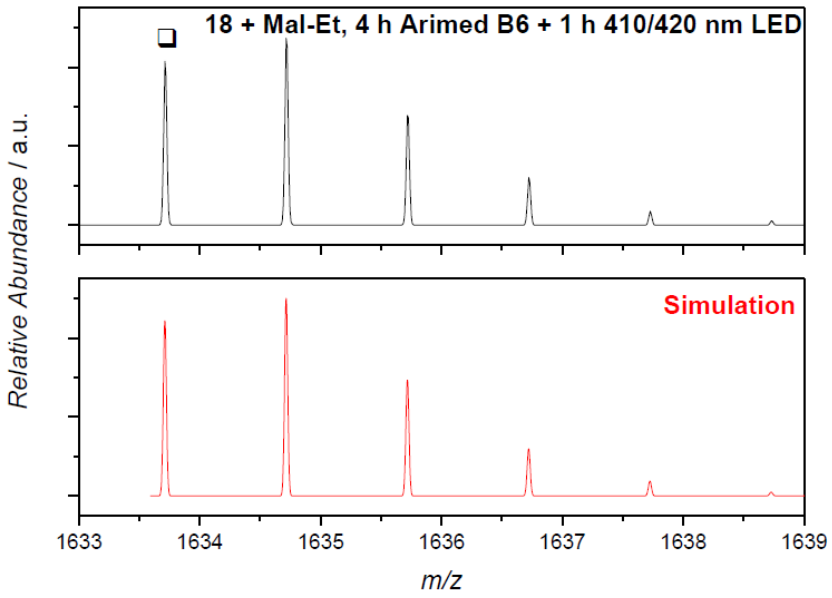


***Figure 22**. Comparison of the experimentally obtained ESI-MS spectrum and a predicted spectrum of the species marked with ❑ in **Table S1**.*

2 Characterisation and Methods

2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H and ^{13}C nuclear magnetic resonance (NMR) experiments were conducted on a Bruker Ascend 400 instrument, performing at 400 MHz. The *δ*-scale is referred to the respective deuterated solvent in which the spectrum was measured. Either chloroform-*d* ($CDCl_3$), dimethyl sulfoxide-*d6* (DMSO-*d6*) acetone-*d6* or deuterated dichloromethane were used as solvents. 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).

2.2 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 can be collected between 200 and 800 nm.

2.3 Gas Chromatography-Mass Spectroscopy (GC-MS)

GC-MS (EI) chromatograms were recorded by using a Varian 431-GC instrument with a capillary column FactorFourTM VF-5ms (30 m × 0.25 mm × 0.25 µm), and a Varian210-MS detector. Scans were performed from 40 to 650 m/z at rate of 1.0 scans × s^{-1}. Measurements were performed in the split–split mode (split ratio 50:1) using helium as carrier gas (flow rate 1.0 mL × min^{-1}). The oven temperature

program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C min^{-1} to 200 °C, hold for 2 min, ramp at 15 °C × min^{-1} to 325 °C, hold for 5 min. The injector's transfer line temperature was set to 250 °C.

2.4 Size Exclusion Chromatography (SEC)

2.4.1.1 Agilent SEC

Unless indicated otherwise size exclusion chromatography (SEC) analysis was performed on an Agilent 1200 system, consisting of an autosampler, a Plgel 5 µm bead-size guard column (50 × 7.5 mm), one Plgel 5 µm Mixed E column (300 × 7.5 mm), three Plgel 5 µm Mixed C columns (300 × 7.5 mm), a differential refractive index detector and a UV detector, using THF as eluent at 35°C with a flow rate of 1 mL min^{-1} . The SEC system was calibrated using linear poly(styrene) standards ranging from 370 to 2.5×10^6 g mol^{-1} or poly(methyl methacrylate) standards ranging from 800 to 2.2×10^6 g mol^{-1}. Typically, 100 µL of a 2.0 mg mL^{-1} polymer solution was injected into the columns.

2.4.1.2 Tosoh SEC

SEC was performed on a TOSOH Eco-SEC HLC-8320 SEC System, consisting of an autosampler, a SDV 5 µm bead-size guard column (50 × 8 mm, PSS) followed by three SDV 5 µm columns (300 × 7.5 mm, subsequently 100 Å, 1000 Å and 105 Å pore size, PSS), and Waters 2487 dual wavelength absorbance detector (analysis at 254 nm) in series with a refractive index detector using tetrahydrofuran (THF) as the eluent at 30 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated using linear polystyrene standards ranging from 266 to $2.52 \cdot 10^6$ g mol^{-1}.

2.5 Photoreactors and Lamps

2.5.1 UV-A light Irradiation

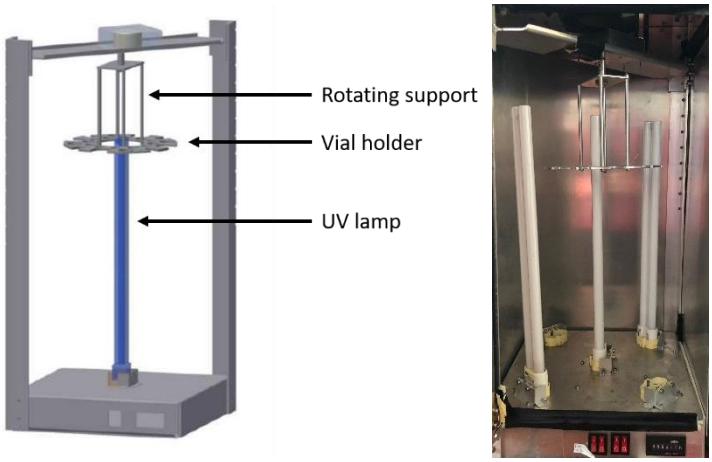


Figure S23. *UV photoreactor that can be equipped with up to 5 UV lamps (one in the middle of the rotating sample holder and four surrounding it).*[1]

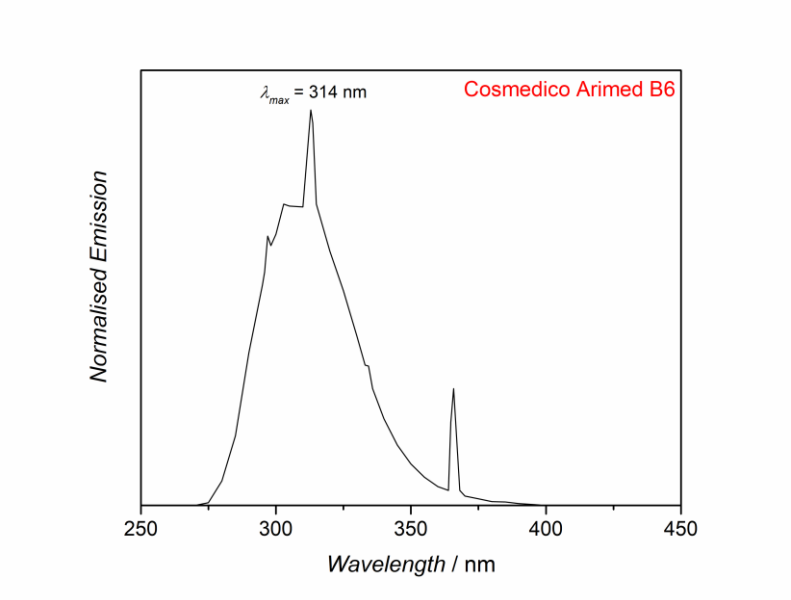


Figure S24. *Emission spectrum of the lamps used for UV-A irradiation: 3 x Cosmedico Arimed B6.*

2.5.2 Visible light Irradiation

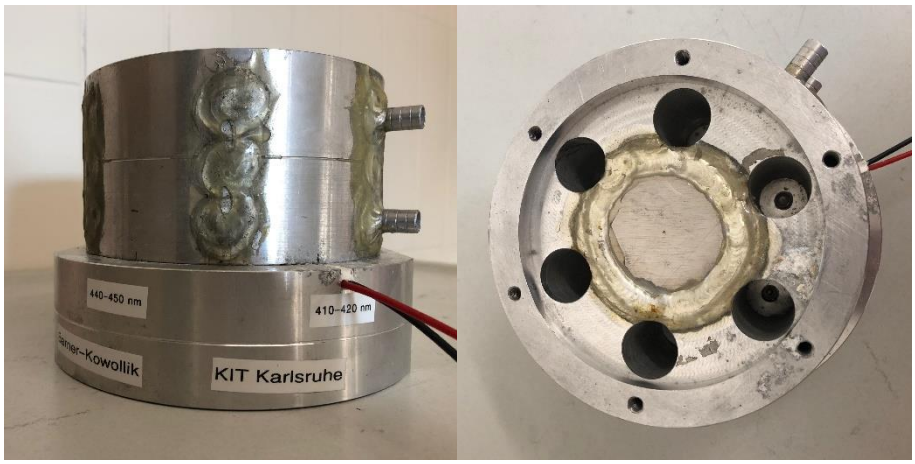


Figure S25. *Photoreactor used for irradiation with visible light.*

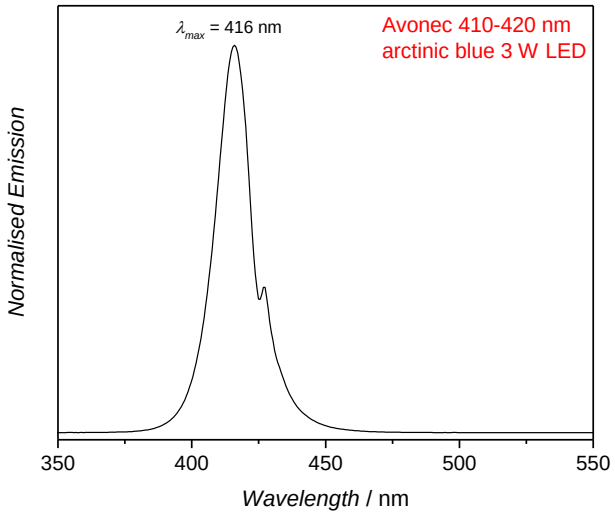


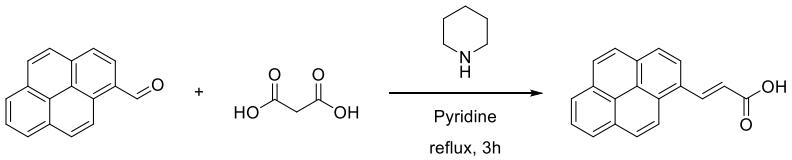
Figure S26. *Emission spectrum of the lamp used for UV-A irradiation: Avonec 410-420 nm arctinic blue 3 W LED.*

3 Synthetic Procedures

3.1 Photoreactions – General Procedure

Unless stated otherwise, photoreactions were carried out in crimped quartz glass vials. 10 mM solutions of the respective molecules in deuterated dichloromethane (or dry dichloromethane for the polymer study) were degassed with inert gas (i.e. nitrogen) for 5 minutes, and subsequently irradiated with light. Irradiation with visible light took place at λ_{max} = 416 nm for 5 h, while reactions under UV-A light at λ_{max} = 314 nm were carried out for 3 h. Emission spectra of the used lamps can be found in chapter 2.5.

3.2 Synthesis of (*E*)-3-(pyren-1-yl)acrylic acid

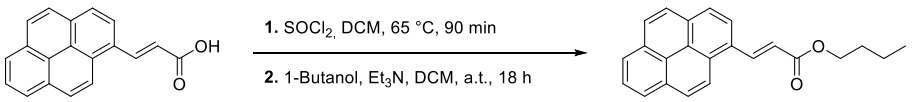


(*E*)-3-(pyren-1-yl)acrylic acid was synthesized according to a literature procedure (949 mg, 3.49 mmol, 73.0 %).[2]

^{1}H NMR (400 MHz, DMSO-*d6*): δ (ppm) = 12.61 (s, 1H), 8.71 (d, 3*J* = 15.7 Hz, 1H), 8.56 – 8.08 (m, 9H), 6.84 (d, 3*J* = 15.7 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*): δ (ppm) = 167.81, 141.16 – 120.39 (m).

3.3 Synthesis of butyl (*E*)-3-(pyren-1-yl)acrylate (2)



500 mg (*E*)-3-(pyren-1-yl)acrylic acid (1.84 mmol, 1.00 eq.) was suspended in anhydrous DCM (15 mL) in a flame-dried flask equipped with a reflux condenser. 1.33 mL $SOCl_2$ (2.18 g, 18.4 mmol, 10.0 eq.) were added to the suspension and the mixture was heated to 65 °C for 90 min. Excess $SOCl_2$ and the solvent were evaporated under reduced pressure. The remaining solid was dissolved in anhydrous DCM (15 mL) and 255 µL NEt3 (185.8 mg, 1.84 mmol, 1.00 eq.) were added. A solution of 185 µL 1-butanol (149.7 mg, 2.02 mmol, 1.10 eq.) in 10 mL anhydrous DCM was added dropwise to the stirred mixture at ambient temperature. After stirring for 18 h, the reaction was quenched by carefully adding ice-cold water. DCM (100 mL) was added and the phases were separated. The aqueous phase was extracted with DCM (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. The solvents

were evaporated, and the crude product was recrystallised in EtOH to yield a yellow solid (497 mg, 1.71 mmol, 93.1 %).

^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 8.83 (d, *J* = 15.7 Hz, 1H), 8.48 (d, *J* = 9.3 Hz, 1H), 8.31 – 7.99 (m, HH), 6.72 (d, *J* = 15.7 Hz, 1H), 4.31 (t, *J* = 6.7 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.57 – 1.43 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CDCl3): δ (ppm) = 167.70, 143.61 – 117.58 (m), 65.04, 31.34, 19.75, 14.28.

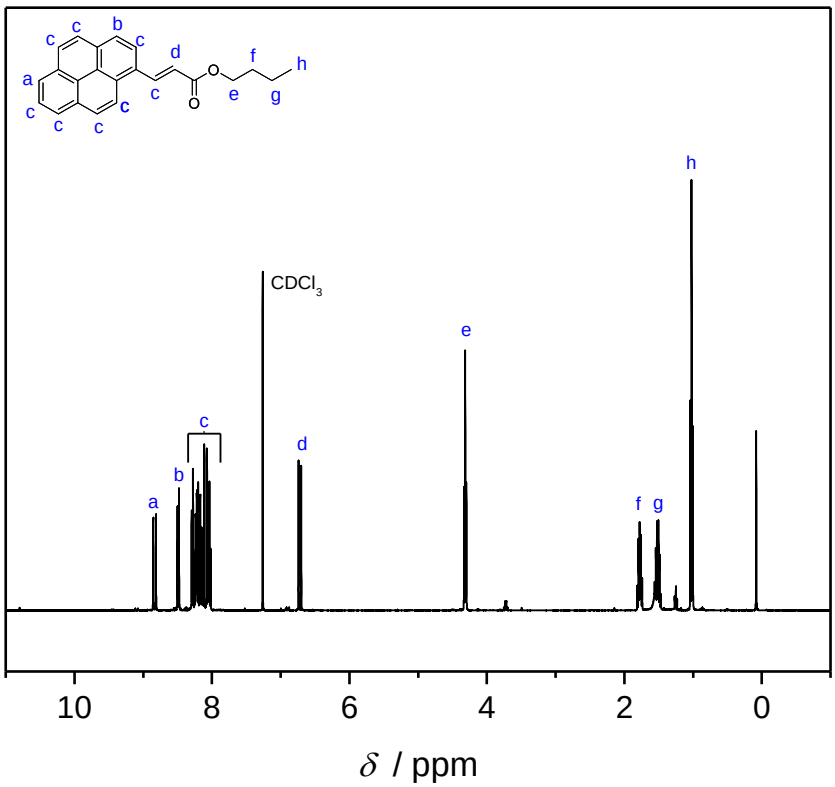


Figure S27**. Proton NMR spectrum (measured in deuterated chloroform, 400 MHz) of **2.

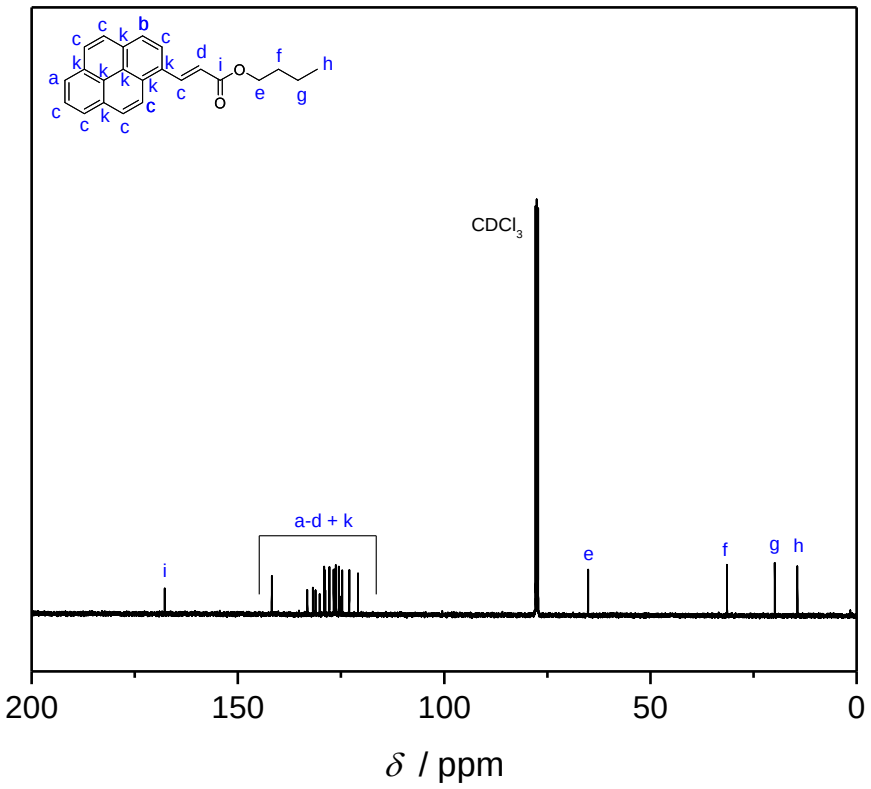
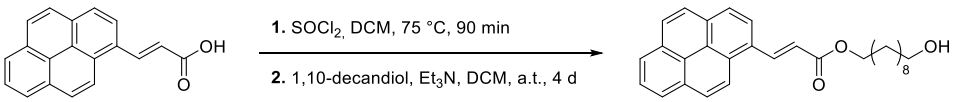


Figure S28**. Carbon NMR spectrum (measured in deuterated chloroform, 400 MHz) of **2.

3.4 Synthesis of 10-hydroxydecyl (*E*)-3-(pyren-1-yl)acrylate

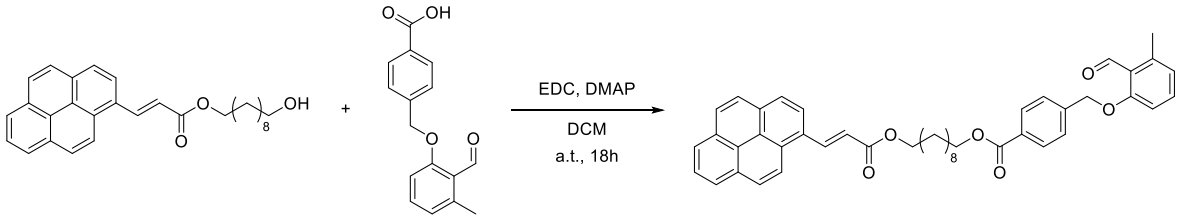


500 mg (*E*)-3-(pyren-1-yl)acrylic acid (1.84 mmol, 1.00 eq.) were suspended in anhydrous DCM (15 mL). 1.33 mL $SOCl_2$ (2.19 g, 18.4 mmol, 10.0 eq.) were added and the mixture was heated to 75 °C for 90 min. The solvent and excess $SOCl_2$ were removed under reduced pressure and the remains were dissolved in dry THF (25 mL) and added dropwise to a solution of 1.60 g 1,10-decandiol (9.18 mmol, 5.00 eq.) as well as 205 µL NEt_3 (185 mg, 3.68 mmol, 1.00 eq.) in 30 mL dry THF. The reaction mixture was stirred at ambient temperature for four days. The reaction mixture was filtered and quenched by adding water. The aqueous phase was extracted with DCM (3 × 100 mL). The organic phase was dried over Na_2SO_4 and all volatiles were evaporated subsequently. The residue was purified by column chromatography (cyclohexane/ethyl acetate, 2:1, Rf = 0.41). The product was received as yellow solid (508 mg, 1.19 mmol, 64.6 %).

^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 8.83 (d, *J* = 15.7 Hz, 1H), 8.48 (d, 3*J* = 9.3 Hz, 1H), 8.33 – 7.98 (m, 8H), 6.71 (d, 3*J* = 15.8 Hz, 1H), 4.30 (t, 3*J* = 6.7 Hz, 2H), 3.63 (t, 3*J* = 6.6 Hz, 2H), 1.78 (qu, 3*J* = 8.0, 6.5 Hz, 2H), 1.57 (qu, *J* = 6.8 Hz, 2H), 1.50 – 1.24 (m, 12H).

^{13}C NMR (101 MHz, CDCl3): δ (ppm) = 167.70, 141.76, 134.01 – 119.58 (m), 65.32, 63.52, 33.26, 30.04 – 29.70 (m), 29.26, 26.49, 26.19.

3.5 Synthesis of (*E*)-10-((3-(pyren-1-yl)acryloyl)oxy)decyl 4- ((2-formyl-3-methylphenoxy)methyl)benzoate (1)



227 mg 4-((2-formyl-3-methylphenoxy)methyl)benzoic acid (0.84 mmol, 1.20 eq.), 410 mg EDC·HCl (2.10 mmol, 3.00 eq.) and 43.0 mg DMAP (0.75 mmol, 0.50 eq.) were dissolved in anhydrous DCM (20 mL) under argon atmosphere and cooled to 0 °C. A solution of 300 mg 10-hydroxydecyl (*E*)-3-(pyren-1-yl)acrylate (0.70 mmol, 1.00 eq.) in anhydrous DCM (150 mL) was added dropwise and the reaction mixture was allowed to reach ambient temperature. After stirring for 18 h, the reaction was quenched by adding water (50 mL) and diluted with DCM (50 mL). The mixture was diluted with DCM (100 mL) and the phases were separated. The organic phase was washed with a saturated sodium bicarbonate solution as well as brine and all solvents were evaporated under reduced pressure. The residue was purified by column chromatography (cyclohexane/ethyl acetate, 3:1, Rf = 0.55). The product was obtained as yellow solid (325 mg, 0.48 mmol, 68.2 %).

^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 10.74 (s, 1H), 8.83 (d, *J* = 15.7 Hz, 1H), 8.48 (d, *J* = 9.3 Hz, 1H), 8.29 – 7.99 (m, 11H), 7.49 – 7.45 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 6.83 – 6.80 (m, 2H), 6.71 (d, *J* = 15.8 Hz, 1H), 5.18 (s, 2H), 4.31 (dt, *J* = 9.8, 6.7 Hz, 4H), 2.58 (s, 3H), 1.77 (ddd, *J* = 8.4, 6.5, 1.9 Hz, 4H), 1.50 – 1.30 (m, 12H).

^{13}C NMR (101 MHz, CDCl3): δ (ppm) = 192.12, 167.36, 166.40, 162.03, 142.42, 141.43, 136.29 – 109.28 (m), 70.05, 65.38, 65.00, 29.74 – 29.32 (m), 28.91 (d, *J* = 9.2 Hz), 26.18, 21.62.

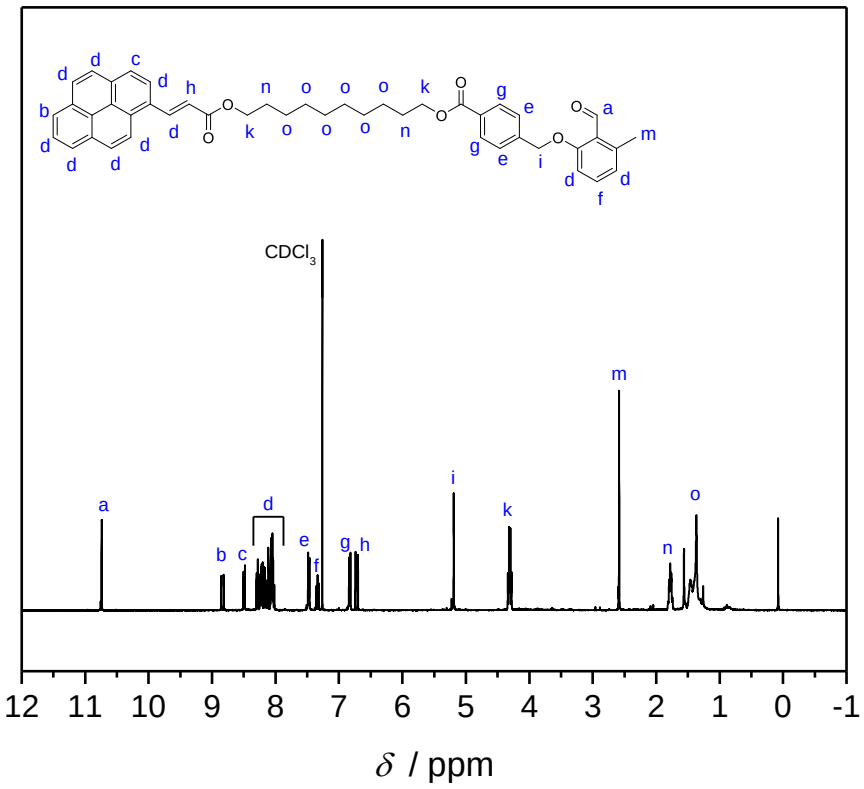


Figure S29. *Proton NMR spectrum (measured in deuterated chloroform, 400 MHz) of* ***1****.*

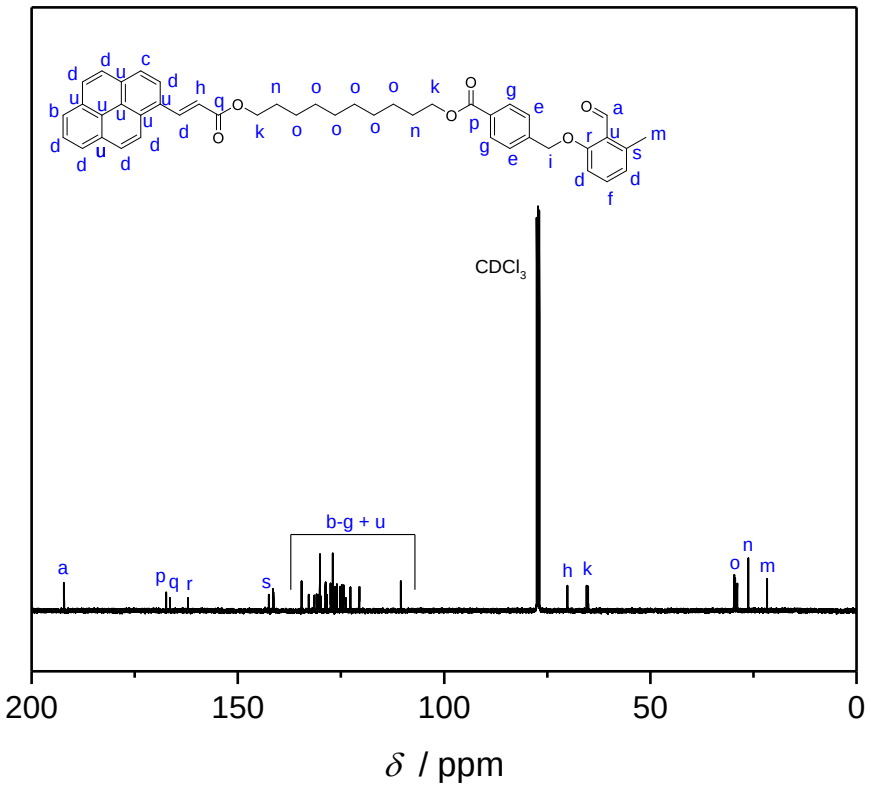


*Figure 30. Carbon NMR spectrum (measured in deuterated chloroform, 400 MHz) of **1**.*

(1) Glassner, M.; Oehlenschlaeger, K. K.; Gruendling, T.; Barner-Kowollik, C. Ambient Temperature Synthesis of Triblock Copolymers via Orthogonal Photochemically and Thermally Induced Modular Conjugation. *Macromolecules* **2011**, *44* (12), 4681–4689.

(2) Oh, J.; Hong, J.-I. Discrimination of Redox-Responsible Biomolecules by a Single Molecular Sensor. *Org. Lett.* **2013**, *15* (6), 1210–1213.